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Review

# Transition and post-transition metal ion chemistry of dibenzo-substituted, mixed-donor macrocycles incorporating five donor atoms

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ABSTRACT

The transition and post-transition metal ion chemistry of a wide range of potentially pentadentate dibenzo-substituted macrocyclic ligands incorporating nitrogen, oxygen and/or sulfur donors is reviewed and shown to result in a diverse range of structural types. Aspects of metal ion recognition, bulk membrane transport, systems incorporating appended chromophores, a sulfate binding system, induced Cu(I)/Cu(II) redox switching, coordination polymers, and unsymmetric macrocyclic ligand systems are all discussed.

## 1. Introduction

Following the pioneering work of a number of groups (including those of Busch, Pedersen, Lehn and Curtis) [1] on fundamental aspects of the metal ion chemistry of macrocyclic ligands – often motivated by the desire to understand the structure and function of related natural macrocycles [2] – there developed a strong interest in the design and synthesis of macrocyclic ligands for applications such as metal ion recognition, solvent extraction and sensing [3–10]. In this review, we present an account of investigations from the authors' laboratories that have involved the interaction of mixed donor macrocyclic ligands of the general structure **1** (together with corresponding substituted derivatives) with a selection of both transition and post-transition metal ions. Aspects of the metal ion chemistry of ligands of this general type were reviewed in 1997 by one of us [3] and brief details of these early studies are only included where necessary to provide a context for post-1997 work. With respect to this, it is noted that the original studies were

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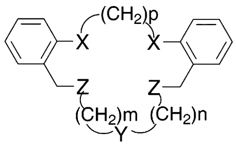
initially concerned with the transition and post-transition metal chemistry of solely diimine mixed-donor rings related to the systems of type **1** [11–13]. At that time these new ligand systems were designed to fall structurally between the two major categories of macrocyclic ligands then being widely investigated – the all-oxygen crown ethers introduced by Pedersen [14] and a range of all-nitrogen donor rings investigated by a number of groups, including those of Busch et al. [15] and Curtis [16].



X,Y = O,N and/or S
Z = N or S
m = 2, 3 or 4
n = 2 or 3
p = 1, 2, 3 or 4

**1**

In our initial studies, while a range of solid complexes of the mixed oxygen–nitrogen diimine systems were successfully characterised, there was a tendency for these derivatives to undergo hydrolysis or solvolysis of their imine functions on coordination which rendered them less than suitable for quantitative solution studies such as the potentiometric determination of metal binding constants. As one of our interests was to probe the potential of such mixed-donor systems for metal ion recognition/discrimination (including their use in metal ion sensors), related series of derivatives in which the imine functions were reduced to secondary amines were synthesised [17–19]. In particular, wide-ranging investigations on the use of 16- to 18-membered ring ligands of type **1** (with Z = NH and X, Y varying between O, S, and/or NH) were undertaken. For these macrocyclic systems the incorporation of dibenzo groups was seen to be advantageous since their presence yielded ligands of intermediate flexibility which hence restricted the number of configurations that the coordinated ligand could adopt. In addition, these ligand systems generally favour 1:1 (metal:ligand) complexation, thus simplifying the interpretation of solution results [3]. Following this earlier ligand development, new synthetic and characterization studies for macrocycles of type **1** and their substituted derivatives have continued up to the present [20–29].

## 2. Metal ion recognition and related studies

In our earlier studies, one strategy for attaining recognition was to 'tune' the structural and electronic features of a given macrocyclic ligand from the above category towards the binding of a metal ion of interest [5,20,30–37]. In this approach, the number, type and arrangement of the donor atoms present, the macrocyclic ring size, the electronic and structural nature of the macrocyclic backbone, the effect of ring substitution and the number and size of the chelate rings formed on metal binding were all used as variables in order to promote such recognition. In essence, this process corresponds to 'tuning' the electronic and steric complementarity between the macrocycle and the metal ion of interest. From the perspective of the metal ion, the properties of interest include the metal's ionic radius, its oxidation state, its overall hardness or softness, its typical coordination number(s) and, in the case of transition metal ions, the nature of any crystal field effects that may affect properties such as the spin state and/or preferred coordination geometries. In these studies, particular attention was given to mixed-donor macrocyclic systems tailored for the recognition of the following industrially important metal-ion groups: Co(II)/Ni(II)/Cu(II), Zn(II)/Cd(II) and Ag(I)/Pb(II) [38].

In a study aimed at probing the possible effect of macrocyclic ring substituents on metal ion recognition, structure–function relationships involving the interaction of the 17-membered, C-methyl substituted $O_2N_3$-derivatives **2** and **3** with Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Pb(II) were investigated [39]. Stability constants for a range of corresponding complexes were determined potentiometrically in 95% methanol (I = 0.1; $Et_4NClO_4$). However, as for the parent (unsubstituted) ligand derivative (**1**; X = O, Z = NH and Y = NH, $n = m = p = 2$), the stabilities in both cases also follow the normal Irving-Williams order, with a small drop in the respective log *K* values for the complexes of the substituted derivatives, attributable to steric effects, being evident where corresponding values were obtained.

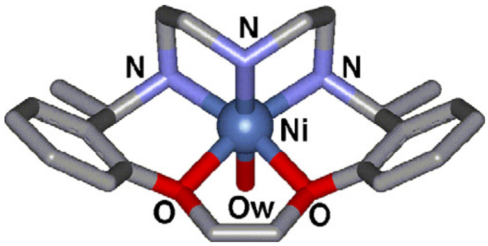
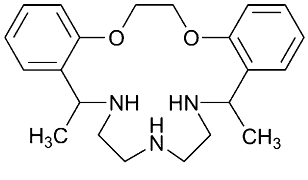
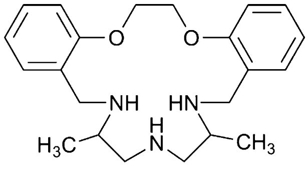


**Fig. 1.** X-ray structure of the complex cation in $[NiL(H_2O)](ClO_4)_2$ (L = **2**).



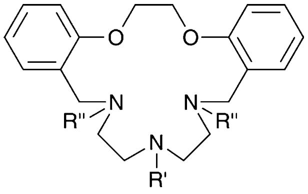
**2**



**3**

The solid state structure of $[NiL(H_2O)](ClO_4)_2$ (L = **2**) shows that it exhibits a $N_3$-*fac*ial octahedral geometry, with the nickel being bound to all five donor atoms of **2** (in its meso form) and a water molecule (Fig. 1). Molecular mechanics modelling of this complex cation indicated that the observed facial configuration is favoured over possible alternative facial or meridional arrangements [39].

As an extension of the above study, the interaction of Co(II), Ni(II), Cu(II), Zn(II), Cd(II), Ag(I) and Pb(II) with the N-alkylated $O_2N_3$-donor macrocycles **4** (R′, R″ = methyl and R′, R″ = benzyl) [3,26] was also investigated [40]. As expected, comparison of the log *K* values for the respective 1:1 complexes of the unsubstituted $O_2N_3$-ring **1** (X = O, Y = Z = NH, $n = m = p = 2$) [41] with those for **4** (R′, R″ = methyl) and **4** (R′, R″ = benzyl) confirms that, in general, the presence of N-substituents leads to formation of weaker complexes than those occurring for the unsubstituted macrocycle (where R′, R″ = methyl). The marked exception is for Ag(I). The general decrease in the log *K* values for the other six metal ion complexes has again been attributed to steric hindrance (together with electronic effects) from the 'R' groups inhibiting complex formation; the greatest effect being seen for the bulky benzyl substitution. However, the presence of such N-substitution results in significantly enhanced discrimination for Ag(I) relative to the other ions measured (Table 1). That is, for Ag(I), the log *K* values remain consistently high; in the case of the tribenzylated derivative (**4**, R′, R″ = benzyl) the value is even slightly higher than that obtained for the parent macrocycle. Overall, the results serve to illustrate what we have termed 'selective detuning' as a means for achieving metal ion selectivity – in this instance in favour of Ag(I).



**4**

**Table 1**
Log stability constants for the $ML^{n+}$ complexes of **1** (X = O, Y = Z = NH, *n* = *m* = *p* = 2) and **4** (R′, R″ = methyl and R′, R″ = benzyl) in 95% methanol; $Et_4NClO_4$, *I* = 0.1; 25 °C.

| Ligand | Co(II) | Ni(II) | Cu(II) | Zn(II) | Cd(II) | Ag(I) | Pb(II) |
|---|---|---|---|---|---|---|---|
| **1**[a] | 7.6 | 10.0 | 14.4 | 7.5 | 8.7 | 8.7 | 8.1 |
| **4**; R′, R″ = $CH_3$ | <3.5 | <3.5 | –[b] | 5.1 | 6.1 | 10.3 | 6.6 |
| **4**; R′, R″ = $CH_2C_6H_5$ | <3.5 | <3.5 | –[b] | ~3.5 | ~3.5 | 9.3 | 4.3 |

[a] **1** with X = O, Y = Z = NH; *n* = *m* = *p* = 2.
[b] Precipitation prevented log *K* determination.

As an extension of the above study, a comparative investigation involving the analogous monobenzylated macrocycle **4** (R′ = benzyl, R″ = H) [26] and the above metal ions has been performed [42]. Monobenzylation again gives rise to marginally enhanced stability for Ag(I), with the log *K* values for all the other metal ion complexes again being reduced (even though the Cu(II) complex still displays the highest overall stability). As might be predicted, the drop in the log *K* values for these latter metal complexes is less for this mono-substituted system than observed for the corresponding complexes of the tribenzylated system **4** (R′, R″ = benzyl) complexes (see Table 1). 'Selective detuning' of the type just discussed seems to be a general phenomenon since related detuning of complex stability for the above metal ions except Ag(I) has also been observed for other amine-containing macrocyclic ligand systems on N-alkylation and N-benzylation [40,43–45]. In keeping with these results, N-alkylation of tetraazalkane ligands (both linear and cyclic) has been shown by Meyerstein [46] to favour stabilization of lower valent metal complexes [46–48]. Several factors have been proposed to account for such behaviour, with solvation effects suggested to be dominant.

