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Labile Interactions and Inert Entities in Supramolecular Chemistry—the Identification of Recognition Mechanisms for Macrobicyclic Amine Complexes

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Labile Interactions and Inert Entities in Supramolecular Chemistry—the Identification of Recognition Mechanisms for Macrobicyclic Amine Complexes

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Consideration of crystallographic data concerning metal complexes of hexa-azabicyclo[6.6.6]icosane, "sarcophagine", and various derivatives provides evidence for the importance of hydrogen-bonding, labile metal ion coordination, aliphatic- and aromatic-group interactions in determining the lattice structures. These "cage amine" complexes not only involve different metal ions, almost all rendered kinetically inert towards substitution by their complexation, but they can be obtained in conformationally locked forms and with a wide variety of substituents, so that they have considerable potential as supramolecular tectons.

Keywords: Macrobicyclic amine complexes; Chirality; Conformations; Labile interactions; Supramolecular synthesis

INTRODUCTION

A possible operational definition of supramolecular synthesis is as the use of labile centres to link kinetically inert functional entities ("tectons") into complex structures with multifunctional characteristics. These characteristics may derive from both the labile and inert components, hydrogen-bonding, such as between the base pairs of DNA, being an example of where the labile centre (formally, H^+) is actually part of a larger, kinetically inert unit (carbon–carbon bonds, of course, being typified by their kinetic inertness). The characteristics of the components in simpler environments are usually significantly modified as a result of the labile interaction. Bountiful exemplification of this fact is found in the binding of polyatomic organic ligands to labile transition metal ions, where, to choose but two instances, redox properties associated with the central metal ion of a complex may vary enormously with the nature of the bound ligand or reactions of the bound ligand may differ completely from those of the "free" (usually solvated) form [1]. While there is some debate [2] as to whether such conventional "coordination chemistry" should be termed supramolecular, its use in synthesis can certainly be encompassed in the definition above. More importantly, one of the useful features of all metal ion chemistry is that the appropriate choice of ligand, typically a macro-, mono- or -bi-cycle, can be used to convert a labile to an inert centre (or, more subtly, to a centre with some inert and some labile sites) [3]. Thus, metal ions may have an extraordinary diversity of roles in the creation of supramolecular systems [4], and so provide supramolecular chemistry with much of its fascination.

To develop the supramolecular chemistry of an inert species containing a metal ion, it is necessary to understand the labile interactions in which it may become involved. This may be a complicated and difficult task, especially in a quantitative sense, since most such species are capable of several modes of labile (and usually weak) interaction. Particularly valuable in defining the stereochemistry and possibly an energetic ranking of such interactions is structural information obtained by X-ray crystallography and, since considerable information of this type is available for complexes of the cage hexamine "sarcophagine" (3,6,10,13,16,19-hexa-azabicyclo[6.6.6]icosane; Fig. 1) and numerous of its simple derivatives [5–50], the present report is concerned with its analysis in order to establish the potential of such species as supramolecular tectons. Sarcophagine ligands constitute but one group of "cage" ligands [3,4] and some closely related species with larger or more complicated cavities or

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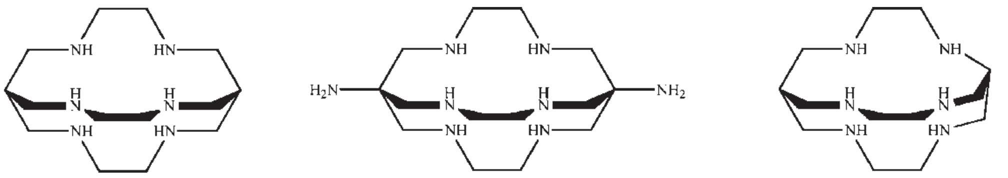

3,6,10,13,16,19-hexa-azabicyclo[6.6.6]icosane
"sarcophagine" = sar

1,8-diamino-3,6,10,13,16,19-hexa-azabicyclo[6.6.6]icosane
"diaminosarcophagine" $(NH_2)_2$sar

2,5,9,12,15,18-hexa-azabicyclo[5.6.6]nonadecane
"ablated sarcophagine" = absar

FIGURE 1 Parent structures and their designations for the ligands presently discussed.

unsaturated centres within the cage framework are known but so far have provided much more limited structural data [51–55]. An important property of sarcophagines is that they are ligands capable of complexing (and rendering inert) a variety of metal ions, the resulting chiral complexes having a number of potential applications at least partly dependent upon the possibility of their incorporation into more sophisticated structures.

BASIC PROPERTIES OF SARCOPHAGINE COMPLEXES

Although not the first such ligand to be prepared, "sarcophagine" = sar (Fig. 1), may be considered as the "parent" member of the group [9,56]. In common with those of numerous derivatives, its complexes are typically substitutionally inert [56]. This does not mean that they are conformationally rigid, since the free ligand is flexible [32,56], explaining the rapidity of its formation of complexes, and some of this flexibility is retained after complexation [39]. The template synthesis which provides sarcophagine and its derivatives is most effectively applied using Co(III) [9,46,56] and thus description of the basic characteristics of Co(III) cage species is a convenient point at which to commence analysis.

A precursor to many Co(III) cage complexes is $[Co(en)_3]^{3+}$ (en = ethane-1,2-diamine), also a configurationally and substitutionally inert but conformationally labile species. The room-temperature ^{1}H NMR spectrum of this diamagnetic complex shows a single peak for the methylene proton resonances, indicating a rapid interconversion between conformers [57]. Thus, this chiral complex is considered to exist as stable, substitutionally inert enantiomers, designated Δ and Λ in accord with IUPAC rules for helicity definition [58], with each of these enantiomers existing in four diastereomeric forms depending upon the chirality, designated *δ* or *λ*, of the conformation adopted by each of the three chelate rings. (Though any five membered, saturated chelate ring such as formed by ethane-1,2-diamine can in principle adopt an achiral, "envelope" conformation, calculations suggest [59] that this should not be an energy minimum and there is no evidence of its adoption in any system where the ring is not part of a more complicated ligand. Even in such cases, the conformation may be considered that of an envelope twisted to avoid true eclipsing of the methylene hydrogen atoms [43].) Thus, on a short time scale, $[Co(en)_3]^{3+}$ may be considered to exist (Fig. 2) in eight diastereomeric/enantiomeric forms: Δ(δδδ), Δ(δδλ), Δ(δλλ), Δ(λλλ), Λ(δδδ), Λ(δδλ), Λ(δλλ) and Λ(δδδ). (In early recognition of this [60], a different nomenclature was used.) These isomers are also commonly described by considering the orientations of the central C-C bond of the en chelate rings relative to the effective C_3 axis of the complex (passing through Co and the centroids of the faces which do not have edges spanned by the chelate rings). If the bond is essentially parallel to this axis, the conformation is designated "*lel*", while, if the bond is essentially oblique to this axis, the conformation is "*ob*" [61]. The relationship between the two terminologies is such that Δ(δδδ) ≡ Δ-*ob*$_3$, Δ(δδλ) ≡ Δ-*ob*$_2$*lel*, etc., it being common to leave designation of the configurational chirality implicit and thus to say that the complex exists as four conformers *ob*$_3$, *ob*$_2$*lel*, *lel*$_2$*ob* and *lel*$_3$. Although differences in energy between the isomers are small and entropic factors must significantly influence the isomer distribution [59], introduction of a *lel* ring is always favourable. A significant feature of the *lel*$_3$ conformation (Fig. 2) is that it poses three NH bonds (from separate chelate units) nearly perpendicular to a trigonal face and ideally poised for H-bonding to a tritopic H-bond acceptor such as phosphate anion. Recognition of this possibility provided an explanation of the effect of $[PO_4]^{3-}$ on the circular dichroism spectrum of resolved $[Co(en)_3]^{3+}$[62], and subsequent structural studies confirmed this form of interaction [63]. Interestingly, if the three NH...O interactions are replaced by three N-CH_2 bonds, with the methylene units connected to a central (bridgehead) atom, the dimensional match is again good and it is precisely a "cap" of this form which is generated in the template reactions of $[Co(en)_3]^{3+}$ which lead to the formation of sarcophagine ligands, though in fact this cap is not incompatible with the *ob* configuration. Thus, the nomenclature used to describe the stereochemistry

