DALTON PERSPECTIVE

π Stacking and the co-ordinate bond: sometimes conflicting factors in molecular recognition, as revealed in the structures of metal picrates

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Crystallographic studies of anhydrous and hydrated 2,4,6-trinitrophenoxides, 'picrates', of metal ions from the main-group, transition, lanthanide and actinide metal series show that picrate may be a ligand of comparable donor ability to hydroxide and often is one of remarkably high denticity, but that these characteristics do not guarantee its co-ordination in preference to water. It is argued that this may be attributable to its 'self-co-ordinating' ability through π stacking, a structural feature which is universally observed regardless of whether picrate is also co-ordinated, and that the π stacking interaction energy must be comparable to the difference between hydroxide and water co-ordinate bond energies.

A fundamental requirement for the design of molecules and molecular aggregates having particular desired functions is an understanding of the magnitude and direction of the forces that exist between their constituent units. The lability of these interactions is an important aspect of the functioning of complex molecular aggregates and since it is usually true that weak interactions are associated with fast kinetics, the development of supramolecular chemistry[1] has led to a focus on many forms of weak interaction for which it is true that knowledge is commonly far less complete than that of a strong interaction such as the two-centre, shared-electron-pair covalent bond. In the particular cases of so-called 'donor–acceptor', 'charge-transfer' or 'π–π stacking' interactions of aromatic molecules,[2-4] the direction is rather well characterised both experimentally and theoretically, and spectacular examples of its application in synthesis are well known.[5] However, experimental information on the magnitude of the interaction energies, in solution especially, is most abundant for systems of uncharged molecules or ones where any charges are remote from the interaction sites.[4] This experimental work has led to the expectation by and large that π–π stacking should be a useful but relatively minor perturbation of interactions based on formal bond formation.[4,6] Studies recently made of the solid-state structures of a number of hydrated and some anhydrous metal picrate (= 2,4,6-trinitrophenoxide) 'salts'[7-21,*] have, however, indicated that this may be a misleading conclusion, at least where the π–π stacking of picrate anion is compared with its ability to form a co-ordinate bond to a metal ion. Consideration of this point raises a number of issues relevant to the understanding of selectivity in the interaction of any one chemical species with another ('molecular recognition')[1] and indeed to the way in which a particular chemical entity is identified.

Co-ordination of Picrate Ion

Although as late as 1986 it could be claimed that picrate anion was still commonly regarded as a 'non-co-ordinating' species,[22] this view was perhaps merely a consequence of the fact that most structural information then available was for simple main-group metal picrates where weak co-ordinate bonding would have been expected (another myth?) or for derivatives formed by interaction with an apparently strong macrocyclic ligand, and where the focus was upon the cationic component of the basic stoichiometric unit.[23] It is an interesting sign of the times that the definition of supramolecular chemistry has engendered a return to consideration of crystal structures in terms of the extended lattice and not simply in terms of the essential molecular unit. For co-ordination complexes of main-group metals in particular, it is not that long since their structures could be described in terms of weak interactions (for example, hydrogen bonding) between ligands without any indication of co-ordinate bonding to the metal.[24] The contemporary view would be that both are important, though is it possible that the position remains that this is based on bold assumptions rather than quantitative measurements of relative weight?

The stoichiometrically simplest co-ordination complex of picrate anion is that with the proton, *i.e.* picric acid. Despite two published structural reports[25,26] and at least one unpublished study,[27] it is not possible to define the position of the proton with precision, partly because these studies have all been based on X-ray diffraction but also because the proton may be disordered over at least two equivalent sites [Fig. 1(*a*)] in which it may be regarded as chelated by the picrate anion. A crystal structure determination may be regarded as one definitive means of establishing the molecular formula of a given compound and the conventional view of picric acid as being 2,4,6-trinitrophenol is reflected in the representation of the asymmetric unit of the structure (derived from the coordinates given in ref. 26) shown in Fig. 1(*b*). A slightly puzzling feature of this is the relative orientation of the two inequivalent 'molecules', where one of the unsubstituted aromatic carbon atoms of one picric acid unit is approximately within the sum of the van der Waals radii of one oxygen atom of a nitro group on the other picric acid unit. Consideration of the extended lattice reveals evidence of possibly much more significant interactions than this, however, the view down *a* [Fig. 2(*a*)], for example, showing that there are extended stacking interactions. Interestingly, this extended structure is much more complex than in a picric acid 'adduct' such as picric acid–benzene[28] where beautiful stacks of alternating $(benzene)_2$ and $(picric\ acid)_2$ units constitute the whole lattice. Crudely, the picric acid lattice can be considered as double pleated sheets separated by herringbone stacks, as indicated in Fig. 2(*b*). Whatever the reasons for this complexity, it is apparent that the nature of picric acid in the solid state is rather inadequately described in terms of a 2,4,6-trinitrophenol unit. The material is a

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[*] Note an erroneous claim is made in ref. 16 that the structure of hydrated sodium picrate had not previously been determined. The present author is fully responsible for this omission of mention of ref. 17 herein. Earlier studies of the other alkali-metal picrates are mentioned.

