

# Chiral metal complexes

## 38\*. Coordination control in complexes of an optically active macrocyclic ligand

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### Abstract

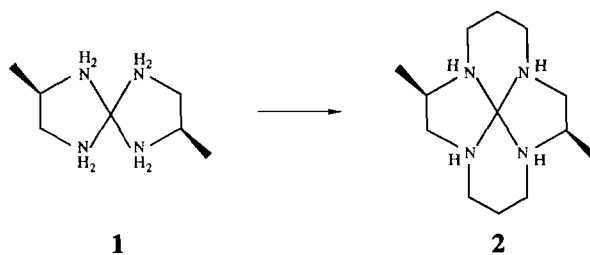
The macrocyclic complex  $[\text{Cu}(\text{S-mac})]^{2+}$ , where S-mac is 6*S*,16*S*-(4*R*,14*R*-dimethyl)-1,5,11,15-tetraazatricyclo-[14,4,1,1<sup>6,11</sup>]docosane, has been synthesized stereospecifically using a template reaction and reduction of an intermediate diimine. Reduction of the diimine was achieved in quantitative yield and proceeds with absolute stereospecificity, as far as can be practically determined. The single-crystal X-ray structure of the complex, as its anhydrous diperchlorate salt, has been determined at low temperature. Crystal data:  $\text{C}_{20}\text{H}_{40}\text{N}_4\text{O}_8\text{Cl}_2\text{Cu}$  is orthorhombic, space group  $P2_12_12_1$ , with  $a = 8.350(2)$ ,  $b = 12.525(3)$ ,  $c = 24.817(7)$  Å,  $Z = 4$ . The structure was refined by full-matrix least-squares methods to  $R = 0.041$  for 2025 non-zero reflections. Each cation is five-coordinate with square-based pyramidal geometry, formed by the four nitrogen donors of the macrocycle in the square plane, and an oxygen atom (two partially occupied positions) of a disordered perchlorate ion (Cu–O 2.442(9), 2.401(21) Å). Both carbon atoms attached to the methyl groups of the macrocycle have absolute configuration *R*. Folding of the seven-membered rings of the ligand produces a conformation such that only one face of the complex is available for axial coordination of unidentate ligands. The complex has been demetallated. The free ligand thus generated reacts with Cu(II) to give a complex which has all features of the original stereochemistry preserved. Analogous Ni(II) and Pd(II) complexes have also been prepared and characterized using NMR techniques.

### Introduction

For some time, we have been interested in exploring the origins of chiral discriminations in coordination complexes of optically active multidentates [1]. In particular, we have sought to develop systems which enforce particular modes of coordination in the remaining sites of octahedral metal ions with a view to applying the complexes to chiral syntheses of organic molecules, and to resolutions of certain enantiomeric and diastereoisomeric substances [2].

More recently we have turned our attention to the possibilities offered in these respects by chiral macro-

cyclic systems with regard to the stereoselective coordination of unidentates. Our approach has been to use chiral tetradentate macrocycles which distinguish between the two faces of the complex (or, between



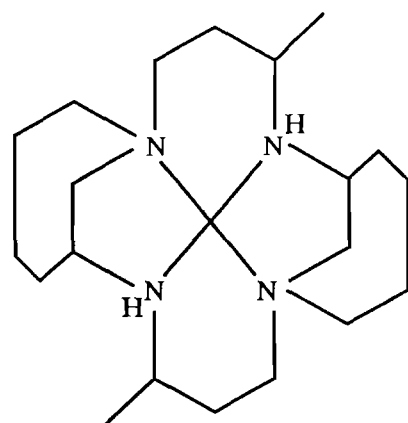
the two available *trans*-axial positions which would constitute an octahedral complex with the macrocycle occupying the square plane). This is achieved in principle by the synthesis of macrocycles based on the *trans* coordination of two homochiral, but unsymmetrical, 1,2-

\*Part 37 see ref. 1.

