Preparation, Stereochemistry, and Crystal Structures† of Some Complexes of the Macrocycle 3,3,7,7,11,11,15,15-Octamethyl-1,9-dithia-5,13-diazacyclohexadecane with Co^{II}, Ni^{II}, Cu^{I}, Cu^{II}, Zn^{II}, Rh^{III}, Ag^{I}, Cd^{II}, Pt^{II}, and Hg^{II} Salts

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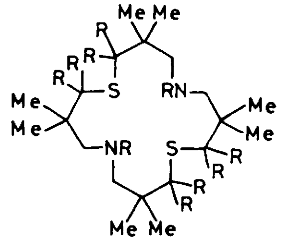
The preparation of some complexes of the macrocycle 3,3,7,7,11,11,15,15-octamethyl-1,9-dithia-5,13-diazacyclohexadecane (L) with Co^{II}, Ni^{II}, Cu^{I}, Cu^{II}, Zn^{II}, Rh^{III}, Ag^{I}, Cd^{II}, Pt^{II}, and Hg^{II} salts is reported. *X*-Ray structural studies have been carried out on $[CoLX_2]$ (X = Cl or Br), $[RhLCl_2]PF_6$, and $[CuLCl_2]\cdot 0.5C_7H_8$. These structures are compared with those found earlier for $[AgL(O_2CMe)]\cdot 2H_2O$, $[PdL][PF_6]_2$, and $[PdL]Cl_2\cdot 2H_2O$. In all of them the metal ions bond with the macrocyclic ligand atoms in a square-planar, or near square-planar, array and no example of tetrahedral or 'folded' co-ordination geometry was obtained. In these structures, the macrocycle displays four of the five possible relative configurations for the NH hydrogens and sulphur lone pairs. The chelate rings vary from chairs to flattened chairs and twist-boats. Proton and ^{13}C n.m.r., u.v.–visible, and conductivity properties of these complexes are also summarised. In solution, facile conversion between two or more configurational isomers occurs for Co^{II}, Rh^{III}, Pt^{II}, and Cd^{II} complexes, although these are slow on the n.m.r. time-scale. Exchange processes are even faster for Cu^{I}, Ag^{I}, Zn^{II}, and Hg^{II} complexes although these exist as essentially one configurational isomer. Conformational rigidity of the chelate rings does not appear to complicate the ^{1}H and ^{13}C n.m.r. spectra for any of these complexes.

Several years ago we synthesised[1] the macrocycle 3,3,7,7,11,11,15,15-octamethyl-1,9-dithia-5,13-diazacyclohexadecane (L), in part, because of the growing interest in ligands containing an N_2S_2 donor set as possible models for the 'blue' copper proteins. At that time, although a vast number of macrocyclic complexes were known, a relatively large proportion of this number involved[2] the first-row transition metal ions and tetra-aza macrocycles (especially those with 14-membered rings) and n.m.r. studies were relatively rare.[2,3] The availability of L presented an opportunity to extend our knowledge into novel areas and we proceeded to study the structures of its complexes with a variety of cations including some diamagnetic second- and third-row transition and post-transition (Group 2B) metals. The design of the ligand is such that ^{1}H n.m.r. spectra of its complexes are generally much more useful in structural studies than those of similar ligands lacking the methyl groups. We hoped that (*i*) the nature and disposition of the heteroatoms, (*ii*) the size and flexibility of the macrocyclic ring, and (*iii*) the presence of the bulky methyl groups would lead to unusual co-ordination geometries for some of the cations. We have already reported the structures of the complexes of L with palladium(II) hexafluorophosphate[4] and chloride.[4,5] The present paper deals with the complexing properties of this ligand towards a variety of additional metal ions.

Results and Discussion

Preparation of the complex $[PtLCl_2]$ was achieved by heating a solution containing L and $PtCl_2$ to reflux for several days. Interruption of the preparation after only a few hours of refluxing resulted in the isolation of a very insoluble pink precipitate, probably the Magnus salt, $[PtL]^{2+}[PtCl_4]^{2-}$. The required complex was purified by preparative t.l.c. and crystallisation, and analysed for $[PtLCl_2]\cdot H_2O$. The ^{1}H n.m.r. spectra of the complex were strikingly similar to those of $[PdLCl_2]\cdot H_2O$[4,5] and indicated the presence of two isomeric species in both $CDCl_3$ and in D_2O. The principal differences observed were that, in the former solvent, the platinum derivative displayed a smaller proportion of the more symmetrical isomer and, at 60 MHz, gave evidence of ^{195}Pt–^{1}H couplings. There was no evidence for such coupling at 400 MHz, presumably because of a field-dependent relaxation mechanism.[6] Analogy with the palladium analogue[4,5] suggests that the complex exists in solution as a mixture of *c,c,c* and *c,c,t*(N) isomers (see Scheme), with square-planar platinum in D_2O and trigonal-bipyramidal platinum in $CDCl_3$.



L ; R = H
L^{1} ; R = D

Reaction of L with $RhCl_3\cdot 3H_2O$ in refluxing ethanol afforded a product which ran as one clean band on preparative t.l.c., but the recovered material, upon crystallisation, formed a mixture of yellow plates and orange rods. This mixture analysed well for

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† *Supplementary data available* (No. SUP 56599, 11 pp.): H-atom co-ordinates, thermal parameters. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1986, Issue 1, pp. xvii—xx. Structure factors are available from the editorial office.

