

Oxygen, sulfur, selenium and tellurium†

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As in previous years, this review will emphasise synthetic, structural and spectroscopic aspects of discrete molecular species containing Group 16 elements. Notable advances include the increasing prominence of organochalcogen-nitrogen heterocycles for materials applications and the wealth of structural motifs and forms of reactivity afforded by simple chemical transformations.

1. Sulfur, selenium and tellurium

We begin by reviewing carbon-free rings, cages and clusters. $[\text{As}_3\text{S}_5][\text{AlCl}_4]$ and $[\text{As}_3\text{Se}_4][\text{AlCl}_4]$ are obtained by reaction of S_8 or selenium respectively with $\text{As-AsCl}_3\text{-AlCl}_3$ melts at 80 °C, followed by slow cooling to 50 °C.¹ The cation structures are derived from As_3E tetrahedra (E = S or Se) with three edge-bridging selenium atoms in $[\text{As}_3\text{Se}_4]^+$ and four edge-bridging sulfurs in $[\text{As}_3\text{S}_5]^+$. The geometry, phase stability and electronic properties of isolated selenium chains incorporated into nanoporous $\text{AlPO}_4\text{-5}$ crystals were investigated,² $[\text{2,2,2-crypt-Na}]^+$ salts of $[\text{Ti}_4\text{Se}_8]^{4-}$ and $[\text{Ti}_2\text{Se}_4]^{2-}$ are generated by extracting $\text{NaTi}_{0.5}\text{Se}$ into ethylenediamine in the presence of 2,2,2-crypt and 18-crown-6,³ and $[\text{cyclo-Te}_4][\text{Ga}_2\text{Br}_7]_2$ is available from the reaction between Te and GaBr_3 in benzene.⁴ Potential energy hypersurfaces of S_7 and of $[\text{LiS}_7]^+$ were investigated by Steudel and co-workers using *ab initio* MO calculations at the G3X(MP2) level of theory.⁵ The boatlike *cyclo-S*₇ conformer is less stable (by $\approx 12 \text{ kJ mol}^{-1}$) than the chairlike form, for the fifteen $[\text{LiS}_7]^+$ complexes modelled, the calculated binding energies were -93.8 to $-165.7 \text{ kJ mol}^{-1}$. The same workers have also investigated Li^+ complex formation with H_2S , Me_2S_n ($n = 1\text{--}5$) and isomers of S_6 .⁶ The first telluradistibirane and telluradibismirane $(\text{Bbt})_2\text{E}_2\text{Te}$ (E = Sb or Bi), containing E_2Te rings, were obtained by treating $(\text{Bbt})\text{E}=\text{E}(\text{Bbt})$ with ${}^n\text{Bu}_3\text{PTe}$ at room temperature.⁷ The telluradistibirane is stable in solution up to 140 °C, whereas the bismuth analogue eliminates $(\text{Bbt})\text{Bi}=\text{Bi}(\text{Bbt})$ and $(\text{Bbt})_2\text{Te}_2$ at 100 °C. The S–S bond order in $[\text{S}_2\text{I}_4]^{2+}$, judged by crystallography, vibrational spectroscopy and normal co-ordinate analysis to be 2.2–2.4, is among the highest values determined for heavier main-group elements in an isolated compound.⁸ Passmore and Laitinen have applied MP2, B3PW91 and PBE0 methods to predict structural and spectroscopic parameters for $[\text{SeX}_3]^+$ and SeX_2 (X = Cl, Br or I),⁹ finding close agreement with experimental data, while the mixed-valence bromoselenate $[\text{Et}_4\text{N}]_2[\text{Se}_3\text{Br}_8(\text{Se}_2\text{Br}_2)]$ is accessible from the reaction between selenium and Br_2 in acetonitrile, in the presence

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† This chapter reviews the literature reported during 2005 on the chemistry of the Group 16 elements.

