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Schiff-base compartmental macrocyclic complexes

Andrew J. Atkins,[a] Daniel Black,[b] Alexander J. Blake,[a,b] Armando Marin-Becerra,[c] Simon Parsons,[a] Lena Ruiz-Ramirez[c] and Martin Schröder*[a,b]

[a] *Department of Chemistry, The University of Edinburgh, West Mains Road, Edinburgh, UK EH9 3JJ*
[b] *Department of Chemistry, The University of Nottingham, University Park, Nottingham, UK NG7 2RD*
[c] *UNAM Facultad de Quimica, Departamento di Quimica Inorganica, Ciudad Universitaria 04510, Mexico DF, Mexico*

The synthesis of a range of new compartmental macrocyclic complexes based on 2,6-diformyl and -diketo phenol groups is described. The metal-free ligands have been prepared and structurally characterised for the first time, and this has led to the synthesis of novel cubane and platinum-group metal complexes. The synthesis of related dithiophenolato-bridged compartmental complexes of Ni^{II}, Cu^{II} and Zn^{II} has been achieved and the relevance of these species to metalloproteins is discussed.

Introduction

The chemistry of metal template cyclisations to form Schiff-base macrocyclic ligands was first developed by Curtis,[1] Busch[2] and Jäger,[3] and pre-dates the first synthesis of crown ethers reported by Pederson.[4] Over the past 30 years a very wide range of cyclised and open-chain Schiff-base metal complexes has been prepared,[5] and these have found uses in O_2-binding chemistry,[6] as bioinorganic models,[7] in hydrometallurgy[8] and catalysis.[9]

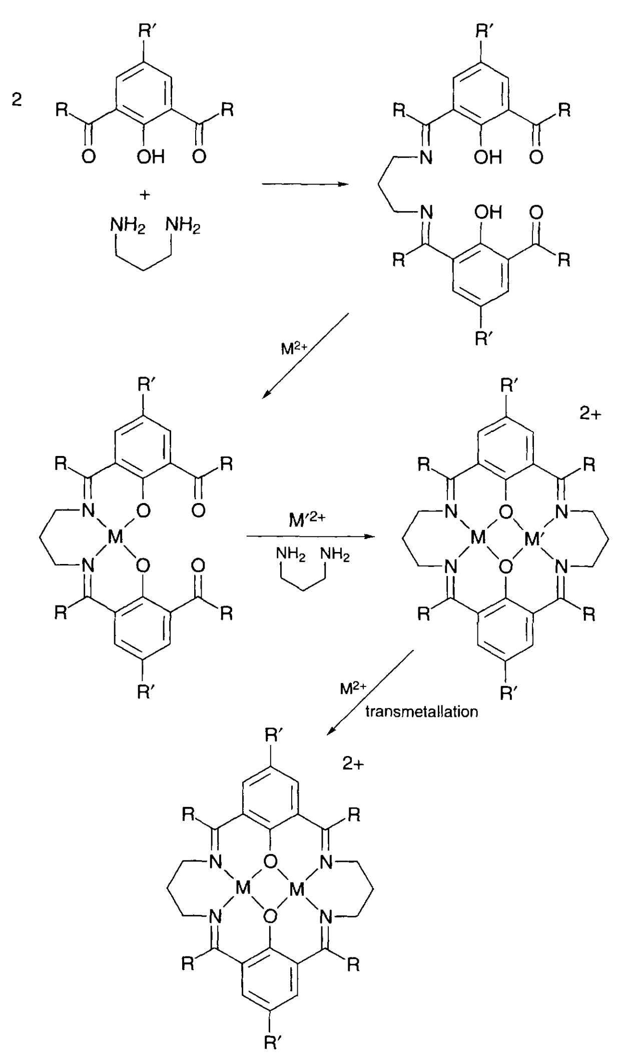
In 1970 Robson and co-workers reported the synthesis of a new compartmental macrocyclic system based upon the metal template Schiff-base condensation of 2,6-diformyl-4-methylphenol with 1,3-diaminopropane in the presence of a range of first row transition metal ions.[10] This unique system achieves the aim of bringing two metal centres into close proximity, with important implications for metal–metal interactions and magnetic exchange,[11] and binuclear metal reactivity.[12] The synthesis of these compartmental ligands (Scheme 1) hinges upon the use of metal-directed template methods for bringing the constituent components of the cyclic ligand together.[13] In the absence of a metal ion, typically a labile first-row transition metal or d^{10} metal ion such as Ni^{II}, Cu^{II}, Zn^{II} or Ag^{I}, cyclisation does not occur cleanly and often intractable polymers and oligomers are produced, with no cyclised ligand(s) being isolable. The unique features of the Robson-type macrocycle led us to investigate potential routes to the synthesis of complexes incorporating non-labile platinum metal complexes. In general, metal-directed template reactions fail with such metal ions,[14] and so routes to metal-free ligands had to be developed.

We report herein our recent results on the synthesis of metal-free compartmental macrocyclic ligands and their complexation with first- and second-row transition-metal ions. This work has been extended to the synthesis of related thiophenolate compartmental complexes which show unusual dithiolato-bridged structural motifs.

Phenolate macrocycles

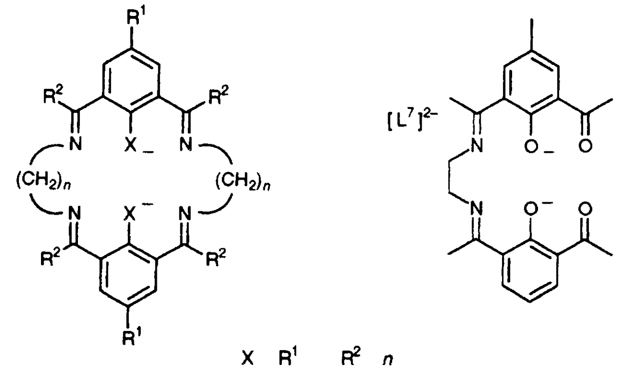
Synthesis and structures of metal-free ligands. Attempts to prepare metal-free compartmental ligands by reaction of 2,6-diformyl-4-methylphenol with 1,3-diaminopropane under a variety of conditions (*e.g.* high and low dilution) and in a variety of solvents generally fail to afford the required cyclised ligand. Direct condensation of 1,3-diaminopropane with 2,6-diformyl-4-methylphenol in thf affords a yellow product containing the free binucleating ligand $[H_2L^1]$. However, some free ketonic and free amine-containing impurities are usually observed in these products, and purification is inevitably dogged by hydrolysis and side-reactions. We therefore undertook an alternative strategy using H^+ as a template ion.

