Journal of the Iranian Chemical Society, Vol. 1, No. 1, September 2004, pp. 1-9.

JOURNAL OF THE
Iranian
Chemical Society

New Super- and Supramolecular Receptor Systems - Cages, Chains, Squares, and Dendrimers Incorporating Macrocycles as Structural Elements

L.F. Lindoy
Centre for Heavy Metals Research, School of Chemistry, University of Sydney, NSW 2006, Australia

(Received 27 October 2003, Accepted 6 December 2003)

The selective use of *tert*-butoxycarbonyl protecting group chemistry has enabled efficient syntheses of multilinked macrocyclic derivatives incorporating tetraaza and aza-thia donor rings. Mixed ring species have also been prepared as well as a dendrimer incoporating nine N_2S_2-donor macrocyclic sites. The interaction of these species with selected metal ions is discussed. A series of cage molecules with varying cavity sizes has been prepared and their interaction with both (selected) metal ions and small molecules described. The formation of new large molecular squares and catenanes involving self-assembly is also presented.

Keywords: Macrocycle, Cage, Square, Catenane

INTRODUCTION

Over recent years there has been very considerable interest in the design and synthesis of larger supramolecular and supermolecular receptor molecules for binding both small molecules and ions (both cations and anions) [1]. Both the strength of binding and the degree of ionic or molecular recognition will depend upon both the structural and electronic complementarity between host and guest. While virtually all host-guest systems exhibiting molecular recognition will show some degree of both steric and electronic complementarity, it should be noted that the distinction between each of these is not always clear cut. Macrocyclic rings have frequently been used as structural components in both supramolecular and supermolecular systems, especially for binding metal ions. In part, this is a reflection of the tendency of such ligands to yield complexes that exhibit both enhanced kinetic and thermodynamic stabilities - a reflection that the donor sites in such compounds are more or less restrained by the cyclic nature of the ring [2].

In recent times we have been interested in the design and synthesis of new examples of multicomponent systems of the above category displaying a range of molecular architectures. In particular cases, the resulting nanometer scale structures incorporate hetero macrocyclic rings and are designed to bind different metal ions simultaneously. Systems of this type show potential for generating unusual electronic and other properties - including novel charge transfer, electron transfer, allosteric and/or catalytic behaviour. Even when no cooperativity occurs between metal binding sites, the prospect that the metal-containing species may act as a multi-electron redox reagents exists. Further, such systems may also serve as simple models for related metallo-biochemical systems.

LINKED MACROCYCLIC LIGAND SYSTEMS

One category of this type involves structures composed of covalently linked macrocyclic ligand species capable of binding transition and other heavy metal ions. While there are now many examples of such systems incorporating two linked macrocycles [3]; examples incorporating three or more linked rings are much less common [4,5].

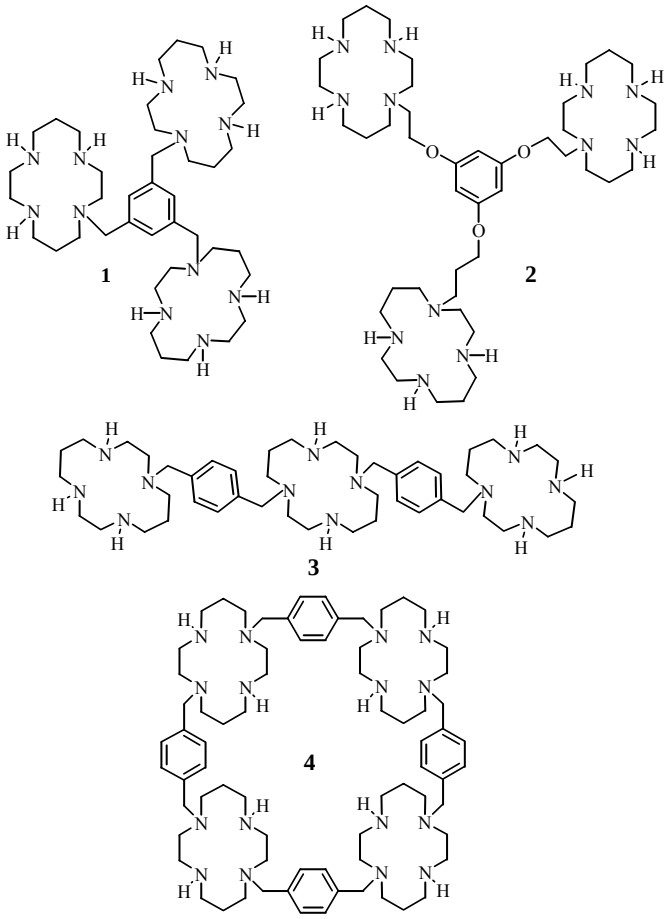
As a continuation of our previous studies in the area [5,6], we have employed *tert*-butoxycarbonyl (Boc) and