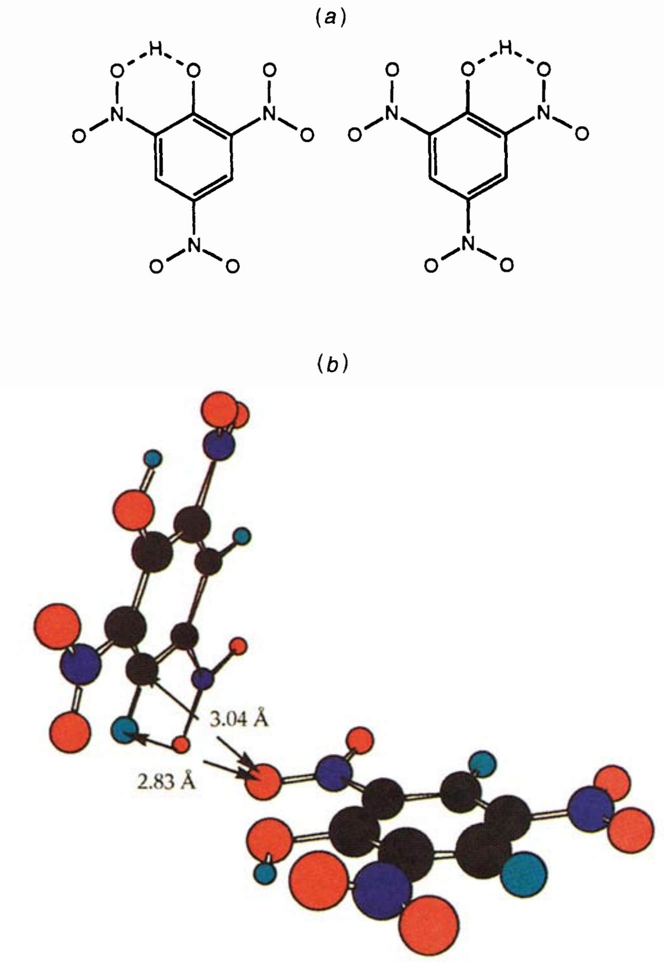

Fig. 1 (*a*) Equivalent proton locations in picric acid. (*b*) The asymmetric unit of the picric acid lattice[26] with indication of the two closest atom contacts within this unit (atom colours: black = C, blue = N, red = O, light blue = H)

chameleon (quite literally, given that the colours of its adducts are varied), its nature changing with its environment, and it is interesting to consider the 2,4,6-trinitrophenolate moiety as the basic unit of a labile polymer which maintains its identity to varying degrees depending upon the nature of other species present. Thus, the possibility arises that self-association may dominate where the picrate–'other species' interaction is relatively weak. In particular it is possible that non-co-ordination of picrate to a metal ion may reflect not so much the weakness of the co-ordinate bond interaction as the strength of the picrate–picrate association.

Some Structural Chemistry of Metal Picrates

There is long-standing structural evidence of the efficacy of picrate ion as a ligand towards all types of metal ions. The structures of the alkali-metal picrates[16,17] provide excellent illustration of its versatility in that forms between bi- and septa-dentate binding are revealed. In lithium picrate monohydrate the picrate can be regarded as binding to one lithium cation in a bidentate manner but also as bridging through the formal phenoxide oxygen atom to a second lithium, defining the 'molecular unit' of the lattice as the binuclear species containing two square-pyramidal lithium ions as shown in Fig. 3(*a*). Again, however, it is misleading not to consider the extended lattice, since it is clear that there is stacking of the picrate units, *viz*. the picrate moieties retain an ability to 'self-co-ordinate' in addition to their ability to co-ordinate the lithium ions [Fig. 3(*b*)]. In sodium picrate monohydrate the similar stoichiometry does not ensure a similar structure to that of the lithium compound

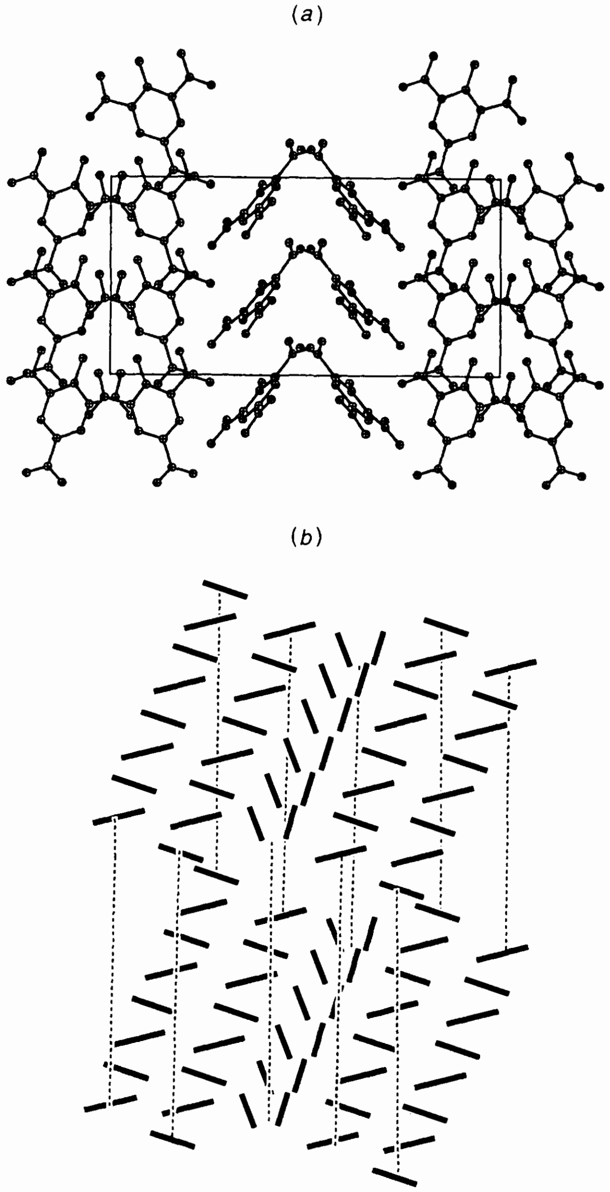

Fig. 2 (*a*) The picric acid lattice viewed down *a*. (*b*) A simplified, 'exploded' view of the picric acid lattice. Bars represent picric acid ($C_6H_3N_3O_7$) moieties, a pair of bars in a 'V' arrangement being the asymmetric unit of Fig. 1(*b*)

