Strong Closed-Shell Interactions in Inorganic Chemistry

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I. Introduction

Chemical systems consist of chemical elements and chemical bonds. Strong, covalent bonds are expected between open-shell species, when more bonding molecular orbitals than antibonding ones will be filled. Strong ionic bonds are expected between closed-shell species, if they carry opposite electric charges. Between closed-shell species of zero charge or, anathema, the same nominal charge, no strong attractions are expected.

Indeed, two closed-shell metal cations would normally be expected to repel each other. In the case of inorganic or organometallic compounds, evidence has, however, recently been accumulated for an entire family of cation−cation interactions between d^8−d^{10}−s^2 systems. They are weaker than most covalent or ionic bonds but stronger than other van der Waals bonds, and roughly comparable in strength with typical hydrogen bonds. Little ab initio theory and

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almost no comprehensive summaries exist on this topic, despite the large amount of rather scattered data and many reviews on a single topic. Therefore it seems timely to try to summarize what is available.

Also being debated is whether an attraction exists at all for the lighter elements, the other possibility being that the observed short distances come from anisotropic atomic shapes, a packing effect. For the heavier elements there are data on the interaction strengths but the question is one of interpretation.

Actually the idealized pictures of covalent, ionic, and van der Waals bonding are appealing and helpful, but they never occur in pure form, and certainly not near the equilibrium distance. The simple picture of a covalent bond, made by an excess of electrons in bonding molecular orbitals, in a single-determinant picture, must be completed by correlation effects. Then, inevitably, the van der Waals attraction is also introduced. The ionic bonds will always have some covalent character. Finally, all three interactions will experience increasing Pauli repulsion of their closed-shell cores, for diminishing bond length, R, and in fact this "penetration" [1] energy will create the $V(R)$ minimum at R_e.

Types of Interaction. Consider two subsystems A and B at a distance R. Even in the absence of any

overlap, if they are polyatomic systems having static electric multipole moments, Q_L, the multipole–multipole interactions must be added. If the subsystems

$$V \cong Q_L(A) \, Q_{L'}(B) R^{-L-L'-1} \tag{1}$$

are polarizable, induction terms occur between the moments of A and the polarizabilities of B. This includes the charge–polarizability ($L = 0$) interactions between a charge Z and a dipole polarizability α_1.

$$V = -\alpha_1 Z^2/2R^4 \tag{2}$$

Numerous reviews exist on these closed-shell interactions[2–15] known as "van der Waals" or "dispersion" interactions. This is actually an idealization.

$$V_{vdW} = C_6 R_{AB}^{-6} \tag{3}$$

In addition to these R^{-6} interactions, there are contributions arising from the higher (than $L = 1$) multipoles in second-order perturbation theory.[7,8] Including three dipole operators in third-order perturbation theory will lead to three-body terms.

At large R, this C_6 coefficient can be expressed by the Casimir–Polder formula,[16]

$$C_6 = \frac{3}{\pi}\int_0^\infty \alpha_1^A(iE)\alpha_1^B(iE) \, dE \tag{4}$$

where $\alpha_1(iE)$ is the frequency-dependent electric dipole polarizability. It is a monotonically decreasing function of E. For the analogous formulas for C_8 and C_{10}, see ref 8.

As recently summarized,[1] writing the wave function for the system AB in the configuration interaction (CI) form,

$$\Psi = \Psi_{Aa,Bb} + \sum_{a',b'} C_{a',b'}^{AB}\Psi_{Aa',Bb'} \tag{5}$$

the leading term is

$$\Psi_{Aa,Bb} = K_{ab}|\Phi_{Aa}\Phi_{Bb}| \tag{6}$$

Φ_{Rr} being the wave function for system R in state r and K_{ab} a normalization factor.

Then eq 6 will already contain the Pauli repulsion energy due to the antisymmetrization, single excitations of the unperturbed functions describe the "polarization" terms, eq 2, and double excitations describe the "dispersion" terms, eq 3. In calculations on the "supermolecule" AB, the terms up to C_4 are obtained at the Hartree–Fock (HF) level. The C_6 ones require inclusion of correlation.

Most of the existing theoretical studies of such interactions refer to well-defined, light-element systems such as rare-gas dimers, $(H_2O)_2$, $(C_6H_6)_2$, biological systems, or their combinations, like (C_6H_6)-Ar.[17] Barrow and Crozet[14] just reviewed the available, accurate gas-phase data. The case of one closed-shell and one open-shell system has also been considered.[18,19] The interactions between metal atoms, in their ground or excited states, and rare gases were reviewed in ref 20.

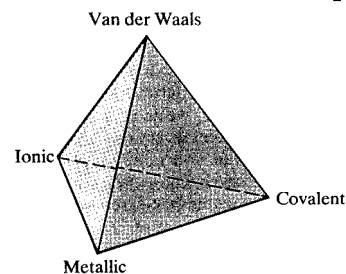**Hydrogen Bonds.** A further common concept in descriptive chemistry are the "hydrogen bonds",

Figure 1. Covalent, ionic, metallic, and correlation bonding. (Reprinted from ref 34. Copyright 1993 Royal Society of Chemistry.)

which could be attributed to a combination of electrostatic, induction, and covalent terms.

The "Donor–Acceptor" or "Charge-Transfer" Complexes. These were a popular subject some time ago. At ab initio level it is not obvious that they would actually result from a simple mixing of a few states,

$$\Psi(D,A) = a\Psi_0(D,A) + b\Psi_1(D^+A^-) + c\Psi_2(D^-A^+) \tag{7}$$

where D refers to the donor and A to the acceptor, as originally proposed by Mulliken.[21,22] For the structural chemistry of the phenomenon, see especially the reviews.[23,24]

Recently the model has been used in a natural bond orbital (NBO) framework.[25] A density-functional theory (DFT) approach to the donor–acceptor interactions was presented by Cioslowski.[26] For a valence-bond formulation, see ref 1. A charge decomposition analysis using fragment orbitals is presented by Dapprich and Frenking.[27]

Some examples on these complexes[28–32] were $(CH_3)_3N\cdots I_2$, ether- or thioether$\cdots I_2$, $I_2\cdots C_6H_6$, or $Ag^+\cdots C_6H_6$. Recently, the analogous complexes between phosphines, PR_3, and dihalogens, X_2, have received attention.[33]

Types of Bonding: Continuous Transitions. At this point it is good to point out that the bonding type may continuously shift from one type to another type as function of a chemical or physical variable. A classical example is the Ketelaar–van Arkel triangular diagram, applied to the present problem as a covalent/ionic/metallic/van der Waals tetrahedron by Laing,[34] see Figure 1.

The previously quoted $L_3E\cdots X_2$ systems, E = N–Bi, X = F–I, are another example. As discussed earlier,[33,35] there is a continuous transition from the donor–acceptor adduct $Me_3N\cdots I_2$, I–I = 283 pm (for free I_2 267 pm), via $Ph_3As\cdots I_2$, I–I = 300 pm, to the iodophosphonium iodide, $(^tBu_3PI^+)(I^-)$, with $I\cdots I$ = 336 pm. A third, classical case is the interdependence of intramolecular and intermolecular distances for linear, triatomic $I-I\cdots I$,[23] $Cl-Sb\cdots Cl$,[36] or $S-S\cdots S$ groups[24] in Figure 2.

A fourth example are the complexes of the heavier rare gases with Au^+. At large R they follow eq 2 but near R_e they acquire in addition a strong covalent character, as seen in Figure 3.[37]

Types of Bonding: Metals. Finally, it is being argued that no specifically "metallic" bonding exists but that metals should be regarded just as big molecules with a close-lying HOMO and LUMO.[38] [It
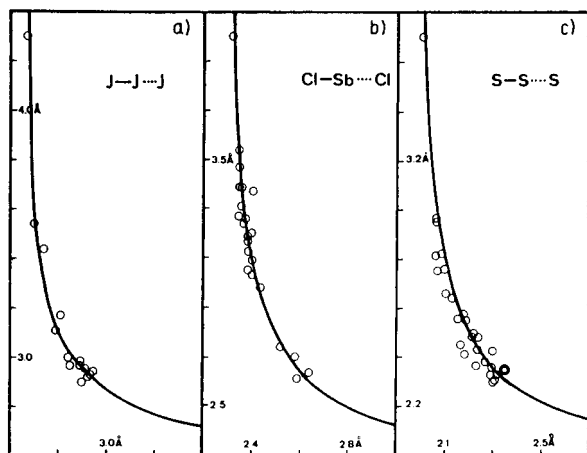
Figure 2. Intermolecular distances as function of intramolecular ones (in Å): (a) iodine and iodides (abscissa 2.5−3.5 Å), (b) antimony chlorides, (c) sulfur and sulfides. (Reprinted from ref 24. Copyright 1975 VCH Verlagsgesellschaft.)
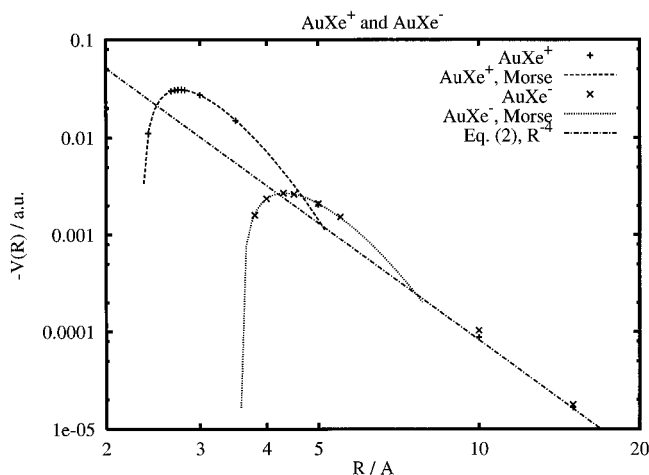

Figure 3. Calculated potential curves for AuXe$^+$ and AuXe$^-$. Adapted from ref 37. The straight line is the common long-distance R^{-4} limit.

must be noted that under these circumstances qualitatively new phenomena appear: metallic conductivity, optical reflectivity, Friedel oscillations around excess charges, etc.]

Heavy-Element Systems. The closed-shell attraction mechanisms quoted above can also be operative in many other inorganic and organometallic systems, including pairs of metal ions.[39−93] They are then commonly referred to as "semibonding interactions",[93] "secondary bonds",[78] "nonbonded interactions",[79] or "specific nonbonded interactions".[86,89]

Particularly strong evidence has now been accumulated on an attraction between two or more d^{10} ions, especially in the case of Au(I). Both ample structural evidence from crystallographic data and some energetic measurements from NMR data exist.[39−70] The paradoxical aspect is that we then formally have two closed-shell cations strongly attracting each other. More generally, reviews exist on both $s^2 \cdots s^2$ (such as Tl(I))[60,75−77] and $d^{10} \cdots d^{10}$ interactions, mainly in solid-state chemistry.[56,89] An entire coordinated research program on "new phenomena in the chemistry of metallic elements with closed inner electron shells" was recently completed.[60]

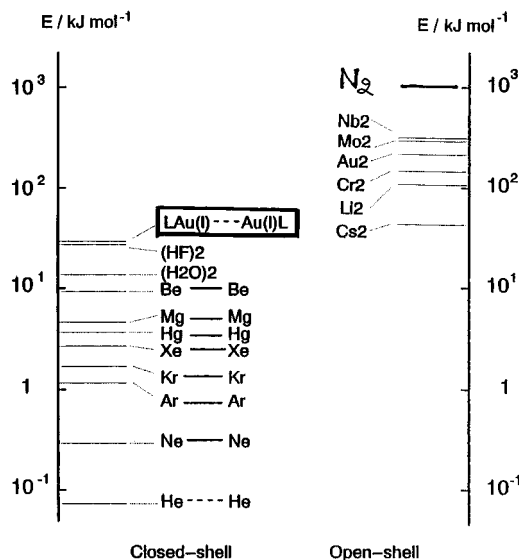Between closed-shell main-group systems such interactions[78−89] were also recognized quite early.

Figure 4. The range of closed-shell and open-shell interaction energies.

Main-group elements and the $5d^{10}$ systems Hg(II)[90] or Au(I)[91] or various d^n−d^m combinations[92] also interact.

As seen from Figure 4, the strength of the Au$^I \cdots$Au^I interaction can be between the strongest hydrogen bonds and the weakest covalent bonds, which makes the effect really striking. Apart from its fundamental interest, it may play a role in the medical applications[42] or possess useful optical properties.

Although most of the available evidence is structural only, we here point out the generality of the phenomenon and call attention to its theoretical interpretation. The earliest, extended Hückel theory (EHT) calculations attributed the metal−metal attraction to hybridization.[45,46,76,77] The later, ab initio calculations however find no attraction at Hartree−Fock (HF) level, precluding that interpretation, and recover the attraction as a correlation effect. Furthermore, although not inherently relativistic, it is considerably strengthened by the large relativistic effects[94−97] for heavy elements, like gold.

Some earlier reviews on closed-shell attractions in heavy-element systems are summarized in Table 1.

II. Methods

A. Ab Initio Methods

All the mechanisms, outlined in the Introduction, will be automatically included in correlated ab initio calculations using the many-electron Hamiltonian

$$H = \sum_{i=1}^{N} h_i + \sum_{i<j}^{N} h_{ij} \qquad (8)$$

Here h_i is the one-electron (Schrödinger or Dirac) Hamiltonian and h_{ij} the two-electron Hamiltonian, r_{ij}^{-1} + eventual Breit terms.

For compounds containing heavier elements, most calculations are now carried out using pseudopotentials (also called effective core potentials). This eliminates both the inner electron shells and the

Table 1. Articles Reviewing Closed-Shell Attractions Involving Heavier Elements (See also the papers in Table 12)

year	author (ref)	subject
1961	Hesse (41)	coinage-metal thiocarbamates
1968	Bent (23)	donor–acceptor structural chemistry
1972	Alcock (78)	main-group complexes
1975	Bürgi (24)	correlations between "long" and "short" bond lengths
	Glidewell (79)	main-group closed-shell systems
	Taylor (75)	metal-to-metal bonded states
1976	Sadler (42)	the biological chemistry of Au
	Fackler (92)	multinucl. d^8–d^{10} complexes with S ligands
1978	Avdeef and Fackler (44)	seven cases of $Cu^I \cdots Cu^I$
1980	Puddephatt (47)	Au
1981	Jones (48)	Au
1982	Puddephatt (50)	Au
	van Koten and Noltes (51)	Cu, Ag
1985	Kucsman and Kapovits (80)	S
1986	Melnik and Parish (54)	Au; structure and Mössbauer
1987	Puddephatt (55)	Au
	Jansen (56)	$d^{10} \cdots d^{10}$, mostly Ag
1989	Desiraju (82)	"crystal engineering"; main-group organic
1990	Schmidbaur (57)	Au
	Balch (58)	structure and luminescence of d^8, d^{10}, and s^2 MM′M trimers
	Cui and Kertesz (59)	chains of d^{10} systems
1992	Krebs, Ed. (60)	all closed-shell cases
	Mingos and Watson (61)	heteronuclear Au clusters
1992–1995	Housecroft (62)	coordination chemistry of Au
	Welch and Chapman, Eds. (63)	Cu, Ag, Au
	Virovets (89)	chalcogenide ions of Mo and W
1994	Grandberg and Dyadchenko (64)	Au organometallics
	King (67)	clusters of Cu, Ag, Au; Hg, hybridization picture
1995	Angermaier (68)	Au
	Grohmann and Schmidbaur (69)	Au
	van Koten et al. (70)	Cu, Ag
1996	Dance (71)	"supramolecular inorganic chemistry"
	Mingos (72)	Au
1997	Fackler (73)	oxidative addition to dinuclear Au species
	Pell and Ibers (74)	layered metal chalcogenides

sharp atomic orbitals needed for them, without a significant loss of accuracy.

The intermolecular interaction between closed-shell systems can be divided into short-range, electrostatic, induction, and dispersion terms.[8] In such ab initio calculations the three first-mentioned terms already exist at Hartree–Fock (HF) level while the last one is only obtained at correlated level. Obviously the three first ones are influenced by correlation, too.

For finite basis sets, the Boys–Bernardi counterpoise correction[98–100] for the basis set superposition error can be substantial and should be included. Briefly, this amounts to calculating the interaction energy, ΔE, of the supermolecule AB and its components A and B using the basis set of the supermolecule,

$$\Delta E^{CP}(R) = E^{AB}(R) - E^{A(AB)}(R) - E^{B(AB)}(R) \quad (9)$$

at every point, R.

Periodic Systems. Almost no theoretical work is available on vdW interactions in crystals. One study of 1- and 2-dimensional helium lattices does exist.[101] A periodic version of the Møller–Plesset method has been developed by Suhai.[102] Both cooperative and correlation effects play a role in the cohesive energy of the hydrogen-bonded formamide crystal. The "increment method" by Stoll, based on local orbitals, has been successfully applied to III–V semiconductors[103] and MgO.[104] (See also section III.D, "The cubic ionic crystals".)

Correlation effects usually increase bond lengths because the bonding MO's are occupied in the ground state at HF level and antibonding ones are partially occupied in the other Slater determinants. The opposite situation suggests attractive dispersion forces, and it is interesting that it often occurs, to a varying extent, in charge-transfer complexes.[105]

Density functional theory (DFT) works well for ionic, covalent, or metallic bonds. It does treat dynamic correlation. However, the dispersion-type, R^{-6} terms resulting from the dipole–dipole Hamiltonian in second order, are not explicitly included in the derivation of the DFT, and do not seem to come out, either.[106,107] Thus systems of the present type cannot be handled using a supermolecule approach.

An example of this failure are the too long interchain distances, obtained for the trigonal phase of tellurium.[108] A molecular application of DFT on the polyiodide problem was published in ref 109.

For the long-range C_6 coefficient of eq 3, one can first calculate the dipole polarizabilities of the subsystems, $\alpha_1^A(iE)$, and then use the Casimir–Polder equation.[16,110–112] Gross et al.[113] maintain that the full inhomogeneous RPA correlation energy already contains the essence of the vdW interaction, even for overlapping systems, and say that "the details are currently being worked out".

Dobson and Dinte[114] present for nonoverlapping systems an energy expression involving the local densities, $n_i(r_i)$, and the local plasma frequencies, $\omega_{P,i} = [4\pi e^2 n_i(r_i)/m]^{1/2}$, of the two subsystems. A similar

approach was used earlier by Rapcewicz and Ashcroft[115] to successfully obtain the C_6 of rare-gas dimers, and also the Axilrod–Teller three-body interaction constants.

B. Semiempirical Methods

In the extended Hückel theory, an effective one-electron Hamiltonian is diagonalized and the electrons are assigned to the lowest orbitals. No electron–electron interaction is explicitly included, let alone any correlation.

Yet, the EHT treatments of the present phenomenon,[45,46,76,77] (and further references below) do find an attraction, conveniently interpreted as a hybridization effect.

C. The Simplest Models: Radii

The covalent radius, R^{cov}, of an element is preferably defined for a given oxidation state and coordination number (e.g. Au(I), $CN = 2$). It is a purely operational quantity, satisfying

$$R(A - B) = R_A + R_B \qquad (10)$$

(+ eventual electronegativity or hardness/softness corrections). The two ways of obtaining R_A are either halving an A–A distance, for every A,

$$R_A = R(A - A)/2 \qquad (11)$$

or defining first *one* standard radius, R_X, often from eq 11, and obtaining then the covalent (or ionic) radii of all other elements as statistical fits to

$$R_A = R(A - X) - R_X \qquad (12)$$

A usual choice for the primary radius are the Pauling halogen radii, $R_F = 64$ pm, $R_{Cl} = 99$ pm, $R_{Br} = 114$ pm, and $R_I = 133$ pm. For ionic radii, the "IR" system of Shannon and Prewitt[116] starts from R_O and R_F of 140 and 133 pm, respectively (for *their* CN = 6) and fits the other radii. Their "CR" system uses 126 and 119 pm, respectively.

More complicated sequences are possible, like that for the "electropositive metal radii".[96,117,118] There the Pauling halogen radii and metal halide molecules yield the metallic radii, R_M, and subsequently the M–L distances for other ligands (such as H or C(sp³)) their effective radii, R_L, which then differ from the Pauling ones.

The van der Waals radius, R^{vdW}, of an element A could similarly be derived by halving the A···A distance in a nonbonding interaction, eq 11, see ref 119 or, in principle, by using eq 12. As well-known to the originators of the concept,[120,121] the use of eq 11 is problematic because the A···A distances in different compounds vary a great deal. It is simply not obvious, especially for the heavier elements, which case represents a "normal" van der Waals distance. An example of the scatter is given in Figure 5.

Pauling also considered the approximations $R^{vdW} = r^i$ (the ionic radius, in his scale on p 154 of ref 118) or the approximations $R^{vdW} = R^{cov} + 80$ pm (p 263).

Bondi[123] derived vdW radii from molar volumes. As a further possibility he mentions the estimate of
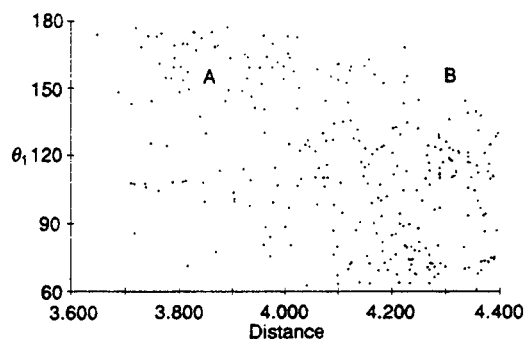

Figure 5. The scatter of intermolecular I–I distances as function of C–I···I angles, Θ. (Reprinted from ref 122. Copyright 1994 Royal Society of Chemistry.)

R^{vdW} from the first ionization potential, IP:

$$R^{vdW} = (\text{const})\lambda_B \qquad (13)$$

$$\lambda_B = h/\sqrt{(m_e \text{IP})} \qquad (14)$$

λ_B being the de Broglie wavelength. Values for metallic elements in organometallic compounds were included.

Nyburg and Faerman[124] carried out a statistical analysis using the Cambridge database and found that N and O could be regarded as spherical while E = F, S, Cl, Se, Br, and I, all bound to carbon, were smaller along the C–E axis than perpendicular to it, a trend already noted by Pauling (ref 119, p 264). This flattening of the atoms E in the C–E direction was attributed to the repulsive part of the interaction in refs 124 and 125 using a He atom as a "test particle".

As the present, formally nonbonding E···E distances vary a great deal, the entire notion of a van der Waals radius is therefore rather unclear, as one nonbonding situation is not more priviledged than another one. Previously Bondi[123] warned against using the intralayer, intermolecular X···X distances of the halogens, X_2, as estimates for R^{vdW}. The solid halogens have relatively high cohesive energies. Such values would be 166, 167, and 177 pm instead of his preferred values 175, 185, and 198 pm for Cl, Br, and I, respectively.

Reviews on van der Waals radii and their applications, mostly on main-group systems, were given by Desiraju[82] or Zefirov and Zorkii.[127] Further examples on contact distance histograms are given by Rowland and Taylor.[128] They first eliminate the covalent cases, and then pick for the typical A···B distance that corresponding to half-height of the first maximum in the remaining (R,n) histogram, where n is number of compounds, and finally fit these A···B distances to a set of $R^{vdW}(A)$. Their final radii turn out to be close to those of Bondi,[123] especially for halogens and sulfur.

The Ratio Q. A better measure on the weakness of the interaction seems to be the ratio

$$Q = (A \cdots A)/(A-A) \qquad (15)$$

where A···A is the intermolecular and A–A the intramolecular distance.[129,130]

Reed et al.[25] introduce as another measure the "covalency ratio"

Table 2. Rg–Rg Distances in Gaseous Dimers[a] and in Solids[b] (The present radii are given in the last column. Their sum is given in brackets.)

	Ne	Ar	Kr	Xe	R^{vdW}
Ne	309[a] (316)[b] [310]	348[a] [343]	365[a] [355]	388.8[a] [373]	155
Ar		376[a] (376)[b] [376]	389.4[a] [388]	409.2[a] [406]	188
Kr			401.7[a] (400)[b] [400]	420[a] [418]	200
Xe				436[a] (434)[b] [436]	218
Rn					224[c]

[a] From Xu, Y.-J.; Jäger, W.; Djauhari, J.; Gerry, M. C. L. *J. Chem. Phys.* **1995**, *103*, 2827–2833, Table 9. [b] Data for the *fcc* structure at 4 K from Kittel, C. *Introduction to Solid State Physics*, 6th ed.; Wiley: New York, 1986; Table 4. [c] Theoretical value from RnXe and Rn$_2$.[130]

$$\chi = (\sum R^{vdW} - R_e)/(\sum R^{vdW} - \sum R^{cov}) \quad (16)$$

Additive, "Rare-Gas" van der Waals Radii. Little information was available on the eventual additivity, eq 10, of the van der Waals radii.[79] Very recently, reliable experimental R_e values in all gas-phase AB dimers, A, B = Ne–Xe, have become available. For diatomic RnXe and Rn$_2$, theoretical values were produced.[131] As shown in Table 2, the corresponding R^{vdW} are closely additive for A ≠ B (for Ar, Kr, and Xe), and also close to those, obtained from solid, *fcc* rare gases.

We then propose to use the gas-phase dimer data in Table 2 to obtain the R^{vdW} in Table 3.

D. Bond Length–Force Constant Correlations

Raman studies have been used to look at the totally symmetrical M···M vibrations (M = Ag(I), Au(I), Pt-(IV), Tl(I), Pb(II), Bi(III)), since the work of Spiro.[133,134] The data can be correlated using the equation proposed by Herschbach and Laurie,[135]

$$R_e/pm = a + b \ln[F/(10^2 N/m)] \quad (17)$$

between the equilibrium distance, R_e, and the force constant, F. Harvey has used this relation for Au–Au distances over the entire range from 247 to 355 pm.[139] Theoretical calculations on $(XAuPH_3)_2$ dimer models[137] follow the same line. See Table 4 for the available parameters for various metal and Harvey[138] for a review, including heteronuclear examples.