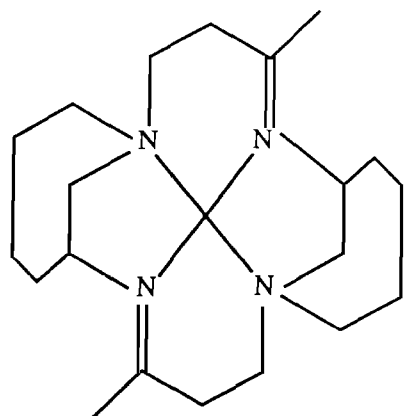
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diamines, as shown in **1** and **2**. A number of methods are then available to limit further coordination to that of only a single unidentate. Strapping the macrocycle is one possibility, either to produce a penta-coordinated ligand or to block access to one face for simple steric reasons. A 'suicide' ligand might be coordinated such that it could not be substituted during subsequent reactions. Both these approaches have their own attendant difficulties with respect to synthesis and separation of resulting diastereomers. Alternatively, an appropriate choice of starting 1,2-diamine could itself yield complexes which permitted the coordination of a unidentate on but one face. We have chosen to pursue this approach, and report here the stereochemical characteristics of complexes of 6*S*,16*S*-(4*R*,14*R*-dimethyl)-



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1,5,11,15-tetraazatricyclo [14, 4, 1, 1<sup>6,11</sup>]docosane, *S*-mac (**3**), based on a previously reported [3a] diimine precursor **4**, which incorporates the desired stereochemical features mentioned above in a ligand of the Me<sub>2</sub>[14]ane-N<sub>4</sub> type. The stereochemistry of related complexes of 3*S*-aminohexahydroazepine has been discussed elsewhere [3b].

## Experimental

Electronic and CD spectra were measured using a Perkin-Elmer Lambda 5 and a Jobin-Yvon CNRS Dichrographe III, respectively. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded with a Bruker WM 360 spectrometer at 22 °C in dmsO-d<sub>6</sub>, using TMS as internal standard. Elemental analyses were carried out by Mrs A. Dams of the School of Chemistry and Applied Chemistry, Cardiff.

### Syntheses

**Caution:** Perchlorate salts of complex ions can be explosive and must be handled with care.

The complex [Cu**4**](ClO<sub>4</sub>)<sub>2</sub> was synthesized according to the method of Saburi and co-workers [3]. In a typical synthesis, [Cu(*S*-mac)](ClO<sub>4</sub>)<sub>2</sub> was prepared by the following method. To a stirred solution of [Cu**4**](ClO<sub>4</sub>)<sub>2</sub> (0.5 g, 0.84 mmol) in methanol (350 cm<sup>3</sup>) was added NaBH<sub>4</sub> (0.5 g, 13.2 mmol), in portions. During the addition, the solution became a brown colour. When the addition was complete, the mixture was refluxed with stirring for 90 min. It was then cooled to room temperature, and the volume reduced *in vacuo* by half, whereupon the complex crystallized. The red product was collected at the pump, washed with methanol (3 × 5 cm<sup>3</sup>), and air dried (yield 0.35 g). The CD spectrum of the mother liquor was the same, within experimental error, as that of the complex dissolved in methanol. Crystals suitable for X-ray analysis were obtained by recrystallization from water. *Anal.* Calc. for C<sub>20</sub>H<sub>40</sub>N<sub>4</sub>O<sub>8</sub>Cl<sub>2</sub>Cu: C, 40.1; H, 6.7; N, 9.4. Found: C, 40.1; H, 6.6; N, 9.1%.

[Cu(*S*-mac)](ClO<sub>4</sub>)<sub>2</sub> (1.16 g) was refluxed in conc. HCl (60 cm<sup>3</sup>) for 4 h, cooled to room temperature, and reduced *in vacuo* to a small volume. Aqueous NaOH (2 M, 175 cm<sup>3</sup>) was added, and the white solid obtained was extracted into ether (2 × 200 cm<sup>3</sup>). The extract was dried over anhydrous sodium sulfate and removed *in vacuo* to yield a slightly hygroscopic white solid, *S*-mac. m.p. 99–101 °C (uncorrected). *Anal.* Calc. for C<sub>20</sub>H<sub>40</sub>N<sub>4</sub>: C, 71.4; H, 12.0. Found: C, 71.5; H, 12.7%.