except in that stacking is still observed, and the solid can be regarded as both a co-ordination polymer and a stacking polymer. The sodium cations are found in two environments, one involving exclusive picrate-oxygen co-ordination and the other a mixture of picrate nitro-group oxygen chelation and bridging-water co-ordination [Fig. 4(*a*)]. The picrate stacking [Fig. 4(*b*)] is similar but not identical to that observed in the lithium complex. The phenyl group carbon atoms do lie in essentially parallel planes but the overlap as measured by the projection of one picrate onto another is not the same, an observation which immediately gives rise to the question as to whether the stacking interactions may be described in terms of the 'slipped', partial-charge-matching model developed to explain porphyrin association.[29] This is a question that is difficult to answer since there is no experimental measure of the charge distributions independent of the crystal structures but, if so, it would be unsurprising if the exact charge distribution were to depend upon the cation associated with the picrate. Qualitatively, the charge distributions associated with the (valence bond) canonical forms shown in Fig. 5 are consistent with the notion that the nitro-group oxygen atoms would be relatively negative and the *meta* ring carbon atoms relatively

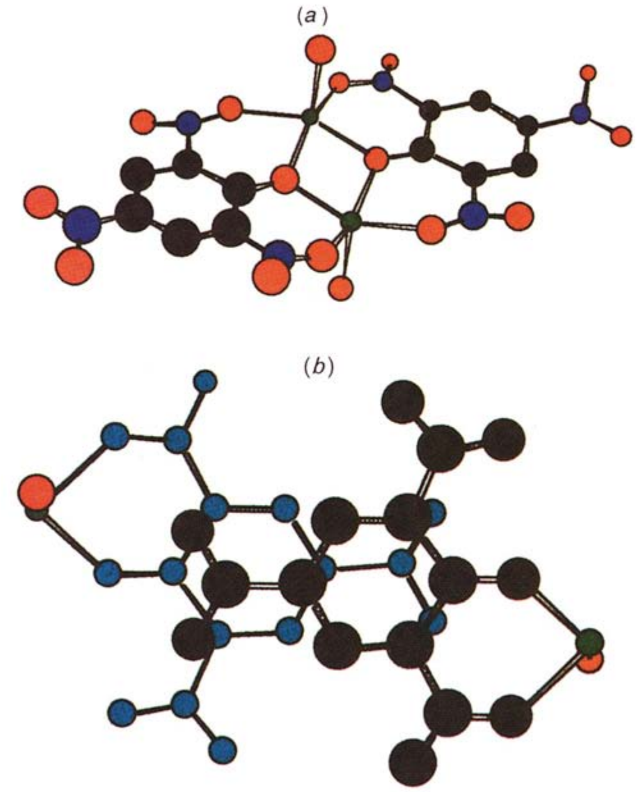

Fig. 3 (*a*) The binuclear 'molecular unit' present in lithium picrate monohydrate. [Figure prepared using the modelling software CHEM 3D PRO, Cambridge Scientific Computing, and the coordinates given in ref. 16. Atom colours are as in Fig. 1(*b*), plus green = metal = Li.] (*b*) Overlap of picrate moieties at (x, y, z) and ($1 - x$, $-y$, $1 - z$) in lithium picrate monohydrate.[16] All atoms in one picrate unit are shown in light blue, those in the other in black

positive, thus 'explaining' the orientation of the two molecules in the asymmetric unit of the H^+ complex (picric acid), but obviously a much more sophisticated approach would be necessary to explain differences in structure associated with changes of cation and the exact reasons for differences in stacking overlap.

In the anhydrous alkali-metal [plus ammonium and thallium(I)*] ion picrates the remarkable versatility of picrate ion as a ligand is further revealed. In potassium picrate (isomorphous with the ammonium salt), for example, it is quinquedentate, with both phenoxo- and nitro-group oxygen atoms having bridging functions, while in caesium picrate (isomorphous with the rubidium and red thallium salts) all seven oxygen atoms of any picrate moiety can be considered bound to a metal cation. Particular views of the lattices illustrating these points are shown in Fig. 6. Picrate stacking rather similar to that found in hydrated lithium picrate is obvious in the view given of the potassium salt. For caesium picrate the picrate phenyl carbon atoms are found in (two sets of nearly orthogonal) parallel planes separated by the 'usual' distance of ≈ 3.5 Å but the projected overlap of one picrate on another is much smaller than for the potassium salt. The significant point, however, is that picrate stacking is a common feature regardless of considerable variations in the co-ordinative interactions. Perhaps, therefore, it is energetically of comparable importance and perhaps further the structures should be regarded as being primarily determined by the optimisation of stacking.