Table 1. Important bond lengths, configuration of the macrocycle, and conformations of the chelate rings in the complexes

Molecule[a]	M–S	M–N	M–X[b]	Config.	Molecular symmetry	Ring conformations
$[CoLBr_2]$	2.464(4)	2.253(9)	2.612(2)	*c,t,c*	$\bar{1}$	chair, twist-boat
$[CoLCl_2]$	2.485(1)	2.246(2)	2.431(1)	*c,t,c*	$\bar{1}$	chair, twist-boat
$[RhLCl_2]PF_6$ (a)	2.344(3)	2.132(8)	2.325(3)	*c,t,c*	$\bar{1}$	chair, twist-boat
(b)	2.303(4)	2.260(5)	2.308(3)	*c,t,c*	$\bar{1}$	chair, twist-boat
$[PdL][PF_6]_2$	2.307(1)	2.090(4)		*c,t,c*	$\bar{1}$	chair, chair
$[PdL]Cl_2 \cdot 2H_2O$ (a)	2.296(5), 2.290(5)	2.14(2), 2.07(2)		*c,c,c*	approx. *m*	2 chair, 2 twist-boat
(b)	2.293(6), 2.297(6)	2.05(2), 2.12(2)		*c,c,t*(N)	none	1 chair, 3 twist-boat
$[CuLCl_2] \cdot 0.5C_7H_8$ (a)	2.386(6), 2.395(6)	2.26(1), 2.07(1)	2.594(5), 2.951(6)	*t,t,t*	none	all twist-boat
(b)	2.394(6), 2.409(6)	2.26(1), 2.11(1)	2.547(5), 2.932(5)	*t,t,t*	none	all twist-boat
$[AgL(O_2CMe)] \cdot 2H_2O$	2.589(1), 2.589(1)	2.481(2), 2.430(2)	2.686(2)	*t,t,t*	none	all twist-boat

[a] (a) and (b) refer to two independent molecules. [b] X = Br, Cl, or O.

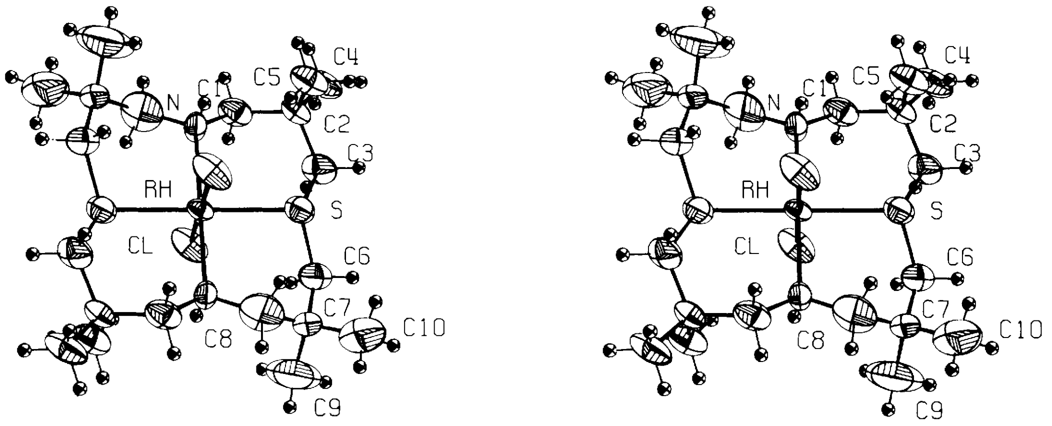
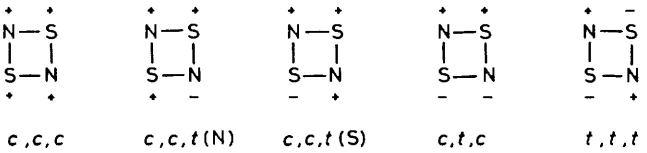


Figure 1. Stereoview of one of the two independent centrosymmetric $[RhLCl_2]^+$ cations



Scheme. The five possible configurations of L when acting as a quadridentate ligand; the positive and negative signs denote the relative orientations of the NH protons and the S lone pairs with respect to the ring plane

$[RhLCl_2]Cl$ but, unfortunately, neither type of crystal was suitable for *X*-ray work. Conversion of this complex into $[RhLCl_2]PF_6$ was effected by metathesis with ammonium hexafluorophosphate. This new complex gave only a single type of crystal, which proved suitable for *X*-ray crystallography. This revealed unco-ordinated hexafluorophosphate ion, as expected, and two types of cation (Figure 1) both lying on inversion centres. Both of these have six-co-ordinate geometry, the chlorides *trans*, and the macrocycle in planar co-ordination with the *c,t,c* configuration (see Scheme). They differ only in the degree of twist in two of the chelate rings.* Both the trichloride and the hexafluorophosphate conduct as 1 : 1 electrolytes and give electronic spectra in solution which are indicative[7] of six-co-ordinate rhodium(III) with the chlorides *trans* and the macrocycle co-ordinated in a planar fashion. The revealing feature is the position and intensity of the lowest energy band which in such cases appears at *ca.* 440 nm, whereas the related *cis* complexes generally absorb in the 350—360 nm region. The intensity of the absorption in the present case is intermediate between that of the *trans* rhodium(III) complex[8] of 1,4,8,11-tetra-azacyclotetradecane and that of the corresponding all-sulphur analogue.[9] The ^1H n.m.r. spectra of the two complexes are very similar but exceedingly complicated and indicate the presence of a mixture of isomers in solution. In order to simplify the task of interpreting these ^1H n.m.r. spectra, the deca-deuteriated ligand L^1 was synthesised and converted into $[RhL^1Cl_2]Cl$ and $[RhL^1Cl_2]PF_6$. This led to much simpler spectra since not only were the resonances from the SCH_2 and NH protons eliminated, so also were the couplings of the latter

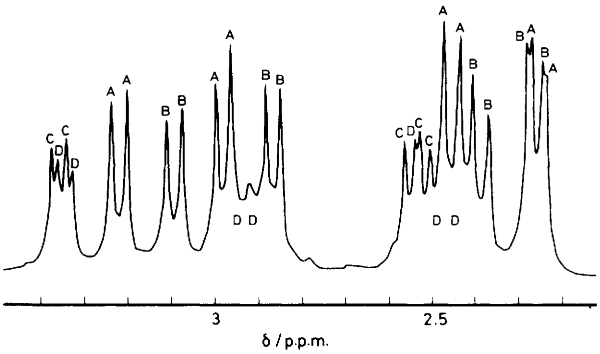


Figure 2. The NCH region of the proton n.m.r. spectrum of $[RhL^1Cl_2]Cl$ at 400 MHz in D_2O

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* Some important aspects of the structures of the various complexes of L, which we have determined by *X*-ray analysis, are compared in Table 1.

to the NCH_2 protons. The NCH region of the ^1H n.m.r. spectrum of $[RhL^1Cl_2]Cl$ at 400 MHz in D_2O is shown in Figure 2. By careful intensity measurements and decoupling experiments, we tentatively attributed the 14 doublets present (12 resolved, two hidden) in this region to the presence of significant amounts of four (A—D) of the five possible configurational isomers (see Scheme). It was assumed that the missing isomer was of the *c,c,c* or *t,t,t* type since, if the chelate rings are flexible, each of these would be expected to give two doublets while the other three, less symmetrical isomers should give four each. The existence of four isomers appears to be supported by the methyl region of the ^{13}C n.m.r. spectrum in which 14 lines attributable to methyl groups can be discerned.