The copper(II) complex was resynthesized from the free ligand (0.272 g) and anhydrous copper(II) chloride (0.1 g) by refluxing the mixture in methanol (30 cm<sup>3</sup>) for 24 h. The mixture was cooled to room temperature and the complex precipitated by the addition of solid sodium perchlorate hydrate. The red complex was recrystallized from water (yield 0.367 g).

[Ni(*S*-mac)](ClO<sub>4</sub>)<sub>2</sub> was synthesized by refluxing a mixture of *S*-mac (0.2 g) and NiCl<sub>2</sub>·6H<sub>2</sub>O (0.15 g) in methanol (40 cm<sup>3</sup>) for 24 h. To the cooled reaction mixture was added solid sodium perchlorate, when the pale peach coloured complex salt crystallized. It was

collected at the pump, washed with methanol and air dried (yield 0.29 g). *Anal.* Calc. for  $C_{20}H_{40}N_4O_8Cl_2Ni$ : C, 40.4; H, 6.8; N, 9.4. Found: C, 40.2; H, 6.7; N, 9.7%.

$[Pd(S\text{-}mac)](ClO_4)_2$  was synthesized using a method analogous to that employed for the Ni(II) complex, except that  $K_2PdCl_4$  (0.06 g) was used. A minor amount of a black precipitate was filtered off after reflux. Sodium perchlorate was added to the filtrate from which the pale yellow product crystallized (yield 57 mg). *Anal.* Calc. for  $C_{20}H_{40}N_4O_8Cl_2Pd$ : C, 37.4; H, 6.3. Found: C, 37.1; H, 6.1%.

#### Crystal and molecular structure of $[Cu(S\text{-}mac)](ClO_4)_2$

*Crystal data.*  $C_{20}H_{40}N_4O_8Cl_2Cu$ ,  $M_r = 599.0$ , orthorhombic,  $a = 8.350(2)$ ,  $b = 12.523(3)$ ,  $c = 24.817(7)$  Å,  $U = 2595.0$  Å<sup>3</sup>,  $Z = 4$ ,  $D_c = 1.533$  g cm<sup>-3</sup>,  $D_m = 1.51$  g cm<sup>-3</sup> (by flotation),  $F(000) = 1260$  and  $\mu(Mo K\alpha) = 11.0$  cm<sup>-1</sup>, space group  $P2_12_12_1$  (No. 19).

Unit cell data were established from precession photographs and were obtained accurately from a least-squares fit to diffractometer data. Intensities were collected at  $-120$  °C on a Nicolet XRD P3 four-circle diffractometer [4] in the range  $4.0 < 2\theta < 52.0^\circ$  using graphite monochromatized Mo  $K\alpha$  radiation. The crystal used for the data collection was  $0.2 \times 0.2 \times 0.5$  mm in size. The intensities were corrected for Lorentz, polarization and empirically for absorption effects. With respect to the latter, the maximum and minimum transmission factors were 0.752 and 0.730, respectively. Of the 2915 reflections measured, 2025 gave counts for which  $I > 3\sigma(I)$ , and these were used for the structure determination.

The structure was solved by the heavy-atom method and refined by full-matrix least-squares calculations in which  $\sum w\Delta^2$  was minimized and with a weighting scheme of unity. Difference Fourier maps revealed that the oxygen atoms of both perchlorate ions were disordered, but in an identifiable pattern; fractional occupancies were assigned to the oxygen atoms so that comparable thermal parameters were ultimately obtained for them, and so that the total occupancies were stoichiometric. The individual perchlorate ions each involve two sets of O atoms. For Cl(1) these are (abcd) and (abcf) each with 20% occupancy and (acde) and (bghi) with 30%. For Cl(2) these are (abcd) and (befg) with occupancies of 60% and 40%, respectively. The positions of the hydrogen atoms in the ligand were calculated assuming the appropriate geometries of the atoms to which they are attached with bond lengths of 1.0 Å. The final structure refinement was carried out with anisotropic thermal parameters for all non-hydrogen atoms and unit weights. When the maximum shift in any parameter was less than  $0.1\sigma$  the refinement process was terminated. The final value for  $R$  was 0.041 and  $R' \{ = (\sum w(F_o -$

$F_c)^2 / \sum w(F_o)^2 \}^{0.5}$  was 0.044. A final difference Fourier map showed no unusual features.