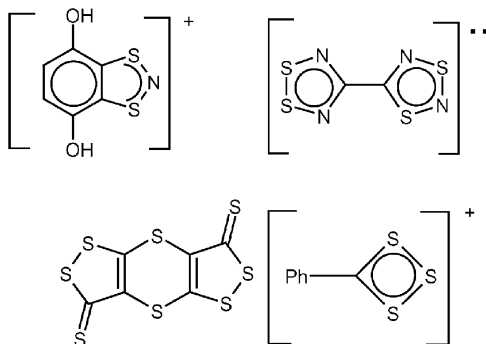
of $[\text{Et}_4\text{N}]\text{Br}$.¹⁰ Highlights from the field of “inorganic” chalcogen-nitrogen systems include investigations into the bonding and spectroscopic properties of $[\text{CoCp}(\text{S}_2\text{N}_2)]$,¹¹ the unexpected availability of Se_4N_4 from reactions of Ph_2SNBr with selenium sources (Ph_3PSe , Me_3PSe , Et_3AsSe or selenium)¹² and synthesis of *tris*(pentafluorophenyl)boron adducts of $\text{OTe}(\mu\text{-NBu}^t)_2\text{TeNBu}^t$ and $[\text{OTe}(\mu\text{-NBu}^t)_2\text{Te}(\mu\text{-O})_2]$ upon hydrolysis of $^t\text{BuNTe}(\mu\text{-NBu}^t)_2\text{TeNBu}^t$ by $(\text{C}_6\text{F}_5)_3\text{B} \cdot \text{H}_2\text{O}$.¹³ Passmore and co-workers have isolated $[\text{SNS}][\text{SbF}_6]$ by reacting either $\text{S}_3\text{N}_2\text{Cl}_2$ or $(\text{NSCl})_3$ with $\text{Ag}[\text{SbF}_6]$ and S_8 in liquid SO_2 ;¹⁴ the $[\text{SNS}]^+$ cation participates in a cycloaddition reaction with 1,4-benzoquinone, affording a benzo-1,3,2-dithiazolium salt.¹⁵ The reaction between Ph_2SNH and $\text{Ph}_2\text{FS} \equiv \text{N}$ in the presence of *dbu* produces $\text{Ph}_2\text{S}(=\text{N}-\text{Ph}_2\text{S} \equiv \text{N})_2$, which has two terminal $\text{S} \equiv \text{N}$ bonds.¹⁶

Chalcogenadiazoles and dichalcogenadiazoles (C_2EN_2 and CE_2N_2 rings, respectively), when fused to aromatic ring systems, exhibit useful conducting and optical properties;^{17–30} prominent results include the synthesis of a biradical containing 1,2,3,5- and 1,3,2,4-isomeric dithiadiazolyl rings,²³ the polymorphism of the sterically crowded radical 2,4,6-(CF_3)₃ $\text{C}_6\text{H}_2\text{CNSSN}^\bullet$,²¹ and the first monomeric π -stacked *bis*-1,2,3-thiaselenazolyl radical.¹⁹