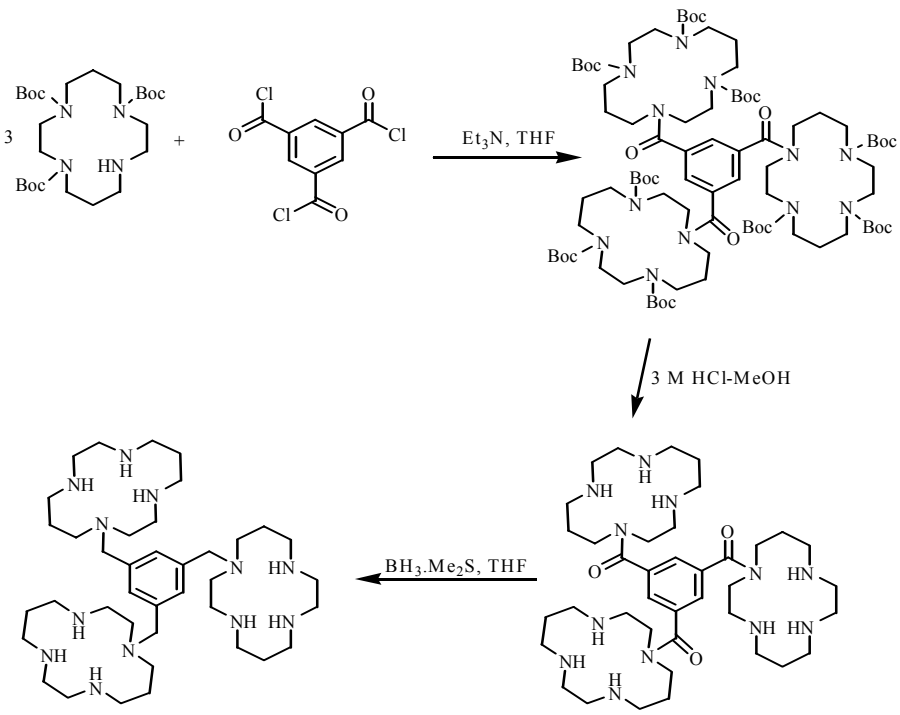
* Corresponding author. E-mail: lindoy@chem.usyd.edu.au

2,2,2-trichloroethoxycarbonyl (Troc) protecting group chemistry (for the protection of secondary amine sites) to prepare a range of linked macrocyclic rings systems incorporating three or four linked rings. The first series of this type was based on the tetraaza cyclam nucleus.

Cyclam, with its 14-membered ring, has long been shown to complex with a very wide range of metal ions, including ions with less common metal oxidation states such as nickel(III), copper(III), silver(II) and silver(III) [7]. Differentially Boc-protected cyclam derivatives[8,9] have been used as key intermediates for the synthesis of each of the linked cyclam derivatives **1**- **4** [10]. Thus, for example, the tris(N-Boc)cyclam species was employed as the cyclam-containing precursor for the preparation of **1** and **2**. The synthesis of 1,3,5-tribenzyl-linked compound **1** (Scheme 1) is a representative synthetic strategy employed by us (a brief report of the synthesis of this product using a different (non protecting group) procedure has also appeared) [11].

It was anticipated that the species **1**- **4** might yield a wide range of interesting new metal derivatives, whose properties, at least in part, reflect the relatively defined





Scheme 1

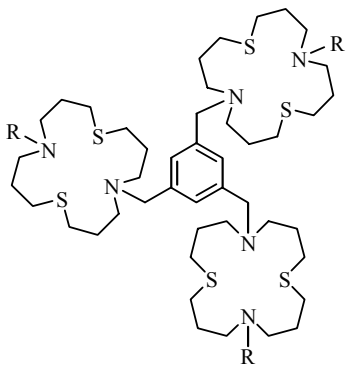
spatial and electronic environments associated with the metal binding sites in these structures. Further, the novel tetra-linked derivative **4** incorporates a large central cavity that has the potential to acting as a large receptor for inclusion of a suitable guest. Variation of the coordinated metal in such a system should provide a means for 'tuning' the electronic nature of this cavity and hence influence the electronic environment of an included guest-experiments of this type are planned for the future.

Each of **1** - **4** have been demonstrated to form complexes with some or all of the following transition and post-transition metal ions, Ni(II), Cu(II), Zn(II), Cd(II), and Pd(II), with emphasis being given to Ni(II) and Cu(II). In each case, it was postulated that the respective metal ions occupied all the available macrocyclic sites. This was confirmed to occur for the Ni(II) complex of **1** and the Cu(II) complex of **3** in solution by means of spectrophotometric titration [12,13]. Similarly, a synchrotron structure determination using a small crystal of $[Ni_3(\mathbf{1})]^{6+}$ confirms that each nickel occupies one of the three macrocyclic cavities in a low-spin, square planar coordination arrangement. Each of the macrocyclic rings adopts the stable trans-III arrangement in this case.

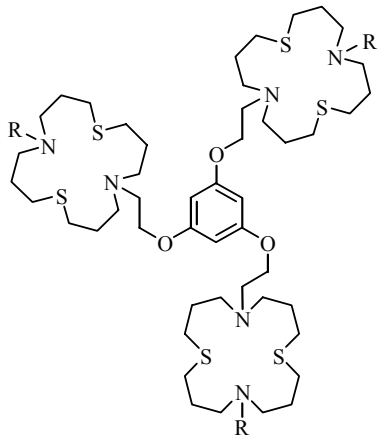
In general, where measurements were possible magnetic, electrochemical and epr studies indicate that there is little communication between individual metal centres in the complexes of **1**-**4**; this is undoubtedly a reflection of the use of *p*-xylyl groups as (extended) spacers in these four ligand systems. Using **3** as an example, cyclic voltamograms of both the trinuclear Ni(II) (low-spin) and Cu(II) complexes of this ligand system gave evidence for the presence of M(II)/M(III) as well as M(I)/M(II) couples in acetonitrile [13].