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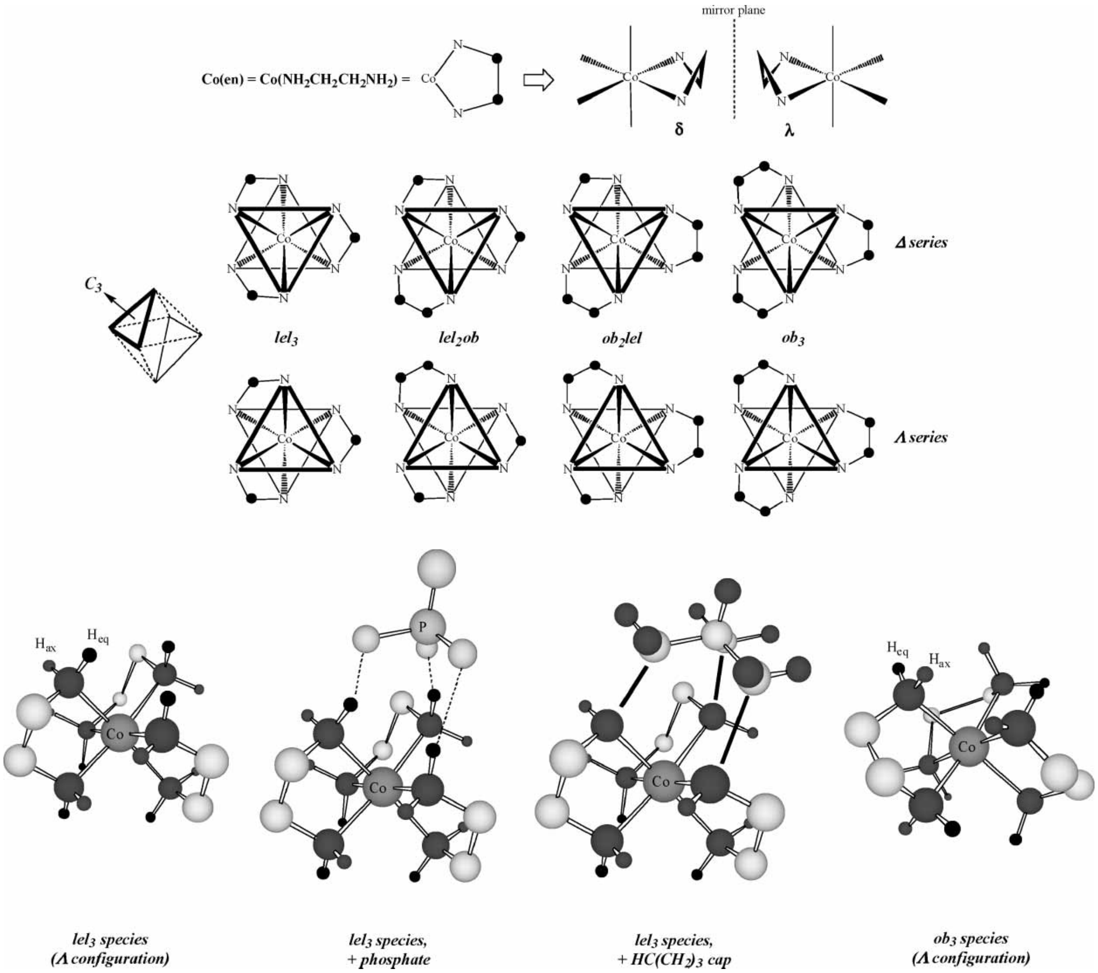

FIGURE 2 Aspects of the stereochemistry of $[Co(en)_3]3^+$ and related cage complexes. In the lower set of figures, it is the equational NH protons of the *lel*$_3$ species which are aligned approximately normal to one octahedral face.

of $[Co(en)_3]^{3+}$ is usefully transferred to sarcophagine complexes [64]. A complication does arise in that the cap may be chiral (and there are other subtleties [59,64]), though this can be designated by use of the conventional IUPAC rules as applied to the projections of the N-C bonds upon one another [58]. (In all known cases, deviations of the cap conformation from its achiral form are very slight.) A further complication is that the capping reaction converts all coordinated N-donors to asymmetric centres, potentially a source of considerable isomeric complexity, though it turns out that the syntheses in this sense are completely stereospecific, with all N-centres of a given cation being of the same configuration and the configurational chirality at Co and N being associated in such a way that Δ-Co is always paired with *R*-N and Λ with *S* [56].

Thus, to fully designate a form of $[Co(sar)]^{3+}$ of, say, true D_3 symmetry, its formula could be written $\Delta(\lambda\lambda\lambda)(R,R,R,R,R,R)(\delta_{cap})_2\text{-}[Co(sar)]^{3+}$. This is cumbersome and, given the facts that there is no diastereoisomerism associated with the N-centres, that the differences between enantiomeric forms of the caps usually correspond to very minor structural changes and that very few instances [24,49,50,55] of mixed conformers (δδλ or δλλ) are known (in the solid state), it is convenient to discuss cage complexes as supramolecular tectons by considering just their *lel*$_3$ and *ob*$_3$ forms.

LABILE INTERACTIONS INVOLVING SARCOPHAGINE COMPLEXES

Hydrogen Bonding

Early structural studies [11] showed that the six secondary-*N* donor atoms of a sarcophagine cage could provide an environment for a metal varying from near-octahedral to near-trigonal-prismatic, depending upon the metal ion. In the case of near-octahedral Co(III) complexes, these and later studies have led to the characterisation of numerous *lel*$_3$ and *ob*$_3$ species and a simplified representation of the differences in coordinated-*N* proton orientations in these chiral cations is given in Fig. 3. The shortest H...H separations, those for NH units on "open"

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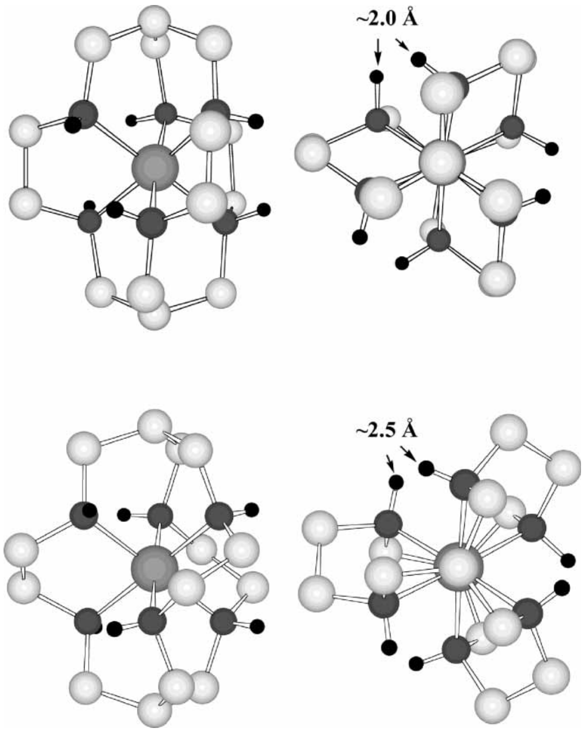

FIGURE 3 Representations, perpendicular to and along the molecular C_3 axes, of (upper) *lel*$_3$ and (lower) *ob*$_3$ forms of octahedral $[M(sar)]^{n+}$ species. NH-atoms are shown in black.

edges of the octahedron not spanned by chelate arms, differ for the two isomers by ~0.5 Å, the shorter distance (~2.0 Å) being that of the *lel*$_3$ species. Thus, it is found for an H-bond acceptor such as chloride ion, a *lel*$_3$ species may act as a chelator, the pairs of NH units just referred to binding to the one chloride, whereas an *ob*$_3$ species becomes involved in multiple "unidentate" NH interactions with independent chloride ions. Though commonly observed in this role [27,40,41], there is no evidence that there is a marked preference for chloride as the species chelated, since both sulfate- and water-*O* may also take the rôle [40] and nitrate [40,41], triflate [15] and carboxylate [40,47] provide examples of anions chelated by *lel*$_3$ species via interactions with two different oxygen atoms (Fig. 4).

Of course, in conformationally flexible systems, it might be argued that it is the choice of counteranion that determines the conformation adopted in the solid state and that a cage complex does not act as an H-bond orienting entity of unique configuration. The to-date unique instance of a Co(III) complex of a sarcophagine ligand adopting a "mixed" conformation (*ob*$_2$*lel*, associated with *ob*$_3$ in the one lattice), for example, is found when Δ-$[Co((NO_2)_2sar)]^{3+}$ is used to resolve $[Gd(dipic)_3]^{3-}$ (dipic = pyridine-2,6-dicarboxylate), hydrogen-bonding between the cation and the anion involving two separate, uncoordinated carboxylate-*O* atoms interacting with two NH [50] (Fig. 5(a)). It is, however, possible to fix the conformation of an octahedral cage species