Moving onto chalcogen-halogen species, the phenylselenium(IV) trihalides PhSeX_3 ($\text{X} = \text{Cl}$ or Br), derived by halogenation of Ph_2Se_2 with SO_2Cl_2 or Br_2 , exhibit very different structures.³¹ The trichloride forms polymeric chains analogous to other RSeCl_3 , whereas PhSeBr_3 is not isostructural with either PhSeCl_3 or PhTeBr_3 , displaying instead a combination of molecular, ionic and charge-transfer bonding modes. Treatment of R_2Te_2 ($\text{R} = \text{Ph}$ or β -naphthyl) with I_2 and $[\text{Et}_4\text{N}]\text{I}$ affords $[\text{Et}_4\text{N}][\text{RTeI}_4]$,³² metathesis reactions of R_2TeF_2 with Me_3SiCN afford $\text{R}_2\text{Te}(\text{CN})_2$ ($\text{R} = \text{Ph}$ or *Mes*) or R_2Te ($\text{R} = \text{Me}$ or *Trip*).³³ $[\text{Te}(\text{CN})_4(\text{MeCN})_2]_n$ and $[\text{Te}(\text{CN})_4(\text{thf})_3]_n$ are available by reacting TeF_4 with Me_3SiCN in acetonitrile or *thf*, respectively; both polymers comprise trigonal pyramidal $[\text{Te}(\text{CN})_3]$ units linked by CN groups, but differ in the connectivities of the $[\text{Te}(\text{CN})_3]$ moieties and coordination of the solvent molecules.³⁴ Raman spectroscopy of SO_2 dissolved in $\text{HF}-\text{SbF}_5$ at -90°C reveals that, in addition to the known adduct $\text{SO}_2 \cdot \text{SbF}_5$, the protonated species $[\text{FS}(\text{OH})_2][\text{SbF}_6]$ is generated.³⁵ This salt was also characterised crystallographically. Fluoride abstraction during the reaction of SF_6 with $[\text{Ti}(\eta^5\text{-1,3-C}_5\text{H}_3\text{tBu}_2)(6,6\text{-dimethylcyclohexadienyl})(\text{PMe}_3)]$ affords $[\text{Ti}(\eta^5\text{-1,3-C}_5\text{H}_3\text{tBu}_2)\text{F}_2]_4$.³⁶ Oxysulfur radicals SF_5O_x ($x = 0\text{--}3$) were analysed in an O_2 matrix at 16 K by IR spectroscopic and DFT methods;³⁷ such species are likely oxidation products upon photolysis of SF_6 in the upper atmosphere. Turning now to halogen adducts of Group 16-containing molecules, the reaction of benzimidazole-2-thione (*mbzim*) with I_2 generates $\{[(\text{mbzim})_2\text{I}][\text{I}_3]\} \cdot [(\text{mbzim}) \cdot \text{I}_2]$, which contains ionic (for the cation) and “spoke” (for the I_2 adduct) structural forms.³⁸ Diiodine adducts of *N,N'*-dimethylperhydrodiazepine-2,3-dithione and $\text{NH}(\text{Ph}_2\text{PS})_2$ dissolve Pd and Au powders, respectively,^{39,40} the palladium reaction being of possible importance for recovery of this metal from spent catalytic converters, and thioether adducts $(\text{PhCH}_2)_2\text{S} \cdot \text{IX}$ ($\text{X} = \text{Cl}$ or Br) were structurally characterised.⁴¹

Frère and Skabara have reviewed the relationships between the molecular structures of the salts of extended tetrathiafulvalene analogues with their electrochemical properties and stacking modes,⁴² and *peri*-ditellurium bridged polyacenes were examined crystallographically as neutral molecules and, upon oxidation, as radical cations.⁴³ In the newly described β -polymorph of C_6S_8 , the dihedral angle between the C_3S_5 planes along the $\text{S}-\text{S}$ axis of the central 1,4-dithiine ring is 133° , whereas in α - C_6S_8 the molecule is essentially planar.⁴⁴ Slow concentration of a

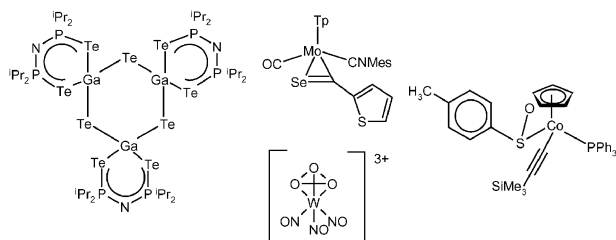
carbon disulfide solution of C_{60} and Se_8 affords a co-crystal $C_{60} \cdot Se_8 \cdot CS_2$, in which Se_8 and CS_2 molecules fill octahedral voids of the distorted hexagonally close-packed fullerene molecules.⁴⁵ The reaction of $PhCS_3Cl$ and $Ag[MF_6]$ ($M = As$ or Sb) gives trithietanium salts $[PhCS_3][MF_6]$, the 6π -C SSS^+ ring being calculated to possess some aromatic character.⁴⁶ Reports on phosphorus-chalcogencompounds include a new route for the bulk-scale preparation of the selenating agent $[PhP(Se)(\mu-Se)]_2$ (Woollins' Reagent),⁴⁷ ammonium salts of pyridine-stabilised monometatrithiophosphate $[py \rightarrow PS_3]^+$,⁴⁸ and the synthesis and reactivity of *O*-acylselenophosphates⁴⁹ and enantiomerically pure *P*-chiral phosphinoselenoic chlorides.⁵⁰