Reaction of 1,3-diaminopropane and 2,6-diformyl-4-methylphenol in MeOH in the presence of 48% HBr, followed by addition of Br_2,[15] affords the protonated 2 + 2 condensation product $[H_4L^1][Br_3]_2$ as a relatively insoluble salt (Scheme 2). Metathesis of this salt with NH_4PF_6 or $NaBF_4$ in MeOH affords $[H_4L^1][PF_6]_2$ or $[H_4L^1][BF_4]_2$. The single-crystal X-ray struc-



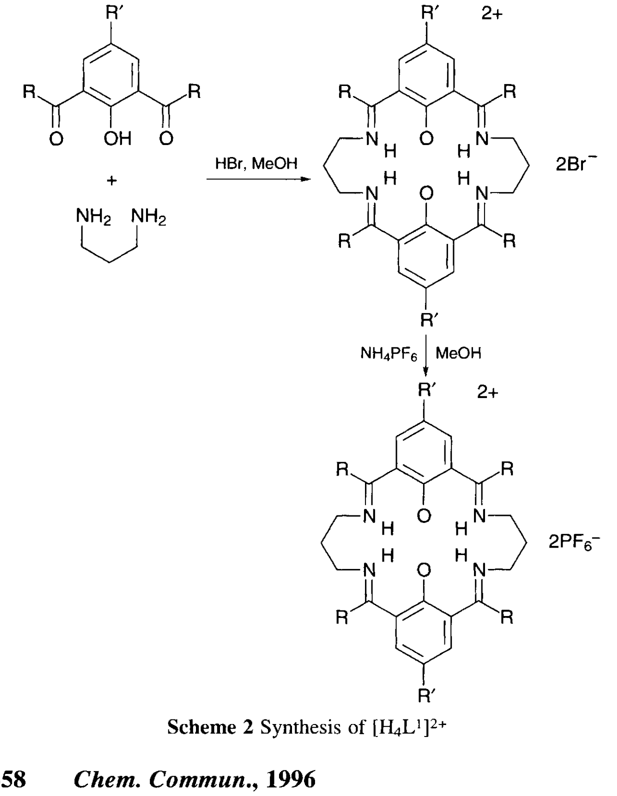
Scheme 1 Synthesis of phenolate compartmental macrocyclic complexes by metal-directed template reaction

ture of $[H_4L^1][PF_6]_2$ shows (Fig. 1)[16] that the protonated Schiff-base macrocycle adopts a highly unusual folded conformation with the two phenyl rings involved in inter- and intra-molecular stacking interactions. The conformation of $[H_4L^1]^{2+}$ is reminiscent of calixarenes[17] and of related Schiff-base macrocycles,[18] with the phenyl rings folded downwards to leave the N- and O-donor atoms on an exposed face. The dihedral angle between the phenyl ring planes in $[H_4L^1]^{2+}$ is 14°.



	X	R¹	R²	n
$[L^1]^{2-}$	O	Me	H	3
$[L^2]^{2-}$	O	Bu^t	H	3
$[L^3]^{2-}$	O	Me	Me	2
$[L^4]^{2-}$	O	Me	H	2
$[L^5]^{2-}$	S	Me	H	3
$[L^6]^{2-}$	S	Me	H	3 $(CH_2\underset{OH}{C}HCH_2)$

A series of related free ligands $[L^1]^{2-}$–$[L^6]^{2-}$ has been prepared. Fig. 2 shows the single-crystal X-ray structure of $[H_4L^2][PF_6]_2$ in which the Me group at the 4-position of the phenol moieties has been replaced by a *tert*-butyl group. The conformation of $[H_4L^2]^{2+}$ is very similar to that observed for $[H_4L^1]^{2+}$ except that the dihedral angle between the planes of the phenyl rings has increased to 25° due to the greater steric bulk of the *tert*-butyl groups.



Scheme 2 Synthesis of $[H_4L^1]^{2+}$

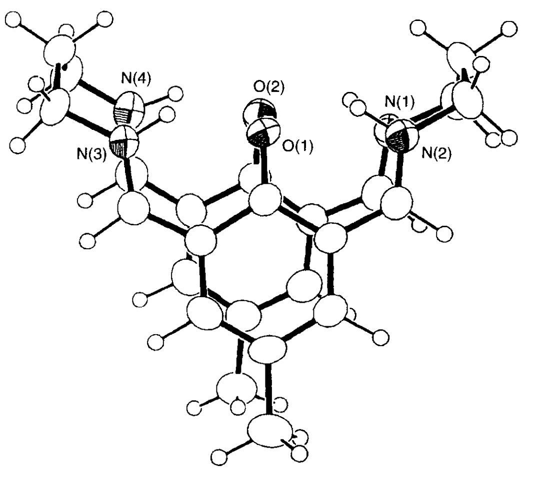


Fig. 1 View of the structure of $[H_4L^1]^{2+}$

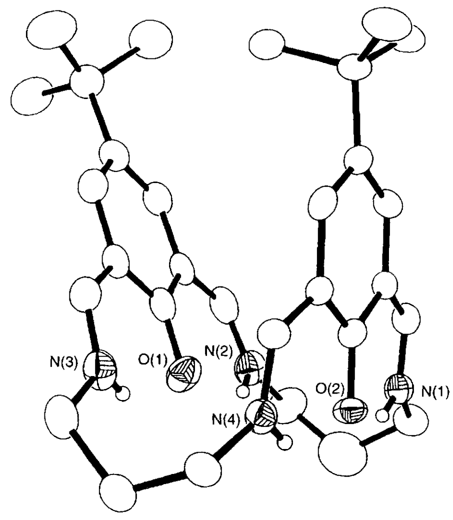


Fig. 2 View of the structure of $[H_4L^2]^{2+}$

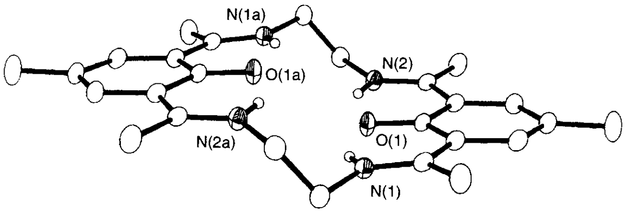


Fig. 3 View of the structure of $[H_4L^3]^{2+}$

A more planar arrangement for these metal-free ligand species is observed on replacement of the C_3 linker with a C_2 linker. The single-crystal X-ray structures of $[H_4L^3][PF_6]_2$ (Fig. 3) and $[H_4L^4][PF_6]_2$ both show a 'stepped' conformation in which the planes of the two diimino-phenol fragments of the macrocycle are approximately parallel but offset. Thus, the degree of folding of the macrocycle can be controlled not only by the steric bulk of the substituent at the 4-position of the phenyl groups, but also by variation of the linker unit, with odd C_3 linkers affording bent conformations, and even C_2 linkers more planar conformations.[19]

Metal complexation reactions. The salt $[H_4L^1][Br_3]_2$ and related halogeno salts are not as useful starting materials for the preparation of complexes as their PF_6^- or BF_4^- analogues due to their relative insolubility and competition reactions with Br^- ion during metal insertion reactions.

