PAPER

Coordinating ability of anions and solvents towards transition metals and lanthanides†

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A scale that attempts to quantify the weakly coordinating character of a variety of solvents and anions is presented. For each group (solvent or anion), a coordinating ability index has been calculated, based on the probability of it being coordinated in the presence of a transition metal atom, compared to the probability of finding it as a solvation molecule or as non-coordinating counterion in a crystal structure. The corresponding index is also defined for the same groups in the presence of lanthanides, and the similarities and differences are discussed.

Introduction

One of the assumptions made usually in coordination chemistry is that some anions and solvent molecules belong to the metal's second coordination sphere, *i.e.*, they are not directly bound to the metal atom. However, it is also frequent to find the supposed counteranions or solvation molecules directly coordinated to the central metal atom of the complex.[1] Traditionally, some oxo- and fluoro-anions were considered to have a poor coordinating ability, a fact that has led to their extensive use in coordination chemistry. Typical examples are the nitrate (NO_3^-), perchlorate (ClO_4^-), acetate (CH_3COO^-), methanesulfonate ($CH_3SO_3^-$), triflate ($CF_3SO_3^-$), tetrafluoroborate (BF_4^-) or hexafluorophosphate (PF_6^-) ions, all having highly electronegative external atoms.[2] These are often used in synthesis as counteranions to avoid interference with the ligands that one wishes to introduce into the metal coordination sphere. Alternatively, weakly coordinating anions (WCA) can be used as labile ligands to support the creation of vacant coordination sites that are a must if a metal atom has to act as a catalyst, and a similar role can be played by weakly coordinating solvents. The importance of weakly coordinating anions in homogeneous catalysis is associated to their ability to withstand the existence of vacant coordination sites on metal centres.[3] WCAs also find application as supporting electrolytes in electrochemical reactions, to prevent the cations produced in anodic processes undergoing nucleophilic attack by the anions traditionally used as electrolytes, such as perchlorate,

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† Electronic supplementary information (ESI) available: A data sheet with the numerical data of the searches, including the two alternative sets of indices a^{TM} and b^{TM}, and the a^{Ln} indices, and also the results of the structural database searches for groups for which an insufficient data set prevented us to deduce coordinating ability indices. ConQuest (cqs) files for the Cambridge Structural Database searches.

tetrafluoroborate or hexafluorophosphate.[4] A similar application aims at stabilizing salts of unusual and reactive cations.[3]

Attempts to create new anions with a very weak coordinating ability have focused on increasing their size and the charge delocalization, as in BPh_4^-, $B(C_6F_5)_4^-$, $OTeF_5^-$, or the fulleride anion C_{60}^-. The optimal characteristics of weakly coordinating anions, thus, were proposed to be:[3,5] (i) low negative charge (monoanions preferred), (ii) a high degree of charge delocalization, (iii) a large size and (iv) the presence of only very weakly basic sites on the periphery (H or F atoms). Still, for instance, BPh_4^- is found coordinated through the π system of one phenyl group in a variety of complexes of several transition metals, and a carbaborate anion, ($CB_{11}H_{12}^-$), has been shown to coordinate thanks to the hydridic character of its hydrogen atoms. Representative of the quest for the weakest possible coordinating anions are the icosahedral carbaborate anions of the type $[H\text{-}CB_{11}H_5X_6]^-$ (X = Cl, Br, I) and their methylated analogues $[H\text{-}CB_{11}Me_5X_6]^-$ proposed by Reed[6,7] (Fig. 1), that have the advantage of providing better visibility in ^{1}H NMR spectroscopy.

Rosenthal had claimed that even the "noncoordinating anions" are really noncoordinating only in aqueous solution, because they are displaced from the coordination sphere by water molecules, whereas they can remain coordinated in the absence of water.[8] The ability to coordinate is a property that is difficult to define; neither the ligand field splitting, nor the pK_a provide an adequate measure of the coordinating ability of a certain group (within this paper we will use the word "group" as a synonym of "solvent or anion").[8]

It now becomes clear that, depending on the purpose for which it is used, a solvent or counterion should be required to have a coordinating ability larger (or smaller) than that of other ligands present in the metal coordination sphere. Some semiquantitative indication of the relative coordinating ability of the most common groups, therefore, should be of interest for researchers involved in the fields of synthesis, catalytic applications or electrochemical reactions of transition metal complexes. In an attempt to calibrate the coordinating ability of a given group

Fig. 1 Molecular structure of the weakly coordinating carbaborate anions $[H-CB_{11}H_5X_6]^-$ (X = Cl, Br, I).

toward transition metals, we have chosen to compare the number of crystal structures in which that group is coordinated with the number of structures in which it coexists with a transition metal without being coordinated. We must consider, however, that it is frequent to find complexes in which a group is weakly bound to a metal atom, in what is often called "secondary coordination", "contact", or "semi-coordinating interaction".[1] We will thus refer to those structures in which a non-bonded group forms a contact to a transition metal at a distance shorter than the Van der Waals radii sum as "semicoordinated", and consider semicoordination also as an indication of the coordinating ability of a group. We can therefore define a coordinating ability index of a group toward transition metals, a^{TM}, as in eqn (1), where c, s and u are the number of structures with the group coordinated, semicoordinated and uncoordinated, respectively. The ways in which values for c, s and u for each group were obtained from a structural database search are described in the Procedures section.

$$a^{TM} = \log (c+s)/u \qquad (1)$$

With such a definition, a positive value of a^{TM} indicates that the group has more chance to coordinate to a transition metal atom than to remain uncoordinated in its presence. The larger the positive value of a, the greater its coordinating ability. At the other extreme of the scale, large negative values of a indicate a poor tendency to coordinate. Finally, a coordinating ability index close to zero tells us that the corresponding species is an *ambiguous coordinator*, with similar probabilities to appear coordinated than uncoordinated. In the present work we specifically analyze the coordinating ability of anions and solvents with respect to transition metals or lanthanide ions. We will represent the coordinating ability index for the latter as a^{Ln} throughout this paper.

