

Review Article

Labile Interactions Defined in Crystalline Metal Complexes

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(Received: 14 October 2003; in final form: 9 February 2004)

Key words: complex compounds, inter-atomic contacts, labile interactions, weak attractions

Abstract

The problems involved in identifying and quantifying labile interactions considered to influence complex compound structures are highlighted through the assessment of four different families of metal complexes for which extensive crystallographic data are available. Modification of the charge distribution within a ligand molecule as a result of coordination is one factor with a number of ramifications. A detailed analysis of evidence for both intra- and intermolecular attractions in dimethylsulfoxide complexes of metal perchlorates is used to provide a basis for the consideration of weak interactions between complex ions involving forces including phenyl-group attractions, hydrogen bonding and cavity inclusion.

Introduction

Much of contemporary chemistry is concerned with the construction of functional edifices through the linking of kinetically inert mesomolecular units *via* labile, though not necessarily weak interactions [1–3]. These interactions, which have their origins in exactly the same fundamental attractions and repulsions between nuclei and electrons as are responsible for the association of kinetically inert species, are conventionally and conveniently divided into many types depending upon the chemical species involved [1–23]. Thus, labile interactions may include ‘bonds’, such as ‘covalent’ and ‘coordinate’ bonds (which, of course, may also be inert) and hydrogen bonds, as well as a variety of ‘intermolecular forces’ [24, 25], such as π -stacking, ‘multiple phenyl embraces’ and dispersion forces. Even when weak, such forces are important, since the energies involved can easily exceed 10 kJ mol^{-1} , a figure which corresponds to a change in an equilibrium or rate constant by a factor of approximately 100, often more than sufficient to be the difference between joy and despair. The rise of ‘supramolecular’ chemistry [1, 2, 26] has focussed attention upon the problem of the understanding and rational exploitation of labile interactions, one of the most familiar objectives of this field being the design of macrocyclic receptors capable of the selective inclusion of substrates [1, 6, 27, 28].

In the crystalline state, molecular motions are greatly restricted compared to the solution state in which most

syntheses are conducted, and atomic positions derived from a crystal structure determination can be used to deduce a great deal concerning both bonding and intermolecular forces [4, 7–9, 15, 20]. Thus, labile interactions can be characterised [1–23] even under conditions where their lability is not apparent. There is a problem of fundamental importance associated with attempts to do so, however, in that it is not possible to tell simply from the positioning of any two atoms whether any interaction between them is overall attractive or repulsive. This issue has been discussed at length in relation to the identification of attractive $\text{CH}\cdots\text{O}$ interactions, for example [4]. An associated issue is that the conventional approach to description of chemical interactions is based upon the identification of closest pairs of atoms except in certain well-known cases such as aromatic rings (though even here, representations of 2-centre/2-electron components remain popular) and ‘ionic’ systems. The latter pose an interesting problem in that in a complex compound such as $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$, for example, formation of the solid lattice is commonly viewed as due to attractions between Co^{3+} and Cl^- centres, centres which are much further apart than those involved in ‘covalent’ bonding and between which other atoms are interposed. Recognition that the assigned charges are formal does not change the fact that an unusually remote interaction is treated as dominant, nor does it provide any greater insight into the full complexity of the interactions which may occur in such a compound. Indeed, given the conventional chemical model of matter as built up from aggregation of positive nuclei and negative electrons, it is somewhat anomalous that qualitative descriptions of chemical bonding are

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based upon interactions between species identified as atoms and ions. Given that the establishment of charges to be associated with centres involves both philosophical and practical difficulties [29, 30], for the purposes of the present discussion it will be assumed that formal charges are at most only qualitatively indicative of deviations from a uniform charge distribution within a given chemical species. This raises the same problem as encountered in assessing the existence of $\text{CH}\cdots\text{O}$ bonds, expressible in terms of the example taken of $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ in that a close approach of Cl to an H of NH_3 might be taken as an attractive (H-bonding) interaction or as simply a consequence of secondary coordination to the Co (or, of course, both). Again as before, one way to find a response to such questions is to examine many structures which may be subject to such ambiguity and to search for common geometrical features which may facilitate a decision. This must still be done with caution, as chemical perspectives can be time dependent, the original crystal structure determination of $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ [31], for example, having been described in terms of the enclosure of $[\text{Co}(\text{NH}_3)_6]^{3+}$ entities within 14-vertex polyhedra of Cl^- ions (the point being to explain differences in site symmetry reflected in ^{59}Co NMR spectra), with no mention of $\text{NH}\cdots\text{Cl}$ interactions, despite the fact that many of the $\text{N}\cdots\text{Cl}$ separations (3.2–3.3 Å) are consistent with such H bonding.

Assuming that various attractive forces can be identified and associated with particular features of a chemical structure, an immediately ensuing problem is that a structure alone provides no direct experimental information on the magnitude of the energies involved. Again, a careful analysis of numerous related structures may, however, allow some conclusions to be drawn as to the relative magnitude of various factors [4, 7–9, 32]. It is the purpose of this article to consider a number of metal complex systems to which this statement applies. The focus is largely, though not exclusively, upon very heavy metal systems, since the high and usually irregular coordination environments commonly observed there can often be rationalised in terms of a balance between various bonding and intermolecular forces. It is convenient to begin with a consideration of metal-based electrolytes, since even in such seemingly simple systems it is apparent that a full analysis of the interactions occurring is far from facile.

Ion solvation and ion–ion interactions

A conventional view is that the dissolution of many metal compounds in water is accompanied by rapid reactions giving rise to hydrated cations (containing the metal) and anions [33], though it is clear even for well-studied aqueous systems that much remains to be understood [34, 35]. A kind of chemical myopia is tolerated presently because experimental definition of

other than the primary coordination spheres of the nuclei at the centres of the ions remains generally uncertain [35, 36]. The nucleophilicity and abundance of water molecules are considered to be the factors giving rise to the displacement of anions into the second and higher coordination spheres of the metal, though there is good evidence that the structure of the primary coordination sphere is not independent of that of the secondary, at least [37]. Certainly, the process of solvent-assisted dissociation is reversible and crystallisation of metal ‘salts’ from water does not necessarily produce materials which would be considered ‘ionic’ [38]. Given that crystallisation occurs from relatively concentrated solutions, if the solids obtained reflect the nature of the species present in such solutions, then once the influence of water on equilibria derived from its simple abundance is removed, the subtlety of factors influencing complex ion equilibria may be revealed in a detailed consideration of these structures. The fact that anhydrous sodium chloride crystallises from aqueous solutions, for example, may be considered to demonstrate the importance of chloride anion hydration in determining the nature of the solution species. In aqua-complex systems such as the thoroughly studied ‘alums’ and related ‘Tutton Salts’ [39], hydrogen bonding appears to be extensive in the solid state and the sulfate anions remain outside the primary coordination spheres of the metal cations present, despite the relatively strong Lewis basicity of sulfate ion. This not the case with many other metal sulfates crystallised from water, especially when very heavy metals such as the lanthanides(III) are involved [40]. This suggests that the balance between metal–water, metal/sulfate and coordinated ligand/lattice water (and its converse) interactions may be such as to depend significantly upon variations in properties of the metal due to its position in the Periodic Table, *viz.*, that changes in bond energies down a group of the Periodic Table may define approximately the magnitude of factors such as the difference in H bonding interaction energies for ligands in the primary and secondary coordination spheres of a metal ion.

Evidence consistent with this suggestion being a specific instance of a rationalisation applicable to more than just aqueous systems may be found in examining the properties of complexes of so-called dipolar, aprotic solvents such as dimethylsulfoxide (dmsO) [41]. A particular group is that of the dmsO solvates of metal perchlorates, one reason for their study having been the consideration of perchlorate as an exceptionally poor Lewis base [42], so that its occupancy of the primary coordination sphere in these materials would not be expected. Structural studies of several [43–50] (but not all [51–55]) $\text{M}(\text{ClO}_4)_x \cdot n(\text{dmsO})$ species have shown that their representation as $[\text{M}(\text{dmsO})_n](\text{ClO}_4)_x$ (all, in these cases, with *O*-bound dmsO) is justified, in agreement with solution studies for a broader range of metals [45, 49, 50, 56–59] which indicate that dmsO is the sole occupant of the primary coordination sphere, even in

Table 1. Selected features of the geometry of crystalline $[M(\text{dms})_n](\text{ClO}_4)_x$ complexes (all values truncated to three significant figures to allow for differing uncertainties. Where disorder was resolved, values for the major component only are given).

M, <i>n</i> , <i>x</i>	M—O(Å)	M—O—S(°)	S···O ^a	Ref.
UO ₂ , 5, 2	2.33–2.43	121–141	2.96–3.07 ^b	[47]
Mg, 6, 2 ^c	2.05, 2.06, 2.08	140, 130, 128	3.34 ^d , 3.25, 3.03	[55]
Sr, 6, 2 ^c	2.42, 2.45, 2.47	151, 133, 143	> 3.50 ^d	[55]
Co, 6, 2 ^c	2.10, 2.11	121, 116	3.18, 3.26; 2.99, 3.28	[62]
Ni, 6, 2 ^c	2.05, 2.08	120, 116	2.98, 3.20; 3.16, 3.19	[62]
Zn, 6, 2 ^c	2.10, 2.11	120, 116	3.20, 3.25; 3.00, 3.28	[45, 62]
Hg, 6, 2 ^c	2.32, 2.32, 2.38	117, 132, 120	3.30, 3.38; 3.54 ^d ; 3.14	[43]
Al, 6, 3 ^c	1.88, 1.89, 1.89, 1.89, 1.89, 1.89	128, 125, 126, 126, 126, 124	3.12, 3.17; 3.03, 3.12; 3.06, 3.12; 3.10, 3.12; 3.08, 3.11, 3.40 ^d ; 2.99, 3.11	[67]
Ga, 6, 3 ^c	1.96, 1.96, 1.96, 1.96, 1.97, 1.98	125, 123, 123, 124, 122, 123	3.15, 3.22; 3.09, 3.14; 3.09, 3.14; 3.10, 3.16; 3.03, 3.16; 3.13, 3.16	[67]
Tl, 6, 3 ^c	2.22	121	3.21, 3.54, 3.86 ^d	[50]
Cr, 6, 3 ^c	1.96, 1.97, 1.97, 1.98, 1.98, 1.98	125, 123, 123, 122, 124, 123	3.17, 3.24; 3.11, 3.15; 3.09, 3.15; 3.04, 3.18; 3.17, 3.17; 3.14, 3.18	[67]
Dy, 8, 3 ^c	2.33, 2.34, 2.34, 2.36, 2.37, 2.38, 2.38, 2.41	137, 124, 134, 126, 126, 129, 129, 126	3.02; 3.02, 3.11; 2.96; 3.03, 3.11; 2.97, 3.23; 3.03, 3.25; 3.11, 3.13; 3.00, 3.21	[67]
Bi, 8, 3 ^c	2.39, 2.40, 2.40, 2.44, 2.45, 2.45, 2.47, 2.47	125, 133, 138, 127, 130, 123, 123, 129	3.10, 3.17; 3.06, 3.71 ^d ; 2.98, 3.77 ^d ; 3.17, 3.23; 3.13, 3.26; 2.94, 3.25; 3.12, 3.16; 3.40, 3.34	[49]
Th, 9, 4 ^c	2.47, 2.49, 2.49 (caps); 2.40, 2.42, 2.43, 2.44, 2.44, 2.45 (prism)	124, 124, 123; 138, 137, 136, 129, 129, 137	2.96, 3.00; 2.94, 3.02; 2.97, 2.98; 3.06, 3.48; 3.11, 3.41, 3.01, 3.51, 3.08, 3.09; 3.08, 3.11; 3.03, 3.58	[69]

^a Intramolecular S···O(dms) approaches <3.5 Å except where otherwise indicated.