Nickel. The brown complex $[Ni_2(L^1)(NCMe)_4]^{2+}$ can be prepared by reaction of $[Ni(OH_2)_6]^{2+}$ with $[H_4L^1]^{2+}$ in MeCN in the presence of NEt_3. The single-crystal X-ray structure of $[Ni_2(L^1)(NCMe)_4]^{2+}$ (Fig. 4) shows two octahedral Ni^{II} centres. The macrocycle is essentially flat with only the middle carbons of the propylene chains deviating from the $[L^1]^{2-}$ ligand plane. Each Ni^{II} centre occupies an octahedral environment and is coordinated to two imine N-donors, two bridging phenoxy O-donors and two axial MeCN ligands. The Ni···Ni separation is 3.136(1) Å; this is similar to the $Cu^{II}\cdots Cu^{II}$ distance [3.091(3) Å] found in $[Cu_2(L^1)(H_2O)_2(ClO_4)_2]$[20] and the $Fe^{II}\cdots Fe^{II}$ distance [3.117(3) Å] found in $[Fe_2(L^1)(Him)_4]^{2+}$[21] (Him = imidazole) where the metal centres are also in octahedral environments and located in the ligand plane. Robson[10] and Gagné[21] have reported related octahedral complexes of Ni^{II} and $[L^1]^{2-}$. In $[Ni_2(L^1)(NCMe)_4]^{2+}$ the Ni–N≡C angle deviates significantly from the expected linear geometry [157.2(4), 166.5(4)°], and we ascribe this to relief of steric interactions between the MeCN ligands. We suggest that the non-linearity of the Ni^{II}–NCMe groups and the relative instability of the complex are caused by unfavourable steric interactions of the axial ligands. The structure of $[Ni_2(L^1)(NCMe)_4]^{2+}$ confirms the conclusion of Okawa and Kida[22] that Ni^{II} ions will adopt an octahedral geometry when coordinated to $[L^1]^{2-}$. Thus, due to its size $[L^1]^{2-}$ does not give a sufficiently large ligand field to enforce a square-planar geometry on Ni^{II}.

The reaction of 2 equiv. of $[Ni(O_2CMe)_2]\cdot 4H_2O$ with $[H_4L^1][PF_6]_2$ in the presence of an excess of NEt_3 in MeCN gives a green product. The single-crystal X-ray structure of this species shows (Fig. 5) it to be the tetranuclear cluster $[Ni_4(L^1)_2(O_2CMe)_2]^{2+}$, with $[Ni_2(L^1)(O_2CMe)]^+$ units having dimerised to give an Ni_4O_4 cubane-type structure. Each Ni^{II} centre is in a distorted octahedral environment, being equatorially bound to the N_2O_2 donor set of one $[L^1]^{2-}$ macrocycle and with axial interactions to a carboxylic O-donor of a bridging $MeCO_2^-$ group and a phenoxy O-donor from a macrocycle from the other half of the cluster. The macrocycle $[L^1]^{2-}$ in each $[Ni_2(L^1)(O_2CMe)]^+$ unit is non-planar and the angle between the planes defined by the two phenol groups is 104°, the macrocycles having to bend to accommodate both the Ni_4O_4 cube and the $MeCO_2^-$ ligands.[23]

There have been a number of Ni_4O_4 cubane-type structures reported in the literature;[24] however, to our knowledge this is the first example where the Ni ions are incorporated within a macrocycle. The driving force for the dimerisation is probably the requirement of the Ni^{II} centres for octahedral coordination.[16,22]

The complex $[Ni_2(L^3)]^{2+}$ incorporating a C_2 linker was first prepared by Okawa and Kida,[22] and was found to bind anions very readily. The Ni^{II} ions were proposed to be square planar in contrast to nickel(II) complexes of $[L^1]^{2-}$. Reducing the ring size by replacing C_3 with C_2 linkers would be expected to increase the ligand field of the resultant macrocycle and afford potentially square-planar nickel(II) products. Indeed, we have confirmed this by the single-crystal X-ray structure determination of $[Ni_2(L^3)][PF_6]_2$ which shows square planarity at each Ni^{II} centre (Fig. 6). We can therefore control the stereochemistry of the metal ion in the resultant complex by control of the ring size of the macrocycle.

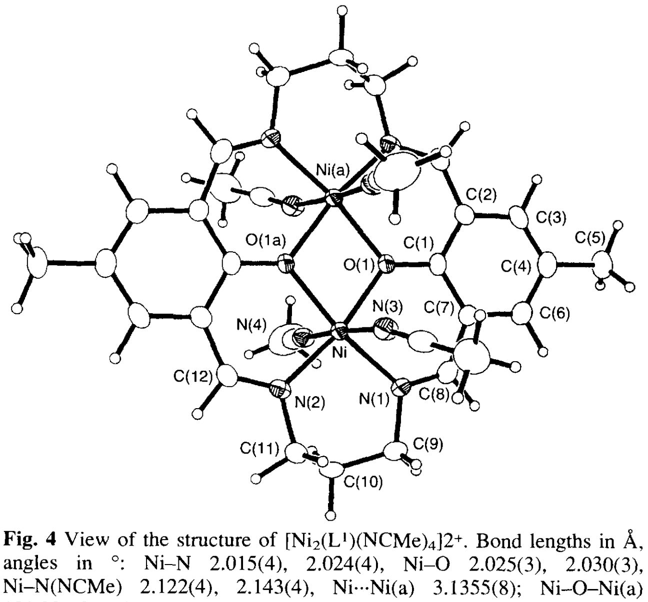


Fig. 4 View of the structure of $[Ni_2(L^1)(NCMe)_4]^{2+}$. Bond lengths in Å, angles in °: Ni–N 2.015(4), 2.024(4), Ni–O 2.025(3), 2.030(3), Ni–N(NCMe) 2.122(4), 2.143(4), Ni···Ni(a) 3.1355(8); Ni–O–Ni(a) 101.32(13), Ni–N–C(NCMe) 157.2(4), 166.5(4).

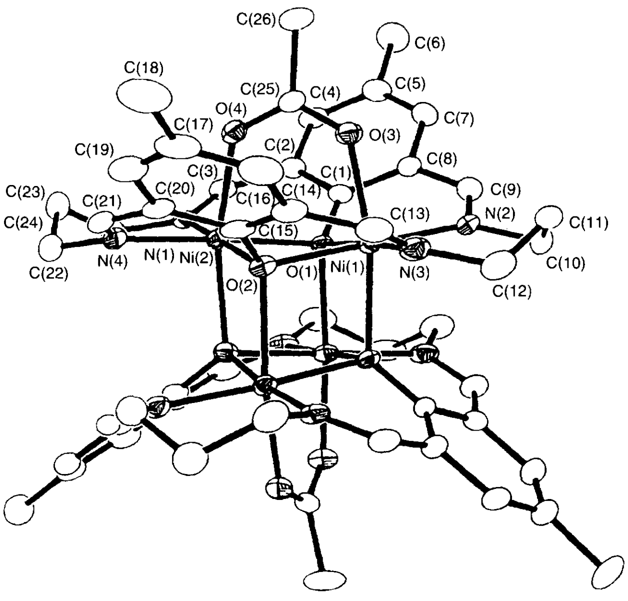


Fig. 5 View of the structure of $[Ni_4(L^1)_2(O_2CMe)_2]^{2+}$. Bond lengths in Å, angles in °: Ni–N 2.014(4), 2.027(4), 2.027(4), 2.028(4), Ni–O(O_2CMe) 2.080(3), 2.095(3), 2.099(3), 2.081(3), Ni–O(OPh intramolecular) 2.031(3), 2.035(3), Ni–O(OPh intermolecular) 2.152(3), 2.168(3), Ni(1)···Ni(2) 3.0240(9); Ni(1)–O(2)–Ni(2) 92.70(12), Ni(1)–O(2)–Ni(1a) 98.50(13).