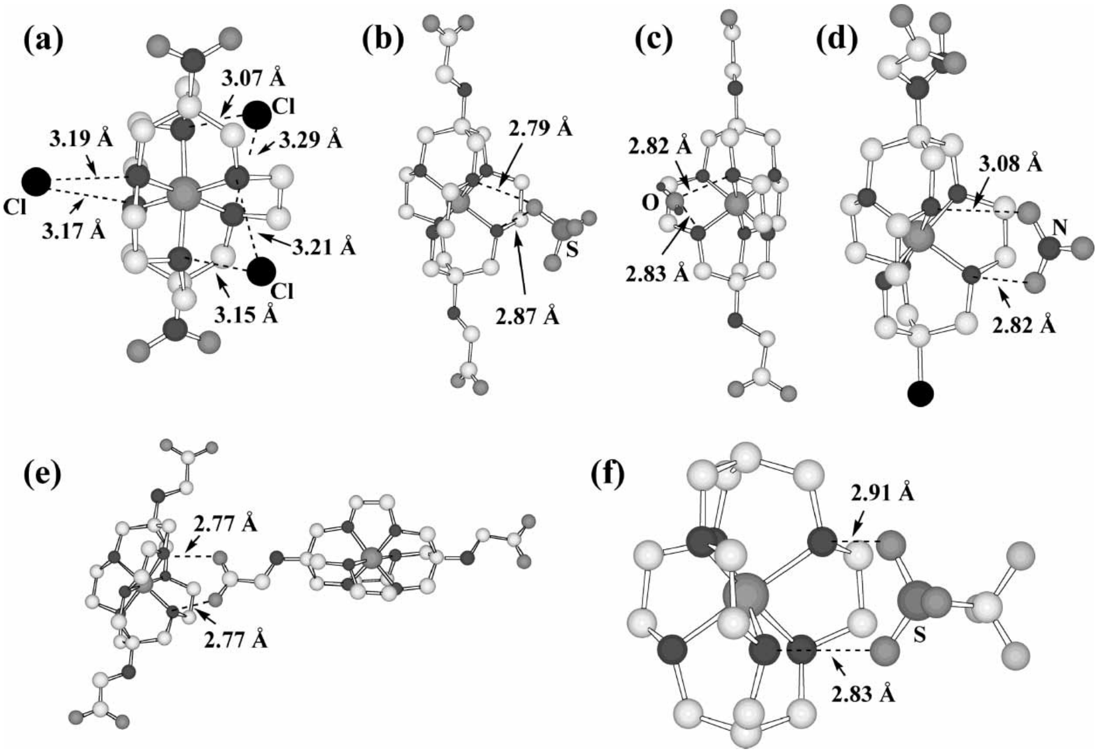

FIGURE 4 Examples of "H-bond chelation" of simple species by essentially octahedral metal-sarcophagine complexes: (a) chloride in $[Co((NO_2)_2sar\}Cl_3$ [27]; (b) sulphate in $[Co((HO_2CCH_2NH_2)_2sar](SO_4)_2Cl\bullet5H_2O$ [40]; (c) water in $[Co((HO_2CCH_2NH_2)_2sar](SO_4)_2Cl\bullet5H_2O$ [40]; (d) nitrate in $[Co(Cl)(HO_2CCH_2N(NO))sar](NO_3)_3\bullet H_2O$ [40]; (e) carboxylate in $[Co((O_2CCH_2NH)_2sar]ClO_4\bullet7.5H_2O$ [40]; (f) triflate in $[Ru(sar)](CF_3SO_3)_3$ [15].

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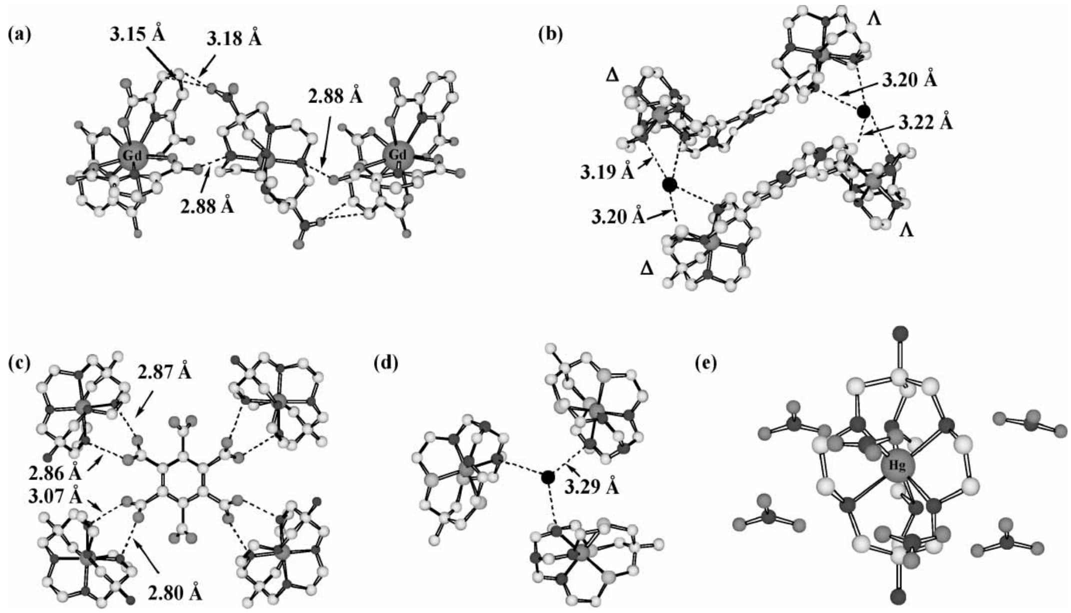

FIGURE 5 Cation-anion aggregates in various cage amine complexes: (a) Bridging of two $[Gd(dipic)3]^{3}$- (dipic = pyridine-2,6-dicarboxylate) anions by Δ-$[Co((NO_2)_2sar)]^{3+}$ [50]. (Note also short O(nitro)…C(aromatic) contacts are indicated - see text.); (b) Symmetrical chloride ion bridging of pairs of centrosymmetric dicage octapositive cations [44]. (Chirality at the cation centres is designated.); (c) The twofold-symmetric array of Δ-$[Co((CH_3)(NH_3)sar)]^{4+}$ cations about a benzene-hexacarboxylate anion [49]; (d) The threefold-symmetric array of Λ-$[Co(azacapten)]^{3+}$ cations about a chloride anion [7]; (e) The cation Δ-$[Hg((NH_3)_2sar)]^{4+}$ and its environment of six nitrate ions, each chelating one coordinated NH [11,49].

by appropriate substitution of the chelate arms. This may be done, for example, by using species such as $[Co(chxn)_3]^{3+}$[46,65] or $[Co(pn)_3]^{3+}$[66,67] (chxn = *trans*-1,2-cyclohexanediamine; pn = 1,2-propane diamine) as reactants in the template synthesis, though not all diastereomers of these complexes can be reacted successfully [65,67]. At least in the case of *R,R*-chxn, however, only two or even one such rings of fixed conformation (in this case, λ) appear sufficient to fix the conformation of the other five-membered rings in the cage complex product (at least in the solid state). Thus, starting from Δ(λ,λ)-$[Co(R,R\text{-chxn})_2en]^{3+}$ and Δ(λ)- or Λ(λ)-$[Co(R,R\text{-chxn})en_2]^{3+}$, the cage products, characterised crystallographically as their chlorides, have *lel*$_3$, *lel*$_3$ and *ob*$_3$ conformations, respectively [49]. As in Δ-*lel*$_3$-$[Co((CH_3)_2char)]Cl_2(ClO_4)$ (a cage species derived from Δ-*lel*$_3$-$[Co(R,R\text{-chxn})_3]^{3+}$) [46], the two *lel*$_3$ species involve H-bond chelation of chloride, while this does not occur in the *ob*$_3$ complex. It is not presently possible to say whether or not such interactions persist in solution or whether chelation is especially favourable in energy but an octapositive cation incorporating two heterochiral Co(III) cage units grafted onto a bipyridinium dication crystallises in the presence of chloride and perchlorate with but one chloride (and seven perchlorates) and that chloride is chelated by NH units, in such a way, in fact, that it is *bis*(chelated) by two separate complex units of the same chirality, leading to cyclic structures in the solid (Fig. 5(b)) [44]. Consistent with the persistence of at least some form of association in solution, the solution electrochemistry of the complex shows a very marked sensitivity to the concentration of chloride in the medium. Cyclic voltammograms of the homochiral analogue of this octapositive cation are markedly different in the presence of *R,R*- and *S,S*-hydrogentartrate monoanions [44], suggesting that the interactions (presumed to involve H-bonding) may be quite selective but it is possible that the unusually high charge of the complex somehow enhances this selectivity, since in the lattices of cage complexes of lower charge, H-bonding between cage NH units and carboxylate oxygen atoms of $[Sb_2(R,R\text{-tart})_2]^{2-}$ takes very similar forms in cage complexes of opposite chirality [47]. Nonetheless, it is remarkable that in the complex $\{\Delta(\lambda\lambda\lambda)\text{-}[Co\{(NH_3)(CH_3)sar\}]\}_{2}$-$Cl_2(C_6(CO_2)_6)\cdot 26H_2O$ [49], H-bonding between the resolved cation and the benzenehexacarboxylate anion is of a form such that each carboxylate unit is tilted in the same way with respect to the benzene ring, meaning the anion is fixed (in the solid state) in a chiral form (Fig. 5(c)).