Calculations were carried out on a FACOM M350S computer using programs written by F.S.S. Neutral atom scattering factors, corrected for anomalous dispersion (see also 'Supplementary material'), were taken from the International Tables for X-ray Crystallography [5].

Final atomic coordinates for the non-hydrogen atoms are listed in Table 1. Coordinates for hydrogen atoms (Table 2) are given here rather than being deposited because of their relevance to the molecular modelling

TABLE 1. Final atomic coordinates (fractional  $\times 10^4$ ) for non-hydrogen atoms with e.s.d.s. in parentheses for  $[Cu(S\text{-}mac)](ClO_4)_2$

	Occ <sup>a</sup>	x/a	y/b	z/c
Cu		1326.5(11)	539.1(7)	1473.5(4)
N(11)		877(8)	1888(5)	1064(2)
N(12)		2539(7)	1481(5)	2015(3)
N(21)		1894(7)	-817(5)	1862(3)
N(22)		448(8)	-426(5)	871(2)
C(11)		930(10)	2761(6)	1481(4)
C(12)		2317(11)	2652(7)	1873(4)
C(13)		3875(14)	3176(7)	1698(4)
C(14)		4312(13)	3116(9)	1103(5)
C(15)		3817(13)	2100(8)	802(4)
C(16)		2048(11)	2071(7)	622(3)
C(17)		-764(12)	1917(8)	832(4)
C(18)		-1146(12)	1007(7)	444(3)
C(19)		-1185(12)	-118(7)	670(3)
Me(1)		-1746(16)	-863(9)	215(4)
C(21)		763(10)	-1635(7)	1654(4)
C(22)		535(11)	-1596(7)	1049(3)
C(23)		1742(12)	-2221(7)	708(4)
C(24)		3484(14)	-2244(8)	888(4)
C(25)		4080(11)	-1225(7)	1171(4)
C(26)		3596(11)	-1115(7)	1762(4)
C(27)		1635(10)	-740(8)	2458(3)
C(28)		2598(12)	112(8)	2745(3)
C(29)		2222(10)	1259(8)	2611(3)
Me(2)		3232(12)	1972(9)	2982(4)
Cl(1)		-2599(2)	718(1)	2187(1)
O(1a)	0.70	-1045(10)	1088(8)	1999(4)
O(1b)	0.70	-3848(33)	966(15)	1778(9)
O(1c)	0.70	-2742(10)	-421(6)	2175(4)
O(1d)	0.50	-2737(36)	937(22)	2771(10)
O(1e)	0.30	-3741(72)	1299(29)	1938(19)
O(1f)	0.20	-3005(57)	1292(43)	2627(22)
O(1g)	0.30	-2252(24)	1796(14)	2359(8)
O(1h)	0.30	-3119(29)	49(18)	2592(10)
O(1i)	0.30	-1200(24)	271(14)	1915(7)
Cl(2)		1616(3)	206(2)	4477(1)
O(2a)	0.60	1749(19)	-463(13)	4013(5)
O(2b)		1682(14)	1276(6)	4324(4)
O(2c)	0.60	3147(18)	1(11)	4773(5)
O(2d)	0.60	406(21)	-190(19)	4814(8)
O(2e)	0.40	1576(28)	253(19)	5017(6)
O(2f)	0.40	-52(32)	-18(19)	4294(13)
O(2g)	0.40	2617(28)	-501(18)	4259(9)

<sup>a</sup>Fractional occupancies are included for relevant atoms.

TABLE 2. Hydrogen atom coordinates (fractional  $\times 10^3$ ) for  $[\text{Cu}(\text{S-mac})](\text{ClO}_4)_2$ 