In support of this argument, the structures of the alkaline-earth-metal picrates[18,19] also show picrate stacking as a common feature despite great differences in the cation co-ordination behaviour. Though the structure of beryllium picrate remains unknown, that of hydrated magnesium picrate perhaps exemplifies the extreme situation where stacking has won out over (picrate) co-ordination and the lattice contains $[Mg(OH_2)_6]^{2+}$ cations along with a picrate 'polymer' anion

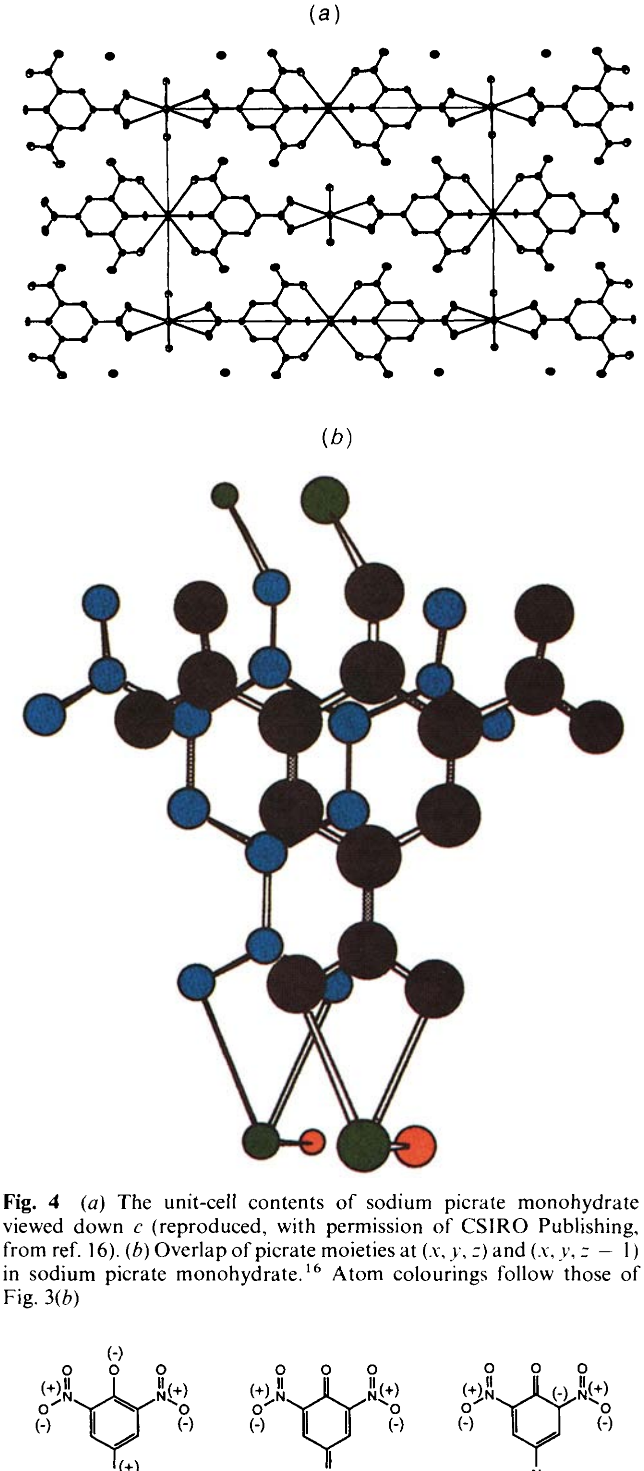

Fig. 4 (*a*) The unit-cell contents of sodium picrate monohydrate viewed down *c* (reproduced, with permission of CSIRO Publishing, from ref. 16). (*b*) Overlap of picrate moieties at (x, y, z) and (x, y, $z - 1$) in sodium picrate monohydrate.[16] Atom colourings follow those of Fig. 3(*b*)

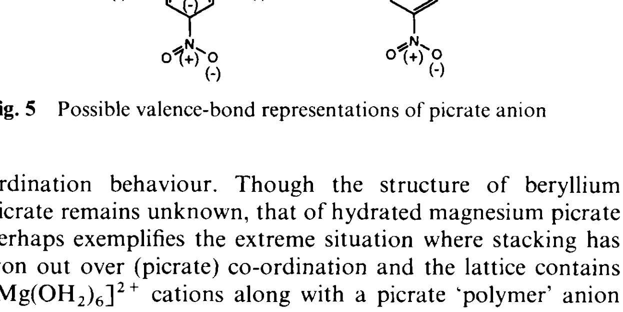

Fig. 5 Possible valence-bond representations of picrate anion

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* Ref. 30 describes a recent study of the yellow form of thallium picrate. Earlier studies of the red form are noted in ref. 16.