Competitive mixed-metal transport experiments from an aqueous source phase across a bulk chloroform membrane into an aqueous receiving phase have been performed using both single-ring macrocycles of type **1** (and selected substituted derivatives) as well as a related spiro-linked double-ring system as the ionophore in the organic phase. Thus the ionophores include the unsubstituted ring (**1**; X = O, Y = Z = NH, *n* = *m* = *p* = 2), the related *t*-butyl substituted derivatives **5** (R = *t*-Bu, *p* = 2 and 3) and double rings of type **6** (R = H and *t*-Bu) [41]. The organic phase also contained palmitic (hexadecanoic) acid to act as a source of lipophilic anion for use in the transport process. Equimolar concentrations of Co(II), Ni(II), Cu(II), Zn(II), Cd(II), Ag(I) and Pb(II) were present in the source phase. Transport was performed against a pH gradient, with the aqueous source and receiving phases being buffered at pH 4.9 and 3.0, respectively; the transport process is shown schematically in Fig. 2.

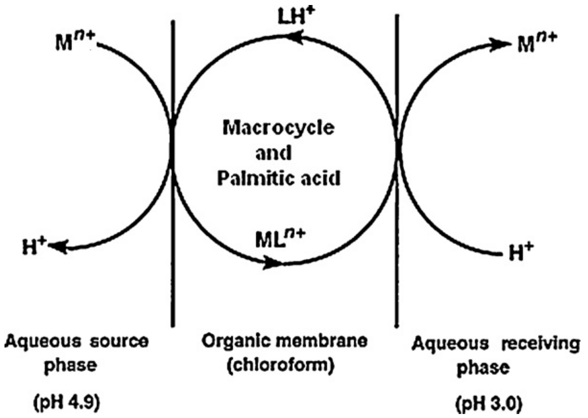
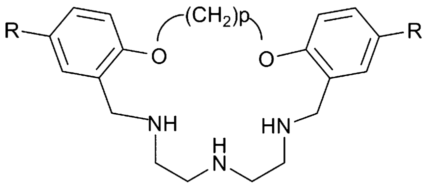


**Fig. 2.** Schematic representation of the arrangement used for the transport of a metal ion across a chloroform membrane phase [49].



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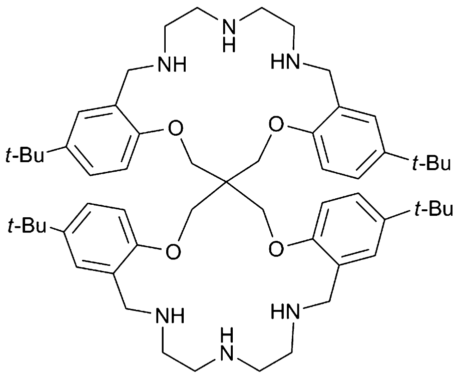
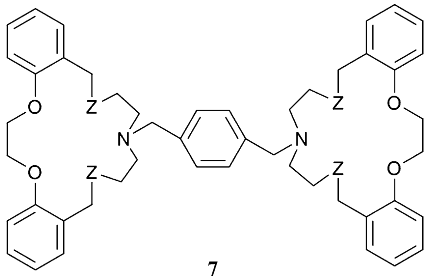


**6**

Transport selectivity for Cu(II) over the other six metal ions present was observed for all the above systems. In this study the metal ion concentration in each of the three phases was measured at the termination of each run. This allowed the metal-ion mass balance across all three phases to be determined – resulting in a fuller understanding of the nature of the transport process for systems of this type.

Other competitive seven-metal transport experiments across a bulk chloroform membrane to those just described have also been performed [42] using the monobenzylated derivative **4** (R′ = benzyl, R″ = H) [26] and its tribenzylated analogue **4** (R′, R″ = benzyl) [40] as ionophores. The results were again compared with those for the parent unsubstituted macrocycle (**1**; X = O, Y = Z = NH, *n* = *m* = *p* = 2) under similar conditions. Both the unsubstituted ligand and its monobenzylated derivative **4** (R′ = benzyl, R″ = H) yielded transport selectivity for Cu(II). In contrast, and in parallel with the log *K* results discussed earlier, the tribenzylated ligand system **4** (R′, R″ = benzyl) yielded sole transport selectivity for Ag(I).

Finally, a similar bulk membrane transport study employing the linked ligand system **7** (Z = NH) [26] has also been performed, with once again sole selectivity for Cu(II) being observed [42]. Interestingly, when compared on a 'per macrocyclic cavity' basis with the transport behaviour of the monobenzylated analogue **4** (R′ = benzyl, R″ = H), there is little difference in the efficiency of either ligand for Cu(II) transport under the (similar) conditions employed.



**7**

As mentioned already, in earlier studies a number of examples of substantial metal ion discrimination employing macrocycles of type **1** were documented; for example, stepwise 'tuning' of the donor set present within such 17-membered rings resulted in >$10^9$ discrimination for Ag(I) over Pb(II) – metals that are found together in nature [37]. Discrimination for Ag(I) over Cu(II) [50], while less spectacular, was still ~$10^4$. In these early wide-ranging studies four design elements that can be employed to 'tune' the discrimination for Ag(I) over the above transition and post-transition ions were documented: (i) the macrocyclic ring size, (ii) the macrocyclic donor set, (iii) macrocyclic donor atom sequence and (iv) the nature of any donor atom substituents present.

More recently, the 'lessons learnt' in these prior studies have been applied to the design and synthesis of the new macrocyclic ligand **8** which was thus anticipated to yield enhanced discrimination for Ag(I) over the series of other transition and post-transition ions mentioned earlier [51].

In our initial studies, and as expected from a consideration of HSAB theory [52,53], it was demonstrated that progressive substitution of sulfur atoms for oxygen in the $O_3N_2$-donor ring **1** (X = Y = O, Z = NH, $n = m = p = 2$) leads to increased silver ion discrimination. Secondly, in these studies it was found that both the strength of binding as well as discrimination for Ag(I) tended to peak for 17-membered ring systems of the above type, corresponding to the formation of three five-membered and two six-membered chelate rings when all donors were bound to the central metal. With respect to this, the X-ray structures of the 1:1 ($Ag^+$:L) complexes, where L = **1** [X = S, Y = O, Z = NH; $n = m = p = 2$ [37], **1** (X = S, Y = NH, Z = NH; $n = m = p = 2$) [54] and **1** (X = S, Y = S, Z = NH; $n = m = p = 2$)] [54] confirmed coordination of all five macrocyclic ring donors to Ag(I) in each case, with no other ligands present in the coordination sphere. Thirdly, the presence of a $NHCH_2CH_2YCH_2CH_2NH$ (Y = O or S) donor atom sequence rather than the corresponding sequence with Y = NH, was also demonstrated to promote enhanced silver discrimination [37], even though the absolute log *K* values across the series tend to be smaller when Y = O. Fourthly, as discussed earlier, it has been well documented that N-benzylation of a secondary amine donor in a variety of aza-macrocyclic systems leads to enhanced discrimination for silver over a range of transition and post-transition metal ions such as those discussed so far [3].

All the above four previously documented ligand design strategies for achieving Ag(I) discrimination were applied to the design of the new N-benzylated $S_2N_3$-donor macrocycle of structure **8** which does yield enhanced selectivity for Ag(I) over Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Pb(II) in both log *K* and bulk membrane transport studies. The silver complex is at least $10^5$ more stable than any of the remaining complexes investigated. As expected, the steric and electronic consequences on N-benzylation result in a general tendency towards reduction of the respective log *K* values relative to the similar complexes of the corresponding unsubstituted derivative **1** (X = S, Y = S, Z = NH; $n = m = p = 2$). However, the effect is greater for Cu(II) than for Ag(I) – a further example of 'selective detuning' of the type discussed above (see Fig. 3).

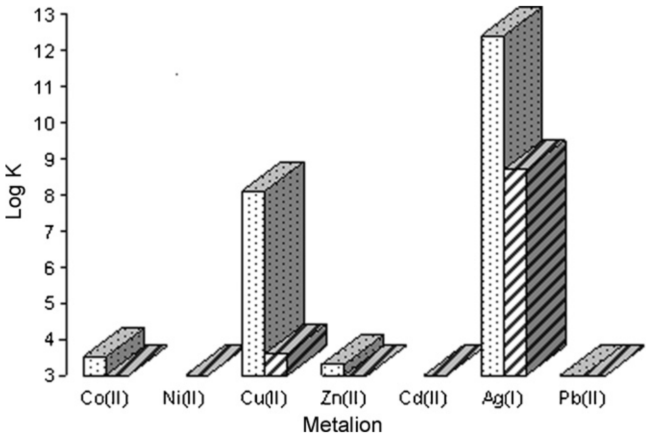
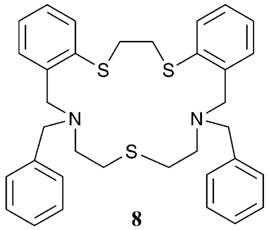


**Fig. 3.** Comparison of the log *K* values for **1** (X = S, Y = S, Z = NH; $n = m = p = 2$) (dotted bars) versus **8** (striped bars) for the metal ions shown.



**8**

A bulk membrane transport experiment (see Fig. 2) with **8** as ionophore and the above seven metals in the aqueous source phase yielded sole transport selectivity for Ag(I); that is, no transport of the other six metals present in the source phase occurred under the conditions employed. Apart from the possibility of employing **8** for the sensing or separation of silver, overall the study serves to exemplify the use of a stepwise strategy for rational ligand design leading, in this case, to enhanced discrimination for silver.