Although possibly only a consequence of the relatively limited structural information available, conformational variability of cage complexes in the solid state seems much more infrequent when N donors are replaced by larger atoms such as S [7,13,18–22,30,38,45], when the cage itself is contracted by the loss of a methylene group in the cap [27,34,39,49], or when metals giving a coordination geometry closer to trigonal prismatic than is found for Co(III) (which is close to octahedral) are bound

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[6,10,11,31,32,35,49]. In any case, it is presently true to say that such systems define particular NH-bond donor arrays. The replacement of NH by S means that the number of H-bond donor centres is reduced, and the complex $[Co(azacapten)]^{3+}$ (azacapten = 1,3,10,16-tetra-aza-8-methyl-6,13,19-trithiabicyclo[6.6.6]icosane), for example, provides a species which can be regarded as a source of three divergent NH units, as in Λ-$[Co(azacapten)][ZnCl_4]Cl$ (a *lel*$_3$ species) [7], where each chloride is three-coordinated as a result of its interaction with NH units from three separate cations (Fig. 5(d)). Hydrogen bonding in cage complexes can also be restricted by N-methylation but the only structural studies known are for polymethylated species, and such a level of functionalisation produces such dramatic changes in the coordinating ability of the ligand that, for example, Co(III) complexes cannot be obtained [31,32]. The 3-carboxymethyl derivative of 1,8-diaminosarcophagine does, however, give a Co(III) complex and here the characterised solid contains *lel*$_3$ cations in which two NH units are spanned not by a single chloride but by a hydrogen-bonded water/chloride entity [40].

Complexes of "ablated sarcophagine", "absar" (absar = 2,5,9,12,15,18-hexa-aza-bicyclo[5.6.6]nonadecane) [29,34,49] and its trithia-analogue [39] have been characterised structurally for Co(III) only and all adopt a *lel*$_2$*ob* conformation. The form of the ligand is such that the bridgehead atoms are linked by two chains identical to those in sarcophagine, while the third chain is shorter by one methylene unit but it is not this shorter chain which has the ethylene link of *ob* conformation. Nonetheless, NH units from the two lel chains are able to chelate chloride or nitrate in various derivatives, while the remaining four NH units are involved in individual H-bonding interactions.

Despite the retention of six NH units and almost always of a conformation which is describable as *lel*$_3$, metal(II) sarcophagine complexes [11,35,49] are not known to act as H-bond chelating units, twisting of the ligand in these complexes towards a trigonal-prismatic form [11] causing the shortest NH...HN separation to be at least 1 Å longer than in Co(III) analogues, and they appear to be better regarded as sources of six divergent NH entities. In the isomorphous series, $[M(II)((NH_3)_2sar)](NO_3)_4\cdot H_2O$ [35,49], each NH is asymmetrically chelated by a separate nitrate ion (a situation in fact very similar to that in *ob*$_3$-$[Co((Me_3N)_2sar)](NO_3)_5\cdot 3H_2O$ [29]) (Fig. 5(e)), this necessitating that the anions bridge cation units, the space group being such that, within a given crystal, all cations are of the same absolute configuration. Interestingly, although the complexes $[M((CH_3)(NH_2)sar](ClO_4)_2$ (M = Mg, Cu, Zn) [49] also adopt the *lel*$_3$ conformation, with each coordinated-NH involved in a separate H-bonding contact (here, in a centrosymmetric crystal, though with an H-bond array that is complicated to describe because of perchlorate disorder), in the protonated analogues $[M((CH_3)(NH_3)sar)](NO_3)_3$ (M = Ni, Zn) [49], the conformation is *lel*$_2$*ob*, providing a subtle variation on a divergent, 6 NH bond donor.

The examples just discussed involve cage complexes with "external" substituents (here, amino groups) capable of protonation/deprotonation reactions which convert them between H-bond donor and H-bond acceptor systems. In the above discussion, this was ignored because of the focus on examining the "core" of the cage complex as a hydrogen-bonding entity but these additional groups are certainly involved in H-bonding which, in many cases, forms an extended system involving also the core NH groups. A special case arises when a 1:1 mixture of amino and ammonium forms can be obtained, the complexes $[Ni\{(CH_3)(NH_2)sar\}]_2H(ClO_4)_5$ and $[(Cu\{(NH_3)(NH_2)sar\}]_2H(NO_3)_7\cdot H_2O\cdot 2EtOH$ [49] providing examples of where H-bonding between these two forms serves to link cage cations into heterochiral dimeric units. Thus, they can then be regarded, in terms of their "cores", as providing divergent, 12 NH bond donors. It should also be noted that several simple external substituents other than amino groups, such as Cl, OH and NO_2 [9,27,32], are readily available and these, too, can add variety to H-bonding (and other—see Fig. 5(a)) interactions of cage species. Further, subtle effects on the relative orientations of NH bonds result from the substitution of the larger S for N in mixed donor cages [7,20–22,28,30,38,39,45].

External Binding of Labile Metal Ions

The introduction of functionality to the exterior of a cage complex appropriate for metal ion binding raises the possibility of the formation of coordination polymers, at least in the case where the donor atoms in the introduced functional groups are insufficient in number to occupy all coordination sites of the metal. The very readily prepared cage ligand $(NH_2)_2sar$, might be considered the simplest species giving complexes suitable for this purpose and the proton-bridged Cu(II) complex referred to above can be viewed as an example of a coordination dimer as well as an H-bond dimer. While no examples of true metal complexes of this type have been structurally characterised, related species derived from introduction of carboxymethylamino (glycine) substituents to the cage [42] illustrate that there are important complications to be considered in any attempt to build up multimetallic units in this way. Thus, the unresolved complex $[Co((O_2CCH_2NH)_2sar]^+$ reacts with Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) to give very insoluble 1:1 complexes which are difficult to crystallise but which have been shown by

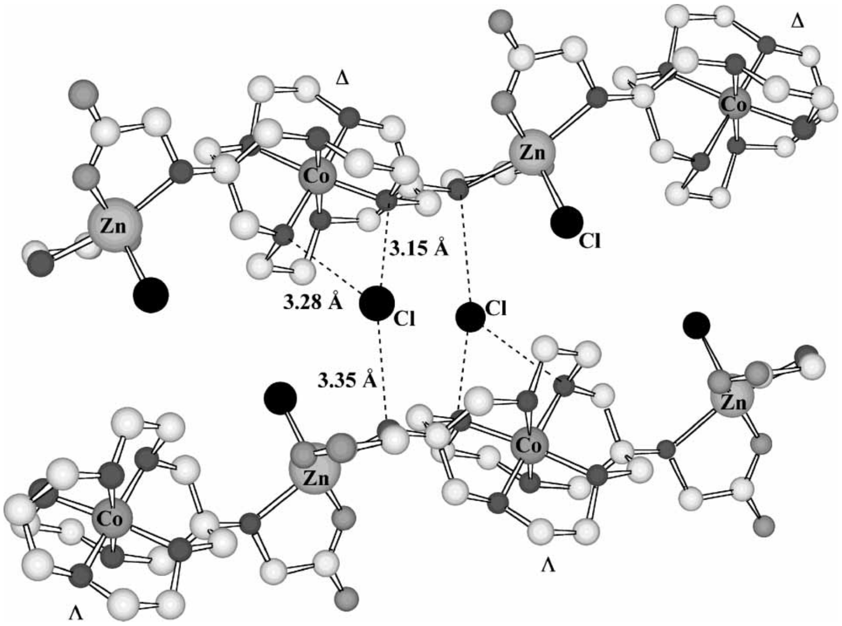

FIGURE 6 Partial view of the lattice of $[Co((O_2CCH_2NH)_2sar)ZnCl]Cl_2{\bullet}3.5H_2O$, showing segments of two adjacent polymer strands of opposite chirality and the centrosymmetric entity produced by H-bonding to two chloride ions.

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crystallographic studies for the Mn, Co and Zn derivatives [42] to be polymeric species in which the M(II) ion binds to the pendent substituents and so bridges cage units. The nature of the bridges and/or of the sequence of cage units linked by them differ in all 3 cases, however. The simplest system is that of the Co(III)·Zn(II) complex, where the Zn(II) centres are chelated by two "glycine" tails from separate cage units, with both chiral N-centres bound to Zn having the same chirality, as do the attached cages, so that individual polymer strands are chiral, though each is formally associated with one of opposite chirality in the crystalline form isolated. The strands are linked together by H-bonding networks which obviously make an important contribution to the overall lattice energy, since an attempted synthesis based on the resolved Co(III) complex as reactant provided no precipitate, even from very concentrated solutions. One of the 3 chloride ions per stoichiometric unit is coordinated to Zn, giving the Zn essentially square pyramidal 5-coordination, while the other two can be considered H-bond-chelated by one *lel*$_3$ Co(III) complex ion and H-bonded to the substituent NH units of two separate Co(III) complexes, each in a different strand, of opposite chirality to the first (Fig. 6). This is perhaps a partial explanation of the relative insolubility of the racemic material. In the Co(III)·Co(II) complex, once again the bridging metal is chelated by two glycine tails but here the two bound-N centres are of opposite chirality and any one polymer strand is racemic with respect to the cage units. In the Co(III)·Mn(II) complex, two types of bridges are found, one mono- and the other bi-nuclear but otherwise the complex resembles the Zn species in that any given strand contains cage units of one chirality, although, at least in the binuclear links, the two bound N-atoms are of opposite configuration. Use of the resolved Co(III) complex does provide readily precipitated complexes with Co(II), Ni(II) and Cu(II) but only as amorphous powders, providing further indications that there is much yet to be understood about the factors controlling the assembly of even such seemingly simple systems in the solid state.