^b Plus one intermolecular approach to uranyl-O of 3.22 Å and several contacts to perchlorate-O between 3.5 and 3.7 Å.

^c Entries in the columns M—O—S and S···O are in order associated with the M—O bond lengths given in the second column.

^d Intermolecular contact to perchlorate-O.

relatively concentrated solutions. Importantly, the structural studies show significant bond length changes in the coordinated dms) molecule by comparison with the molecule in the gas phase or the pure, crystalline solvent (and this is generally true for other compounds as well as perchlorates [41]). This effect may be rationalised by considering that the charge distribution represented by the Valence Bond Theory ‘resonance form’ $(\text{CH}_3)_2\text{S}^+-\text{O}^-$ is favoured as a result of coordination, the question then arising as to what effect this may have on further interactions of the dms). One effect that might be anticipated is some depletion of the electron density at C and H of the methyl groups, leading to more effective H bonding ability and indeed, in all published $[M(\text{dms})_n](\text{ClO}_4)_x$ structures, perchlorate-O atoms can be found within 3.2–3.8 Å of methyl-C atoms, consistent with the occurrence of weak $\text{CH}\cdots\text{O}$ interactions. While these approaches are remote and may at most be indicative of weak interactions, they are usually numerous, a beautiful example [50] being provided by $[\text{Tl}(\text{dms})_6](\text{ClO}_4)_3$, where a perchlorate-O atom situated on the crystallographic and molecular threefold axis of the structure is 3.52 Å from the C atoms of methyl groups of three equivalent dms) ligands (Figure 1). This same perchlorate-O is 3.63 Å from Tl, making a decision between secondary coordination and $\text{CH}\cdots\text{O}$ bonding as the primary cause (if they are not simply comparable) of the approaches difficult.

In many instances, a form of ‘chelation’ of perchlorate-O by the two methyl groups of one dms) entity may be discerned and a particular instance of such chelation in the case of $[\text{Zn}(\text{dms})_6](\text{ClO}_4)_2$ [45] provides evidence for further complication in the analysis of the interactions occurring. Thus, the approaches of one perchlorate-O to methyl carbons (3.45, 3.61 Å), with a second perchlorate-O at only slightly longer distances (3.59, 3.63 Å), are associated with another approach (3.56 Å) of the first oxygen to the S centre of the dms) (Figure 2).

This approach to sulphur can be rationalised in terms of the (negative) charge depletion at S leading to an attractive interaction of its nucleus with the charge accumulation at perchlorate-O. That this S-contact is not invariably observed when C-contacts are apparent may mean that the latter are energetically more important, although there is another consideration of possible importance and that is the extent to which S as well as O of formally O-bound dms) may interact with the metal. It has been noted [50] in the case of $[\text{Tl}(\text{dms})_6](\text{ClO}_4)_3$, for example, that although $\langle\text{Tl}-\text{O}\rangle$ (2.224(3) Å) is considerably shorter than $\langle\text{Tl}-\text{S}\rangle$ (3.292(2) Å), justifying the description of the complex as one of O-bound dms), the M—O—S bond angle is relatively small. It has been suggested that this may be indicative of some tendency towards η^2 coordination of the SO unit, reflecting the ‘softness’ of Tl(III) as a Lewis acid, and, consistent with this view, the corresponding angle in $[\text{Hg}(\text{dms})_6](\text{ClO}_4)_2$ [43], containing ‘soft’ Hg(II), is smaller while that

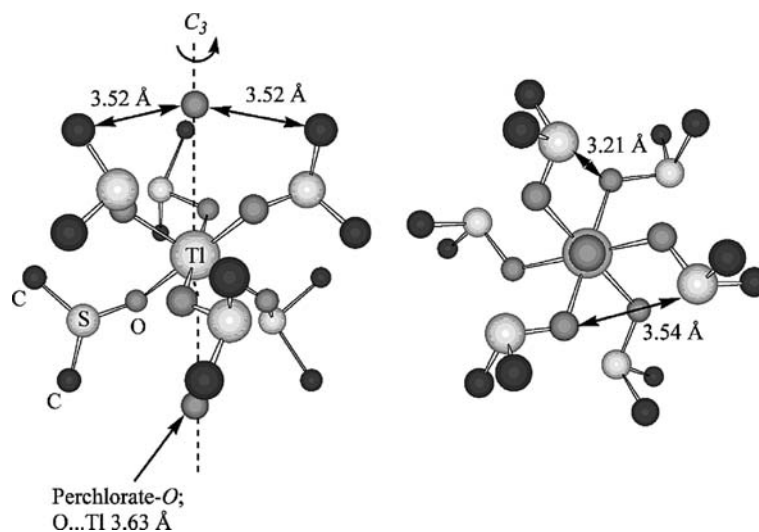


Figure 1. Views perpendicular to (L) and down (R) the threefold axis of the $[\text{Tl}(\text{dmso})_6]^{3+}$ cation [50]. The two perchlorate-O atoms lying on the threefold axis above and below the cation are also shown.

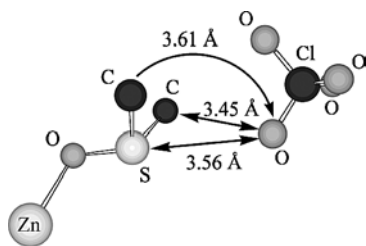


Figure 2. Portion of the lattice of $[\text{Zn}(\text{dmso})_6](\text{ClO}_4)_2$ showing contacts between perchlorate and a coordinated dmso.

in $[\text{Sc}(\text{dmso})_6]_3$ [57, 59], containing ‘hard’ Sc(III), is significantly larger. However, yet a further complication in these systems is the possibility of an interaction between the O-atom of a coordinated dmso with the S-atom of an adjacent dmso. This is analogous to that identified between O and carbonyl-C of coordinated dmf molecules [60] and may of course be considered as an aspect of the interaction to be expected between dipolar molecules, regardless of the rest of their environment. In crystalline dmso itself [61], columnar arrays of head-to-tail SO entities are found, with an ‘intermolecular’ S \cdots O separation of 3.84 Å (and with O \cdots H 2.40–2.70 Å, i.e., $\langle \text{O}\cdots\text{C} \rangle$ 3.5 Å, and H \cdots H 2.80–2.90 Å noted). Again, the $[\text{Tl}(\text{dmso})_6]^{3+}$ cation provides a striking example of evidence that ‘dipolar’ S \cdots O interactions may indeed be fortified by coordination of dmso. Each sulphur atom in this highly symmetrical species can be viewed as bridging (unsymmetrically) two oxygen atoms which occupy the vertices of a trigonal face completed by the oxygen to which the sulphur is considered bound in an inert manner (Figure 1). The S \cdots O distances are 3.21 and 3.54 Å, both significantly shorter than the S \cdots O separation in crystalline dmso itself. If indeed some attractive interaction is involved, then some consequences concerning the M \cdots S distances and M—O—S bond angles might be anticipated and for present

purposes it is useful to focus on the latter. (As noted above, variations in the ratio of MO to MS separations in some dmso complexes have been considered in terms of the Lewis acid character of the central metal.) The Tl—O—S bond angle is 120.7(2)°, a value which may be considered relatively small (see ahead) and thus indicative that some attractive interaction indeed is occurring. Whether or not this involves principally S and O centres of bound dmso molecules is unclear but it is instructive to consider other dmso complexes in these terms. Relevant data are summarised in Table 1.

In the family of essentially octahedral $[\text{M}(\text{dmso})_6](\text{ClO}_4)_2$ species (M = Mg, Co, Ni, Zn, Cd, Hg), the Co, Ni and Zn [45] compounds are isomorphous and in recent structure determinations at low (~150 K) temperature [62], many aspects of the disorder well known [46, 47, 55–59] to plague structure determinations on complexes containing both perchlorate and dmso proved to be resolvable, providing greater precision on most aspects of geometry. Approaches of perchlorate to bound dmso as noted above for the Zn species can be found in all but also there are close parallels to the features noted above for the Tl(III) complex. Thus, in columns parallel to *c*, the lattices in part involve alternating cation and perchlorate entities, one of the Cl—O bonds being coincident with the crystallographic 3 axis and the oxygen atom involved being equidistant from three dmso methyl groups associated with three ligands on one trigonal face. Above the opposite trigonal face, the perchlorate here is inverted and now each of the three oxygen atoms appears to be ‘chelated’ by two methyl groups. (This is unlike the Tl(III) system, where the orientation of two perchlorate groups towards opposite trigonal faces is the same.) Within the $[\text{M}(\text{dmso})_6]$ unit, there are slightly differing but both relatively small ‘upper’ and ‘lower’ M—O—S angles, associated with slightly different pairs of S \cdots O (dmso)

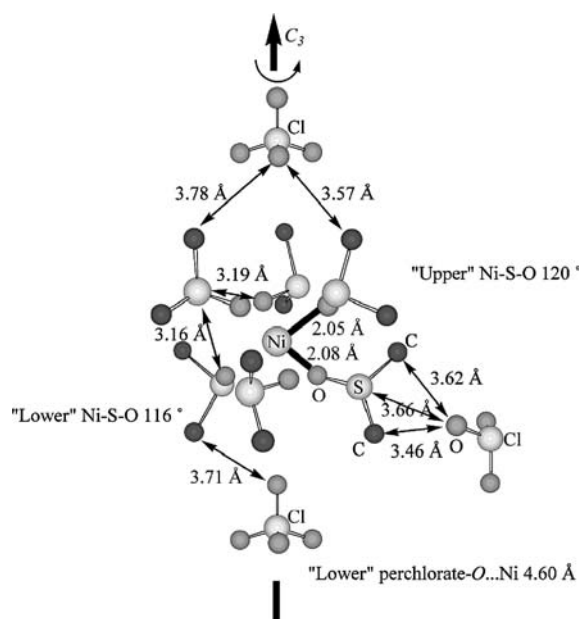


Figure 3. Geometry of a portion of the $[\text{Ni}(\text{dmsO})_6](\text{ClO}_4)_2$ lattice. For clarity, only two of the Ni—O vectors are shown.

approaches, all even shorter than those in the Tl(III) complex. The various interatomic distances and angles observed in the major component of the partly disordered Ni complex are shown in Figure 3 (see also Table 1).