An interesting puzzle is the dimeric $[IAuPMe_3]_2$, whose predicted Au–Au vibration could not be seen at all in the domain predicted by eq 17.[143]

An estimate for the M···M interaction energy can be obtained by deriving the Herschbach–Laurie eq 17 from the assumed potential

$$V(R) = Ae^{-BR} - CR^{-n} \quad (18)$$

The ab initio calculations for the $[XAuPH_3]_2$ models[137] suggest an effective n of about 2.5. Assuming that the first term dominates the force constant,

$$F = V''(R_e) \cong AB^2 e^{-BR_e} \quad (19)$$

Table 3. A Comparison of Isotropic van der Waals Radii, R_E^{vdW} (in pm) from Pauling (Ref 119, p 260), Bondi (Ref 123), the VCH Periodic Table (Ref 132), and the Present Rare-Gas Scale

E	Pauling	Bondi	VCH	present
H	120	120	100	**164**[a]
He		140		
Li		182		
C		170	170	
N	150	155	150	
O	140	152	140	
F	135	147	140	
Ne		154	150	**155**
Na		227		
Mg		173		**194**[b]
Si		210		
P	190	180		
S	185	180	180	
Cl	180	175	180	
Ar		188	180	**188**
K		275		
Ca				**214**[b]
Ni		163		
Cu		140		
Zn		139		
Ga		187		
As	200	185		
Se	200	190		
Br	195	185	200	
Kr		202	190	**200**
Sr				**222**[b]
Pd		163		
Ag		172		
Cd		158		
In		193		
Sn		217		
Sb	220			
Te	220	206		
I	215	198	220	
Xe		216	210	**218**
Ba				**244**[b]
Pt		175		
Au		166		
Hg		155		**208**
Tl		196		
Pb		202		
Rn				**224**
U		186		

[a] For a free hydrogen atom in vacuum. [b] Half of the M$_2$ dimer bond length, see: Allouche, A. R.; Aubert-Frécon, M.; Nicolas, G.; Spiegelmann, F. *Chem. Phys.* **1995**, *200*, 63–77, Table 4.

Table 4. Herschbach–Laurie Parameters for Eq 17 (Note that F is expressed in 10^2 N/m = 1 mdyn/Å)

system	a, pm	b, pm	ref
Cr–Cr	250	−74.6	138
Mo–Mo	287	−53.8	138
Rh–Rh	278	−28.7	140
Pd–Pd	267	−38.7	141
Ag–Ag	250	−30	139
	253	−28.4	138
W–W	293	−47.1	138
Re–Re	289	−45.8	138
Ir–Ir	292	−16.0	138
Pt–Pt	286	−22.3	141
Au–Au	268	−29.0	139
Au–Au	289	−20.6	137[a]
Hg–Hg	269	−24	142

[a] Ab initio values for $(XAuPH_3)_2$ model systems.[137]

one gets eq 17 with

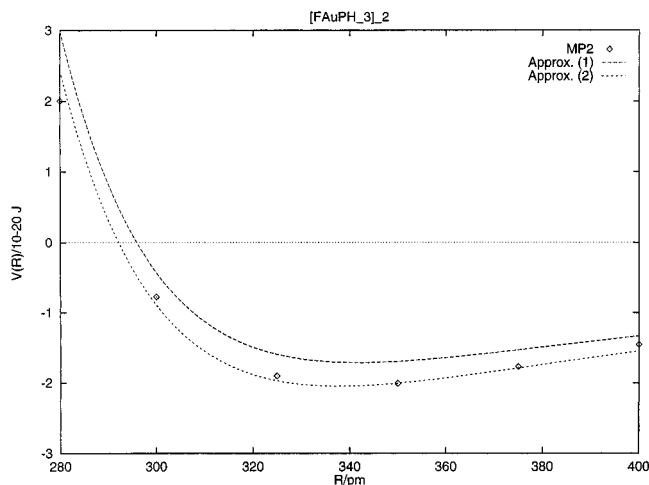$$a = B^{-1} \ln(AB^2) \quad b = -1/B \quad (20)$$

Figure 6. A fit of the ab initio points[137] for a perpendicular $[FAuPH_3]_2$ dimer to eq 18. Approximations 1 and 2 correspond to eqs 22 and 23, respectively.

Then, assuming that the attractive term dominates $V(R_e)$, and using $V(R_e) = 0$,

$$D_e = V(R_e) \cong -R_e F b / n \qquad (21)$$

Here b comes from the (experimental or theoretical) fit for a particular M···M pair while (R_e, F) come from measurements. For C one obtains the approximations

$$C^{(1)} = R_e^n D_e \qquad (22)$$

$$C^{(2)} = C^{(1)} + R_e^n b^2 F \qquad (23)$$

For an example, see Figure 6. Finally eqs 17 and 21 can be combined to

$$D_e = -(R_e b / n)(10^2 \text{N/m}) \, e^{(R_e - a)/b} \qquad (24)$$

III. Experimental Data

A. The d^{10}–d^{10} Case

Examples on short d^{10}···d^{10} distances exist for all three coinage metals.[39−71] Some of the earliest examples were AuCN,[144] Ag_2PbO_2 (304−328 pm), and $Ag_5Pb_2O_6$ (304 pm).[39] The *aurophilic*[57,145] or, more generally, *metallophilic*[137] attraction can lead to the formation of dimers, oligomers, infinite chains, or infinite, two-dimensional sheets. Statistical analyses of the structural data for gold(I) have been published in refs 146 and 147.

Literally hundreds of structural data exist. Some force constants have been obtained from Raman spectroscopy (see section II.D). A handful of experimental values for the Au^{I}···Au^{I} interaction strengths, $V(R_e)$, have been obtained from temperature-dependent NMR measurements, see Table 5. They vary from 29 to 46 kJ/mol.

Calorimetric measurements exist for the dimerization enthalpy of AgL^{+}. In propylene carbonate solution it has been measured to be −5(7) and −13(20)

Table 5. Measured Au^{I}···Au^{I} Interaction Strengths

system	R_e, pm	$V(R_e)$, kJ mol^{-1}	ref
RPC[(PPh$_2$)AuCl]$_2$	300.0(1)	29−33	148
(butadiene)[(PPh$_2$)AuCl]$_2$	302.3	29	149
(bicyclopropyl)[(PPh$_2$)AuCl]$_2$	308.5	29	150
H$_2$C[(PPh$_2$)-Au-S-tolyl]$_2$		42(4)	151
(CH$_2$)$_3$PPh$_2$AuS(CH$_2$)$_3$SAuPPh$_2$		42(4)	151
1,1′-(AuPPh$_3$)$_2$(C$_2$B$_{10}$H$_{10}$)$_2$	311.9	46	152

kJ mol^{-1} for L = dppe and dppm, respectively[153] (see the same paper for earlier DMSO work). Although of a reasonable order of magnitude, the results are too inaccurate for any conclusions to be drawn.

The dimers occur as unbridged ones, e.g. **1**,[154] singly bridged ones,[148] **2**, including the open A-frames,[155] **3**, as a special case, or doubly bridged, transannular ones, **4**. The bridges can be very long (nicely proving the metallophilic attraction). Local dimers can be identified in clusters,[158] **5**, or infinite chains, **6**. For concrete examples, see Figure 7.
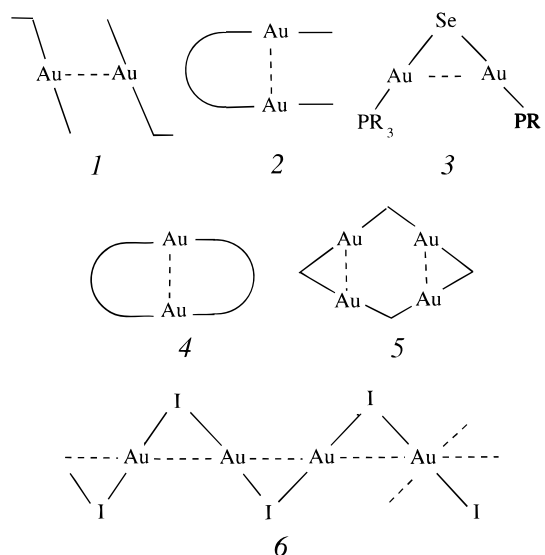
Various X−Au···Au−X dihedral angles can occur in the dimer, for two linearly coordinated metal atoms.

When comparing the three coinage metals, only silver is "normal". Copper, like other 3d metals, is anomalous having the compact, nodeless first d shell. Gold again mainly differs from silver due to relativistic effects.[94,159] Because relativistic effects considerably strengthen the aurophilic attraction, we start the discussion from gold.

Open A-Frames with Au···Au Interactions. The dimers with A-frame motifs, **3**, merit separate attention, see Table 6.

A neat example is (Ph$_3$PAu)$_2$C(CN)$_2$, where the Au−C−Au angle is only 87.7°, while the C−C−C of 113.4° is close to the tetrahedral angle.

In the extreme when the corner atom is Pt or a third Au, the A-frame approaches an equilateral triangle, with particularly short Au−Au distances. In the early examples,[160,173] three-center covalent bonding was thought to occur.

As a counterexample, in the [(PhHg)$_2$OH]$^{+}$ ion the Hg···Hg is 364 pm but the open angle Hg−O−Hg = 126° precludes a metallophilic attraction.[188]
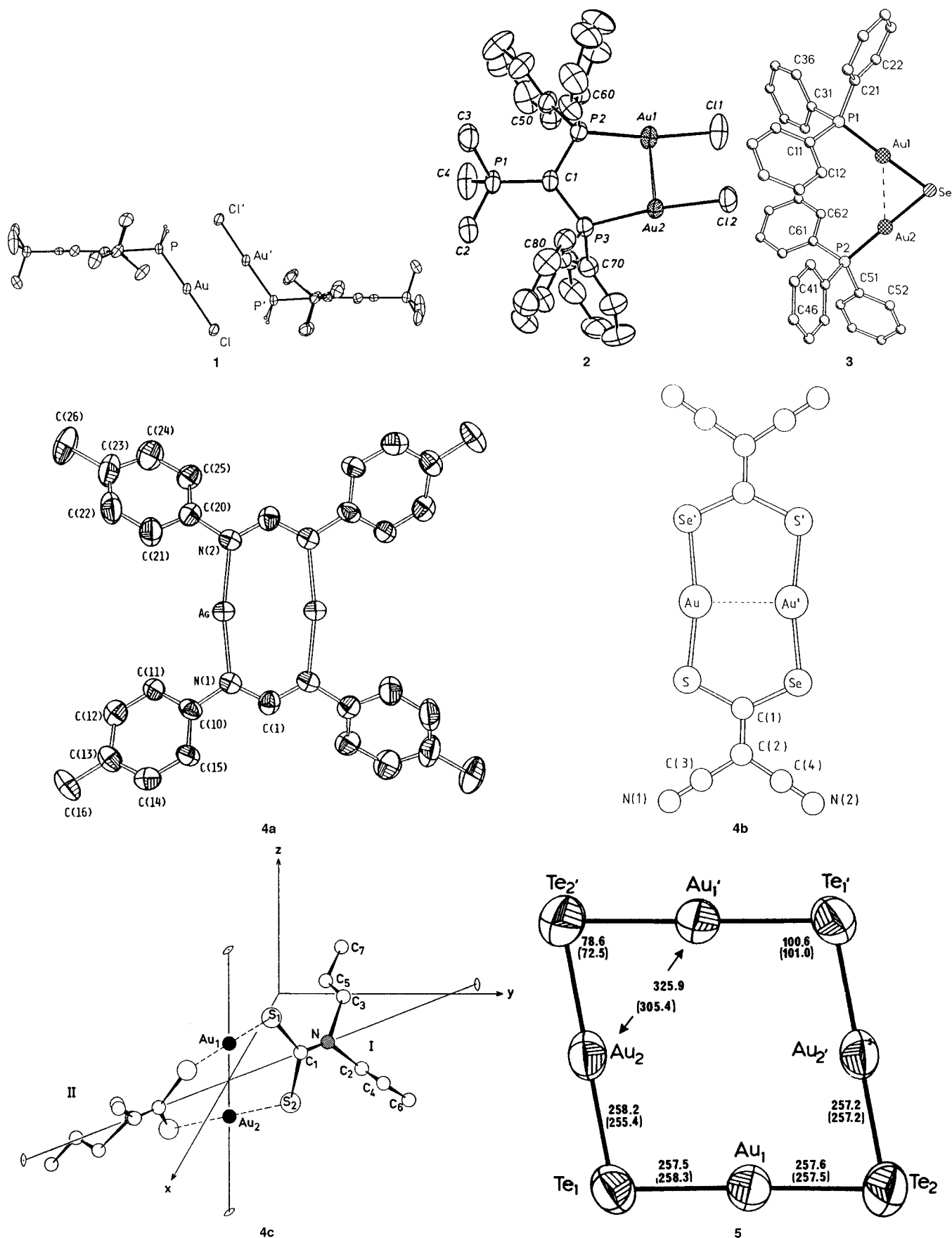
Figure 7. Experimental structures of 2,4,6-(ʹBu)₃C₆H₂PH₂]AuCl (Au···Au = 344 pm): **1**,[154] (Me₃P)=C[PPh₂AuCl]₂ (300 pm), **2**,[148] Se[AuPPh₃]₂ (305.1 pm), **3**,[155] Ag₂(form)₂(270.5 pm), (the analogous Cu···Cu is 249.7 pm), **4a**,[156] [Au(i-mnts)]₂²⁻ (281 pm), **4b**,[157] [Pr₂NCS₂Au]₂ (276 pm), **4c**,[41] Te₄Au₄⁴⁻ (305 or 326 pm), **5**.[158] (**1**: Reprinted from ref 154. Copyright 1990 Weinheim. **2**: Reprinted from ref 148. Copyright 1988 VCH Verlagsgellschaft. **3**: Reprinted from ref 155. Copyright 1991 Weinheim. **4a**: Reprinted from ref 156. Copyright 1988 American Chemical Society. **4b**: Reprinted from ref 157. Copyright 1992 Barth. **4c**: Reprinted from ref 41. Copyright 1961 MacMillan. **5**: Reprinted from ref 158. Copyright 1985 VCH Verlagsgellschaft.)

Table 6. Geometries of A-Frame Systems ($n = 2$), Tripodes ($n = 3$), and Tetrapodes ($n = 4$), $L'_m E(ML)_n$

n	E	M–E	M···M	M–E–M	system	ref
2	C	211(av)	289	86.3	$(Ph_3PAu)_2\mu\text{-}C(PPh_3)CO_2Et^+$	160
2	C	210	291	87.7	$(Ph_3PAu)_2C(CN)_2$	161
2	C	210,211	299	90.2	$[(Ph_3PAu)_2C(PPh_2AuPPh_2)_2]^{2+}$	162
2	N	220	303		$(NO_2)(o\text{-}C_6H_4)N(AuPPh_3)_2$	163
2	P[g]	240.6(av)	296.5		isophosphindoline Ag_2	164
2	S	216	302	88.7	$(Ph_3PAu)_2S$	165
2	Cl		306(av)	81.7(av)	$(Ph_3PAu)_2Cl^+ClO_4^-$	166
2	Fe	253.8(av)	291.9(av)	70.2	$[Fe(CO)_4(AuPPh_3)_2]$	167
2	Se	239.6	305	79.1	$Se(AuPPh_3)_2$	155
2	Se	239.6		75.4	$Se(AuPH_3)_2$	168[a]
				87.3		b
				97.8		c
				111.9		d
2	Se	227	313	87.2	$SeCu_2$	169[c]
2	Se	220	252	69.9	$SeCu_2$	170[a,e]
2	Se	220	269.5	75.4	$Se(CuPH_3)_2$	170[a,e]
2	Se	221	269.0	74.9	$Se(CuPMe_3)_2$	170[a,e]
2	Te	257	326	78.6	$[Ph_4P]_2[K_2Au_4Te_4(en)_4]$	158
2	Te	257	305	72.6	$[Ph_4P]_2[K_2Au_4Te_4(dmf)_2(CH_3OH)_2]$	158
2	I	262(2×)	308(4×)	72	$[AuI]_\infty$	171
2	Os	266(av)	293	66.9	$[Os(CO)_4(AuPPh_3)_2]$	172
2	Pt	260	274	63.5	$[Cl(Et_3P)_2Pt(AuPPh_3)_2]^+$	173
3	N[h]	203(av)	309	99(av)	$[R\text{-}N(AuPPh_3)_3]^+$	174
3	O	197	303–321	103	$(Ph_3PAu)_3O^+BF_4^-$	175
	O	205(av)	309(av)	97.8(av)	$((o\text{-}tol)_3PAu)_3O^+BF_4^-$	176
	O	203	319.8	103.7	$(^iPr_3PAu)_3O^+BF_4^-$	177
3	S	228	325	90.8	$(^iPr)_3PAu]_3S^+BF_4^-$	178
3	Te	251	313(av)	77	$[KAu_9Te_7]^{4-}$	158
3	Te	260(av)	324(av)	75(av)	$[(Ph_3P)Au]_3Te^+$	179
4	B[f]	216–219	282(av)	81	$(Cy_3P)B[Au(PPh_3)_3]_4^+BF_4^-$	180
4	C[f]	213	279–282	82–83	$HC[Au(PPh_3)_4]^+$	181
4	P	237	297(av)	77.6	$[(o\text{-}Tol)P(AuPPh_3)_4]^{2+}$	182
4	P[f]	237	294(av)	76.7(av)	$[P(AuPPh_3)_5]^{2+}$	183
4	P[f]	237	293.6	76.6	$[(Ph_3PAu)_4\text{-}PAuP\text{-}(AuPPh_3)_4]^{3+}$	184
4	S	240(av)	291(av)	74.6(av)	$(Ph_3PAu)_4S^{2+}$	185
4	As	250	290	70.7	$As(AuPPh_3)_4^+$	186
4	As	261	296	69.1	$As(AuPPh_3)_4^+$	187

[a] Relativistic and correlated (MP2) calculation. [b] Nonrelativistic and correlated. [c] Relativistic SCF. [d] Nonrelativistic SCF. [e] The CCSD(T) results are closely similar. [f] Capped tetrapode, $m = 1$. [g] Capped A-frame, $m = 2$. [h] Capped tripode, $m = 1$.

In addition to these "open A-frame" structures there are bridged ones, **7**, typically with two d^8 metal atoms.[189]

7
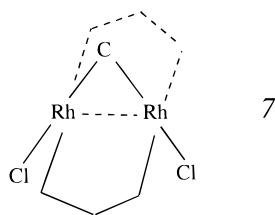
Further Examples on d^{10} Dimers. Both Ag(I) and Hg(II) have a lesser tendency for M···M interactions than Au(I).[190] A summary on early work on attractions between Ag(I) ions was given in ref 191. Karsch and Schubert[192] find for the doubly bridged $[CMe_2PCH_2PMe_2)]_2Ag_2^{2+}$ an Ag···Ag of 304 pm. Tsuda et al.[193] find in $[Ag_2(C_8H_6N_2)_2]\cdot 2ClO_4$, **8**, an Ag···Ag distance of only 275.6(1) pm. Obviously, the bridging naphthyridine rings play a role.

Constable et al.[194] prepared double-helical Cu(I) and Ag(I) quaterpyridine complexes, in which the Ag···Ag of 310.7 pm suggests an interaction while the Cu···Cu of 317 pm does not. Potts et al.[195] have a double helix with Cu···Cu = 263 pm.

Adams et al.[196] found two silver ions with Ag···Ag = 317 pm in one macrocycle complex. The crystal structure of silver oxalate, $Ag_2C_2O_4$, contains pairs of Ag^+ ions at 294.5 pm.[197]


8
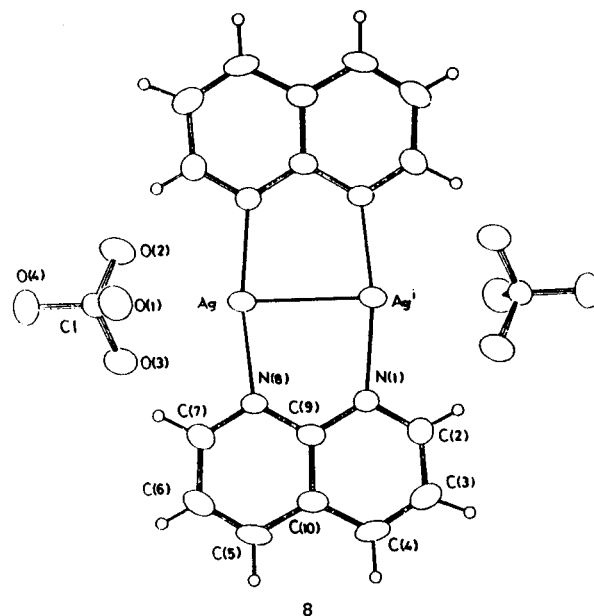
In ref 198, an $[Ag_3L_2I_3]$ complex with a particularly short, triply iodine bridged Ag···Ag of 280.5 pm is found. The corresponding force constant, F, is 47 N m^{-1}. For an F versus R plot, see ref 139.

Heine et al.[199] find a Cu(I)···Cu(I) distance of 236.9(1) pm in $[Cu_2R_2BrLi(thf)_3]$, R = Si(SiMe_3)_3, **9**. Note that the other two ligands are soft, $2 \times$ Si for Cu(1), and Si and Br for Cu(2).
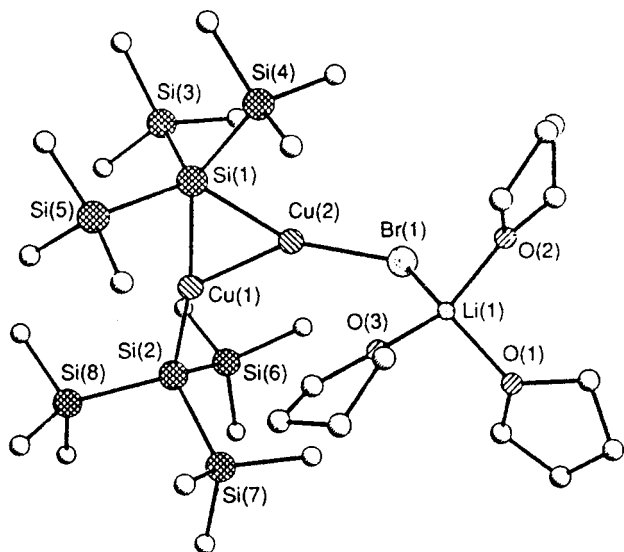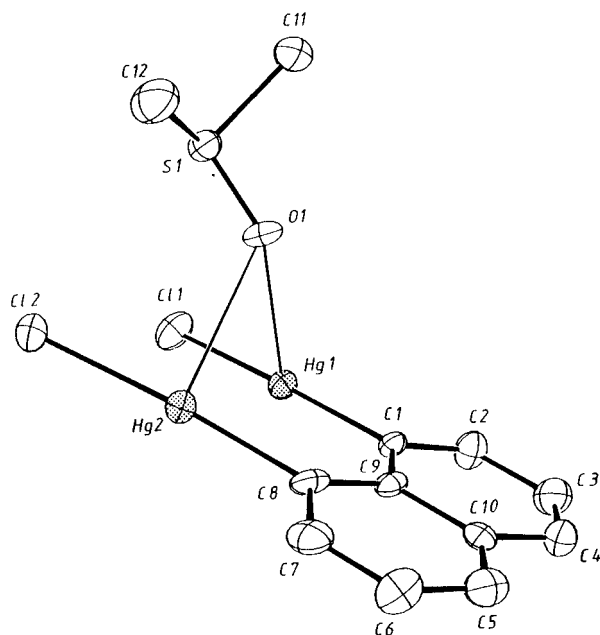
9

The Hg^{II}···Hg^{II} examples are not numerous. In Hg$_2$[Pt(μ_2-CO)$_3$L$_3$]$_2$, L = −PPh^{i}Pr$_2$, a Hg···Hg of 322.5 pm is found.[200] In this compound, however, the Pt−Hg distances are short, 293−308 pm. A very short Hg^{II}···Hg^{II} distance of 279.7(1) pm occurs in the *peri*-dimercurated naphthalene dimer [C$_{10}$H$_6$]$_2$Hg$_2$, **10**; in the half-open DMSO complex **11** the distance is 310.2(1) pm.[201]
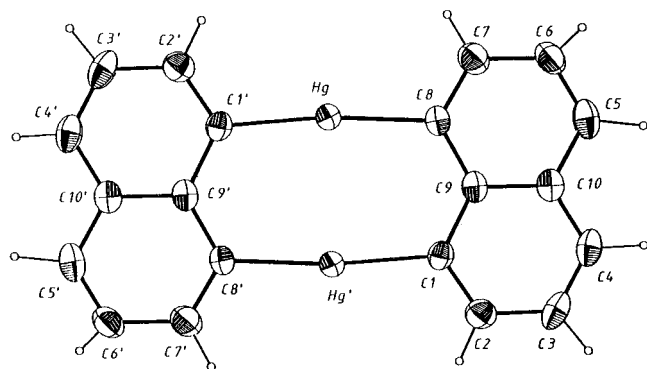

10

11

Ag versus Au. There are few examples that would permit a clean comparison of Ag···Ag and Au···Au metallophilic bonding.

With the reservation that the anions are different, it is interesting to note that in [Ag(NH$_3$)$_2$]NO$_3$ and the recently prepared [Au(NH$_3$)$_2$]Br the M−N distances are 212 and 201−203 pm but the M···M distances 313 and 341 pm, respectively.[202] In other words, gold makes here shorter intramolecular but longer intermolecular bonds.