	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>
H(m1a)	-279	-61	6
H(m1b)	-185	-163	32
H(m1c)	-93	-85	-10
H(m2a)	316	274	288
H(m2b)	293	188	337
H(m2c)	442	176	295
H(N12)	367	127	193
H(N22)	123	-29	58
H(11a)	103	346	130
H(11b)	-8	274	170
H(12)	193	305	220
H(13a)	379	395	179
H(13b)	475	283	190
H(14a)	551	317	109
H(14b)	382	374	92
H(15a)	449	202	48
H(15b)	398	146	105
H(16a)	180	276	45
H(16b)	192	148	35
H(17a)	-155	189	114
H(17b)	-90	260	63
H(18a)	-220	115	29
H(18b)	-29	102	17
H(19)	-197	-17	98
H(21a)	116	-235	175
H(21b)	-32	-151	182
H(22)	-52	-193	101
H(23a)	135	-297	69
H(23b)	172	-190	34
H(24a)	356	-285	115
H(24b)	413	-237	57
H(25a)	528	-124	115
H(25b)	367	-59	98
H(26a)	381	-182	194
H(26b)	431	-56	193
H(27a)	193	-145	262
H(27b)	48	-60	252
H(28a)	243	0	313
H(28b)	375	-2	265
H(29)	108	143	270

For hydrogen atoms  $B = 1.5 \text{ \AA}^2$ .

of the complex cation. Selected bond lengths and angles are listed in Table 3.

## Results and discussion

### Crystal and molecular structure of $[\text{Cu}(\text{S-mac})](\text{ClO}_4)_2$

A view of the complex cation [6], together with the atom labelling scheme, is shown in Fig. 1. The complex cation is five-coordinate (square-pyramidal) with an oxygen atom of a disordered perchlorate anion occupying two alternative, adjacent positions, separated by 0.96 Å, on one side of the  $\text{N}_4$  plane. Variations in the Cu–N bond lengths are minimal and the Cu atom lies slightly

TABLE 3. Selected bond lengths and angles with e.s.d.s. in parentheses for the complex

Distances (Å)			
	<i>n</i> = 1	<i>n</i> = 2	
Cu–O(1a)	2.442(9)		
Cu–O(1i)	2.401(21)		
Cu–N(n1)	2.007(6)	2.055(6)	
Cu–N(n2)	2.009(6)	2.057(6)	
N(n1)–C(n1)	1.506(11)	1.486(10)	
N(n1)–C(n6)	1.486(10)	1.491(11)	
N(n1)–C(n7)	1.487(11)	1.498(9)	
N(n2)–C(n2)	1.519(10)	1.502(11)	
N(n2)–C{(n+1)9}	1.528(10)	1.533(10)	
C(n1)–C(n2)	1.518(12)	1.513(12)	
C(n2)–C(n3)	1.521(14)	1.531(12)	
C(n3)–C(n4)	1.520(14)	1.521(15)	
C(n4)–C(n5)	1.533(14)	1.539(13)	
C(n5)–C(n6)	1.543(14)	1.527(12)	
C(n7)–C(n8)	1.526(13)	1.514(13)	
C(n8)–C(n9)	1.517(12)	1.506(14)	
C(n9)–Me(n)	1.538(12)	1.535(12)	
Angles (°)			
N(11)–Cu–O(1a)	85.2(3)	N(11)–Cu–O(1i)	100.6(5)
N(12)–Cu–O(1a)	84.9(3)	N(12)–Cu–O(1i)	102.4(5)
N(21)–Cu–O(1a)	97.9(3)	N(21)–Cu–O(1i)	82.5(5)
N(22)–Cu–O(1a)	103.9(3)	N(22)–Cu–O(1i)	86.3(5)
N(11)–Cu–N(21)	176.8(3)	N(12)–Cu–N(22)	171.1(3)
N(11)–Cu–N(12)	86.6(3)	N(21)–Cu–N(22)	86.4(3)
N(11)–Cu–N(22)	93.4(3)	N(12)–Cu–N(21)	93.2(3)