The present approach is per force oblivious of a large number of complexes synthesized in the presence of a given group (solvent or anion), which is nevertheless not incorporated into the crystal structure. Therefore, the significance of the coordinating ability scale proposed here relies on the hypothesis that the number of crystal structures with an uncoordinated group present is roughly proportional to the number of complexes that show no trace of the participation of that group in its synthesis.

Results

Our structural database searches were designed to detect all possible coordination modes of the groups under consideration, even unsuspected ones, in order to properly evaluate the overall coordinating ability of each group. We note, for instance, that the BPh_4^- anion coordinates to transition metals through π-bonding, and forms contacts through either the H or C atoms. Similarly, BAr_4^- (Ar = C_6H_3-3,5-$(CF_3)_2$) was found coordinated only *via* π interaction, whereas $B(C_6F_5)_4^-$ was found coordinated and semi-coordinated through the fluorine atoms but not *via* π-bonding. Also CH_2Cl_2 was found in similar proportions semicoordinated to transition metals through its Cl or H atoms. Finally, it is worth mentioning that solvents such as fluorobenzene or chlorobenzene are more prone to coordination through the aromatic ring than through a lone pair of the halogen.

The results of the structural database searches are provided as ESI,† and the corresponding coordinating ability indices a^{TM} and a^{Ln} for a variety of commonly used anions and solvents are shown in Tables 1–4. One might consider as an alternative measure of the coordinating ability of a group the percentage of the total structures with simultaneous presence of the group and of a transition metal that show signs of coordination (given also in Tables 1–4). While the use of percentages may be more intuitive, the a indices have the advantage that they better discriminate the coordinating abilities of those groups at the two ends of the scale, where the strongest and weakest coordinating groups appear, as seen in Fig. 2. As a rule of thumb we note that those groups with indices of 1.8 and higher appear coordinated or semicoordinated in at least 99% of the structures, and so could be called strong coordinators. Conversely, groups with indices of −1.8 or less appear uncoordinated in at least a 99% of their occurrences, and should be named weak coordinators. A coordinating index close to zero indicates an ambiguous coordinator, with nearly an equal chance of appearing coordinated than uncoordinated.
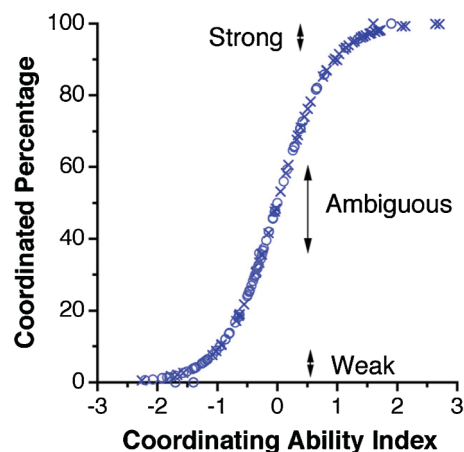
Fig. 2 Scattergram of the coordinating ability indices a^{TM} and the percentages of structures with each anion (crosses) or solvent (circles) coordinated to a transition metal or a lanthanide (Tables 1–4).

While we have chosen to consider semicoordination as indicative of the coordinating ability of a given group in defining the coordinating index a (eqn (1)), one might well prefer to adopt a more stringent criterion and count semicoordinated structures

Table 1 Coordinating ability results for anions towards transition metals: number of structures analyzed, coordinating ability index a^{TM} and percentage of structures in which the anion is found coordinated or semicoordinated to a transition metal

Anion	Structures	a^{TM}	%
O^{2-}	5,619	3.3	100
CN^-	4,689	3.1	100
S^{2-}	3,044	2.7	100
PhS^-	865	2.6	100
N_3^-	2,190	2.1	99
PO_4^{3-}	966	2.1	99
NO_2^-	864	1.7	98
PhO^-	199	1.7	98
SCN^-	4,101	1.6	97
F^-	1,507	1.5	97
$C_2O_4^{2-}$	1,881	1.4	96
CH_3COO^-	5,022	1.4	96
HPO_4^{2-}	438	1.4	96
CO_3^{2-}	509	1.3	95
Cl^-	47,635	1.3	95
Br^-	8,853	1.0	90
CF_3COO^-	1,378	1.0	90
I^-	7,019	0.9	90
$H_2PO_4^-$	200	0.8	87
$CH_3SO_3^-$	50	0.5	74
SO_4^{2-}	1,342	0.3	69
HCO_3^-	66	0.2	61
NO_3^-	7,629	0.1	58
$RCB_{11}H_{11-x}X_x^-$	124	0.0	48
ReO_4^-	158	0.0	48
$AlCl_4^-$	89	−0.1	42
HSO_4^-	69	−0.3	33
SiF_6^{2-}	136	−0.3	31
$CF_3SO_3^-$	5,009	−0.4	31
ClO_4^-	14,495	−0.6	19
$Al(OC(CF_3)_3)_4^-$	42	−0.6	19
AsF_6^-	130	−0.6	18
SbF_6^-	1,014	−0.9	10
BF_4^-	7,212	−1.1	8
PF_6^-	9,595	−1.6	3
$B(C_6F_5)_4^-$	286	−1.7	2
BPh_4^-	2,311	−1.8	2
BAr_4^-	733	−2.3	1

Ar = $(C_6H_3$-3,5$(CF_3)_2)$.