M(0)···M(0), M = Pd, Pt. Unsupported bonds between two Pt(0) centers were reported by Otsuka.[203] In [Pt(^{t}Bu)$_2$P(CH$_2$)$_3$P(^{t}Bu)$_2$]$_2$, the Pt(0)···Pt(0) distance is 276.5(1) pm and the P−Pt−P angle only 102.6°. Pan et al.[204] report the bridged Pd(0)···Pd(0) dimer **12** with an intermetallic distance of 276.11(5) pm. The P−Pd−P angles are 164.96(4) and 162.74-
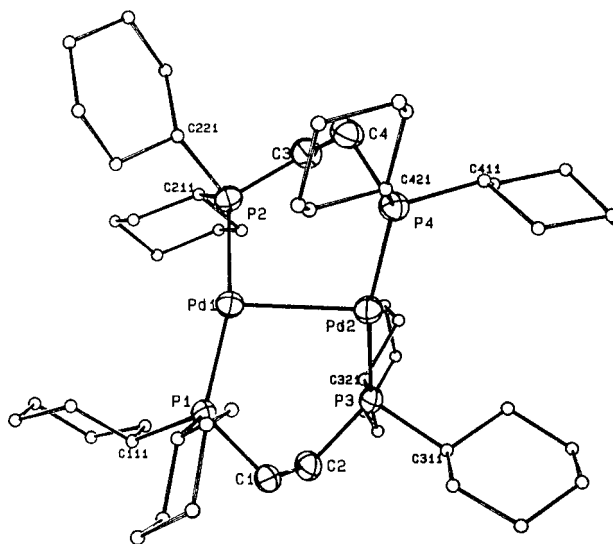
12

(5)°. An appealing example is the "manxane" structure **13** of [Pt$_2$(μ-dppm)$_3$] with Pt···Pt of 302 pm.[205] The chemistry of diplatinum centers was reviewed by Anderson;[206] the Pt^I−Pt^I range is 262−277 pm.
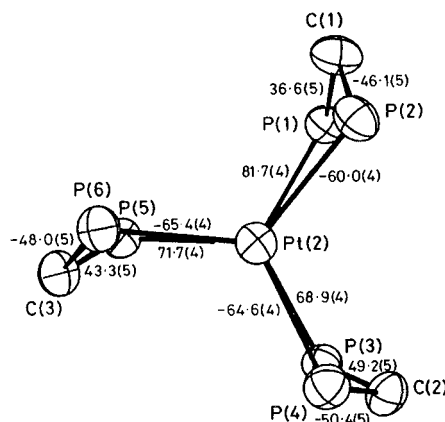
13

Mixed Dimers. Many dimers of two different d^{10} atoms are known. Bennett et al.[207] found in the singly bridged ClHg(*o*-C$_6$H$_4$)(PPh$_2$)AuCl an Hg^{II}···Au^I of 311 pm. Other examples by Wang and Fackler are [HgAu(CH$_2$SPPh$_2$CH$_2$)$_2$]PF$_6$ (293.4(1) pm)[208] or [HgAu-(CH$_2$P(S)Ph$_2$)$_2$]PF$_6$ (308.8(1) pm).[209]
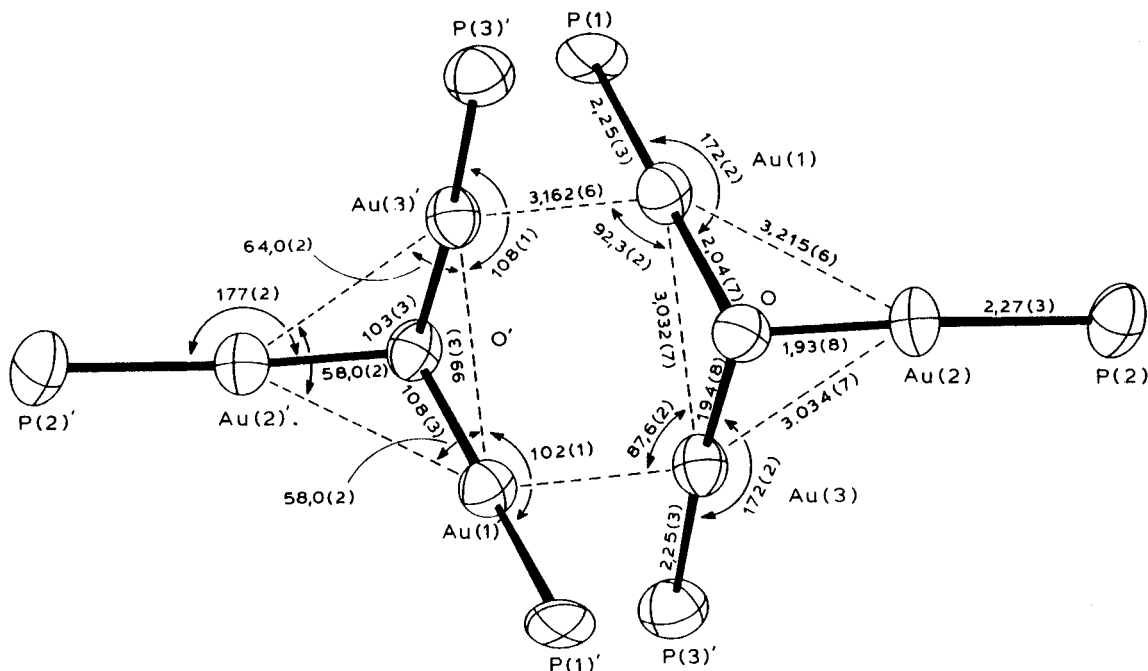
Figure 8. The coupled tripodes in the cation **14**. (Reprinted from ref 175. Copyright 1980 Elsevier.)

For structural data on Au−Ag−Au trimers, and a summary on Au−Ag interactions, see ref 210.

Bridged, Diamond-Shaped M(μ-X)$_2$M Systems. Alemany and Alvarez[211] summarized experimental data and EHT-level calculations for $L_2M(\mu\text{-}XR_n)_2ML_2$ systems for the d^{10} metals M = Cu(I), Zn^{II}−Hg^{II}.

Allshouse et al.[212] reported Ag_2S_2 ring motifs with Ag···Ag of 307−335 pm.

Tripodes. Several E(AuL)$_3$ motifs, like **14**, with more or less C_{3v} local symmetry, are mentioned in Table 6. An interesting case is (Ph$_3$PAu)$_3$O(BF$_4$) (Figure 8),[175] in which two real, charged (Ph$_3$PAu)$_3$O$^+$ cations in the tetrafluoroborate salt are held together by interionic Au···Au interactions at 316 pm. The intraionic, average Au···Au distance is 309 pm.

If the phenyl groups are replaced by the smaller methyl groups, the OAu$_3$ motifs form a tetrahedral intermolecular arrangement with average Au···Au of 325 pm.[213]

Tetrapodes. Perhaps the most remarkable tetrapode so far is the C_{4v} tetragonal pyramidal [As-(AuPPh$_3$)$_4$]$^+$ ion, **15**.[186] Our ab initio MP2 calculations[187] on [E(AuPH$_3$)$_4$]$^+$ models indeed give a lower energy for C_{4v} than for T_d for both E = P and As, and indeed give a tetrahedral geometry, as observed,[214] for E = N. At HF level all three systems remain tetrahedral.

Experimentally, only approximate (pyramidal, four-coordinate) E = P tetrapodes have been reported so far.[215]

In ref 216 the corner atoms are S or Te, with Au···Au 326 and 362 pm, respectively. In ref 217, the corners are Ru(CO)$_4$ and the Hg^{II}···Hg^{II} are 353 pm, with the Ru−Hg−Ru = 172°.

Dimers of Dimers. The structure of silver(I) glutarate consists of an intramolecular Ag···Ag pair at 280 pm in one plane and 320 as well as 342 pm between the planes.[218]

**Particularly short Au···Au distances** tend to occur when the ligands are "soft". Anticipating the discussion in the theoretical section, we list a number of such cases in Table 7. Note that the M···M
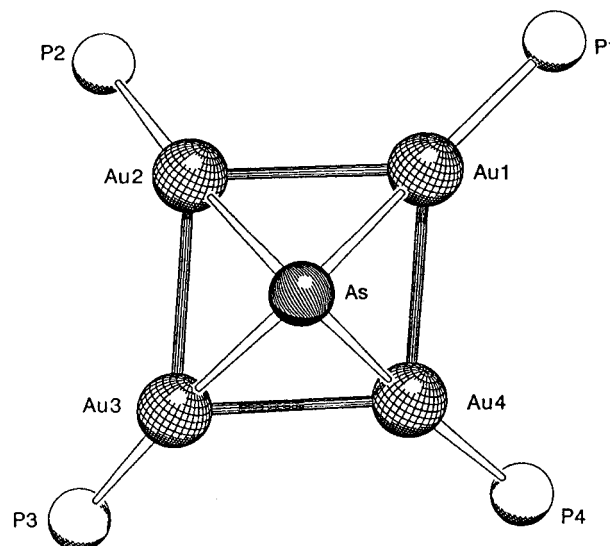
15

distances between M(I) ions (M = Cu, Ag, Au) can be shorter than in the metal. Further examples can be found in ref 54.

Concerning the influence of the organic group R in the PR$_3$ phosphines on the secondary Au···Au distance, Dávila et al.[229] find a decrease in the order:

$$PCy_3 > PMe_3 > PPh_3 > PEt_3 > P(OPh)_3 \qquad (25)$$
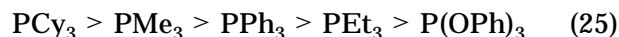
Even shorter Au−Au distances occur in formally Au(II) compounds. As emphasized by Hoffmann[230] (see their **9**), the border between Au(I) and Au(II) may be diffuse. Consider as an example the chain of four gold atoms in Figure 9. Recall the existence of the ClO$_4^-$ anions outside the Au^I···Au^I axis in **8**, of ref 193. [Recent calculations on Au^I···Au^I interactions across ring systems suggest that the effect of explicitly including the counterions is minimal.[232]]

Halogenocuprates(I) and Halogenoargentates-(I). Hartl et al.[233] report intraionic Cu^I···Cu^I dis-

Table 7. M(I) Systems with Particularly Short M···M Distances (In metallic Cu, Ag, and Au the M−M are 256, 289, and 288 pm, respectively. For further examples, see Table 2 of ref 56.)

M···M, pm	compound	coordination	ref
235	(CuN$_5$R$_2$)$_3$, R = p-tolyl	see **41**	219
243.7(8)– 249.6(9)	Cu$_5$Mes$_5$	(−C−Cu−)$_5$ ring	220
245	Cu$_2$[PhNNNPh]$_2$	(−N−Cu−N−)$_2$	52, p 1104
249.7(2)	Cu$_2$(form)$_2$	(−N−Cu−N−)$_2$	156
270.5(1)	Ag$_2$(form)$_2$	(−N−Ag−N−)$_2$	156
273.3(3)	Ag$_4$Mes$_4$	(−C−Ag−)$_4$ ring	220
269.7(1)	Au$_5$Mes$_5$·2(thf)	(−C−Au−)$_5$ ring	220
276	R$_2$N−C[SAuS]$_2$C−NR$_2$, R = Pr	(S−Au−S)$_2$	41, 221
278	[Au$_2$(i-MNT)$_2$]$^{2-}$		222
284.6(2)	Au$_2$(dtsq)$_2$$^{2-}$	(S−Au−S)$_2$	223
286.7(1)	[Au$_2$-μ-(i-MNT)μ-(dppee)]	(P−Au−S)$_2$	224
287.2(2)	[Au$_2$(dmpe)$_2$](ClO$_4$)$_2$·H$_2$O	(−P−Au−P−)$_2$	225
292.0(1)	[Au(TPAH)I][AuI$_2$]		226
296.0(1)	(Ph$_3$P)AuGeCl$_3$		227
297.7(10)	[Co$_2$Au$_2$(CO)$_6$(μ-dppm)$_2$]	(−Co−Au−P−)$_2$	228

3

Figure 9. The chain of four gold atoms in [(pta)$_3$Au]$_2$Au$_2$(i-mnt)$_2$·0.5Me$_2$CO·0.5MeCN. Au(1)−Au(2) = 312.0(1), Au(2)−Au(3) = 279.9(1), Au(3)−Au(4) = 311.1(1) pm. (Reprinted from ref 231. Copyright 1994 Royal Society of Chemistry.)
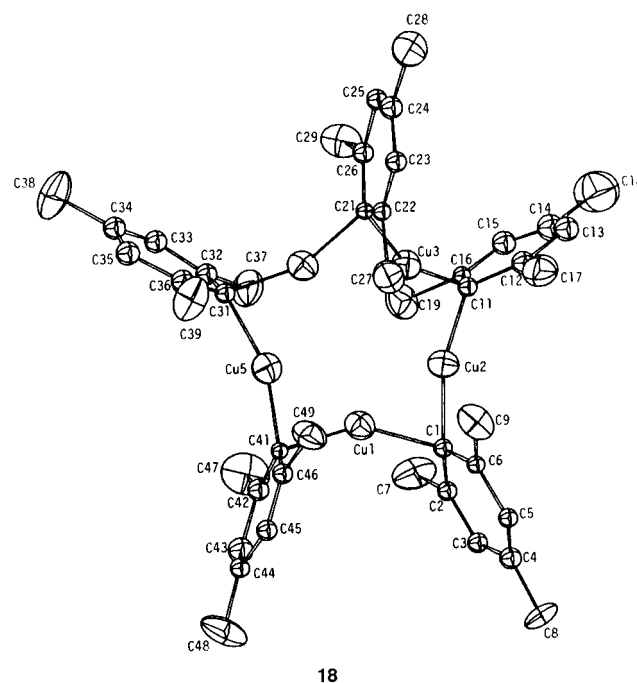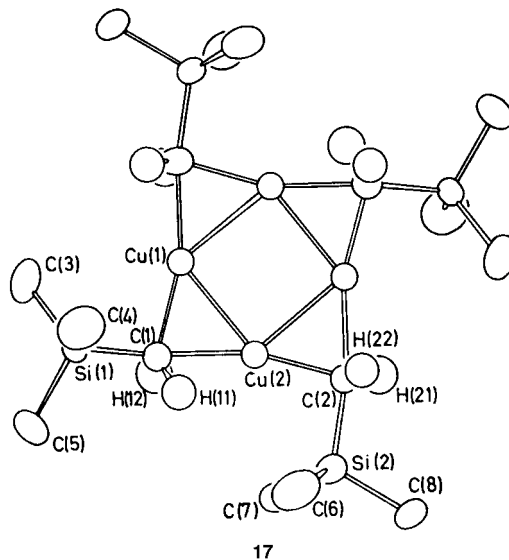
tances from 265 to 295 pm for various [Cu$_2$I$_4$]$^{2-}$ groups, **16**.

Jagner and Helgesson review all these species, like the doubly bridged [Cu$_2$X$_4$]$^{2-}$, X = Cl, Br, I, reaching Cu···Cu distances of >243 pm and small Cu−X−Cu angles of >61°.[234] For a theoretical analysis of the halogenocuprates at EHT level, see Subramanian and Hoffmann.[235]

16

Hou et al.[236] found a case with an analogous [Ag$_2$I$_4$]$^{2-}$ anion having Ag···Ag of 311 pm. Piché and Harvey[237] report for the central, Ag$_2$X$_2$ "diamond" of Ag$_2$(dmb)$_2$X$_2$ an Ag···Ag distance of 345.1, 334.5, and 337.8 pm for X = Cl, Br, and I, respectively. The trend perhaps reflects a balance between softness and ionic size.

Bridged, n-Membered Rings, n > 2. As examples of tetramers and pentamers, we show [CuCH$_2$-SiMe$_3$]$_4$, **17**, Cu···Cu = 241.7 pm;[238] [Cu(2,4,6-Me$_3$-(C$_6$H$_2$)]$_5$, **18**, Cu···Cu(av) = 249 pm; and the corresponding [Au(2,4,6-Me$_3$(C$_6$H$_2$))]$_5$·2(thf), Au···Au = 269.7 pm.[220]

17

18

In ref 239 the metals are Cu(I) and Ag(I) and the four corners are amide nitrogens, with the N−M−N bond angles slightly bent inward.

Kühnel and Range[240] find in Rb[Ag(CN)$_2$]·0.4H$_2$O the Ag(I) ions in 3- and 8-membered rings, with the shortest Ag···Ag equal to 305 pm. In [Ag$_4$(μ_2-Fe-(CO)$_4$)$_4$],$^{4-}$ Figure 10, there are two short Ag···Ag of
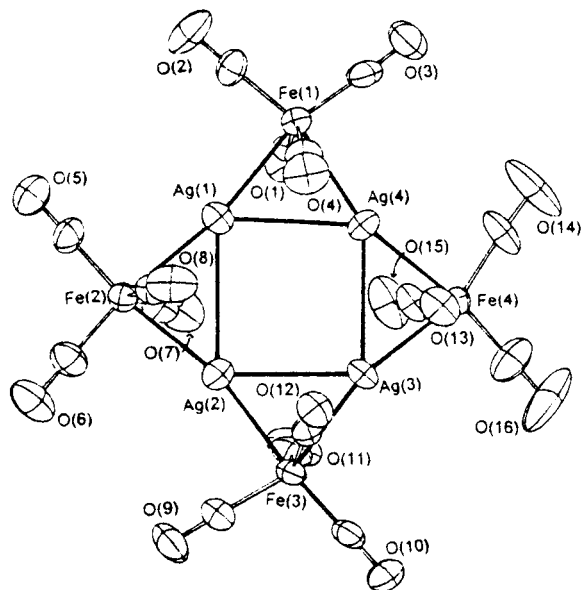
Figure 10. The structure of $[Ag_4Fe_4(CO)_{16}]^{4-}$ (Reprinted from ref 241. Copyright 1994 American Chemical Society.)

Table 8. Binary Coinage-Metal Compounds, MX, with Short M···M Distances (The number of M−M contacts is denoted by "CN".)

case	M−X, pm	CN	M···M, pm	M−X−M	ref	comments
Au_2P_3	232−234	2	293		248	$P_{3n}{}^{2n-}$
		2	314			polyanion
AuCl	236	4	337	92	249	
"I"-AuBr	240	4	347	92.3	250	"AuCl", lemon-yellow
"P"-AuBr	244	4	304	77.1	250	"AuI", yellow-brown
AuI	262	4	308	72.6	251	

Three-, five-, and six-atomic gold chains with mixed valencies were reported by the Zaragoza group.[245] In the symmetrical six-atomic chain, starting from the end, the Au−Au distances were 265.4, 273.7, and 283.8 pm. That middle distance was shorter than the 297.7 pm in the parent compound $[Au(CH_2PPh_2-CH_2)_2Au]$.

A bent, four-atomic Ag chain with Ag···Ag distances of 318, 305, and 312 pm was found in $[Ag_6(PPh_2)_6(P^tBu_3)_2]$ in ref 246.

Furet et al.[247] list a number of $M_8(\mu_4\text{-}E)_6L_n$ species (E = S, Se, PR), such as the 120 VE $Ni_8(\mu_4\text{-}PPh)_6-(CO)_8$, with a Ni···Ni of 265 pm, and attribute a part of it to a through-space M−M interaction.

Binary compounds of coinage metals with short $M^I···M^I$ distances are discussed in Table 8. While the silver halides, AgX, have a NaCl structure for X = F, Cl, and Br and either ZnS or wurtzite structures for AgI,[251] the gold halides AuX (X = Cl, Br, I) have infinite chain structures −Au−X−Au−X−, **6**. Actually each Au is surrounded by *four* such neighboring Au atoms. The Au−X−Au angle and Au···Au distance are large in AuCl and much smaller, despite of the longer primary bond length, in AuI. AuBr is bistable, having four modifications[252] of which the "I" phase resembles AuCl and the "P" phase resembles AuI. In the latter structure, the Au···Au attraction may indeed be the driving force. The role of these metal−metal interactions was discussed earlier in refs 171 and 253.

Short Cu···Cu distances occur in copper sulfides, like in chalcocite, Cu_2S (259 pm) and djurleite $Cu_{1.96}S$ (264 pm).[254]

Ternary Compounds of Coinage Metals. Hoppe[255] found in KAgO almost square $Ag_4O_4{}^{4-}$ groups with Ag···Ag of 291 pm and Ag−O−Ag of 84.2°. CsAgO, CsAuO, and KCuO[256] share the same structure.

Infinite chains, exhibiting ···M···M···M··· secondary bonding, occur in the isoelectronic $[AuE^-]_\infty$ chains of MAuE, M = K, Rb, Cs; E = S, Se, Te.[257,258] It is noteworthy that the shortest Au···Au of 297 and 311 pm occur for RbAuTe and CsAuTe, having E = Te and containing the 2-dimensional structure in Figure 11b. The single chains in Figure 11a have Au···Au of 326−343 pm.[258] Of the nine combinations, KAuTe has a different structure. For further examples of ternary systems, see section III.D.

More Chains. Cui and Kertesz[59] compiled data for 26 linear, nine zigzag, and four helical chains involving the d^{10} metals Cu(I), Ag(I), Au(I), Cd(II),

304 pm (av) and two long ones of 325 pm (av).[241] The analogous $[Au_4Fe_4(CO)_{16}]^{4-}$ anion can assume either a nearly square, D_{4h} conformation (Au···Au 297 and 283 pm) or a strongly distorted, D_{2h} one (293 and 340 pm).[242] In solid $[Fe(CO)_4(AuPPh_3)_2]$ A-frame,[167] the Au···Au vary from 290 to 294 pm.

Jarvis et al.[243] found in 1973 for $(Me_3SiCH_2Cu)_4$ a square-planar, tetranuclear Cu(I) structure with Cu···Cu 241.7 pm and the C−Cu−C of 164° bent inward.

As for copper, Abraham et al.[244] compare the $Cu^I···Cu^I$ in (μ-(phenylimino)(2,6-dimethylphenoxy)-methanethiolato)copper(I) tetramers and hexamers. The results are 260−277 and 281−325 pm, respectively.

Other d^{10} Oligomers. Eastland et al.[191] found in $[Ag(imid)_2(ClO_4)]_6$ the unbridged structure **19** with an Ag−Ag of 349 pm in the central triangle and 305 pm in the peripheral ones.

19

a
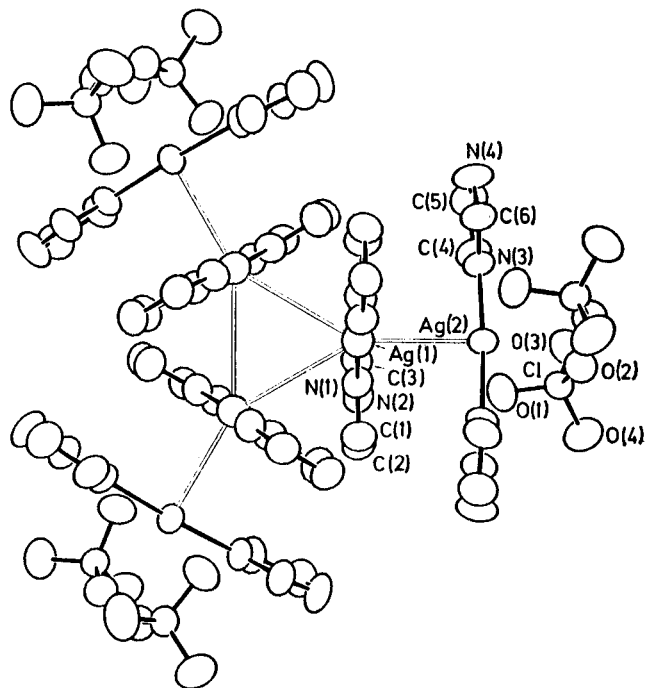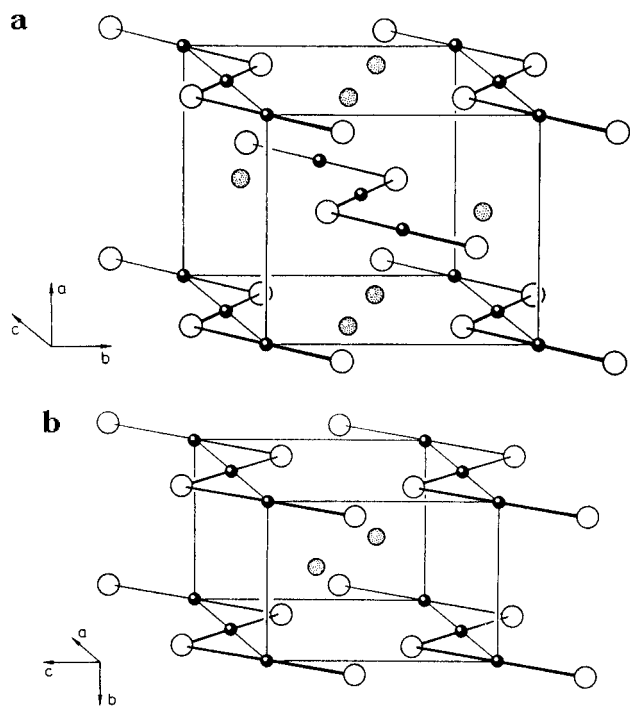

b

Figure 11. The chain structures of (a) KAuS, RbAuS, CsAuS, KAuSe, RbAuSe, and CsAuSe as well as of (b) RbAuTe and CsAuTe. (Reprinted from ref 258. Copyright 1992 Elsevier.)
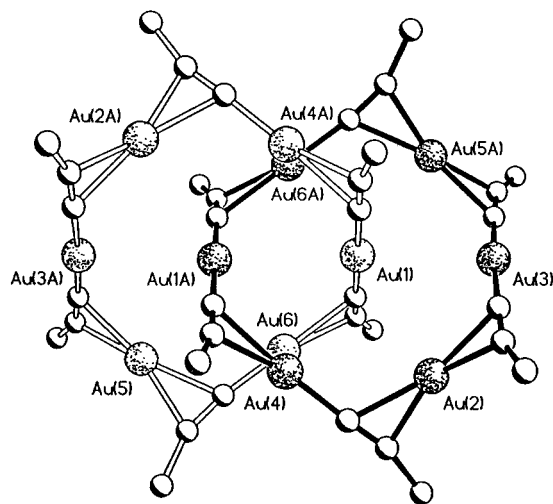

Figure 12. A [2]catenane [[Au(C≡C-^{t}Bu)]$_6$]$_2$ of monovalent gold. (Reprinted from ref 264. Copyright 1995 VCH Verlagsgesellschaft.)
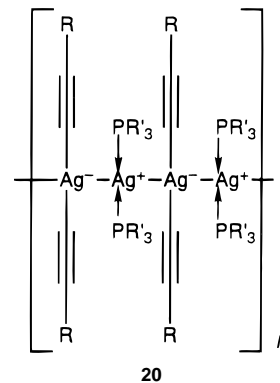
or Hg(II). They also present an EHT- or MNDO-level band structure analysis and conclude that electronegative bridging groups diminish and electropositive ones increase the M···M interaction. Further data exist for Cu(I)···Cu(I) chains in dithiosquarates (ref 259, Cu−Cu 257−276 pm).