Despite such indications, the solid state structures do show that the pendent glycine units of $[Co((O_2CCH_2NH)_2sar]^+$ are effective chelating units even in the presence of a nearby highly charged cation. Hence, there are prospects (yet to be realised) that metal ion binding in solution might be used to cause aggregation of cage units and so enable the creation, for example, of multi-electron redox systems from one-electron components. In this regard, the higher solubility of species derived from resolved cage cations may be seen as an advantage, since assembly from such species would lead to fewer isomeric possibilities for the products.

Interactions of Cage Complexes Involving Aliphatic Components

It has been noted above that H-bond chelation of chloride is apparent in the crystal structure of Δ-*lel*$_3$-$[Co((CH_3)_2char)]Cl_2(ClO_4)$ [46]. It is, however, also apparent that there is a segregation of polar and apolar components of the lattice (Fig. 7(a)) consistent with some attractive interactions (in the conventional view, dispersion forces) between the methylene chains of the cyclohexano-rings in this complex.

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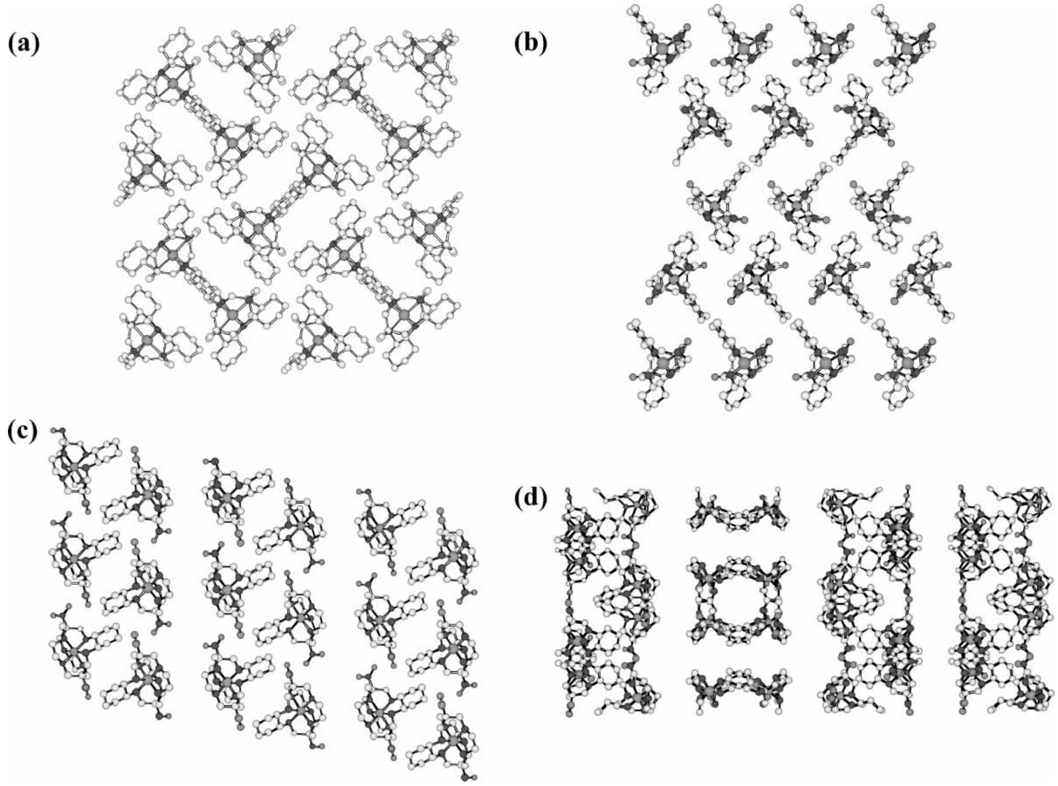

FIGURE 7 Partial views of the lattices, anions and solvent molecules deleted, of various cyclohexano-substituted cage complexes: (a) Δ-*lel*$_3$-$[Co((CH_3)_2CHAR)]Cl_2(ClO_4)$ [46], down *c*; (b) Δ-*lel*$_3$-$[Co((NO_2)_2cy_2sar)]Cl_3{\bullet}2.5H_2O$ [49] down *b*; (c) Δ-*lel*$_3$-$[Co((NO_2)_2cysar)]Cl_3{\bullet}4H_2O$ [49] down *b*; (d) Λ-*ob*$_3$-$[Co((NO_2)_2cysar)]Cl_3{\bullet}9H_2O$ [49] down *a*. Different congregations of cyclohexano units are apparent. (In the nomenclature used for (b)-(d) [49], "CHAR" = cy_3sar.)

There is no reason to assume that the various forces which may be operative within the lattice of such a complex must be in competition, so that, unfortunately, it cannot be concluded that these observations mean that H-bonding and dispersion forces here are necessarily of similar energetic significance. However, in the other cage complexes referred to above, containing one and two cyclohexano rings and for which there are different NH…Cl bonding patterns, proximity of the cyclohexano methylene groups (C…C 3.70–3.95 Å) is, in every case, also observed (Fig. 7(b–d)) [49]. This is associated with some quite spectacular channel structures within the lattices.

When the additional aliphatic functionality to the basic cage structure consists of C_4 units attached to the external amino groups (rather than bridging an NCCN unit as in the cyclohexano compounds), as in $[Co((BuNH_2)_2sar)]^{5+}$, the solid state structure (Fig. 8) again shows evidence for association of these "greasy" components, even though the complex shows no evidence of surfactant properties in solution [48]. With but a single N-butyl substituent, this time on a coordinated nitrogen atom, substituent association is not observed but this is perhaps because of alternative interactions (CH/π plus CH…O [68]) with the large aromatic counteranion present. With a single, long (C_{13}) chain attached to an external nitrogen atom and simple counteranions, the lattice [48] shows a bilayer structure expected when dispersion interaction become dominant, though they do not, in this case, exclude NH-bonding interactions of the cation. Thus, while it is not yet possible to place quantitative values upon the energies of interaction associated with H-bonding and alkyl-chain dispersive forces in cage amine complexes, both effects can clearly play an important rôle in determining solid state structures. In solution, numerous cage complexes with long-chain substituents on the cap are known to show true surfactant properties associated, in some cases, with biological activity which is presumed to be due to the insertion of the "tails" into cell membranes [69–71].

In surveying crystal structures for evidence of contacts between aliphatic entities, which commonly involve C…C distances of 3.7–4.3 Å, other "remote" contacts frequently become apparent. Thus, while the presumed H-bonding contacts to Cl discussed above involve relatively short N…Cl separations in the range 3.1–3.3 Å, in many cases they are accompanied by Cl…C separations <0.5 Å longer. There is, of course, independent evidence for CH…Cl bonding [72] and such interactions may well be responsible for the somewhat irregular geometries seen for Cl…$(NH)_n$ units in the complexes presently discussed. In principle, however, every component (electrons and nuclei) of every

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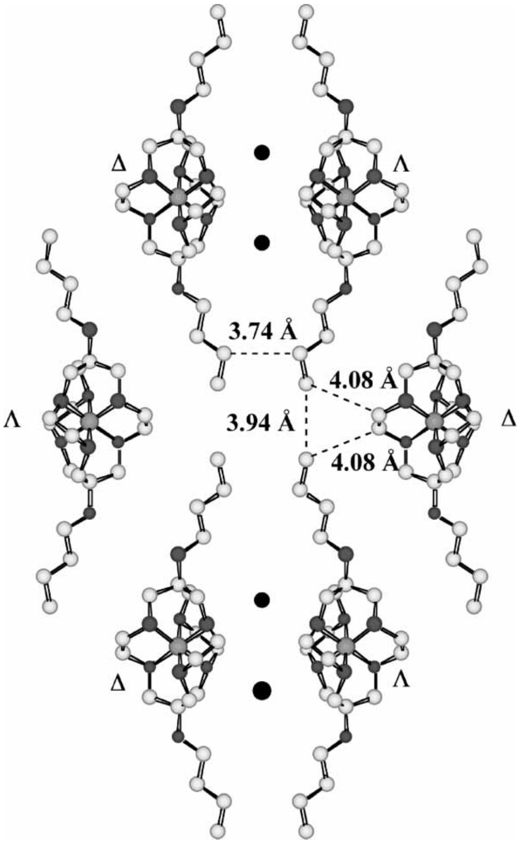

FIGURE 8 Repeat unit of the racemic (${}_{ob3}$-cation + chlorides) sheets parallel to -2,0,1 in $[\mathrm{Co}((\mathrm{C_4H_9NH_2})_2\mathrm{sar})]\mathrm{Cl_5 \bullet 6H_2O}$ [48]. Sheets above and below are displaced so that two more cage ethylene links contact the aggregate shown.

atom in a molecular or lattice aggregate interacts with every other one, so a point must come when it is futile to attempt dissection of forces on the basis of internuclear separations provided by X-ray crystallography. Unfortunately, that point is difficult to discern!