Table 2 Coordinating ability results for anions towards lanthanides: number of structures analyzed, coordinating ability index a^{Ln} and percentage of structures in which the anion is found coordinated or semicoordinated to a lanthanide. The corresponding coordinating ability indices relative to transition metals are also given for comparison

Anion	Structures	a^{TM}	a^{Ln}	%
F^-	49	1.5	1.7	98
PhS^-	36	2.9	1.6	100
$C_2O_4^{2-}$	484	1.4	1.6	98
SO_4^{2-}	141	0.3	1.5	97
O^{2-}	83	3.3	1.4	96
CH_3COO^-	326	1.6	1.3	95
CN^-	460	3.1	1.2	94
NO_3^-	2,028	0.1	1.1	93
$AlCl_4^-$	30	−0.1	1.1	93
CF_3COO^-	59	1.0	1.1	93
CO_3^{2-}	47	1.3	1.0	91
SCN^-	175	1.6	0.8	87
Cl^-	1,609	1.3	0.8	85
I^-	451	0.9	0.5	76
Br^-	176	1.0	0.4	71
N_3^-	34	2.1	0.3	68
$CF_3SO_3^-$	303	−0.4	0.1	53
S^{2-}	45	2.7	−0.3	36
ClO_4^-	588	−0.6	−0.6	22
BPh_4^-	76	−1.8	−0.7	17
PF_6^-	38	−1.6	−0.9	10

phenoxide and sulfide anions, which are practically not found as independent anions in the presence of a transition metal. Halides, pseudohalides, carboxylates and oxalate (among others), with good coordinating abilities, are neither good choices as counterions because they may compete with other ligands for available coordination sites. Among the oxoanionic groups, only hydrogensulfate and perchlorate have negative coordinating indices. It is interesting that hydrogen- or alkyl-coated carboranes still have a relatively high coordinating ability. Fluoro-coated anions, on the other hand, form a class of generally weakly coordinating species, in contrast with the highly coordinating power of the naked fluoride ion. Only the tetraphenylborate BPh_4^- or the related BAr_4^- anions join the perfluorinated species in the category of very weakly coordinating anions.

In a classical review on weakly coordinating anions,[8] Rosenthal pointed out that "perchlorate is rarely coordinated when its complexes are prepared in aqueous solution". The present study places perchlorate as a not-too weak coordinator (a^{TM} = −0.6), but if the searches are restricted to structures in which water solvation molecules are also present, its index drops to −1.1 (the percentage of coordinated structures decreases from 19 to 8%), clearly an indication that part of the coordinating power attributed to this anion here may correspond to compounds synthesized in non aqueous solvents, as proposed by Rosenthal. While these results provide qualitative support to Rosenthal's assertion, they also show that perchlorate has a non-negligible probability of coordinating to a transition metal even in the presence of water. The same author also stated that "BF_4^- is similar in its coordinating properties to perchlorate, though it seems slightly less likely to coordinate". The present results confirm such an assertion in qualitative terms, but also quantify the different coordinating abilities of these two anions, which is certainly non negligible, since the tetrafluoroborate anion coordinates in about 10% less of its appearances than perchlorate.

as indicative of the lack of coordinating ability, thus defining an alternative index $b = \log c/(s + u)$. In the case of a^{TM}, most of the groups analyzed show differences between the two alternative indices of at most 0.3 units. The most relevant exceptions correspond to groups with large negative values of a^{TM} and a ratio of semicoordinated to coordinated structures greater than two: dichloromethane, chloroform, SbF_6^- and PF_6^-. In those cases, if we measure the coordinating ability of a group by the proportion of strictly coordinated structures, using the alternative indices b^{TM} and b^{Ln} (included in the ESI†) a weaker coordinability would be attributed to those groups. Having noted this, the subsequent discussion of the results will be based on the wider definition of the coordinating ability implicit in the a^{TM} and a^{Ln} indices given in eqn (1), keeping in mind that differences in a^{TM} values of 0.2 or less may not be significant.

Discussion

A look at the a^{TM} indices for anions (Table 1) tells us that the strongest anionic coordinators seem to be the oxide, cyanide,

Table 3 Coordinating ability results for solvents relative to transition metals: number of structures analyzed, coordinating ability index a^{TM} and percentage of structures in which the anion is found coordinated or semicoordinated to a transition metal

Solvent	Structures	a^{TM}	%
Pyridine	4,513	1.4	96
Formamide	29	0.3	66
Dimethylsulfoxide	2,038	0.3	65
Hexamethylphosphoramide	59	0.2	59
Triethylamine	50	0.1	56
n-Propanol	82	0.0	50
Water	48,284	−0.1	46
Dimethoxyethane	407	−0.2	40
Dimethylformamide	3,478	−0.2	37
Ethylene glycol	90	−0.2	37
Acetonitrile	10,572	−0.2	37
Trifluoroacetic acid	42	−0.3	36
i-Propanol	316	−0.3	35
Acetic acid	198	−0.3	34
p-Xylene	116	−0.3	33
Diglyme	88	−0.3	32
Tetrahydrofuran	6,615	−0.3	32
n-Butanol	60	−0.4	30
Methanol	8,119	−0.4	30
1,4-Dioxane	274	−0.4	29
Carbon disulfide	131	−0.4	28
t-Butanol	26	−0.4	27
Dimethylacetamide	187	−0.5	26
Fluorobenzene	82	−0.5	26
Ethanol	2,871	−0.5	24
o-Xylene	50	−0.5	24
Benzene	4,381	−0.7	17
Ethyl acetate	215	−0.8	13
Acetone	3,013	−1.0	9
Cyclohexane	248	−1.0	9
Nitrobenzene	143	−1.1	8
Toluene	4,723	−1.2	6
Bromobenzene	36	−1.2	6
Nitromethane	516	−1.4	4
Phenol	48	−1.4	4
Diethyl ether	3,356	−1.4	4
o-Dichlorobenzene	118	−1.4	4
Chlorobenzene	267	−1.5	3
1,2-Dichloroethane	495	−1.6	3
Dichloromethane	9,619	−1.7	2
n-Hexane	1,755	−1.8	1
Carbon tetrachloride	84	−1.9	1
n-Heptane	170	−1.9	1
n-Pentane	964	−2.1	1
Chloroform	4,052	−2.2	1