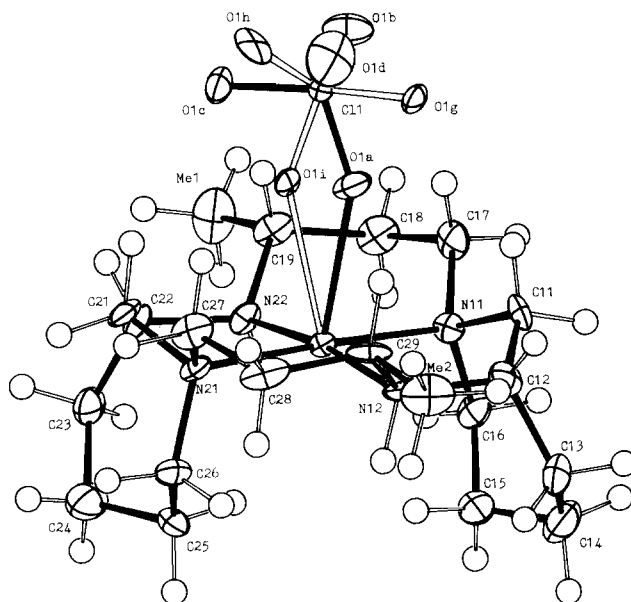


Fig. 1. A perspective drawing [6] of the complex cation  $[\text{Cu}(\text{S-mac})]^{2+}$  showing the coordination of the disordered perchlorate ion to give a square-pyramidal geometry in the solid state. Non-hydrogen atoms are scaled to include 35% probability.

TABLE 4. Intermolecular contacts with e.s.d.s. in parentheses for the complex

Proposed hydrogen bonding <sup>a</sup>			
N(12)H(N12)···O(1b <sup>I</sup> )	3.14(3)	N(22)H(N22)···O(2c <sup>II</sup> )	3.02(2)
N(12)H(N12)···O(1e <sup>I</sup> )	3.12(6)	N(22)H(N22)···O(2e <sup>II</sup> )	3.27(2)
Contacts $\leq 3.3$ Å <sup>a</sup>			
C(13)···O(1h <sup>III</sup> )	3.00(2)	C(14)···O(2g <sup>V</sup> )	3.22(3)
C(13)···O(1e <sup>I</sup> )	3.14(5)	C(18)···O(2c <sup>II</sup> )	3.26(2)
C(25)···O(2e <sup>II</sup> )	3.16(2)	C(24)···O(2e <sup>II</sup> )	3.30(2)
C(27)···O(1g <sup>IV</sup> )	3.16(2)		

<sup>a</sup>Roman numeral superscripts refer to the following equivalent positions relative to  $x, y, z$ : I:  $1+x, y, z$ . II:  $1/2-x, -y, z-1/2$ . III:  $-x, 1/2+y, 1/2-z$ . IV:  $-x, y-1/2, 1/2-z$ . V:  $1-x, 1/2+y, 1/2-z$ .

out of the N<sub>4</sub> basal plane (0.11 Å), displaced towards the oxygen atom. Cu–O bond lengths are 2.442(9) and 2.401(21) Å, being somewhat shorter than the average Cu<sup>II</sup>–OCIO<sub>3</sub><sup>-</sup> distance (five- or six-coordination), reported by Orpen *et al.* [7] as 2.508 Å. The disordered nature of the oxygen atom mirrors the behaviour of the coordinated nitrate ion in another macrocyclic complex of Cu(II) [8]. Bite angles of the six-membered rings are, as expected, somewhat greater than 90°, whereas those of the five-membered rings are less than 90°. The conformation of both latter rings is  $\lambda$  and the stereochemistry at the tertiary nitrogens is *R*, in accord with the particular chosen chirality of the diamine. Both six-membered rings adopt the stable chair conformation, with the absolute configurations of C-methyl and coordinated secondary nitrogen atoms being *R*. The stereochemistry of the latter is enforced by the substituents on the six-membered chelate rings which adopt the favoured equatorial orientation [9]. The seven-membered rings of the ligand possess somewhat distorted twist-chair conformations.

The observed stereospecificity of the hydrogenation of [Cu4]<sup>2+</sup> may be explained in terms of the accessibility of the prochiral faces of the imine groups of the precursor. As one side of the CuN<sub>4</sub> plane is blocked by the axially projecting hexahydroazepine rings, only the *pro-R* face of each imine is accessible for hydride addition. The *pro-S* face is sterically concealed to such an extent that no product containing *S*(C)–Me centres is detected. During the reaction both secondary nitrogen atoms adopt the *R* configuration so as to ensure the methyl groups of the six-membered chelate rings adopt the energetically favoured equatorial orientation. These facts unambiguously establish the stereochemical nature of the course of the reduction, mentioned in passing by other workers [10].