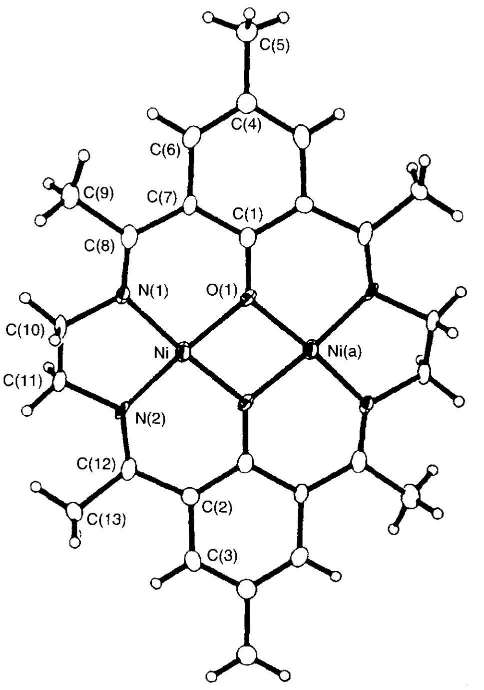


Fig. 6 View of the structure of $[Ni_2(L^3)]^{2+}$. Bond lengths in Å, angles in °: Ni–O 1.837(4), 1.847(4), Ni–N 1.850(5), 1.839(4), Ni···Ni(a) 2.781(2); Ni–O–Ni 98.0(2).

Copper. We wished to monitor further the differences between C_2- and C_3-linked macrocycles and investigated the binding of copper(II) to these compartmental ligands. Reaction of $[H_4L^3][PF_6]_2$ with $Cu(O_2CMe)_2\cdot H_2O$ in the presence of NEt_3

affords two binuclear copper(II) species, green $[Cu_2(L^3)(O_2CMe)]PF_6$ and brown $[Cu_2(L^3)][PF_6]_2$, the former being the major product. Recrystallisation of the crude product from MeCN–Et_2O yields single crystals of both complexes. The single-crystal X-ray structure of $[Cu_2(L^3)(O_2CMe)]^+$ shows (Fig. 7) that the two Cu^{II} ions both adopt a square-pyramidal geometry with each being coordinated to two imino N-donors, two phenoxy O-donors, and to an O-donor of the bridging acetate. The Cu$\cdots$Cu separation of 2.824 Å is somewhat less than that of *ca.* 3.1 Å found in analogous C_3-bridged systems.[20] Both Cu^{II} ions lie slightly out of their N_2O_2 basal plane [Cu(1) by 0.254(2) Å and Cu(2) by 0.206(2) Å]. The macrocycle adopts a more buckled conformation than in its protonated form: in particular, the benzene rings are not coplanar but are twisted by 12.8° with respect to each other.

The single-crystal X-ray structure of $[Cu_2(L^3)]^{2+}$ shows (Fig. 8) that in this species each Cu^{II} centre is coordinated in a square-planar fashion by an N_2O_2 donor set from the macrocycle. The Cu$\cdots$Cu separation of 2.897 Å is similar to that found in $[Cu_2(L^3)(O_2CMe)]^+$. It is evident from the structures of both $[Cu_2(L^3)]^{2+}$ and $[Cu_2(L^3)(O_2CMe)]^+$ that the macrocycle $[L^3]^{2-}$ enforces a marginally smaller Cu$\cdots$Cu separation than in comparable C_3-bridged systems. It should be noted that $[Cu_2(L^3)(O_2CMe)]^+$ and $[Cu_2(L^3)]^{2+}$ can be interconverted: suspension of $[Cu_2(L^3)(O_2CMe)]PF_6$ in EtOH followed by the addition of HPF_6 (60 mass% solution in water) results in the quantitative generation of $[Cu_2(L^3)][PF_6]_2$.

The reaction of $[H_4L^2][PF_6]_2$ with $Cu(O_2CMe)_2{\cdot}H_2O$ in MeCN–EtOH in the presence of an excess of NEt_3 leads to the formation of a binuclear species of formulation $[Cu_2(L^2)(NCMe)_2][PF_6]_2$. A single-crystal X-ray structure determination shows (Fig. 9) that the $[Cu_2(L^2)(NCMe)_2]^{2+}$ units dimerise in the solid state to produce $[Cu_4(L^2)_2(NCMe)_4]^{4+}$ units which have a distorted Cu_4O_4 cubane-type structure. The Cu$\cdots$Cu separation is 3.119 Å within each Cu_2O_2 unit. Each Cu^{II} ion is in a tetragonally distorted octahedral coordination environment.

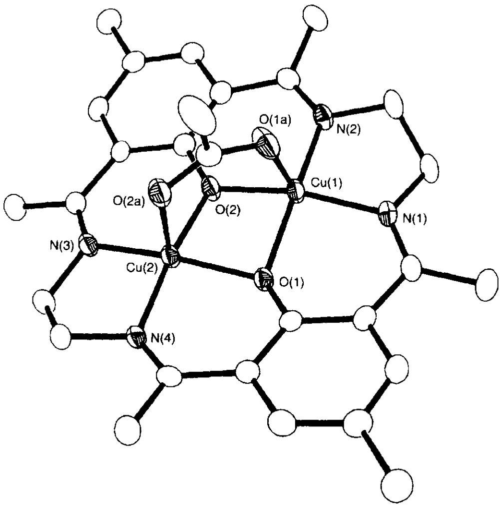


Fig. 7 View of the structure of $[Cu_2(L^3)(O_2CMe)]^{2+}$. Bond lengths in Å, angles in °: Cu–O 1.907(3), 1.916(3), 1.923(3), 1.926(3), Cu–N 1.908(3), 1.911(4), 1.914(4), 1.916(4), Cu–O(O_2CMe) 2.184(3), 2.243(3), Cu(1)$\cdots$Cu(2) 2.8237(7); Cu–O–Cu 94.36(12).

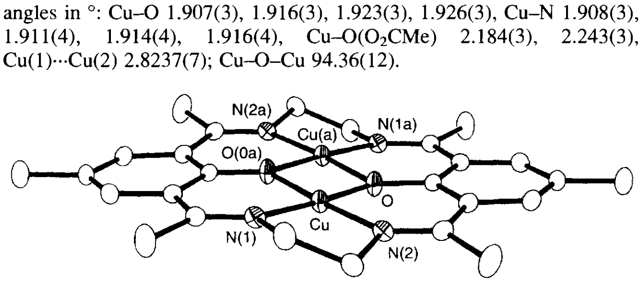


Fig. 8 View of the structure of $[Cu_2(L^3)]^{2+}$. Bond lengths in Å, angles in °: Cu–O 1.897(2), Cu–N 1.890(2), 1.897(2), Cu$\cdots$Cu(a) 2.8971(11); Cu–O–Cu(a) 99.54(9).