Interactions of Cage Complexes Involving Aromatic Components

Interactions between aromatic molecules have long been of interest [73–76], various terms, such as "pi-stacking", "edge-to-face", "vertex-to-face" and "multiple embraces", having been used to describe the relative orientations of essentially planar aromatic entities seemingly involved in weak mutual interactions. Longest recognised are pi-stacking interactions, well characterised in "donor-acceptor" complexes where the planes of the aromatic rings lie close to parallel [77]. While these parallel ring plane orientations are often associated with close ring atom contacts, typically ~ 3.5 Å, for which a relatively simple model based on charge localisation within the aromatic units can, in many cases, provide an adequate rationalisation of the contacts, this is not invariably the case [78]. An example is provided in the case of the cage amine complex having an unusual composition which may be defined by the formula $[\mathrm{Co}((\mathrm{CH_3})(\mathrm{C_{12}H_9CH_2NH_2})\mathrm{sar})]_8(\mathrm{NO_3})_{20}\mathrm{Cl_{4}}$-$\cdot\mathrm{33H_2O}$ [41], where the biphenyl units can be seen to

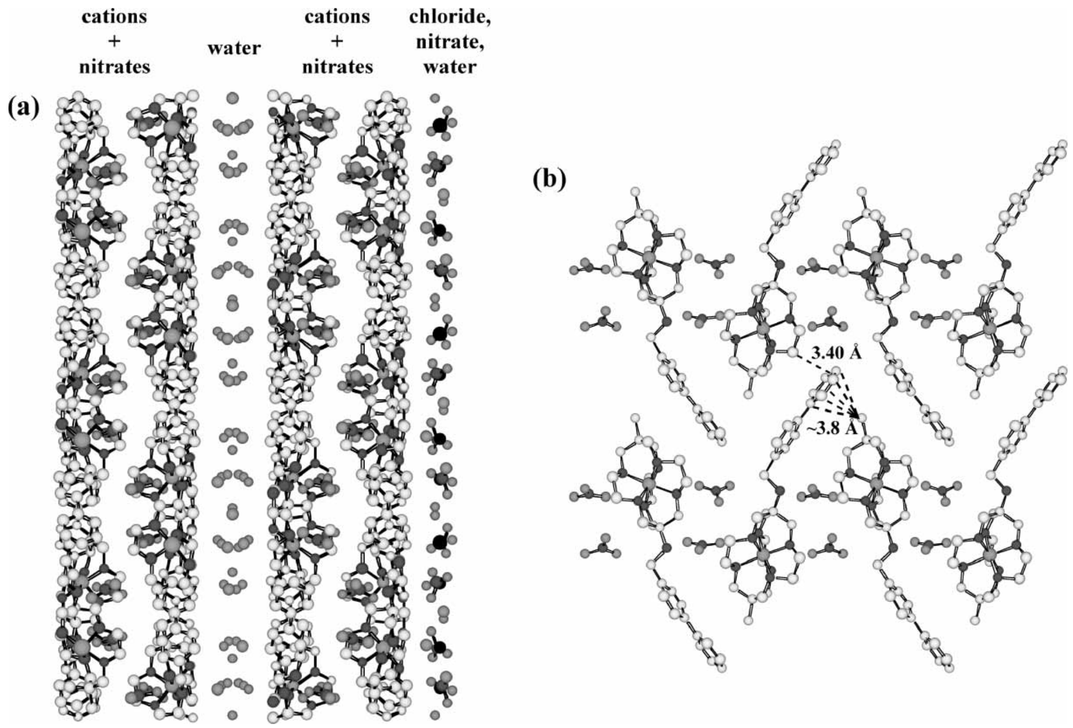

FIGURE 9 Partial views of the lattice of $[\mathrm{Co}((\mathrm{CH_3})(\mathrm{C_{12}H_9CH_2NH_2})\mathrm{sar})]_8(\mathrm{NO_3})_{20}\mathrm{Cl_4 \bullet 33H_2O}$: (a) down *c*, showing the repeat array of various layers (seen edge on); (b) perpendicular to one of the (cations + nitrates) layers, showing some of the short contacts to the biphenyl unit.

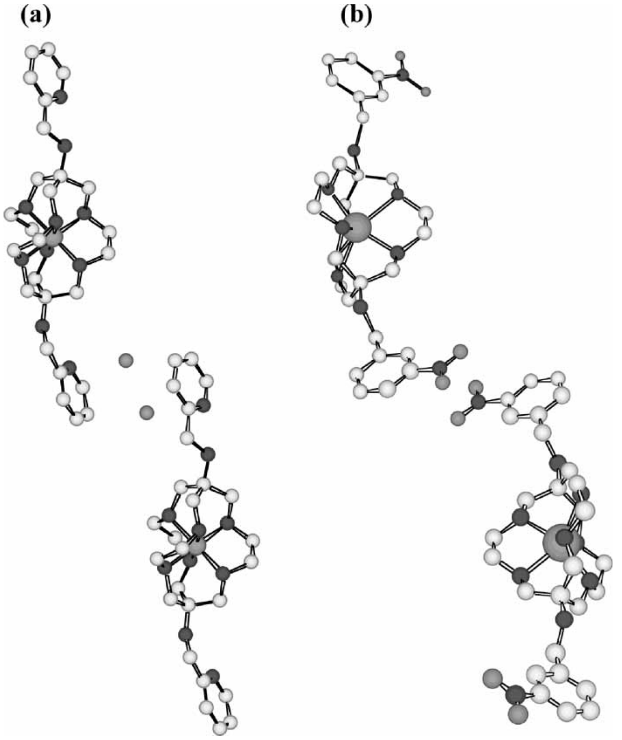

FIGURE 10 Contacts involving aromatic substituents on cage amine complexes: (a) a water molecule dimer (O…O 2.75 Å) sandwiched between pyridyl groups (O…N 3.11 Å) in the complex *ob*$_3$-[Co((2-(pyH)CH$_2$NH)$_2$sar)](S$_2$O$_6$)$_2$Cl•6H$_2$O [41]; (b) portion of a strand of cations present in the lattice of [Cu((3-NO$_2$-C$_6$H$_4$CH$_2$NH$_2$)$_2$sar)]Cl$_4$•5H$_2$O [49], apparently linked by close nitro-group contacts (O…N 3.03, O…C 3.15 Å).

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define a "herringbone" array, frequently seen in stacked aromatic lattices [78], but where each biphenyl is rather well isolated from another. In fact, the lattice of this complex, as is evident from a view down *c* (Fig. 9(a)), has a quite remarkable structure in which a layer containing only water molecules is sandwiched between layers containing only cations and nitrate anions, both these layers being flanked by another layer of cations plus nitrates which is in turn next to a layer of chloride and nitrate anions plus water molecules. In terms of such layers, the repeat unit of the lattice is thus (Cl$^-$, NO$_3^-$, H$_2$O);(cations, NO$_3^-$);(cations, NO$_3^-$);(water);(cations, NO$_3^-$);(cations, NO$_3^-$). This was not predicted on the basis of what was previously known of labile interactions involving cage complexes! The very similar (cations, NO$_3^-$) layers all contain both enantiomers of the cations (*viz.* they are racemic) and the biphenyl units define a herringbone array within these layers. There is one C(aromatic)…C(aromatic) contact ~3.7 Å but there are various shorter contacts involving O(nitrate)…C(aromatic) ~3.2 Å, C(cage methylene)…C(aromatic) ~3.4 Å, and a near-symmetric contact of the terminal methyl group of one cage with the "outer" phenyl group C atoms of another at ~3.6 Å (Fig. 9(b)). Contacts of nitrate anions with extended aromatic systems are seen in other complexes [79] (and bear some parallel to contacts observed in metal picrates [80]) and, here, this interaction of the nitrate anions may explain why they are also seen to adopt the unusual mode of bridging two NH units of the *lel*$_3$ cage by a single oxygen.