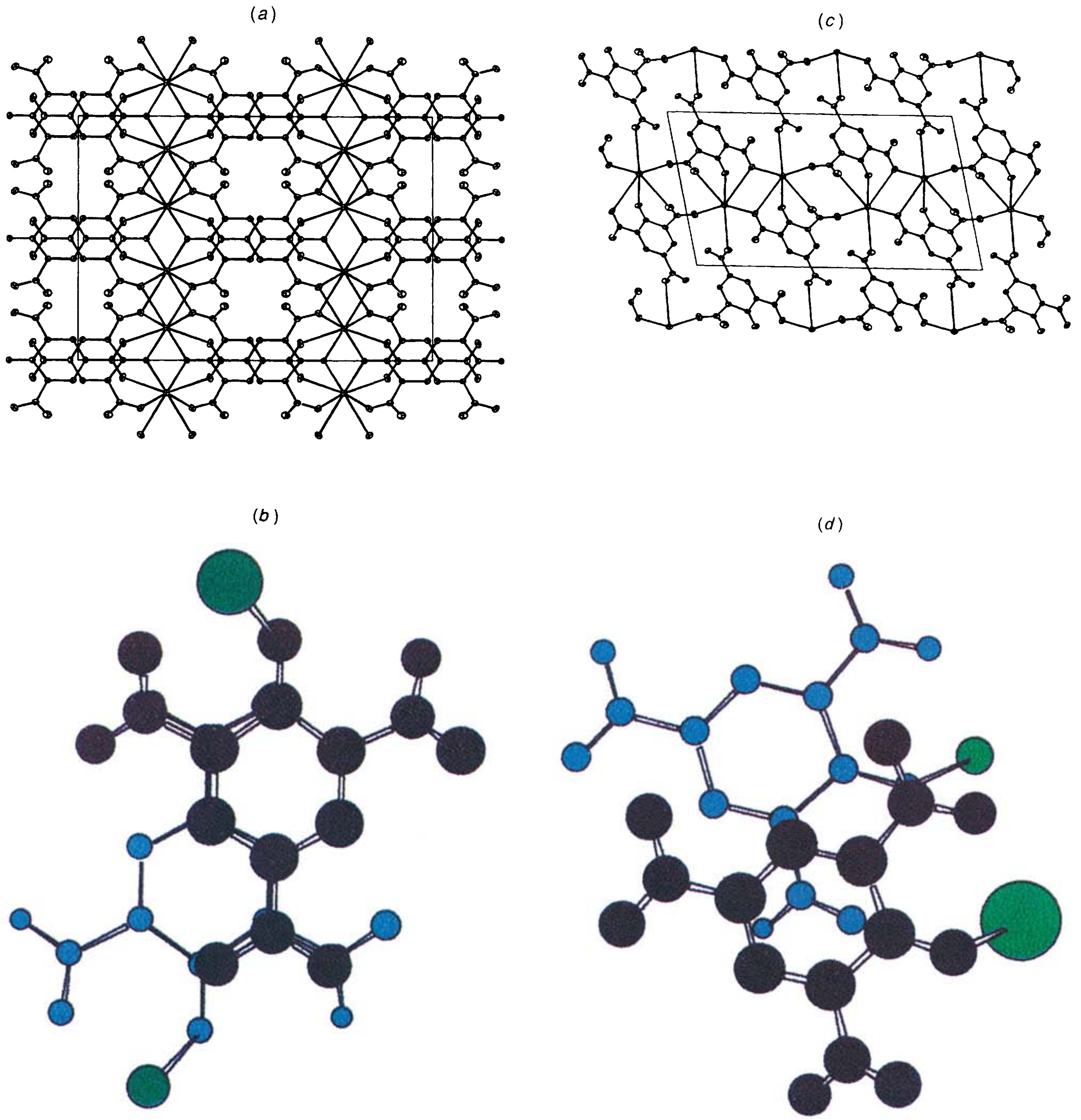

Fig. 6 (*a*) The unit-cell contents of anhydrous potassium picrate, projected down *c* (reproduced, with permission of CSIRO Publishing, from ref. 16). (*b*) Overlap of picrate moieties at (x, y, z) and $(x, \frac{1}{2} - y, \frac{1}{2} + z)$ in anhydrous potassium picrate.[16] Atom colourings follow those of Fig. 3(*b*). (*c*) The unit-cell contents of anhydrous caesium picrate, projected down *b* (reproduced, with permission of CSIRO Publishing, from ref. 16). (*d*) Overlap of picrate moieties at (x, y, z) and $(x, 1 + y, z)$ in anhydrous caesium picrate.[16] Atom colourings follow those of Fig. 3(*b*)

forming by stacking in a manner closely similar to that observed in both potassium and lithium picrates. The hydrated picrates of the heavier alkaline-earth metals calcium, strontium and barium have structures which are more complicated in that picrate co-ordination at least in a bidentate form occurs in all and picrate stacking occurs in different, less symmetrical ways. Views of the very different magnesium and barium picrate lattices are shown in Fig. 7. Picrate overlap seems to reach a minimum for strontium, where the groups form two sets of parallel planes as in the caesium compound. It is not simple to dissect all the factors which may be operative in these systems but obviously a possible interpretation is that there is close to a balance for picrate between the metal co-ordination (in place of water ligand) and self-co-ordination (stacking) energies and since these bonding modes are not necessarily exclusive frequently they are both seen to be optimised. Considering stacking as a common factor, it might be surmised that it should dominate for the heavier metals, where co-ordinate bond strengths would be weaker, but again it is interesting to ask whether for oxyanion ligands on very heavy metals this is a plausible expectation. Allowance for relativistic effects,[31,32] for example, may mean that bond strengths do not decrease down a Periodic Group, and the importance of nitrato complex formation for lanthanides and actinides[33] and the surprisingly varied co-ordination chemistry of perchlorate anion with Pb^{II},[34] for example, are at least empirical evidence for an exceptional strength of oxyanion binding to heavy metals. Of course, there are simple geometrical reasons for expecting chelation of 'small bite' ligands like nitrate and perchlorate to be more effective for larger cations,[35] and the same analysis would lead to the expectation that chelation by picrate would be less effective for larger cations, though again this conclusion