Surprisingly, given the very similar M—O distances and similar lattices (Figure 4) in which columns of alternating $[\text{M}(\text{dmsO})_6]$ and $[\text{ClO}_4]$ units (although, for Mg, two perchlorate units interpose between every pair of Mg, more like the case for Tl) can be discerned, $[\text{Mg}(\text{dmsO})_6](\text{ClO}_4)_2$ ($P\bar{1}$) [55] is not isostructural with its Co, Ni and Zn analogues ($P3_1/c$). All Mg—O—S are significantly larger than in the transition metal species, though the two smaller values are associated with single, ‘intramolecular’ S···O contacts of 3.25 Å (for the dmsO with Mg—O—S 130.2°) and 3.03 Å (for 127.5°). The largest Mg—O—S is found for two *trans*-disposed ligands which have contacts to perchlorate oxygens (S···O 3.34 Å). It would appear that bending of the Mg—O—S angle (to facilitate S···O approaches) is more energetically demanding than that of Zn—O—S, a circumstance possibly to be associated with differences in the metal valence shells, though in general the issue of differences in bending force constants for analogous compounds of groups 2 and 12 has proven complicated to resolve [63]. Whatever the fundamental causes of the differences, a simple rationalisation of the nature of all four systems is that their subtler details reflect the balance of a number of weak interactions, the dominance of one over others being sensitive to minor differences in strong interactions. It should be noted again that in all the lattices considered there are numerous dmsO-methyl-CH···O (perchlorate) approaches between ~3.3 and 3.8 Å which must be of

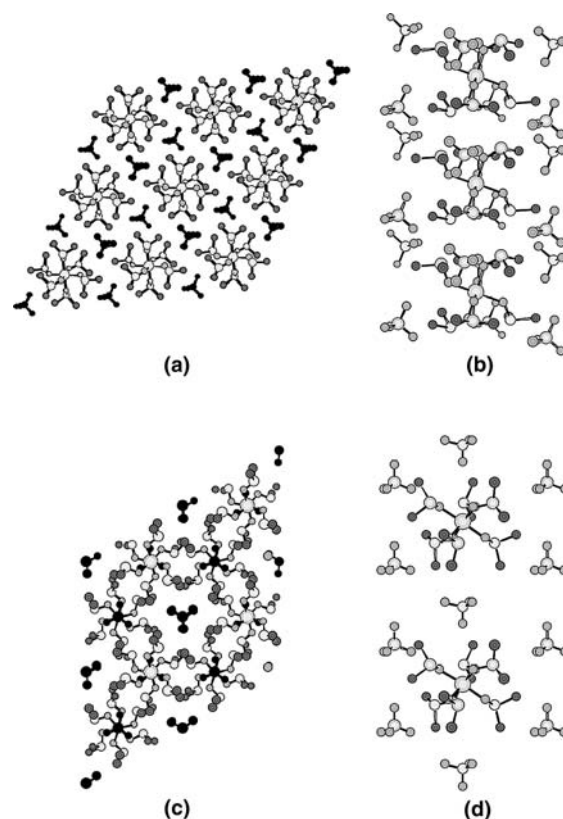


Figure 4. Partial lattice views of $[\text{Mg}(\text{dmsO})_6](\text{ClO}_4)_2$ and $[\text{Zn}(\text{dmsO})_6](\text{ClO}_4)_2$: (a) the Mg lattice viewed down a , showing adjacent cation and anion columns. For contrast, all atoms of the perchlorate units are shown in black. Columns of cations along the bc diagonal are separated by two perchlorate units; (b) a view perpendicular to the cation and anion columns parallel to a ; (c) the Zn lattice (minor disordered component deleted) viewed down c , again with all perchlorate atoms shown in black; (d) a view perpendicular to the mixed cation/anion and purely anion columns parallel to c .

importance in determining the lattice structure (and which presumably, simply because of their number, must give rise to some differences between, for example, $[\text{M}(\text{dmsO})_6](\text{ClO}_4)_2$ and $[\text{M}(\text{dmsO})_6](\text{ClO}_4)_3$ systems).

Other informative contrasts with the Zn system are provided by the other group 12 compounds, $[\text{Cd}(\text{dmsO})_6](\text{ClO}_4)_2$ ($Fd2d$) [44] and $[\text{Hg}(\text{dmsO})_6](\text{ClO}_4)_2$ ($P\bar{1}$) [43], though disorder problems in the structure of the former are quite severe and detailed comparisons with the other species are not justifiable. For Hg(II), marked distortions from octahedral geometry in six-coordinate complexes are common but the fact that $[\text{Hg}(\text{dmsO})_6](\text{ClO}_4)_2$ is isomorphous with its Mg analogue indicates that the special bonding proclivities of Hg(II) may not be the prime cause of the distortions seen in this case. Since $\langle \text{Hg—O} \rangle$ (2.34 Å) is considerably longer than $\langle \text{Mg—O} \rangle$ (2.06 Å), retention of the same S···O approaches in both complexes would require greater bending of the M—O—S unit and this is essentially as observed. Thus, Hg—O—S of 117.3° is associated with S···O of 3.30, 3.38 Å (differing slightly from Mg, where only one contact is <3.5 Å) and

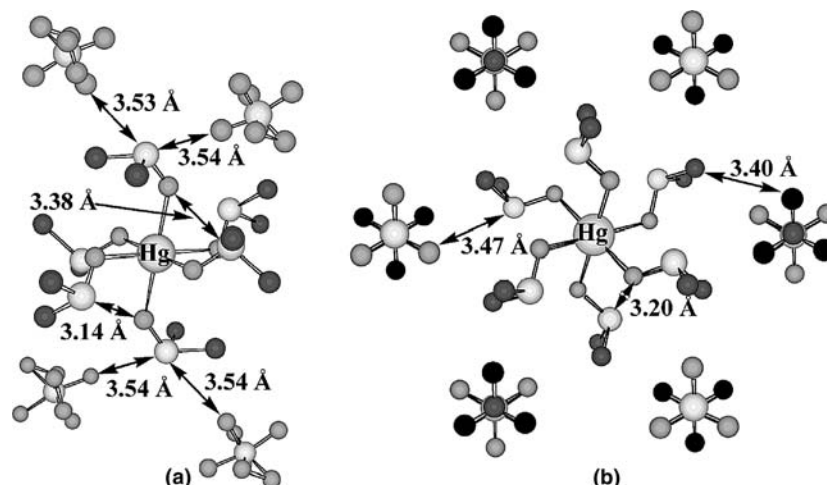


Figure 5. Close approaches in the $[\text{Hg}(\text{dmsO})_6](\text{ClO}_4)_2$ and $[\text{Hg}(\text{dmsO})_6](\text{CF}_3\text{SO}_3)_2$ lattices: (a) a partial view of the perchlorate lattice, showing disordered perchlorate units in proximity to two dmsO ligands; (b) a view down c of the triflate lattice, showing $\text{S}\cdots\text{O}$ (dmsO), $\text{S}\cdots\text{O}$ (sulphonate) and $\text{F}\cdots\text{C}$ approaches. (Fluorine atoms shown in black.)

$\text{Hg}-\text{O}-\text{S}$ of 120.0° is associated with $\text{S}\cdots\text{O}$ of 3.14 \AA . Bending towards one octahedral edge to achieve a given, single $\text{S}\cdots\text{O}$ should be less, of course, than the bending necessary over a face in order to achieve two contacts of the same length. The third $\text{Hg}-\text{O}-\text{S}$ of 132.2° , as in the case of the largest angle for Mg, is not associated with any close intramolecular approach but with perchlorate- O contacts (3.53 \AA) with the S atoms of the two (*trans*) ligands involved (Figure 5(a)). The general argument that there may be a competition between intra- and intermolecular modes of $\text{S}\cdots\text{O}$ interactions dependent in part upon the energy of $\text{M}-\text{O}-\text{S}$ bond bending is supported also by features of the structure of $[\text{Hg}(\text{dmsO})_6](\text{CF}_3\text{SO}_3)_2$ [64] (a compound studied, incidentally, because of an interest in determining the $\text{Hg}\cdots\text{H}$ separations, found to range between 4.00 and 5.48 \AA). In this $\text{P}\bar{3}$ system, all the $\text{Hg}-\text{O}-\text{S}$ angles are the same, all are small ($116.4(2)^\circ$) and each S is found within 3.20 \AA of a coordinated oxygen atom as well as within 3.47 \AA of a sulphonate group oxygen atom (Figure 5(b)). Clearly, the substitution of triflate for perchlorate must introduce new considerations (both geometrical and chemical) and, as in some related systems [65], there is evidence for $\text{CH}\cdots\text{F}$ interactions ($\text{C}\cdots\text{F}$ 3.40 \AA) but it does seem that intramolecular $\text{S}\cdots\text{O}$ interactions of dmsO ligands are a significant attractive force controlling aspects of complex ion structure.

A structure determination is yet to be performed for $[\text{Ca}(\text{dmsO})_6](\text{ClO}_4)_2$ but the cation has been characterised in other environments [66] and the complex $[\text{Ca}(\text{dmsO})_6]_2[\text{W}_4\text{Ag}_4\text{S}_{16}]$ [66(a)] provides some interesting comparisons with $[\text{Hg}(\text{dmsO})_6](\text{ClO}_4)_2$. $\langle\text{Hg}-\text{O}\rangle$ and $\langle\text{Ca}-\text{O}\rangle$ are very similar (2.34 , 2.33 \AA , respectively), suggesting similar degrees of $\text{M}-\text{O}-\text{S}$ angle bending would be necessary for a given intramolecular $\text{S}\cdots\text{O}$ separation. In both complexes, there is a wide range in $\text{M}-\text{O}-\text{S}$, with the values for the Ca species being

generally larger, again perhaps as a result of some fundamental difference in factors determining the force constants. Only the smallest angle (125°) is associated with an $\text{S}\cdots\text{O}$ separation (3.13 \AA) comparable to the shortest observed with Hg (though angles of 126° and 139° are associated with such contacts at 3.36 and 3.48 \AA , respectively). All dmsO-S except that at 3.13 \AA from O are associated with contacts to S atoms of the $[\text{W}_4\text{Ag}_4\text{S}_{16}]$ unit between 3.42 and 3.99 \AA , suggesting that these polysulphide S atoms play a role equivalent to that of perchlorate- O in the Hg complex. That such perchlorate- O interactions may eventually win out when bond length extension requires extreme $\text{M}-\text{O}-\text{S}$ bending to retain intramolecular $\text{S}\cdots\text{O}$ interactions is suggested by the structure of $[\text{Sr}(\text{dmsO})_6](\text{ClO}_4)_2$ [55]. This species has been characterised as a component of the lattice of $\text{Sr}_7(\text{dmsO})_{40}(\text{OH}_2)(\text{ClO}_4)_{14}$ and it is the only $[\text{M}(\text{dmsO})_6](\text{ClO}_4)_2$ complex known to date in which there are no intramolecular $\text{S}\cdots\text{O}$ contacts $<3.8 \text{ \AA}$. $\langle\text{Sr}-\text{O}\rangle$ is 2.46 \AA and $\text{Sr}-\text{O}-\text{S}$ angles are 133.0° , 142.7° and 150.9° , with every dmsO-S having at least one 'intermolecular' contact to perchlorate- O of $<3.5 \text{ \AA}$.

