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# Supramolecular confinement of $C_{60}$, $S_8$, $P_4Se_3$ and toluene by metal(II) macrocyclic complexes

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Treatment of $S_8$ or $P_4Se_3$ with {5,7,12,14-tetramethyldibenzo[*b*,*i*]-1,4,8,11-tetraaza[14]annulenato}metal(II) [= M(TMTAA)] in carbon disulfide afforded the solid state 1 : 2 inclusion complexes [$(S_8)${M(TMTAA)}$_2$], M = Ni or Cu (isostructural), or [$(P_4Se_3)${Ni(TMTAA)}$_2$]. A toluene inclusion complex [$(MeC_6H_5)$Ni(TMTAA)] resulted from the recrystallisation of [Ni(TMTAA)] from toluene. Recrystallisation of [Ni(TMTAA)] from $CS_2$–hexane resulted in the unsolvated complex. All complexes are comprised of interlocking dimers of the macrocycle, and in the inclusion complexes these dimers act as homotopic divergent receptors either through the methyl- or phenyl-lined surfaces. Solid state 1 : 1 $C_{60}$ inclusion complexes of [M(TMTAA)], M = Cu or Zn, have individual macrocycle molecules acting as heterotopic divergent receptors.

## Introduction

Non-planar metal macrocycles based on arrays of unsaturated units for which there are many[1] have the potential to associate *via* weak intermolecular forces with molecules (or ions), especially if the interacting surfaces have curvature complementarity. A readily available macrocycle formed from condensation of 1,2-diaminobenzene with acetylacetone in the presence of nickel(II) acetate, notably {5,7,12,14-tetramethyldibenzo[*b*,*i*]-1,4,8,11-tetraaza[14]annulenato}nickel(II) [Ni(TMTAA)], falls into this category. It adopts a rigid saddle shape[2,3] due to the otherwise unfavourable non-bonding interactions between the hydrogen atoms on methyl groups and the *o*-hydrogen atoms on the aromatic rings, and potentially can act as a divergent heterotopic receptor. Nickel can be removed from the macrocycle and be replaced by many other metal ions.[3]

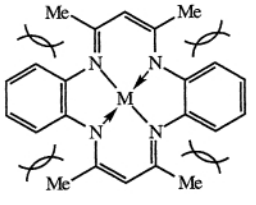
We recently established the ability of [Ni(TMTAA)] to bind a range of disparate globular molecules in two ways. First, as a divergent receptor with $C_{60}$ in a 1 : 1 complex where there is a fullerene cage perched in each cavity in an infinite zigzag array.[2] Secondly, for the smaller globular molecules 1,2-dicarbadodecaborane(12) (= *o*-$C_2B_{10}H_{12}$) and the phosphorus sulfide, $P_4S_3$, the macrocycle self associates through aromatic faces into dimers. These dimers now act as divergent homotopic receptors, the complexes having a 1 : 2 ratio of guest to host species.[2] Other studies have demonstrated the ability of $C_{60}$ and *o*-$C_2B_{10}H_{12}$ to bind to cyclotriveratrylene which is also a rigid non-planar molecule, albeit bowl shaped[4–7] in contrast to the saddle structure of [Ni(TMTAA)]. Similarly bowl shaped calix[5]arene forms complexes with the same cage molecules.[8,9] The complex of [Ni(TMTAA)] with $P_4S_3$ is the only authenticated inclusion complex of a Group 15 chalcogenide cage species.

We now report new findings on the supramolecular/host–guest chemistry of the nickel(II) macrocycle, notably: (i) the heavier Group 15 chalcogenide $P_4Se_3$ forms a 1 : 2 inclusion complex with [Ni(TMTAA)]; (ii) $S_8$ also gives a 1 : 2 inclusion complex; (iii) unsolvated [Ni(TMTAA)] as well as a toluene inclusion complex of [Ni(TMTAA)] exist in the solid state with a different extended motif based on macrocyclic dimers associated through methyl-lined faces. These findings further highlight the adaptability of [Ni(TMTAA)] in self dimerisation in the confinement of globular molecules involving inherently weak interactions, as well as the confinement of a planar molecule. The only other related studies of $P_4E_3$ species are the formation of [$Ni(P_4E_3)\{N(CH_2CH_2PPh_2{}^{-2})_3\}$] (E = S[10] or Se[11]) where the nickel(II) centre is attached strongly to the unique P of the cage. Other attempts to complex this cage resulted in cluster fragmentation.[12] We also report the preparation and structures of the supramolecular complexes [$(C_{60})$-M(TMTAA)], M = Cu or Zn, and [$(S_8)${Cu(TMTAA)}$_2$] which are isostructural with the nickel(II) analogues, as well as the preparation and structure determination of unsolvated weakly associated, dimeric [Zn(TMTAA)].