Masciocchi et al.[260] compare the intra- and intermolecular M···M distances in Cu(pz), Ag(pz), and (Cu,Ag)(pz) (pz = pyrazolate). They are 316 and 334 pm for Cu and 340 and 327 pm for Ag, respectively.

Arai[261] found in 1962 a chain structure for ClAuPCl$_3$. Adams et al.[49] find in the pyridine complex AuI·py an −AuX$_2$−Au(py)$_2$−Au(py)$_2$−AuX$_2$−··· chain with shorter Au···Au distances of 299 and 329 pm for X = I and longer ones of 325 and 342 pm for X = Cl. The values are for the Au in X···py and py···py, respectively.

Perreault et al.[136] find an infinite chain with Au···Au of 330.6 pm in Au$_2$(tmb)Cl$_2$ (tmb = 2,5-dimethyl-2,5-diisocyanohexane).

Ahrland et al.[147] find for [Au(C$_4$H$_8$S)Cl] and -Br molecular chains with Au···Au of 332 and 335 pm, respectively, whereas [Au(C$_4$H$_8$Se)I] has alternating Au(C$_4$H$_8$Se)$_2$$^+$ and AuI$_2$$^+$ groups and Au···Au of 299 and 300 pm. An analogous, alternating structure is found in the ethynyl derivative −[Ag(C≡C−CH$_3$)$_2$)]−[Ag(PMe$_3$)$_2$]−$_∞$, **20**, Ag···Ag = 303.3 pm.[262] Several other oligomers and chains are mentioned by King,[67] who uses hybridization arguments to discuss the results. Jaber et al.[263] report Ag···Ag = 315 pm in amminesilver(I) p-nitrobenzoate.

20

A striking, catenane gold chain structure with both intraring and inter-ring Au···Au interactions was just reported by Mingos[264] for [Au(C≡C(^{t}Bu))]$_n$, see Figure 12. The structure of ZnAu$_2$(CN)$_4$ consists of six interpenetrating quartz-like nets and has Au···Au contacts of 311 pm.[265]

Sheets. Of the two linear gold compounds, AuCN forms infinite Au−CN−Au chains, with a hexagonal, Au···6Au (340 pm) arrangement, in the cation plane.[144] The latest data[266] report a lattice parameter, a, of 339.5 pm. The compressibility along the a axis is 4.0 times larger than along the c axis. AgCN has a similar structure, with Ag···Ag 347 pm.[267] Esperås[268] found in cyano(methylisocyanide) gold(I) a roughly hexagonal surrounding around each Au atom with the six Au···Au 352−372 pm. He points out that the insolubility of the sample in both organic solvents and water gives further support for weak gold−gold bonding. The (OC)AuCl forms a square lattice of antiparallel molecules, Au···4Au (338 pm).[269] Both silver ketenide, Ag$_2$C=C=O, and its pyridine adduct contain a square lattice of Ag(I) ions with an Ag···Ag or 284 and 285 pm, respectively.[270] Now the ketenide stands in the middle of the square.

The structure of CsFe$_{0.72}$Ag$_{1.28}$Te$_2$ has tellurium-capped squares of the metal M (Ag or Fe) with M···M of 319 pm.[271]

A hexagonal Ag$^+$ plane is found in KAgCO$_3$ (Ag···Ag ≥ 297 pm)[56] while in Ag$_3$BO$_3$ and AgBO$_2$ the three Ag$^+$ triangles form more complicated patterns.[272] In Eu[Ag(CN)$_2$]$_3$·3H$_2$O, the arrangement is shown in Figure 13.

In Na$_2$PdH$_2$, the Pd(0) form a square lattice with Pd···Pd of 360 pm.[274]

Fischer et al.[275] report neutron diffraction structures of TlAu(CN)$_2$ as function of temperature. The nearest-neighbor Au^I···Au^I distances are 290−300 pm and decrease by about 5 pm when T decreases from
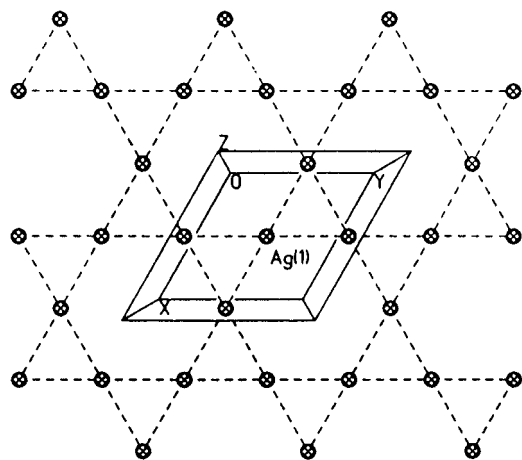
Figure 13. The arrangement of Ag$^+$ ions in Eu[Ag-(CN)$_2$]$_3$·3H$_2$O from Assefa et al.[273] (Ag···Ag 334 pm). (Reprinted from ref 273. Copyright 1995 Munksgaard.)

Figure 14. The Ag^I···Ag^I framework in Ag(4,4′-bpy)·NO$_3$. Reprinted from ref 282. G is a guest molecule.

300 to 5 K. The next-nearest-neighbor Au···Au distances are about 350 pm and the Au^I···Tl^I distances in the same crystal are about 340−350 pm.

Two-dimensional arrays of Au(I) ions occur in M[Au(CN)$_2$], M = K, Cs, etc.[276] Large pressure-induced effects are observed on the optical emission energies.

Liquid Crystals. Liquid crystals containing Pd, Pt, Rh, or Au have been prepared but no unequivocal evidence exists for the M···M attraction in the formation of liquid crystalline structures.[277] A closer look, however, reveals dimers of Pd, Ag, and possibly Pb in various liquid-crystal materials.[278] The liquid-crystalline gold−isonitrile complexes of Kaharu et al.[279] do not show short Au···Au distances in the solid state. The role of coinage-metal M^I···M^I dimers in certain double-helical structures is discussed in "Further Examples on Dimers" and "More Chains".

Knitted Polymeric Structures. Balch et al.[280] show that (AuI)$_2$(μ-dpph) forms interwoven polymeric chains with Au···Au = 312.4 pm while the corresponding AuCl$_2$ compound has no comparable interaction. Rigid-rod polymers were built from binuclear alkynyl(isocyanide)gold(I) complexes by Puddephatt et al.[281]

Yaghi and Li[282] use Ag···Ag contacts (297.7 pm) between rodlike silver 4,4′-bipyridine units to form the T-shaped assembly in Figure 14.

Chirality. A phosphine with three different substituents is chiral. Angermaier et al.[283] found that [Me(Ph)HP]AuX, X = Cl, Br, crystallizes in infinite chains with a constant Au−Au of 324.0(1) and 324.9-(1) pm for the two halogens, respectively. The chain was a RSRS... one, with neighbors having the opposite chirality.

Dimetal-linked open frameworks of adamantanoid Ge$_4$S$_{10}$$^{4-}$ groups occur in [(CH$_3$)$_4$N]$_2$(M$_2$)-
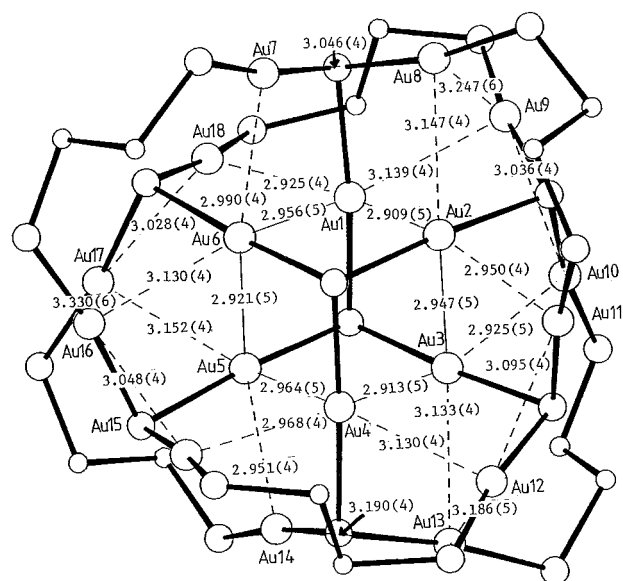
Au−S   2.31(2) − 2.42(2) Å

Au−P   2.16(3) − 2.31(2)

Figure 15. A "loosely bound cluster" **21** of 18 gold atoms.

Ge$_4$S$_{10}$.[284] The M^I···M^I are short, 240.9 and 276.1 pm for M = Cu, Ag, respectively.

"Loosely bound clusters" would exhibit E···E interactions but no E−E covalent bonds. Examples are the Cu$_8$S$_{18}$ clusters with Cu···Cu distances of 276−279 pm.[285] A further one is the [Au$_{18}$S$_8$(Ph$_2$PCH$_2$CH$_2$PPh$_2$)$_6$] cluster, **21** (Figure 15), with an inner cube and an outer ring of Au atoms.[286] Further copper sulfide systems are discussed in section III.E under "biological systems".

Even larger clusters with a Cu$_{44}$Se$_{22}$ core were prepared by Dehnen and Fenske.[287] The Cu···Cu are 251−300 pm and the Se···Se 341−462 pm. For a theoretical analysis, see section IV.A. Another example is [Cu$_{96}$P$_{30}$(P(SiMe$_3$)$_2$)$_6$(PEt$_3$)$_{18}$] with Cu···Cu of 240−280 pm.[288]

The [Ag$_{12}$Se$_7$]$^{2-}$ ion in its potassium salt[289] shows Ag···Ag = 307 pm. All Ag−Ag vectors are bridged by selenides. Similarly, [Ag$_4$(TeR)$_6$]$^{2-}$ has the Ag···Ag of 313 pm bridged by Te atoms, but the Ag−Te−Ag angles are acute, 69°.[290] Inversely, an [Ag$_6$S$_4$]$^{2-}$ Ag(I) octahedron, with Ag−Ag of 306.6 pm, bridged by the four sulfurs, occurs in NaAg$_3$S$_2$ (Figure 16).[291]

When such tetrahedra or octahedra receive some bonding valence electrons, their M−M distances are shortened, see the "partially covalent cases" below.

Cluster−Cluster Attractions. Wood et al.[292] report that the structure of M$_2$Ag$_6$S$_4$ (M = Na, K) consists of Ag$_6$ octahedra with an intramolecular Ag···Ag distance of 308.5 pm. The trigonal faces of two neighboring octahedra form an antiprism with Ag···Ag of 333.1 pm.

Metals: Zinc and Cadmium. Jansen[56] quotes the high c/a ratios of hexagonal Zn and Cd, 1.856 and 1.886, respectively, as a further example on attractions between ionic cores within an atomic layer. The ideal c/a value for a hexagonal close-packed structure is 1.63.

Also in the case of liquid or solid mercury it is interesting to ask which percentage of the cohesive energy comes from the correlation mechanism.
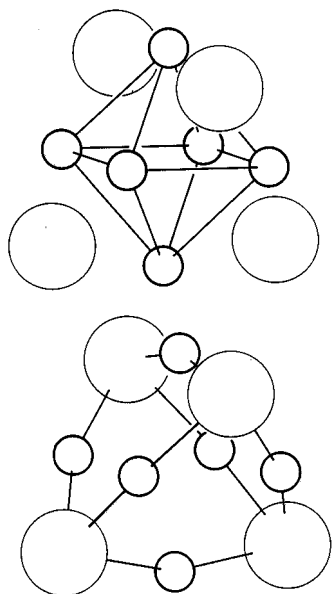
Figure 16. Two representations of the structure of the $[Ag_6S_4]^{2-}$ anion. (Reprinted from ref 291. Copyright 1993 Barth.)

B. The s^2–s^2 Case

The mercury dimer, **Hg_2**, is spectroscopically well characterized with $R_e = 363(4)$ pm. Note that the sum of the "rare-gas" vdW radii would be much larger, 416 pm. The dissociation energy, D_e, equals 0.0434(25) eV. This dimer provides a neat model system for the weak closed-shell interactions; the theoretical calculations[293,294] are discussed in the section IV.A. Upon ionization, a covalent Hg–Hg bond appears.[296]

$Tl^I \cdots Tl^I$. Abundant evidence exists for attractions between monovalent thallium atoms; see refs 76 and 77 for both molecular and solid-state examples. The molecular motifs include the $[(C_5Bz_5)Tl]_2$ dimers (see Figure 17,[295] Bz = benzyl, $-CH_2C_6H_5$), the $[RO\text{-}Tl]_4$ alkoxythallium tetramers **23**,[297] and the interchain $Tl \cdots Tl$ of 399 pm in $[(C_5H_5)Tl]_\infty$.[298] The intermolecular configuration of the difulvalene–Tl_2 systems[299] rather resembles that in **22**.
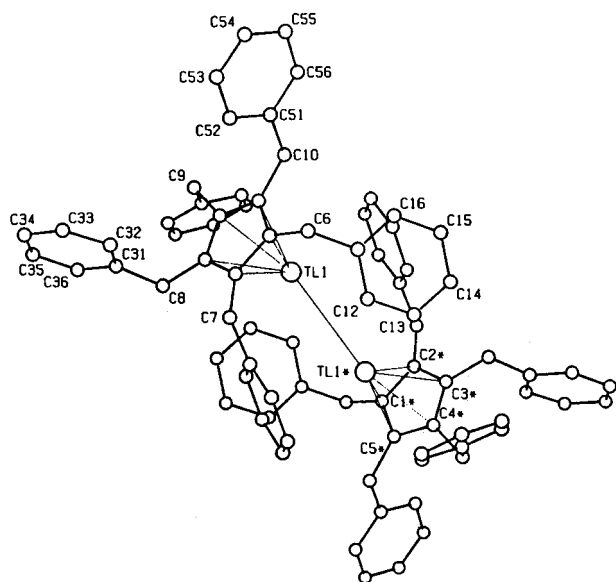

Figure 17. The structure of dimeric $[(C_5Bz_5)Tl]_2$, **22**. (Reprinted from ref 295. Copyright 1987 VCH Verlagsgesellschaft.)
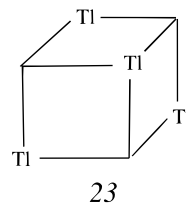
23

An interesting case are the M(I) dialkyl dithiocarbamates, as summarized by Jennische:[300–302] As discussed above, the coinage metals, M = Cu, Ag, form oligomers while the M = Au form well-defined dimers with a nearly planar core, coupled to chains, Figure 18. If M = Tl, the two metal atoms lie above and below the $(CS_2)_2$ plane and these dimers are coupled to chains, as shown in Figure 19.

For further data for thallium as well as the dimers, hexamers **24** and infinite chains of indium, see Table 9.

24
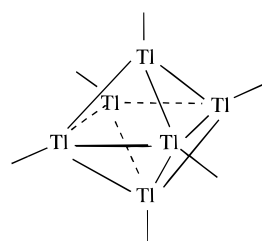
$Pb^{II} \cdots Pb^{II}$. Some examples on possible $Pb^{II} \cdots Pb^{II}$ interactions are listed in Table 9. No theoretical analysis exists, apart from EHT studies on solid PbO^{303} and on various hydroxo, oxo, and halide systems.[304]

The simplest groups, thought to exhibit the Pb⋯Pb attraction, are the triangular XPb_2^{3+} with X = F, Cl, Br, I, OH. Their Pb⋯Pb are all about 340 pm and the Pb–X–Pb angles 84, 84, 81, 75, and 78°, respectively.[304] Note that a species such as Pb_2F^{3+}, in a melt, is the association product of two cations, Pb^{2+} and PbF^+! Bridging with anions in the liquid may however play a major role here.

Note that $Pb_4(OH)_4^{4+}$ is μ_3-bridged by the oxygen atoms, like its thallium analogue $Tl_4(OR)_4$. Therefore an M⋯M attraction may or may not contribute to the stability of this structure. The Raman frequencies and intensities of $Tl_4(OEt)_4$, $Pb_4(OH)_4^{4+}$, and $Bi_6(OH)_{12}^{6+}$ were interpreted as evidence for M⋯M interaction.[75]

The doubly bridged $Pb_2(OH)_2^{2+}$ has also been seen.[304] Again the possible role of further counterions must be mentioned. The triply bridged $MM'Se_3^{2-}$ (M,

Figure 18. The structure of gold dipropyl dithiocarbamate, **4c**. (Reprinted from ref 301. Copyright 1959.)

Figure 19. The crystal structure of the A and B chains of thallium diethyl dithiocarbamate. (Reprinted from ref 302. Copyright 1975 Munksgaard.)

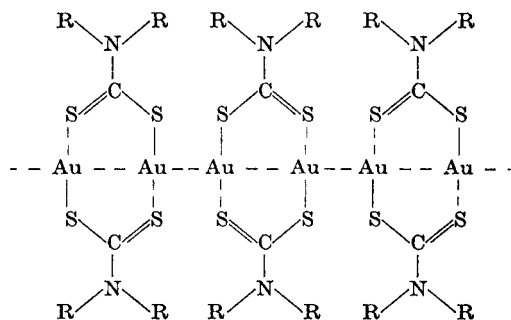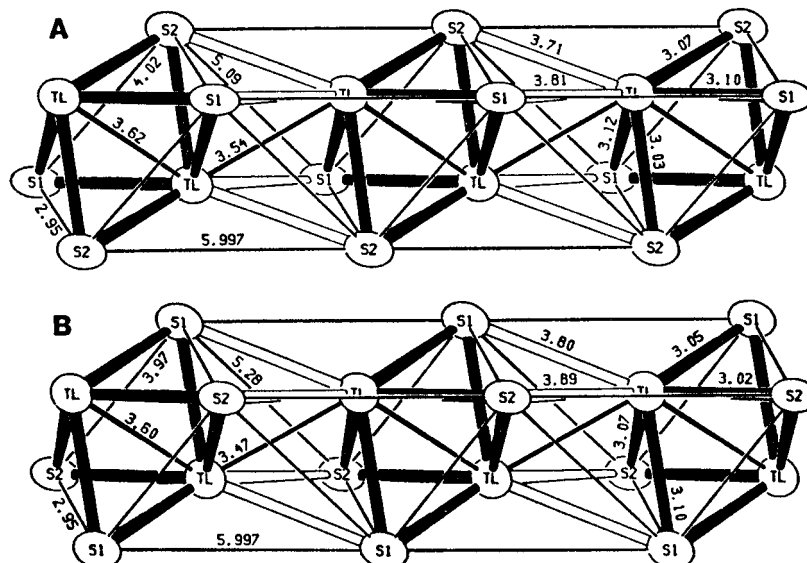M′ = Sn, Pb) shows experimentally an Sn···Sn of 309 pm.[305] Theoretical calculations (K. Klinkhammer and P. Pyykkö, unpublished results) closely reproduce it, at both HF and MP2 level, suggesting a stiff system and no major role of an M···M correlation contribution. The analogous Pb···Pb is 318 pm, below that of metallic lead, or 349 pm.

Alkalides. A rather special example on presumed $s^2 \cdots s^2$ attractions are the ones at $M^- \cdots M^- = 490$ and 513 pm for M = K and Rb, respectively, in crown ether compounds.[306] Rubidium also showed infinite chain structures with Rb···Rb = 513 pm. No evidence for attractions was found for Na⁻.

C. Other Main-Group Cases

Alkaline Earth Dimers. Analogous with the $d^{10}-d^{10}$ and s^2-s^2 interactions above, one could ask whether any analogous interactions have been observed between main-group p^6 ions? Potentiometric titrations and liquid X-ray scattering on alkaline earth fluorides in molten nitrate media give evidence for M_2F^{3+}, with M···M of 410 and 430 pm for M = Sr and Ba, respectively.[307] Note, however, the role of anion bridging in the liquid.

Pnicogen−Pnicogen Interactions, Group 15. The crystal structures of the elements have Q values, eq 15, of 1.24, 1.15, and 1.15 for As, Sb, and Bi, respectively, see Table 9.

Almost as short Sb···Sb and Bi···Bi distances of 344 and 353 pm, respectively, are found in the intramolecular structure of $[M_2(P_2Se_6)_4]$, M = Sb,Bi of $Cs_8M_4(P_2Se_6)_5$, see Figure 20.[308]

The crystal structures of the binuclear R_2E-ER_2 molecules were reviewed by Ashe[309] and by Becker and Mundt.[129] A recurrent structural motif is the coaxial chain structure, **25**. As seen from Table 9,

25
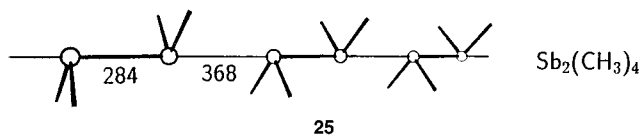
in E_2Me_4, $Q = 1.72$, 1.52, 1.28, and 1.15 for E = P,
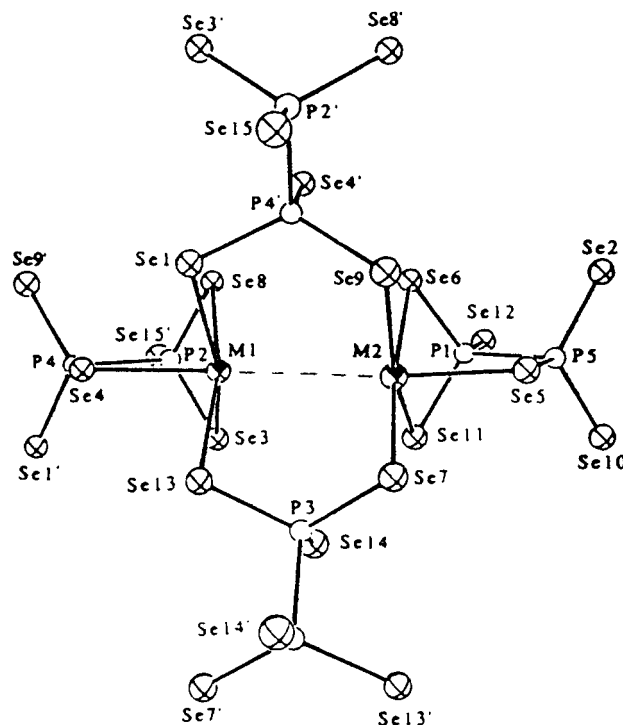
Figure 20. Structure of the $[M_2(P_2Se_6)_4]$ unit, M = Sb, Bi. (Reprinted from ref 308. Copyright 1994 American Chemical Society.)

As, Sb, and Bi, respectively. The E−E gets longer and the E···E shorter from P to Bi.

The intermolecular Sb···Sb force constants, F, of $Me_2Sb-SbMe_2$ and $(Me_3Si)_2Sb-Sb(SiMe_3)_2$ were measured by Bürger et al.[310] The results were 0.125 and 0.18 N cm⁻¹, respectively. The intramolecular force constant was ca. 1.1 N cm⁻¹.

An interesting example is reported by Ashe et al.[311] in the substituted ferrocenes in Figure 21. The two As atoms prefer to stay on opposite sides of the Fe atom while the two Sb atoms adopt an "on the top" position with Sb···Sb of 358 pm. In addition, intermolecular contacts Sb···Sb of 395 pm occur in the solid.