Low-temperature structure determinations for $[\text{M}(\text{dmsO})_6](\text{ClO}_4)_3$ ($\text{M} = \text{Al}$ [67], Ga [67], Tl [50]) provide data which support the analysis above (as do ambient temperature determinations for $\text{M} = \text{Sc}$ [67], In [47], though unresolved aspects of disorder cause greater uncertainties in geometry). The range of $\langle\text{M}-\text{O}\rangle$ in these three Group 13 complexes is nearly as great as that observed in the various $\text{M}(\text{II})$ species described above but here $\text{M}-\text{O}-\text{S}$ systematically decreases in association with the retention of two intramolecular $\text{S}\cdots\text{O}$ for every S atom (Table 1). Every S (except S5 in the Al species) has at least one additional contact to perchlorate- O , invariably longer than the intramolecular contacts, though frequently $<3.5 \text{ \AA}$. Contacts between perchlorate- O and methyl-C, frequently in the range

3.3–3.4 Å and presumably indicative of CH···O bonding, are numerous in all complexes and, given the relative abundance of perchlorate entities relative to that in the M(II) compounds, the fact that S···O(perchlorate) contacts do not displace intramolecular S···O in the M(III) systems suggests that perchlorate-O interaction with S is weaker than that with CH. Again, the energy involved in M—O—S bending must be of some relevance to the retention of intramolecular attractions and the quite small value (119.6(2)°) for the Tl complex is consistent with the normal decrease in the value of the relevant force constant down the Periodic Table. Note that in the beautifully symmetric structures of [M(dmso)₆]I₃ (M = Al, Ga, In and Sc [57, 59]), where anion disorder is not a complication, S···O approaches essentially identical to those in the perchlorates are seen.

Another aspect of periodicity is revealed in the structures determined for the complexes with the empirical formulae Pb(ClO₄)₂·5dmso [54], Pb(ClO₄)₂·3dmso [54], and Ba(ClO₄)₂·5dmso [55]. Here, finally, a property is observed which might be expected when a small-bite chelate interacts with a large metal ion [68] and perchlorate is found to be coordinated in these solids. The ambient temperature Pb complex determinations are affected by disorder but in Pb(ClO₄)₂·5dmso = [Pb(dmso)₅(O₂ClO₂)]ClO₄, the intrusion of perchlorate into the primary coordination sphere appears to have only minor consequences concerning close approaches to the dmso-S atoms. Pb—O—S range from 125 to 144° but all close contacts involve dmso-O except in one case, where S appears poised essentially equidistant from dmso-O and the more closely bound oxygen atom of the unsymmetrically chelating perchlorate ligand. The ligand with Pb—O—S 144°, however, is unusual in that its contact is to a dmso-O coordinated to an adjacent Pb atom. This contact is symmetrical, so that, in effect, a pair of aligned dmso dipoles link two Pb complex entities (Figure 6). The complex Pb(ClO₄)₂·3dmso, with the unexpected composition of mixed dimers, [Pb₂(μ-dmso)₂(dmso)₄(O₂ClO₂)₂][Pb₂(μ-O₂ClO₂)₂(dmso)₆(OCIO₃)₂], is somewhat more complicated to describe but perhaps the only feature of note is that S···O (bound perchlorate) contacts occur at distances which,

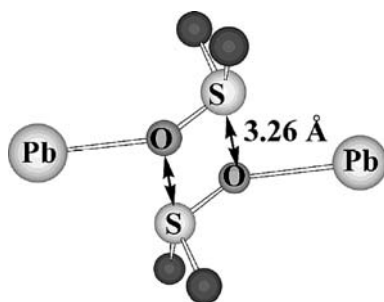


Figure 6. The symmetrical interaction of two dmso ligands on separate complex ion entities within the lattice of [Pb(dmso)₅(O₂ClO₂)]ClO₄.

in some cases, are only slightly longer than S···O (dmso) and which are relatively short (3.1–3.2 Å). The complex Ba(ClO₄)₂·5dmso, defined in a determination free of disorder, is also a centrosymmetric dimer, [Ba₂(μ-dmso)₄(dmso)₆(O₂ClO₂)₂](ClO₄)₂, but provides marked contrasts with the Pb systems. ⟨Ba—O(dmso)⟩ 2.68 Å (for the unidentate ligands) is by far the longest of all systems considered so far and this may explain why the bending only of one of the bridging dmso ligands is sufficient to enable a single and rather long (3.42 Å) S···O contact involving another dmso ligand. ⟨Ba—O(perchlorate)⟩ at 2.99 Å clearly brings these donors further out from Ba and thus closer to the dmso-S atoms and, significantly, the shortest of all S···O (perchlorate) contacts (3.16 Å) is to the more remotely bound oxygen of the chelating pair. Other short (3.2–3.4 Å) contacts of this type involve both the uncoordinated oxygen atoms of chelating perchlorate as well as oxygen atoms of lattice perchlorate.

Neither the Pb nor the Ba systems just discussed involve six coordination of the metal and change in coordination number is of course another factor which depends on the position of an element in the Periodic Table. Considering only homoleptic dmso complexes of metal perchlorates, Bi(III) [49], Dy(III) [67] and Th(IV) (Harrowfield *et al.*, submitted for publication) provides examples where the effects of this change may be considered independently of any effects of perchlorate coordination as seen for Pb(II) and Ba(II). Perchlorate disorder still creates uncertainty in approaches involving perchlorate-O but most dmso configurations are well defined in these three cases. The Bi and Dy complexes provide further examples where all the dmso present is coordinated, while the Th complex is, somewhat surprisingly given the ease with which certain materials containing large amounts of lattice dmso can be crystallised [69], the sole known example of a metal perchlorate which crystallises in a form where both coordinated and lattice dmso are present. Thus, the formulae M(ClO₄)₃·8dmso (M = Bi, Dy) and Th(ClO₄)₄·13dmso correspond to the representations [Bi(dmso)₈](ClO₄)₃, [Dy(dmso)₈](ClO₄)₃ (both of square-antiprismatic coordination geometry) and [Th(dmso)₉](ClO₄)₄·4dmso (of tricapped-trigonal-prismatic geometry), respectively (Figure 7). Given very similar ⟨M—O⟩ (2.43 Å (Bi); 2.36 Å (Dy); 2.45 Å (Th)), any effects of specific metal properties and differences in O—M—O angles associated with 8- or 9-coordination might be anticipated to be revealed in comparisons of these compounds. In fact, all three show rather close similarities in M—O—S angles and closest S···O (dmso) approaches, the two 8-coordinate metals differing only rather subtly in that for Dy each dmso-S has two very similar approaches, whereas for Bi the two values are rather more divergent, with two ligands appearing to have but a single contact <4 Å. This could be seen as a consequence of the small difference in ⟨M—O⟩, the longer Bi—O meaning that for the same degree of bending, a single contact would be more readily

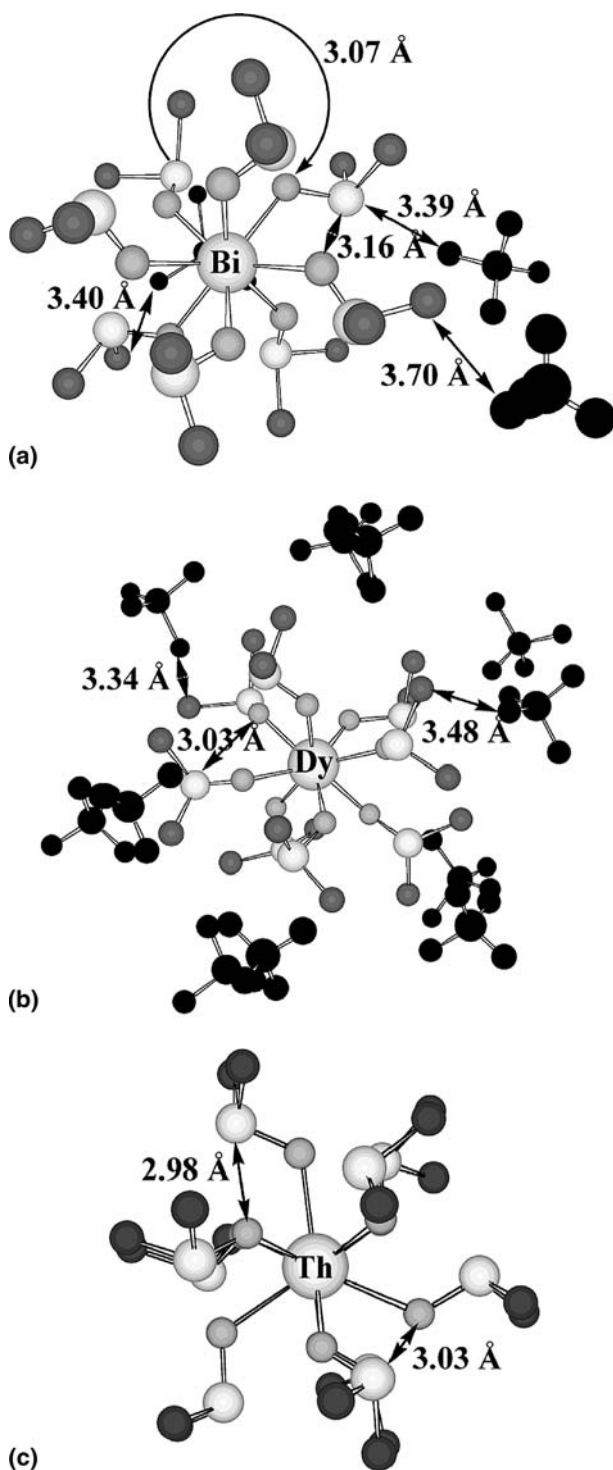


Figure 7. (a) Section of the lattice of $[\text{Bi}(\text{dms})_8](\text{ClO}_4)_3$, showing one 'stoichiometric unit', viewed perpendicular to one square face of the square-pyramidal coordination sphere, and various close atomic approaches. All atoms of the perchlorate units are shown in black; (b) a $[\text{Dy}(\text{dms})_8]$ unit of $[\text{Dy}(\text{dms})_8](\text{ClO}_4)_3$, showing more comprehensively its immediate environment of perchlorate units (black) and some close atomic approaches; (c) the $[\text{Th}(\text{dms})_9]$ unit of $\text{Th}(\text{ClO}_4)_4 \cdot 13\text{dms}$, free of its environment of both perchlorate and dms units, viewed down the near-threefold axis and showing the two inequivalent $\text{S} \cdots \text{O}$ approaches.

maintained than two (as previously discussed in relation to $\text{M}(\text{II})$ systems). In all three systems, $\text{S} \cdots \text{O}$ (perchlorate) contacts are also apparent, somewhat longer than $\text{S} \cdots \text{O}$ (dms) at ~ 3.5 Å, uncertainty in these values resulting from partial disorder of the perchlorate moieties. In the Th complex, $\text{S} \cdots \text{O}$ (dms) approaches are amongst the shortest of all observed in the complexes presently discussed, though they do not differ greatly from those of the Dy complex, possibly consistent with the fact that the smallest $\text{O}-\text{M}-\text{O}$ bond angles in the two species are very similar (and slightly smaller on average than those of the Bi complex). $\text{M}-\text{S}-\text{O}$ values vary considerably over each of the three complexes but all lie within an intermediate range (~ 124 – 138°) for the present systems, consistent with the fact that a higher coordination number brings ligands into closer proximity than in, say, an octahedral complex with the same $\langle \text{M}-\text{O} \rangle$ and thus does not necessitate extreme $\text{M}-\text{O}-\text{S}$ bending to maintain a particular $\text{S} \cdots \text{O}$. Within the $[\text{Th}(\text{dms})_9]$ moiety, which has close to C_{3h} symmetry, the closer oxygen atoms making up the trigonal prism are associated with the larger $\text{M}-\text{O}-\text{S}$ and the more remote oxygen atoms making up the capping species are associated with the smaller, providing yet further support to the notion that the $\text{S} \cdots \text{O}$ (dms) interactions must be attractive. As well, within the dms molecules which are not within the primary coordination sphere of the Th, there is a pair aligned exactly as would be expected for antiparallel dipoles, with an $\text{S} \cdots \text{O}$ separation of 3.79 Å, essentially equal to that observed within the lattice of pure dms. Longer contacts to perchlorate- O are also evident, indicating quite striking differences between dms in the primary and higher coordination spheres of the metal with respect to both forms of contact.