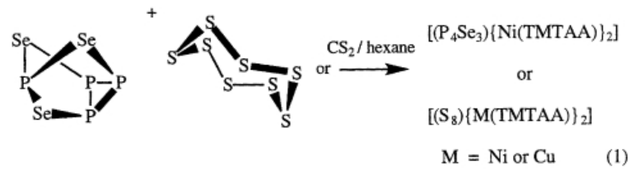
## Results and discussion

### $P_4Se_3$ and $S_8$ complexes

Slow evaporation of $CS_2$–hexane solutions of the macrocyclic complex with $P_4Se_3$ or $S_8$ gave the discrete crystalline 1 : 2 complexes [$(P_4Se_3)${Ni(TMTAA)}$_2$] and [$(S_8)${Ni(TMTAA)}$_2$] respectively, eqn. (1). The 1 : 2 complex is favoured even for an excess of the cage, and indeed these conditions are best for



= M(TMTAA)



(1)

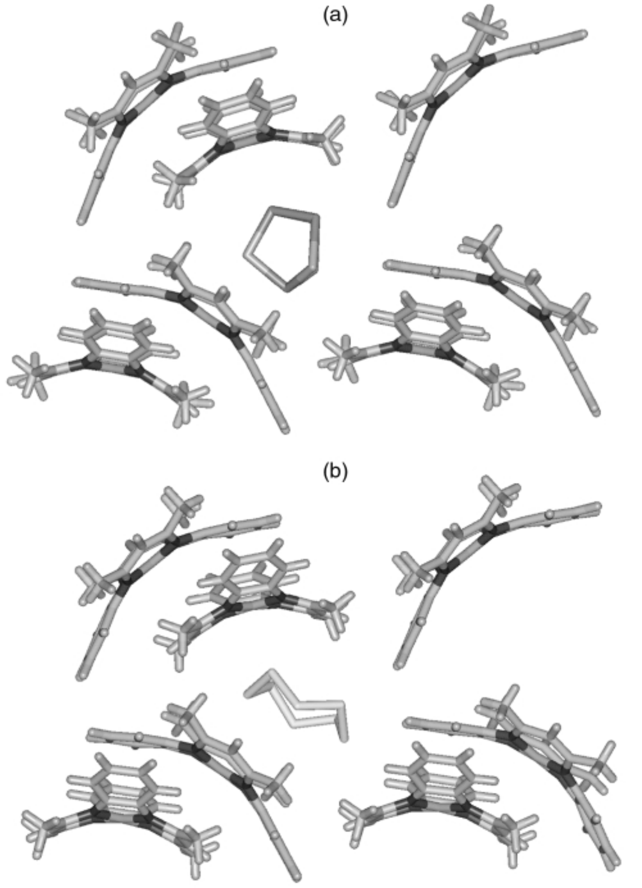


**Fig. 1** Projection of the supramolecular interplay found in (a) [$(P_4Se_3)$-{Ni(TMTAA)}$_2$] and (b) [$(S_8)${Ni(TMTAA)}$_2$].

driving the precipitation of the complex from solution, the complex being more soluble than [Ni(TMTAA)] itself. Similarly, [$(S_8)${Cu(TMTAA)}$_2$] crystallised from $CS_2$–hexane solutions containing an excess of $S_8$ over [Cu(TMTAA)].

The complex [$(P_4Se_3)${Ni(TMTAA)}$_2$] crystallises in the space group *Pnma* and is isomorphous with the $P_4S_3$ analogue.[2] Supermolecules of {Ni(TMTAA)}$_2$ are locked through their pendant aromatic rings. The $P_4Se_3$ cages are cradled within the methyl-lined faces of two supermolecules in a bent arrangement, with additional contacts to hydrogen atoms of other [Ni(TMTAA)] dimers, which also involve weak intermolecular forces, Fig. 1. The formation of dimers of the macrocycle is driven by the complementarity of curvature of the two components, as well as by nickel–π-arene interactions (see below). There are no inter-cage contacts and $P_4Se_3$ is disordered over two sites related by a mirror plane perpendicular to the crystallographic mirror plane passing through Se–P–Se. At 173 K $P_4Se_3$ is apparently disordered over the two sites in a 75:25 ratio but was difficult to resolve. At 123 K the disorder was at a 90:10 ratio and refined giving the major component well resolved and yielding meaningful contact distances. The major site has the same orientation as the major component of $P_4S_3$ in [$(P_4S_3)${Ni(TMTAA)}$_2$].[2]

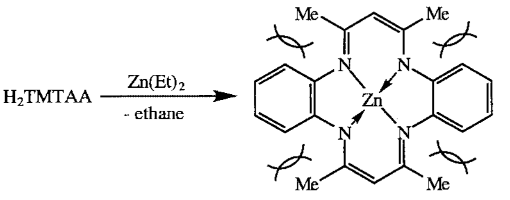
In the dominant orientation a selenium atom and the unique phosphorus are closest to the metal centre of one [Ni(TMTAA)] molecule at 3.26 and 3.72 Å respectively. A phosphorus in the $P_3$ ring of $P_4Se_3$ is 3.18 Å from the metal centre in the second [Ni(TMTAA)] molecule. The other two phosphorus atoms of the $P_3$ ring are 2.97 and 3.02 Å from a methyl hydrogen of this second [Ni(TMTAA)]. The third and fourth [Ni(TMTAA)] molecules have closest contacts at 3.49 (phosphorus in $P_3$ ring to phenyl hydrogen) and 3.22 Å (one of the two adjacent selenium atoms to phenyl hydrogen).