The strategies employed in the above studies have been extended to the preparation of linked mixed-donor macrocyclic systems. The metal ion binding properties of the symmetrical tri-linked species **5** and **6**, incorporating 16-membered, N_2S_2-donor macrocycles and 1,3,5-tribenzyl or phloroglucinol cores has been carried out. The complexation of all these unusual N_2S_2-ring systems with the soft metal ions silver(I) [14], palladium(II) [15] and platinum(II) [15] has been investigated, and microanalytical as well as mass spectrometric data are in accord with all three macrocyclic sites once again being occupied in each complex. Selected complexes of type $[Ag_3L](NO_3)_3$ and $[M_3L](PF_6)_6$ (M = Pd or Pt) were isolated [14,15] and their properties compared with complexes of the those of the analogously substituted single-ring macrocycles. For example, the X-ray structure of $[PdL](PF_6)_2$ (where L is a single *N*-benzylated derivative of the N_2S_2-donor macrocycle), showed that the palladium is coordinated to all four donor atoms of the macrocycle in a square planar manner. NMR titrations in the case of silver(I) [14], and spectrophotometric titrations for palladium(II) and platinum(II) [15], all confirm that 3:1 (metal:ligand) stoichiometries also occur for the complexes of the tri-linked ligands in non-aqueous solution.

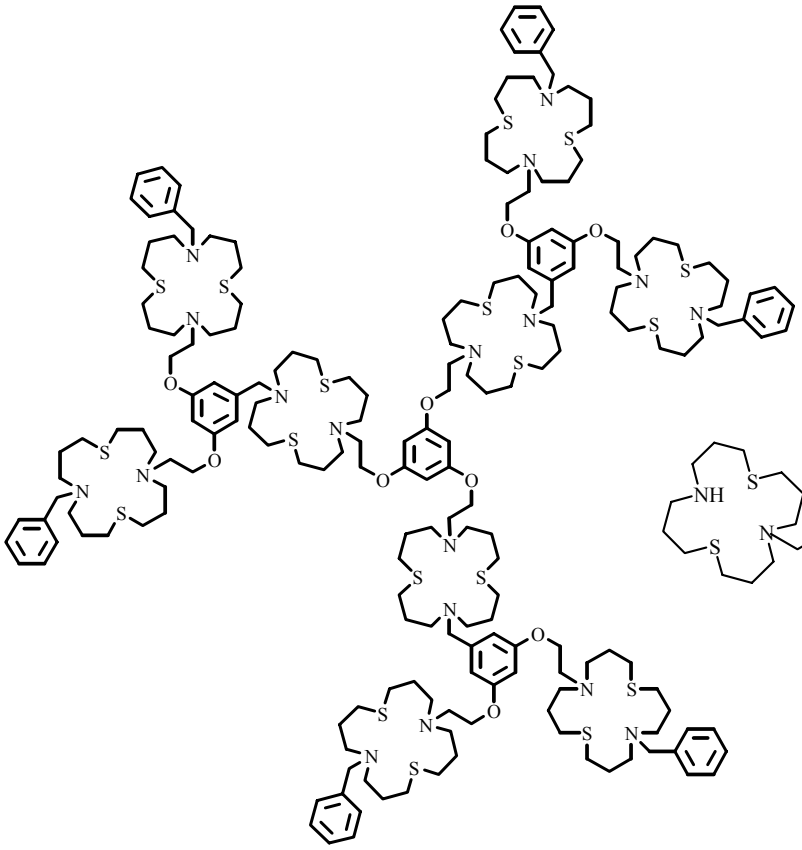
Macrocycle **6** (R = H) represents a first generation core for higher order dendritic systems and as an extension of these studies a related system incorporating nine linked N_2S_2-macrocycles has been synthesized; namely, this core has been employed for the synthesis of the second generation system **7**. Frustratingly, the palladium(II) derivative of **7** resisted mass spectral characterisation using a variety of ionisation methods (EI, FAB, MALDI or



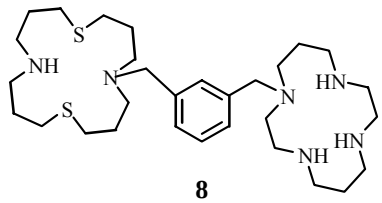
5



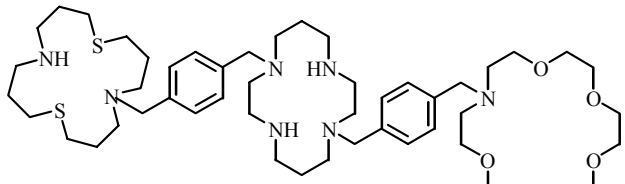
6



7



8



9

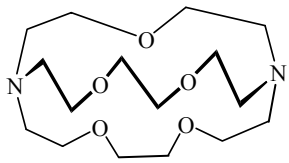
ES), perhaps reflecting the 18+ charge that is associated with a nona-nuclear cation of the type proposed. However, the binding of nine palladium(II) ions to **7** was demonstrated by means of a spectrophotometric titration involving the addition of the nine-ring dendrimer to palladium(II) chloride in acetonitrile and plotting the increase in absorbance at 300 nm; a clear endpoint at a 9:1 ratio of palladium to dendrimer was obtained [16].