The overall result of this analysis is the conclusion that for a molecule such as dms, coordination can result in a considerable enhancement of secondary interactions of the molecule, and a qualitative ordering based on just the data presently discussed is that the energy of $\text{S} \cdots \text{O}$ (dms) exceeds that of $\text{S} \cdots \text{O}$ (perchlorate). Quantitatively, it would appear that the $\text{S} \cdots \text{O}$ (dms) interaction has an energy at least equal to that required for the bending of an $\text{M}-\text{O}-\text{S}$ unit by $\sim 20^\circ$, an energy perhaps as great as 4 kJ mol^{-1} . Obviously, it would be useful to extend such analyses in many dimensions. Evidence that coordinated dimethylformamide (dmf), for example, may be involved in weak intramolecular attractions has been noted for the complex $[\text{Al}(\text{dmf})_6](\text{ClO}_4)_3$ [60] (and is discussed further ahead) but, to remain briefly under consideration of dms, uranyl ion complexes of this molecule provide evidence of the diversity of its possible interactions. In $[\text{UO}_2(\text{dms})_5](\text{ClO}_4)_2$ [47], each dms ligand has a similar orientation with respect to the equatorial UO_5 pentagonal plane which gives rise to a short (2.96–3.07 Å) $\text{S} \cdots \text{O}$ contact involving an adjacent dms. Other, more remote contacts involve both uranyl- O and perchlorate- O , with the uranyl- O contacts (~ 3.7 Å) being such that it is the same oxygen which is

the closer to all dms_o-S. In [UO₂(dms_o)₅](CF₃SO₃)₂ (Harrowfield *et al.*, submitted for publication), disorder problems are rather severe but it appears that sulphonate-*O* contacts with dms_o-S (~3.6 Å) influence the conformations of the sulfoxide ligands in such a way that four turn slightly to give contacts ~3.5 Å with one uranyl-*O* while one turns in the opposite manner to similarly contact the other uranyl-*O*. S···*O* (dms_o) contacts ~3.0 Å are retained for all, nonetheless. The apparently greater influence of triflate compared to perchlorate is consistent with their relative basicity. On such grounds, it is unsurprising to find that in [UO₂(dms_o)₂(NO₃)₂] (Harrowfield *et al.*, submitted for publication), dms_o-S has a close contact with coordinated nitrate-*O* (3.25 Å) and a slightly longer contact to uranyl-*O* (3.33 Å), that in [UO₂(dms_o)₃(pic)₂] (Harrowfield *et al.*, submitted for publication) (pic = 2,4,6-trinitrophenoxide, picrate) short contacts are to phenoxide-*O* (3.09 Å), nitro-*O* (3.15, 3.27 Å) and uranyl-*O* (3.37 Å), and that in [(UO₂)₄(μ₃-O)₂(dms_o)₄(O₂CCH₃)₄] (Harrowfield *et al.*, submitted for publication) an unusually short contact to acetate-*O* (2.87 Å) occurs (along with a contact to uranyl-*O* of 2.93 Å as the shortest for the other, inequivalent S of this complex). In all these structures, there is evidence for other specific examples of weak interactions which may be of structural influence, uranyl-*O* approaches to nitrate-*N* (3.14 Å) and acetate-*C* (3.30 Å) being but two examples (Figure 8; see ahead also).

Al(dmf)₆(ClO₄)₃ has been mentioned as another homoleptic solvento complex of a perchlorate in which

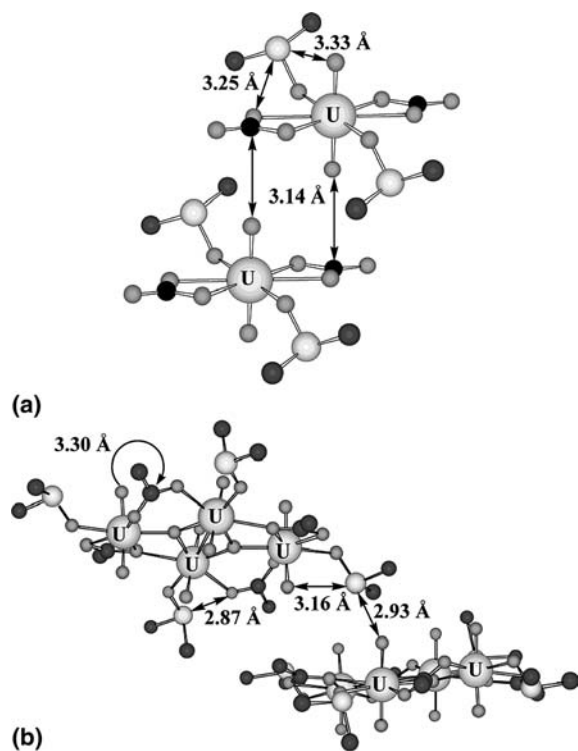


Figure 8. Partial views of the lattices of (a) 'mononuclear' [UO₂(NO₃)₂(dms_o)₂] and (b) 'tetrameric' [(UO₂)₄(μ₃-O)₂(dms_o)₄(O₂CCH₃)₄] showing both intra- and inter-molecular contacts.

close intramolecular approaches (2.88–2.92 Å; of carbonyl-*C* to coordinated oxygen) have been identified as indicative of a significant attractive force. In support of this analysis, in complexes of dmf with the lanthanides Gd, Tb and Ho [70] where both M—O—C bond angles and M—O bond lengths differ significantly from those of the Al complex and where the relative positionings of the dmf ligands vary considerably, a close *O*-contact for each carbonyl-*C* is maintained. Thus, in [H₂N(CH₃)₂]-[Gd(dmf)₈](ClO₄)₄, such C···*O* contacts range from 2.86 to 3.09 Å, in [Tb(dmf)₈](ClO₄)₃ from 2.82 to 3.31 Å, and in [Ho(dmf)₇(OH₂)](ClO₄)₄ from 2.97 to 3.27 Å. Given the general chemical importance of the amide unit and the common observation of metal ion catalysis of its reactions, recognition and exploitation of intra-complex interactions of this type may prove to be useful.

Labile interactions involving aromatic ligands

Intense interest has been focussed on both aromatic-aromatic interactions such as face-to-face (π -stacking, charge transfer interactions), edge-to-face and vertex-to-face attractions of aza-aromatics in particular, as well as aromatic-metal interactions (polyhapto- π -coordination, cation- π interactions) and their importance is undoubted [5–7, 10, 11, 14, 16–18, 20, 23]. As exemplified by the extensive chemistry of metallocenes [71], polyhapto-aromatic binding need not be labile but there are many systems, particularly involving alkali metal ions [72], where this is the case. While the term 'cation- π bonding' [10] implies that this interaction can be regarded as coordinative, with the aromatic behaving as a Lewis base, there are instances of ambiguity in the interpretation of aromatic unit approaches to metals. An instructive example is provided in comparison of the structures of the three formally dimeric complexes of dibenzoylmethane anion (DBM⁻) with Zn(II) [71], Sn(II) [74] and Pb(II) [75], M₂(DBM)₄. In the Zn species, the primary coordination sphere consists of five oxygen donor atoms and the ZnO₅ coordination geometry is close to trigonal bipyramidal, there being no evidence of unusually close approaches of any of the phenyl group atoms to the metal. If the Sn and Pb species are regarded simply as dimers, it is also true for both that no close approaches of aromatic units to the metals are apparent. However, the SnO₅ and PbO₅ entities have very asymmetric structures, far from trigonal bipyramidal, and both can be seen as having large gaps in the primary coordination sphere. An obvious explanation for this difference from Zn(II) is that both Sn(II) and Pb(II) may be regarded as having a lone pair (5s² or 6s²) in the valence shell and that the structures provide examples of this lone pair being 'stereochemically active'. As in several cases of Pb(II) structures initially considered to provide evidence for this effect, consideration of the complete lattice of the crystalline solid casts doubt on

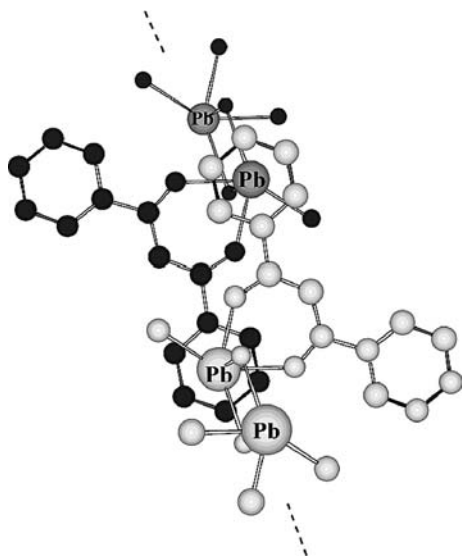


Figure 9. A simplified representation of the linking of $\text{Pb}_2(\text{DBM})_4$ ($\text{DBM} = (\text{C}_6\text{H}_5\text{CO})_2\text{CH}^-$) units by the positioning of a ligand phenyl group within an apparent coordination vacancy on $\text{Pb}(\text{II})$. (All atoms of one dimer unit have the same colour and only the ligands involved in the linking are shown in full.)

this interpretation. Thus, both the Sn and Pb compounds appear to be polymeric rather than dimeric, the dimer units being linked by a phenyl group from one making a close approach to a metal atom of its neighbour, locating itself in an essentially η^6 manner, and so largely occupying the space initially assigned to a lone pair (Figure 9). One rationalisation of this is that it is the lone pair that is involved in donation to an aromatic ring rendered electron deficient by its substituents and, while reasonable, this is the converse of the conventional view of cation– π interactions. While this may do no more than highlight the artificiality of the formalisms involved in analysing the formation of these complexes, it does place metal–aromatic interactions within the broader context of interactions observed in substituted aromatic systems, in particular those termed ‘ π -stacking’ [7]. Note that the term ‘ π -stacking’ has often been applied to describe systems which simply involve parallel arrays of aromatic rings and where there may be no evidence of significant π – π interactions [7(a)] or, if anything, it is the substituents on the rings which are involved in any close intermolecular contacts, and some examples of this are cited ahead.