The complex [$(S_8)${Ni(TMTAA)}$_2$] crystallises in the space group $P2_1/c$, and therefore is not isomorphous with [$(P_4S_3)$-{Ni(TMTAA)}$_2$], although it exhibits the same structural motif with two supermolecules of {Ni(TMTAA)}$_2$, locked through their pendant aromatic rings, associated with an $S_8$ molecule, Fig. 1. There are no inter-$S_8$ contacts and unlike the structures of the $P_4Se_3$ and $P_4S_3$ complexes there is no disorder. The closest sulfur to metal centre distances are 3.32 and 3.52 Å to the separate [Ni(TMTAA)] molecules respectively. The next nearest sulfur atom is 4.04 Å from the first [Ni(TMTAA)] molecule. Methyl hydrogen distances on these two [Ni(TMTAA)] molecules range from 2.76 to 3.67 Å for the sulfur atoms in the $S_8$ ring. Three other [Ni(TMTAA)] molecules have hydrogen atoms within 3.6 Å of sulfur atoms, two with phenyl hydrogens closest at 3.11 and 3.21 Å and the third with a methyl hydrogen at 3.21 Å.

The complex [$(S_8)${Cu(TMTAA)}$_2$] crystallised in an isostructural form to [$(S_8)${Ni(TMTAA)}$_2$] described above. The $S_8$ again lies in the phenyl-lined cavities of two [Cu(TMTAA)] molecules and the closest sulfur to metal centre distances are 3.34 and 3.50 Å to the separate [Cu(TMTAA)] molecules. The Cu atoms are displaced by 0.03 Å from the $N_4$ plane towards the phenyl-lined surface.

### Unsolvated [M(TMTAA)] (M = Ni or Zn) and the toluene solvate of [Ni(TMTAA)]

The complex [Ni(TMTAA)] can be crystallised from $CHCl_3$ as discrete monomeric units.[13] Another report[14] gives [Ni(TMTAA)] isomorphous with [Cu(TMTAA)][15] where the macrocyclic complex self-associates through the methyl-lined surfaces as well as through the aromatic faces, as described in the $S_8$ and $P_4Se_3$ inclusion complexes above. The complex [Zn(TMTAA)] crystallises as dimers from toluene in the space group $P2_1/c$ isomorphous to the [Ni(TMTAA)][14] and [Cu(TMTAA)][15] dimers. It was prepared as a hydrolytically unstable complex from the reaction of diethylzinc with the metal free macrocycle, [$H_2$TMTAA], in toluene under dry, anaerobic conditions, eqn. (2).



(2)

Red crystals of [{Zn(TMTAA)}$_2$] were deposited from toluene solutions and in the solid state the complex forms discrete dimers with zinc atom A situated over the pentanediiminato ring and displaced 0.32 Å out of the $N_4$ plane toward the phenyl-lined surface, Fig. 2. Zinc atom B is situated over a phenyl group of the other Zn(TMTAA) molecule and is displaced 0.20 Å again towards the phenyl-lined surface. The dimer has the same arrangement as for {Ni(TMTAA)}$_2$ dimers in the $P_4Se_3$ and $S_8$ complexes described above. The structure extends into columns of [{Zn(TMTAA)}$_2$] dimers through the interlocking of the methyl-lined surfaces. One interaction consists of a symmetrical overlay of the pentanediiminato rings over the $ZnN_4$ plane with the central CH immediately above zinc atom A (of a dimer as described above). The other interaction consists of an offset of the methyl-lined surfaces related to the $ZnN_4$ plane such that a methyl hydrogen lies above zinc atom B and the central CH.

A third form of [Ni(TMTAA)] can be crystallised from methanol or $CS_2$–hexane, Fig. 3. The asymmetric unit consists of two molecules of [Ni(TMTAA)] arranged such that one of the phenyl rings of one molecule points into the phenyl-lined face of the other in a pseudo host–guest relationship. One of the *meta* aromatic hydrogen atoms of the "guest" molecule