Attempts to obtain the ^{103}Rh n.m.r. spectrum of the complex $[RhLCl_2]Cl$ were unsuccessful. As mentioned above, $[RhLCl_2]PF_6$ gave what appeared to be a single type of crystal, one of which was shown by *X*-ray crystallography to contain ligand co-ordinated only in the *c,t,c* configuration. Thus, since $[RhL^1Cl_2]PF_6$ in CD_3CN gives a very similar ^1H n.m.r. pattern to that shown in Figure 2, it appeared that slow (on the ^1H n.m.r. time-scale) equilibration of isomers takes place in solution. Three possible modes of equilibration can be envisaged, *viz*. (*i*) dissociation–reassociation of sulphur[10] and/or nitrogen, (*ii*) inversion at sulphur, and (*iii*) deprotonation–inversion–reprotonation at nitrogen. The first was viewed as unlikely in light of the well-accepted kinetic stability of Rh^{III} complexes. It was then concluded that both other modes of equilibration are operative since if only one were in effect then a maximum of two isomers should be observable starting from crystalline $[RhL^1Cl_2]PF_6$.

Sulphur inversion alone would give a mixture of *c,t,c* and *c,c,t*(N) at equilibrium, while nitrogen inversion would give *c,t,c* and *c,c,t*(S). Based on earlier work[11] with polyaza macrocycles it would be expected that nitrogen inversion would be inhibited by dissolving the complex in a solvent containing a protic acid. Suppression of NH exchange splits the five possible isomers into two groups, one having the two NH protons on the same face of the complex [*c,c,c*; *t,t,t*; *c,c,t*(S)], and the other with the NH protons on opposite faces [*c,t,c*; *c,c,t*(N)]. Indeed, when some yellow crystals of $[RhL^1Cl_2]Cl$ were separated by hand from the original mixture and their ^1H n.m.r. spectrum obtained in acidified D_2O the NCH region showed appreciable changes in the relative intensites of the various signals from those present in neutral solution (Figure 2). Two sets of signals (from isomers A and C) were enhanced in intensity relative to the remainder. Since one of the former sets of resonances (C) must arise from the symmetrical isomer present (*c,c,c* or *t,t,t*) the other set (A) may be ascribed to the isomer with the *c,c,t*(S) configuration. The remaining resonances (B and D) should then correspond to the *c,t,c*, and *c,c,t*(N) configurations. Support for these conclusions was sought using $[RhL^1Cl_2]PF_6$, but unfortunately, this complex is not soluble in D_2O and the use of *p*-$CH_3C_6H_4SO_3H$–CD_3CN or CF_3CO_2H as solvents led to only minimal changes in its ^1H n.m.r. spectrum relative to that run in CD_3CN.

The complexes of $CoCl_2$ and $CoBr_2$ with L (Figure 3) are both pink but differ markedly in solubility, the latter being almost totally insoluble in all solvents tested while the former is quite soluble in solvents such as CH_2Cl_2. Nevertheless, when *X*-ray analyses were carried out on them, the crystals proved to be isomorphous and each contains a single centrosymmetric species in which the cobalt has essentially octahedral geometry, the halides are *trans*, and the macrocycle has the *c,t,c* configuration.

In deuteriochloroform the ^1H n.m.r. spectrum of the chloride is spread over a range of 230 p.p.m. Distinction between NC*H* and SC*H* resonances was achieved by comparison of this spectrum with that of the decadeuterio analogue, $[CoL^1Cl_2]$.

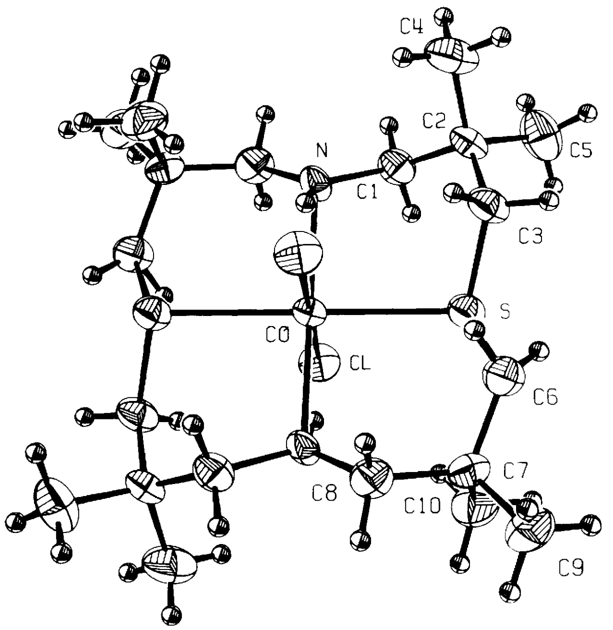

Figure 3. A view of the centrosymmetric $[CoLCl_2]$ molecule

These spectra show the presence of two major isomers (ratio *ca.* 9:7) and probably a minor one. The more prominent of the former shows two ^1H resonances ascribable to each of CMe, NCH, and SCH and has therefore either the *c,c,c* or *t,t,t* configuration. The less prominent major isomer shows four CMe and NCH proton resonances, while only two of the expected four SCH resonances are assignable with some certainty. This isomer must have one of the three less symmetrical configurations. Since cobalt(II) complexes are known to be labile with respect to bond dissociation, it cannot be assumed that these isomers have the *trans*-octahedral stereochemistry found in the solid state. Five-co-ordinate structures, formed by dissociation of chloride, or *cis*-octahedral geometry are both possible, although the latter may be relatively unfavourable for saturated macrocycles with rings larger than 14-membered.[12]

The fact that n.m.r. spectra are obtainable indicates little about the spin state for Co^{II}, but the pink colour is characteristic of high-spin cobalt(II) and indicates[13,14] that the ligand-field strength is fairly weak in this case. This accords not only with the known[2,15] low ligand-field strength of tetrathia macrocycles as compared to their tetra-aza analogues, and with the expectation that the 16-membered ring is larger than the optimum required to produce a strong ligand field,[16] but also with our failure to prepare Co^{III} complexes of L by oxidation of its Co^{II} complexes. This type of oxidation has been reported as difficult for complexes with weak ligand fields,[17] including some[18] with sulphur-containing macrocycles. A brown colour observed on heating cobalt(II) perchlorate with L under air in nitromethane may well indicate the formation of a binuclear μ-peroxo species,[13] although attempts to isolate a characterisable product have been unsuccessful.