An appealing rationalisation of many stacked structures is that they involve the projection of relatively positive centres of a functionalised aromatic onto relatively negative centres of the same molecule [76]. (On the basis of simple packing considerations, it would not be expected that stacking would lead to a direct projection of all interacting centres one upon the other and ‘offset’ or ‘slipped’ stacking is in fact the usual observation [7].) Such a mode of interaction need not mean that the parallel arrays of near-planar molecules which engender the term ‘stacking’ are the only possible

result and herring-bone arrays of aromatics, for example, occur with essentially the same frequency as stacks [7(a)]. Significantly, stacking appears to be a flexible motif in the sense that parallel orientations can often be maintained for various projections of the molecules. This is exemplified in numerous structures [7, 77] of complexes of nitrophenoxides and aza-aromatic carboxylates where stacking is maintained in spite of major changes in both the nature and the coordination mode of the metals involved. One conclusion which may be drawn from this work is that the energy of stacking interactions may be comparable to coordinate bond energies, at least for alkali and alkaline earth metals and some heavy metals such as Tl, Ag and Pb. A very speculative estimate [78] (although having some theoretical [79] and experimental [80] support) of the energy of picrate-pair stacking of 40 kJ mol^{-1} is certainly consistent with this conclusion. As with $\text{M}(\text{ClO}_4)_x \cdot n\text{dmso}$ compounds, it is possible to find numerous systems where various weak interactions appear to be in competition and where the balance may change from one system to another. Several examples (and ones where the interactions may not be particularly weak, though they are labile) are provided by metal complexes of nitrophenoxides [7(b), (Harrowfield *et al.*, submitted for publication), 79(b), (d), 81–84].

For 2-nitrophenoxide (2NP^-), the coordination environments of the metals in its $\text{M}(\text{I})$ ($\text{M} = \text{alkali metals, Ag, Tl}$) complexes vary greatly but in all structures infinite parallel arrays of aromatic units can be discerned [77(b)]. Projections perpendicular to the aromatic ring plane (for adjacent pairs dissected from the infinite arrays) show, however, that the overlap of adjacent units is not of a common form (Figure 10). Indeed, in the case of $\text{Rb}(\text{I})$, there is no overlap at all, with the closest approach (3.36 \AA) being of a nitro-group oxygen to the carbon attached to phenoxide oxygen. Further, even where there is overlap, atom separations are not always such as to indicate significant interaction (using a value of 3.5 \AA as the critical point [7(a)], though greater values have been taken [10]). In the case of the $\text{Na}(\text{I})$ complex, several short $\text{C} \cdots \text{C}$ contacts (3.32 , 3.33 , 3.47 and 3.50 \AA) are apparent, though the shortest contact (3.29 \AA) is that of nitro- N with the carbon bearing the nitro substituent on the adjacent ring. In contrast, even though the ring projections appear very similar, in the $\text{Tl}(\text{I})$ complex the only contact under 3.5 \AA is between nitro- N and nitro- O at 3.34 \AA . In the $\text{Ag}(\text{I})$ complex, overlap in projection is very slight and no short contacts are evident, the closest approach (3.57 \AA) being of nitro- N to the 4-carbon of the adjacent ring, though here a reason for this special character of the Ag complex may be that it is the only one of the series discussed in which binding of the metal to the aromatic ring occurs. Ag is η^2 -bound to carbons 5 and 6 of the phenoxide ring (as well as to nitro- and phenoxide- O) and obviously this may produce a rather different perturbation of the ring to

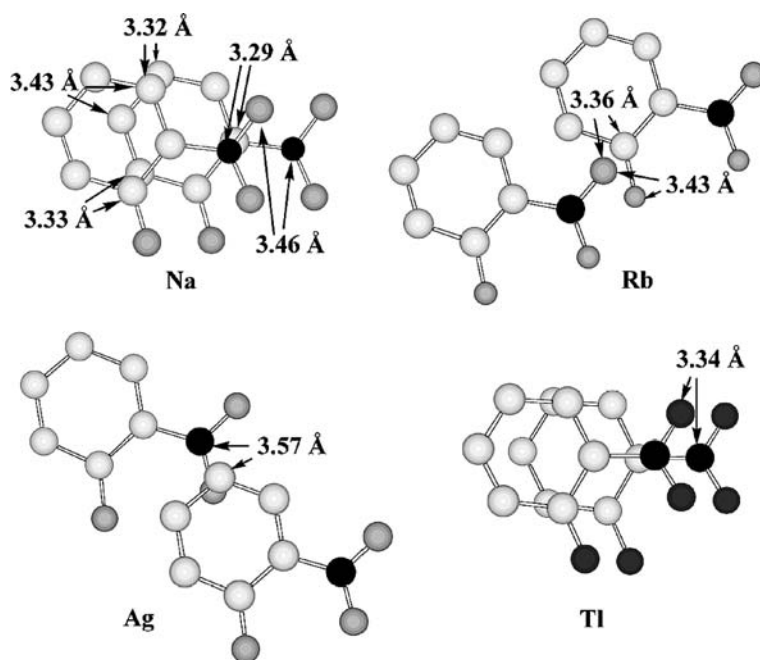


Figure 10. Projections, perpendicular to the aromatic ring plane, of adjacent 2-nitrophenoxide units within stacks in the lattices of the M(I) complexes. Only the shortest inter-atomic approaches are indicated.

systems where the metals form their primary coordination spheres with oxygen-donors only.

A different contrast of Ag(I) and Tl(I) is provided [77(b)] in their 4-nitrophenoxide ($4NP^-$) complexes, where again Tl is *O*-coordinated and Ag is involved in an η^2 interaction with the aromatic ring along with *O*-coordination. In the case of 4-nitrophenol, two polymorphs are known [85] in which quite different stacking patterns occur, and the Ag(4NP) and Tl(4NP) complexes display essentially these two modes (Figure 11). The head-to-head, tail-to-tail mode in the Ag complex is associated with relatively short C \cdots O (phenoxide) and C \cdots O (nitro) contacts of 3.30 and 3.20 Å, respectively, though with the shortest contact (3.16 Å) being N(nitro) \cdots O(nitro) and no C \cdots C contacts apparent. The head-to-tail mode found in the Tl complex involves C \cdots C contacts of 3.40 and 3.46 Å along with N \cdots C of 3.47 Å and a short nitro-*O* \cdots phenoxide-*O* contact of 3.30 Å. (Note that given the occurrence of attractive interactions between bound halogen and nitro groups [8], it would seem reasonable to expect that such O \cdots O contacts might also be attractive.)

The structures of complexes of higher nitrophenoxides display similar characteristics to those discussed above, the Pb(II) complex of 2,4-dinitrophenoxide, for example, [77(d)] being another instance of parallel arrays of the aromatic being associated with different adjacent-ring projections and in particular projections where contacts appear to involve primarily the ring substituents rather than the ring atoms themselves, one of the reasons for this perhaps being that a group such as $-\text{NO}_2$ can rotate out of the aromatic plane to facilitate contact, so that in this Pb complex a C \cdots O

(nitro) contact as short as 3.02 Å is found. In the widely investigated complexes of 2,4,6-trinitrophenoxide (picrate) [7(b), (Harrowfield *et al.*, submitted for publication), 78, 81–84], stacked arrays of at least some of the aromatic units are invariably observed, and in the case of the Ag(I) complex (incorporated in the publication concerning mono-nitrophenoxides [77(b)]), the metal is not involved in direct interaction with the ring and the complex is isomorphous with that of sodium. Here, the stacking projection involves significant overlap of the rings, though only producing C \cdots C contacts of 3.45, 3.46, 3.46 and 3.49 Å, along with N \cdots C of 3.45, 3.49 Å,

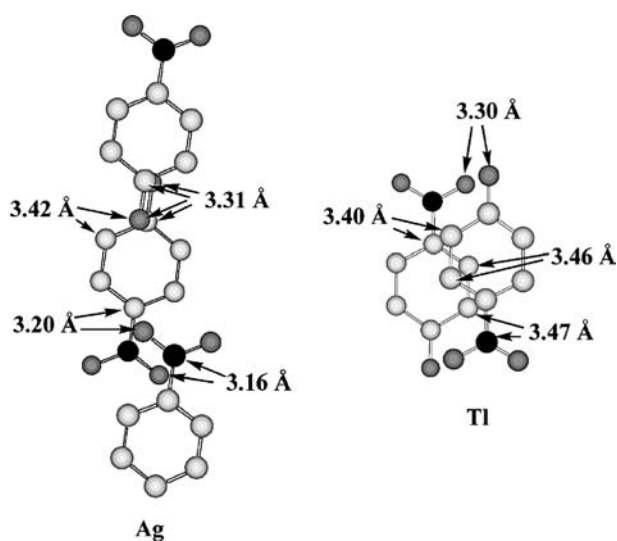


Figure 11. Projections and close approaches within 4-nitrophenoxide arrays of the Ag(I) and Tl(I) complexes.

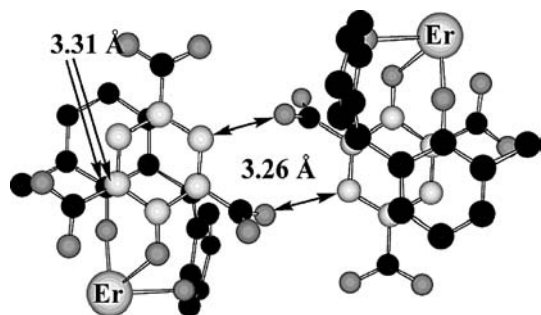


Figure 12. Partial view of adjacent coordinated picrate entities within the lattice of the Er(III) complex of a functionalised calix[4]arene dianion [83]. Carbon atoms of the calixarene are shown in black.

$N \cdots O$ of 3.32 Å and $O \cdots O$ of 3.10, 3.39 Å. The nitro groups are not significantly tilted from the aromatic planes but in another complex of 1:1 M:picrate stoichiometry (though of a rather complicated structure), tilting of one nitro group appears to result in what might be termed ‘edge-to-edge’ interaction of picrate units. Thus, in the Er(III) complex of a doubly-deprotonated calix[4]arene derivative [83], coordinated picrate lies nearly parallel to one phenyl ring of the calixarene and projection indicates significant overlap of the aromatic rings, though only one $C \cdots C$ is short (3.31 Å) (Figure 12). The uncoordinated 6-nitro group is tilted at an unusually large angle (72°) to the aromatic plane, resulting in one of its oxygen atoms coming within 3.26 Å of carbon-5 of a picrate of an adjacent complex moiety (which reciprocates the interaction). In fact, a very similar situation arises in the complex of Cu(II) picrate with 15-crown-5 [82], where one array of parallel picrate units shows in projection overlap of only two nitro groups ($N \cdots O$ 3.30 Å) but is in contact ($O \cdots C$ 3.09 Å) with an oxygen of a strongly tilted (55°) nitro group from a picrate in a separate array. Even more complicated forms of picrate interactions are found in various solvates of the lanthanide picrates, which are known in forms which vary from those with no picrates restrained within the metal’s primary coordination sphere to those where all three picrates are chelated. In the case of $[\text{Ho}(\text{cis-DTSO}_2)_4(\text{OH}_2)_2](\text{pic})_3$ (*cis-DTSO*₂ = *cis*-1,3-dithiane-1,3-dioxide) [81(c)], although the uncoordinated picrate ions are involved in H bonding to coordinated water, it is clear also that they form parallel arrays. Contacts both within and between these arrays are numerous and complicated, a degree of disorder involving the nitro substituents making detailed estimation of approaches difficult but three different modes of parallel unit overlap are shown in Figure 13. In all of these, many contacts fall in the range 3.5–3.6 Å but shorter contacts are quite sparse, the shortest $C \cdots C$ being 3.38 Å, $N \cdots C$ being 3.41 Å, $O \cdots C$ being 3.36 Å and $N \cdots O$ 2.97 Å (associated with $O \cdots O$ 3.01 Å). Chelation of all three picrates to the one metal, as in $[\text{Nd}(\text{hmpa})_3(\text{pic})_3]$ [81(h)], prevents these three picrate entities from adopting parallel orientations but does not