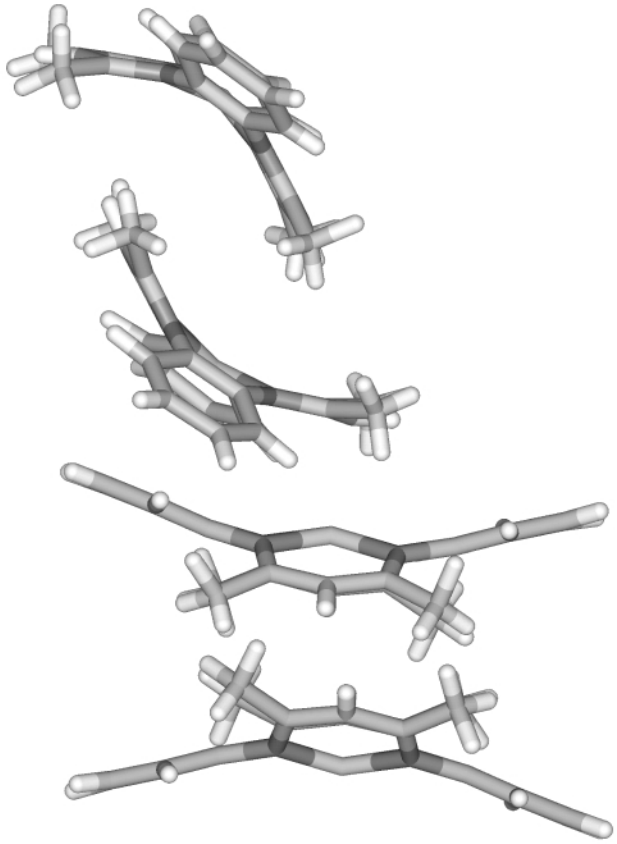


**Fig. 2** Intramolecular interactions in [{Zn(TMTAA)}$_2$].

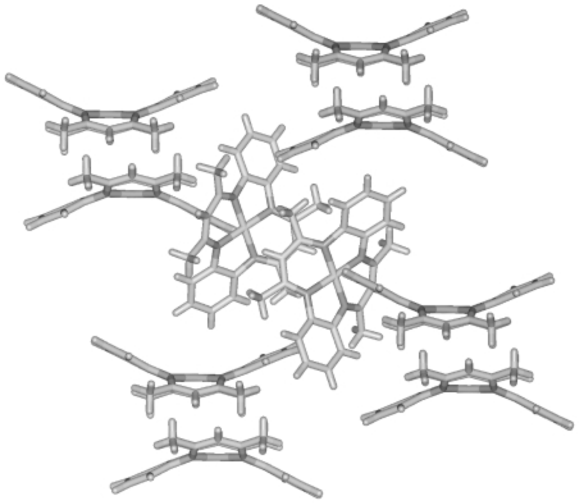


**Fig. 3** Projection of the supramolecular interplay found in [Ni(TMTAA)].

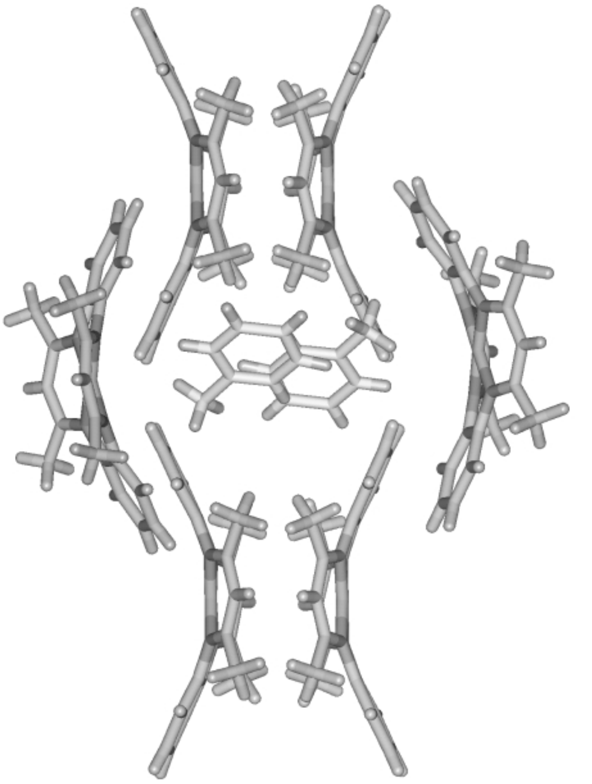


**Fig. 4** Projection of the supramolecular interplay found in [(MeC$_6$H$_5$)-Ni(TMTAA)].

makes close contact with the "host" nickel atom (H $\cdots$ Ni 2.92 Å) while the other is nearest one of the nitrogen atoms (H $\cdots$ N, 3.43 Å). The closest contact between the molecules, however, is between one of the pentanediimine methyl groups of the "guest" and the *meta* aromatic carbon atoms of the "host" ($CH_3 \cdots C$ 2.86, 3.04; $CH_3 \cdots C$ 3.41, 3.55 Å). To maximise this interaction the phenyl of the "host" is tilted 3.05° toward the "guest" methyl. These units stack together through an interlocking of the methyl-lined surfaces of each [Ni(TMTAA)] molecule. The molecules are slightly offset with the central hydrogen in the pentanediimine group making closest contact to the nickel atom at 3.06 Å. This interaction is within the extremes of the two similar interlocks described for [{Zn(TMTAA)}$_2$] above. The "host–guest" and dimer interactions for [Ni(TMTAA)] form the basis of two dimensional sheets of the pentanediimine wrapped dimers. These sheets in turn stack together in an alternating fashion so that the gross dimples in each sheet are complemented by those in alternating sheets. Although many points of van der Waals contact are made between molecules in alternating sheets, they do not appear significant in this context.