Table 4 Coordinating ability results for solvents relative to lanthanides: number of structures analyzed, coordinating ability index a^{Ln} and percentage of structures in which the anion is found coordinated or semicoordinated to a transition metal. The corresponding indices relative to transition metals are also given for comparison

Solvent	Structures	a^{TM}	a^{Ln}	%
Hexamethylphosphoramide	81	0.2	1.9	100
Dimethylacetamide	23	−0.5	1.3	96
Dimethylsulfoxide	193	0.3	1.1	93
Dimethylformamide	506	−0.2	0.8	86
Diglyme	78	−0.3	0.7	82
Water	6,764	−0.1	0.6	82
Tetrahydrofuran	2,186	−0.3	0.4	73
Dimethoxyethane	317	−0.2	0.4	71
i-Propanol	41	−0.3	0.4	71
Pyridine	222	1.4	0.3	66
Acetic acid	23	−0.3	0.0	48
Methanol	663	−0.4	0.0	48
1,4-Dioxane	35	−0.4	−0.1	46
Ethanol	336	−0.5	−0.1	42
Acetone	91	−1.0	−0.5	25
Dichloromethane	148	−1.7	−0.6	19
Acetonitrile	548	−0.2	−0.7	18
Triethylamine	73	0.1	−0.8	14
Diethyl ether	242	−1.4	−0.9	12
Cyclohexane	20	−1.0	−1.0	10
Benzene	217	−0.7	−1.2	6
Toluene	494	−1.2	−1.2	6
Nitromethane	19	−1.5	−1.3	5
Chloroform	127	−2.2	−1.4	4
Carbon disulfide	23	−0.4	−1.4	0
n-Pentane	54	−2.1	−1.7	0
n-Hexane	144	−1.8	−1.7	1

The strong influence of the CF$_3$ peripheral groups in several anions must be noticed, making them much less coordinating despite the possibility of coordinating or forming contacts through the fluorine atoms. Compare, for instance, the coordinating abilities of the following pairs of anions: CF$_3$COO$^-$ and CH$_3$COO$^-$, CF$_3$SO$_3^-$ and CH$_3$SO$_3^-$, or BAr$_4^-$ and BPh$_4^-$. Also protonation of an anion clearly decreases its coordinating power, as can be seen in the a^{TM} values for the anions derived of phosphoric acid: PO$_4^{3-}$ > HPO$_4^{2-}$ > H$_2$PO$_4^-$. Also significantly smaller coordinating ability is found for hydrogensulfate than for sulfate, and similar differences appear between the carbonate and bicarbonate anions, as well as between the acetate and trifluoroacetate anions and their respective acids. Although in those cases one might be tempted to associate the varying coordinating ability to the net charge of the anion, no general correlation has been found between a^{TM} and the charge of the anions.

The (HCB$_{11}$Me$_5$X$_6$)$^-$ carbaborate anions have been proposed to be as close as any to the concept of a universal weakly coordinating anion,[7] but so far only one structure of that type of anion in the presence of a transition metal has been solved, and that assertion cannot be evaluated with the presently used approach. Hope also rested on the (CB$_{11}$H$_{12}$)$^-$ anion, but the present study shows that it often coordinates to transition metals through the H atoms in much the same way that (BH$_4$)$^-$ does, in bidentate or tridentate fashion, and it has a positive coordination index of 0.4. Also the (RCB$_{11}$H$_{11-x}$X$_x^-$) halogenated carbaborates are found to coordinate with similar probabilities through the hydrogen or the halogen atoms, becoming coordinatively ambiguous anions. All in all, the present results put the family of carbaborate anions as ambiguous coordinators rather than as the weak coordinators they are claimed to be. Some purportedly weak coordinating anions examined, OTeF$_5^-$, RCB$_{11}$H$_{11}^-$ and C$_{60}^{n-}$, have not been included in Table 1 because of the insufficient number of structures available, although the results of our searches are included in the ESI.†

Since the number of available structural data for lanthanides is an order of magnitude smaller than for transition metals, we have been able to evaluate a^{Ln} values (Table 2) for only half of the anions, and also the statistics are in most cases poorer. Therefore, those lanthanide indices should be taken as semiquantitative at most. Some of the most dramatic changes on going from the transition metals to lanthanides are found for the SO$_4^{2-}$, NO$_3^-$ and AlCl$_4^-$ anions and, to a lesser degree, PF$_6^-$ and CF$_3$SO$_3^-$. Their enhanced coordination ability reflects the favorable coordination to lanthanides by groups with donor atoms of high electronegativity, in keeping with the marked ionic character of the lanthanide–ligand bonding. The strong coordinating ability of the former three

anions should probably also be attributed to their capacity to act as small bite bidentate ligands toward lanthanides. Other remarkable differences, but in the opposite direction, are observed for other anions with less electronegative donors S^{2-}, CN^-, N_3^-, SPh^-, and SCN^- ions, whose coordination indices decrease by between one to three units. An importantly decreased coordinating ability of O^{2-} to lanthanides compared to transition metals is due to the fact that the oxido ion often appears uncoordinated to a lanthanide but coordinated to a transition metal present in the same structure, so it probably reflects its relative coordination ability rather than its intrinsic affinity for lanthanides. The important decrease in the index corresponding to SPh^- is not significant, due to the comparatively small number of structures found for lanthanides with this anion and to the use of an approximate value of a in this case with no uncoordinated structures. Finally, it is worth stressing that the BPh_4^- anion seems to be a better π-coordinator towards lanthanides than towards transition metals.