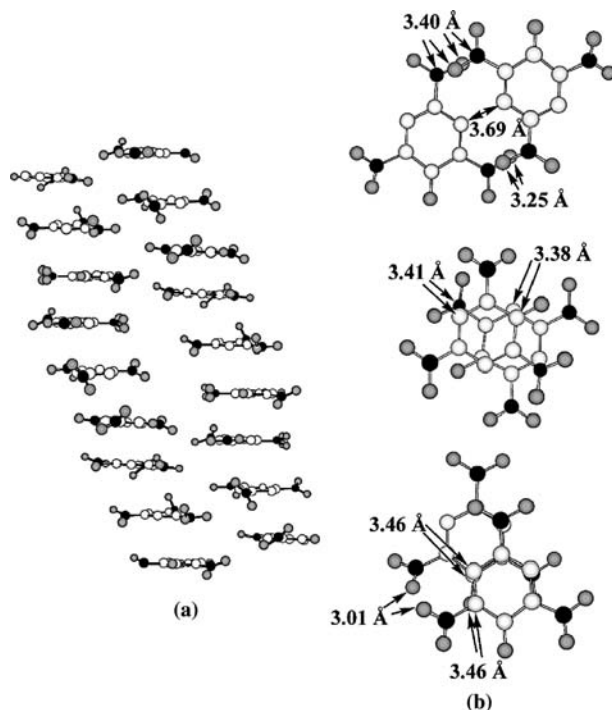


Figure 13. $[\text{Ho}(\text{cis-DTSO}_2)_4(\text{OH}_2)_2](\text{pic})_3$: (a) a view of the picrates moieties in the lattice, showing the parallel orientations of the ring planes; (b) three different modes of ring overlap observed within these stacks.

preclude stacking between picrates from separate complex units. Also apparent are ‘non-stacking’ approaches between picrates, both intra- and inter-molecular, the latter being exemplified in what might be termed an ‘edge-to-edge’ ($\text{CH} \cdots \text{O}$) interaction causing two picrate units to be essentially coplanar, as shown in Figure 14.

Although it appears that for various nitrophenoxides it is the interactions involving the substituent atoms that are prominent in inducing nitrophenoxide–nitrophenoxide association and that ring stacking may therefore be more a consequence of the optimisation of these interactions than the result of (carbon) π – π attractions, stacking is nonetheless a remarkably persistent motif within a very large number of solid state structures. Since even one particular nitrophenoxide may show

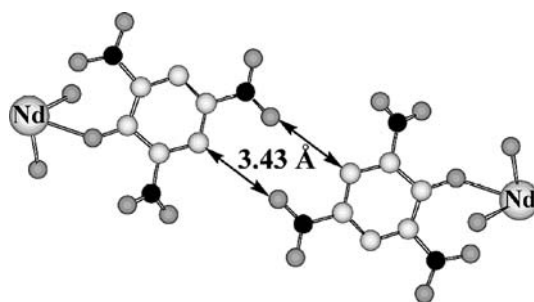


Figure 14. Partial view of the lattice of $[\text{Nd}(\text{hmpa})_3(\text{pic})_3]$ [83(h)], showing ‘edge-to-edge’ ($\text{CH} \cdots \text{O}$) contact of two coplanar picrate ligands bound to separate Nd complex units.

various forms of stacking overlap, the contribution of this effect to the lattice energy must vary but approximate upper limits may be estimated. If, in the case of 2-nitrophenoxide, it is assumed that the remoteness of aromatic–aromatic approaches in the Ag(I) complex is a consequence of the binding of the metal to the ring carbons, then the Ag(I)/C₂ binding energy must exceed that of stacking. In the gas phase, the bond enthalpy for the Ag⁺/ethene complex is 140 kJ mol⁻¹ [86] but it is known that this interaction enthalpy diminishes significantly with the binding of co-ligands [87], so that a figure of half this value might be taken as appropriate for the 2-nitrophenoxide complex. Since a given aromatic unit has others to both sides in a stack, then this number could be halved again to obtain a ‘stack-pair interaction enthalpy’ of ~35 kJ mol⁻¹, a plausible figure if stacking effects are to be regarded as some of the stronger intermolecular forces (and one that happens to agree with the crude estimate made for picrate systems).

Hydrogen bonding and ligand conformations

Hydrogen bonding is far too diverse and important a topic to be adequately considered in a brief review but some specific cases occurring in metal complex systems are worthy of present consideration in order to provide some indication of the importance of H bonding as a factor relative to other labile interactions. In many systems, such as some of those [81] just discussed, H bonding is as prominent a motif in the crystal lattices as is stacking. In the case of [Fe(OH₂)₆](pic)₂ [84], for example, both the phenoxide- and nitro-group-*O* atoms are involved in approaches (2.1–2.2 Å) to the aqua-ligand hydrogen atoms consistent with strong H bonds and, significantly, the picrate stacks are not only ‘slipped’ but the mean aromatic planes of consecutive units in a stack are at approximately 36° to one another. In this, the Fe(II) compound differs from its otherwise closely similar Mg(II) analogue [88] and if the greater acidity of [Fe(OH₂)₆]²⁺ compared to that of [Mg(OH₂)₆]²⁺ [89] is interpreted as meaning that its aqua-ligands would act as stronger H-bond donors, then the subtle differences between the two may be taken as an indication that H bonding and stacking are interactions of comparable energy for picrates at least.

Implicit in arguments such as that just advanced is the notion that the formal charge on a cation is delocalised over the entirety of any complex it may form and thus that the strength of an interaction such as H bonding may depend on this formal charge [90]. Because X···H distances provided by X-ray structure determinations are frequently rather imprecise and because H bonding arrays are usually rather complicated, it is difficult to provide clear evidence that effects of this factor are dramatic but it is certainly easy to find examples where different patterns of H bonding are associated with significant differences in the coordina-

tion sphere of a metal. In the case of Co(III) complexes of derivatives of 3,6,10,13,16,19-hexa-azabicyclo[6.6.6]jucosane, ‘sarcophagine’ (sar), two extreme conformations, designated as *le*₃ or *ob*₃ depending upon whether the C–C bonds of the ethylene bridges are parallel or oblique, respectively, to the C₃ axis of the complex have been well characterised [91]. The *le*₃ conformation is invariably associated with approaches to the coordinated NH units, interpreted as H bonding, in which a single acceptor binds to 2NH entities situated at the extremes of an octahedral edge not spanned by a chelate arm, whereas the *ob*₃ conformation is associated with approaches by a separate acceptor to each NH unit. In the complex [Co((NO₂)₂sar)Cl₃·2H₂O [91(b)], a situation found in many complexes including those of the simple bidentate ligand ‘en’ (ethane-1,2-diamine) arises in which every chloride is ‘H-bond chelated’ by two NH units, and here one of these chlorides is also chelated by two NH units from an adjacent complex cation (of the opposite chirality) (Figure 15(a)). Though this particular form is rare, four-coordination of chloride in these systems is usual and consistent with regarding the cation–anion interactions as occurring through specific (adjacent atom) bonding pathways rather than through a non-directional ‘electrostatic’ interaction. A sarcophagine complex which has been characterised in both *le*₃ and *ob*₃ forms is [Co((HO₂CCH₂NH₂)₂sar)]⁵⁺ [91(d)], which, as the pentachloride is *ob*₃ and, as the

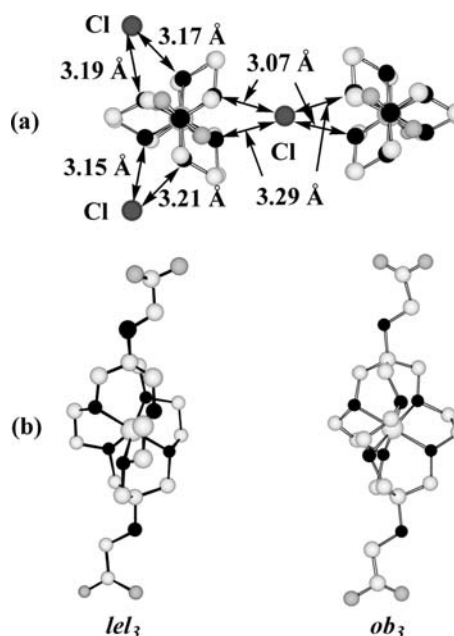


Figure 15. Sarcophagine complexes: (a) a view, down the threefold molecular symmetry axes, of an adjacent pair of *le*₃ cations of opposite chirality found in the lattice of [Co((NO₂)₂sar)Cl₃·2H₂O]. The nearest-neighbour chloride ions for one cation are shown, one chloride being in equivalent interaction with the other cation; (b) the *le*₃ and *ob*₃ cations found in [Co((HO₂CCH₂NH₂)₂sar)]Cl(SO₄)₂ and [Co((HO₂CCH₂NH₂)₂sar)]Cl₅.

chloridebis(sulphate) is lel_3 (Figure 15(b)). In the former, there is no chelation of Cl and in the latter, it is sulphate-*O* which is chelated, showing that the situation in $[\text{Co}(\text{NO}_2)_2\text{sar}]\text{Cl}_3 \cdot 2\text{H}_2\text{O}$ is not some peculiarity due to chloride. As there is no evidence in this a various other cases for the association of unusual $\text{X} \cdots \text{H}$ distances with the different conformers and since the total numbers of H bonds to the cation is constant, it would appear that the energy difference between the two arrays must be a relatively small fraction of the total H-bond energy or, in other words, that the lel_3/ob_3 difference, estimated from molecular mechanics calculations as $\sim 4 \text{ kJ mol}^{-1}$ [92] must be small relative to the H bonding energy. If, as argued above, H bonding and stacking energies may be comparable and stacking energies may be $\sim 30\text{--}40 \text{ kJ mol}^{-1}$, a consistent, if rather imprecise picture arises. Note that hydrogen bonds from an NH centre may be expected to have an enthalpy of at least 20 kJ mol^{-1} [19].