In the crystal, weak hydrogen bonds are evident between NH groups and perchlorate oxygen atoms and the details of these, together with the closest non-bonded contacts, are given in Table 4. The latter indicate that there are no abnormalities induced in the complex cation due to crystal packing effects. This is important

for conclusions based on molecular modelling outlined below, in that it justifies the use of the crystal structure coordinates for such purposes.

Previous workers [3, 10] have suggested that this class of complex generates a chiral ‘pocket’ as a consequence of the folding of the two seven-membered ligand rings on one side of the square plane formed by the macrocycle. This is not observed to be the case, and a correct description of the structure of the cation is all the more startling when space-filling considerations are brought to bear. Figure 2 shows space-filling [11] projections of the complex cation viewed from either side of the plane of the macrocycle. Whilst one side is accessible to coordination by a unidentate (as evidenced by the structure in the solid state), the conformation of the seven-membered rings of the macrocycle blocks completely the other side. Indeed, the chiral ‘pocket’ formed on this side is so small that it lacks any molecular significance.

The outstanding structural feature of the complex is that the nature of the chiral macrocyclic framework distinguishes the two sides of the plane, thus permitting the further coordination of but one unidentate. Consequently, the introduction of a ‘suicide’ ligand, or the strapping of one face is superfluous by virtue of the ligand design. In turn, these observations point to a new class of macrocyclic complexes which can be used for the unambiguous exploration of discriminatory interactions of unidentates.

#### Spectroscopic studies

Characteristic electronic and CD spectroscopic data for the complexes are listed in Table 5. The former are entirely consistent with planar coordination of the macrocycle at the metal atoms. CD spectra are of the vicinal kind, with no configurational contribution possible for these complexes.

<sup>1</sup>H and <sup>13</sup>C NMR data for the Ni(II) and Pd(II) complexes are given in Table 6. The patterns of resonances in the spectra are consistent with C<sub>2</sub> symmetry, as expected on the basis of the structure of the ligand obtained from the X-ray structure determination, pro-

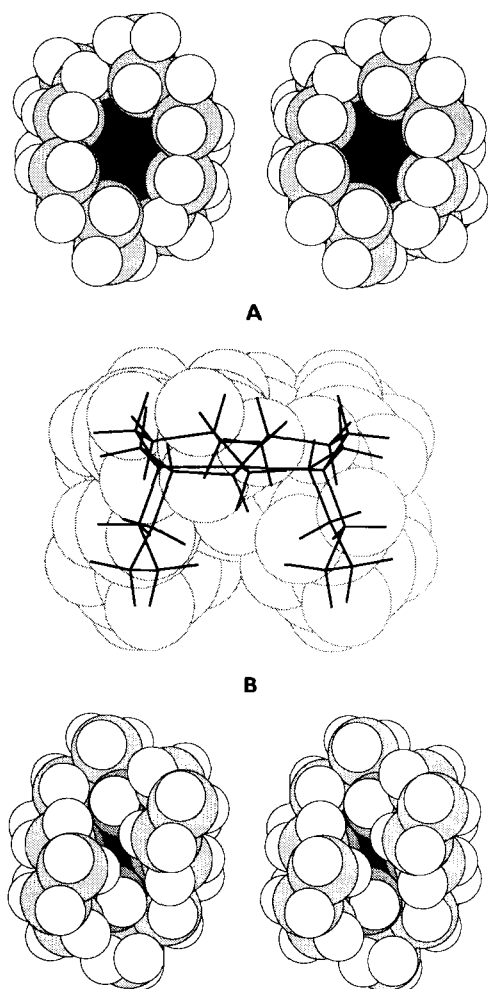


Fig. 2. Space-filling stereo views [11] of the complex cation, drawn with van der Waals' radii, viewed from either side of the  $\text{CuN}_4$  plane. Coordinates are taken from Tables 1 and 2. The more heavily shaded areas in the centres of the ring structures represent fractions of the metal ion accessible for further coordination. Faces A and B are indicated by reference to a view of the molecule from either side of the square plane. Oxygen atoms of the perchlorate groups have been omitted for clarity.