The complex [Ni(TMTAA)] crystallised from toluene produces the toluene inclusion complex containing two [Ni(TMTAA)] molecules associated through the methyl lined surfaces, Fig. 4. Toluene molecules are perched in the exposed phenyl lined cavity of the [{Ni(TMTAA)}$_2$] dimer with closest approaches being for one hydrogen atom, *ortho* to the methyl group of toluene, at 3.21 (to nickel atom), 3.11 (to nitrogen) and 3.11 Å (to phenyl carbon bound to nitrogen, the centre of the C $\cdots$ N bond being 3.03 Å from the hydrogen atom). One methyl hydrogen atom of the toluene is 3.81, 3.51 and 3.11 Å from the nickel atom and the nitrogen and carbon atoms diagonally opposed to the above nitrogen/carbon pair respectively. Toluene has hydrogen–carbon distances of less than 3.5 Å to two other [Ni(TMTAA)] molecules which comprise the walls of the channel within the extended structure. Within the channel toluene molecules are almost coplanar and alternate in methyl group orientation but are offset. Closest approaches are for hydrogen–hydrogen at 2.82 Å and carbon–carbon at 3.39 Å.

## $C_{60}$ Complexes

The complexes [(C$_{60}$)M(TMTAA)] (M = Ni, Cu or Zn) form on mixing [M(TMTAA)] and C$_{60}$ solutions (toluene– or CS$_2$–hexane) with either equimolar or up to 2 : 1 equivalent ratios of reagents, eqn. (3).

$$[\mathrm{M(TMTAA)}] + \mathrm{C_{60}} \xrightarrow[\text{or toluene–hexane}]{\mathrm{CS_2}\text{–hexane}} [(\mathrm{C_{60}})\mathrm{M(TMTAA)}] \quad (3)$$

The complex [(C$_{60}$)Cu(TMTAA)] crystallises from CS$_2$–hexane in the monoclinic space group $P2_1/n$, isostructural to the previously reported [(C$_{60}$)Ni(TMTAA)]$^2$ and [(C$_{70}$)-

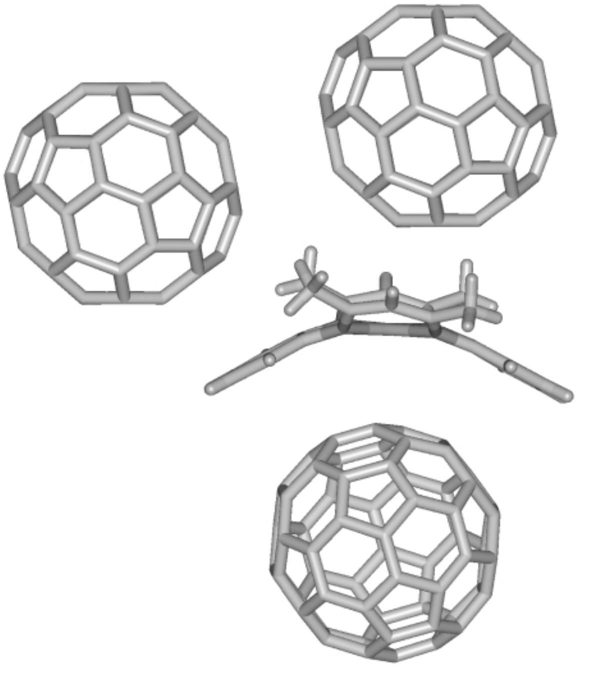


**Fig. 5** The $C_{60}$ interactions with Cu(TMTAA) in [($C_{60}$)Cu(TMTAA)].

Ni(OMTAA)][16] (OMTAA = 2,3,6,8,11,12,15,17-octamethyldibenzo[*b*,*i*]-1,4,8,11-tetraaza[14]annulene). The structure consists of sheets of $C_{60}$ (five close $C_{60}$ geometric centre to centre distances at 9.96–10.08 Å and a sixth fullerene at 12.82 Å) isolated by layers of Cu(TMTAA) such that each $C_{60}$ molecule lies in a phenyl-lined surface of one Cu(TMTAA) and a methyl-lined surface of another Cu(TMTAA) molecule with a third Cu(TMTAA) molecule interacting through a smaller surface defined by a phenyl and two methyl groups, Fig. 5. The closest contacts between $C_{60}$ and the copper centres are at 3.18 and 3.37 Å for the phenyl- and methyl-lined surfaces respectively. The Cu atoms are displaced from the $N_4$ plane of the macrocycle by 0.04 Å towards the phenyl-lined surface (*cf.* displacement in [{Cu(TMTAA)}$_2$],[15] 0.069 and 0.071 Å towards the phenyl-lined surface).