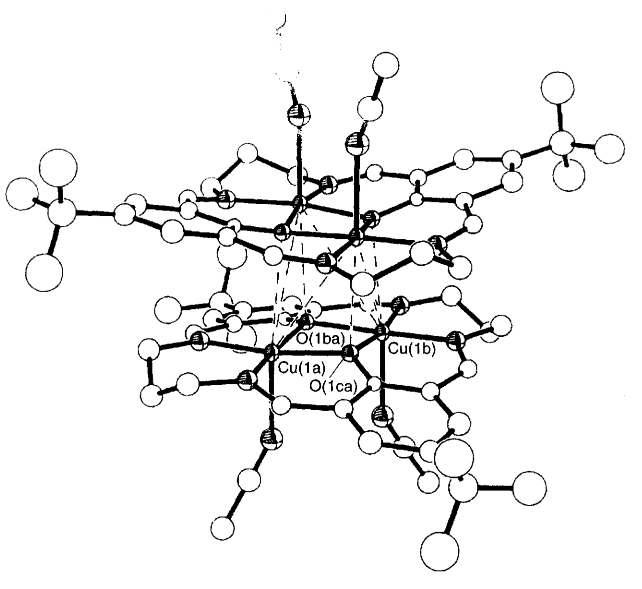


Fig. 9 View of the structure of $[Cu_4(L^2)_2(NCMe)_4]^{4+}$. Bond lengths in Å, angles in °: Cu–O 1.992(7), Cu–N 1.975(11), Cu–N(NCMe) 2.33(2); Cu–O–Cu 103.1(5).

The bond lengths to the four atoms of the N_2O_2 donor set provided by the macrocycle lie in the range 1.97–1.99 Å with the axial MeCN ligands being coordinated at a somewhat greater distance [2.33(2) Å]. A long-range interaction of 3.115 Å to the phenoxy oxygen atom of an adjacent Cu_2O_2 unit completes the coordination sphere of each Cu^{II} ion. The more elongated nature of the $[Cu_4(L^2)_2(NCMe)_4]^{4+}$ cube compared to that of $[Ni_4(L^1)_2(O_2CMe)_2]^{2+}$ reflects the expected Jahn–Teller distortion at Cu^{II} and the greater degree of electrostatic repulsion between the two halves of the Cu_4O_4 system. Whilst these long-range interactions between neighbouring Cu_2O_2 units are too long to be regarded as genuine bonds, the interaction causes each macrocycle to deviate noticeably from planarity. The angle subtended by the normals to the two benzene rings is 27.3(3)°. As already observed in the structure of $[Ni_2(L^1)(NCMe)_4]^{2+}$, the MeCN ligands in $[Cu_4(L^2)_2(NCMe)_4]^{4+}$ do not coordinate in a linear fashion, the Cu–N≡C angles being *ca.* 148°. Interestingly, the complex $[Cu_2(L^1)(O_2CMe)]^+$ does not form a tetranuclear species but consists of discrete binuclear units [Cu–O 1.948(5)–1.980(5), Cu–O(O_2CMe) 2.209(6), 2.138(5), Cu–N 1.948(6)–1.952(6), Cu$\cdots$Cu 2.945(2) Å].

Palladium. $[H_4L^1][PF_6]_2$ and $[H_4L^1][BF_4]_2$ are useful starting materials for the synthesis of complexes of inert metal ions such as those of the platinum group. Thus, reaction of $[H_4L^1][BF_4]_2$ with MCl_2 (M = Pt, Pd) or $[Pd(O_2CMe)_2]_3$ in the presence of a tenfold molar excess of NEt_3 in MeCN affords $[M_2(L^1)]^{2+}$ (M = Pd or Pt) in up to 75% yield. Reaction with $RhCl_3{\cdot}3H_2O$ with 2 molar equiv. of $TlPF_6$ under the same conditions affords $[Rh_2Cl_4(L^1)]^{2+}$. The single-crystal X-ray structural determination of $[Pd_2(L^1)][BF_4]_2{\cdot}2MeNO_2$ shows[16] [Fig. 10(*a*)] each square-planar Pd^{II} centre bound to two O- and two N-donors of the macrocycle. The Pd$\cdots$Pd distance is 3.1511(6) Å. In contrast to the folded conformation of the protonated ligand $[H_4L^1]^{2+}$, the macrocycle in $[Pd_2(L^1)]^{2+}$ is planar, thus removing the possibility of intramolecular π interactions between phenyl rings. However, intermolecular stacking of the phenyl rings occurs in the solid state to give a staggered array of cations [Fig. 10(*b*)].[16]

Ruthenium. Reaction of the open-chain ligand $[H_2L^7]$ with $[RuCl_2(PPh_3)_3]$ affords a red–brown species tentatively assigned as $[Ru(HL^7)Cl(PPh_3)]$. Further reaction with 1,2-diaminoethane in the presence of $Zn(O_2CMe)_2$ and $[RuCl_2(PPh_3)_3]$

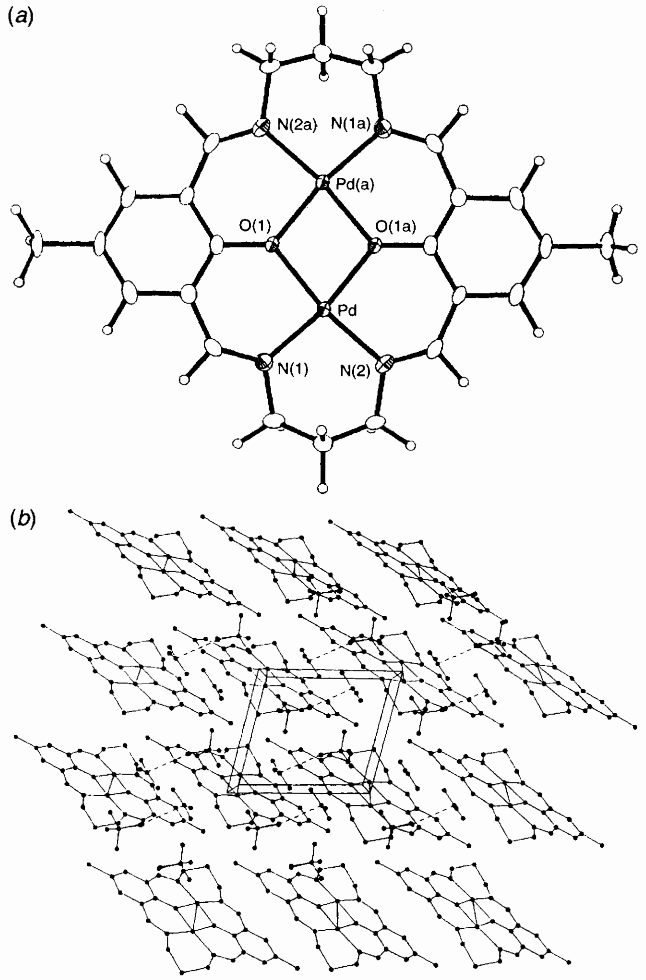


Fig.10 (*a*) Views of the structure of $[Pd_2(L^1)]^{2+}$. Bond lengths in Å, angles in °: Pd–O(1) 2.016(4), Pd–O(1a) 2.014(4), Pd–N(1) 1.981(4), Pd–N(2) 1.993(4), Pd···Pd 3.1514(6); O(1)–Pd–N(1) 93.30(17), O(1)–Pd–N(2) 170.34(17), N(1)–Pd–N(2) 96.36(18), O(1)–Pd–O(1a) 77.13(15), Pd–O(1)–Pd(1a) 102.88(16). (*b*) Crystal packing arrangement.