The phosphate anion appears uncoordinated to lanthanide cations practically always when it is forming part of a robust polyoxometallate. Therefore, no coordinating ability index has been derived for the phosphate anion toward lanthanides, since there is little data available on structures with the phosphate not forming part of a polyoxometallate. All other anions present in Table 1 but not in Table 2 were also searched for lanthanides, but coordinating ability indices are not reported because of the insufficient number of structures found. The corresponding search results can be found as ESI.†

Before discussing the results for solvents in general, it is in order to devote a few words to the way in which the coordinating ability indices of alkanes have been obtained. Alkanes can in principle be attached to a metal via σ-CH or σ-CC coordination, but no structures of this type have been found for n-pentane, n-hexane, n-heptane or cyclohexane. Alternatively, one could think of alkanes interacting with a metal complex via oxidative addition reactions that could leave behind a σ-bonded alkyl group. This is not what one would usually expect, since the corresponding alkyl complexes can readily give β-elimination reactions. However, a few structures of σ-bonded complexes of those alkyl groups have been found, which may provide a semiquantitative indication of their non-innocence toward transition metal centers. A drawback of this approach is that the coordinated alkyl ligands may not come from the corresponding alkane used as a solvent, but most likely from an alkyl halide or other alkylating agent. For those reasons, the coordinating indices given here for alkanes are probably overestimated and should be used with caution. In spite of the arbitrariness of our definition of the coordination ability index for alkanes, it must be noted that n-alkanes appear as poor coordinators, and that a great deal of their coordinating ability index comes from semicoordination through H···M contacts rather than from alkyl complexes.

Let us now take a perspective view at the ranges of a^{TM} values (Table 3) found for some families of related organic solvents (Fig. 3). *n*-Alkanes appear at the lower end of the scale as weak coordinators, although cyclohexane has a quite higher index, a value that is probably biased by the existence of a significant number of organometallic cyclohexyl complexes. Even if those complexes may arise from oxidative addition reactions of cyclohexane used as a solvent, therefore reflecting its coordinating ability,[9] in other instances they do not result
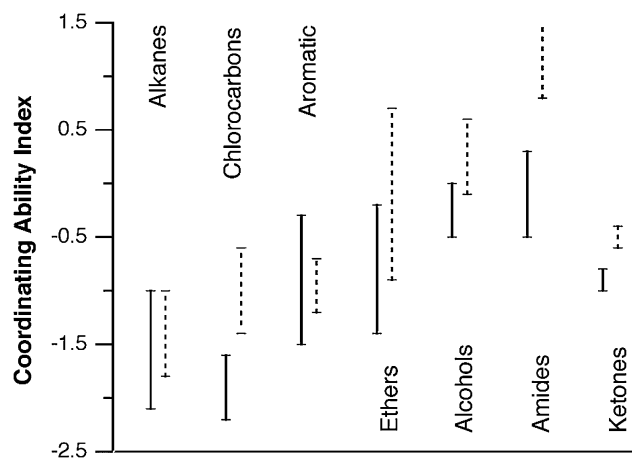

Fig. 3 Ranges of coordinating ability indices a^{TM} for several families of solvents (continuous lines), compared to the corresponding ranges for the a^{Ln} indices (dashed lines).

from reaction of the solvent, but from, *e.g.*, transmetallation reactions with the corresponding Grignard reagent,[10] or through reaction of a hydrido complex with cyclohexene.[11] Chlorocarbons (chloroform, dichloromethane, carbon tetrachloride and 1,2-dichlorethane) also form a family of weakly coordinating solvents. Derivatives of benzene appear with a wide range of coordinating abilities, depending on the substituents at the aromatic ring: while chlorobenzene and phenol are weak coordinators, *o*-xylene, fluorobenzene and *p*-xylene are rather ambiguous toward transition metals. We must recall, however, that these solvents coordinate mostly through their π systems rather than through substituents having lone pairs, such as F, Cl, Br or NO_2. Aliphatic alcohols form a family whose members are all rather ambiguous coordinators, but comparison of the a^{TM} values for n-propanol and i-propanol, or for n-butanol and *t*-butanol, suggests that linear alcohols are slightly less coordinating than their branched isomers. Phenol, on the other hand, is far less coordinating than the aliphatic alcohols. Finally, other oxygen-containing solvents cover a wide range of coordinating abilities, with a^{TM} indices ranging from +0.3 to −1.4. However, if we distinguish three subfamilies, amides (formamide, hexamethylphosphoramide, dimethylformamide, dimethylacetamide), ketones (methyl-ethyl ketone, acetone) and ethers (ethylene glycol, dimethoxyethane, diglyme, tetrahydrofuran, 1,4-dioxane, diethyl ether), we find the former to be clearly more coordinating than ethers or ketones.

To single out the most representative cases of the full scale of coordinating indices, we may note that n-propanol is the most ambiguous solvent, with $a^{TM} = 0.0$, while pyridine is the strongest coordinator, and n-pentane and chloroform appear presently as the least coordinating solvents towards transition metals.