Based on the above synthetic approaches, it has proved possible to prepare linked hetero-macrocyclic systems [17]. Two representative systems of this type, capable of binding two or three different metal ions simultaneously, are given by **8** and **9**. In particular, these systems were designed to take up metals selectively into the respective cavities, especially with respect to the metal's hardness or softness. Preliminary studies employing both **8** and **9** as well as other related hetero-ring systems indicate that this does occur and further studies are currently underway.

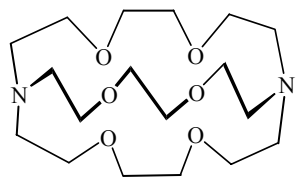
MOLECULAR CAGES

We have also been involved in the design and synthesis of new 'cage' structures containing three- dimensional cavities for selectively binding 'guest' metal ions or small molecules. Relative to two-dimensional ligands, molecular cages (cryptands) are potentially able to present a more defined receptor cavity to an incoming guest of the above type. Namely, complementarity with the guest ion or molecule may, in principle, be able to be achieved more readily due to the presence of a three-dimensional receptor and hence may lead to higher selectivity for binding a guest of interest.

The now classic study by Lehn *et al*. [18] demonstrated that a range of aza-capped flexible polyether cages, **10** and **11** are examples, show cavity size selectivity towards particular alkali and alkaline earth ions. Nevertheless, cages of this type incorporate flexible $-O(CH_2)_nO-$ (n = 2 or 3) 'links' between their donor atoms and hence are able to



10



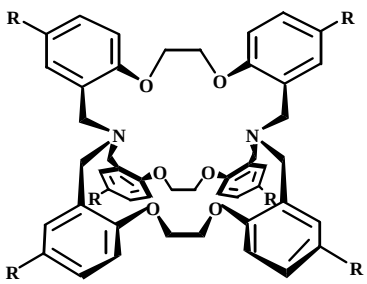
11

accommodate to some degree the requirements of an included guest. While a higher degree of rigidity may correspond to increased preorganisation for complexation and hence aid the thermodynamics of complexation for particular guests, it may also play an unfavourable role by inhibiting the entry of the guest into the cavity.

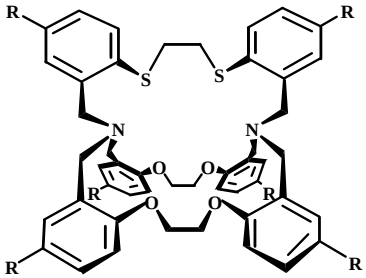
In our initial studies, we set out to investigate the effects of cage rigidity on complexation behaviour and our early studies clearly revealed that the N_2O_6-cages of type **12** (R = H or *t*-Bu) [19] and **13** [20] are poor coordinating agents for metals [21]. For example, the reasons for the poor affinity of **12** for alkali metals were probed using structural and molecular modelling (including DFT) studies [19,22] It is clear that these systems do not adopt an *endo* arrangements of the lone pairs on the nitrogen caps but rather adopt an six benzyl $-CH_2-$ groups into the central cavity such that the latter's volume is much reduced. The cavity is no longer large enough to accommodate an alkali metal ion.

In contrast to the above, we observed that when one or two of the aromatic ring-containing 'straps' linking the terminal nitrogen atoms of **13** (R = *t*-Bu) was replaced by an aliphatic strap of type $-CH_2CH_2OCH_2CH_2OCH_2CH_2-$ to yield **14** (R = *t*-Bu) and **15** (R = *t*-Bu) then uptake of individual alkali metals was observed to occur and the X-ray structure of the sodium complex of the cage incorporating two aliphatic straps confirmed that this metal ion now occupies the central cavity of the cage [22]. This behaviour is a direct consequence of the additional flexibility present in the new derivatives, which enables them to achieve *endo-endo* arrangements of the nitrogen bridgeheads (with a corresponding increase in the cavity size available for metal ion binding). A series of solvent extraction experiments (water/chloroform) involving the extraction of sodium picrate by the cages (four in all) in which the dibenzo-containing straps are successively replaced by aliphatic ones is now complete. Under the conditions employed, a progressive increase in extraction efficiency occurred as the number of aliphatic 'straps' increased from zero to three.