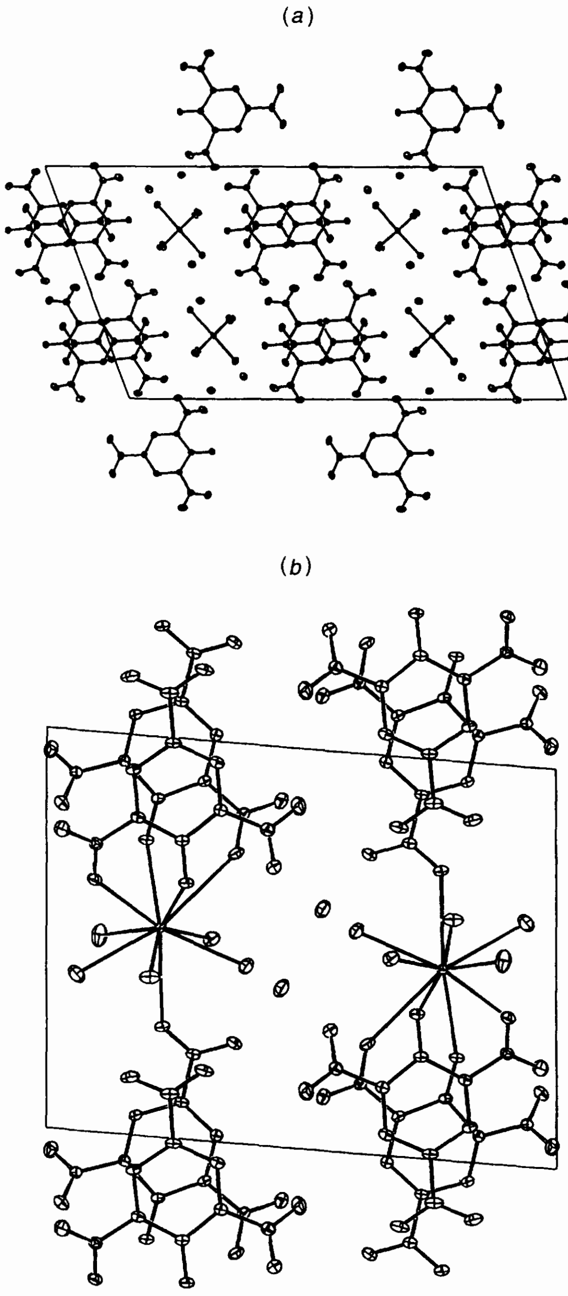

Fig. 7 (*a*) The unit-cell contents of (*a*) hydrated magnesium picrate, projected down *b*, and (*b*) hydrated barium picrate, projected down *c* (reproduced, with permission of CSIRO Publishing, from ref. 19)

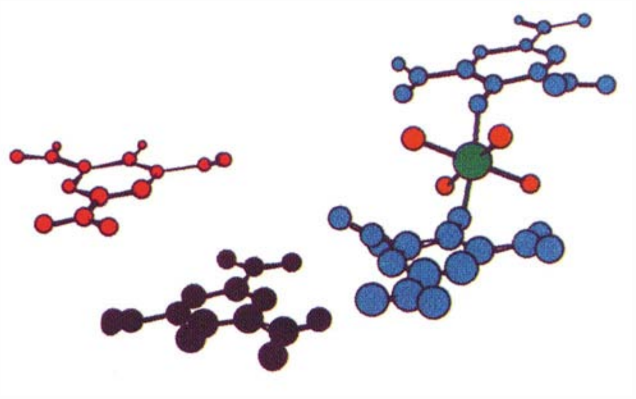

Fig. 8 The stoichiometric unit (excluding lattice water) of the picric acid adduct of hydrated scandium picrate,[15] showing the near-parallel orientation of all picrate moieties. All atoms in the co-ordinated picrate units are shown in light blue, while atoms in the unco-ordinated picrate/picric acid units are shown in black and pink (reproduced with permission of CSIRO Publishing)

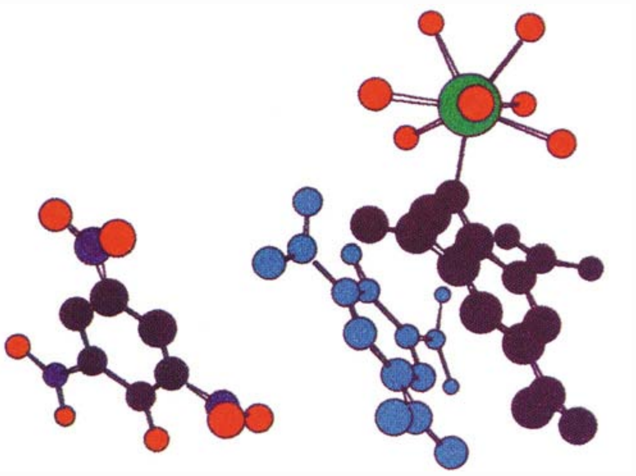

Fig. 9 A view of the stoichiometric unit (excluding lattice water) in hydrated erbium picrate,[12] showing a stacking interaction between 'free' and bound picrates. Atoms in the stacked units are shown in light blue and black (reproduced with permission of CSIRO Publishing)

must be qualified by allowing that relativistic factors may influence bond lengths in such a way that effective cation sizes do not vary uniformly.

The influence of cation size upon picrate binding is apparently a factor which cannot be separated from that of cation charge, and the structure[15] of the hydrated picrate of Sc^{3+} shows that a small cation is certainly not necessarily one to which picrate binds in a bidentate fashion. In the *trans*-[Sc(OH$_2$)$_4$(pic)$_2$]$^+$ cation found in the solid the two bound picrate (pic) moieties are present as unidentate, phenoxo-*O* ligands, with a mean Sc–O bond length of 2.03$_3$ Å. This Sc–O (anion) separation is essentially identical with that found in *cis*-[Sc(OH$_2$)$_4$(ts)$_2$]$^+$ cation (ts = tosylate = toluene-4-sulfonate)[36] and thus it may be that steric factors within the scandium(III) co-ordination sphere determine the co-ordination geometry, though since picrate stacking continues to be a feature of the extended lattice, with the two co-ordinated picrate groups in particular lying in closely parallel planes (Fig. 8), once again it is possible that the optimisation of stacking determines the preferred co-ordination mode. (It is well known that in several formally similar systems[37] the actual co-ordination mode within the solid seemingly depends on very subtle influences.)