We focus now on the co-ordination chemistry of chalcogen donor ligands, beginning with phosphorus chalcogenides. The first ditelluroimidodiphosphinate complexes were reported: $Na[N(Pr^i_2PTE)_2]$ reacts with the appropriate metal halides to form $[M\{N(Pr^i_2PTE)_2-Te,Te'\}_2]$ ($M = Zn, Cd$ or Hg) or $[M\{N(Pr^i_2PTE)_2-Te,Te'\}_3]$ for antimony or bismuth,⁵¹ by contrast, bi- and trimetallic complexes with central M_2Te_2 and M_3Te_3 rings were obtained with gallium(III) and indium(III).⁵² Square-planar $[M\{N(Pr^i_2PSe)_2-Se,Se'\}_2]$ ($M = Sn$ or Se) were prepared by reaction of $K[N(Pr^i_2PSe)_2]$ with tin(II) chloride or $Se\{S_2P(OPr^i)_2\}_2$.⁵³ The formation of zinc phosphate polymers from insertion reactions of metathiophosphates into zinc dialkyldithiophosphates was explored using molecular simulation techniques,⁵⁴ the reaction between $[Cu(MeCN)_4][BF_4]$, *dp*pm and dialkyldithiophosphates affords polynuclear copper(I) complexes with bridging diphosphine ligands.⁵⁵ A macrocyclic silver(I) complex $[Ag_{12}(PhS_2P-PS_2Ph)_6(dppeS)_6]$ was generated upon oxidation of the one-dimensional co-ordination polymer $\{[Ag_2(PhS_2P-PS_2Ph)(dppe)] \cdot dppe\}$.⁵⁶ Complexes containing tripodal $[AnPO_3]^{2-}$ and $[AnPS_3]^{2-}$ ligands were synthesised from metal alkoxides and carboxylates using Lawesson's Reagent.⁵⁷ Crystallisation of $Ag[O_2CCF_3]$ from chloroform solutions containing Ph_3PS affords $\{[(CF_3CO_2)Ag]_6(Ph_3PS)_4\}$, which has a 24-membered $[AgOCO]_6$ ring.⁵⁸

Oxidative addition reactions from appropriate precursors deliver naphthalene-1,8-dithiolate and biphenyl-2,2'-dithiolate complexes of titanium(IV),⁵⁹ phenylchalcogenate complexes $[SmCp^*_2(EPh)(thf)]$ and $[SmCp^*_2(\mu-EPh)]_2$ ($E = S, Se$ or Te)⁶⁰ and trigonal-bipyramidal platinum(II)-phenylseleno complexes.⁶¹ Estimates of E–E and Cr–E bond strengths ($E = Se$ or Te) were made from kinetic measurements of reactions involving $[CrCp^*(CO)_3]$ and Ph_2E_2 ,⁶² application of DFT methods to the oxidative addition of R_2E_2 ($R = H$ or Me ; $E = S, Se$ or Te) to $[M(PR'_3)_2]$ ($R' = H$ or Me ; $M = Pd$ or Pt) has demonstrated that activation barriers are higher for platinum than palladium for all R, R' and E combinations studied.⁶³