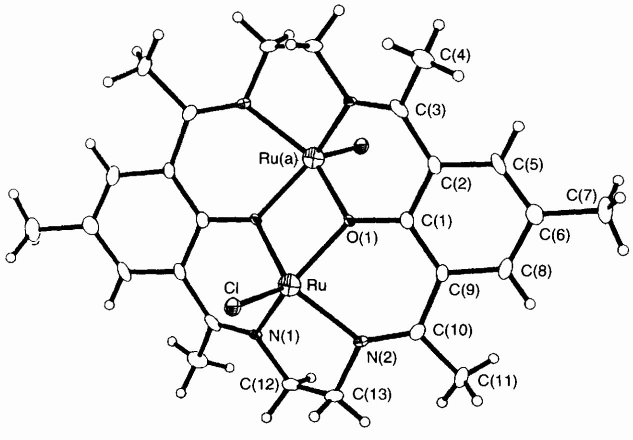


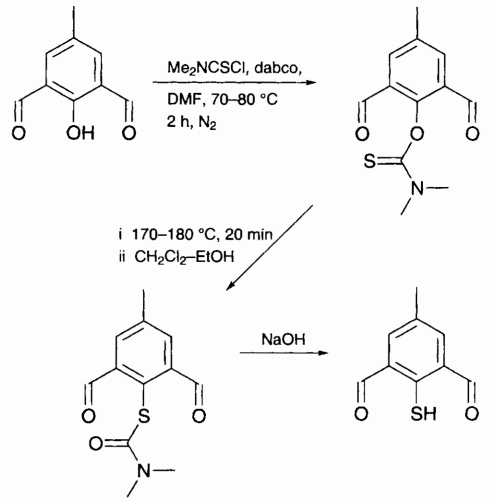
Fig. 11 View of the structure of $[Ru_2(L^3)Cl_2]$. Bond lengths in Å, angles in °: Ru–O 1.992(3), Ru–N 2.061(4), 2.073(4), Ru–Cl 2.241(2), Ru···Ru 3.230(2); Ru–O–Ru(a) 105.1(2).

affords a most unusual ruthenium(II) complex in low yield. The single-crystal X-ray structure of $[Ru_2(L^3)Cl_2]$ shows (Fig. 11) five-coordination to Ru^{II} with each metal centre bound to two imine N-donors, two bridging phenoxy O-donors and one Cl^- ligand. Each symmetry-equivalent Ru^{II} centre lies 0.790 Å out of the N_4O_2 plane with the Ru^{II} centres mutually *anti* with respect to the macrocyclic ligand. Thus, the hole size of the macrocycle appears to be too small for the relatively large Ru^{II} centres. This complex $[Ru_2(L^3)Cl_2]$ represents a rare example of coordinatively unsaturated d^6 Ru^{II}, and we are currently investigating further the mechanism(s) and structures of intermediates in its preparation. Interestingly, we have been unable to prepare this complex with R^2 = H, which may reflect the results of Chakravorty and coworkers[25] who confirmed that decarbonylation of 2,6-diformyl-4-methylphenol can occur in the presence of Ru^{II}.

Thiophenolate macrocycles

Modification of the macrocyclic donor set from N_4O_2 to N_4S_2 might be expected to increase the ligand-field strength of the macrocycle due to potential π back-donation and the weaker σ-donor abilities of RS^- compared to RO^-. The synthesis of complexes of $[L^5]^{2-}$ incorporating bridging dithiolato units was therefore undertaken and 2,6-diformyl-4-methylthiophenol was prepared according to Scheme 3.[26]

Reaction of $[Ni(O_2CMe)_2]\cdot 4H_2O$ with 2,6-diformyl-4-methylthiophenol and 1,3-diaminopropane in MeCN in the presence of NH_4PF_6 gives $[Ni_2(L^5)][PF_6]_2$ as a red product in low yield (Scheme 4). The single-crystal X-ray structure of $[Ni_2(L^5)][PF_6]_2\cdot 2dmf$ shows[23] (Fig. 12) each Ni^{II} ion bound to two bridging thiophenolate S-donors and two imine N-donors; additional interactions with O-donors from two dmf molecules are observed. The coordination geometries at the Ni^{II} centres are therefore distorted square-planar with the Ni^{II} ions displaced by approximately 0.1 Å out of the least-squares plane defined by the N_2S_2 donor set. The angle between the two square planes defined by the N_2S_2 arrays about Ni and Ni(a) is 144.4°. The metal–metal distance in $[Ni_2(L^5)]^{2+}$ [Ni··· Ni(a) 3.163(4) Å] is similar to those observed in the macrocyclic complexes of $[L^1]^{2-}$, which suggests that there is a well defined metal–metal distance that can be accommodated by two bridging phenolate or thiophenolate donors within the Schiff-base macrocyclic framework. In order to accommodate the coordination geometries about the Ni^{II} ions in $[Ni_2(L^5)]^{2+}$, the macrocycle $[L^5]^{2-}$ adopts a folded conformation. This folding allows the bridging thiophenolate S-donors to form a *syn–endo* Ni_2S_2 ring, and the geometries about the S-atoms are pyramidal, Ni–S–C(1) 99.3(7), Ni(a)–S–C(1) 101.6(7)°. The folded conformation of ligand $[L^5]^{2-}$ also permits a lengthening of the S···S distance within the macrocycle, S···S(a) 2.87(2) Å, thus minimising repulsive S···S interactions. If $[L^5]^{2-}$ were to adopt a planar conformation, the S···S distance would become prohibitively short. Although complexes of open-chain analogues of $[L^5]^{2-}$ have been reported,[27,28] this is, to our knowledge, the first report of the cyclised system: a related cyclised system has been reported by Lawrence *et al.*[29] Thus, the observed ligand donor coordination at Ni^{II} in $[Ni_2(L^5)]^{2+}$ is rare and potentially