The complex [Zn(TMTAA)] also reacts with $C_{60}$ and although suitable single crystals of [($C_{60}$)Zn(TMTAA)] could not be obtained the powder diffraction pattern indicated a material isomorphous with [($C_{60}$)Ni(TMTAA)][2] and [($C_{60}$)-Cu(TMTAA)].

Bond distances and angles within the macrocycles in the present study are unexceptional,[2,3] as for the bond distances and angles in the $P_4Se_3$ cage[11,17] and $S_8$.[18]

### Solution studies

We have evidence (uv-vis spectra) for a strong interaction between [Ni(OMTAA)] and $C_{60}$ in toluene solution[19] however [Ni(TMTAA)], [Zn(TMTAA)] and [Cu(TMTAA)] interactions with $C_{60}$ have proved difficult to study due to stability and solubility problems. The other ligands do not appear to bind strongly in solution (uv-vis studies).

## Conclusion

The extended structures for the inclusion complexes differ with $P_4Se_3$ or $S_8$ units being situated in isolated pockets and toluene molecules occupying channels. The self assembly of two M(TMTAA) moieties at 90° to each other is common as in the Ni(TMTAA) supermolecules containing *o*-dicarborane, $P_4S_3$, $P_4Se_3$ and $S_8$ guests, [($S_8$){Cu(TMTAA)}$_2$] and also with the structures of [Zn(TMTAA)] and [Cu(TMTAA)].[15] The $M^{2+}$ ion of one macrocycle sits below a phenyl ring of the other macrocycle common for all seven compounds, Table 1.

**Table 1** Intramolecular contacts for [{M(TMTAA)}$_2$] (phenyl-lined surface/methyl-lined surface linkage) in [M(TMTAA)] and its inclusion complexes

| Complex | Metal–phenyl centroid distance/Å (M···C range/Å) | Metal–imine geometric centre distance/Å (M···C range/Å) |
|---|---|---|
| [($o$-$C_2B_{10}H_{12}$){Ni(TMTAA)}$_2$][2] | 3.55 (3.78–3.85) | 3.66 (3.84–3.85) |
| [($P_4S_3$){Ni(TMTAA)}$_2$][2] | 3.51 (3.73–3.85) | 3.60 (3.76–3.77) |
| [($P_4Se_3$){Ni(TMTAA)}$_2$] | 3.51 (3.76–3.82) | 3.62 (3.75–3.79) |
| [($S_8$){Ni(TMTAA)}$_2$] | 3.40 (3.69–3.89) | 3.52 (3.59–3.74) |
| [($S_8$){Cu(TMTAA)}$_2$] | 3.37 (3.55–3.75) | 3.36 (3.41–3.60) |
| [{Zn(TMTAA)}$_2$] | 3.26 (3.45–3.60) | 2.71 (2.62–3.08) |
| [{Cu(TMTAA)}$_2$][15] | 3.49 (3.67–3.83) | 3.29 (3.23–3.53) |

**Table 2** Intramolecular contacts for [{M(TMTAA)}$_2$] (methyl-lined surface/methyl-lined surface linkage) in [M(TMTAA)] and its inclusion complexes

| Complex | Metal–imine geometric centre distance/Å | M···C distance/Å |
|---|---|---|
| [($MeC_6H_5$)Ni(TMTAA)] | 3.71 | 3.46–4.05 |
| [{Ni(TMTAA)}$_2$] | 3.83 | 3.57–4.36 |
| [{Zn(TMTAA)}$_2$] (offset) | 4.93, 5.06 | 4.37–6.01 |
| [{Zn(TMTAA)}$_2$] | 4.17 | 3.98–4.63 |
| [{Cu(TMTAA)}$_2$][15] (offset) | 4.31 | 3.91–5.17 |
| [{Cu(TMTAA)}$_2$][15] | 3.76 | 3.54–4.18 |
| [{Fe(TMTAA)}$_2$][19] | 4.31 | 3.91–5.17 |

In [($MeC_6H_5$)Ni(TMTAA)] and [{Ni(TMTAA)}$_2$] described above the interplay of the macrocycles is different to that of the foregoing complexes, now with the methyl-lined faces locked together. This association is also evident in the structure of unsolvated [Zn(TMTAA)] and [Cu(TMTAA)].[15] Here there is greater variation in packing with the "symmetrical" arrangement placing the metal closest to the pentanediimine geometric centre, Table 2. The arrangement occurs for [($MeC_6H_5$)Ni-(TMTAA)], [Zn(TMTAA)] and [Cu(TMTAA)].[15] A slight offset occurs in [Ni(TMTAA)] and a greater mismatch is seen in [Zn(TMTAA)], [Cu(TMTAA)][15] and [Fe(TMTAA)].[20]

The opposite interaction of the macrocycles to above (methyl-lined surface linkage) occurs in [{Fe(TMTAA)}$_2$][20] whereby the phenyl-lined surfaces are locked together. The iron–phenyl centroid contact distance is 3.58 Å with two carbon atoms at 2.98 and 3.21 Å from the Fe and the other phenyl carbon atoms span out to 4.55 Å.