Mono-, bi- and tetranuclear platinum group metal complexes of cyanodiselenoimidocarbonate, $[\text{C}_2\text{N}_2\text{Se}_2]^{2-}$, and triselenocarbonate, $[\text{CSe}_3]^{2-}$ were prepared by Woollins and co-workers,^{64,65} ruthenium complexes bearing $[\text{Se}_n]^{2-}$ or $[\text{Te}_n]^{2-}$ chains were available by reacting $[\text{RuClCp}(\text{PPh}_3)_2]$ with polychalcogenide salts.⁶⁶ The heterocubane cluster $[\text{Rh}_3\text{Cp}^*\text{Sb}_2\text{S}_5]$, available from $[\text{RhCp}^*\text{Cl}(\mu\text{-Cl})_2]$ and $\text{K}_3[\text{SbS}_3]$ in boiling thf, has a very short antimony-sulfur distance $[2.297(1) \text{ \AA}]$ which, in conjunction with DFT calculations on model compounds, is strong evidence for a stable $\text{Sb}=\text{S}$ bond.⁶⁷ Reaction of $[\text{Cu}(\text{tmeda})(\text{MeCN})][\text{OTf}]$ with S_8 affords $[\text{Cu}_2(\text{S}_2)_2(\text{tmeda})_2][\text{OTf}]_2$, which was formulated on the basis of UV-Vis, RR and crystallography to possess a bis($\mu\text{-S}_2^{2-}$) dicopper(II) core,⁶⁸ the tetranuclear niobium complex $[\text{Nb}_4\text{SO}_5(\text{NCS})_{10}]^{6-}$ is capped by a μ_4 -sulfido ligand.⁶⁹ The counterion and crystallisation solvent are the dominant factors in determining the solid-state structures of $[\text{9}]\text{aneS}_3$ and $[\text{18}]\text{aneS}_6$ complexes of platinum(II),⁷⁰ while the first mononuclear selenoaryl complexes were prepared from molybdenum alkylidene precursors using mesityl isoselenocyanate.⁷¹ The bicyclic system $\text{CF}_3\text{CN}_5\text{S}_3$ is a monodentate donor through its N5 atom with Zn^{2+} , Co^{2+} and Cu^{2+} , whereas with cadmium(II) bidentate co-ordination (the nitrogen atom adjacent to carbon is the second donor) is supplemented by a $\text{Cd}\cdots\text{F}$ interaction.⁷² The possible existence of complexes of *cyclo*- O_3 and *cyclo*- S_3 was investigated, using the 18-electron rule to construct candidate species and optimising structures with the DFT-B3LYP method.⁷³ Genuine η^3 complexes of the *cyclo*- E_3 ligands for Groups 6 and 8 metals were suggested to be available with strong π -acceptor co-ligands such as nitrosyl. Voltammetric measurements on Group 8 metal complexes of (formally monoreduced) *N*-substituted thiazolidine-2,4,5-trithione demonstrate that this new class of dithiolene complex is stable in neutral, monoanionic and dianionic forms.⁷⁴



Two unusual C–S bond activation reactions have appeared. The alkynylsulfoxide $\text{Me}_3\text{SiC}\equiv\text{CS}(\text{O})(p\text{-tolyl})$ reacts with $[\text{CoCp}(\text{PPh}_3)_2]$ to give a cobaltosulfoxide complex, which can be further oxidised to a metallosulfone.⁷⁵ CuSCN reacts with methanol and acetonitrile under solvothermal conditions to afford a three-dimensional co-ordination polymer containing dodecanuclear copper(I) clusters with μ_3 - and μ_4 - CH_3S^- groups.⁷⁶ This *in situ* generation of thiolate ligands provides a model for the geothermally induced conversion of ‘inorganic’ sulfur into organosulfur species. Power and co-workers have used the bulky 2,6-Trip₂C₆H₃ aryl group to stabilise quasi two-coordinate dithiolate complexes $[\text{M}^{\text{II}}(\text{SAr})_2]$ ($\text{M} = \text{Cr}, \text{Mn}, \text{Fe}, \text{Co}, \text{Ni}$ or Zn) which possess almost linear S–M–S axes (with the exception of the iron complex) and exhibit interactions between M and *ipso* carbon atoms from the Trip rings.⁷⁷ Wiegardt and co-workers have examined the electronic structures of benzene-1,2-dithiolate complexes of iron and concluded that highvalent iron(IV) is not accessible with these ligands,⁷⁸ copper(I) and zinc(II) complexes of

silylchalcogenate ligands have been synthesised,⁷⁹ and sulfur reacts with lanthanocene alkyls to give lanthanide thiolate, sulfide and disulfide species.⁸⁰