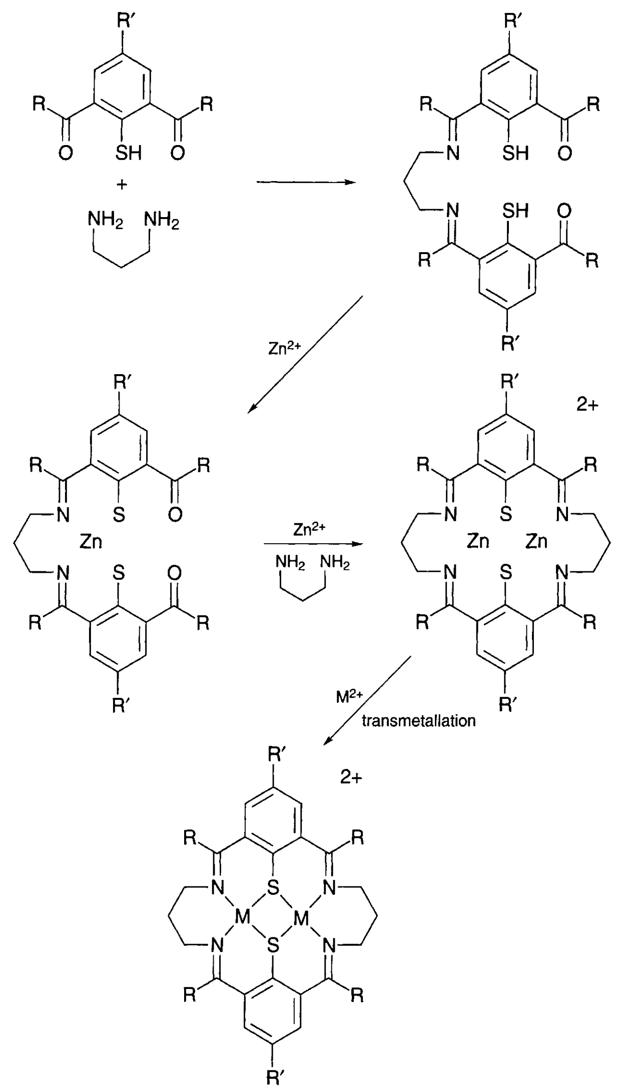


Scheme 3 Preparation of 2,6-diformyl-4-methylthiophenol

provides a structural model for nickel-containing hydrogenase enzymes involving thiolate-bridged binuclear Ni^{II} centres.[30] Interestingly, recrystallisation of $[Ni_2(L^5)]^{2+}$ from $MeNO_2$ affords $[Ni_2(L^5)]^{2+}\cdot MeNO_2$ which shows the $MeNO_2$ solvate molecule sitting inside the cleft formed by the folded $[L^5]^{2-}$ macrocycle (Fig. 13). The related nickel(II) complex $[Ni_2(L^6)]^{2+}$ incorporating pendant OH groups has also been synthesised (Fig. 14) and shows a similar configuration and conformation to the nickel(II) complexes of $[L^5]^{2-}$.

We found that the metal-directed template synthesis of $[L^5]^{2-}$ in the presence of Ni^{II}, although successful, did not afford the desired product in high yield. Furthermore, attempted synthesis by template methods of the copper(II) analogue $[Cu_2(L^5)]^{2+}$, a potential model for the binuclear copper sites in N_2O reductase and cytochrome c oxidase,[31] invariably failed in our hands. Thus, a more efficient synthetic route to these types of compartmental complexes was required. We reasoned that redox side-reactions were occurring during the template process, the reaction of Cu^{II} with thiolate leading to the potential formation of Cu^{I} and disulfides. Thus, template synthesis of $[L^5]^{2-}$ around redox-inert Zn^{II} was investigated.

Reaction of $[Zn(O_2CMe)_2]$ with 2,6-diformyl-4-methylthiophenol and 1,3-diaminopropane affords a yellow product assigned as $[Zn_2(L^5)(O_2CMe)]^+$. Transmetallation of $[Zn_2(L^5)(O_2CMe)]^+$ with Ni^{II} affords $[Ni_2(L^5)]^{2+}$ in high yield



Scheme 4 Synthesis of thiophenolate compartmental macrocyclic complexes by metal-directed template reaction

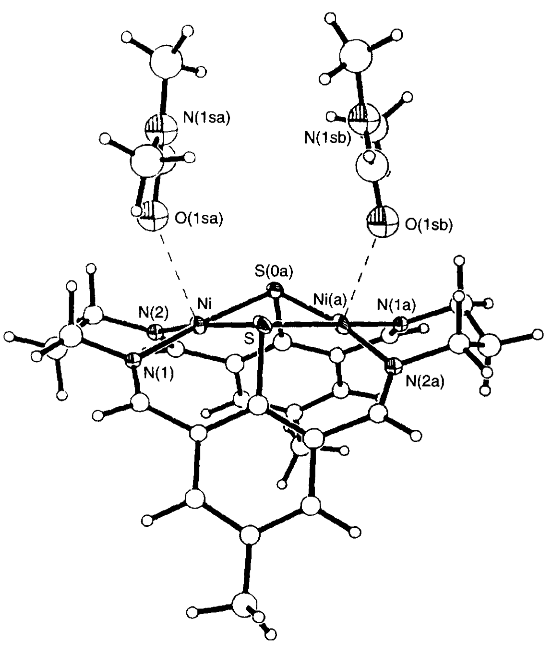


Fig. 12 View of the structure of $[Ni_2(L^5)]^{2+}\cdot 2dmf$. Bond lengths in Å, angles in °: Ni–S 2.181(6), 2.171(6), Ni–N(1) 1.927(15), 1.906(15), Ni–O(dmf) 2.644(15), S···S 2.872(20), Ni–Ni(a) 3.163(4); Ni–S–Ni(a) 93.24(22).

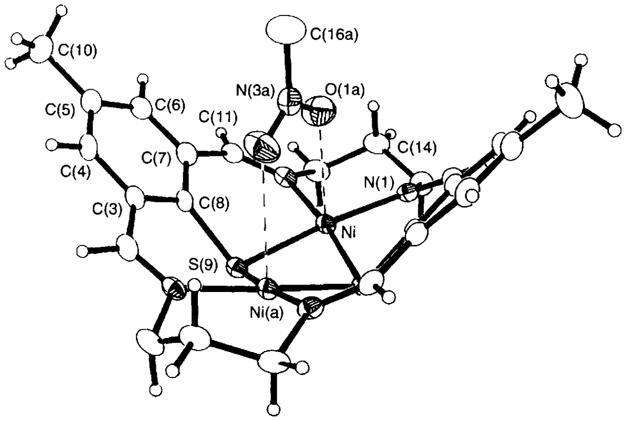


Fig. 13 View of the structure of $[Ni_2(L^5)]^{2+}\cdot MeNO_2$. Bond lengths in Å, angles in °: Ni–S 2.163(2), 2.184(2), Ni–N 1.919(3), 1.939(3), Ni–O($MeNO_2$) 2.834(3), Ni···Ni 3.167(2); Ni–S–Ni(a) 93.50(3).

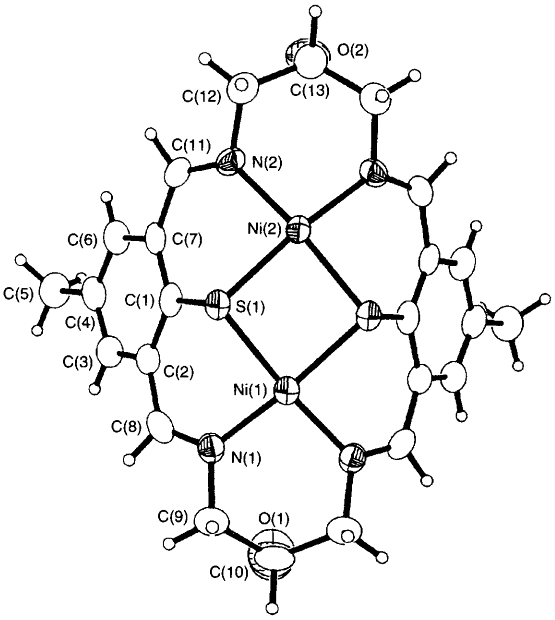


Fig. 14 View of the structure of $[Ni_2(L^6)]^{2+}$. Bond lengths in Å, angles in °: Ni–S 2.164(3), Ni–N 1.903(8), 1.906(8); Ni(1)–S–Ni(2) 92.43(11).