The complex of $NiCl_2$ with L readily forms blue crystals, unsuitable for *X*-ray work, but which analyse well for the simple complex $[NiLCl_2]$. The u.v.–visible spectrum shows absorption at 398 ($\varepsilon = 30$ dm^3 mol^{-1} cm^{-1}) and 650 nm ($\varepsilon = 16$) and strong charge-transfer bands below 350 nm in ethanol, consistent with the presence of high-spin octahedral nickel(II).[16] A ^1H n.m.r. spectrum could not be obtained, although n.m.r. studies[19] on the comparable paramagnetic complex, dichloro-

Table 2. Hydrogen-1 n.m.r. data (δ/p.p.m.) for complexes at 400 MHz

Compound	Temperature	CH_3	NCH	SCH	NH
$[CuL]BF_4$	20 °C	1.07 (s)	2.59 (s)	2.82 (s)	2.57 (s)
$[AgL(NO_3)]$[a]	20 °C	1.06 (s)	2.43 (s)	2.96 (s)	2.02 (s)
$[AgL(NO_3)]$	−50 °C	1.03 (s), 1.13 (s)	2.26 (d)[b], 2.69 (t)[b]	2.50 (d)[c], 3.32 (d)[c]	2.03 (t)[b]
$[CdLCl_2]$[d]	−10 °C	1.10 (s), 1.17 (s)	2.17 (d)[b], 3.49 (t)[b]	2.46 (d)[c], 4.01 (d)[c]	1.98 (t)[b]
$[ZnLCl_2]$	−10 °C	1.07 (s), 1.18 (s)	2.07 (d)[b], 3.54 (t)[b]	2.36 (d)[e], 4.02 (d)[e]	2.56 (t)[b]
$[HgLCl_2]$	−20 °C	1.11 (s), 1.22 (s)	2.30 (d)[b], 3.41 (t)[b]	2.50 (d)[c], 4.17 (d)[c]	2.60 (br t)

[a] At 60 MHz. [b] J 12.5 Hz. [c] J 11.5 Hz. [d] Major isomer only. [e] J 11.0 Hz.

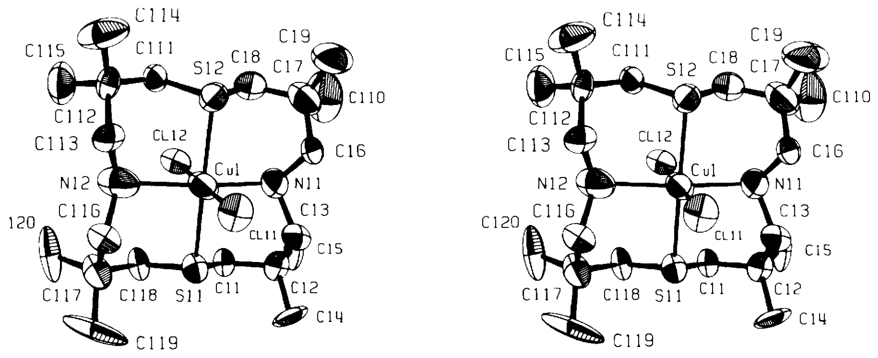

Figure 4. Stereoview of one of the two independent $[CuLCl_2]$ molecules

(1,5,9,13-tetra-azacyclohexadecane)nickel(II) have been taken to indicate the presence of a mixture of configurational isomers, the predominant one having the *c,c,c* configuration.

The bright green $CuCl_2$ complex of L (Figure 4) was purified by preparative t.l.c. and crystallised from dichloromethane–toluene to afford crystals of $[CuLCl_2]\cdot0.5C_7H_8$ which were suitable for *X*-ray structure analysis. This revealed the presence of two closely related species, each of which contains copper with essentially square-pyramidal geometry. One chloride is axial and the macrocycle has the *t,t,t* configuration, in which all of the chelate rings are forced to adopt twist-boat conformations. The other chloride occupies the second axial site, but at a significantly greater distance from the metal.*

The electronic spectrum of this complex (in ethanol) displays four well-defined absorptions which appear to suggest[22] that a similar structure is retained in solution although it has been noted[23] that electronic spectra of copper(II) complexes are unreliable as indicators of co-ordination geometry. The analogous deep blue complex $[CuL][BF_4]_2$ also displays four well-defined absorptions in its u.v.–visible spectrum. However, the replacement of chloride by the non-co-ordinating anion BF_4^- leads to a shift of the lowest energy absorption from 720 to 620 nm in ethanol (567 nm in dichloromethane). The positions and intensities of the three lowest energy bands in ethanol are similar to those reported[24] for the analogous complex 1,9-dithia-5,13-diazacyclohexadecanecopper(II) perchlorate in aqueous solution. Unfortunately, the crystals of $[CuL][BF_4]_2$ proved to be unsuitable for *X*-ray crystallography. It would be of particular interest to see if the macrocycle in this complex retains the *t,t,t* configuration found for the chloride, since the copper in the 'blue' proteins is believed[25] to have a distorted tetrahedral co-ordination sphere, and the *t,t,t* configuration of L is that most suited to accommodate tetrahedral stereochemistry. Distortion of L from the approximately planar co-ordination mode found in $[CuLCl_2]\cdot0.5C_7H_8$ towards a tetrahedral mode, with retention of the *t,t,t* configuration, would be favoured since this would allow the chelate rings to relax from twist-boats to chairs.