The X-ray structure of $[AgL]PF_6{\cdot}MeCN$ (L = **8**) was determined as a part of the above study. The structure shows that the Ag(I) ion is bound to all five donor atoms of **8** and that the complex cation adopts a 'tight' (Fig. 4) distorted trigonal bipyramidal geometry, consistent with the strong ligand-to-silver coordination inferred from the solution studies.

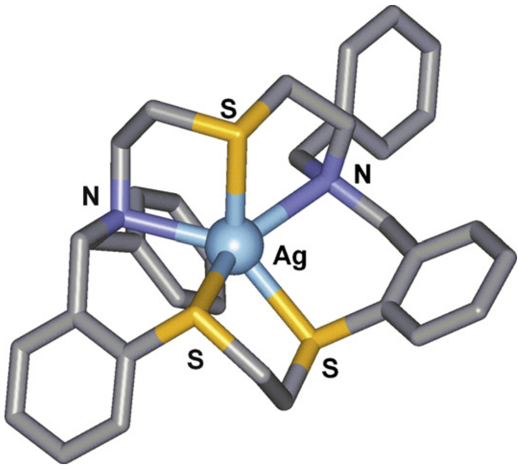
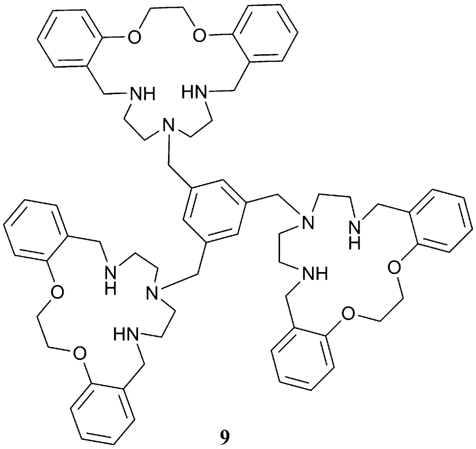


**Fig. 4.** X-ray structure of the complex cation in $[AgL]PF_6{\cdot}MeCN$ (L = **8**).

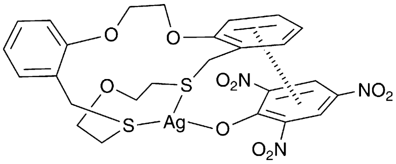
Competitive membrane transport studies involving the N-phenyl (**4**; R″ = H, R′ = –$C_6H_5$) and tri-linked (**9**) substituted derivatives of the parent $N_3O_2$-ring **1** (X = O, Y = NH, Z = NH; *n* = *m* = *p* = 2) have been carried out [55]. The transport experiments again involved seven-metal competitive studies, with in this case (**4**; R″ = H, R′ = –$C_6H_5$) and **9** being employed as the ionophores in the respective chloroform membrane phases. As before, the aqueous source phase contained equal concentrations of Co(II), Ni(II), Cu(II), Zn(II), Cd(II), Ag(I) and Pb(II) (as their nitrate salts). The results were compared with those obtained previously for the related mono-ring (**4**; R″ = H, R′ = benzyl) and di-linked (**7**; Z = NH) ring systems. For both **4** (R″ = H, R′ = –$C_6H_5$) and **9**, sole transport selectivity for Cu(II) was observed and, on a per macrocyclic cavity basis, the tri-linked analogue **9** is a less efficient ionophore for Cu(II) transport than its monomeric or di-linked analogues under the conditions employed. This may reflect the observed tendency for the tri-linked derivative **9** to form a 2:1 complex (metal/ligand) with Cu(II) under similar conditions. However the situation is not straight forward since the higher overall charge on such a species (and its effect on complex lipophilicity) is clearly an additional factor that will influence transport efficiency.



**9**

An investigation of the influence of host–guest assembly between the 17-membered $N_3O_2$-donor macrocycle **1** (X = O, Y = NH, Z = NH; *n* = *m* = *p* = 2) [as well as its di-*t*-butyl derivative **5** (R = *t*-Bu; p = 2)] and lipophilic carboxylic or phosphinic acids on the solvent extraction of Cu(II) has been reported [56]. Host–guest formation between the macrocycle and such lipophilic organic acid guests (that are themselves potential metal-ion ligands/extractants) results in synergistic solvent extraction of Cu(II) in a two phase (water/chloroform) extraction system. A series of 2:1 (organic acid:macrocycle) assemblies was demonstrated to form by NMR titration of 4-tert-butylbenzoic, hexadecanoic, phenylphosphinic, diphenylphosphinic and salicylic acid into a solution of macrocycle in deuterochloroform (with evidence for the stepwise formation of 1:1 intermediates in some cases being observed). Host–guest adducts of this type were then employed as the ionophores in the solvent extraction (water/chloroform) experiments to probe the influence of such assembly formation on metal ion binding. From entropy considerations it was anticipated that the formation of particular 1:2 host–guest species of the above type might result in enhanced metal ion binding (and hence enhanced metal ion extraction) since the components of the coordination sphere are, at least in part, preassembled for complex formation. Enhanced (synergistic) extraction of Cu(II) ions was indeed observed in each case. The isolation of host-guest adducts of both **1** (X = O, Y = NH, Z = NH; *n* = *m* = *p* = 2) and **5** (R = *t*-Bu; *p* = 2) with 4-*t*-butylbenzoic acid and salicylic acid, respectively, has proved possible and their solid state structures were confirmed by X-ray diffraction.

The 17-membered $S_2O_3$-donor dibenzo macrocycle (**1**; X = O, Z = S, and Y = O; *n* = *m* = *p* = 2) and a 20-membered analogue incorporating a $S_2O_4$ donor set together with the corresponding rings devoid of benzo-substituents were employed as metal picrate extractants in a series of two phase (water/chloroform) solvent extraction experiments involving aqueous phases containing equimolar concentrations of Co(II), Ni(II), Cu(II), Zn(II), Cd(II), Ag(I) and Pb(II) [57]. Sole extraction selectivity for Ag(I) was observed across all four ligand systems. As expected, the more lipophilic benzo substituted rings showed enhanced extraction efficiency for this ion than occurred for their all-aliphatic analogues. From X-ray crystal structure and comparative NMR studies, it was proposed that the formation of π–π stacking interactions between the picrate anion and the benzo-substituents in the dibenzo-containing macrocycles (see **10**) also contribute to the observed enhanced extraction efficiency of the dibenzo-systems under the conditions employed.



**10**

## 3. Sulfate binding study

A series of comparative solvent extraction (water/chloroform) studies of Ni(II) and Cu(II) employing a di-nonyl-substituted $N_3O_2$-donor macrocycle of type **5** as extractant have been undertaken from sulfate, chloride, nitrate and acetate-containing aqueous source phases [58]. Unexpectedly, efficient extraction of both metal sulfates was observed, the degree of extraction being comparable (or slightly enhanced) relative to that for each of the remaining mono-charged anion systems. X-ray diffraction studies show that for the corresponding (unsubstituted) solid state complexes, $[NiL(H_2O)_3]SO_4{\cdot}4H_2O$ and $[CuL(H_2O)]SO_4{\cdot}6.67H_2O$ (where L = **1**, X = O, Y = NH, Z = NH), each complex occurs as a hydrogen bonded dimer, with the sulfate anions involved in hydrogen bonded networks involving ligand amine protons and water molecules (Fig. 5). In the Cu(II) complex, simultaneous sulfate binding to a copper site is also present. In each complex the macrocyclic ligand does not coordinate via its ether oxygen donors but instead is arranged so that it forms a partial hydrophobic shield around the metal ion and sulfate anions which are hence in part isolated from the exterior of the complex cluster assembly. Since hydrophobicity normally aids extraction into an organic phase, the unexpected enhanced extraction of the doubly charged sulfate species into chloroform solution was attributed to the occurrence of a related shielded arrangement; that is, one in which the hydrophobicity of the extracted species is maintained on passing into the chloroform phase.

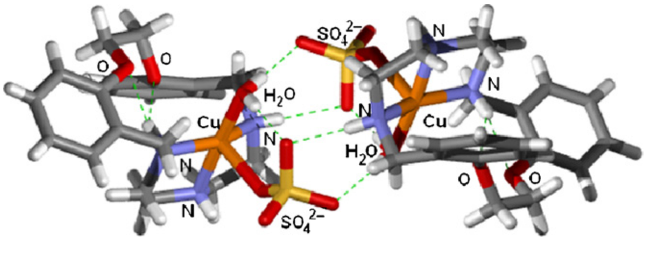


**Fig. 5.** X-ray structure of $[CuL(H_2O)]SO_4{\cdot}6.67H_2O$ (where L = **1**, X = O, Y = NH, Z = NH); hydrate waters are not shown.

## 4. Systems incorporating an appended aza chromophoric group

The complexation of Co(II), Ni(II), Cu(II), Zn(II), Cd(II), Ag(I), Pb(II) and Hg(II) with the azo-appended $N_3O_2$-donor derivative, **4** (R″ = H, R′ = $-C_6H_4-N{=}N-C_6H_4-NO_2$), results in metal-dependent hypochromic shifts in the electronic spectrum of this ligand, with strongly bound copper inducing the largest shift [55]. Thus the azo-coupled derivative **4** (R″ = H, R′ = $-C_6H_4-N{=}N-C_6H_4-NO_2$) yields a red solution in acetonitrile. On addition of Cu(II), a shift of the $\lambda_{max}$ of the peak at 495 nm to 321 nm was observed, accompanied by a concomitant solution colour change to pale yellow. In part, the solid state X-ray structures of the red hydronitrate salt of **4** (R″ = H, R′ = $-C_6H_4-N{=}N-C_6H_4-NO_2$) and its yellow $[CuLNO_3]NO_3{\cdot}CH_2Cl_2$ complex, as well as of $[(CuL)_2(\mu\text{-}OH)_2](ClO_4)_2{\cdot}2CH_2Cl_2{\cdot}2H_2O$ (dark red), have provided insight into the structure-function relationships governing the above observed colour changes. While the latter are of interest in terms of potential colorimetric sensor applications, it is noted that, as yet, a complete rationale for the observed behaviour has not yet been achieved.