The molecular conformations of $\text{CH}_3\text{N}=\text{S}(\text{CF}_3)_2$,⁸¹ $\text{FC}(\text{O})\text{N}=\text{S}(\text{O})\text{F}_2$,⁸² $\text{FC}(\text{O})\text{SSC}(\text{O})\text{CF}_3$ ⁸³ and $\text{E}(\text{SCH}_3)_2$ (E = Se or Te)⁸⁴ were determined by electron diffraction studies and by *ab initio* and DFT geometry optimisation. *Ab initio* MO calculations at the G2(MP2) level demonstrate that branched isomers of dialkyl triselenides $\text{RSe}(=\text{Se})\text{SeR}$ (R = Me or Et) are less stable (by $\approx 60 \text{ kJ mol}^{-1}$) than linear RSeSeSeR , casting doubt on claims made during 2004 of their existence.⁸⁵

We conclude this section by reviewing chalcogenide-containing materials. Two new mixed-valent tellurium oxides $\text{A}_4[(\text{Te}^{6+})_5(\text{Te}^{4+})_3]\text{O}_{23}$ ($\text{A}^+ = \text{Rb}^+$ or K^+) contain corrugated $[\text{Te}_6\text{O}_{23}]$ layers, constructed from corner-connected TeO_6 octahedra and TeO_5 square pyramids, which are interconnected by tetravalent tellurium atoms.⁸⁶ Two polymorphs of $[(\text{N}_2\text{H}_4)_2\text{ZnTe}]$, prepared at ambient temperatures using solution-based techniques, possess one-dimensional zinc telluride chains whose conformations differentiate the polymorphs.⁸⁷ In related studies $[\text{N}_2\text{H}_5]_4[\text{Ge}_2\text{Se}_6]$ and $[\text{N}_2\text{H}_5]_4[\text{Sn}_2\text{Se}_6] \cdot (\text{N}_2\text{H}_4)_3$ were decomposed to metal selenide films at 200–300 °C.⁸⁸ Two new members of the $(\text{Sb}_2\text{Te}_3)_m \cdot (\text{Sb}_2)_n$ homologous series, Sb_4Te_3 and Sb_8Te_9 , were reported,⁸⁹ and the crystal structure of $[\text{Sb}_2\text{Te}_2][\text{AlCl}_4]$, obtained from $\text{Te-Sb-SbCl}_3\text{-NaCl-AlCl}_3$ melts, contains one-dimensional chains of linked $[\text{Sb}_2\text{Te}_2]^+$ rings.⁹⁰ The semiconducting materials Li_2TE_3 (E = S or Se), synthesised from Li, Te and E (molar ratio 2 : 1 : 3) contain layers of trigonal pyramidal $[\text{TE}_3]^{2-}$ dianions,⁹¹ the charge-density wave materials MTe_3 (M = rare earth metal) contain $[\text{Te}_2]^-$ square nets which, the authors noted, propagate in a fashion incommensurate from the $[\text{MTe}]^+$ sub-lattice.⁹²