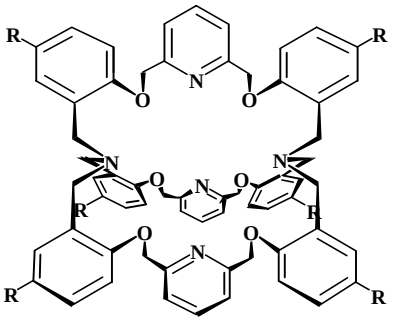
In view of the above behaviour, the studies were extended to include the synthesis of new cages in which the 'straps' in **12** were elongated to enlarge the central cavity with the aim of incorporating a suitable guest. The first product of this type incorporated three pyridyl groups between the ether heteroatoms of **12** to yield the extended cage **16** [23]. The rigidity associated with the tribenzylamine bridgeheads in this cage, once again, introduces a measure of preorganisation into this system. Molecular modelling indicated that the central cavity now approximated that of a 'slot', centred on the plane passing through the three pyridyl nitrogens (the calculations also confirmed that the *exo-exo* arrangement of the nitrogen caps remains strongly favoured). The cavity appeared ideal for insertion of flat aromatic-like rings. The X-ray structure of this compound, recrystallised from benzene, shows that



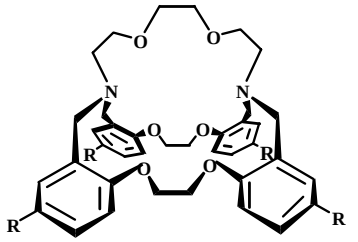
12



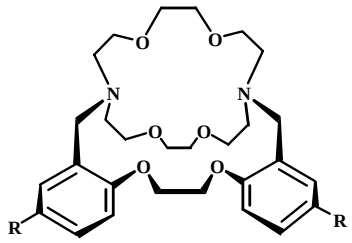
13



16



14



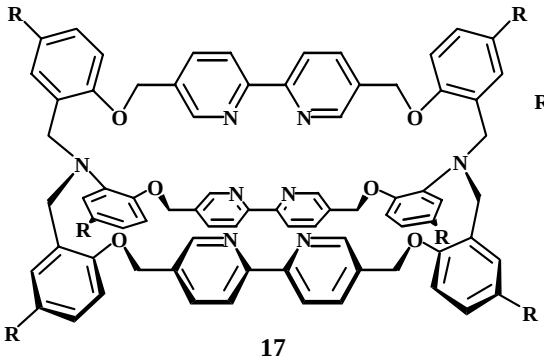
15

the bridgehead methylene groups 'intrude' somewhat into the cavity such that it is significantly truncated [24]. In this case a benzene guest is encapsulated centrally in this cavity, being held in position by 'T'-shaped, π-stacking interactions of the edge-to-face type between the pyridine rings (orientated 'sidewise') of the host and alternate hydrogens on the benzene guest. The latter is aligned symmetrically with respect to the overall pseudo 3-fold symmetry of the cage.

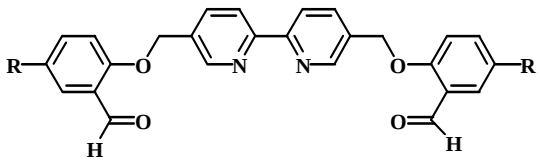
The diameter of the cavity, as defined by the positions of the heterocyclic nitrogen atoms, suggested that that this cage was ideal for accepting a phloroglucinol guest, with the latter being suitably orientated to undergo hydrogen bonding, via its phenol hydrogens, to the trigonally orientated nitrogens. Accordingly, **16** (R = *t*-Bu) was found to solubilise phloroglucinol in dichloromethane and chloroform and NMR evidence showed that it interacts in a 1:1 ratio with this triphenol. The NMR data in are in accord with this guest occupying the central cavity of **16** as postulated above. Molecular mechanics and semi-empirical molecular orbital (AM1) calculations also supported the formation of such a host-guest complex. Further evidence for the role of hydrogen bonding in stabilising the above host-guest complex was obtained by repeating the experiment using the corresponding cage in which the three pyridyl groups of **16** had been replaced by three *m*-xylyl groups. In contrast to the previous situation, there was no evidence for host-guest formation when this new cage was mixed with phloroglucinol; that is, the respective ^{1}H NMR chemical shifts for this cage were unaffected on addition of this potential guest. Significantly, the NMR induced chemical shift data indicate that **16** (R = *t*-Bu) interacts more strongly with phloroglucinol relative to a range of other mono-, di- and tri-phenolic derivatives whose steric properties make them less than ideal for simultaneous binding to the trigonally disposed pyridyl nitrogens of **16**. Clearly, both the steric and electronic properties of **16** result in it being an ideal (and selective) synthetic receptor for phloroglucinol.

As a direct extension of the above studies it was decided to expand the available cavity in the N_3O_2-cage in another way; namely, by insertion of 2,2'-bipyridyl moieties in the centre of each 'strap' to yield an extended cage of type **17** (R = H or *t*-Bu) [25]. While this product was initially synthesised in small yield by a conventional 'multi-step' procedure, it was subsequently shown to be best obtained by means of a metal template procedure involving the reductive amination of three equivalents of the dialdehyde **18** in the presence of iron(II), cobalt(II) or nickel(II), an excess of ammonium acetate, and sodium cyanoborohydride in acetonitrile. The ammonium ion ultimately forms the bridgehead nitrogens by means of sequential imine condensation and reduction steps.