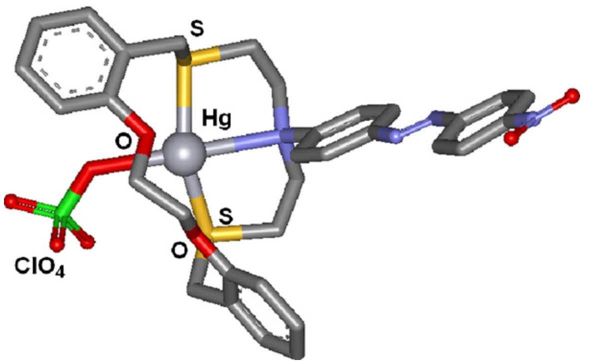
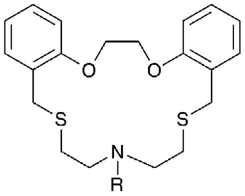


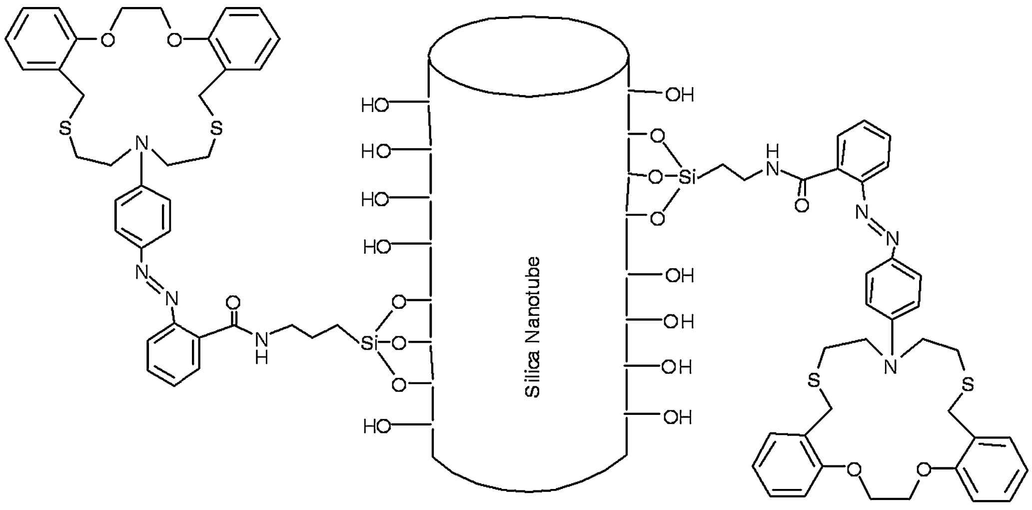
**Fig. 6.** X-ray structure of the complex cation in $[HgL_2(ClO_4)]ClO_4$ (where L = **11**, R = $-C_6H_4-N{=}N-C_6H_4-NO_2$).



**11**

A related investigation to the above in which the above azo-containing substituent was appended at the amine site of the corresponding 17-membered $NO_2S_2$ donor ring to yield **11** (R = $-C_6H_4-N{=}N-C_6H_4-NO_2$) has been carried out [59]. As expected, this ‘softer’ ligand derivative also acts as a chromoionophore and exhibits selectivity for Hg(II). The colour generation process is anion dependent both in solution and the solid state. The crystal structures of the two different coloured species obtained with perchlorate (pale yellow) and iodide (red) were determined, with the structure of the yellow perchlorate complex, $[HgL_2(ClO_4)]ClO_4$ (L = **11**), shown in Fig. 6. The colour-switching results were rationalised in terms of a cooperative ‘push-n-pull’ process, which depends upon the coordinating ability of the anion controlling the colour change through generation of endo- or exo-metal complexes (endo relates to complexes in which the metal is bound to donor atoms whose bonding electron pairs are orientated towards the macrocyclic ring cavity, while exo refers to complexes in which the donor pairs point outwards, away from the cavity). Thus, for example, the structure of the red exo-coordinated dimeric $HgI_4$-bridged species, $[Hg_2L_2I_4]$ (L = **11**), unequivocally shows that the N donor of **11** is not bound to the Hg(II) ion, with the latter located outside of the cavity (exo-coordination). This result was explained in terms of the strong coordination (‘pull’) of the iodides acting to inhibit Hg–N bond formation. In contrast, the presence of the less-coordinating perchlorate anion was postulated to allow the Hg(II) to engage the N lone pair (‘push’) resulting in direct Hg–N bonding in an endo-mode, reflected by the observed colour change to yellow. The use of KI and NaCl to induce red-yellow colour switching for the $[HgL_2(ClO_4)]ClO_4$ complex was also demonstrated.

In a further study immobilization of the related azo-coupled macrocyclic receptor **11** (R = $-C_6H_4-N{=}N$-*o*-$C_6H_4-C(O)-NH-(CH_2)_3-Si(OEt)_3$) shows $-(CH_2)_3-$ while structure (**12**) shows $(CH_2)_4$ on a silica nanotube substrate via a sol-gel reaction involving solvolysis of the terminal $-Si(OEt)_3$ functions to yield **12** was carried out [60]. The use of the resulting material for optical sensing of Co(II), Fe(II), Cu(II), Zn(II), Cd(II), Pb(II), Hg(II) and Ag(I) was probed. While a colour change was observed from yellow to violet when an aqueous solution Hg(II) nitrate was added to a suspension of the functionalised nanotubes, no significant change occurred in the presence of the other seven-metal ions listed above. Thus the functionalised silica nanotubes show much promise as a useful material for the selective colorimetric detection of Hg(II) in aqueous media.



**12**

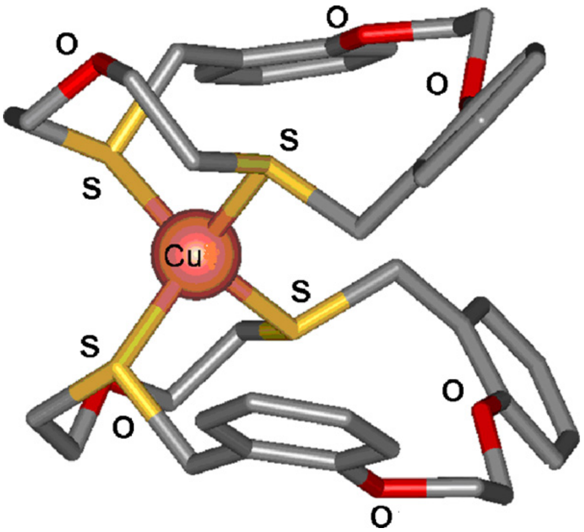


**Fig. 7.** Crystal structure of the cationic sandwich complex, $[Cu(L)_2]^+$ (L = **1**; X = O, Y = O, Z = S; $n = m = p = 2$).

## 5. Donor induced Cu(I)/Cu(II) redox switching

The interaction of the 17-membered $O_2S_2Y$-macrocycles (**1**; X = O, Z = S, and Y = S, NH or O; $n = m = p = 2$) with Cu(II) perchlorate in acetonitrile results in 1:1 (M:L) square-pyramidal Cu(II) complexes of type $[CuL(H_2O)(ClO_4)]ClO_4$ (in which the macrocyclic ring ether oxygen atoms remain uncoordinated) when Y = S or NH but yielded a rare 1:2 (M:L) 'sandwich' tetrahedral Cu(I) complex when Y = O [61]. The structures of all three complexes were confirmed by X-ray diffraction. The pseudo-tetrahedral structure of the Cu(I) complex with Y = O is shown in Fig. 7. Hence substitution of O for S or NH at position Y in the ligand structure (to yield **1**; X = O, Z = S, Y = O, $n = m = p = 2$) results in donor-set-induced coordination sphere switching (square-pyramidal to tetrahedral) in the solid state which is accompanied by a Cu(II) to Cu(I) oxidation-state change.

Spectrophotometric studies (including Job plots) in acetonitrile are in agreement with similar behaviour occurring solution. Interestingly, the corresponding 16- and 18-membered analogues of the above 17-membered macrocycle with Y = O also induce a similar Cu(II/I) redox change in acetonitrile and such behaviour was maintained when the reaction solvent was changed from acetonitrile to methanol or ethanol. Other (isolated) examples of the spontaneous generation of Cu(I) complexes from Cu(II) starting reagents in the presence of thioether-containing ligands have also been reported [62–66]. In particular instances such behaviour has been proposed to involve concomitant oxidation of the reaction solvent and/or of the thioether ligand.

## 6. Other X-ray structural and related studies

As outlined in the prior (1997) review [3] and also exemplified so far throughout the present discussion, X-ray diffraction studies have played a central role in the investigations involving the present class of ligands in the past and this has continued over recent years.

### *6.1. Single-ring macrocyclic systems incorporating mixed N, S and/or O donors*

For example, a comparative structural study of the complexation behaviour of the soft metal ions Ag(I), Cd(II), Hg(II) and Pd(II) with the 17-membered $O_2N_3$-donor macrocycle **1** (X = O, Z = NH, Y = NH; $n = m = p = 2$) has been reported [67]. The X-ray structures of 12 complexes incorporating the above metal ions were determined and the results serve to illustrate the diverse coordination arrangements that may be generated with this ligand. Both mononuclear and dinuclear species form and in particular cases the effect of varying the anion was also observed to induce a major structural change in the resulting complex.