2. Oxygen

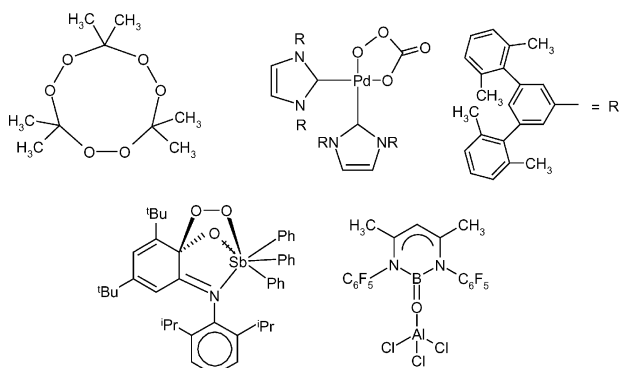
Among the investigations into peroxy species which appeared during 2005 were the O–O bond cleavage of $\text{C}_{60}(\text{O})(\text{OOBu}^t)_4$ by AlCl_3 to yield [5,6]- and [6,6]-oxohomofullerenes,⁹³ and computational studies of the decomposition of triacetone triperoxide^{94,95} and the water-mediated degradation of peroxyacetyl nitrate $[\text{CH}_3\text{C}(\text{O})\text{OONO}_2]$.⁹⁶ Dihydrogen trioxide (HOOH) has been detected for the first time in a supersonic jet and studied by microwave spectroscopy.⁹⁷ From the rotational constants for the molecule and its deuterated isotopomer structural parameters were identified: $d(\text{H-O})$ 0.963 Å, $d(\text{O-O})$ 1.428 Å, O–O–O 107.0°, H–O–O 101.1°. The cerium(III)-catalysed photoinitiated reaction between $[\text{SO}_3]^{2-}$ and dioxygen in aqueous medium proceeds *via* formation of cerium(IV), which initiates a radical chain reaction involving $[\text{SO}_3]^-$, $[\text{SO}_4]^-$ and $[\text{SO}_5]^-$.⁹⁸

Through *ab initio* methods the rapid removal of $^1\text{O}_2$ from solution by 1,5-dithiacyclooctane compared with either thiane or 1,4-dithiane was found to result from a conformational change of the molecule, which electrostatically stabilised the intermediate persulfoxide and raised the barrier for physical quenching of $^1\text{O}_2$.⁹⁹ Generation of $^1\text{O}_2$ from H_2O_2 is promoted by La^{3+} salts when incorporated into zeolites Beta and USY,¹⁰⁰ or when used in conjunction with $[\text{MoO}_4]^{2-}$ and HO^- ,¹⁰¹ with optimal catalysis at a $[\text{MoO}_4]^{2-} : \text{La}^{3+} : \text{HO}^-$ ratio of 1 : 4 : 12.

Mixing ethanolic solutions of 1-[(ethoxycarbonyl)methyl]-3-hydroxy-2-pyridinone (HL) and hydrated nickel(II) nitrate, followed by addition of H_2O_2 and Et_3N , gives $[\text{Ni}_8\text{L}_{12}(\mu_6\text{-O}_2)][\text{NO}_3]_2$ in which six nickel(II) ions form an octahedral cage around the central $[\text{O}_2]^{2-}$, with the $[\text{Ni}_6(\text{O}_2)]$ core end-capped by two further Ni^{2+} ions.¹⁰²

The Ni...Ni distances [3.234(2)–3.330(2) Å] confirm the absence of metal–metal bonds.

The considerable number of publications covering dioxygen activation by *d*- and *f*-block metals permits only a brief survey. In contrast with many oxygen-storage materials, the sulfur centre in the lanthanide oxysulfates Ln₂O₂SO₄ (Ln = La, Pr, Nd or Sm) is the redox-active site.¹⁰³ Thus, reduction by H₂ or hydrocarbon and subsequent re-oxidation with O₂ between Ln₂O₂SO₄ and Ln₂O₂S achieves an oxygen storage of 2 (mol of O₂) mol⁻¹, which is eight times higher than CeO₂–ZrO₂. Crystals of a two-coordinate palladium(0)-carbene complex rapidly fix O₂ and CO₂ to form a palladium(II)-peroxocarbonate, *via* a peroxo intermediate.¹⁰⁴ RR and DFT computational studies of the Ni₂O₂ core in the *trans*-μ-1,2-peroxo bridged complex [(tmc)Ni]₂(O₂)²⁺ disclose that the reduced covalency of the Ni-peroxo bonds relative to a structurally similar dicopper(II) complex results from the lower effective nuclear charge of nickel(II) compared to copper(II).¹⁰⁵ Exposing sterically hindered copper(I)-anilidoimine complexes to dioxygen at low temperatures gives side-on bound O₂ complexes; the O–O bond length in one example examined crystallographically [1.392(2) Å] indicates significant copper(III)-peroxo character, which is supported by theoretical calculations.¹⁰⁶ Vibrational spectroscopic studies of GaO₂ and InO₂, produced by matrix-isolation techniques from the Group 13 atoms and O₂, show that the cyclic MO₂ (M = Ga or In), which form spontaneously, photoisomerise to linear OMO molecules, in accord with the slightly greater calculated stability of the latter.¹⁰⁷ The Pt–Pt bond in the 1,2-diplatinaborane cluster [(PMe₂Ph)₄Pt₂B₁₀H₁₀] reacts with dioxygen to give[(PMe₂Ph)₄Pt₂(O₂)B₁₀H₁₀], in which *d*(O–O) = 1.434(6) Å.¹⁰⁸ The bound O₂ molecule is readily displaced by CO or SO₂. The reversible addition of dioxygen to a non-transition metal complex has been reported for the first time. Oxygenation of a solution of an *o*-amidophenolatoantimony(V) complex at room temperature generates a spiroendoperoxide which, upon heating to 50 °C, eliminates dioxygen.¹⁰⁹ This capability arises from the redox behaviour of the amidophenolate group, which in the peroxide adduct exists as an iminobenzosemiquinonate.