TABLE 5. Electronic and chiroptical spectroscopic data for the complexes, recorded in  $\text{H}_2\text{O}$

Complex	$\lambda$ (nm)	$\epsilon$ ( $\text{M}^{-1} \text{cm}^{-1}$ )	$\Delta\epsilon$ ( $\text{M}^{-1} \text{cm}^{-1}$ )
[Cu( <i>S</i> -mac)]( $\text{ClO}_4$ ) <sub>2</sub>	484	196	
	555		-0.16
	470		+0.21
	420		-0.34
[Ni( <i>S</i> -mac)]( $\text{ClO}_4$ ) <sub>2</sub>	458	95	
	475		+0.93
	425		-1.26
[Pd( <i>S</i> -mac)]( $\text{ClO}_4$ ) <sub>2</sub>	286	900	
	300		+0.92
	270		-2.01

TABLE 6. Characteristic NMR data for the complexes ( $\delta$ , ppm, relative to TMS as internal standard; solvent  $\text{dmsO-d}_6$ ; 22 °C)

Complex	$^1\text{H}$	$^{13}\text{C}$
[Ni( <i>S</i> -mac)]( $\text{ClO}_4$ ) <sub>2</sub>	1.05d ( $\text{CH}_3$ )	15.2 ( $\text{CH}_3$ ), 23.3, 28.6, 32.0, 32.8, 52.4, 55.1 ( $\text{CH}_2$ , one obscured by solvent), 57.4, 61.7 (CH)
[Pd( <i>S</i> -mac)]( $\text{ClO}_4$ ) <sub>2</sub>	1.09d ( $\text{CH}_3$ )	16.1 ( $\text{CH}_3$ ), 22.2, 28.2, 33.0, 33.3, 53.8, 58.2 ( $\text{CH}_2$ , one obscured by solvent), 58.5, 64.1 (CH)

viding the mode of coordination is the same in each complex. Since Cu(II) recoordinates to the free ligand to produce a complex with exactly the same geometry as that imposed during the template synthesis, it is certain that this indeed occurs, and all of the complexes are assigned an analogous geometry to that shown in Fig. 1.

The stereochemical properties of these complexes make them ideal for use in a systematic study involving variation of the chiral topologies of the exposed face containing the metal ion in an environment amenable to coordination by a suitable unidentate. We will report studies of such systems in the near future.

### Supplementary material

Lists of observed and calculated structure factors, anisotropic thermal parameters, proposed hydrogen bond parameters and a comprehensive table of bond lengths and angles are available from the authors on request.

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### References

- 1 R. R. Fenton, F. S. Stephens, R. S. Vagg and P. A. Williams, *Inorg. Chim. Acta*, 197 (1992) 233, and refs. therein.
- 2 M. A. Cox, T. J. Goodwin, P. Jones, P. A. Williams, F. S. Stephens and R. S. Vagg, *Inorg. Chim. Acta*, 127 (1987) 49.

- 3 (a) K. Miyamura, K. Hata, T. Makino, M. Saburi and S. Yoshikawa, *J. Chem. Soc., Dalton Trans.*, (1987) 1127; (b) K. Miyamura, M. Saburi, S. Tsuboyama, K. Tsuboyama and T. Sakurai, *J. Chem. Soc., Dalton Trans.*, (1988) 1543.
- 4 G. M. Sheldrick, *SHELXTL User Manual*, Revision 3, Nicolet XRD Corporation, Cupertino, CA, 1981.
- 5 *International Tables for X-ray Crystallography*, Vol. IV, Kynoch, Birmingham, UK, 1974, pp. 72-79, 149.
- 6 C. K. Johnson, *ORTEP, Rep. ORNL-3794*, Oak Ridge National Laboratory, TN, USA, 1965, revised 1971.
- 7 A. G. Orpen, L. Brammer, F. A. Allen, O. Kennard, D. G. Watson and R. Taylor, *J. Chem. Soc., Dalton Trans.*, (1989) S49.
- 8 G. Patrick, M. P. Ngwenya, S. M. Dobson and R. D. Hancock, *J. Chem. Soc., Dalton Trans.*, (1991) 1295.
- 9 Y. Saito, *Top. Stereochem.*, 10 (1978) 96.
- 10 T. Makino, K. Hata and M. Saburi, *Chem. Lett.*, (1979) 287.
- 11 R. S. Vagg, *3D-MOL*, integrated microcomputer programs for molecular graphics, Macquarie University, 1992.