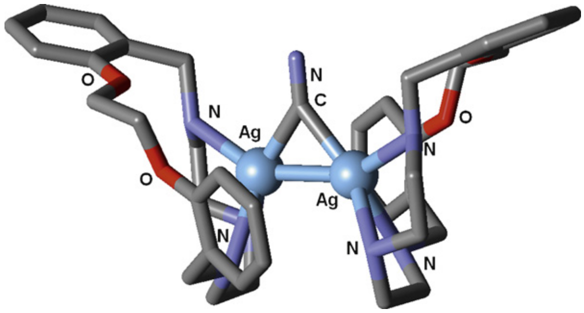


**Fig. 8.** Dimeric structure of the complex cation in $[Ag_2L_2(\mu\text{-CN})][Ag(CN)_2]\cdot H_2O$.

For Ag(I), five related 2:2 (metal:ligand) complexes incorporating **1** (X = O, Z = NH, Y = NH; $n = m = p = 2$) were obtained using silver salts of the following anions: $NO_3^-$, $ClO_4^-$, $PF_6^-$, $OTf^-$ and $CN^-$ [67]. In each complex the respective silver centres bind to two N atoms from one macrocyclic ligand and one N atom from a second, with the ether oxygen donors remaining uncoordinated. A weak Ag···Ag interaction between adjacent silver ions is also present in each case. The $[Ag_2L_2(\mu\text{-CN})][Ag(CN)_2]\cdot H_2O$ (L = **1**; X = O, Z = NH, Y = NH; $n = m = p = 2$) complex (Fig. 8) represents a rare example of a discrete binuclear silver complex incorporating a two-electron $\mu_2$-$\kappa$C:$\kappa$C bridging cyanide group [68].

With Hg(II), **1** (X = O, Z = NH, Y = NH; $n = m = p = 2$) yielded 1:1 (M:L) complexes of types $[HgL(ClO_4)_2]$ and $[HgL(SCN)_2]\cdot CH_3CN$ [67]. In the first of these, all macrocyclic donor atoms are bound to the central metal as are two monodentate perchlorato ligands thus yielding a coordination geometry of seven (Fig. 9).

In $[HgL(SCN)_2]\cdot CH_3CN$ the mercury is five-coordinate, being bound to three N donors from the ligand and two S atoms from the thiocyanato groups. Hg(II) also yields a further two structural types. In $[Hg_2L_2](HgI_4)$ (L = **1**; X = O, Z = NH, Y = NH; $n = m = p = 2$) each Hg(II) centre has a distorted tetrahedral geometry, being bound to three ligand nitrogen atoms with a Hg–Hg bond occupying the fourth position; this results in formation of the 2:2 dinuclear complex. In $[HgL_2](NO_3)_2\cdot 2CH_3OH$ the coordination geometry is

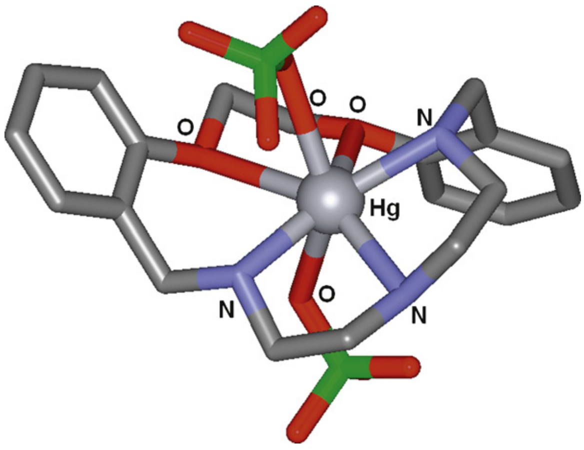


**Fig. 9.** Crystal structure of the seven-coordinate complex, $[HgL(ClO_4)_2]$ (L = **1**; X = O, Z = NH, Y = NH; $n = m = p = 2$).

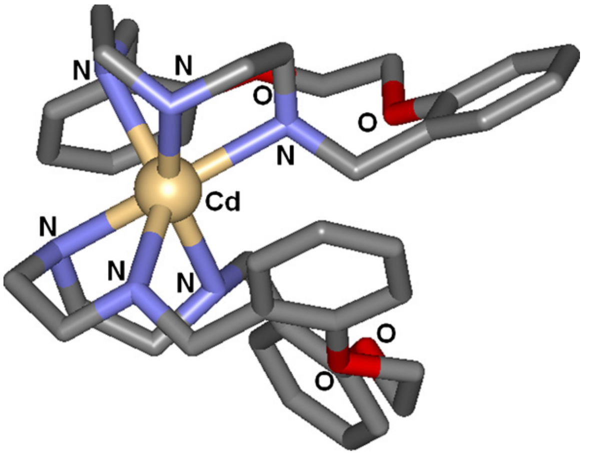


**Fig. 10.** Crystal structure of the cationic sandwich complex present in $[CdL_2](ClO_4)_2 \cdot CH_3CN$ (L = **1**; X = O, Z = NH, Y = NH; *n* = *m* = *p* = 2).

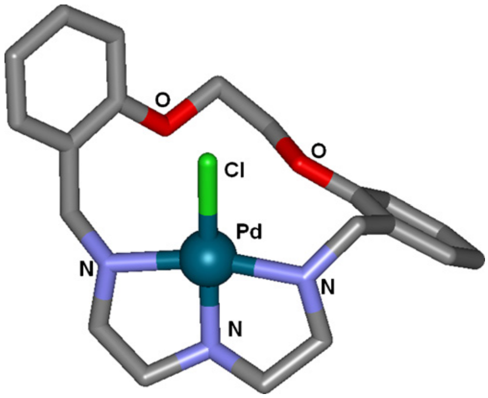
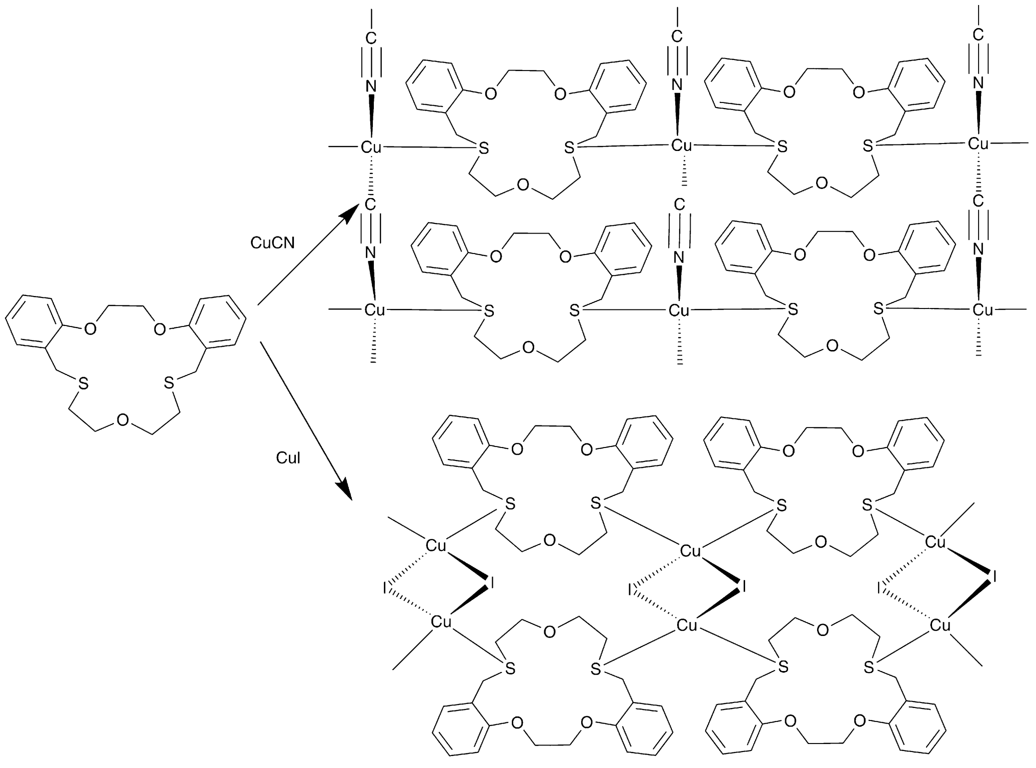


**Fig. 11.** Crystal structure of the complex cation in $[PdLCl]Cl \cdot H_2O$ (L = **1**; X = O, Z = NH, Y = NH; *n* = *m* = *p* = 2).

best described as distorted octahedral in which each of the two macrocyclic ligands coordinate to the metal centre via three nitrogen atoms. The macrocyclic oxygen atoms and the nitrate anions are not coordinated.

Cd(II) forms a 1:2 complex of type $[CdL_2](ClO_4)_2 \cdot CH_3CN$ (L = **1**; X = O, Z = NH, Y = NH; *n* = *m* = *p* = 2) (Fig. 10) in which two macrocyclic units bind to the Cd(II) centre via a facial arrangement of their nitrogen donors (the ether oxygen atoms do not coordinate) to form a distorted octahedral array of six N atoms [69]. This contrasts with the distorted pentagonal–bipyramidal coordination geometry of the related 1:1 complex, $[CdL(NO_3)_2]$, reported earlier [33]. In this latter case all macrocyclic donors coordinate, with the Cd(II) ion lying in the macrocyclic cavity and two monodentate nitrate groups occupying the axial sites such that the Cd(II) centre achieves a seven-coordinate geometry.