Heating of the tetrafluoroborate with fine copper ribbon in CD_3CN under nitrogen yielded a colourless solution which gave a ^1H n.m.r. spectrum at 400 MHz very similar to that of the silver nitrate complex at ambient temperature (see Table 2). This solution became green quite rapidly on exposure to air. Thus, perhaps not unexpectedly,[26] the copper tetrafluoroborate complexes of L display stability behaviour which is intermediate between that of related tetrathia- and tetra-azacyclohexadecanes. For the tetrathia complexes, with non-co-ordinating ligands, the Cu^I state is preferred,[20,27] while for their tetra-aza counterparts, the Cu^{II} state is favoured.[28]

The silver nitrate complex of L was prepared and purified by crystallisation. The resulting very thin plates analysed for the unsolvated, 1:1 complex but were unsuitable for *X*-ray crystallography. However, the analogous silver acetate complex, when crystallised from moist solvent, gave a dihydrate which was suitable for *X*-ray structure analysis. This revealed[29] a five-co-ordinate complex with approximately square-pyramidal co-ordination, an acetate oxygen atom being apical. The macrocycle has the *t,t,t* configuration and all rings are twist-boats. ^1H N.m.r. spectra of the nitrate at ambient temperature showed only three rather broad signals, downfield from those of the free ligand resonances. Cooling to −50 °C gave a very clean spectrum at 400 MHz (see Table 2 and Figure 5). This consists of two methyl resonances, two SCH doublets, two NCH multiplets, and a broad NH resonance, with the last proton strongly coupled to one NCH and weakly to the other. This coupling behaviour has been a consistent feature of all diamagnetic macrocyclic complexes prepared with L when NH exchange is slow on the n.m.r. time-scale.

The acetate complex showed very similar ^1H n.m.r. behaviour

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* The related macrocycle, 1,5,9,13-tetrathiacyclohexadecane, acts as a bridging, bidentate ligand for two copper(II) centres, in the presence of co-ordinating anions, while with non-co-ordinating anions, a copper(II) cation occupies the cavity.[20] The crystal structure of the perchlorate has been reported recently[21] and shows that the sulphur lone pairs have the *c,t,c* configuration.

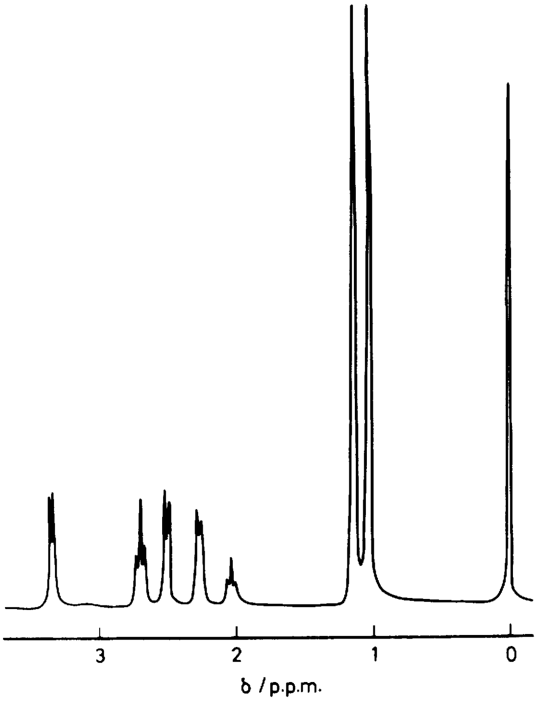

Figure 5. The proton n.m.r. spectrum of [AgL(NO_3)] at 400 MHz in $CDCl_3$ at −50 °C

except that a lower temperature was required to obtain limiting spectra. These low-temperature spectra were taken to indicate the freezing out of a symmetrical macrocycle configuration, presumably the *t,t,t* situation found in the solid state for the acetate, with the ligand now adopting tetrahedral co-ordination geometry. The lower temperature required to obtain the limiting spectrum with the acetate would then be rationalised as this counter ion would be expected to be more reluctant to separate from silver than nitrate. At higher temperatures an exchange process leads to equivalence of the geminal pairs, a situation which also explains the observation that the ^{13}C spectrum of the nitrate (see Table 3) displays only four signals at ambient temperature. Possibly in this exchange process, individual silver–heteroatom bonds dissociate, the heteroatom inverts, and then the bond reforms, without dissociation of the entire macrocycle. In the presence of excess of L, free and bonded macrocycle are not in fast equilibrium on the n.m.r. time-scale at ambient temperature.

Complexes of three post-transition metal ions, Zn^{II}, Cd^{II}, and Hg^{II}, were prepared by adding the appropriate chloride salt in two portions to a slight excess of L in a suitable solvent. ^1H N.m.r. spectra were obtained after each addition and showed, in all cases, separate signals for free and complexed macrocycle. The cadmium(II) bromide complex was also prepared in this fashion but, like its Co^{II} analogue, proved to be exceedingly insoluble. The cadmium(II) chloride derivative was purified by crystallisation and analysed well for the simple 1:1 complex.

Table 3. Carbon-13 n.m.r. data (δ/p.p.m.) for complexes at 400 MHz and ambient temperature

Compound	CH_3	*C*Me	SC	NC
[AgL(NO_3)]	27.5	34.3	44.7	61.4
[CdLCl_2][a]	27.5, 27.8	35.3	41.7	60.9
[CdLCl_2][b]	22.9, 27.0	34.6	41.4	61.4
	28.0, 32.4		44.7	65.0
[ZnLCl_2]	27.3, 27.9	34.8	41.3	63.1
[HgLCl_2]	27.4	35.0	43.6	61.4

[a] Major isomer. [b] Minor isomer.