Both derivatives of type **17** readily form 1:1 complexes with a number of transition and post-transition metal ions. Initial molecular modelling suggested that **17** would interact with a single octahedral metal ion such that a helical twist is induced. X-ray structure determinations on both the free cage and its manganese(II), iron(II), nickel(II) and copper(II) metal complexes have been determined. All structures show a triple helical twist, with the structure of the nickel(II) derivative being given in Figure 1. Intriguingly, the structures fall into two categories - those in which the bridgehead nitrogen lone-pairs are *exo* nickel(II) and copper(II)] and those in which they are *endo* [manganese(II) and iron(II)]. For the systems showing *exo-exo* configurations of their lone pairs, the central metal ion



17



18

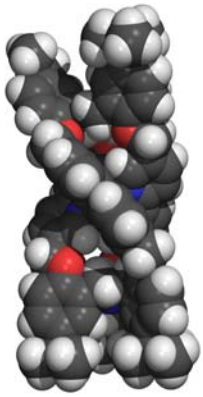


Fig. 1. X-ray structure of the triple helical cation, $[Fe(\mathbf{17})]^{2+}$.

is seen to induce a helical twist that extends about 22 Å along the axial length of the molecule (around 26 Å for each strand when measured around the outside of the helix). Such behaviour is unusual relative to other helical structures reported recently in which multiple metal-ion coordination is required to induce a helical twist along the length of the system [1].

SELF-ASSEMBLED SYSTEMS

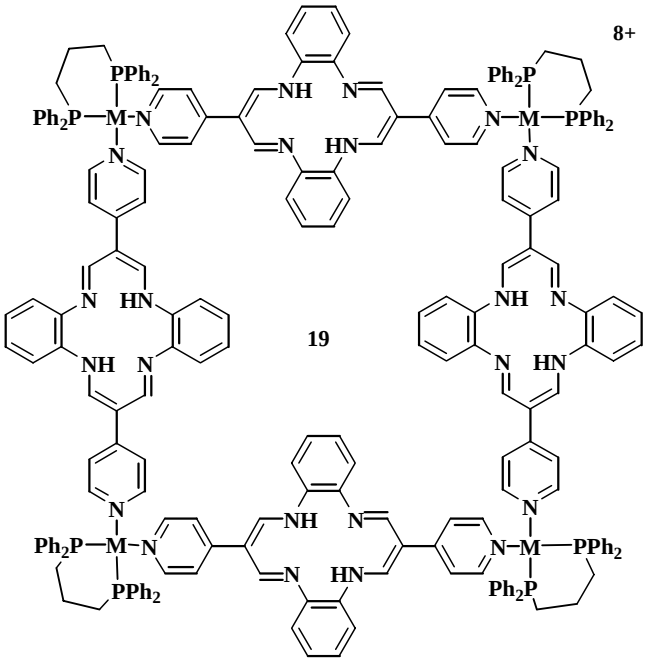
A Molecular Square

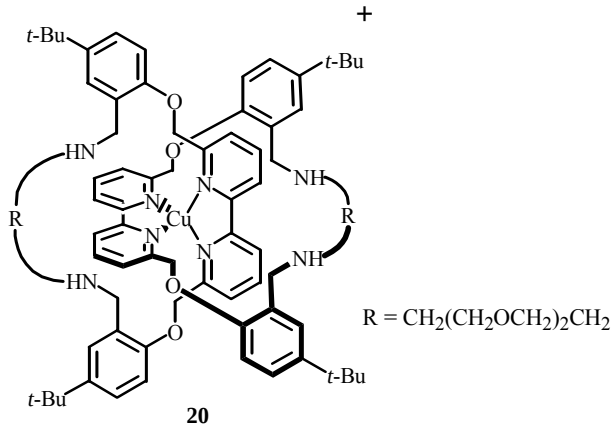
In work in progress we have investigated the prospect of inducing the self-assembly process given in Scheme 2 to produce the supramolecular square **19** [26]. Accordingly, the precursor to the 'corner unit', [Pt(1,3-bis(diphenylphosphino)propane)$(NO_3)_2$], and the required dipyridyl-substituted, tetraaza macrocycle (see **19**) were mixed in dichloromethane in a 1:1 ratio and the reaction solution monitored by ^{31}P NMR. Under the conditions employed, three main phosphorus-containing products were occurrence of more than one product in some instances [29,30] when using generally smaller side units (such as 4,4'-bipyridine) in analogous syntheses.

In the present study, NMR diffusion measurements indicated that the molecular weight of the major product was in the range expected for the molecular weight of the square. However, attempts to isolate single crystals of this product for X-ray confirmation of its structure have so far eluded us. Nevertheless, suitable crystals of a second product were obtained and its X-ray structure showed that it was the interesting metallocycle formed between two corner and two side units, with the macrocyclic sides bent such that the overall geometry of the adduct ellipsoidal, terminated at each end by a Pt(1,3-bis(diphenylphosphino)propane) group. Although not yet confirmed, it seems likely that the remaining product is the analogous cyclic trimer since such as has been documented to form in equilibrium with the target molecular square in the earlier studies [29-31].