Since one of the most relevant properties that one considers when choosing a solvent for a given synthesis is its polarity (of course, other properties may be as important: boiling point, flammability, toxicity or cost), it is worth analyzing the coordinating ability of solvents according to their dielectric constant.[12] Thus, mapping the two parameters as in Fig. 4 may be of some help to select the most appropriate solvent in each case. The first thing to be noticed is that no correlation whatsoever is found between the coordinating ability index of a solvent and its dielectric constant. We can notice, however, that the a^{TM} values presented by families
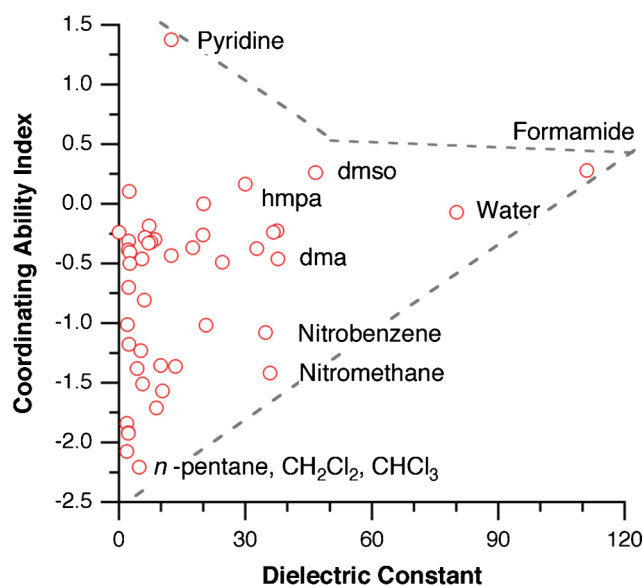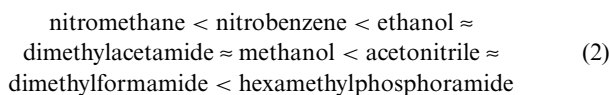
Fig. 4 Scattergram of the dielectric constant and the coordinating ability index a^{TM} for the set of solvents analyzed (dmso = dimethylsulfoxide, dma = dimethylacetamide, hmpa = hexamethylphosphoramide).

of high, intermediate and low polarity solvents cover different coordinability ranges. The most polar solvents (dimethylsulfoxide, water and formamide) are highly ambiguous regarding their coordinating ability, with indices between −0.1 and 0.3, and the chances for getting them coordinated or uncoordinated are roughly similar. Solvents of intermediate polarity (with dielectric constants of about 30) cover a wide range of coordinating abilities, from weakly coordinating to ambiguous, according to their a^{TM} values between −1.4 and 0.2, in the following order:

$$\text{nitromethane} < \text{nitrobenzene} < \text{ethanol} \approx$$
$$\text{dimethylacetamide} \approx \text{methanol} < \text{acetonitrile} \approx \quad (2)$$
$$\text{dimethylformamide} < \text{hexamethylphosphoramide}$$

Finally, low polarity solvents cover all the spectrum of coordinating abilities, from strongly coordinating (pyridine) to very weakly coordinating (n-pentane and chloroform).

If we compare now the coordinating abilities of solvents toward lanthanides (Table 4) to those referred to transition metals, we observe that most values present significant changes. Clear trends in those differences can be summarized as follows. All O-donor solvents and chlorocarbons become more coordinating to lanthanides than to transition metals, alkanes vary little their indices, and N-donor solvents and CS_2 become less coordinating to lanthanides than to transition metals. Also the π-coordinating aromatic solvents benzene and toluene slightly decrease their coordinating ability when switching from transition metals to lanthanides. For the wide family of O-donor solvents, however the relative coordinating power is similar for the two types of metals, as can be seen by a fair correlation between their a^{TM} and a^{Ln} values (Fig. 5).

These results suggest that the lanthanides have an enhanced affinity for O-donor ligands relative to transition metals, in agreement with the generally accepted more ionic character of the metal–ligand bonding in the former. To support such a conclusion, we observe that the ratio of structures showing M–O and M–N bonds is 1.9 among the lanthanides, but only 0.7 among
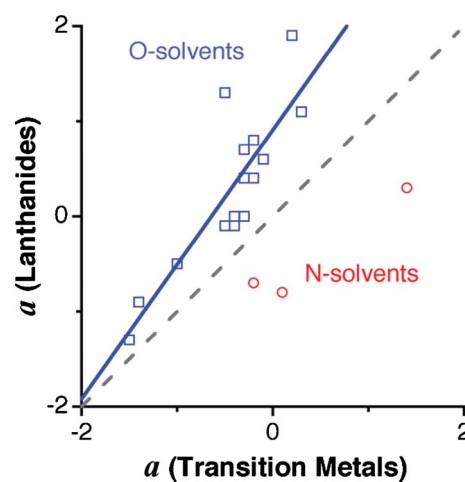

Fig. 5 Coordination ability indices of solvents toward lanthanides (O-donor solvents: squares; N-donor solvents: circles) as a function of the corresponding indices relative to transition metals.

transition metals. Moreover, if one analyzes the structures in which a transition metal, a lanthanide and a water molecule coexist, the number of occurrences of water coordinated to a lanthanide but not to a transition metal is about seven times the number of structures in which the opposite behavior is found.

Ligand competition

If the indices presented here are to be of some use, they should not only provide a good estimate of the probability of a given group to coordinate or not to a metal ion, but should also reasonably predict the competitive behavior of two groups in the presence of a metal. Hence, we have analyzed structures in which two groups A and B coexist with a transition metal, being A the one with the higher a^{TM} index, and the difference between the indices will be referred to as Δa^{TM} (eqn (3)). We then determine $n(A)$, the number of structures in which only A is coordinated, those in which only B is coordinated, $n(B)$, and those in which both groups appear coordinated, $n(A+B)$. Then, the ratio of the total number of structures in which A is coordinated to that with B coordinated, r (eqn (4)), should give an indication of the better coordinating ability of A with respect to B.