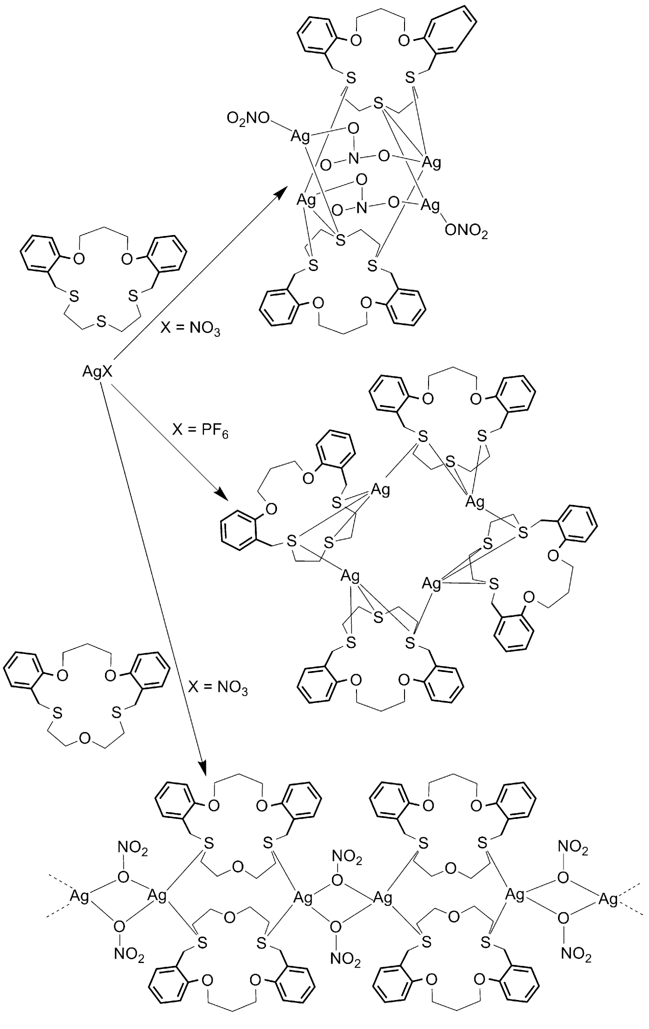
Interaction of $K_2PdCl_4$ and $Pd(NO_3)_2$ with **1** (X = O, Z = NH, Y = NH; *n* = *m* = *p* = 2) yields the respective 1:1 complexes, $[PdLCl]Cl \cdot H_2O$ and $[PdL(NO_3)]NO_3 \cdot CH_3OH$ (L = **1**; X = O, Z = NH, Y = NH; *n* = *m* = *p* = 2), in which the metal is bound to the $N_3$ donors of L and a chloro or nitrato group occupies the remaining site [67]. Each palladium centre adopts a distorted square-planar coordination geometry; once again, the ligand's ether oxygen atoms do not coordinate. The X-ray structure of the cation in $[PdLCl]Cl \cdot H_2O$ is shown in Fig. 11. Both structures in this case are analogues of the previously reported acetate-containing complex, $[PdL(OAc)]OAc \cdot H_2O$ ((L = **1**; X = O, Z = NH, Y = NH; *n* = *m* = *p* = 2) [69].



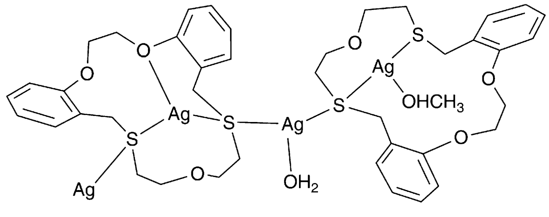
**Scheme 1.**

The combination of the 'framework-building' components, Cu(I) and **1** (X = O, Y = O, Z = S; $n = m = p = 2$), together with a 'framework-regulator', $CN^-$ or $I^-$, has led to the formation of two new extended frameworks exhibiting square-grid and a double-stranded polymeric arrangements, respectively [70]. Thus, for this metal ion/macrocycle combination, a change of anion promotes the assembly of very different network arrays (Scheme 1). The generation of the two-dimensional square-grid structure, $[CuLCN]_n$ (L = **1**; X = O, Y = O, Z = S; $n = m = p = 2$), involved the interaction of **1**; (X = O, Y = O, Z = S, $n = m = p = 2$) with Cu(I) cyanide. The two-dimensional sheets in $[CuLCN]_n$, are considerably puckered due to the distorted tetrahedral geometry adopted by the copper ions with the dimensions of individual rectangular units, incorporating copper ions at the corners, being approximately 4.9 × 10.3 Å. The parallel reaction of this ligand with Cu(I) iodide gave the one-dimensional double-stranded polymeric species $\{[CuLI](MeCN)\}_n$. Each Cu(I) centre has a distorted tetrahedral coordination geometry.

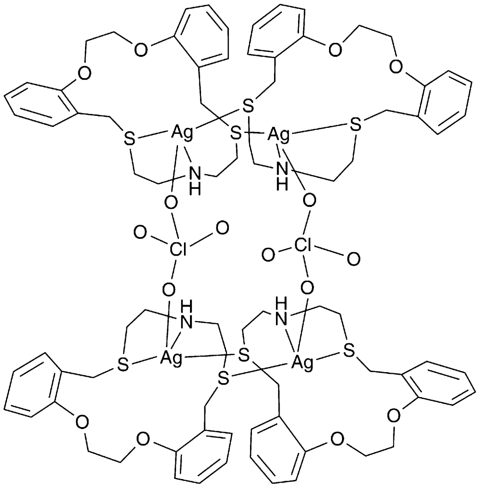
In other studies, the effect of varying the single donor Y from S to O to NH in the 17-membered $O_2S_2Y$-macrocycles of type **1** showed that such a variation results in marked changes in the coordination geometries of the resulting Ag(I) complexes [71]. Four complexes with different topologies were isolated. A sandwich complex of type $[Ag(L)_2](ClO_4)$ was obtained when Y = S (namely, with L = **1**; X = O, Y = S, Z = S; $n = m = p = 2$). When Y = O (namely, with L = **1**; X = O, Y = O, Z = S; $n = m = p = 2$) the results were solvent dependent: in the presence of acetonitrile a complex crystallised in a cofacial dimeric arrangement with two $[AgL(CH_3CN)]^+$ units connected by an argentophilic Ag–Ag interaction at 3.33 Å such that product was of type $\{[AgL(CH_3CN)](ClO_4)\}_2$. In contrast, a one-dimensional coordination polymer of type $\{[Ag_4L_2(CH_3OH)_2](ClO_4)_4\}_n$ (L = **1**; X = O, Y = O, Z = S; $n = m = p = 2$) (**13**) was obtained when the product was obtained from methanol. Finally, in the case where Y = NH (namely, for L = **1**; X = O, Y = NH, Z = S; $n = m = p = 2$) an interesting tetrameric bowl-type complex of composition $[Ag_4L_4(\mu\text{-}ClO_4)_2](ClO_4)_2$ (**14**) was obtained in which the overall geometry around each silver centre is distorted tetrahedral.



Scheme 2.

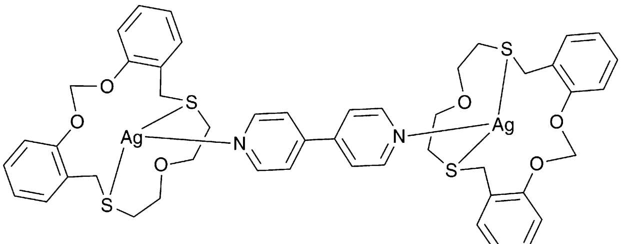


**13**



**14**

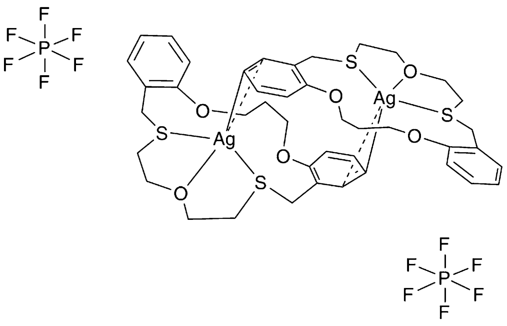
Reaction of the 16-membered $S_2O_3$-donor macrocycle **1** (X = O, Z = S, Y = O; $n = m = 2$, $p = 1$) (L) with Ag(I) perchlorate affords a mononuclear 'half-sandwich' Ag(I) complex of type $[AgL(MeCN)](ClO_4)$ which then reacts 4,4′-bipyridine (bpy) through replacement of the bound acetonitrile ligand to yield the corresponding linked di-silver complex, $[(Ag_2L_2(\mu\text{-bpy})](ClO_4)_2$ (**15**) [72]. Both the mono- and dinuclear silver complexes as well as the free ligand were structurally characterised by X-ray diffraction.



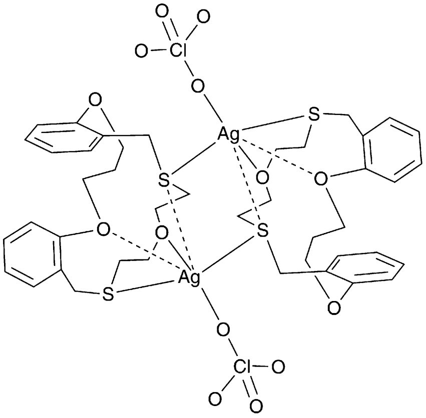
**15**

The interaction of the corresponding 18-membered thiaoxamacrocycles, **1** (X = O, Z = S, Y = S, $n = m = 2$, $p = 3$) and **1** (X = O, Z = S, Y = O, $n = m = 2$, $p = 3$), with Ag(I) nitrate and hexafluorophosphate has also been investigated [29]. Three exo-coordinated complexes displaying different architectures were obtained: a tetranuclear sandwich species of type $[Ag_4L_2(NO_3)_4]$ (where L = **1**; X = O, Z = S, Y = S, $n = m = 2$, $p = 3$), a cyclic tetramer of type $[Ag_4L_4](PF_6)_4$ (where L = **1**; X = O, Z = S, Y = S, $n = m = 2$, $p = 3$) and a polymeric product of type $[AgLNO_3]_n$ (where L = **1**; X = O, Z = S, Y = O, $n = m = 2$, $p = 3$) (Scheme 2). Once again, variation of both anion and donor atoms is seen to have a marked influence on the type of complex generated by these ligand types.