In the picrates of larger tripositive cations such as Y^{3+} and the lanthanides both bi- and uni-dentate co-ordination of picrate are observed.[7-14,21] Interestingly, despite the fact that M–OH$_2$ bond lengths are generally found to be significantly longer than M–O (picrate), in the higher hydrates of these picrates only partial, unidentate anion co-ordination is apparently preferred. The fact that with the lighter (larger) lanthanides co-ordination of two picrates (one quasi-bidentate) can occur may indicate that lower torsional barriers about longer bonds allow more ready adaptation of a co-ordinated picrate into a stacking array. In the hydrated picrate of a heavier lanthanide, [Er(pic)(OH$_2$)$_7$][pic]$_2$·5H$_2$O, it is apparent (Fig. 9) that bound picrate stacks with 'free' picrate, but within the complete lattice extensive stacking of free picrates is also observed,[12] and hence it may be that, as a moderately good ligand for the metal, water largely sets picrate free to stack on its own. The extreme of the situation found with hydrated magnesium picrate is, however, not realised even at the end of the lanthanide series.

The only structure yet recorded for the picrate of a metal with a formal charge greater than 3+ is that of thorium(IV) picrate.[20] The material studied was actually a 'basic thorium picrate', [Th(OH)(pic)$_3$]·16H$_2$O, shown crystallographically to contain a hydroxo-bridged thorium dimer in which one

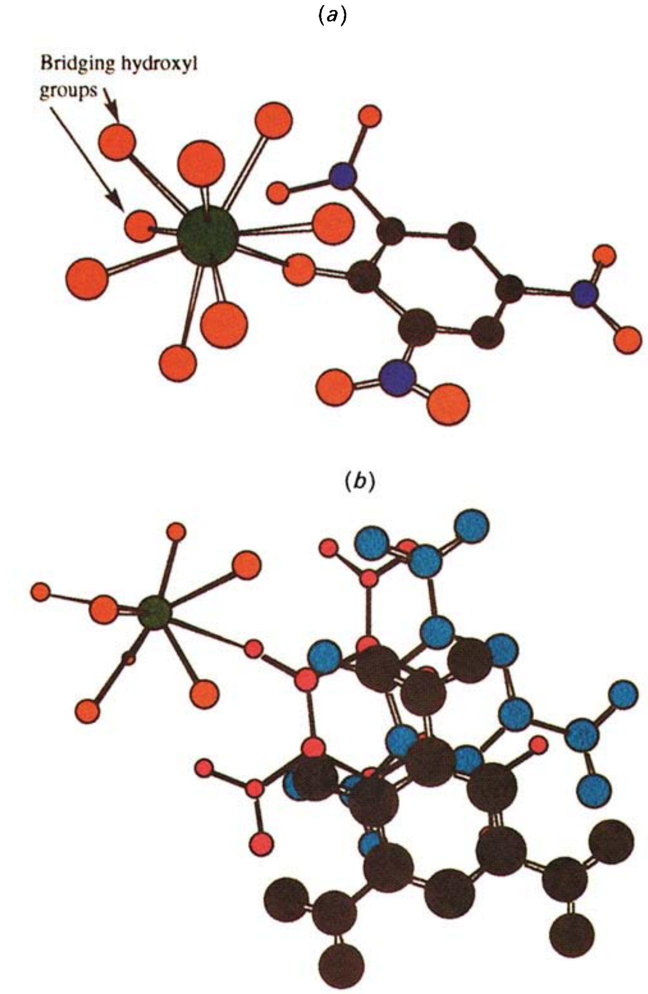

Fig. 10 Views of (*a*) one half of the centrosymmetric dimer unit (excluding lattice water) found in hydrated 'basic thorium picrate'[20] [atom colours are as in Fig. 3(*a*), with metal = Th], and (*b*) the two adjacent 'free' picrate anions (light blue and black) projected onto the ring plane of the co-ordinated picrate moiety (pink) (reproduced with permission of CSIRO Publishing)

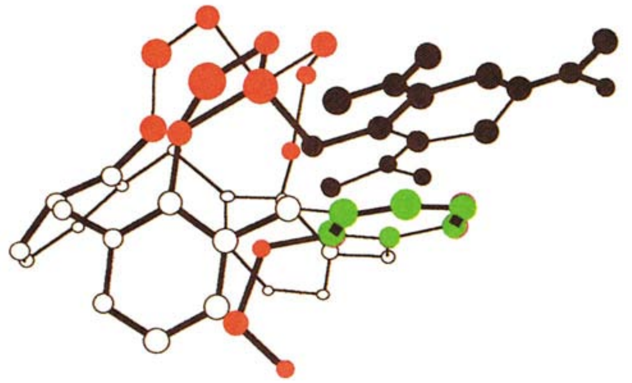

Fig. 11 A possible form of π stacking between a co-ordinated picrate anion (black) and a phenyl ring (green) of a co-ordinated, 'partial cone' form tetraphosphorylated calix[4]arene. For simplicity, two alkoxy substituents on each phosphorus are not shown, nor is the full co-ordination of the arbitrarily chosen metal ion

picrate is bound to each thorium atom in a unidentate manner through the formal phenoxo oxygen atom [Fig. 10(*a*)]. The Th–O (picrate) bond length [2.366(3) Å] is essentially identical to that of the Th–OH (bridging) bond [2.374(4) Å, mean] and significantly shorter than that of the Th–OH_2 bonds [2.507(6) Å, mean] also present in the dimer unit. If these bond lengths are to be taken as directly indicative of bond strengths, then the thorium(IV)–picrate interaction must be appreciably stronger than Th–OH_2 and the fact that the unco-ordinated picrate anions are actually involved in stacking with the co-ordinated ones [Fig. 10(*b*)] suggests that stacking energies may exceed the difference in Th–O (picrate) and Th–O (water) co-ordinate bond energies. Though difficult to estimate on the basis of currently available information, crude considerations of Morse potentials and the experimentally defined dependence of thorium–ligand bond-disruption energies on ligand structure[38,39] suggest this energy difference might lie between 10 and 40 kJ mol^{-1}. Though not of a magnitude comparable to most ligand-binding enthalpies, this certainly could explain an apparent weakness of picrate as a ligand compared to those unlikely to self-associate and could be a factor related with marked selectivity if exploitable in a chemical discrimination.