Chalcogen−Chalcogen Interactions, Group 16. Presumed attractions between nonbonded chal-
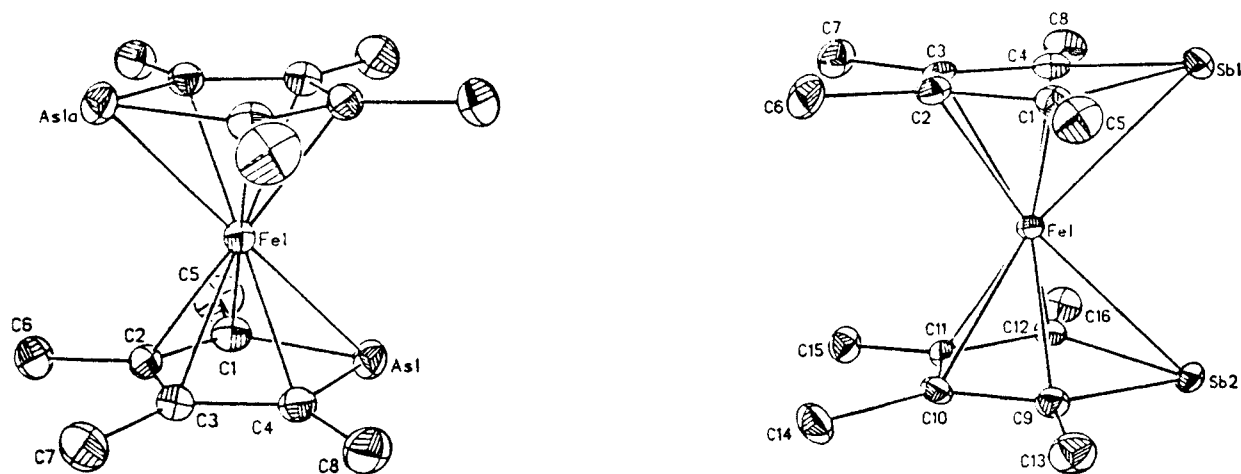
Figure 21. The structures of [Me$_4$C$_4$E]$_2$Fe, E = As, Sb. (Reprinted from ref 311. Copyright 1994 American Chemical Society.)
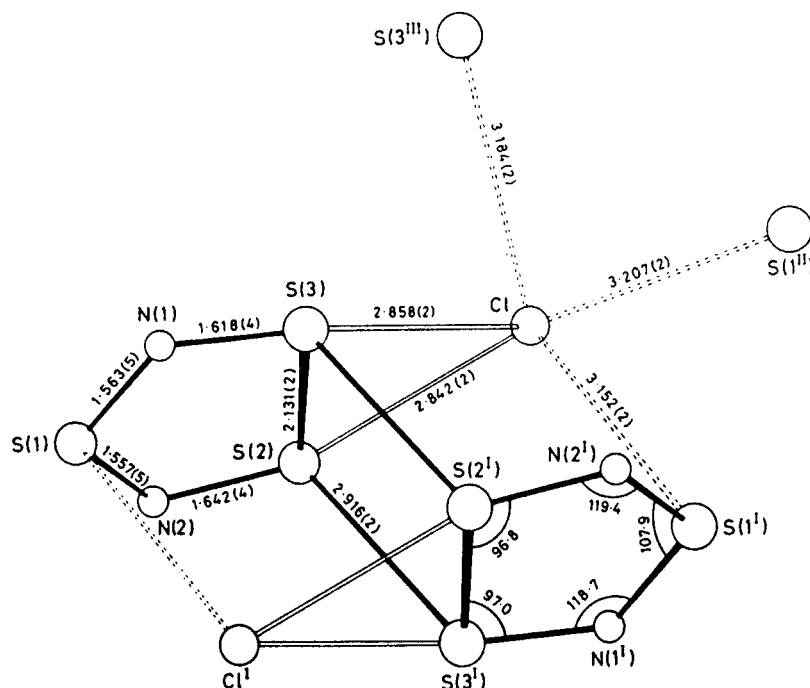
Figure 22. The dimeric structure of S$_6$N$_4$Cl$_2$, **27**. (Reprinted from ref 335. Copyright 1984 Royal Society of Chemistry.)

cogen atoms have been observed inside a number of molecules and solids.[74,78−89,129,312−336]

Starting with the elements (see Table 9), the ratios Q for the eight-atomic α-S and α-Se are 1.60 and 1.53, respectively.[313,314] The Q for the trigonal, chain structures are 1.61,[315] 1.53,[314] and 1.23[316] for S, Se, and Te, respectively. In cubic Po, $Q = 1$.

Cross-ring E···E distances of 283, 284, and 299 pm were observed inside the S$_8^{2+}$,[317] Se$_8^{2+}$,[318] and Te$_8^{2+}$ [319] ions, respectively. These Q ratios of 1.40, 1.22, and 1.09, respectively, also decrease down the column.

A particularly neat example on intermolecular interactions are the crystal structures of the dichalcogenanes, forming infinite [RE-ER]$_\infty$ chains **26**.[129]

26
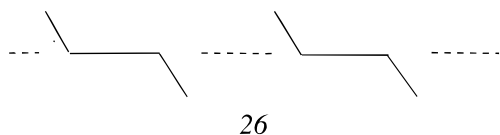
Theoretical, ab initio results on coaxial dimer models [HE-EH]$_2$ are again purely repulsive at HF

level and reproduce the attraction at MP2 level.[329]

Newton et al.[327] prepared an infinite polymer of [Te$_2$(S$_2$PPh$_2$)$_2$]$_\infty$, with intramolecular Te−Te of 272.3 pm and intermolecular ones of 351.4 and 366.8 pm.

A neat dimeric structure occurs in S$_6$N$_4$Cl$_2$, **27**; see Figure 22. There are both short S−S of 213 pm inside the rings and long S···S of 291.6 pm between the rings.[335]

Between different chalcogen atoms, the analogous, nonbonded S···O interactions at 203−325 pm have been reviewed by Kucsman and Kapovits.[80] The lower limit would correspond to a ratio S···O/S−O = 203/170 = 1.19.

Barton et al.[320] found in selenoiminoquinones **28** an intramolecular attraction between the carbonyl oxygen and the selenium. The experimental O···Se was 208 pm, the calculated HF and MP2 ones 244 and 211 pm, respectively, suggesting that the electronic correlation energy again plays a major role. It then is natural that HF-level calculations for related Se···N distances give larger values than experiment.[321]

2.08
(2.44, 2.11)

Cl

2.30 (2.26, 2.35)

O

Se

1.28
(1.25, 1.36)

1.77 (1.79, 1.80)

91.1
(94.1, 92.1)

N

1.31 (1.30, 1.41)

116.6
(123.6, 113.6)

116.4
(118.9, 117.9)

experimental: R = Cl; (theoretical R = Cl: HF, MP2)

28

Figure 23. Four diiodoacetylenes, pyramidally coordinated to an iodide in **29**. (Reprinted from ref 350. Copyright 1996 Weinheim.)
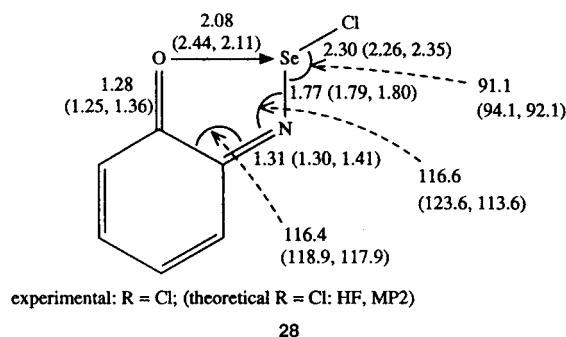
For further examples on interactions between two molecules or polyatomic chalcogenide ions, see refs 323−327. The transition-metal chalcogenide cluster ions were just reviewed by Virovets.[89] In organic superconductors, Williams et al.[323] quote interstack S···S distances in the range 342−394 pm. The role of these presumed S···S interactions in organic conductors[324] or semiconductors[325] has been discussed.

Numerous examples exist on interactions between chalcogen layers in solids.[330,388,520] Monconduit et al.[330] report Te···Te distances of 334−362 pm in layered ternary tellurides $Nb_3Ge_xTe_6$ ($x \approx 0.9$).

In organometallic polytellurides,[331−333] Te···Te distances in the range 331−360 pm are also found.

An interesting case is the $(Te_8^{4+})_\infty$ polyanion in Te_8-$(VOCl_4)_2$.[334] The intraionic Te−Te range from 274.3 to 301.0 pm and the interionic Te···Te in the chain is 359 pm.

As emphasized by Alcock (ref 83, p 296), the layers of chalcogen or halogen atoms are able to *intercalate* atoms, molecules, or ions.

Halide−Halide Interactions, Group 17. The simplest examples are the crystal structures of the halogens Cl_2, Br_2, and I_2 themselves, see Table 9. Note the decrease of the ratio Q down the series: 1.68, 1.46, and 1.29, respectively.

For data on the Cl···Cl case, see refs 82, 122, and 337−339. The last-mentioned authors argue on the basis of calculations that the observed, short Cl···Cl distances are not due to any specific attraction but rather are caused by an anisotropic repulsive wall of the −Cl group. The Cl···Cl distances, as function of the Cl−Cl···Cl angle, follow the sum of the elliptical radii of ref 124.

While the polyhalonium cations, such as I_3^+ or I_5^+ have stronger covalent contributions, the polyhalide anions, such as I_3^-, I_5^-, or I_4^{2-} will partially belong to the present class, see ref 340 for references. They can often been seen as loose complexes between I^-, I_2, and I_3^- motifs.[341] A remarkable example is the I_{12}^{2-} anion of Tebbe and Kavoosian.[342] It consists of two I^- ions and five I_2 molecules.

Lin and Hall[340] find that for I_5^- correlation effects (MP2 versus HF) shorten the central bonds by 16 pm and lengthen the end ones by 7 pm. The Br_5^+ geometry and vibrational frequencies were adequately reproduced by DFT theory.[109]

In $(C_5Br_5)_2Ru$, the bromine atoms are slightly bent outward from the inter-ring distance of 361 pm but they are eclipsed, rather than staggered.[343]

Halide−halide attractions are thought to exist between I^- ions in CdI_2.[344] Note, however, that the I···I of 423 pm in the solid, and more in the liquid,
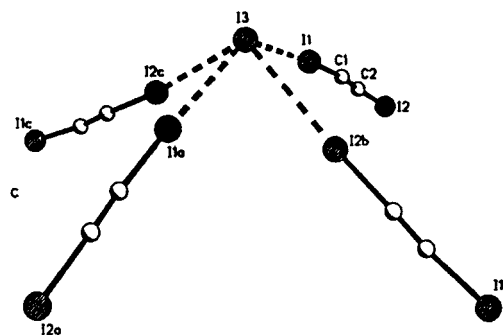
are at the high end in Table 9. In the organic superconductor $(ET)_2I_3$, I···I distances of 388 pm occur between neighboring I_3^- groups.[323]

Vogt et al.[345] quote a number of cases where an iodide ion is attracted to an iodine atom, belonging to a cation, such as an iodophosphonium cation. In that case the I···I are 346.5 and 356.3 pm. Another such case is the iodocarbenium iodide, with a nearly linear C−I···I group (I···I 333, 344 pm) of Weiss et al.[346]

Stenzel et al.[347] study the influence of the I···I interactions on the P−I distance of various $(R_2PI_2)^+$, I^-, I_3^- systems. The P−I of PI_4^+, 240(1) pm, is elongated to 244.5 pm in R_2PI_3 (R = ^tBu), where the I···I is 336 pm.

An infinite, linear polyiodide with almost identical I−I (328.3 and 329.9 pm) occurs in $(Me_4Sb)_3I_8$.[348] For the latest references on extended polyiodides, see Blake et al.[349] In $PPh_4[X(ICCI)_2]$, X = Cl, Br, I, each halide ion is pyramidally four-coordinated to four diiodoacetylenes (see Figure 23). The authors[350] point out that in crystals with big cations, such as PPh_4^+, and consequently low lattice energies, the halide ions acquire a Lewis-base character.

Halogen−chalcogen interactions occur in a number of cases in Table 9. Notable examples are the short Te···I distances between a $Mo_3Te_7^{2-}$ cluster core and an iodide in ref 351.

The Pnicogen Triiodides. AsI_3, SbI_3, and BiI_3 have a decreasing ratio (E···I)/E−I of 1.39, 1.16, and 1, respectively; the last case is cubic (see Table 9). As noted by Alcock,[78] the long bond becomes shorter and the short one longer down the series.

A Cambridge Crystallographic Database study of Bi···X versus BiX distances (X = Cl, Br, I)[352] preliminarily suggests in each of the three cases *two* curves, see Figure 24. For X = Cl, the symmetrical distances would be about 270 and 290 pm, respectively.

Lone-pair−lone-pair interactions have been suggested as the reason behind the tetrahedral packing of the tetrahedral E_4O_6 molecules, E = As, Sb. The lone pairs of four E atoms meet in a tetrahedral geometry, with the shortest E···E = 395 and 362 pm, respectively.[353,354]

Galy et al.[355,356] have reviewed the stereochemistry of crystals with s^2 lone pairs from groups 13−18. Attractive interactions are thought to exist between the cation layers, such as the Pb(II) layers in tetragonal (yellow) PbO, whose Pb···Pb = 363 pm.[357] Other possible examples are quoted by von Schnering
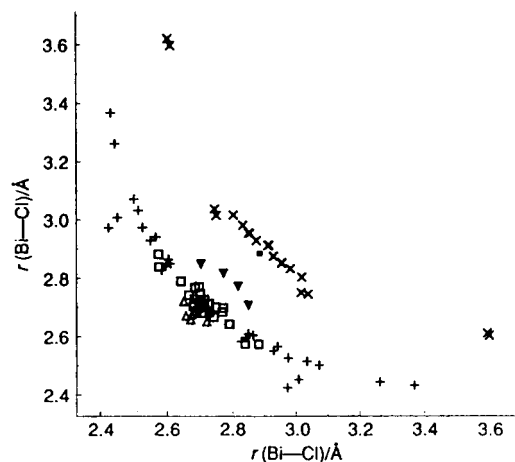
Figure 24. The Bi···Cl distance as function of the Bi−Cl distance in Bi(III) complexes. (Reprinted from ref 352. Copyright 1992 Royal Society of Chemistry.)

and Nesper.[358] In RhBi$_4$ the Bi lone pairs stand in contact between interpenetrating chiral nets.[359]

D. Further Examples

The d^8 metal ions can be regarded, in a sense, as closed shells, if the crystal-field splittings are large. In the case of 20 Pt^{II}···Pt^{II} simple salts with metal cations, the Pt···Pt vary from 309 to 375 pm, as quoted by Nagle et al.[360] In partially oxidized systems the distance drops to 280−300 pm. A notable feature of the Pt···Pt in the unoxidized, solid Pt(bpy)-Cl$_2$ is that it drops from 345 to 337 pm when the temperature decreases from 294 to 20 K.

In addition to infinite chains, there are d^8 dimers and oligomers,[361] for summaries, see ref 362. Tanase et al.[363] found an unbri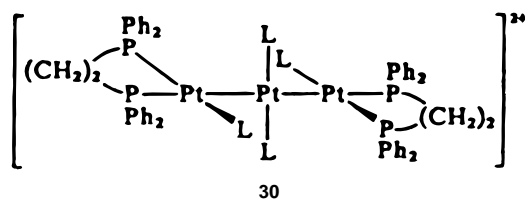dged Pt−Pt−Pt linear trimer **30** with average Pt−Pt of only 264 pm, suggesting covalent bonding. The authors count the oxidation states as Pt^I−Pt^0−Pt^I, not as Pt^{II}−Pt^{II}−Pt^{II}. The L is an isocyanide.

30

A nice, half-bridged example with a short Pd^{II}···Pd^{II} distance of 288.6 pm is shown in Figure 25.

Despite of the higher formal charges of the Au(III) atoms, the AuO$_4^-$ groups of MAu$_2$O$_4$ (M = Sr, Ba) are stacked at Au···Au of 321 and 309 pm, respectively.[365] Similarly, LnAu$_2$O$_9$ (Ln = Nd, Gd) contain stacked square-planar AuO$_4$ groups at Au···Au = 310 pm.[366]

Stone[367] finds Pt···Pt distances such as 291 pm in the system in Figure 26 but interprets the result as "little" or no direct Pt−Pt bonding. The dihedral angle between the two Pt−C−C planes is 96.9°.

In [[PtCl(dmso)]$_2$(μ-OH)$_2$], the intramolecular Pt^{II}···Pt^{II} is 305 pm.[368]

For reviews and EHT discussions on bridged d^8−d^n dimers, n = 8, 9, see ref 369.

d^8−d^{10}. Examples of this case are the Au^{III}···Au^I contacts of 331 pm in [Au^{I}Au^{III}(PMe$_3$)$_2$(C$_4$F$_6$)], **31**, in
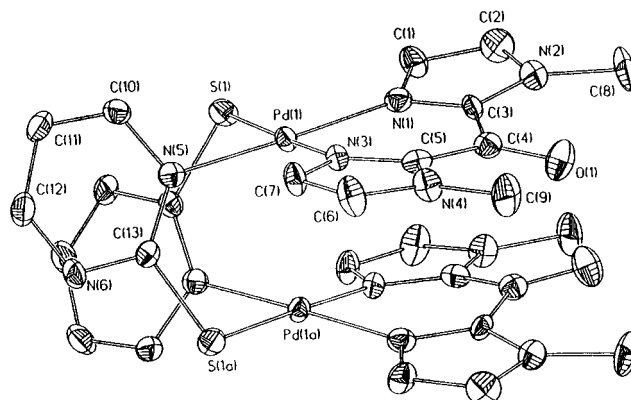
Figure 25. The structure of the pyridinethiolate complex [Pd$_2$(bmik)$_2$(pymt)$_2$](NO$_3$)$_2$·5H$_2$O. (Reprinted from ref 364. Copyright 1994 VCH Weinheim.)
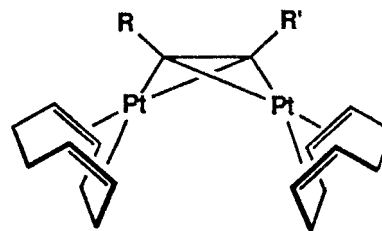
Figure 26. The structure of Pt$_2$(μ-PhC$_2$SiMe$_3$(cod)$_2$. (R = Ph, R′SiMe$_3$, cod = cycloocta-1,5-diene.) (Reprinted from ref 367. Copyright 1981 Royal Society of Chemistry.)

Figure 27,[370] of 305 pm in [Au^I[Ph$_2$P-(CH$_2$)S]$_2$···Au^{III}I$_2$],[371] or of 353 in [S(Au$_2$dppf)(Au-(C$_6$F$_5$)$_3$)$_2$.[372]

M···M Interactions in Complex Hydrides. The d^{10}−d^{10} case of Na$_2$PdH$_2^{274}$ was quoted above. The Li$_2$PdH$_2$ also has a tetragonal structure. For an unknown reason, the analogous Li$_2$PtH$_2$ distorts: each Pt(0) has as its neighbors two Pt atoms at 299.2 pm and two others at 326.8 pm.[373]

In the crystal structure of the d^8 compound Mg$_2$-RuD$_4$ the Ru···Ru distances of 324 pm form a bent chain. In Li$_3$RhH$_4$,[374] the Rh···Rh are 388 pm.

d^n−d^n, n < 8. The structure of [Cp*Ru(OMe)]$_2$ is bent, with Ru···Ru = 295.5 pm.[375] The analogous [C$_5$-Me$_4$EtRuSEt]$_2$ has 307.5 pm.[376] Whether these structures, see Figure 28, indicate metal−metal bonding, has not been theoretically studied. For an early review, contrasting d^n M···M and ligand S···S interactions, see Fackler.[92]

Structural Isomers. The bistability of the AuBr chains was quoted under "Binary Compounds of Coinage Metals". Another example is the Pt$_3$ core of Pt$_3$(μ-PPh$_2$)$_3$Ph(PPh$_3$)$_2$. This compound can adopt, depending on the crystallization process, two geometries. One is nearly D_{3h}, Pt−Pt = 2 × 295.6 and 307.4 pm. The other one breaks one Pt−Pt bond and has 2 × 275.8 and 358.6 pm.[377]

Attractions between the d^{10} metals Hg(II) or Au(I) and the main-group heteroatoms have been reviewed by Kuz'mina, see refs 90 and 91, respectively.

In the case of Hg^{II}···Cl interactions, a remarkable range of chloromercury anions is obtained. For example, in [Hg$_2$Cl$_7$]$^{3-}$, the intraionic Hg−Cl distances vary from 234 to 297 pm and the interionic ones are ≥336 pm.[378] Similarly, a large family of Hg-(II) iodomercurates exists with both Hg···I and I···I interactions.[379]
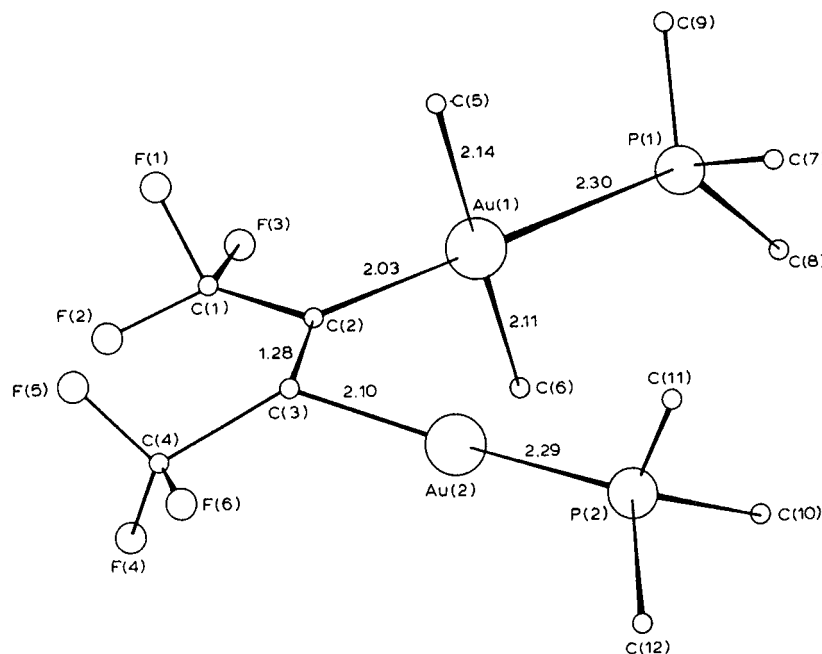
Figure 27. The structure of the Au^{I}Au^{III} compound, **31**. (Reprinted from ref 370. Copyright 1973 Royal Society of Chemistry.)
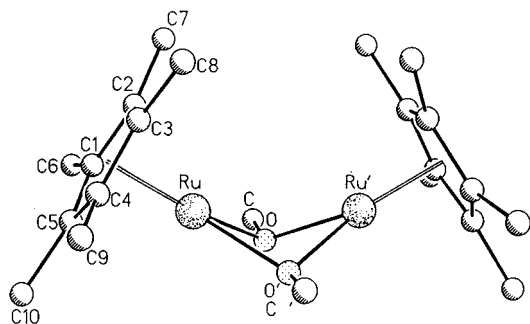
Figure 28. The experimental solid-state structure of [Cp*Ru(OMe)]$_2$. (Reprinted from ref 375. Copyright 1989 Elsevier.)

Gold–Chalcogen Interactions. Eikens et al.[380] observe nonbonding, intermolecular Au···Se distances in the range 323–326 pm in gold selenolates. The ubiquitous Au···Au interactions also occur. For a review on sulfido- and selenoaurates, see Ibers et al.[87]

It is interesting that the intermolecular Au···Te in the dimeric crystal[216] should be so much larger than the intramolecular ones in the gold–tellurium anions (see Table 9).

Heavy Atoms and Aromatic Rings. This subject was reviewed in ref 30; see also ref 60. An example is shown in Figure 17, in which case the Tl–ring distance is 249 pm.

Schmidbaur et al.[381] report for [E(1,3,5-Me$_3$C$_6$H$_3$)-X$_3$] average E···D (ring center) distances of 324 and 303 pm for (E,X) of (Sb,Br) and (Bi,Cl), respectively. Note that Bi is 21 pm smaller than Sb. Frank et al.[382] report for [(C$_6$H$_6$)BiCl$_3$]$_2$ mean Bi–C of 340 and 345 pm, both Bi atoms being η^6. A rather different case, involving otherwise pentacoordinate Bi(V) and the η^1 nitrogen of pyridine, Ph$_5$Bi···NC$_5$H$_5$, with Bi···N 321(2) pm, was observed by Seppelt et al.[383]

Ag$^+$ enjoys strong interactions both with benzene rings and fullerene, see ref 384.

Heavy Atoms and Hydrogens. Novoa et al.[385] studied theoretically the H$_3$C—H···X$^-$ interactions with the polyhalide ions X$^-$ = I$_3^-$, IBr$_2^-$, ICl$_2^-$. The BSSE corrections were essential and the interaction was mainly due to correlation. The final, MP2 interaction energies were 2.5, 3.1, and 3.2 kJ/mol, respectively.

Other Intermolecular Bonds. Reddy et al.[386] report a N···Br distance of 261(6) pm in the carbon tetrabromide:hexamethylenetetraamine 1:1 complex and suggest that the order of "stickiness" is N···Br > C—H···N > Br···Br.

Further cases are listed in Table 9, in the order Z_X > Z_Y.