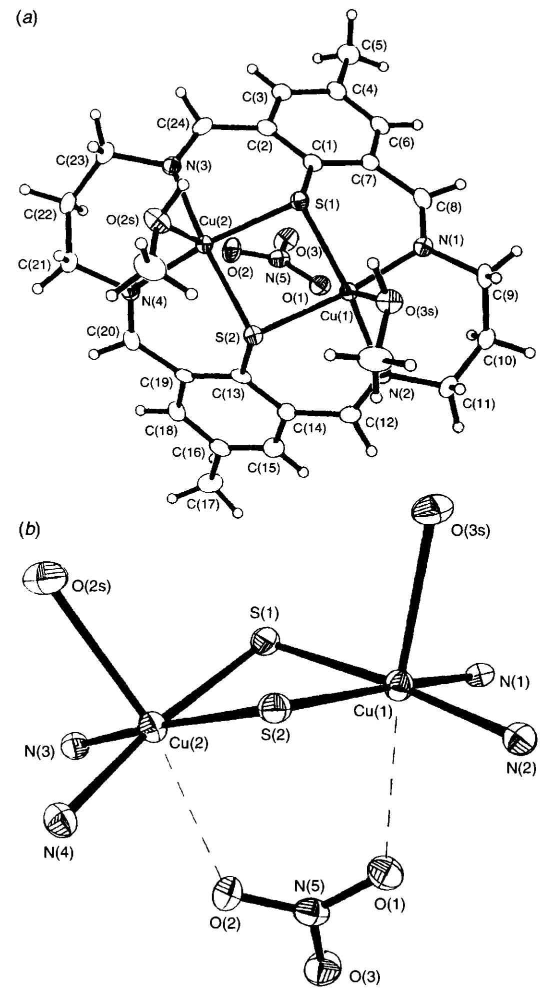


Fig. 15 (*a*) View of the structure of $[Cu_2(L^5)]^{2+}{\cdot}2MeOH{\cdot}NO_3^-$. Bond lengths in Å: Cu(1)–N(1) 2.011(4), Cu(1)–N(2) 2.000(4), Cu(1)–S(1) 2.290(2), Cu(1)–S(2) 2.306(2), Cu(2)–N(3) 2.005(4), Cu(2)–N(4) 2.000(4), Cu(2)–S(1) 2.306(2), Cu(2)–S(2) 2.294(2), Cu(1)–O(3S, MeOH) 2.359(4), Cu(2)–O(2S, MeOH) 2.386(4). (*b*) Interaction of the dicopper unit and nitrate ion.

(up to 80%). More importantly, template reaction of $[Zn_2(L^5)(O_2CMe)]^+$ with Cu^{II} affords the $[Cu_2(L^5)]^{2+}$ cation as a very dark green product in high yield (75–85%). The single-crystal X-ray structure of $[Cu_2(L^5)(MeOH)_2(NO_3)]PF_6$ shows (Fig. 15) two Cu^{II} centres each bound to two N-donors and bridged by two thiolate donors of the compartmental macrocycle. The coordination about each Cu^{II} is completed by one O-donor from MeOH. The conformation of the thiolate macrocycle is very similar to that observed for the corresponding nickel(II) complexes (Figs. 12 and 13) with a Cu···Cu separation of 3.264(2) Å. Interestingly, one NO_3^- counter anion occupies the cleft formed by the folded macrocycle, Cu···O(NO_3^-) 2.702 Å. Although binuclear and polynuclear copper(I) species with bridging thiolates are well known,[32] few examples of stable thiolate copper(II) species have been reported.[28,33]

Current work is investigating the redox and magnetochemical properties of the above systems and to develop their chemistries further.

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Dr Andrew J. Atkins gained a BA Degree in Chemistry from the University of Cambridge in 1989, and his PhD under the supervision of M. Schröder from the University of Edinburgh in 1993. He is currently an Assistant Editor at the Royal Society of Chemistry.

Daniel Black gained his BSc Degree in Chemistry from the University of Bristol in 1993. He is currently a third-year PhD student under the supervision of M. Schröder in Nottingham.

Dr Alexander J. Blake gained a BSc (1976) and PhD in Chemistry (1980) under the supervision of G. P. McQuillan from the University of Aberdeen. After postdoctoral research at the University of Exeter (with A. G. Osborne and D. R. Rosseinsky) and the University of Edinburgh (with E. A. V. Ebsworth and A. J. Welch) he was appointed Research Fellow in Edinburgh in 1985. In 1995 he was appointed Manager of the Crystal Structure Service at the University of Nottingham. He is currently a co-editor of *Acta Crystallographica* and a member of the IUCr Commission on Journals.

Armando Marin-Becerra gained a BSc Degree in Chemistry in 1988 and a MSc in Inorganic Chemistry in 1992, both from the National Autonomous University of Mexico. He is currently a third-year PhD student at the same University.

Dr Simon Parsons gained a BSc Degree in 1987 from the University of Durham and PhD in Chemistry in 1991 from the University of New Brunswick, Canada under the supervision of J. Passmore. After postdoctoral research at the University of Oxford (with A. Downs), he was appointed to a postdoctoral position in crystallography at the University of Edinburgh in 1993. In 1995 he was appointed Staff Crystallographer in the same Department.

Professor Lena Ruiz-Rammrez gained a BSc in Chemistry from the National Autonomous University of Mexico in 1968 and a PhD in Chemistry from the University of Edinburgh under the supervision of T. A. Stephenson in 1974. She undertook postdoctoral studies with R. Wilkins at New Mexico State University at Las Cruces in 1980, with J. Lewis at Cambridge in 1982, and with M. Bressie at The Institute of Catalysis (CNRS) in Lyon, France in 1991. She was appointed as full-time Professor (A) at the National Autonomous University of Mexico in 1974, and has been a Professor (C) since 1984. She has been awarded the CANIFARMA award in 1994, and the Aida Waiss award in 1995.

Professor Martin Schröder gained a BSc Degree in Chemistry from the University of Sheffield in 1975, and a PhD in Inorganic Chemistry from Imperial College, University of London under the supervision of W. P. Griffith in 1978. After postdoctoral research at the ETH, Zürich (with A. Eschenmoser) and Cambridge (with J. Lewis), he was appointed in 1982 to a Demonstratorship in Inorganic Chemistry at the University of Edinburgh. He was subsequently promoted in Edinburgh to lecturer, reader, and in 1994 to a Personal Chair in Inorganic Chemistry. In 1995 he was appointed to the Chair of Inorganic Chemistry at the University of Nottingham. He was awarded the Corday Morgan Medal and Prize of the Royal Society of Chemistry in 1991.

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