Conclusion

Although it has been suggested that in all the systems analysed above a competition between self-association and co-ordination may be seen for picrate, there is no reason to expect that in general a positive co-operativity between co-ordination and π–π stacking cannot occur. Obviously, this could arise when a ligand containing an aromatic functionality is present and such a situation has in fact been fully characterised in the solid state for the complex formed between lithium picrate and dibenzo-36-crown-12 (5,6,8,9,11,12,14,15,17,18,23,24,26,27,29,30,32,33,35,36-icosahydrodibenzo[*b*,*t*][1,4,7,10,13,16,19,22,25,28,31,34]dodecaoxacyclohexatriacontine).[40] This particular case may be rather appropriately contrasted with that of the rubidium picrate complex of a cryptand where the picrate does not co-ordinate but forms columnar stacks (with staggered ring substituents) with an interplanar spacing of only ≈ 3.6 Å despite the fact that it is formally a stacking of units of like charge.[41] The intermediate case of a picrate anion stacking with an aromatic unit of a bound ligand while remaining unco-ordinated itself is also known.[42] In all such cases and the systems referred to earlier any thermodynamic assessment of the interactions occurring is difficult because equilibria are not observed. An attempt[40] to determine the association equilibrium constant between picrate ion and the lithium complex of dibenzo-36-crown-12 in dichloromethane solvent failed because in fact no clear evidence of association could be obtained, and although there is considerable information on π–π stacking interaction equilibria in solution involving nitroaromatics in general,[43] the specific comparison of picrate–picrate (or picrate–aromatic) with picrate–metal ion association cannot yet be made in a quantitative sense. In contrast to the results for the Li(pic) complex of dibenzo-36-crown-12, there is indirect evidence that π stacking by picrate may influence important solution processes. For example, stacking of unco-ordinated picrate with a bound calixarene characterised in the solid may persist in solution, and further work is intended to reveal any effect this may have on solvent extraction;[42] solution ^1H NMR spectra of alkali-metal picrate complexes of calixcrown ligands designed for possible use in nuclear waste treatment show multiple picrate resonances possibly indicative of the presence of different associated species;[44] the greater efficiency of the partial cone compared to the cone form of tetrakis(diethoxyphosphoryl)-*p*-*tert*-butylcalix[4]arene in the solvent extraction of lanthanide picrates may be indicative of stacking-assisted co-ordination as illustrated in Fig. 11;[45] the extraction of potassium picrate by benzo-18-crown-6 (2,3,5,6,8,9,11,12,14,15-decahydro-1,4,7,10,13,16-benzohexaoxacyclooctadecine, L) is favoured over that of other alkali metal picrates at least partly because of the relatively high value for the formation constant of [KL(pic)],[46] which may reflect optimum stacking of the type characterised in solid [LiL(pic)] (L = dibenzo-32-crown-12), but interestingly not observed in the potassium picrate complex of benzo-15-crown-5

(2,3,5,6,8,9,11,12-octahydro-1,4,7,10,13-benzopentaoxacyclopentadecine).[23]

The ultimate question of course is not whether the particular association properties of picrate ion can be characterised but how far π–π stacking can be rationally exploited as a factor in co-ordination chemistry (and generally in supramolecular chemistry). In the solid state it is clearly important in determining structure in systems ranging in sophistication from helicates[47–49] to simple complexes of bidentate heteroaromatics.[50] The magnetic and electrical properties of 'charge-transfer salts', which usually display beautifully stacked structures in the solid state, have long been of interest.[51] In solution the properties known for molecules such as the porphyrins show how important π stacking may be in determining electron and energy transfer.[29] The structural chemistry of metal picrates offers an indication that even rather small and simple stacking units may be associated with energy factors large enough to be usefully exploited. It is salutary that Nature has of course provided elegant demonstration of this in the structures of nucleic acids and here at least rather thorough investigations have been made of the consequences of introducing stacking with metal-ion complexes.[52–54] The use of aromatic receptors to control the reactions of nucleobases has been rather elegantly explored recently[55] and this chemistry forms part of a quite extensive backdrop of known simple effects of π–π stacking on reactivity.[56] To conclude with one further comment on picrate systems, it is worthy of note that in no case stacking of picrate involves coplanarity of all three nitro substituents with the aromatic ring. Perhaps, and this obviously a concept of general significance, twisting of at least one nitro group from coplanarity is a mechanism for control of stacking ability.

Acknowledgements

One of the singular pleasures of chemistry is the growth of crystals. The appearance of any chemical in a well defined crystalline form is a comforting, if sometimes misleading, indicator of purity and stoichiometric exactitude. Thus, many reagents such as picric acid have long been used because of the ease with which they can provide derivatives beautiful in appearance and highly crystalline in form. Captivated thus by picrates, I have been fortunate in having a collaborator, Allan White, able to reveal the complexity of the structures of many. The eclectic choice of references in this article is in part intended to be a tribute to his efforts.

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