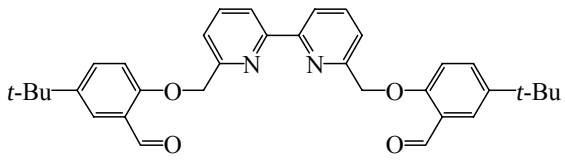
Synthesis of Catenanes

In initial studies it has proved possible to demonstrate the formation of the copper-containing catenane **20** [25]. Reaction of two molar equivalents of dialdehyde **21** to one





20



21

of $[Cu(CH_3CN)_4]^+$ in methanol followed by the dropwise addition of a solution of two equivalents of $NH_2CH_2(CH_2OCH_2)_2CH_2NH_2$ to this bright yellow solution resulted in Schiff base condensation occurring. The course of the reaction was monitored by electrospray mass spectrometry and the formation of a product corresponding to the target tetraimine catenane was indicated. This product was then reduced *in situ* by the addition of sodium cyanoborohydrate. While the above technique indicated the clean formation of a complex of stoichiometry corresponding to the required catenane, the latter proved difficult to isolate in pure form.

Based on molecular modelling studies at the semi-emperical level, it was predicted that the use of the corresponding bis-dialdehyde derived from *p*-salicylaldehyde would provide a more favourable orientation for ring closure of the aldehyde groups on copper(I) complex formation. The bis-ligand copper complex of this bis-dialdehyde was isolated as a deep red crystalline solid and its X-ray structure confirmed the above prediction, at least for the solid state. The presence of π-stacking of the aromatic rings in this complex clearly aids orientation of the aldehyde groups for catenane formation over the other two possibilities -namely, the formation of a single large ring or of two non-interlinked rings.

Comparative semi-empirical calculations indicated that 1,6-diaminehexane appeared of ideal length to span the adjacent aldehyde groups in this precursor for catenane formation. Accordingly, this diamine was employed him for the reaction illustrated in Scheme 2. In this case crystals of the product complex were obtained and the formation of the required catenane was confirmed by X-ray diffraction. The π-stacking observed in the precursor bis-dialdehyde complex is preserved in this product and clearly plays a significant role in the success of the reaction procedure.

ACKNOWLEDGMENTS

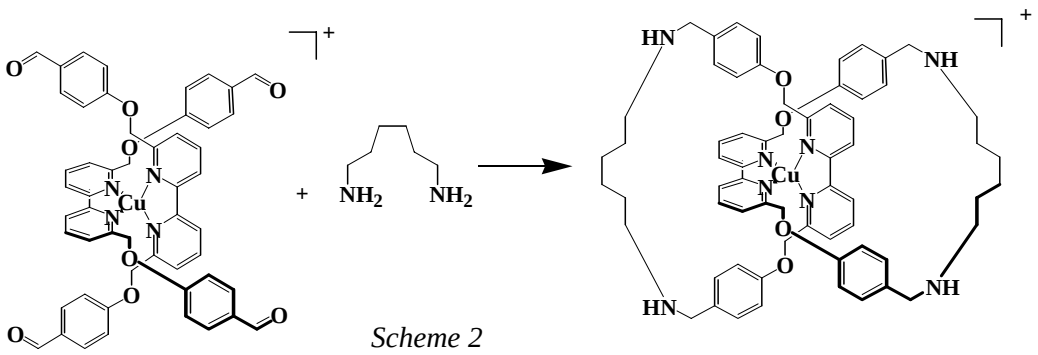
The author sincerely thanks his many students and collaborators, both past and present, for their contributions to the work outlined in this paper. Their names are given in the references cited in the text. The author also thanks the Australian Research Council for financial support and especially thanks the Iranian Chemical Society for the opportunity to visit Iran during which the material discussed above was presented as a lecture to the Second Seminar of Macrocyclic Chemistry Iranian Chemical Society May 3-4, 2003.

REFERENCES

[1] L.F. Lindoy, M. Atkinson. 'Self-assembly in Supramolecular Chemistry'. (Royal Society for Chemistry, Cambridge 2000).

[2] L.F. Lindoy. 'The Chemistry of Macrocyclic Ligand Complexes' (Cambridge University Press: 1989).

[3] L.F. Lindoy, Adv. Inorg. Chem. 45 (1998) 75; J. D. Chartres, L.F. Lindoy, G.V. Meehan, Coord. Chem. Rev. 216-217 (2001) 249.



Scheme 2

[4] L. Spiccia, B. Graham, M.T.W. Hearn, G. Lazarev, B. Moubaraki, K.S. Murray, E.R.T. Tiekink, J. Chem. Soc., Dalton Trans. (1997) 4089; B. Graham, M.J. Grannas, M.T.W. Hearn, C.M. Kepert, L. Spiccia, B.W. Skelton, A.H. White, Inorg. Chem. 39 (2000) 1092; E. Kimura, S. Aoki, T. Koike. M. Shiro, J. Am. Chem. Soc. 119 (1997) 3068; E. Kimura, M. Kikuchi, H. Kitamura, T. Koike, Chem. Eur. J. 5 (1999) 3113; S. Sun, J. Saltmarsh, S. Mallik, K. Thomasson, Chem. Commun. (1998) 519; P.V. Bernhardt, E.J. Hayes, J. Chem. Soc., Dalton Trans. (1998) 3539; K. Wang, X. Han, R.W. Gross, G.W. Gokel, J. Chem. Soc., Chem. Commun. (1995) 641; E. Abel, G.E.M. Maguire, O. Murillo, I. Suzuki, S.L. De Wall, G.W. Gokel, J. Am. Chem. Soc. 121 (1999) 9043.