The complexes [M(TMTAA)] are rigid, remarkably adaptable macrocycles, able to accommodate molecules of different size and shape, either as discrete macrocycles or associated dimers of the macrocycles. As evident in the structures of unsolvated [Ni(TMTAA)],[11] [Cu(TMTAA)],[12] [Zn(TMTAA)] and [Fe(TMTAA)][20] the macrocyclic complexes associate through both the phenyl- and methyl-lined surfaces. In the presence of toluene the association through the phenyl-lined surface is broken in preference for incorporation of toluene into the structure. The globular molecules *o*-carborane,[2] $P_4S_3$,[2] $P_4Se_3$ and $S_8$ compete for the methyl-lined surface leaving the phenyl-lined surface association intact; $C_{60}$[2] effectively competes for both the methyl-lined surface (as a globular molecule) as well as for the phenyl-lined surface (as an aromatic guest).

## Experimental

All solvents and starting materials were obtained from Aldrich and used without further purification. X-ray powder diffractions patterns were collected on a Scintag PADV, with a

**Table 3** Crystal data and details of the data collection and structure refinement for $[(S_8)\{Ni(TMTAA)\}_2]$ **1**, $[(S_8)\{Cu(TMTAA)\}_2]$ **2**, $[(P_4Se_3)\{Ni(TMTAA)\}_2]$ **3**, $[\{Ni(TMTAA)\}_2]$ **4**, $[(MeC_6H_5)Ni(TMTAA)]$ **5**, $[\{Zn(TMTAA)\}_2]$ **6** and $[(C_{60})Cu(TMTAA)]$ **7**

| | **1** | **2** | **3** | **4** | **5** | **6** | **7** |
|---|---|---|---|---|---|---|---|
| Formula | $C_{44}H_{44}N_8Ni_2S_8$ | $C_{44}H_{44}Cu_2N_8S_8$ | $C_{44}H_{44}N_8Ni_2P_4Se_3$ | $C_{22}H_{22}N_4Ni$ | $C_{29}H_{30}N_4Ni$ | $C_{44}H_{44}N_8Zn_2$ | $C_{82}H_{22}CuN_4$ |
| Collection temperature/K | 123 | 123 | 123 | 123 | 173 | 298 | 123 |
| $M$ | 1058.77 | 1068.46 | 1163.06 | 401.15 | 493.28 | 815.7 | 1126.65 |
| Crystal system | Monoclinic | Monoclinic | Orthorhombic | Monoclinic | Triclinic | Monoclinic | Monoclinic |
| Space group | $P2_1/c$ (no. 14) | $P2_1/c$ (no. 14) | $Pnma$ (no. 62) | $P2_1/c$ (no. 14) | $P\bar{1}$ (no. 2) | $P2_1/c$ (no. 14) | $P2_1/n$ (no. 14) |
| $a$/Å | 18.0406(6) | 18.1070(6) | 19.0407(8) | 15.9494(8) | 10.4126(5) | 14.107(6) | 14.5538(6) |
| $b$/Å | 13.8560(2) | 13.8843(3) | 17.3568(8) | 14.9208(8) | 13.3634(7) | 16.371(8) | 17.5225(8) |
| $c$/Å | 18.1661(6) | 18.0489(5) | 13.5731(4) | 15.6235(7) | 17.5322(9) | 16.670(1) | 18.3011(7) |
| $\alpha$/° | | | | | 92.595(1) | | |
| $\beta$/° | 97.2162(5) | 96.791(1) | | 91.070(3) | 90.591(1) | 99.94(3) | 107.8447(9) |
| $\gamma$/° | | | | | 101.863(1) | | |
| $V$/Å$^3$ | 4505.0(0.2) | 4496.0(0.2) | 4485.7(6) | 3717.4(3) | 2384.5(2) | 3792(3) | 4442.6(3) |
| $D_c$/g cm$^{-3}$ | 1.561 | 1.575 | 1.722 | 1.434 | 1.374 | 1.429 | 1.68 |
| $Z$ | 4 | 4 | 4 | 8 | 4 | 4 | 4 |
| $\mu$/cm$^{-1}$ | 12.51 | 13.59 | 34.61 | 10.58 | 8.39 | 13.1 | 5.6 |
| Unique reflections | 11252 | 12943 | 5602 | 18550 | 14446 | 6662 | 11332 |
| No. observed data | 4925 | 4621 | 2521 | 4286 | 10009 | 4047 | 2698 |
| $R$ | 0.060 | 0.080 | 0.062 | 0.092 | 0.0900 | 0.041 | 0.111 |
| $R'$ | 0.054 | 0.073 | 0.060 | 0.162 | 0.2204 | 0.049 | 0.104 |