The endo- and exocyclic dinuclear complexes, $[Ag_2L_2](PF_6)_2$ and $[Ag_2L_2(ClO_4)_2]0.5H_2O$, were obtained on reaction of the 18-membered $S_2O_3$-donor macrocycle, **1** (X = O, Z = S, Y = O; $n = m = 2$, $p = 3$) with Ag(I) hexafluorophosphate and perchlorate, respectively [73]. In this study the observed endo- and exo-coordination arrangements were rationalised in terms of the stronger coordination ability of perchlorate over hexafluorophosphate towards Ag(I). Thus the structure of $[Ag_2L_2](PF_6)_2$ (**16**) shows that each Ag(I) is accommodated inside the macrocyclic cavity, with the uncoordinated hexafluorophosphates acting as counterions. Each Ag(I) centre is four coordinate with a distorted tetrahedral geometry, being bound to two sulfur and one oxygen donor from the surrounding macrocycle and one aromatic carbon (at 2.62 Å) via Ag-$\pi$ coordination from an adjacent (also bound) macrocycle.



**16**



**17**

In contrast to the above complex, in the exo-coordinated species $[Ag_2L_2(ClO_4)_2]·0.5H_2O$ (**17**), each Ag(I) centre bridges two facing macrocycles to again form a cyclic dimer. Accordingly, the Ag(I) centre is four-coordinated by a sulfur and an oxygen atom from one macrocycle and one sulfur atom from another (long-range silver oxygen and sulfur interactions are also present). The remaining site is occupied by a perchlorate oxygen [at 2.78 Å].

In another structural study [27], Cd(II) and Hg(II) complexes of the $NS_2O_2$-donor macrocycle **1** (X = O, Y = NH, Z = S; $n = m = p = 2$) and its ditopic xylyl-bridged analogue **7** (Z = S) (see later) have been investigated. Interaction of Cd(II) nitrate with **1** (X = O, Y = NH, Z = S; $n = m = p = 2$) results in formation of $[CdL(NO_3)_2]·0.5CH_2Cl_2$ (L = **1**; X = O, Y = NH, Z = S; $n = m = p = 2$) (**18**) in which L acts as a tridentate ligand via its $S_2N$ donors and binds in an exo manner such that the cadmium centre is not contained in the macrocyclic cavity. The remaining coordination positions are filled by two bidentate nitrate ions such that, overall, the cadmium is seven-coordinate.

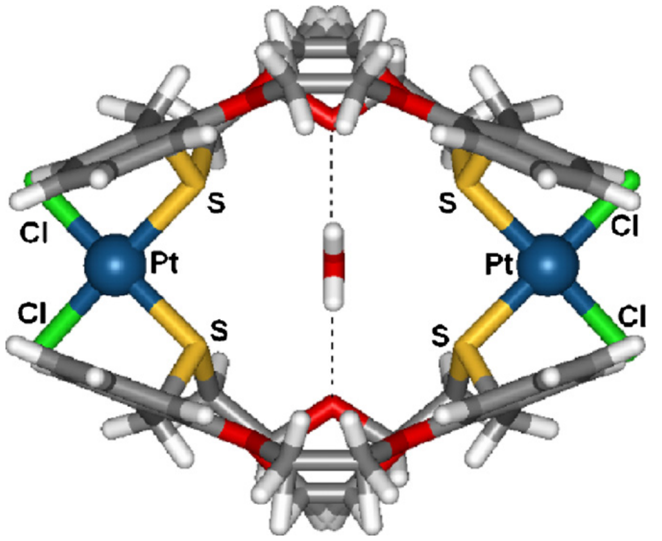
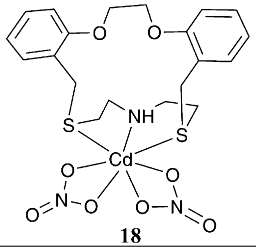
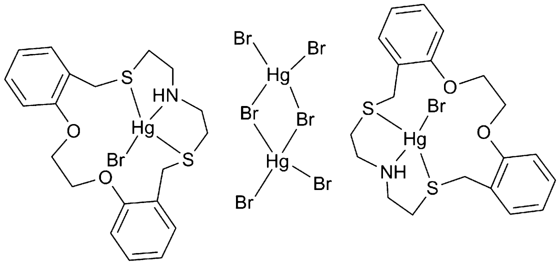


**Fig. 12.** X-ray structure of $[Pt_2L_2Cl_4]·H_2O$ showing the hydrogen bonded water in the cavity.



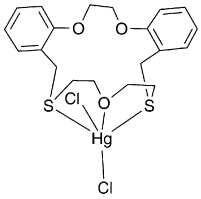
**18**

$HgX_2$ (X = Br or I) interact with **1** (X = O, Y = NH, Z = S; $m = n = p = 2$) to give complexes of type $[HgLBr]_2[Hg_2Br_6]·2CH_2Cl_2$ (**19**) and $[HgLI_2]$ (**20**). The Hg(II) centre in the first complex has a distorted tetrahedral coordination geometry, with the central metal being bound to a $S_2N$ donor subset from (**1**; X = O, Y = NH, Z = S; $m = n = p = 2$) together with a bromo ligand. In $[HgLI_2]$ (L = **1**; X = O, Y = NH, Z = S; $m = n = p = 2$) the coordination is best described as distorted tetrahedral, with the macrocycle coordinating in an exodentate manner via only one S and one N donor atom. The remaining two coordination sites are occupied by iodide ions. In contrast, interaction of **1** (X = O, Y = NH, Z = S; $m = n = p = 2$) with Hg(II) perchlorate led to isolation of $[HgL(ClO_4)]ClO_4$ in which all macrocyclic ring donors are bound to the central metal. The coordination geometry is distorted octahedral in which the $O_2S_2$-donors from the macrocyclic ring occupy the equatorial plane while the axial sites are occupied by the macrocyclic ring nitrogen as well as by an oxygen from a monodentate perchlorato ligand.

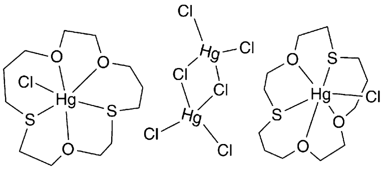


**19**

The reaction of Hg(II) chloride with the $O_3S_2$-donor macrocycle **1** (X = O, Y = O, Z = S, $n = m = p = 2$) (L) and with the corresponding $O_3S_2$-donor, all-aliphatic analogue L′ yielded complexes of type $HgLCl_2$ (**21**) in which the macrocycle is exo-coordinated, and $[HgL'Cl]_2[Hg_2Cl_6]$ (**22**) in which the macrocycle is endo-coordinated [74]. This change in the solid state coordination behaviour was attributed to the difference in the degree of ring rigidity of the respective ligands. A comparative NMR study provided evidence that the above different coordination modes are maintained in solution.

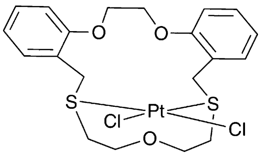


**21**



**22**

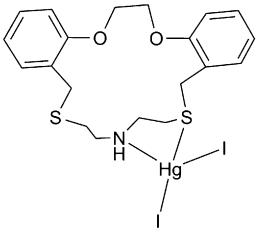
The $O_3S_2$-macrocycle **1** (X = O, Z = S, Y = O, $n = m = p = 2$) also reacts with $K_2PtCl_4$ to yield both mono- and dinuclear complexes, the formation of which reflected the conditions used for their isolation [75]. For the first complex, an aqueous solution of $K_2PtCl_4$ was added to a dichloromethane solution of **1** (X = O, Z = S, and Y = S, NH or O, $n = m = p = 2$) and the mixture was stirred for 24 h at room temperature. Slow evaporation of the separated dichloromethane phase yielded yellow crystals whose X-ray analysis revealed them to be a species of type $[cis\text{-}PtLCl_2]\cdot CH_2Cl_2$. The Pt(II) centre in this complex has a square-planar coordination environment (see **23**), being bound to two chloro ligands and to two sulfur donors from the macrocycle, which is present in a bent configuration. All three ether oxygen atoms of the macrocycle remain uncoordinated.



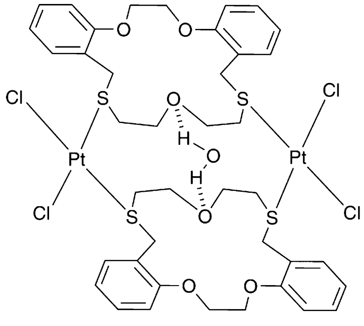
**23**

In contrast, the reaction of the above ligand with $K_2PtCl_4$ in acetonitrile/water for 24 h yielded a yellow powder. Vapour diffusion of diethyl ether into a solution of this powder in dimethylsulfoxide gave a yellow crystalline product whose X-ray analysis (Fig. 12) revealed an unusual 2:2 (M:L) cyclic dimer of type $\{[Pt_2L_2Cl_4](H_2O)\}\cdot 3CH_3CN$ (where L = **1**; X = O, Z = S, Y = O; $n = m = p = 2$).

Each Pt(II) centre is located out of the cavity and adopts a distorted square-planar geometry, being bound to two sulfur donor atoms from different macrocycles and two chloro groups in a *cis* arrangement to form a small metallacycle (see **24**). Interestingly, a bridging hydrogen bonded water molecule is contained in the cavity of the dimer, likely contributing to the overall stability of the dimeric arrangement adopted by this unusual species.