[5] I.M. Atkinson, D.M. Boghai, B. Ghanbari, L.F. Lindoy, G.V. Meehan, V. Saini, Aust. J. Chem. 52 (1999) 351.

[6] A.M. Groth, L.F. Lindoy, G.V. Meehan, J. Chem. Soc. Perkin Trans. 1, (1996) 1553; I.M. Atkinson, A.M. Groth, L.F. Lindoy, O.A. Matthews, G.V. Meehan, Pure & Appl. Chem. 68 (1996) 1231; J. D. Chartres, A.M. Groth, L.F. Lindoy, M.P. Lowe, G.V. Meehan, J. Chem. Soc. Perkin Trans. 1, (2000) 3444.

[7] A. De Blas, G. De Santis, L. Fabbrizzi, M. Licchelli, P. Pallavicini, Pure Appl. Chem. 65 (1993) 455.

[8] B. Boitrel, B. Andrioletti, M. Lachkar, R. Guilard, Tetrahedron Lett. 36 (1995) 4995.

[9] S. Brandes, C. Gros, F. Denat, P. Pullumbi, R. Guilard, Bull. Soc. Chim. Fr. 133 (1996) 65.

[10] Y. Dong, L.F. Lindoy, Aust. J. Chem. 54 (2001) 291.

[11] Shuguang Sun, J. Saltmarsh, S. Mallik, K. Thomasson, Chem. Commun. (1998) 519.

[12] Y. Dong, L.F. Lindoy, P. Turner, G. Wei, Dalton Trans. (2004) in press.

[13] Y. Dong, L.F. Lindoy, Coord. Chem. Rev. 245 (2003) 11.

[14] J.D. Chartres, A.M. Groth, L.F. Lindoy, G.V. Meehan, J. Chem. Soc., Dalton Trans. (2002) 371.

[15] I.M. Atkinson, J.D. Chartres, A.M. Groth, L.F. Lindoy, M.P. Lowe, G.V. Meehan, B.W. Skelton, A.H. White, J. Chem. Soc., Dalton Trans. (2001) 2801.

[16] I.M. Atkinson, J.D. Chartres, A.M. Groth, L.F. Lindoy, M.P. Lowe, G.V. Meehan, Chem. Commun. (2002) 2428.

[17] J.D. Chartres, L.F. Lindoy, G.V. Meehan, unpublished work.

[18] B. Dietrich, J.-M. Lehn, J.P. Sauvage, J. Chem. Soc., Chem. Commun. (1970) 1055; J.-M. Lehn, J.P. Sauvage, J. Am. Chem. Soc. 97 (1975) 6700; B. Dietrich, J.-M. Lehn, J.P. Sauvage, J. Blanzat, Tetrahedron 29 (1973) 1629.

[19] I.M. Atkinson, L.F. Lindoy, O.A. Matthews, G.V. Meehan, A.N. Sobolev, A.H. White, Aust. J. Chem. 47 (1994) 1155.

[20] I.M. Atkinson, D.C.R. Hockless, L.F. Lindoy, O.A. Matthews, G.V. Meehan, B.W. Skelton, A.H. White, Aust. J. Chem. 53 (2000) 799.

[21] I.M. Atkinson, A.M. Groth, L.F. Lindoy, O.A. Mathews, G.V. Meehan, Pure and Appl. Chem. 68 (1996) 1231.

[22] K.R. Adam, I.M. Atkinson, J. Kim, L.F. Lindoy, O.A. Matthews, G.V. Meehan, F. Raciti, B.W. Skelton, N. Svenstrup, A.H. White, J. Chem. Soc., Dalton Trans. (2001) 2388.

[23] I.M. Atkinson, A.R. Carroll, R.J.A. Janssen, L.F. Lindoy, O.A. Matthews, G.V. Meehan, J. Chem. Soc., Perkin Trans. 1, (1997) 295.

[24] R.J.A. Janssen, L.F. Lindoy, O.A. Matthews, G.V. Meehan, A.N. Sobolev, A.H. White, J. Chem. Soc., Chem. Commun. (1995) 735.

[25] L.F. Lindoy, G.V. Meehan, J.R. Price, D.F. Perkins, unpublished work.

[26] G. Wei, J. Beves, L.F. Lindoy, unpublished work.

[27] M. Fujita, J. Yazaki, K. Ogura, J. Am. Chem. Soc., 112 (1990) 5645; M. Fujita, J. Yazaki, K. Ogura Tetrahedron Lett. 32 (1991) 5589; M. Fujita, J. Yazaki, K. Ogura, Chem. Soc. Jp., Chem. Lett. (1991) 1031.

[28] P.J. Stang, D.H. Cao, J. Am. Chem. Soc. 116 (1994) 4981.

[29] S. Leininger, B. Olenyuk, P. Stang, Chem. Rev. 100 (2000) 853.

[30] M. Schweiger, S.R. Seidel, A.M. Arif, P.J. Stang, Inorg. Chem. 41 (2002) 2556; M. Fujita, K. Ogura, Coord. Chem. Rev. 148 (1996) 249.

[31] A. Sautter , D. Schmid, G. Jung, F. Wurthner, J. Am. Chem. Soc. 123 (2001) 5424.