Partially Ionic Cases, s^2–d^8 and s^2–d^{10}. In a case like Tl$_2$Pt(CN)$_4$, **32**, Tl^I–Pt^{II} = 314.0 pm,[360] there are two closed-shell metal ions in close contact. A preliminary theoretical analysis[436] however supported the intuitive expectation of a mainly ionic bond between 2Tl$^+$ and [Pt(CN)$_4$]$^{2-}$ ions, with some covalent character. A closer analysis suggested that also the correlation and the crystal-field contributions are important, see below.[437]

32

Table 9. Comparison of Bonding X−Y and Nonbonding X···Y Distances and Their Ratio (X···Y)/(X−Y)

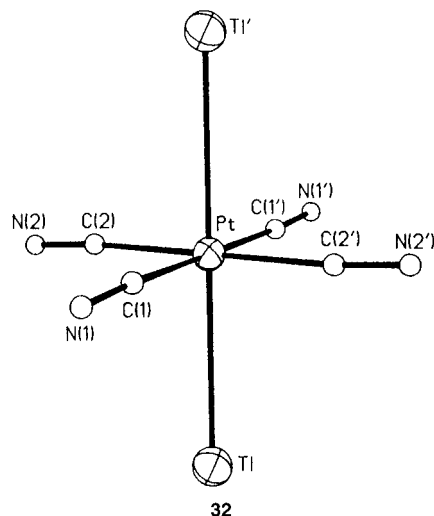| case	X−Y, pm	X···Y, pm	ratio	system	ref
S−S	213	292	1.37	$S_6N_4Cl_2$	335
	204(av)	286	1.40	$(S_8^{2+})(AsF_6^-)_2$	317
	204	327?	1.60	α-S	313
	207	333	1.61	S(chain)	315
		321		α-P_4S_3	387
		341,346		TiS_2	388
		342−394		thioorganic superconductor	323, pp 174,178
	228	348	1.53	$Nb_2S_4(S_2NCEt_2)_4$	89
	203	378	1.86	α-S_2Me_2	129
	−	411		$(H_2S)_2$	389
Cl−Cl	198	332,382	1.68	$Cl_2(s)$	390
Ar−C		384		Ar···C_6H_6	17
K−K		490		K^-···K^-	306
As−As	252	312	1.24	As(s)	52, p 876
		395		$As_2O_3(s)$(cubic)	353
	243	370	1.52	$[As_2Me_4]_\infty$	129
Cu−Cu		237		$[Cu_2R_2BrLi(thf)_3]$	199
		242		$(Me_3SiCH_2Cu)_4$	243
		263−270		chelated Cu_4N_4 amide square	239
Se−N	187	215,218	1.16	$[(C_6H_3)(NMe_2)_2(Se)]^+$	391
Se−P		365		α-P_4Se_3	392
Se−Se	232(av)	284	1.22	$(Se_8^{2+})(AlCl_4^-)_2$	318
	237	344	1.45	Se(trigonal chain)	314
	231	355	1.54	Se_2Me_4	
		355		$TiSe_2$	388
		363−380		α-P_4Se_3	392
Br−Br	227	331,379	1.46	$Br_2(s)$	390
		349		W_6Br_{14}	393
Pd−Pd		276		$[(dcpe)Pd(0)]_2$, **12**	204
Ag−S	243	289,300	1.19	$[AgSCN]_\infty$ (interchain)	394
		318,334		$(BEDT-TTF)Ag_4(CN)_5$	395
Ag−Ag		284		Ag_2CCO	270
		292−302		chelated Ag_4N_4 amide square	239
Cd−N		259,267		$Me_2Cd(dabco)$	396
In−In		361−368		InCl	75, p 160
		ca. 360		InBr, InI	75, p 160
		363		$[(Bz_5C_5)In]_2$	295
		394,396		$[(Me_5C_5)In]_6$	397
		399		$[(C_5H_5)In]_\infty$ (interchain)	398
Sn−O	208	256(av)	1.23	$Ph_2Sn(O_2CMe)_2$	399
Sb−O		264,273		$[O(CH_2CH_2S)_2Sb]_2(SCH_2CH_2)_2O$ (transannular Sb···O)	400
Sb−S	248,251	356,332	1.3−1.4	$[(p-tolyl)_2SbS_2PEt_2]_2$	93
Sb−Sb	291	336	1.15	Sb(s)	52, p 876
		358		$[Me_4C_4Sb]_2Fe$	311
	284	368	1.30	Sb_2Me_4	129
	288	388	1.35	$Sb_2(SnMe_3)_4$ (type A)	129
	287	399	1.39	$Sb_2(SiMe_3)_4$	129
Te−O	216	299	1.38	$Ph_2Te(O_2CMe)_2$	see ref 399
Te−S		270−300		intramolecular	see ref 328
		301−370		intramolecular	see ref 328
Te−Cl		316,331		$(Te_8^{2+})(WCl_6^-)_2$	319
Te−Sb	268	321	1.20	$[Sb_9Te_6]^{3-}$	401
Te−Te	270−278	299	1.09	$(Te_8^{2+})(WCl_6^-)_2$	402
		305,309		$CsTh_2Te_6$	403
	278	320−345	>1.15	$RbTe_6$	403
	282	328	1.16	$[Fe_4(Te_2)_2(Te)_2(TeMe)_2(CO)_8]^{2-}$	404
	272−283	331	1.19	$[TMDH]Te_4$	331
		334−362		$Nb_3Ge_{0.9}Te_6$	330
	283	349	1.23	Te	316
	275	346	1.26	$[Sr(15-crown-5)_2]Te_4 \cdot H_2O$	332
	271−277	346	1.26	$[(Te_4)Ag(\mu-Te_4Ag(Te_4)]^{4-}$	87
	272	351,367	1.32	$[Te_2(S_2PPh_2)_2]_\infty$	327
	271	374	1.38	Te_2Me_2	129
	>274	359		$(Te_8^{4+})_\infty$ in $Te_8(VOCl_4)_2$	334
		378		$TiTe_2$	388
I−N		244		Ur·I_2	405
		250		Ur·$2I_2$	405
		275		Ur·$3I_2$	405
I−O		286		$2,4,6-Me_3C_6H_2-I-Ts$	406
	181	289	1.60	$LiIO_3$	78
I−F		331,333		iodofluoroadamantanes	407
I−Cl	244	300	1.23	α-ICl	see ref 407
		318,332		$PPh_4[Cl(ICCI)_2]$	350
I−As	256	356	1.39	AsI_3	78
I−Br		324,339		$PPh_4[Br(ICCI)_2]$	350

Table 9. (Continued)

case	X−Y, pm	X···Y, pm	ratio	system	ref
I−Sb	287	332	1.16	SbI_3	78
I−Se		299		$[Se_2Ph_2 \cdot I_2]_2$ (I−I···Se)	35, p 238
		359		$[Se_2Ph_2 \cdot I_2]_2$ (Se−Se···I)	35, p 238
I−Te		350,358		$[Mo_4Te_7(CN)_6]I^{3-}$	351
I−I	272	300	1.10	$Et_3SI_x(l)$	341
		308		α-ICl	see ref 407
		333,344		$C_5H_{10}N{=}CHI^+I^-$	346
		334,352		$PPh_4[I(ICCI)_2]$	350
		336		$^tBu_3PI_2$	35, p 335
		336		$^tBu_2PI_3$	347
		346,356		$Ph_3P-CH_2I^+I^-$	345
	272	350,397	1.29	$I_2(s)$	390
		388		$(ET)_2I_3$	323, p 100
		393		LaI	408
		423		CdI_2	344
Pt−H		226		$[PtCl_4]cis$-$[PtCl_2(NH_2Me)_2]^{2-}$	409
Pt−Ag		290		$[(NH_3)_2Pt(NHCO\text{-}Me)_2Ag]NO_3 \cdot 4H_2O$	410
Pt−Pt		337		phenanthroline MeNC complex	411
Au−N		263		Ph_3PAu-S-kinolinate	91
		274,280		$[Ph_3PAuO(C_6H_4)N{=}NC_6H_4OAuPPh_3]$	91
Au−O	203	258	1.27	$[RO(AuPR'_3)_2]^+BF_4^-$	412
Au−S	253	311	1.23	$(Ph_3P)_2AuS_2COEt$	413
		306		$[SPPh_2C(AuPPh_3)_2CH(AuPPh_3)COOMe^-$	414
Au−Cl		315		$Ph_3PAu-C_6Cl_5$	91
Au−K		327−361		KAu_5	415
		355−364		$K_2Au_2SnS_4$	416
Au−Se	241−247	323−336	1.35	Au selenolates	380
Au−Te	265(av)	312	1.18	$[AuTe_7]^{3-}$	87
	257	374	1.46	$Ph_3PAuTeC(SiMe_3)_3$	216
Au−Au		276		$[(O)Ph_2PC(PPh_2AuPPh_2)_2CPPh_2(O)]$	417
		290−300		$TlAu(CN)_2$	275
		297		RbAuTe	257, 258
		300		$(Me_3P){=}C[PPh_2AuCl]_2$	148
		305.1		$Se[AuPPh_3]_2$	155
		305, 326		$Te_4Au_4^{4-}$	158
		311		CsAuTe	257, 258
		311		$ZnAu_2(CN)_4$	265
		312.4		$(AuI)_2(\mu\text{-}dpph)$	280
		324.0		$[Me(Ph)HP]AuCl$	283
		324.9		$[Me(Ph)HP]AuBr$	283
		330.6		$Au_2(tmb)Cl_2$	136
		332		$[Au(C_4H_8S)Cl]$	147
		335		$[Au(C_4H_8S)Br]$	147
		338		$(OC)AuCl$	269
		339.5		AuCN	266
		341		$[Au(NH_3)_2]Br$	202
		344		$2,4,6\text{-}(^tBu)_3C_6H_2PH_2]AuCl$	154
				(see also Tables 6−8 and the text)	
Hg−C		371		$Hg\cdots OCS(g)$	14, p 440
Hg−O		244		$Ph\text{-}Hg\text{-}(NMe)(CH_2)(C_6H_4O)$	90, p 76
		257,269		$Hg(C_5H_7O_2)Cl$ (intermolecular)	418
Hg−S	236	310,330	1.31	HgS (interchain)	419
	234	329,339	1.42	$Hg(SEt)_2$	420
Hg−Cl		303		$PhHgOC_6H_3BrCl$	91
Hg−Hg	282	316	1.12	β-Hg	421
		341		Sr_3Hg_2	422
		353		$[HgRu(CO)_4]_4$	217
		363(4)		$Hg_2(g)$	see ref 293
Tl−S	292	340	1.16	$[TlMe_2(S(O)PPh_2)]_\infty$	423
Tl−Se	311	363	1.17	$(N,N\text{-}Et_2\text{-}N'\text{-}benzoylselenoureato)Tl$	424
Tl−Tl		347,354		$[TlS_2CNEt_2]_2$ (intermolecular)	302
		360,362		$[TlS_2CNEt_2]_2$ (intramolecular)	302
	314	354	1.13	$(MeSi)_2(N^tBu)_6Tl_6$	425
		362		$Tl_3Al_7S_{12}$	426
		363		$[(Bz_5C_5)Tl]_2$	295
		365		$[TlN(SiMe_3)_2]_2$	427
		367		$Tl_2B_9H_9C_2Me_2$	428
		369		Tl_2Pc	429
		374		$TlCo_2S_2$	77, p 74
		376,400		$(^tBu)_4$-difulvalene)Tl_2 (intermolecular)	299
		383		β-TlI	430
		384		$Tl_4(OMe)_4$ (intramolecular)	297
		404−452		$Tl_4(OMe)_4$ (intermolecular)	297
		399		$[(C_5H_5)Tl]_\infty$ (interchain)	298
		403		β-TlF	431
Pb−S	288(av)	336(av)	1.16	$Pb(S_2PPh_2)_2$	432

Table 9. (Continued)

case	X−Y, pm	X⋯Y, pm	ratio	system	ref
Pb−Pt	270[a]	331	1.23	$[(CH_3CO_2)Pb(crown-P_2)Pt(CN)_2]^+$	433
Pb−Pb		340		$IPb_2^{3+}(l)$	304
	−	363	−	yellow PbO	357
		367		$Pb(SEt)_2$	434, p 161
	−	385		$Pb_4(OH)_4^{4+}$	75, p 163
Bi−X				X = Cl, Br, I	see ref 352
Bi−I	310	310	1.00	BiI_3	78
Bi−Bi	307	353	1.15	Bi	52, p 876
	312	358	1.15	Bi_2Me_4	129
	304	380	1.25	$Bi_2(SiMe_3)_4$	435

[a] Calculated for a gas-phase dimer.

An even shorter Tl^I−Pd^{II} bond of 289.7 pm was found by Balch et al.[438] in $[Tl(crown-P_2)Pd(CN)_2]^+$. A Pt(II) analogue had a longer bond of 291 and 296 pm.

Against this background, the very short Tl−Au of 295.6 and 300.3 pm in the infinite −Au−Tl−Au−Tl− chain of $AuTl(MTP)_2$, MTP = $Ph_2 P(S)CH_2$, **33**,[439,441] should perhaps rather be viewed as mainly ionic bonds between Tl^+ and $[LAuL]^-$ moieties. The same may hold for oligomers such as the Ir^I−Tl^I−Ir^I and Ir^I−Pb^{II}−Ir^I trimers in the metallomacrocycle $Ir_2(CO)_2$-$Cl_2\mu$-$(Ph_2PCH_2)_2AsPh_2$, **34**.[440] Here Ir−Tl = 295.8 and 297.9 pm.

33
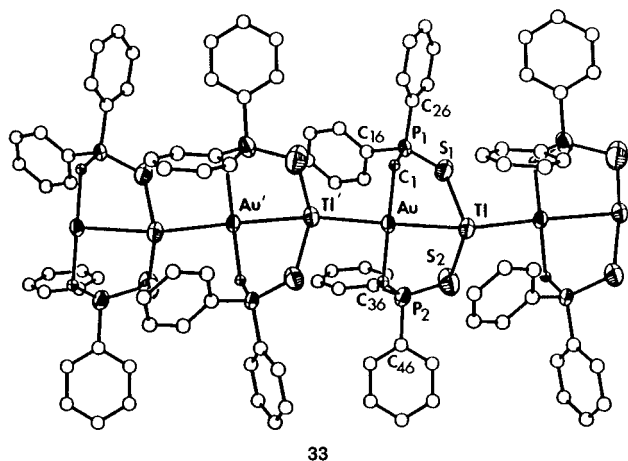
In the infinite, linear $(Au-Pb-Au)_\infty$ chain structure (Figure 29) of $Au_2Pb(MTP)_4$, the Au−Pb distances are 289 and 296 pm and the intermolecular Au−Au distance is 315 pm.[441]

Many trimer combinations involving d^8 metals and closed-shell ones have been reported by Balch et al.[58] and by Fackler et al.: AuPbAu, HgPtHg, and AuPt-Au.[442] In the d^{10}−d^8−d^{10} systems $Au_2Pt(MTP)_4$ and $[Hg_2Pt(MTP)_4]^{2+}$ (MTP = $CH_2P(S)Ph_2$), the M−Pt distances are 303.4 and 313.8 pm for M = Au and Pt, respectively.[443] The Au−Pt−Au system is linear. The Hg^{II}−Pt^{II}−Hg^{II} system is larger and bent (149°).

Lippert et al.[444] quote data for the systems Ag^I−Pt^{II}−Ag^I, Au^I−Pt^{II}−Au^I, Hg^{II}−Pt^{II}−Hg^{II}, Au^I−Au^{III}−Au^I, Au^I−Rh^I−Au^I, and Au^I−Ir^I−Au^I.

Alternatively, one could talk of "donor−acceptor bonds". Usón and Fourniés[445] have reviewed the Pt-(II) → M (M = Ag, Sn, Pb) ones, seeing the Pt(II) as a donor. The shortest Ag−Pt, that in $(tht)(C_6F_5)_3$-Pt−Ag(PPh_3)$, is only 263.7 pm. Yip et al.[446] report much longer distances in doubly bridged complexes, like the Au−Pt of 291 pm in $[AuPt(dppm)_2(C≡CPh_2]^+$. Stone et al.[447] report a Pt^{II}⋯Au^I distance of 300.0(1)

pm in a carborane system with an Au−B(carborane)−$(\mu$-H)−Pt^{II} bridge.

The Cubic Ionic Crystals. AgI and TlI contain nothing but closed-shell ions discussed in the present review. Indeed, both the metal−metal, metal−halide, and halide−halide dispersion coefficients, C_6, are being used in simulations of their phonon spectra or liquid structure. For the $C_6(Ag⋯Ag)$, values from 62 to 375 au. have been suggested, see the AgCl study of ref 448. For a discussion of the changes of the free-ion polarizabilities in the crystal field, see refs 448 and 449. Effects of an Ag⋯Ag attraction on the phonon spectra of AgCl and AgBr were also studied in ref 450. Similarly, Kiang and Goddard[451] had to include Ag−Ag, Ag−Br, and Br−Br van der Waals pair potentials in a calculation of the phonon spectrum of AgBr. The evidence for important two- and three-body van der Waals attractions in silver halides was summarized by Bucher.[452]

Indirect evidence for dispersion effects can be obtained by comparing a good crystal HF result against experiment. For the lattice parameter, a_0, of AgCl, Aprà et al.[453] find 592 and 551 pm at HF and DFT levels, respectively. In this case, the two different density functional corrections actually improve the result, to 556 or 555 pm.

For estimates of the effective C_6 coefficients for alkali halides, see Aquilanti et al.[454] Pyper[455] concludes that the "CsCl" crystal structure of CsCl depends on the dispersion energy between the ions.

Obviously the same interactions will survive after melting, in the liquid, for instance in CsAu(l), where simulations again yield distances of about 300 pm, between the Au-ions.[456]

Partially Covalent Cases. In a number of cases, the system has some covalent character but derives a part of its stability from the metallophilic attraction. For M = Ag or Au, for instance, one could either oxidize the metal atom from d^{10} to M(II) and have some, primarily d σ bonding, or have a subvalent compound, s^x, $x > 0$, with some s bonding. For the known extremes of these two cases, see **35−37**.[457,458]

Both the Ag_6^{4+} clusters in Ag_3O or $Ag_6Ge_{10}P_{12}$ (see ref 56), or in Ag_5GeO_4,[459] Ag_5SiO_4,[460] and the newly synthesized $(AuL)_4^{2+}$, L = $P(^tBu)_3$,[461] L = $P(mesi-tyl)_3$[462] are examples of partial covalent bonding, in the last case of a 2-electron−n-center (2e−nc) bonding, where a part of the stability comes from the metallophilic attraction.[463] The possibility of such a $(AuL)_n^{(n-2)+}$ series was already pointed out by Mingos.[464]
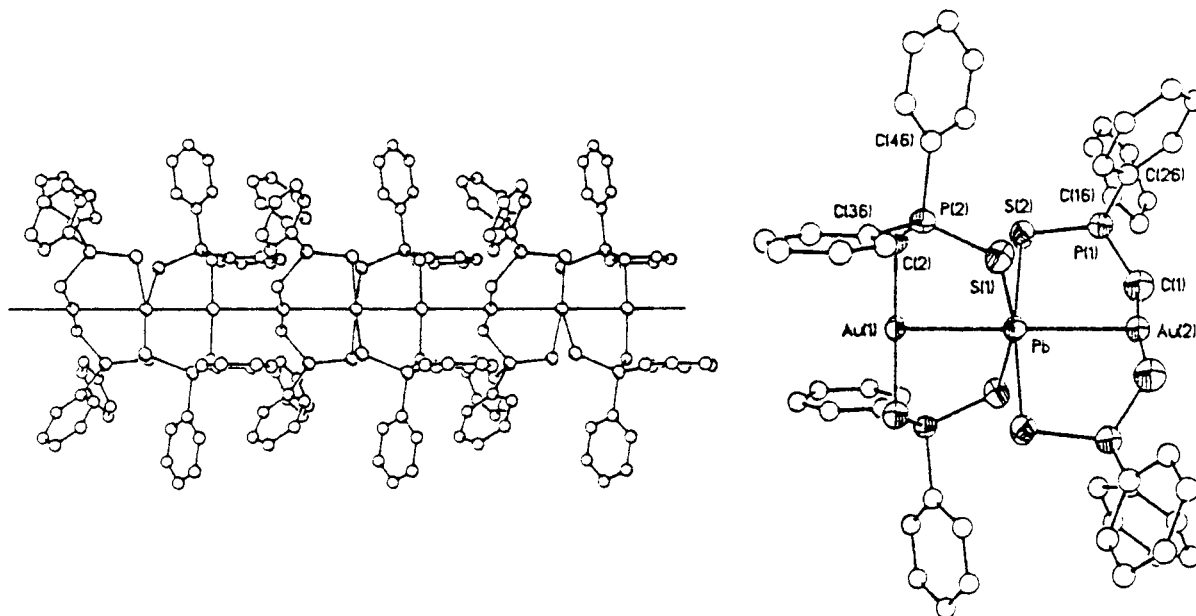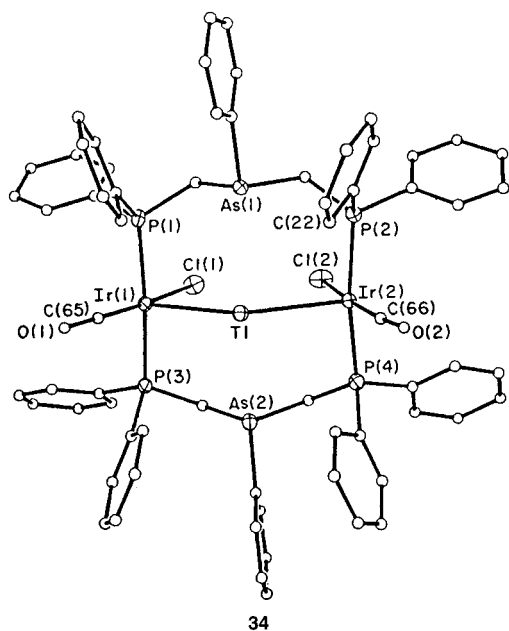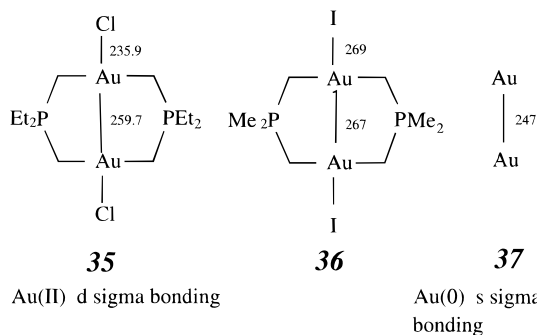
Figure 29. The monomer and chain structures of $Au_2Pb(MTP)_4$. (Reprinted from ref 441. Copyright 1989 American Chemical Society.)

10 have radial Au−X covalent bonds. However, they also can be expected to derive a part of their stability from the periferal Au···Au interactions, see below.

Mingos[474] predicted, at EHT level, the stability of the octahedral cluster with a CAu_6^{2+} core, later prepared as $[C(AuL)_6]^{2+}$ (L = PPh_3).[145] The isoelectronic N^{3+} species and the trigonal bipyramidal, D_{3h} $E(AuL)_5^{n+}$ species with E = C, N, P have also been reported (see ref 475). Although their structure can already be analyzed at HF[476] or density functional theory (DFT)[475] level, Au−Au distances in the 300 pm range occur and a further, aurophilic stabilization of perhaps 25 kJ/mol per Au−Au pair can be expected.[137,463]

E. Related Phenomena

Colors. The systems with metallophilic attractions tend to be both colored and luminescent. AuI is lemon yellow; AuCN bright yellow; etc.

Luminescence. Although some examples of emitting mononuclear Au(I) compounds are known,[326] most luminescent gold compounds contain Au···Au interactions, see ref 226. No correlation has, however, been found,[477,478] between the presence or absence of an Au···Au interaction and the optical properties (absorption or emission). Interestingly, the phosphorescence is assigned to a metal-centered $p_z \rightarrow d_\sigma$ transition. As discussed in the present theoretical section, reasons exist for assigning the aurophilic attraction to a virtual d → p transition. Correlations between the Au···Au distance and the softness of the ligands were studied.[226]

In case of (TPA)AuCl, protonation to (TPA-HCl)-AuCl lengthens the Au···Au of the dimers from 309 to 332 pm and at the same time shifts the emission from red (674 nm) to yellow (596 nm).[479] In Eu-[M(CN)_2], the luminescent properties suggest a stronger M···M interaction for M = Au than for M = Ag.[480]

In view of the importance of both the Au 5d and 6p orbitals in the theoretical description of the attraction,[137,481] it is interesting to speculate that the

34

35   **36**   **37**

Au(II) d sigma bonding   Au(0) s sigma bonding

In metallic systems, many further examples exist on combined metallic and correlation bonding, see ref 56. See also the analysis on large Ni_n clusters[465] in section IV.B. At this point, the −M−M−M− chains in CaCu, CaAg, SrAg, and CaAu should also be quoted; see ref 59.

The symmetrical, centered species of the exact or approximate symmetries T_d, D_{3h}, or O_h in Table

Table 10. Centered XAu$_n$ Species with Peripheral Au⋯Au Interactions (For C_{nv} species, see Table 6.)

symmetry	X	X−Au	Au⋯Au	system	ref
T_d	C			[(2-Me-C$_6$H$_4$)$_3$PAu]$_4$C	466[a]
	N	193−210	301−350[b]	(Ph$_3$PAu)$_4$N$^+$	214
	O	205.7	335.9	[((o-Tol)$_3$PAu)$_4$O]$^{2+}$	467
D_{3h}	C	208.4(av)	290,299(ax-eq)	[(Ph$_3$PAu)$_5$C]$^+$	468
	N	205−208(eq)	289−307(ax-eq)	[(Ph$_3$PAu)$_5$N]$^{2+}$	469
		211(ax)		[(Ph$_3$PAu)$_5$N]$^{2+}$	
	N	207−209(eq)		[(Me$_3$PAu)$_5$N]$^{2+}$	470
		209−216(ax)	297(av ax-eq)		
	P			[(Ph$_3$PAu)$_5$P]$^{2+}$	471
	S			[S(AuP(p-Tol)$_3$)$_2$(AuPPh$_3$)$_3$]$^{3+}$	472
O_h	C	212.4(av)	300.3(av)	[(Ph$_3$PAu)$_6$C]$^{2+}$	145
	P			[(LAu)$_6$P]$^{3+}$, L = ^{t}Bu$_3$P, ^{i}Pr$_3$P	473
	S			[S(AuP(m-Tol)$_3$)$_4$(AuPR$_3$)$_2$]$^{4+}$	472

^{a} No structure known. ^{b} Au−N−Au 94.3−120.7°.

same transitions would cause the optical properties, when real, and the attraction, when virtual.