In general, for cage complexes bearing aromatic substituents, there is little evidence that possibly attractive contacts between aromatic-*C* atoms may have a dominant structural influence. In the *bis*(benzamide) species, *lel*$_3$-[Co((C$_6$H$_5$CONH)$_2$sar)]Cl$_3$·$^{13}/_8$H$_2$O [41], the lattice does display columns (parallel to *c*) of phenyl groups, the two of each complex unit belonging to separate arrays with parallel ring planes but the only close contacts occur between pairs of phenyl groups from the separate arrays, not between phenyl groups of one array. This means the contacts are essentially of the "edge-to-face" type, with the two closest C…C separations being quite long (3.58 and 3.66 Å) and similar to the separation between aromatic C and C of a cage methylene group of an adjacent complex. The shortest contact to an aromatic carbon atom is in fact that of a water oxygen (at 3.29 Å), though here it might be argued that this is simply a consequence of the (H-bonding) contact of this oxygen with the external NH (at 2.97 Å). In the analogous phthalamate complex, *lel*$_3$-[Co{(2-(CO$_2$H)C$_6$H$_4$CONH)$_2$-sar}]Cl$_3$·6.75H$_2$O [41], the phthalamate rings again form parallel arrays but the closest contacts to aromatic-*C* are from carboxylate-*O* (3.42 Å) and carboxylate-*C* (3.62 Å). In the complex *lel*$_3$-[Cu{(C$_6$H$_5$CH$_2$NH$_2$)$_2$sar}][CuCl$_4$]$_2$·2H$_2$O·3EtOH [49], congregation of the phenyl groups is reflected in a layered lattice but, despite disorder which renders detailed analysis imprecise, aromatic-*C* contacts in the phenyl-groups layer are remote (>3.7 Å) and, if anything, it is the ethyl groups of the ethanol of crystallisation which may interact with the aromatic rings. Apparent stacking again involving well-separated (C…C >3.9 Å) rings is also seen in Co(III) cage complexes with hydroxybenzylamino substituents [37] and a Zn(II) complex with anilino substituents [49]. One case where stacking is associated with relatively short aromatic-*C*…aromatic-*C* contacts (3.49 Å) is found in *lel*$_3$-[Co((2-pyCH$_2$NH$_2$)(2-pyCH$_2$NH)sar)](NO$_3$)$_4$·2H$_2$O but this may be contrasted with the situations found in *ob*$_3$-[Co((2-(pyH)CH$_2$NH)$_2$sar)](S$_2$O$_6$)$_2$Cl·6H$_2$O and *lel*$_3$-[Co((NH$_3$)(2-(pyH)CH$_2$NH)sar)](S$_2$O$_6$)$_2$-Cl·3H$_2$O (and note the proton locations implied by these formulae are those derived from the structure solutions) [41]. In the first of these dithionate-chlorides, the aromatic groups are found in pairs with closely parallel ring planes ~6 Å apart with a pair of H-bonded water molecules sandwiched between them (Fig. 10(a)), while in the second, the aromatic groups are widely separated and have only

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various contacts <3.5 Å to chloride and both dithionate- and water-*O*. Adding to such variety, cage complexes with nitroaromatic substituents have structures in which the nitro groups come into close contact (N. . .O $\sim$3.1 Å) (Fig. 10(b)), while introduction of a heteroaromatic substituent such as 3-thiophenylmethyl [41] may be associated with generation of weak S. . .S contacts ($\sim$3.7 Å).

CONCLUSIONS

The discussion of evidence for weak interactions in the lattices of cage complexes bearing aromatic substituents, in particular, illustrates the difficulties involved in assessing the range of forces possibly involved in determining a particular lattice structure. While hydrogen-bonding is pervasive and is presumably, like metal ion coordination, a major force, and the effects of aliphatic substitution can be rendered important simply by increasing its extent, energies $\sim 10\,\mathrm{kJ\,mol^{-1}}$ are sufficient to turn an equilibrium from an unfavourable to a favourable situation, so that even weak interactions must be considered chemically important. Fortunately, in the case of aromatic substituents, it seems that whatever the specific interactions principally responsible, their more usual consequence for lattice structures is some form of aggregation of the aromatic groups. Hence, given the stereochemical and structural diversity that may be built into cage amine systems, there are real prospects for their rational incorporation into sophisticated functional devices using at least the factors of hydrogen-bonding, metal ion coordination, and aliphatic and aromatic functionalisation as controls. A real challenge awaits in attempting to use the information gained from crystal structure determinations to control structures in solution.

References

[1] *Metals and Ligand Reactivity: An Introduction to the Organic Chemistry of Metal Complexes*; Constable, E. C., Ed.; VCH: Weinheim, 1996.
[2] Dance, I. *New J. Chem.* **2003**, *27*, 1.
[3] Lindoy, L. F. Dietrich, B., Viout, P., Lehn, J-M Macrocycle Chemistry, VCH: Weinheim *The Chemistry of Macrocyclic Ligand Complexes*; Cambridge University Press: Cambridge, 1989.
[4] Lehn, J-M. *Supramolecular Chemistry*; Wiley-VCH: Weinheim, 1995.
[5] Creaser, I. I.; Geue, R. J.; Harrowfield, J. M.; Sargeson, A. M.; Snow, M. R.; Springborg, J. *J. Am. Chem. Soc.* **1977**, *99*, 3181.
[6] Creaser, I. I.; Geue, R. J.; Harrowfield, J. M.; Herlt, A. J.; Sargeson, A. M.; Snow, M. R.; Springborg, J. *J. Am. Chem. Soc.* **1982**, *104*, 6016.
[7] Gahan, L. R.; Hambley, T. W.; Sargeson, A. M.; Snow, M. R. *Inorg. Chem.* **1982**, *21*, 2699.
[8] Balahura, R. J.; Ferguson, G.; Ruhl, B. L.; Wilkins, R. G. *Inorg. Chem.* **1983**, *22*, 3990.
[9] Geue, R. J.; Hambley, T. W.; Harrowfield, J. M.; Sargeson, A. M.; Snow, M. R. *J. Am. Chem. Soc.* **1984**, *106*, 5478.
[10] Comba, P.; Engelhardt, L. M.; Harrowfield, J. M.; Lawrance, G. A.; Martin, L. L.; Sargeson, A. M.; White, A. H. *J. Chem. Soc., Chem. Commun.* **1985**, 174.
[11] Comba, P.; Engelhardt, L. M.; Harrowfield, J. M.; Horn, E.; Sargeson, A. M.; Snow, M. R.; White, A. H. *Inorg. Chem.* **1985**, *24*, 174.
[12] Comba, P.; Creaser, I. I.; Gahan, L. R.; Harrowfield, J. M.; Lawrance, G. A.; Martin, L. L.; Mau, A. H. W.; Sargeson, A. M.; Sasse, W. H. F.; Snow, M. R. *Inorg. Chem.* **1986**, *25*, 384.
[13] Hambley, T. W.; Snow, M. R. *Inorg. Chem.* **1986**, *25*, 1378.
[14] Strach, S.; Bramley, R. *J. Chem. Phys.* **1988**, *88*, 7380, (citation of an uupublished structure).
[15] Bernhard, P.; Bürgi, H.-B.; Raselli, A.; Sargeson, A. M. *Inorg. Chem.* **1989**, *28*, 3234.
[16] Höhn, A.; Geue, R. J.; Sargeson, A. M.; Willis, A. C. *J. Chem. Soc., Chem. Commun.* **1989**, 1644.
[17] Höhn, A.; Geue, R. J.; Sargeson, A. M.; Willis, A. C. *J. Chem. Soc., Chem. Commun.* **1989**, 1648.
[18] Gahan, L. R.; Donlevy, T. M.; Hambley, T. W. *Inorg. Chem.* **1990**, *29*, 1451.
[19] Osvath, P.; Sargeson, A. M.; Skelton, B. W.; White, A. H. *J. Chem. Soc., Chem. Commun.* **1991**, 1036.
[20] Donlevy, T. M.; Gahan, L. R.; Hambley, T. W.; Stranger, R. *Inorg. Chem.* **1992**, *31*, 4376.
[21] Bruce, J. I.; Gahan, L. R.; Hambley, T. W.; Stranger, R. *Inorg. Chem.* **1993**, *32*, 5997.
[22] Donlevy, T. M.; Gahan, L. R.; Stranger, R.; Kennedy, S. E.; Byriel, K. A.; Kennard, C. H. L. *Inorg. Chem.* **1993**, *32*, 6023.
[23] Clark, I. J.; Creaser, I. I.; Engelhardt, L. M.; Harrowfield, J. M.; Krausz, E.; Moran, G. M.; Sargeson, A. M.; White, A. H. *Aust J. Chem.* **1993**, *46*, 111.
[24] Engelhardt, L. M.; Harrowfield, J. M.; Sargeson, A. M.; White, A. H. *Aust J. Chem.* **1993**, *46*, 127.
[25] Andersen, P. A.; Creaser, I. I.; Dean, C.; Harrowfield, J. M.; Horn, E.; Martin, L. L.; Sargeson, A. M.; Snow, M. R.; Tiekink, E. R. T. *Aust J. Chem.* **1993**, *46*, 449.
[26] Creaser, I. I.; Engelhardt, L. M.; Harrowfield, J. M.; Sargeson, A. M.; Skelton, B. W.; White, A. H. *Aust J. Chem.* **1993**, *46*, 465.
[27] Clark, I. J.; Engelhardt, L. M.; Geue, R. J.; Harrowfield, J. M.; Sargeson, A. M.; Skelton, B. W.; White, A. H. *Aust J. Chem.* **1993**, *46*, 1485.
[28] Donlevy, T. M.; Gahan, L. R.; Hambley, T. W. *Inorg. Chem.* **1994**, *33*, 2668.
[29] Bernhardt, P. V.; Bygott, A. M. T.; Geue, R. J.; Hendry, A. J.; Korybut-Daszkiewicz, B. R.; Lay, P. A.; Pladziewicz, J. R.; Willis, A. C. *Inorg. Chem.* **1994**, *33*, 4553.
[30] Donlevy, T. M.; Gahan, L. R.; Hambley, T. W.; Hanson, G. R.; McMahon, K. I.; Stranger, R. *Inorg. Chem.* **1994**, *33*, 5131.
[31] Bernhardt, P. V.; Harrowfield, J. M.; Hockless, D. C. R.; Sargeson, A. M. *Inorg. Chem.* **1994**, *33*, 5659.
[32] Bottomley, G. A.; Clark, I. J.; Creaser, I. I.; Engelhardt, L. M.; Geue, R. J.; Hagen, K. S.; Harrowfield, J. M.; Lawrance, G. A.; Lay, P. A.; Sargeson, A. M.; See, A. J.; Skelton, B. W.; White, A. H.; Wilner, F. R. *Aust J. Chem.* **1994**, *47*, 143.
[33] Harrowfield, J. M.; Sargeson, A. M.; Skelton, B. W.; White, A. H. *Aust J. Chem.* **1994**, *47*, 181.
[34] Geue, R. J.; Osvath, P.; Sargeson, A. M.; Acharya, K. R.; Noor, S. B.; Guru Row, T. N.; Venkatesan, K. *Aust. J. Chem.* **1994**, *47*, 511.
[35] Bernhardt, P. V.; Bramley, R.; Engelhardt, L. M.; Harrowfield, J. M.; Hockless, D. C. R.; Korybut-Daszkiewicz, B. R.; Krausz, E. R.; Morgan, T.; Sargeson, A. M.; Skelton, B. W.; White, A. H. *Inorg. Chem.* **1995**, *34*, 3589.
[36] Bashkin, J. K.; Bass, L. A.; Sondhi, S. M.; Robinson, K. D.; Beatty, A. M. *Inorg. Chim. Acta* **1996**, *253*, 91.
[37] Yeh, G. C.; Beatty, A. M.; Bashkin, J. K. *Inorg. Chem.* **1996**, *35*, 3828.
[38] Bruce, J. I.; Donlevy, T. M.; Gahan, L. R.; Kennard, C. H. L.; Byriel, K. A. *Polyhedron* **1996**, *15*, 49.
[39] Osvath, P.; Sargeson, A. M.; McAuley, A.; Mendelez, R. E.; Subramanian, S.; Zaworotko, M. J.; Broge, L. *Inorg. Chem.* **1999**, *38*, 3634.
[40] Donnelly, P. S.; Harrowfield, J. M.; Skelton, B. W.; White, A. H. *Inorg. Chem.* **2000**, *39*, 5817.
[41] Burnet, S.; Choi, M-H.; Donnelly, P. S.; Harrowfield, J. M.; Ivanova, I.; Jeong, S-H.; Kim, Y.; Mocerino, M.; Skelton, B. W.; White, A. H.; Williams, C. C.; Zeng, Z-L.; Eur *J. Inorg. Chem.* **2001**, 1869.