$$\Delta a^{TM} = a^{TM}(A) − a^{TM}(B), \text{ for } a^{TM}(A) > a^{TM}(B) \quad (3)$$

$$r = \frac{n(A) + n(A+B)}{n(B) + n(A+B)} \quad (4)$$

The pairs of groups that can be compared is limited by the number of available structures in which the two groups coexist with a transition metal, and we will analyze only pairs of groups for which more than 35 structures have been found. The results for those cases are reported in Table 5, classified according to the nature of groups A and B. For pairs of competing solvents, we observe that the coordination ratio is always favorable to the group with higher coordination ability index (i.e., it is greater than 1.0), except when one of the competing solvents is pyridine. In the presence of the most coordinating solvent, pyridine, the ratio is less favorable, probably because in many cases it is not present

Table 5 Competitive coordination ratios r (eqn (4)) of two groups that are simultaneously present with a transition metal, and the corresponding difference in coordinating ability indices Δa (eqn (3))

Group A	Group B	Δa	$n(A)$	$n(B)$	$n(A+B)$	r
Solvent/Solvent						
Pyridine	Ethanol	1.9	37	3	5	5.6
Pyridine	Water	1.5	360	89	314	1.7
Acetonitrile	Dichloromethane	1.5	239	0	0	—
thf	Diethyl ether	1.1	36	1	1	18.5
Water	Acetone	0.9	144	5	17	7.3
dmso	Water	0.4	162	42	92	1.9
Water	thf	0.2	121	9	67	2.5
Water	dmf	0.1	275	113	186	1.5
Water	Acetonitrile	0.1	299	204	211	1.2
Solvent/Anion						
Acetonitrile	BPh_4^-	1.5	101	1	0	101.0
Acetonitrile	PF_6^-	1.4	556	2	2	139.5
Acetonitrile	BF_4^-	0.9	587	7	16	26.2
dmso	ClO_4^-	0.9	62	0	3	21.7
Water	ClO_4^-	0.5	2007	147	243	5.8
Acetonitrile	ClO_4^-	0.4	544	43	50	6.4
Pyridine	Br^-	0.4	5	2	106	1.0
Methanol	ClO_4^-	0.2	290	37	50	3.9
thf	$CF_3SO_3^-$	0.1	11	25	27	0.7
Anion/Solvent						
CH_3COO^-	Acetone	2.4	64	0	3	22.3
SCN^-	Acetonitrile	1.8	113	0	18	7.3
NO_3^-	Acetone	1.1	37	15	6	2.0
SO_4^{2-}	Water	0.4	248	234	419	1.0
Anion/Anion						
CN^-	NO_3^-	3.0	63	0	10	7.3
CN^-	Cl^-	1.8	46	0	136	1.3
NO_3^-	ClO_4^-	0.7	50	2	7	6.2
SCN^-	CH_3COO^-	0.2	11	1	57	1.2

*For the definition of Δa^{TM} and of the coordination ratio see eqn (3) and (4).

Fig. 6 Coordination ratio (eqn (4)) of pairs of competing groups toward transition metals, plotted as a function of their difference in coordinating ability indices Δa^{TM} (eqn (3)), and grouped according to the nature of the competing groups.

the solvent that enhances its coordinating ability relative to the anions presumably present in stoichiometric amounts. The scarce number of structural data found for Anion/Anion pairs does not allow us to discuss in detail this type of coordination competition, but the examples found also indicate that there is preferential coordination of the anion with the higher coordinating ability index.

Conclusions

A quantitative evaluation of the coordinating ability of the most common solvents and counteranions has been made by analyzing crystal structures for the presence of coordinated and uncoordinated groups (solvents or anions) in the presence of a transition metal or a lanthanide. From such an analysis we extract the corresponding *coordinating ability indices* a^{TM} and a^{Ln}. As defined, a coordination ability index of 1.8 or higher for a group indicates that the probability of finding it coordinated is at least a 99%, and is characteristic of a strong coordinator. Conversely, an index of −1.8 or lower points to a coordination probability of at most 1%, indicative of a poor coordinator. Indices close to zero are characteristic of ambiguous coordinators, for which there are roughly equal chances of finding the group coordinated than uncoordinated.

Regarding their coordinating ability toward transition metals, the least coordinating anions are found to be the fluoro and borate anions BF_4^-, PF_6^-, BPh_4^-, $B(C_6F_5)_4^-$ and BAr_4^- (Ar = 1,3-$(CF_3)_2C_6H_3$). In contrast, the carbaborate anions are seen to be moderately coordinating species. The presence of CF_3 substituents has been found to significantly decrease the coordinating power of anions such as acetate, methylsulfonate and tetrafluoroborate, while the trifluoromethyl group itself is a very weak coordinator. Also protonation of oxoanions results in an important diminution of their coordinating ability.

The scale of coordinating indices toward lanthanides covers a narrower range, from −0.9 to +1.7, compared to that referred

as a solvent in the reaction medium, but in smaller proportions as an intended ligand, and the actual solvent dominates the coordination equilibrium due to its much larger concentration. Disregarding the pairs that include pyridine and those with Δa^{TM} values of less than 0.2, a qualitative trend (Fig. 6) indicates that the solvent with the larger coordinating ability index is the one that overwhelmingly dominates the competition when the index difference is larger than about 0.7