Concomitantly with the low-temperature contraction of the infinite −Pt^{II}−Pt^{II}− chains in Pt(bpy)Cl$_2$, its emission energy maximum decreases, proportional to R^{-3}.[482]

Magnetic circular dichroism (MCD) data of dimeric Au(I) systems also were interpreted in terms of d$\sigma^* \rightarrow$ pσ processes.[225]

Thermochromism. Distibanes, R$_2$SbSbR′$_2$ crystallize in infinite chains ⋯Sb−Sb⋯Sb−Sb⋯ and become colored while doing so.[327,483] Many other examples on color changes with temperature are known. The explanation for the association is discussed in section IV.A, "Other Main-Group Systems".[329]

Electronic Conductivity. It is interesting to ask whether the systems with infinite chains or sheets of closed-shell atoms could be doped. Janssen and Wiegers[252] found that the "P" and "I" phases of AuBr are intrinsic semiconductors with activation energies of 0.25 and 0.38 eV, respectively. The high-temperature conductivity of the former is as high as 10^{-2} Ω^{-1} cm^{-1}.

"Through-space" NMR spin−spin coupling between two ^{19}F nuclei is well-documented.[484] As several chalcogens and pnicogens are excellent NMR nuclei, this would be a potential way to study the closed-shell interaction. One semiempirical study on through-space J(Se−Se) has appeared.[485] It invokes the overlap of lone pairs.

Experimentally, Fujihara et al.[486] saw a J(Se−Te) of 467 Hz in the tellurium−selenium heterocycle **38**.
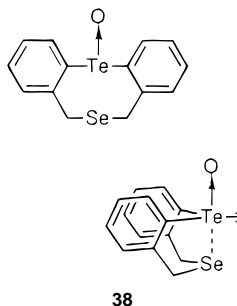
Spin−spin coupling constants of up to 59 Hz were observed for through-space Se⋯N interactions in 2-selenobenzylamine derivatives by Iwaoka and Tomoda.[321]

For covalent Pb−Pt bonds the one-bond J(Pb−Pt) is of the order of 14 to 18 kHz. Balch et al.[433] find that it decreases to 274 Hz in the crown-ether complex [(CH$_3$CO$_2$)Pb(crown-P$_2$)Pt(CN)$_2$]$^+$, whose Pb⋯Pt is 331 pm.

Substantial J(Tl−Tl) of 23.9 and 17.7 kHz are found in α- and β-TlF, respectively.[431]

NMR Chemical Shifts. Jansen[56] quotes for Ag$_{10}$-Si$_4$O$_{13}$ a ^{109}Ag low-field shift of 320 ppm. No systematical studies seem to be available.

Mössbauer and Other Nuclear Quadrupole Coupling Data. In plots,[54,258] of Mössbauer isomer shifts versus nuclear quadrupole coupling data for gold compounds, no difference could be seen between the cases with and without Au^I⋯Au^I interactions. In complexes of I$_2$, changes from free-molecule values are seen.[487]

Role in Biological Systems. Several biological systems contain sulfur-bridged Cu(I) clusters with short Cu−Cu distances. Hollander and Coucouvannis[285] found in a related Cu$_8$S$_{12}$ bridged cluster Cu⋯Cu of 279−291 pm in **39**. EXAFS studies of the protein CUP2, regulating the expression of yeast metallothionein, reveals Cu^I⋯Cu^I of about 275 pm.[488]

39
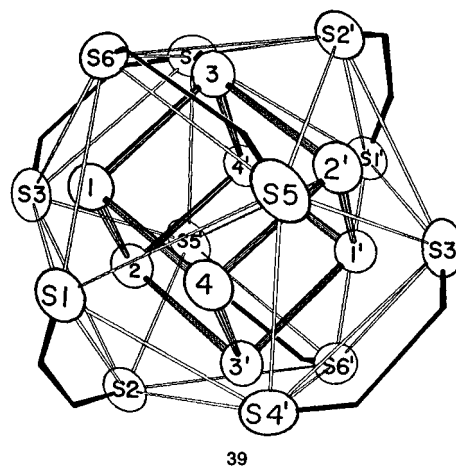
In cytochrome c oxidase, evidence[489] is presented for a doubly sulfur-bridged dinuclear Cu center, whose Cu⋯Cu is 250 pm,[490] see Figure 30. Tolman et al.[491] suggest that a key step in O$_2$ activation may be a transformation from **A** to **B**, as shown in **40**. Inversely, O$_2$ evolution may involve the reverse. In their model system [(LCu)$_2$(μ-O)$_2$](ClO$_4$)$_2$, L = 1,4,7-
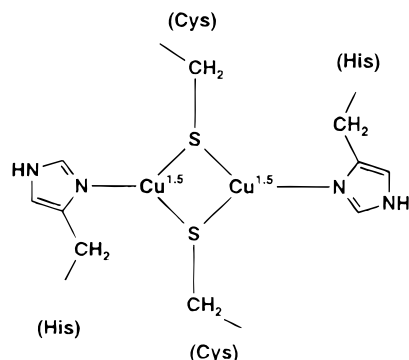
Figure 30. The dinuclear copper center of cytochrome c oxidase. (Reprinted from ref 489. Copyright 1989 VCH Verlagsgesellschaft.)

Table 11. Observed Cu⋯Cu Distances in Metalloproteins and Related Systems (The Cu−S are 225−228 pm.)

system	Cu−Cu, pm	ref
Saccharomyces cerevisiae CuMT	270.3(11)	492
Papilloma virus CuE7	272(2), 307(4)	492
Schizosaccharomyces pombe Cu-(γEC)$_n$G	274.7(8)	492
yeast CUP2	275	488

tribenzyl-1,4,7-triazacyclononane, the structure **B** has Cu⋯Cu of 279 pm.
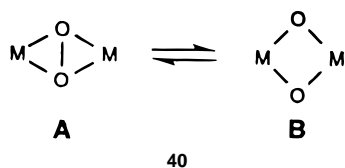
Examples of Cu⋯Cu distances in biological systems are given in Table 11. A typical Cu−S of 226 pm and a concomitant Cu⋯Cu of 272 pm imply a Cu−S−Cu of 74°, comparable with the M−E−M angles of the free A-frames in Table 6, indicating that the Cu⋯Cu attraction is involved. (The iron sulfide proteins have similar Fe−S−Fe angles.)

Pickering et al.[492] diagnose the presence of a copper−thiolate cluster in proteins from these Cu−Cu contacts in the X-ray absorption spectra. Resonance Raman spectra of Cu−Cu vibrations in "copper A" in subunit II of cytochrome c oxidase have been reported.[493] It should be emphasized that both Cu^I, Cu^I systems and mixed-valence Cu^I,Cu^{II} Cu_A[494] systems exist.

IV. Theoretical Data

A. Ab Initio Results

1. Neutral Diatomics

The rare-gas (Rg) dimers are the simplest and best understood among all closed-shell systems. The C_n coefficients, $n = 6, 8, 10$, were reported for Ar_2 to Rn_2 by Hättig and Hess[495] using a quasirelativistic TDMP2 method.

Recent supermolecule calculations on the Rg_2 dimers at levels up to CCSD(T) using relativistic pseudopotentials are reported by Burda et al.[496] and by Runeberg and Pyykkö.[131] The latter authors found
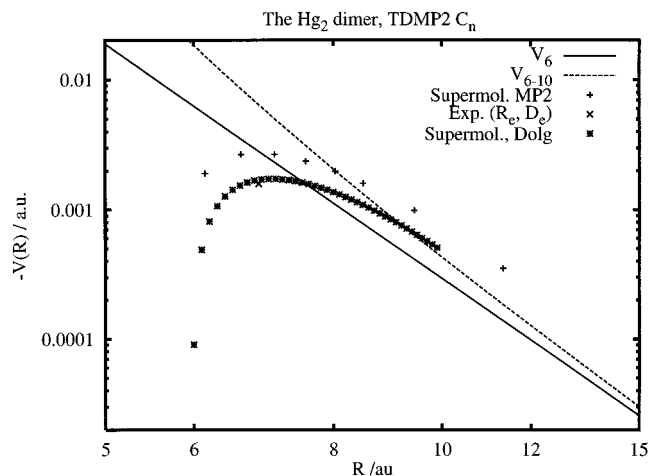

Figure 31. Potential curves for the Hg_2 dimer. The experimental minimum ($\times$) is in excellent agreement with the large-basis supermolecule calculation of Dolg and Flad.[294]

an adequate agreement with the sum of the C_n terms at large R, when compared with supermolecular CCSD(T) ones. The MP2 level supermolecular C_6 are too large. When basis sets up to [9s8p7d7f] were used for Xe_2, with estimated [2g] corrections, a CCSD(T) D_e of 21.4 meV was obtained, compared with 24 meV from experiment. The spin−orbit effects lengthen and strengthen the bond of XeRn and Rn_2.[131]

The neutral Hg_2 dimer in its electronic ground state is perhaps the simplest example of an attractive interaction between closed-shell metal atoms. A state-of-the-art calculation by Schwerdtfeger et al.,[293] using a (9s8p7d2f)/[7s6p4d2f] basis, however, only gave about half of this binding energy. Note that the experimental D_e of 0.0434(25) eV is almost 1 order of magnitude smaller than the strongest aurophilic interactions, which were well reproduced by ab initio calculations. The puzzle was solved by Dolg and Flad[294] who found that a larger, (9s9p8d4f2g) basis was necessary and obtained a D_e of 0.047 eV, in good agreement with experiment. Spin−orbit effects accounted for about 10% of the value.

From Monomers to Dimers. The Casimir−Polder equation, eq 4, can be used to relate the C_n coefficients of the dimer to the dynamic (frequency-dependent) polarizabilities, $\alpha_L(i\omega)$. The latter can be evaluated at the "coupled" or "uncoupled" level, depending on whether or not electron−electron integrals are included in the energy denominator. The latter, uncoupled alternative is less accurate. It was pointed out by Szabo and Ostlund[497] that supermolecular MP2 calculations, with their energy denominators of the type $\Delta E = \epsilon_a + \epsilon_b - \epsilon_i - \epsilon_j$, yield an interaction energy, corresponding to the uncoupled monomer polarizabilities, $\alpha(i\omega)$.

As an example we show the interatomic potential of Hg_2 in Figure 31. First, the supermolecular results of Dolg and Flad[294] closely agree with the experimental minimum. Second, their MP2 level supermolecular results are too strongly binding over the entire range. Third, the TDHF and TDMP2 coefficients, C_n, $n = 6-10$, for Hg_2 were reported by Hess.[498] This "time-dependent" approach corresponds to the "coupled" one. For Hg_2 the higher C_n coefficients

(included in the dashed curve) are seen to be important over the entire range.

For data on the main-group s^2–s^2 systems Mg_2–Ba_2, see footnote b to Table 3.

2. The d^{10}–d^{10} Case

The free $(Au^+)_2$ is not bound in its electronic ground state; the potential curve is dominated by the Coulomb repulsion of the naked ions. If this, R^{-1}, term is subtracted, the R^{-4} and R^{-6} terms of eqs 2 and 3 can be clearly seen.[168] Thus the ligands will be essential for understanding the observed Au^I···Au^I attraction. According to Figure 3 of ref 296, the ("core–core") repulsion is strengthened by relativistic effects. A purely repulsive potential was found earlier for $(Cu^+)_2$.[499]

The A-frames of the type $E(ML)_2$, **3**, with E = Se, Te; M = Au^{168} or with E = Se, M = Cu,[169,170] are the simplest cases where the effects of relativity and/or correlation on the M···M distance can be studied. As seen from Table 6, the correlation effects considerably diminish the M–Se–M angle and shorten the M···M distance for both M = Cu and M = Au. The difference between MP2 and CCSD(T) levels is here small, suggesting that already MP2 captures most of the physics of the Cu^I···Cu^I attraction.

In the case of $Se(AuPH_3)_2$, **3**,[168] the relativistic and correlation effects diminish the Au–Se–Au angle, by 11.9 and 22.3°, respectively. The corresponding Ag–Se–Ag angle is systematically larger than the Au–Se–Au one, indicating a weaker interaction. For $Se(MPH_3)_2$, the values are 87 and 81° at the 11-VE MP2 level, respectively.[168] Here "11-VE" refers to an eleven-electron, $5d^{10}6s^1$ valence space for gold; the 88 core electrons in the shells 1s to 5p are described by the pseudopotential (also called "effective core potential").

The effect of having L = PMe_3, L = PH_3, or L = nothing on the calculated M–Se–M bond angle is also small in this case.[170] The main purpose of the work was to study the higher $(Cu_2Se)_n$ clusters, up to $n = 6$. Then each Se actually bridges three or four Cu atoms. The optimized structure appears to maximize its number of Cu···Cu contacts. The shortest, calculated Cu–Cu contacts were 220 pm. The important role of the correlation effects on the Cu···Cu attraction was demonstrated at both MP2 and CCSD(T) level.

The correlation terms in the Cu···Cu interaction were fitted to a two-body interaction

$$f(r) = -0.632 - 0.184 \exp(-0.423r) \quad (26)$$

in au). A three-body potential was also fitted to Cu_3-As results.[169] For further work on $(Cu_2Se)_n(PH_3)_m$ systems, see ref 500. Related work on sulfide clusters exists.[501]

Earlier Work on Cu. Kölmel and Ahlrichs[499] carried out coupled pair functional (CPF) calculations on the copper dimers $(CuX)_2$ (X = H, F, Cl) and the azenido model compounds $[Cu(RN_5R)]_3$, **41**, and $[Cu(RN_3R)]_2$, **42**, R = H, Ph. The experimental Cu···Cu in the latter case is 245 pm. For the azenido systems, only SCF calculations were performed and a correlation correction, $d\Delta E/dR \approx 0.01$ au, from the dimer was simply added.

41
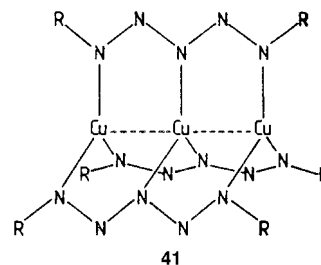
Recall in this context the shortest observed Cu^I···Cu^I of 235 pm in **41**.[219]
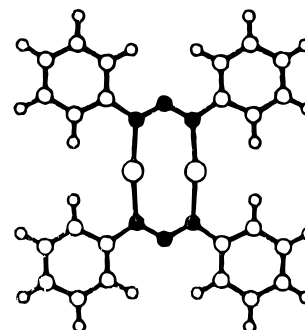
42

For the D_{2h}, diamond-shaped dimers, the correlated calculations were performed at the CPF level, and considerably shortened the Cu···Cu distance from the SCF value. For $(CuH)_2$ the calculated Cu···Cu is only 215 pm, below the 222 pm in Cu_2! The Cu···Cu for X = F, Cl are 252 and 243 pm, respectively. Note that the Cl value is smaller.

The unbridged $(X-Au-PH_3)_2$ dimers, **43**, X = F–I, H, –CN, –CH_3, and –SCH_3, have formed the prototype system for our ab initio studies of the aurophilic attraction.[137,168,481,502] The X–Au–Au–X dihedral angle is mostly taken as 90°, as in **43**, to make the electrostatic dipole–dipole terms vanish.

The central conclusions are seen in Figure 32. All HF level curves go up; they are purely repulsive. Hence a simple hybridization picture cannot be valid. When the correlation effects are included, here at MP2 level, the Au···Au attraction appears, with an Au···Au distance, R_e, and a depth, $\Delta E(R_e)$, comparable with experiment. The interaction energy, ΔE is increased by nearly a factor of 2 when going from the hardest ligand, X = F to the softest ones, X = I and SCH_3, in the order:[137,502]

$$F < H < Cl < CH_3 < CN < Br < HCC <$$
$$I < SCH_3 \quad (27)$$
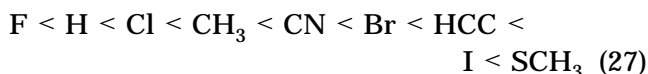
The calculated ΔE was found to correlate with the R_e and also with the MP2 level monomer 6p population.[137]

Some experimental evidence exists for the strengthening and shortening of the M···M interaction by the softer ligands. Toronto et al.[503] found for the dimeric, solid $[(Me_2PhP)AuX]_2$ the predicted Au···Au trend of 323.0, 311.9, and 310.4 pm for X = Cl, Br, I, respectively.

The role of relativity is of particular interest. If relativistic effects are omitted (by using a nonrelativistic pseudopotential for Au) at fixed monomer geometry, the interaction potential $V(R_e)$ was found to decrease by no more than 27% for the perpendicular $[ClAuPH_3]_2$ model.[502]
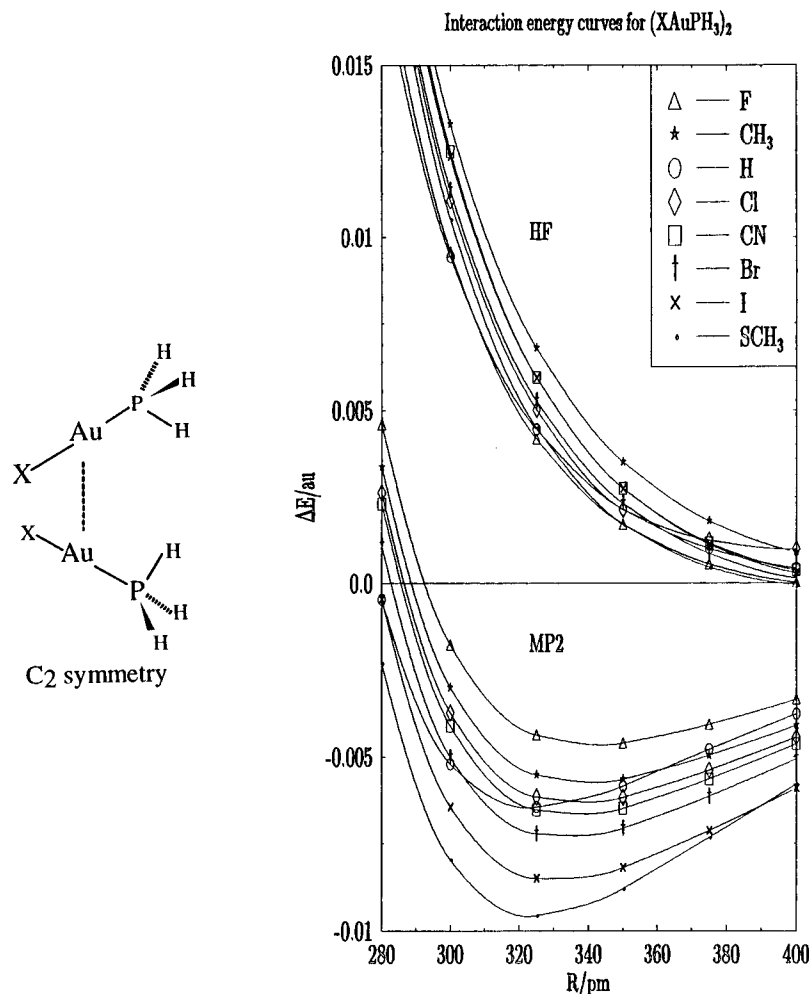
Figure 32. Influence of hard and soft ligands, X, on the gold−gold attraction potential, $V(R)$ of $[XAuPH_3]_2$, **43**. (Reprinted from ref 137. Copyright 1994 Elsevier.)

With concern to the technical requirements, three different quasirelativistic 19-VE pseudopotentials were compared and gave closely similar results. The 11-VE Au pseudopotential exaggerates the Au−Au attraction and should be avoided, as long as possible. Two coinage-metal f functions are desirable (for Au with $\alpha = 1.19$ and 0.2). The compact one is needed for intramolecular and the diffuse one for intermolecular bonding. Further, diffuse spd on Au were not needed.

The attraction survives at higher levels of correlation, going from MP2 to MP3, MP4(SDQ), CCSD and CCSD(T), but the series oscillates quite strongly. This will require further studies. The MP2 studies are likely to exaggerate $V(R_e)$.[502] The oscillations for two cases are shown in Figure 33.

The best proof for the "dispersion" character of the aurophilic attraction is the logarithmic representation in Figure 34. The long-distance MP2 interaction energy of **43** is seen to approximately go over to the R^{-6} law, corresponding to the sum of London and induction terms. Note also that near R_e the calculated correlation energy, ΔE(MP2-HF) (×), is comparable with the dispersion energy, estimated from the London formula (*).[232]

Finally we mention the possibility of nonadditive, three-body induction terms that can be comparable with the pairwise, two-body induction terms.[232] These terms involve the static dipole moments of two
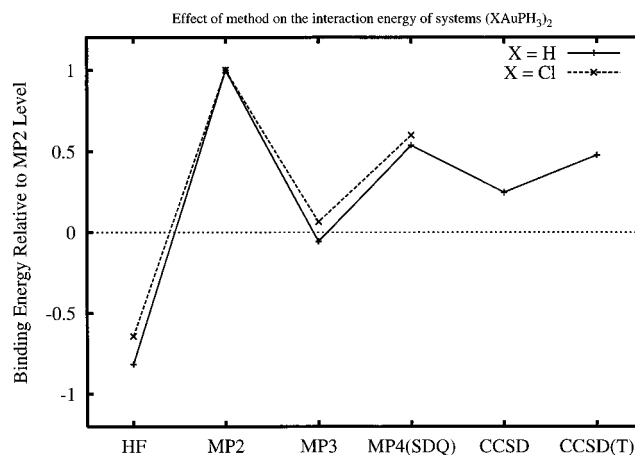
Figure 33. The dependence of the counterpoise-corrected interaction energy for two perpendicular model systems at the MP2 R_e on the method. Two f functions on Au were used. Adapted from ref 502.

monomers and the polarizability of a third one. The induction terms already enter in HF level calculations.

Other Dimers. The first ab initio study of the transannular $Au^I \cdots Au^I$ distance in a $[CH_2(PH_2AuPH_2)$-$CH_2]^{2+}$ model at MP2/LANL1DZ level shows a dramatic reduction by 52.4 pm, from HF to MP2 level.[504] (The term "LANL1DZ" refers to a particular 11-VE pseudopotential.) The final calculated $Au \cdots Au$ is still 347 pm, as compared to the experimental 297−300

Transition from supermolecule to London, $(ClAuPH_3)_2$
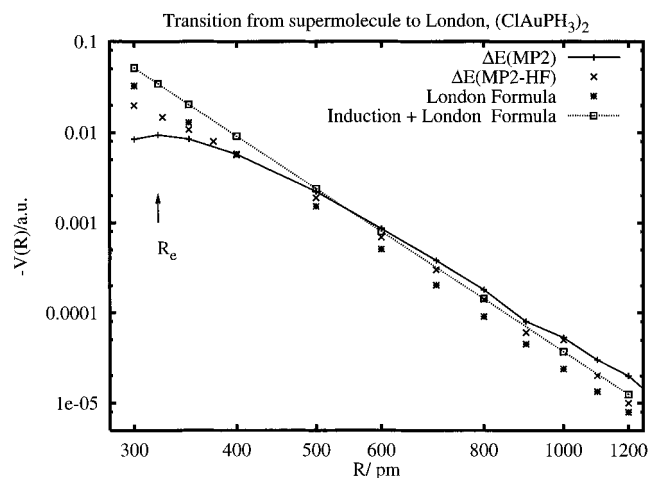
Figure 34. Extension of the long-distance, London + induction R^{-6} law (the dashed line) to the equilibrium Au–Au distance, R_e suggests a van der Waals interpretation of the aurophilic attraction. MP2 level results for [ClAuPH₃]₂, **43**. Adapted from ref 232.

pm in the related compounds **44**. Later results[232] give much closer agreement with experiment, both with 11-VE and 19-VE pseudopotentials.

The pseudopotential calculation on an Ag₂-(NHCHNH)₂ model system[505] was performed at the SCF level only.

The Pt(0) and Pd(0) d¹⁰···d¹⁰ interactions in MM′(PH₃)₄ model systems were considered by Sakaki et al.[506] at levels up to MP4SDQ. The interaction energies were of the order of 18,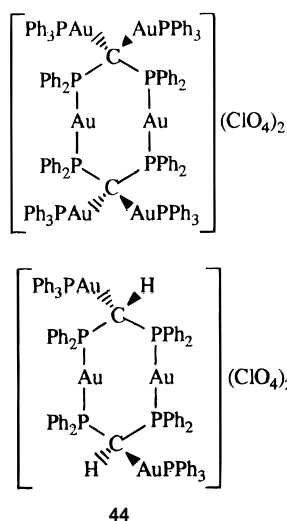 17, and 16 kJ/mol for the pairs Pt–Pt, Pt–Pd, and Pd–Pd, respectively. The calculated Pd–Pd distance of a model for the molecule **12**[204] is about 270 pm, compared with the experimental 276 pm. The introduction of electron correlation was again indispensable. The dihedral angle of 90° (perpendicular PtP₂ planes) was preferred to the coplanar case.

Tripodes. Following the synthesis of the first monomeric S(AuPR₃)₃⁺ compounds, the influence of both correlation and relativistic effects was analyzed in ref 507. If both effects were included, the systems (with R = H, nothing) showed a strong tendency to pyramidalize. As seen from Figure 35, the experimental Au–S–Au angles are close to the calculated ones.

Interaction Energy–Bond-Length Relations. Even the simplest $V(R_e)$ relationships would be of interest. We have collected into Figure 36 the experimental, NMR Au···Au interaction energies from Table 5, the calculated points for the perpendicular (XAuPH₃)₂ dimers,[137] the calculated value for the trimer,[507] and the present eq 24, using the experimental Herschbach–Laurie fit.[139] The experimental values for Au₂ and solid Au ("per bond") are included.

Tetrapodes. The E(AuL)₄ systems can be tetrahedral or C_{4v} pyramidal. The latter case is ascribed to the aurophilic attraction. The first example was the C_{4v} tetragonal-pyramidal [As(AuPPh₃)₄]⁺ ion, **15**.[186] Our ab initio 11-VE MP2 calculations[187] on [E(AuPH₃)₄]⁺ models indeed give a lower energy for C_{4v} than for T_d for both E = P and As, and indeed give a tetrahedral geometry, as observed,[214] for E = N. At the HF level all three systems remain tetrahedral. As seen from Table 6, the calculated geometry is close to the experimental one. Without the phosphines, the correlation-induced decrease of the Au–E–Au angle would be even larger.