Cavity inclusion and catalysis

The idea of using ligand superstructure as a cavity wherein reactions influenced or induced by the bound metal may be conducted has been extensively explored both from the point of view of imitating and understanding various biological processes (e.g. oxygen transport, enzyme catalysis) and from the point of view of synthesising more efficient and more selective catalysts [6, 26, 27, 28, 93, 94]. Particular interest has been focussed on calixarenes [27, 94, 95, 96] and cyclodextrins [26(a), 97, 98] as readily available, cavity-forming molecules which may be used to provide such ligand 'superstructure'. The requirements for success in this domain, however, are so stringent that few examples of successful catalyst design can yet be cited. (Active metallocatalysts based on calix[4]arenes are known [99] but these do not appear to involve reactions within the

ligand cavity.) Part of the reason for this is a need for a better understanding of the factors that lead to selectivity in cavity inclusion of coordinated ligands. In calix[4]arene systems, simple examples where a coordinated metal draws a single ligand into the cavity have long been known [100], as have cases where a ligand on a metal not bound to the calixarene is encapsulated by the calixarene [101], but instances where a metal is bound to the calixarene and also to at least two other, different ligands, either one of which may be inserted into the cavity, remain rare [94, 96]. With the objective being catalysis, it is, of course, essential that whatever interactions may give rise to inclusion be labile.

Phosphine ligands are important in numerous metallocatalyst systems and phosphine derivatives of both calixarenes and cyclodextrins readily form complexes with metals such as Ru, Rh, Pd and Pt which are catalytically active [97, 98]. Diphosphination of the macrocycles provides a chelating unit to strongly bind the metal, upon which two or more other coordination sites are available for binding substrates to be reacted. Ligands held at these other sites may enter the cavity formed by the macrocycle and variation in their nature can provide a system for the exploration of cavity inclusion selectivity towards coordinated ligands. In the case of the calix[4]arene diphosphine derivative L_I (Figure 16), its complexes of the form $[\text{Pd}(\text{CH}_3)(\text{py})L_I]^+$, $[\text{PtH}(\text{PPh}_3)L_I]^+$ and $[\text{RuCl}_2(\text{CO})_2L_I]$ have been shown by spectroscopic measurements to involve preferential inclusion of the CH_3 , H and CO ligands, respectively, and a structure determination on the Ru complex has confirmed its inclusion of CO [97]. While it is appealing, recognising the relatively small size of the calix[4]arene cavity, to rationalise these results simply as reflecting a size preference (an argument supported by some results for a metalocalix[6]arene system [102]), the fact that NO^+ , isoelectronic with CO, is held with remarkable strength within calix[4]arenes [103] and induces a similar conformation (for the *cone*

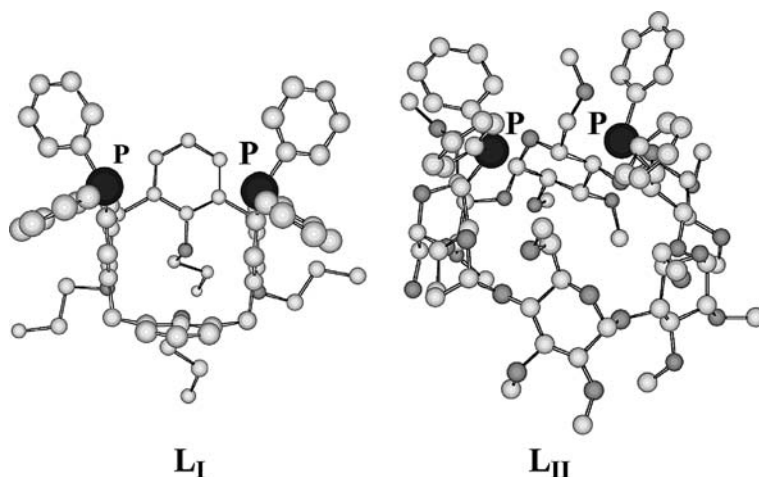


Figure 16. Bis(diphenylphosphino) derivatives of macrocycles: L_I is derived from the tetrapropyl ether of calix[4]arene and L_{II} from permethylated α -cyclodextrin.

form) to that seen in $[\text{RuCl}_2(\text{CO})_2\text{L}_{\text{II}}]$ [97], suggests that other factors may be operative. While coordinated CO does not have the orientational freedom of NO^+ , so that it is necessarily the oxygen atom which penetrates furthest into the cavity, like NO^+ , it does position itself remarkably closely to two distal aromatic rings of the calixarene. The carbonyl-C is 2.81 Å from each of the calixarene aromatic carbons to which P is bound (and 3.08 Å from the two neighbouring ring carbon atoms), while the carbonyl-O is 2.98 Å from the same carbon atoms, as well as having contacts between 3.03 and 3.27 Å with all five other atoms of the rings to which these carbons belong and contacts of 3.30 Å with the carbons bearing phenolic-O of the other two rings and of 3.23 Å with their phenolic oxygen atoms. (Note that the N of included NO^+ comes to within 2.45 Å of one phenolic ether oxygen and 2.78 Å of another.) These are all considerably shorter separations than found in a variety of simple inclusion complexes of calixarenes [104], so that even were it to be argued that inclusion in the metal complex system is enforced by the metal and that the approaches may signify enhanced repulsions rather than attractions, significant modification of the properties of the included ligand might be anticipated. ‘Charge-transfer’ interactions with aromatics (such as that involved in NO^+ inclusion), for example, are known to be dramatically enhanced as separations between the interacting centres fall below ~ 3.5 Å [105]. Any modification of ligand properties resulting from inclusion is, of course, of potential interest in regard to catalysis and, in this regard, it is interesting that the C—O bond length for included CO (1.02(2) Å) is, if anything, actually shorter than that for the non-included

CO (1.08(2) Å). Also worthy of note is the fact that the phenyl groups bound to P, along with the ‘flattened’ phenyl rings of the calixarene, define cavities, each formed by three phenyl groups, which surround the coordinated chlorine atoms. The closest $\text{Cl}\cdots\text{C}$ approaches (involving C2 of the P-phenyl groups) are 3.40 and 3.45 Å, comparable to those seen in a variety of systems where ‘halogen bonding’ [19] has been proposed. Thus, it is certainly possible that to analyse cavity preferences of coordinated ligands in terms of cavity interactions alone may be misleading unless all forms of labile interactions occurring can be catalogued, an objective which can be difficult to realise.

Cyclodextrins provide molecular cavities of quite different chemical character to those of calixarenes and α -cyclodextrin in particular provides a larger cavity than a cone calix[4]arene, so that it is unsurprising to find that complexes of the ligand L_{II} (Figure 16) show different cavity selectivity to those just discussed [98]. Here, there is substantial evidence that the cyclodextrin cavity is ‘chlorophilic’ and the crystal structure of the simple complex $[\text{PtCl}_2\text{L}_{\text{II}}]$ (Figure 17) provides evidence of the nature of the cavity interactions with coordinated chlorine. Given the highly oxygenated nature of the cyclodextrin framework, it is significant that there is no evidence for ‘halogen bonding’ involving these oxygen atoms, the shortest $\text{Cl}\cdots\text{O}$ approaches (involving the ring glycosidic oxygen of two glucose residues) being >4.1 Å. Consistent with spectroscopic measurements [98], the closest approaches to Cl (~ 2.5 Å) appear to involve the hydrogen atoms at C5 on the rings to which the phosphines are attached. Thus, the interaction may be described as $\text{Cl}\cdots\text{HC}$ bonding, though given that

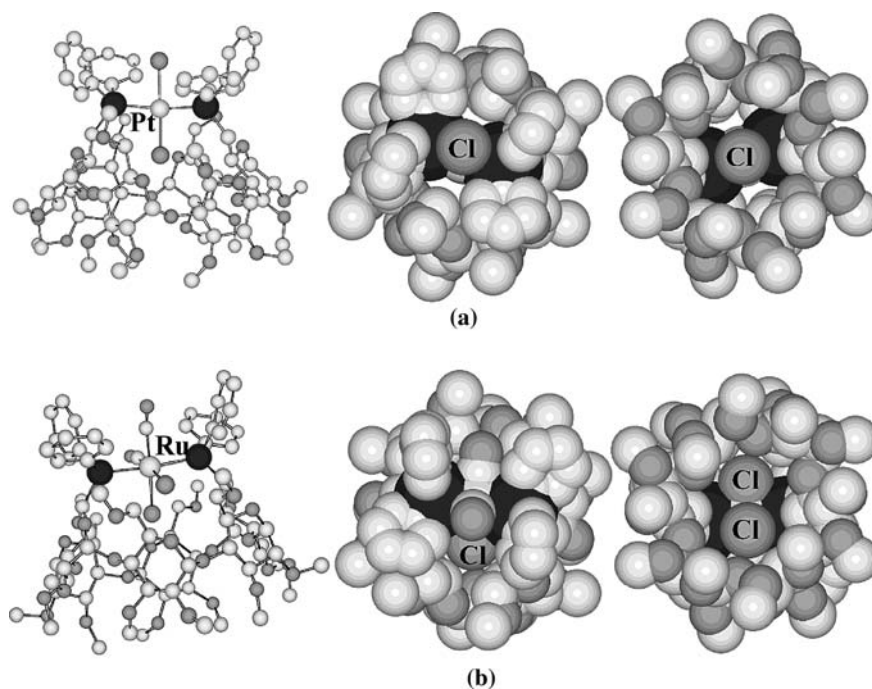


Figure 17. Metal complexes of the A,D-bis(diphenylphosphino)- α -cyclodextrin L_{II} : (a) the PtCl_2 complex, with space-filling views from ‘above’ and ‘below’ the macrocycle; (b) similar views of the major conformer present in the lattice of the $\text{RuCl}_2(\text{CO})_2$ complex.

halogen-bonding energies may sometimes considerably exceed analogous hydrogen-bonding energies [19], it may be that Cl...O interactions are not observable because of the conformational rigidity of the cyclodextrin ring. Certainly, simple rotation about the C5–C6 bond does not bring the pendent CH₃O groups within closer than 4.8 Å of the included Cl. Again, it should also be noted that the four phenyl substituents at the two phosphorus atoms define a shallow upper cavity on the functionalised cyclodextrin and give rise to Cl...C contacts of 3.40 and 3.44 Å (two of each), and it is difficult to say what influence this might have upon the specific positioning of the included chlorine atom. A similar analysis may be made concerning the complex [RuCl₂(CO)₂L₁₁] [98], although assessment of this structure is complicated by its disorder. Nonetheless, again it is clear that orientation of the chloro groups into the cavity is preferred to that of the CO and that this can be associated with contacts to C5 hydrogen atoms (~2.8 Å). Both the carbonyl-C and -O atoms have close contacts to aromatic carbon, as short as 2.91 Å for C and 3.34 Å for O, indicating interactions which may assist in keeping these atoms out of the cyclodextrin cavity.

Conclusions

The discussion above provides a complement to rather more comprehensive reviews (e.g. [23]) focussed on labile interactions in systems including those where any metal ions present are not considered to have a significant influence. There is no reason to expect that labile and weak interactions in metal complex systems should differ in any way other than quantitatively from those in other systems, though as is exemplified in the case of 'agostic interactions' [106] metals may provide a special form for a given interaction, in this case the ability of hydrogen to link at least two centres. As has been noted by others beforehand [4, 7(a), 8, 9], the analysis of crystal structures for evidence of weak interactions is an arduous task and it is extremely difficult to be sure that all inter-atomic approaches of possible significance have been identified. This is particularly true where hydrogen is involved, since hydrogen atom positions are often not established with certainty. The real problem which remains, however, is the assignment of quantitative measures to the energy of all the interactions which may be separately identified on some logical basis and the present discussion, unfortunately, does little more than indicate where the difficulties arise.

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