The reaction between NaH₂PO₄ and [CrCp*I(μ-Ome)]₂ gives [(CrCp*)₂(μ-Ome)₂]₂(μ₄-PO₄)⁺, the first organometallic μ₄-PO₄ complex,¹¹⁰ while Pt(NO₃)₂ reacts with concentrated sulfuric acid at 400 °C to give [NH₄]₂[Pt₂(μ-SO₄)₄(H₂O)₂].¹¹¹ Crystallisation of lithium and sodium aryloxides with dioxane forms co-ordination polymers composed of Li₄O₄ or Na₆O₆ aggregates respectively,^{112,113} nonabismuth polyoxo cations [Bi₉(μ₃-O)₈(μ₃-OR)₆]⁵⁺ (R = H or Et) are available from base hydrolysis and subsequent ethanolsis of BiO(ClO₄).¹¹⁴

Oxidative degradation of the solvent (either dme or thf) occurs when solutions of $[M\{N(Ph_2PO)_2\}_2] \cdot (thf)_n$ ($M = Sr$ or Ba) are exposed to O_2 , giving binuclear complexes $[Sr_2\{N(Ph_2PO)_2\}_4] \cdot 2C_3H_6O_3$ and $[Ba_2\{N(Ph_2PO)_2\}_4] \cdot 2C_4H_8O_3$, which contain co-ordinated carboxylic acids.¹¹⁵

Anderson *et al.* have stabilised a terminal palladium-oxo unit by encapsulation within a cavity defined by two fused $[PW_9O_{34}]^{9-}$ units.¹¹⁶ From crystallographic and EXAFS analyses, $d(Pd-O) \approx 1.65 \text{ \AA}$, ^{17}O nmr studies confirm that in solution the solid-state structure persists. The first stable oxoborane monomer $LB = O$ ($L = \beta$ -diketiminate) was prepared following hydrolysis of the product obtained from the reaction of $LAICl_2$ with BCl_3 ,¹¹⁷ while a new methodology for preparing binary organometallic oxides containing heavy p -block elements was reported, using $[An_2Te(OSn^tBu_2OH)_2]_2$ as a representative example.¹¹⁸

Abbreviations

An	4-CH ₃ OC ₆ H ₄
Bbt	2,6-bis[bis(trimethylsilyl)methyl]-4-[tris(trimethylsilyl)methyl]phenyl
dbu	1,8-diazabicyclo[5.4.0]undec-7-ene
dmphen	2,9-dimethyl-1,10-phenanthroline
dppeS	Ph ₂ PCH ₂ CH ₂ P(S)Ph ₂
Mes	2,4,6-Me ₃ C ₆ H ₂
RR	Resonance Raman
tmc	1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane
Trip	2,6-(2,4,6- ⁱ Pr ₃ C ₆ H ₂) ₂ C ₆ H ₃

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