Dimers of Dimers. The LAuX dimers can undergo a transformation to a (XAuX)⁻(LAuL)⁺ structure. Furthermore, dimers of these dimers are known with the counterintuitive [−++−] or [+−,−+] chain structures, in addition to chain or square [+−+−]. Calculations at the 11-VE MP2 level on the corresponding models with X = Cl, L = PH₃ reveal only small energy differences. Thus these reactions are "permitted by theory". Furthermore the Au atom NBO charges all are around +0.5 to +0.6, providing an interpretation for this energetical closeness.[508]

3. The $d^n–d^n$ Case, n < 10

The d⁸···d⁸ case was studied for the first time using ab initio (MP2) methods by Novoa et al.[362] on [PtCl₂(CO)₂]₂, [PtCl₂HNCH(OH)₂]₂, and [RhCl(CO)₃]₂ at double-ζ basis function level. The effects of Cl···CO interactions and added axial ligands on the L–Pt···Pt–L′ axis were also considered.

Aullón et al.[509] report a statistical analysis between the pyramidality of the monomers and the M···M distance for d⁸···d⁸ dimers, M = Ni(II), Pd(II), Pt(II), Au(III). Assuming that the pyramidalization would come first, and the M···M distance would be a consequence of it, the authors obtain a correlation between the M–M–L angles of an (ML₄)₂ complex and the M···M distance from MP2 calculations on cis-[PtCl₂(CO)₂].

4. Molecular Main-Group Systems

The Tl^I···Tl^I interaction was considered by Schwerdtfeger[510] using a simple HTl···TlH model system. He obtained an attraction of 14 kJ/mol and a Tl–Tl distance of 328 pm at the correlated level. The system was bent, like in **45**. At the HF level, no
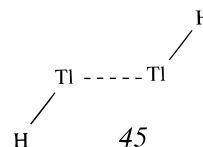
Tl···Tl attraction was found. This again casts doubts
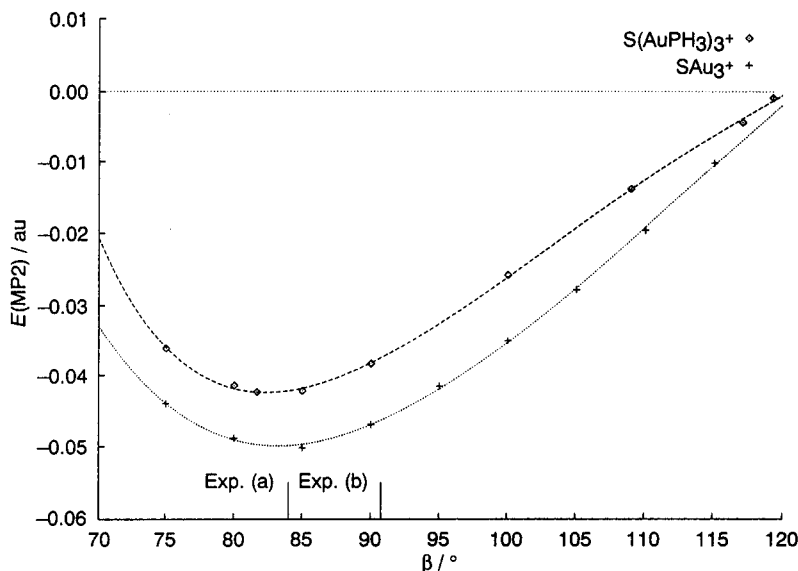
Figure 35. The calculated quasirelativistic MP2 energy of $S(AuPR_3)_3^+$ tripodes as function of the Au–S–Au angle, β. The experimental points a and b refer to R = Ph and ^iPr, respectively. (Reprinted from ref 507. Copyright 1995 Royal Society of Chemistry.)
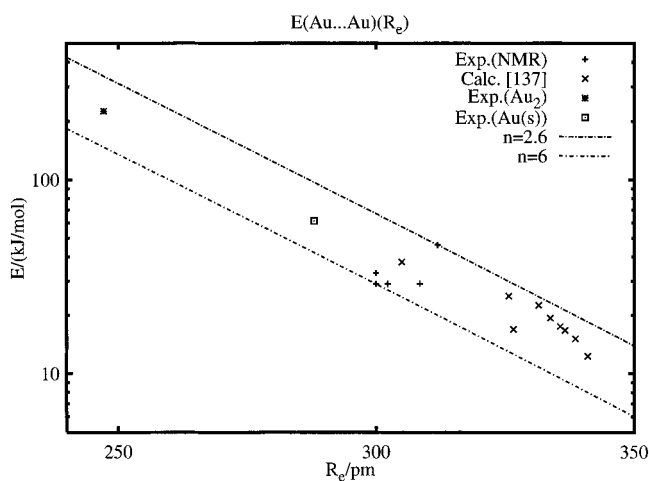
Figure 36. Calculated and experimental $Au^I\cdots Au^I$ interaction energies as function of bond length.

on the EHT hybridization model of Janiak and Hoffmann.[76,77]

Pnicogens and Chalcogens. As discussed in section III.C, closed-shell pnicogen- and chalcogen-containing molecules have a tendency to E⋯E attractions in their intramolecular or intermolecular structures, such as **25** and **26**. To understand the nature of this attraction, Klinkhammer and Pyykkö[329] studied the analogous hydride dimer model systems at MP2 level, again using relativistic pseudo-potentials. Relatively large basis sets, (6s6p3d3f)/[4s4p3d3f], were needed to make the Te⋯Te distance approach convergence. The expectations of predominant contributions from certain virtual excitations were not vindicated. Theoretical, ab initio results on coaxial $[E_2H_4]_2$ dimer models (see Figure 37) are purely repulsive at HF level and yield an attraction of about 10 kJ/mol per pair at MP2 level.[329] We repeat that this attraction arises from a large number of small contributions, AO-wise and MO-wise, precluding any simple pictures of it.

The calculated E⋯E energies ranged from 8 to 13 kJ/mol, increasing from left to right and from top to bottom in the periodic table. The bottom of the
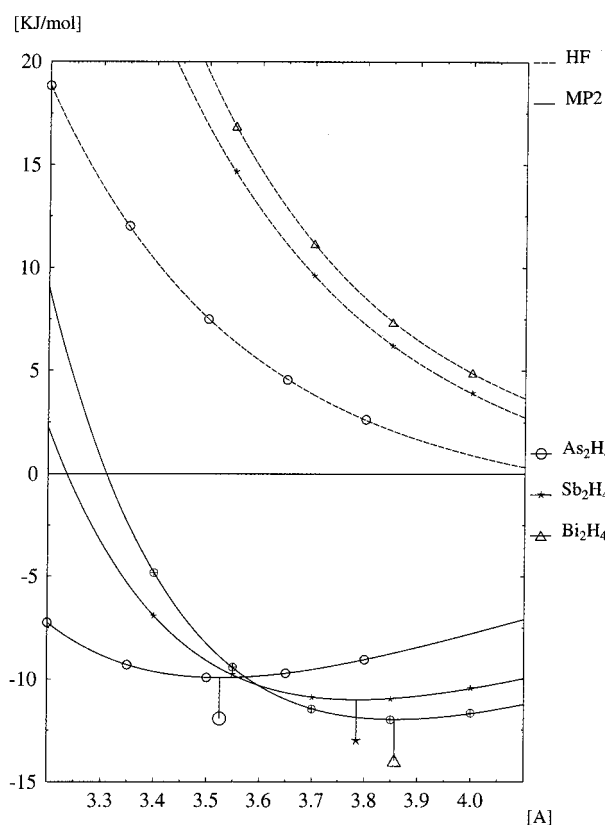
Figure 37. Calculated HF and MP2 intermolecular potentials for the coaxial systems $(H_2E\text{-}EH_2)_2$, E = As, Sb, Bi. (Reprinted from ref 329. Copyright 1995 American Chemical Society.)

potential curve was, however, very flat, making the comparison with experimental crystal distances difficult. The calculated $F(Sb\cdots Sb)$ was 0.05 N cm^{-1}. The experimental intermolecular Sb⋯Sb force constants, F, of $Me_2Sb\text{-}SbMe_2$ and $(Me_3Si)_2Sb\text{-}Sb(SiMe_3)_2$ of Bürger et al.[310] were 0.125 and 0.18 N cm^{-1}, respectively, compared with the intramolecular force constant of ca. 1.1 N cm^{-1}. Both cooperative effects, softer ligands in the experimental case and basis-set effects, may contribute to the difference.

A further example is the intramolecular Se···O interaction in the selenoiminoquinone **28**. Barton et al.[320] performed both HF and MP2 calculations and found an Se–O of 244 and 211 pm, respectively, compared to the experimental value of 208 pm.

5. Interactions between Transition and Main-Group Elements

Ruiz and Alvarez[511] studied the interaction of Cd-$(CN)_2$ with CCl_4 and CMe_4 to get an idea of the host···guest interaction energies in the corresponding clathrates. Actually, charged $[Cd(NC)_4]^{2-}$ and $[Cd(NC)_3]^-$ fragments were considered. At the MP2 level (with counterpoise corrections), an attraction of up to 17 kJ/mol was obtained.

Schwarz et al.[512] considered the structure of the experimentally observed system $PdCH_2I^+$, **46**, and found a secondary bridging interaction between the Pd and I atoms. Methods up to CCSD(T) level were used.

$$\tau(H-C-Pd-I) = 113.9$$
$$\omega(H-C-Pd) = 110.1$$

46
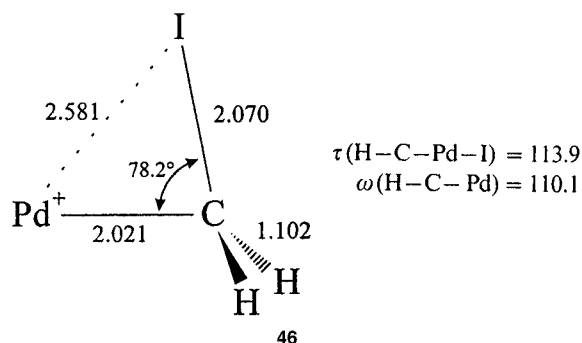
6. Partially Covalent Cases

We recall here the calculations on the systems $(ML)_4^{2+}$ (M = Ag, Au; L = PH_3, nothing).[463] These tetrahedral, two-electron–four-center (2e–4c) bonded systems are already stable at the HF level but become more strongly bound when correlation, at the MP2 level, is included.

7. Partially Ionic Cases

The $Tl_2[Pt(CN)_4]$ s^2–d^8 system was considered at various levels of approximation.[437] Most of the bonding is ionic, with some covalent character, but the correlation-induced strengthening and a crystal field-induced weakening also influence the Tl–Pt bonding.

8. Spin–Orbit Effects

It is possible to divide the different heavy-atom systems in a rather general way into two classes.

Class A molecules have at the dissociation limit open $l > 0$ atomic shells and hence $L > 0$. As reviewed by Pyykkö (ref 96, section IV.B), in this case the larger spin–orbit stabilization at the dissociation limit will diminish the dissociation energy. Well-known examples are BiH^+, Pb_2, PbO, PbH, or Tl_2, the last one being an extreme case.

Class B molecules have at the dissociation limit no heavy atoms with orbital angular momentum, $l > 0$, only closed shells or open s shells. Consequently no S–O effects occur at the dissociation limit, while
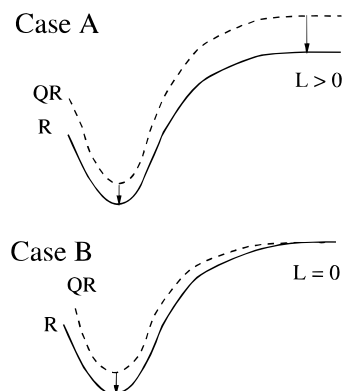
Figure 38. Spin–orbit effects on the dissociation energy of case A and case B molecules. The quasirelativistic (QR) case has no SO effects, the relativistic (R) case includes them.

higher order S–O interactions still can stabilize the molecule, through interactions of the type

$$E_{SO}^{(2)} = \sum_n |\langle X^1\Sigma_g|\lambda\mathbf{L}\cdot\mathbf{S}|n^3\Pi_g\rangle|^2/(E_0 - E_n) < 0 \quad (28)$$

for a homonuclear diatomic. The accumulated examples on this case include Hg_2,[294] the rare-gas dimers,[131] Au_2 and AuH,[513] and CsHg.[514]

The qualitative situation can be seen from Figure 38.

B. Density-Functional Calculations

As stated in section II, density functional calculations on the "supermolecule" are unable to describe van der Waals interactions. These interactions are not related in any simple way to the electron density. Although Cotton et al.[156] or Lee and Trogler[515] failed to find any interatomic electron density between the metal atoms in **4a**, see Figure 7, this does not prove the absence of a bonding interaction. For DFT work on the C_6 coefficients of nonoverlapping systems, see section II.A.

The cluster $[Ni_6(CO)_{12}]^{2-}$, **47**, was considered by Rösch and Pacchioni[465] at DFT level. This system can

47
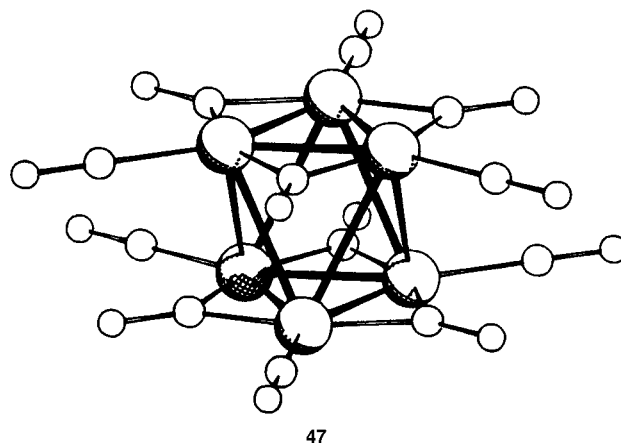
be regarded as a reduced dimer of two D_{3h} $Ni_3(CO)_6$ units, with an intramolecular Ni–Ni of 249 pm. The intermolecular Ni–Ni between the units is only slightly larger, or 277 pm. The calculated intergroup bonding energy at LDF level is only about 20 kJ/mol per Ni–Ni bond, in the hydrogen-bond range. An analysis was presented in terms of the group orbitals

Table 12. EHT Papers on the Closed-Shell Interactions

year	author (ref)	subject
1978	Avdeef and Fackler (44)	$Cu_8S_{12}^{4-}$
	Dedieu and Hoffmann (46)	$Pt^0\cdots Pt^0$
	Mehrotra and Hoffmann (45)	$Cu^I\cdots Cu^I$ dimers and tetramers
	Whangbo and Hoffmann (516)	tetracyanoplatinate chains
1981	Hoffman and Hoffmann (189)	A-frames
1985	Jiang et al. (230)	binuclear and polymeric $Au\cdots Au$
1988	Merz and Hoffmann (517)	$Cu\cdots Cu$
1990	Cui and Kertesz (59)	linear, zigzag, helical d^{10} chains
	Janiak and Hoffmann (76)	$In^I\cdots In^I$, $Tl^I\cdots Tl^I$
1991	Janiak and Hoffmann (77)	$In^I\cdots In^I$, $Tl^I\cdots Tl^I$
1992	Alemany and Alvarez (211)	$L_4M_2(\mu\text{-}XR_n)_2$ diamonds, M = Cu, Al, Ga
	Canadell et al. (388)	interlayer $Te\cdots Te$
	Subramanian and Hoffmann (235)	halocuprates
1993	Abraham et al. (518)	$Cu^I\cdots Cu^I$, with and without $-S-$ bridges
	Alemany and Hoffmann (519)	toroidal Ni thiolates, $S\cdots S$?
	Canadell et al. (520)	interlayer $Te\cdots Te$
1994	Aullón et al. (369)	bridged $(ML)_2$, M = Rh, Pd, Pt
	Burdett et al. (521)	main-group $AX_n(AuPR_3)_m$
	Calhorda and Veiros (522)	Au_5 chains, intra-ring $Au\cdots Au$
	Furet et al. (247)	hexacapped $M_8(\mu_4\text{-}E)_6L_n$
	Norman (523)	coordination of EX_3, EX_2Ph, E = Sb, Bi, X = Cl$-$I
	Ruiz et al. (524)	host$-$guest interactions in clathrates
	Seong et al. (525)	CuTe chains

of the monomer. Briefly, the bonding MO's are too low and the antibonding ones too high to result in a strong interaction.

C. Semiempirical Results

EHT Models. The first theoretical discussion of the attraction between closed-shell metal atoms seems to be that by Mehrotra and Hoffmann.[45] Hybridization of the filled shells ($5d^{10}$ for Au(I) or Pt-(0)) with the empty shells ($6s$ and $6p$) was a logical proposal for the d^{10}–d^{10} interaction mechanism,[45,189,516,517] and did explain it at the extended Hückel level. As these papers contain excellent summaries of the experimental material, we give a summary of the EHT literature in Table 12.

Burdett et al.[521] considered $AX_n(AuPR_3)_m$ molecules at EHT level. They mainly focus on species such as $(AuPR_3)_4I_2$ or the centered species in Table 10. Orbital energies and overlap populations are used as the criterion for $Au\cdots Au$ bonding.

Furet et al.[247] performed an EHT-level bonding analysis for a number of $M_8(\mu_4\text{-}E)_6L_n$ species (E = S, Se, PR), such as the 120-VE system $Ni_8(\mu_4\text{-}PPh)_6\text{-}(CO)_8$, with a $Ni\cdots Ni$ of 265 pm, and attribute a part of it to a through-space M–M interaction.

The $s^2\cdots s^2$ Case. Analogous hybridization models, as for the $d^{10}\cdots d^{10}$ case, were presented for the $6s^2\cdots 6s^2$ $Tl^I\cdots Tl^I$ case.[76,77] The underlying mechanism was the $6s$–$6p$ hybridization.

An EHT analysis for the host$-$guest interaction in the Hofmann clathrate $Ni(NH_3)_2Ni(CN)_4\cdot 2C_6H_6$ was presented in ref 524.

Conclusion on EHT. As the attraction is, however, absent in ab initio treatments at Hartree$-$Fock (HF) level,[137,168,187,481] it must therefore be ascribed to correlation. Hence the EHT model only holds in the allegorical sense that it includes correlation effects. It is successful on more realistic grounds when predicting new, partially covalent species[464,474] and may also be physically meaningful in other, partially covalent situations, such as the strongly bent $L-M^0-L$ (M = Pd, Pt) systems.[46,203,204] EHT level band structure calculations at the distances,

resulting from the correlation effect and leading to band overlap, may also be meaningful.[388,520]

Higher Methods. Boča[526] reported CNDO level calculations on the partially covalent, 2e$-$4c system $[(AuPR_3)_4]^{2+}$, R = ^tBu. He emphasized the better donor properties of this phosphine, as opposed to the simplified PH_3 model. Surprisingly large differences were found between the calculated Au$-$Au between R = H and R = Me on one hand and R = ^tBu on the other hand (243 and 263 pm, respectively, exp 270$-$273). At ab initio level, using R = H, the HF and MP2 results[463] were 290 and 272 pm, respectively.

V. Conclusion: Anything Goes

All neutral closed-shell atoms and molecules are "sticky",[386] anything sticks to anything, including the case of helium, whose dimer has D_e and D_0 of 9.06×10^{-2} and 8×10^{-6} kJ/mol, respectively.[527]

For compounds involving heavier elements these interactions are particularly strong. Imagine a very long, N-dimensional vector of all possible closed-shell monomers. Then many, if not most, of the combinations in the corresponding $N \times N$ matrix may actually exist.

While it would be impossible to review all individual cases, we hope to have mentioned most *types* of nonbonded interactions and the current, very preliminary state of their theoretical understanding. When no other obvious bonding contributions exist, one finds at the ab initio level that the attraction is due to correlation effects, that go over to R^{-6} London forces at large distances. If bridging atoms or strong ionic character exist, they mostly cause the predominant bonding, and already HF level theories can give adequate geometries. Both scalar and spin$-$orbit relativistic effects increase the closed-shell attraction, but only by some 30%, even for gold. The spin$-$orbit effect is of the order of 10% for Hg_2 or Rn_2.

After one's attention has been focused on a given pair of elements, the Cambridge Crystallographic Database can be used for a comprehensive description. The available studies have been quoted.

VI. Some Acronyms and Symbols Used in This Review

symbol	name (formula)
BEDT-TTF	bis(ethylenedithio)tetrathiofulvalene ($C_{10}S_8H_8$)
bmik	bis(1-methylimidazol-2-yl) ketone ($C_9H_{10}N_4O$)
bpy	2,2′-bipyridine ($C_{10}H_8N_2$)
4,4′-bpy	4,4′-bipyridine ($C_{10}H_8N_2$)
Bz	benzyl ($C_6H_5CH_2-$)
Cy	cyclohexyl ($C_6H_{11}-$)
dabco	1,4-diazabicyclo[2.2.2]octane ($C_6H_{12}N_2$)
dcpe	1,2-bis(dicyclohexylphosphino)ethane ($Cy_2P-C_2H_4-PCy_2$)
DFT	density functional theory
dmb	1,8-diisocyano-p-menthane
dmf	dimethylformamide (Me_2NCHO)
dmpe	bis(dimethylphosphino)ethane ($Me_2PCH_2CH_2-PMe_2$)
dmso	dimethyl sulfoxide (Me_2SO)
dppe	bis(diphenylphosphino)ethane ($Ph_2PCH_2CH_2-PPh_2$)
dppee	bis(diphenylphosphino)ethylene ($Ph_2PC=CPPh_2$)
dppf	1,1′-bis(diphenylphosphino)ferrocene ($[Ph_2P-C_5H_4]_2Fe$)
μ-dpph	μ-bis(diphenylphosphino)hexane ($Ph_2P(CH_2)_6-PPh_2$)
dppm	bis(diphenylphosphino)methane (($Ph_2P)_2CH_2$)
dppp	1,3-bis(diphenylphosphino)propane ($Ph_2P-[CH_2]_3PPh_2$)
dtsq	1,2-dithiosquarate ($C_4O_2S_2^{2-}$)
EHT	extended Hückel theory
en	ethylenediamine (($H_2N-CH_2-)_2$)
ET	see BEDT-TTF
EXAFS	extended X-ray absorption fine structure
form	di-p-tolylformamidinate (p-$CH_3C_6H_4NCHN-C_6H_4$-p-CH_3)
i-MNT	1,1-dicyanoethene-2,2-dithiolate (($NC)_2C=CS_2$)
i-mnts	1,1-dicyanoethene-2,2-thioselenolate ($SSeC=C(CN)_2$)
Me	methyl ($-CH_3$)
Mes	mesityl (2,4,6-$Me_3C_6H_2$)
MNT	1,2-dicyanoethene-1,2-dithiolate
o-Tol	o-tolyl (MeC_6H_4)
Pc	phthalocyanine ($C_{32}H_{16}N_8$)
pta	phosphatriazaadamantane ($C_6H_{12}N_3P$)
py	pyridine (C_5H_5N)
pymt	pyridine-2-thiol ($C_4H_3N_2S$)
pz	pyrazolate ($C_3H_3N_2$)
thf	tetrahydrofurane (C_4H_8O)
TPAH	1,3,5-triaza-7-phosphaadamantane ($C_6H_{12}N_3P$)
Ts	tosylate ($O_2SC_6H_4$-4-Me)
ur	urotropine ($C_6H_{12}N_4$)

VII. Acknowledgments

Note Added in Proof

Section II.A. Nonadditive interatomic interactions also arise via exchange (Pauli, Born) repulsion at short distances; see the example of $K^+-W(110)$ collision potentials.[528]

Section III.A. Further support for the predicted[137] shortening and strengthening of the aurophilic attraction by soft ligands on the gold is provided by the structure of $[Au_3(\mu$-tppm)$I_3]$. Its Au−Au is 313.6 pm,[529] as contrasted to 320.1 pm in the corresponding Cl compound.

A new experimental approach to the strength of the aurophilic dimerization in liquids is provided by concentration-dependent studies of optical properties.[530] The room temperature equilibrium constants, K, for $[Au_2(dppm)[(CH_2)_2S(O)NMe_2]]BF_4$ and $[Au_2$-$(dmpm)[(CH_2)_2S(O)NMe_2]]BF_4$ are 33(9) and 52(7) M^{-1}, respectively. These values correspond to ΔG of -8.7 and -9.8 kJ/mol, respectively. By studying $K(T)$, one could obtain also the ΔH (and ΔS) that could be compared with Table 5.

Section III.C. In contrast to the chained Te_8^{2+} groups in $Te_8[WCl_6]_2$ (quoted in Table 9), the new compound $Te_8[ReCl_6]$ has isolated ones with $Q = (Te-Te)/(Te\cdots Te) = 315/272 = 1.16$.[531] The Q still decrease along the series S, Se, Te. In the mixed species $Te_2Se_6^{2+}$, the $Se\cdots Se$ are 334−342 pm.[532]

Further examples on the *soft−soft interactions* between iodophosphonium and mono- and polyiodide ions are given by Stenzel et al.[533]

Sections III.D and IV.A.3. A short Pt−Pt distance of 274.4 pm occurs in the quadruply bridged $[Pt_2(\mu$-mtpo)$_4]\cdot2DMSO$. Both HF and DFT LANL2DZ full geometry optimizations on a $Pt_2[NHCHN(C-(CH_2)(CH_3))]_4$ model give good $Pt^{II}-Pt^{II}$ distances for this d^8-d^8 case.[534]

Copyright Acknowledgment for Structures

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Structure **47**. (Reprinted from ref 465. Copyright 1995 American Chemical Society.)

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