Both the mercury and zinc complexes, however, appeared to be rather unstable in the absence of excess L and could not be purified. The ^1H n.m.r. spectra of all four complexes appeared to derive from a major, symmetrical, isomer (*t,t,t* or *c,c,c* configuration).*

For the cadmium(II) and zinc(II) complexes, the limiting spectra (Table 2) were observed at ambient temperature at both 60 and 400 MHz, although cooling sharpened the signals, whereas for the mercury(II) complex cooling to below −20 °C was necessary even at 400 MHz. In contrast to the mercury and zinc complexes, the cadmium complexes gave spectra containing resonances attributable to a second, minor isomer which was present in easily detectable quantities. It appeared that these signals could arise from one of the less symmetrical configurational isomers, *c,t,c*, *c,c,t*(N), or *c,c,t*(S). This conclusion gains support from the ^{13}C n.m.r. spectrum which displays two sets of signals. One of these showed a five-line pattern, representing the major, symmetrical isomer, with one type of NCH_2, SCH_2, and quaternary carbon and two non-equivalent, methyl-derived resonances. The other gave a much less intense set of signals, each in approximately the same position as a resonance of the major isomer but consisting of two signals where the major isomer displayed only one (see Table 3). Attempts to obtain a ^{113}Cd n.m.r. spectrum on the chloride complex were unsuccessful and ^{113}Cd couplings to either ^1H or ^{13}C were not detected. In the ^{13}C n.m.r. spectra of the zinc and mercury complexes, only one set of signals, corresponding to one of the more symmetrical isomers, is present in both cases. We have not attempted to obtain a ^{199}Hg spectrum on the mercury complex. However, in the ^1H n.m.r. spectrum of this complex at low temperature small satellite signals on both sides of the NCH and SCH resonances are of a magnitude consistent with that expected from coupling to the 16.8% abundant ^{199}Hg nucleus. The couplings to each of the SCH and NCH resonances decrease as one proceeds downfield, being *ca.* 120 Hz for the high-field NCH, 90 Hz for the high-field SCH, 60 Hz for the low-field NCH, and 40 Hz for the low-field SCH. The NCH protons can be identified because, as mentioned above, one of them is always strongly coupled to the NH proton.

Experimental

Melting points were determined with a Kofler hot-stage apparatus and are uncorrected. Proton n.m.r. spectra were recorded on a Varian EM360L or Bruker WH-400 (Southwestern Ontario NMR Centre) spectrometer. Carbon n.m.r. spectra were recorded on the latter instrument or on a Bruker WP-60 spectrometer (*J* values are given in Hz). Electronic spectra were obtained on a Varian DMS 90 instrument and molar conductivities were calculated from the electrical resistance of solutions, in freshly dried solvent, measured with a Beckmann model RC-19A conductance bridge. Preparative t.l.c. plates were spread with Kieselgel G (Merck). Elemental

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* An *X*-ray crystal structure analysis[30] of 1,5,9,13-tetrathiacyclohexadecanemercury(II) perchlorate reveals approximately square-planar co-ordination of the ligand (distorted toward tetrahedral) and the *t,t,t* configuration. In contrast, a ^{13}C n.m.r. solution study[31] of lead(II), cadmium(II), and mercury(II) complexes of 1,5,9,13-tetramethyl-1,5,9,13-tetra-azacyclohexadecane suggests the presence of only one isomer, with the *c,c,c* configuration in the case of lead, and two isomers, with the *c,c,c* and *c,c,t* configurations, for cadmium and mercury.

analyses were performed by Galbraith Laboratories, Knoxville, Tennessee, U.S.A. The ligand, 3,3,7,7,11,11,15,15-octamethyl-1,9-dithia-5,13-diazacyclohexadecane (L) was obtained as described earlier.[1,4] The decadeuterio analogue (L^1) was obtained by an identical procedure starting from $(CD_3)_2SO$ and was purified by crystallisation from CH_3OD.

Complex of Platinum(II) *Chloride with* L.—A mixture of platinum(II) chloride (54.3 mg) and L (76.0 mg) was heated at reflux in a mixture of dichloromethane and acetonitrile for 5 d. An initial precipitate redissolved. The solvent was evaporated and the residue crystallised from acetonitrile–hexane to give pale yellow crystals of $[PtLCl_2]\cdot H_2O$ (130 mg; decomp. 220 °C) which were dried *in vacuo* (Found: C, 36.45; H, 6.75; N, 4.45. $C_{20}H_{42}Cl_2N_2PtS_2\cdot H_2O$ requires C, 36.5; H, 6.75; N, 4.25%); ^1H n.m.r. (in deuteriochloroform), δ (major isomer) 1.14, 1.21, 1.34, 1.41 (all 6 H, s, CMe), 2.6—2.8 (8 H, m, NCH and SCH), 3.07 (2 H, dd, NCH, *J* 13.5, 7), 3.60 (2 H, t, NCH, *J* 12), 3.81 (2 H, d, SCH, *J* 11.5), 5.07 (2 H, d, SCH, *J* 11.5), 5.17 (1 H, br t, NH), and 8.10 (1 H, br t, NH); δ (minor isomer) 1.20, 1.23 (both 12 H, s, CMe), 2.6—2.8 (8 H, m, NCH and SCH), 3.25 (4 H, br t, NCH), 4.52 (4 H, d, SCH, *J* 11), and 6.77 (2 H, br t, NH). When a solution of platinum(II) chloride and L were heated in acetonitrile for 4 h, a very insoluble pink precipitate formed. Addition of a catalytic quantity of tin(II) chloride to this mixture and then heating for a further 3 d led to dissolution of this solid and the appearance of a small amount of a black precipitate. The resulting solution was filtered, evaporated and the residue submitted to preparative t.l.c. (dichloromethane–methanol, 4:1) and gave a band of intermediate polarity which was shown (^1H n.m.r.) to be $[PtLCl_2]$ (94% yield).