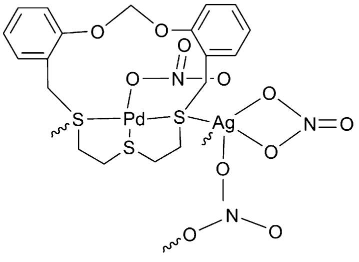
**20**



**24**

### 6.2. A heterobinuclear Pd(II)/Ag(I) system

An unusual example of endo- and exocyclic coordination of Pd(II)/Ag(I) to a single macrocycle to yield a heterobinuclear 2D network structure has been reported [76]. Interaction of the 16-membered ring (**1**; X = O, Y = S, Z = S; $n = m = 2$, $p = 1$) with $K_2PdCl_4$ yields the exo-coordinated square-planar complex $[cis\text{-}PdLCl_2]$. Reaction of this species with excess silver nitrate then leads to isolation of the polymeric heterobinuclear complex, $\{[PdLAg(NO_3)_{2.5}](NO_3)_{0.5}\}_n$, containing endocyclic Pd(II) and exocyclic Ag(I) (see **25**) bound to a single macrocycle. This appears to be a unique example of a macrocyclic complex species incorporating $\mu_2$-S-bridged Pd(II) and Ag(I) centres. The resulting network is composed of honeycomb-like 2-D sheets.



**25**

### 6.3. Xylyl-linked double-ring macrocyclic systems incorporating $O_2S_2N$ donor sets

The interaction of **7** (Z = S) with cadmium nitrate yields a one-dimensional coordination network of type $\{[Cd_2(L)(NO_3)_4]\cdot 2CH_2Cl_2\}_n$ (where L = **7**; Z = S) in which each L is exo-coordinated via two sulfur atoms and one nitrogen atom to its Cd(II) ion [27]. Each metal centre is also bound to one monodentate and one bidentate nitrate anion, with the latter also bridging via one of its oxygen atoms to the neighbouring Cd(II) site

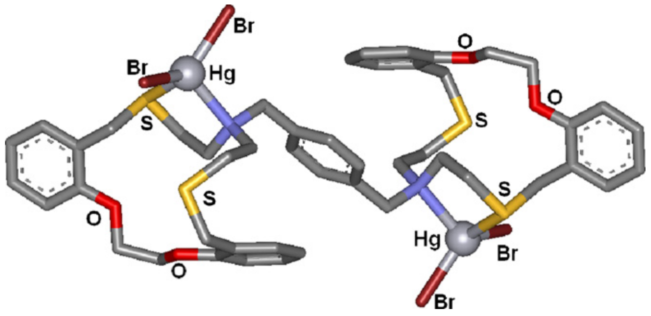


**Fig. 13.** The X-ray structure of $[Hg_2LBr_4]$ (where L = **7**; Z = S).

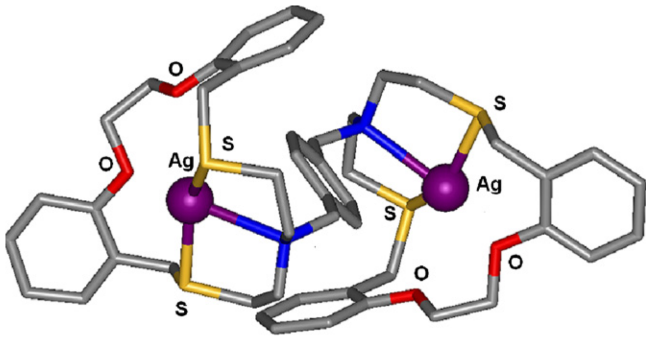


**Fig. 14.** X-ray structure of the complex cation in the endo-coordinated dinuclear complex, $[Ag_2L](ClO_4)_2$ (where L = **7**; Z = S).

via a $\mu_2$-O bridge (namely, there are two such bridges present per dinuclear complex unit). This results in each Cd(II) centre being seven-coordinate. $[Cd(L)_{0.5}(NO_3)_2]$ (L = **7**; Z = S) units are linked by an inversion to yield the polymeric arrangement; the separation between the closest Cd(II) ions bound to different macrocycles is 4.16 Å, while that between the two Cd(II) bound to the same ligand is 12.06 Å.

Contrasting with the above polymeric arrangement, reaction of $HgX_2$ (X = Br or I) with the xylyl-linked bis-macrocycle **7** (Z = S) yields isostructural 2:1 (metal:ligand) complexes of type $[Hg_2LBr_4]$ and $[Hg_2LI_4]$ [where L = **7** (Z = S)] [27]. The structure of $[Hg_2LBr_4]$ is given in Fig. 13. The corresponding chloro derivative $[Hg_2LCl_4]$ was also synthesised in a subsequent study [77]. Both Hg(II) centres in each complex have similar distorted tetrahedral environments; each is made up of one S and one N donor from an exodentate **7** (Z = S) macrocycle and two coordinated halides.

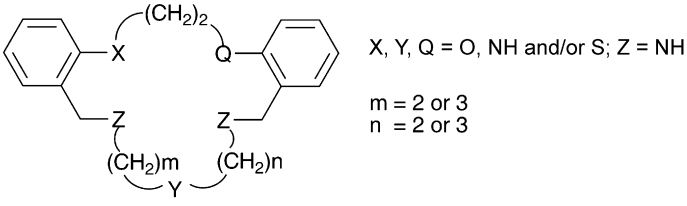
The above xylyl-linked ligand (**7**; Z = S) also gives rise to a dinuclear Ag(I) complex and a one-dimensional Cu(I) iodide coordination polymer [78]. Thus, interaction of this ligand with silver perchlorate yielded the discrete dinuclear endo-coordinated species $[Ag_2L](ClO_4)_2$ (L = **7**; Z = S) in which the Ag(I) ions lie within the respective macrocyclic cavities and are bound to both sulfurs and the nitrogen of each ring (Fig. 14); the ether oxygen atoms do not coordinate.

In contrast, interaction of the above ligand with Cu(I) gave a one-dimensional coordination polymer of type $[Cu_4LI_4]_n$ incorporating twisted-ribbon like $Cu_4I_4$ units as 'connectors' between Cu(I)-bound macrocyclic fragments (Fig. 15). An NMR study suggests that the solid structures are also retained in solution.

## 7. Systems involving unsymmetric macrocycles

As an extension of the macrocyclic ligand systems discussed so far, all of which have symmetrical arrangements of their donor atoms, the more challenging synthesis and characterization of a range of 17- or 18-membered, asymmetric mixed-donor macrocycles of general type **26** have also been carried out [25]. X-ray structures of the representative 17-membered rings incorporating $N_4O$- and $N_4S$-donor sets confirmed the expected connectivity of these ligands.

The development of a simple procedure for modelling the metal complex stability constants of Zn(II), Cd(II), Ag(I) and Pb(II) complexes (in part chosen because these metals are free of crystal field influences) incorporating selected 17-membered symmetrical macrocycles of type **1** as well as unsymmetrical macrocycles of type **26** has been described. The ligand donor sets involved in this initial study are given by OO/NNN, OO/NON, OO/NSN, SS/NNN, SS/NON, SS/NSN, NN/NNN, NN/NON, NN/NSN for type **1** (XX/ZYZ) and OS/NNN, OS/NON, OS/NSN, NO/NNN, NS/NNN for type **26** (XQ/ZYZ) [79]. A motivation for undertaking this structure-function analysis was in part provided by the results from prior studies in which it was demonstrated that for selected complex categories the binding free energy of metal complexation, ΔG, can be partitioned as a sum of contributions from individual metal–donor interactions [80,81] and a related approach was taken in the above study.



**26**

Initial calculations were based on previously determined log *K* data for the 1:1 (M:L) complexes of a selection of the symmetrical ligands of type **1**. Namely, for a given metal ion type, the collective log *K* data for this ligand type were employed to derive parameters that are characteristic of each of the metal–donor bond types present. This parameterization was then employed to compute log *K* values for complexes from both the symmetrical (type **1**)

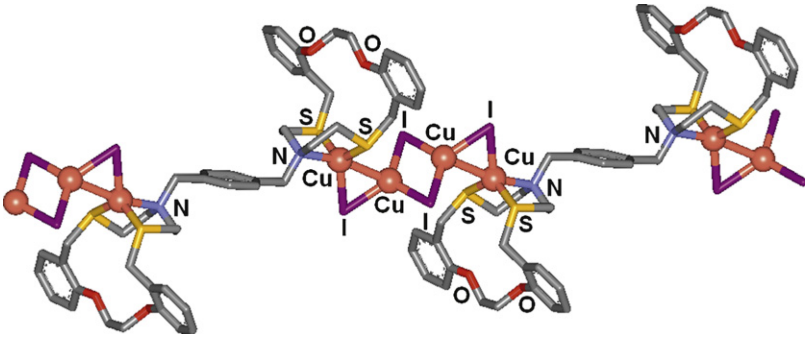


**Fig. 15.** X-ray structure of part of the polymeric chain in $[Cu_4LI_4]_n$ (where L = **7**; Z = S).

and unsymmetrical (type **26**) ligand series. In general, quite good agreement with the experimentally determined log *K* values was obtained across both ligand series. The parameters were also used to predict log *K* values for complexes of other ligands in the series not then synthesised. The results from this study point the way for the calculation of metal complex stabilities for other (suitable) metal complex systems that are also derived from series of closely related ligands.

## 8. Conclusion

The foregoing discussion clearly demonstrates the extraordinary structural diversity that is possible from the use of ligands containing different donor set combinations – with different metal ion affinities – incorporated in a semi-flexible macrocyclic framework when reacted with transition and post-transition ions of the type discussed herein.

## Acknowledgements

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