[42] Donnelly, P. S.; Harrowfield, J. M.; Skelton, B. W.; White, A. H. *J. Chem. Soc., Dalton Trans* **2001**, 3078.
[43] Donnelly, P. S.; Harrowfield, J. M.; Skelton, B. W.; White, A. H. *Inorg. Chem* **2001**, *40*, 5645.
[44] Donnelly, P. S.; Harrowfield, J. M.; Skelton, B. W.; White, A. H. *Aust. J. Chem.* **2001**, *54*, 15.
[45] Sharrad, C. A.; Gahan, L. R. *Polyhedron* **2003**, *22*, 45.
[46] Walker, G. W.; Geue, R. J.; Haller, K. J.; Rae, A. D.; Sargeson, A. M. *Dalton Trans* **2003**, 279.
[47] Bernhardt, P. V.; Dyahningtyas, T. E.; Harrowfield, J. M.; Kim, J-Y.; Kim, Y.; Rukmini, E. *Aust. J. Chem.* **2003**, *56*, 1187.
[48] Harrowfield, J. M.; Koutsantonis, G. A.; Nealon, G. L.; Skelton, B. W.; White, A. H. *Eur. J. Inorg. Chem.* **2005**, 2384.
[49] Choi, M-H.; Clark, I. J.; Donnelly, P. S.; Engelhardt, L. M.; Harrowfield, J. M.; Jeong, S-H.; Kim, Y.; Koutsantonis, G. A.; Lengkeek, N. A.; Mocerino, M.; Nealon, G. L.; Ogden, M. I.; Rukmini, E.; Sargeson, A. M.; Skelton, B. W.; White, A. H. *Inorg. Chim. Acta* **2005**, to be published.
[50] Harrowfield, J. M.; Skelton, B. W.; White, A. H. *Inorg. Chim. Acta* **2005**, to be published.
[51] Gainsford, G. J.; Geue, R. J.; Sargeson, A. M. *J. Chem. Soc., Chem. Commun.* **1982**, 233.
[52] Geue, R. J.; McCarthy, M. G.; Sargeson, A. M.; Skelton, B. W.; White, A. H. *Inorg. Chem.* **1985**, *24*, 1607.
[53] Haller, K. J.; Rae, I. D.; Bygott, A. M. T.; Hockless, D. C. R.; Ralph, S. F.; Geue, R. J.; Sargeson, A. M. *Acta Cryst.* **1999**, *B55*, 380.
[54] Geue, R. J.; Qin, C. J.; Ralph, S. F.; Sargeson, A. M.; Skelton, B. W.; White, A. H.; Willis, A. C. *Chem. Commun.* **1999**, 2351.
[55] Angus, P. M.; Sargeson, A. M.; Willis, A. C. *Chem. Commun.* **1999**, 1975.
[56] Sargeson, A. M. *Pure Appl. Chem.* **1986**, *58*, 1511.
[57] Sudmeier, J. L.; Blackmer, G. L.; Bradley, C. H.; Anet, F. A. L. *J. Am. Chem. Soc.* **1972**, *94*, 757.
[58] HI *Inorg. Chem.* **1970**, *9*, 1.
[59] Comba, P.; Hambley, T. W. *Molecular Modelling of Inorganic Compounds*;, 2nd ed. Wiley-VCH: Weinheim, 2000.
[60] Corey, E. J.; Bailar, J. C. Jr, *J. Am Chem. Soc.* **1959**, *81*, 2620.
[61] , Defined in ref. [58]. See discussion in refs [59,62,63].
[62] Mason, S. F. 7, *Molecular optical activity and the chiral discriminations*; Cambridge University Press: Cambridge, 1982.
[63] Duesler, E. N.; Raymond, K. N. *Inorg. Chem.* **1971**, *10*, 1486.
[64] Comba, P. *Inorg. Chem.* **1989**, *28*, 426.
[65] Geue, R. J.; McCarthy, M. G.; Sargeson, A. M. *J. Am. Chem. Soc.* **1984**, *106*, 8282.
[66] Hendry, A. J.; Naidoo, K. J.; Thornton *J. Chem. Soc., Chem. Commun.* **1989**, 998.
[67] Geue, R. J.; Hendry, A. J.; Sargeson, A. M. *J. Chem. Soc., Chem. Commun.* **1989**, 1646.
[68] Nishio, M.; Hirota, M.; Umezawa, Y. In The CH/π Interaction: Evidence Nature and Consequences. Methods in Stereochemical Analysis, Marchand Marchand, A. P., Ed.; Wiley-VCH: Weinheim, 1998;.
[69] Behm, C. A.; Boreham, P. F. L.; Creaser, I. I.; Korybut-Daszkiewicz, B. R.; Maddalena, D. J.; Sargeson, A. M.; Snowdon, G. M. *Aust. J. Chem.* **1995**, *48*, 1009.
[70] Sargeson, A. M. *Coord. Chem. Rev.* **1996**, *151*, 89.
[71] Walker, G. W.; Geue, R. J.; Sargeson, A. M.; Behm, C. A. *Dalton Trans* **2003**, 2992.
[72] Metrangolo, P.; Resnati, G. *Chem. Eur. J.* **2001**, *7*, 2511.
[73] Russell, V.; Scudder, M. L.; Dance, I. *Dalton Trans* **2001**, 789, Dance, I., Scudder, M.L.J. Chem. Soc., Dalton Trans **1996**, 3755; Dance, I., Scudder, M.L. Chem. Eur. J. **1996**, 2, 481.
[74] Janiak, C. *Dalton Trans* **2000**, 3885.
[75] Jennings, W. B.; Farrell, B. M.; Malone, J. F. *Acc. Chem. Res.* **2001**, *34*, 885.
[76] Adams, H.; Carver, F. J.; Hunter, C. A.; Morales, J. C.; Seward, E. M. *Angew. Chem., Int. Edn* **1996**, *35*, 1542.
[77] Foster, R. *Organic Charge-Transfer Complexes*; Academic Press: New York, 1969.
[78] André, I.; Foces-Foces, C.; Cano, F. H.; Martinez-Ripoll, M. *Acta Cryst.* **1997**, *B53*, 984–996.
[79] Drew, M. G. B.; Guillaneux, D.; Hudson, M. J.; Iveson, P. B.; Russell, M. L.; Madic, C. *Inorg. Chem. Commun.* **2001**, *4*, 12.
[80] Harrowfield, J. M. *J. Chem. Soc., Dalton Trans* **1996**, 3165.

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