Complexes of Rhodium(III) *with* L *and* L^1.—Rhodium(III) chloride trihydrate (26.3 mg) and L (or L^1) (37.5 mg) were heated in refluxing ethanol for 1 h. During this time the initial red colour changed to yellow. The solvent was evaporated and the residue subjected to preparative t.l.c. (dichloromethane–methanol, 9:1). Only one band was observed and this was cut in half. The two fractions recovered therefrom (total 59.8 mg) gave identical ^1H n.m.r. spectra and each, on crystallisation from acetonitrile–toluene, gave $[RhLCl_2]Cl$ as a mixture of orange and yellow crystals (decomp. 300 °C) (Found: C, 41.0; H, 7.35; N, 4.8. $C_{20}H_{42}Cl_3N_2RhS_2$ requires C, 41.15; H, 7.25; N, 4.8%); ^1H n.m.r. exceedingly complex (see Figure 2); ^{13}C n.m.r. in D_2O, δ 27.6, 28.1, 32.0, 32.2, 32.9, 33.2, 33.4, 35.7, 35.9 (all CH_3), 39.2, 40.2, 40.3, 40.5, 40.8 (all CH_3 or *C*Me), 48.6, 48.8, 49.1, 49.3, 49.7, 49.9 (all SC), 70.5, 71.8, 72.3, 73.6, 73.9, 74.6 (all NC); molar conductivity in methanol 155 Ω^{-1} cm^2 mol^{-1} (8.43×10^{-4} mol dm^{-3}); $\lambda_{max.}$ (in water) at 437 (ε 181), 271 (ε 14 850), and 224 nm (ε 22 600 dm^3 mol^{-1} cm^{-1}). A solution of $[RhLCl_2]Cl$ (89.0 mg) in ethanol was mixed with a solution of ammonium hexafluorophosphate (25.3 mg) in aqueous ethanol. The resulting solution was evaporated to dryness, the residue washed with water and crystallised from methanol to give yellow crystals of $[RhLCl_2]PF_6$ (85.9 mg; decomp. 300 °C) which were suitable for *X*-ray analysis. Its ^1H n.m.r. spectrum in deuterioacetonitrile (insufficiently soluble in chloroform) was very complex but similar to that of $[RhLCl_2]Cl$ in deuteriochloroform. Molar conductivity in acetonitrile 144 Ω^{-1} cm^2 mol^{-1} (9.46×10^{-4} mol dm^{-3}); $\lambda_{max.}$ (in acetonitrile) at 437 (ε 182), 272 (ε 16 500), and 225 nm (ε 24 000 dm^3 mol^{-1} cm^{-1}).

Complexes of Cobalt(II) *with* L.—A solution of cobalt(II) chloride hexahydrate (39.6 mg) in ethanol was added dropwise to a warm solution of L (62.5 mg) in the same solvent. Within a few hours the solution changed from blue to pink and crystals of $[CoLCl_2]$ (13 mg) were deposited. These were suitable for *X*-ray analysis. Evaporation of the mother-liquors to small bulk afforded a further crop (66 mg) of the same complex. ^1H N.m.r. (in deuteriochloroform, all resonances broadened singlets), δ (predominant isomer) −24, −6 (both CMe), 42, 56.5 (both SCH), 99.5, and 171 (both NCH); δ (other major isomer) −27, −14, −10.5, −3.5 (all CMe), 57, 87.5, 197, 198 (all SCH; assignment of last two uncertain), 58.5, 86, 127, 152 (all NCH); δ (minor isomer) (CMe not observed), 35, 49, 69, 121 (all NCH), 96.5, 179.5, 184.5 (all SCH); $\lambda_{max.}$ (in chloroform), broad, composite absorption centred at 530 nm (ε 16 dm^3 mol^{-1} cm^{-1}), intense end absorption extending into cut-off region of solvent, shoulder at 295 nm (ε 390 dm^3 mol^{-1} cm^{-1}). Conductivity measurements were attempted in methanol but the compound decomposed. $[CoLBr_2]$ was prepared, in the manner described above for the chloride, from cobalt(II) bromide hexahydrate (16.3 mg) and L (18.7 mg). The initial precipitate (26.4 mg, *ca.* 90% yield) consisted of crystals suitable for *X*-ray analysis. This complex is considerably less soluble than $[CoLCl_2]$ in all solvents tried. Various attempts to produce cobalt(III) complexes of L failed to yield isolable products. These included (*i*) bubbling air through solutions containing cobalt(II) acetate and L in ethanol [or cobalt(II) perchlorate, L, and lithium chloride in nitromethane or acetone]; (*ii*) addition of a bromine solution (0.5 mol equiv.) to $[CoLBr_2]$, of $KHSO_5$ to $[CoLCl_2]$, of sodium hypochlorite to a solution containing cobalt(II) perchlorate and L.

Complex of Nickel(II) *Chloride with* L.—A solution of nickel(II) chloride hexahydrate (12.9 mg) in absolute ethanol was added to a solution of L (19.5 mg) in dichloromethane. The solvent was evaporated *in vacuo* and the residue crystallised twice from absolute ethanol to give blue crystals of $[NiLCl_2]$ (Found: C, 47.45; H, 8.45; N, 5.5. $C_{20}H_{42}Cl_2N_2NiS_2$ requires C, 47.6; H, 8.4; N, 5.5%); $\lambda_{max.}$ (in ethanol) at 650 (ε 16), 398 (ε 30), 288 (ε 7 000), and 230 nm (ε 4 500 dm^3 mol^{-1} cm^{-1}).

Complexes of Copper(II) *and Copper*(I) *with* L.—Copper(II) chloride dihydrate (17 mg) and L (37.5 mg) were heated together in refluxing ethanol for 5 min. On cooling a small amount of a very dark precipitate was deposited and was filtered off. The solvent was then evaporated and the residue subjected to preparative t.l.c. (dichloromethane–methanol, 9:1). The material (39 mg) recovered from the only green band crystallised from dichloromethane–toluene and gave crystals of $[CuLCl_2]$ which were suitable for *X*-ray analysis; $\lambda_{max.}$ (in ethanol) at 720 (ε 385), 390 (ε 5 510), 325 (ε 4 150), and 251 nm (ε 2 030 dm^3 mol^{-1} cm^{-1}). An aqueous solution of copper(II) tetrafluoroborate (1.0 cm^3, 0.10 mol dm^{-3}) was evaporated and the resulting solid stirred with a solution of L (37.5 mg) in ethanol. A dark blue solution was produced rapidly. The solvent was then evaporated and the residue crystallised from methanol to give well formed blue crystals of $[CuL][BF_4]_2$ which were, however, unsuitable (composed of sheets) for *X*-ray work. This material had $\lambda_{max.}$ (in ethanol) at 620 (ε 300), 387 (ε 5 000), 320 (ε 3 000), and 230 nm (ε 1 400 dm^3 mol^{-1} cm^{-1}) and (in trifluoroethanol) at 690 (very broad band, ε 300) and 378 nm (ε 4 000 dm^3 mol^{-1} cm^{-1}). A solution of $[CuL][BF_4]_2$ (30.6 mg) in CD_3CN was heated with fine copper ribbon (31.8 mg) until the dark blue solution became colourless (30 min). The solution was then filtered and its ^1H n.m.r. spectrum recorded (Table 2) at −35 °C. The solution gradually turned green on standing and the spectrum broadened.