Complexes **1**, **2**, **3**, **4** and **7**: Enraf-Nonius KappaCCD diffractometer, crystal mounted in oil; no absorption correction, Mo-Kα radiation, $I > 3\sigma(I)$, refined on $F$. Complex **5**: Siemens SMART CCD, crystal mounted in oil; no absorption correction, Mo-Kα radiation, $I > 2\sigma(I)$, refined on $F$. Complex **6**: Cad4 single counter diffractometer, crystal mounted in a Lindemann capillary; absorption correction applied, Mo-Kα radiation, $I > 3\sigma(I)$, refined on $F$.

germanium solid state detector. Elemental analyses were performed by Chemical and Micro Analytical Services. The complexes [M(TMTAA)], M = Ni or Cu, and $H_2$TMTAA were prepared according to published procedures.[15,21]

### Syntheses

**$[(S_8)\{M(TMTAA)\}_2]$ and $[(P_4Se_3)\{Ni(TMTAA)\}_2]$.** Carbon disulfide solutions (10 ml each) containing $S_8$ (10 mg, 0.10 mmol) or $P_4Se_3$ (18 mg, 0.05 mmol) and [Ni(TMTAA)] (50 mg, 0.10 mmol) were mixed and allowed to evaporate slowly. The complex precipitated and was collected and washed with toluene then hexane. A $CS_2$ solution (10 ml) of [Cu(TMTAA)] (25 mg, 0.06 mmol) was added to a $CS_2$ solution (10 ml) of $S_8$ (32 mg, 0.125 mmol), stirred and layered with an equal volume of hexane. On standing and partial evaporation dark crystals formed. $[(S_8)\{Ni(TMTAA)\}_2]$: mp decomp. >220–221 °C. Found (calc.): C, 50.30 (49.92); H, 3.81 (4.19); N, 10.83 (10.58)%. $[(S_8)\{Cu(TMTAA)\}_2]$: we were unable to separate this compound from coprecipitated $S_8$. $[(P_4Se_3)\{Ni(TMTAA)\}_2]$: mp decomp. >240 °C. Found (calc.): C, 44.98 (45.44); H, 3.82 (3.81); N, 9.82 (10.10)%.

**$[\{Ni(TMTAA)\}_2]$ and $[(MeC_6H_5)Ni(TMTAA)]$.** The complex [Ni(TMTAA)] was recrystallised from $CS_2$–hexane or toluene respectively. $[\{Ni(TMTAA)\}_2]$: we were unable to separate the compound from the coprecipitated solvated species $[(CS_2)Ni(TMTAA)]$.[22] $[(MeC_6H_5)Ni(TMTAA)]$: mp 278.5–279.5 °C. Found (calc.): C, 71.05 (70.61); H, 6.41 (6.13); N, 11.85 (11.36)%.

**$[\{Zn(TMTAA)\}_2]$.** To a stirred toluene solution of $H_2$TMTAA (0.935 g, 2.7 mmol) was added diethylzinc (0.28 ml, 12.73 mmol) dropwise at room temperature. The red solution was warmed, then left to cool slowly. An initial red precipitate was removed and small red crystals deposited overnight. Yield: 0.73 g, 64%. Mp 150 °C (decomp.). Found (calc.): C, 64.50 (64.78); H, 5.40 (5.40); N, 14.01 (13.74)%.

**$[(C_{60})\{Zn(TMTAA)\}]$.** A solution of $[\{Zn(TMTAA)\}_2]$ (4.0 mg, 0.01 mmol) in toluene was combined with $C_{60}$ (2.0 mg, 0.003 mmol) in toluene and warmed gently. The solution was left to cool slowly on a warm water-bath. A dark precipitate was removed and the filtrate left to crystallise. Satisfactory microanalyses could not be obtained for this complex, however infrared, uv-visible and mass spectra were consistent with the given formulation. X-Ray powder diffraction indicated a compound isomorphous with $[(C_{60})\{Ni(TMTAA)\}]$.

**$[(C_{60})\{Cu(TMTAA)\}]$.** Carbon disulfide solutions (50 ml each) containing $C_{60}$ (100 mg, 0.14 mmol) and [Cu(TMTAA)] (62 mg, 0.15 mmol) were mixed and allowed to evaporate slowly. The complex precipitated and was collected and washed with toluene then hexane. Yield: 0.130 mg, 80%. Mp decomp. >400 °C. Found (calc.): C, 87.13 (87.42); H, 1.74 (1.97); N, 4.97 (4.80)%.

### Crystallography

Crystallographic data given in Table 3.

CCDC reference number 186/1563.

See http://www.rsc.org/suppdata/dt/1999/2927/ for crystallographic files in .cif format.

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