Although it is not obvious that the coordinating ability indices for solvents should be comparable at a quantitative level with those for anions, we have applied the coordination competition analysis to pairs formed by a solvent and an anion with a lower (Solvent/Anion competition) or a higher (Anion/Solvent competition) index. The Solvent/Anion and Anion/Solvent pairs show similar trends to the Solvent/Solvent ones, with the curves shifted to lower and higher values, respectively. Such shifts can be understood taking into account the much higher concentration of
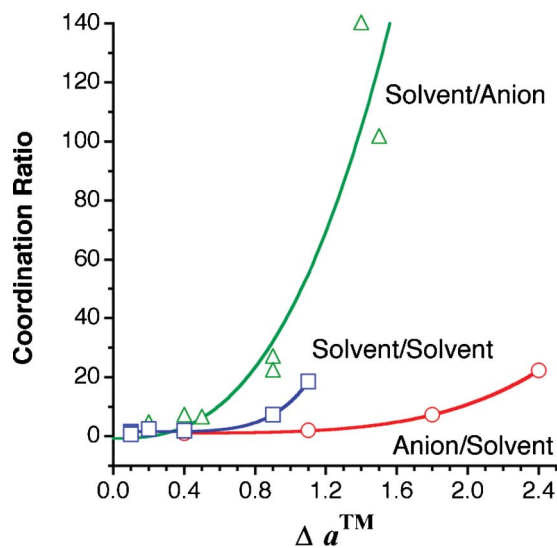
to transition metals, from −2.3 to +3.3. Moreover, anions with electronegative peripheral atoms, such as SO_4^{2-}, NO_3^-, $AlCl_4^-$, CF_3COO^-, $CF_3SO_3^-$ and PF_6^-, are significantly better coordinators toward lanthanides than transition metals. In contrast, anions such as SCN^-, N_3^-, CN^-, PhS^- and BPh_4^- are significantly weaker coordinators toward lanthanides.

As for the coordinating ability of solvents toward transition metals, the weakest coordinators are the alkanes and the chlorocarbons. Ethers and ketones are moderately poor coordinators. Alcohols, aromatic solvents, amides, and even water, are roughly ambiguous coordinators, while pyridine stands out as a quite strong coordinator. When the same solvents are evaluated for their coordinating ability toward lanthanides, chlorocarbons, ethers, alcohols, amides and ketones are seen to be better coordinators than toward transition metals. Aromatic solvents and alkanes, on the other hand, have similarly weak coordinating abilities toward lanthanides and transition metals.

From the analysis of pairs of groups competing for coordination positions at transition metal atoms, we can conclude that there is preferential coordination of the group with the higher coordinating ability index. This means that the chances of having that group coordinated to the metal atom are higher than those for the competing group. For competing solvents, the chances of finding the solvent with the lower index coordinated decrease roughly in a nearly exponential way with the increasing difference between the two indices. For Anion/Solvent and Solvent/Anion pairs, the solvent has an enhanced coordinating ability because of the concentration factor, resulting in similar trends shifted to lower and higher values of the indices, respectively.

Procedure

For each group considered, three searches were conducted in the Cambridge Structural Database (CSD):[13] (i) structures with the group coordinated to any transition metal (or any lanthanide), (ii) structures with the group forming a contact shorter than the van der Waals distance with, but not coordinated to, a transition metal (lanthanide) and (iii) structures in which a group is uncoordinated to a coexisting transition metal (lanthanide) atom. Since more than one copy of the same chemical group can coexist in the same crystal structure, the presence of only one such group coordinated to a metal can be taken as an indication of its coordinating ability, and the whole structure is classified in the "coordinated" set. Similarly, in the absence of a coordinated group, the occurrence of semicoordination of only one group grants the structure its classification in the "semicoordinated" set, irrespective of whether there are copies of the same group that do not form short contacts.

In the searches for coordinated groups, single and polymeric metal–ligand bonds were considered, as well as double or triple bonds when suitable (e.g., for the oxide or sulfide anions). Special care was taken to define each search in such a way that all possible coordination modes could be detected. For instance, κ-S and κ-O coordination, as well as π-bonding were allowed for dimethylsulfoxide; terminal, μ_2, μ_3 and μ_4 bridging modes were allowed for monoatomic anions, and both σ-coordination through the halogen atom and π-coordination (with any hapticity) of the phenyl ring were considered for halobenzenes. In order to distinguish monoatomic anions (F^-, Cl^-, Br^-, I^-, O^{2-} and S^{2-}) from the corresponding atoms within polyatomic groups (e.g.,

halogenated organic molecules, BF_4^-, alcohols, ethers, thiolates, etc.), these atoms were excluded when bonded to any non-transition element except for the alkaline, alkaline-earth and rare earth elements, considering that those are mostly ionic bonds of the otherwise isolated anions.

For the searches of lanthanides, semicoordination was searched for using a van der Waals radius of 3.0 Å for all those elements, taking into account that their covalent radii vary only between 1.87 and 2.07 Å.[14] In the cases of cyanide, sulfide and oxide, "uncoordinated" structures may have the anion coordinated to a transition metal, that is taken as indicative of a weaker coordinating power toward lanthanides than toward transition metals. In the case of sulfide, for instance, even if it is coordinated to a transition metal, the sulfur atom is never four-coordinated, so it could in principle coordinate to a lanthanide with its remaining lone pair.

All searches were carried out on version 5.32 of the CSD with two updates (up to February 11, 2011), comprising a total of 547,174 structures. We restricted our searches to the subset of 525,823 structures with atomic coordinates determined. The reader interested in the specific searches applied for a given group, or in reproducing the results reported here, or in updating them with later versions of the CSD, will find the corresponding search files for the ConQuest software (cqs files) as ESI.† Specific search restrictions were applied to some groups. For n-hexane, to make the search affordable, only contacts at 3.2 Å or less were retrieved for all transition metals, rather than using the van der Waals radii sum. For pyridine, the protonated pyridinium cation was excluded from the search; this cation appears practically always uncoordinated, except for two cases in which it is π-coordinated,[15] indicating that an acidic medium may significantly decrease the coordinating ability of pyridine. Similarly, the triethylammonium cation was excluded from searches for trimethylamine structures. For groups for which no uncoordinated structures were found, the coordinability index was approximated as $a = \log(c+s)$. Conversely, for groups for which no coordinated or semicoordinated structures were found, the index was approximated as $a = \log(1/u)$.

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