Complexes of Silver(I) *with* L.—A solution of silver nitrate (34 mg) in ethanol was added dropwise to a solution of L (75 mg) in ethanol–diethyl ether (1:1) at ambient temperature. The clear solution was evaporated and the residue crystallised from acetone to give colourless plates (decomp. 220 °C) of $[AgL(NO_3)]$ (Found: C, 44.2; H, 7.7; N, 7.65. $C_{20}H_{42}AgN_3$-

Table 4. Crystallographic data

Complex	$[CoLCl_2]$	$[CoLBr_2]$	$[RhLCl_2]PF_6$	$[CuLCl_2]\cdot0.5C_7H_8$
M	504.5	593.4	693.5	555.2
Space group	$P2_1/c$	$P2_1/c$	$P\bar{1}$	$P\bar{1}$
a/Å	8.377(3)	8.360(2)	11.741(4)	12.828(6)
b/Å	10.355(5)	10.475(3)	12.418(12)	21.963(4)
c/Å	14.247(4)	14.419(4)	10.639(6)	10.872(3)
α/°			89.91(6)	93.15(2)
β/°	92.58(3)	93.07(2)	110.95(3)	109.35(2)
γ/°			88.35(5)	82.32(2)
U/Å^3	1 231.3	1 260.9	1 447.9	2 863.9
Z	2	2	2	4
D_c/g cm^{-3}	1.36	1.56	1.59	1.29
$F(000)$	538	610	712	1 184
μ(Mo-K_α)/cm^{-1}	10.2	39.9	10.1	11.3
$2\theta_{max}$/°	54	40	44	40
Unique reflections	3 583	1 162	3 546	5 227
$I > 3\sigma(I)$	2 498	716	2 585	3 514
R	0.045	0.049	0.060	0.102
R'	0.050	0.044	0.052	0.110

Table 5. Final fractional co-ordinates (× 10^5 for Cl, S; × 10^4 for others) for $[CoLCl_2]$ with estimated standard deviations in parentheses

Atom	x	y	z	Atom	x	y	z
Co	0	0	0	C(4)	2 952(5)	−728(5)	2 785(3)
Cl	−16 718(10)	2 401(9)	13 408(5)	C(5)	4 248(5)	−2 402(4)	1 816(3)
S	8 017(9)	−22 452(8)	4 183(5)	C(6)	1 094(4)	3 085(3)	−506(2)
N	2 111(3)	663(2)	902(2)	C(7)	2 097(4)	3 074(3)	418(2)
C(1)	3 331(4)	−400(3)	1 066(2)	C(8)	3 018(4)	1 798(3)	546(2)
C(2)	2 922(4)	−1 390(3)	1 818(2)	C(9)	3 346(5)	4 133(4)	306(2)
C(3)	1 295(4)	−2 025(3)	1 658(2)	C(10)	1 158(5)	3 370(4)	1 276(3)

Table 6. Final fractional co-ordinates (× 10^4) for $[CoLBr_2]$ with estimated standard deviations in parentheses

Atom	x	y	z	Atom	x	y	z
Co	0	0	0	C(4)	3 035(21)	−716(16)	2 764(10)
Br	−1 835(2)	311(2)	1 393(1)	C(5)	4 254(18)	−2 367(15)	1 777(11)
S*	813(5)	−2 187(4)	441(3)	C(6)	−1 083(18)	−3 035(13)	513(10)
N*	2 083(12)	710(8)	914(7)	C(7)	−2 065(16)	−3 062(12)	−401(9)
C(1)	3 333(15)	−370(13)	1 075(8)	C(8)	3 026(16)	1 831(13)	546(10)
C(2)	2 948(17)	−1 329(13)	1 818(9)	C(9)	−3 307(21)	−4 112(14)	−270(12)
C(3)	1 280(18)	−1 976(13)	1 665(9)	C(10)	−1 094(20)	−3 385(15)	1 214(11)

* Atoms S and N are mutually disordered. In the final rounds of anisotropic refinement atom S had an occupancy 0.95(S) and atom N had occupancy 0.49(S), which is in accord with the disordered N–S system and an electron total of 23.

O_3S_2 requires C, 44.1; H, 7.8; N, 7.7%); its ^{13}C and ^1H n.m.r. spectra at 400 MHz were obtained in deuteriochloroform (the latter at −50 °C; Tables 2 and 3, Figure 5). A solution of silver(I) acetate (20.2 mg) and L (45.4 mg) in acetonitrile was heated at 60 °C for 1 h. A very thin pale yellow film formed. The solution was filtered and the solvent removed *in vacuo* to yield a colourless solid (62 mg) which, upon crystallisation from acetone, gave crystals suitable for *X*-ray analysis;[29] the ^1H n.m.r. spectrum of this complex at 400 MHz was virtually identical to that of $[AgL(NO_3)]$ (except that cooling to −65 °C was required to obtain the limiting spectrum).

Complexes of Cadmium(II), *Zinc*(II), *and Mercury*(II) *with* L.—A mixture of cadmium(II) chloride tetrahydrate (6.5 mg) and L (20.0 mg) was dissolved in warm ethanol and then this solvent was removed *in vacuo*. A ^1H n.m.r. spectrum of the colourless residue showed the presence of complexed and free ligand. This material was then treated with a further amount (6.5 mg) of the tetrahydrate as before. The product crystallised from ethanol–chloroform as small colourless crystals (20.2 mg; decomp. 200 °C) of $[CdLCl_2]$ (Found: C, 42.95; H, 7.55; N, 5.0. $C_{20}H_{42}CdCl_2N_2S_2$ requires C, 43.05; H, 7.6; N, 5.0%); ^{13}C and ^1H n.m.r. spectra (latter at −10 °C) were recorded (Tables 2 and 3). Solubility problems frustrated attempts to obtain conductivity data (values obtained in dichloromethane showed very little conductance). The complex $[CdLBr_2]$ was obtained in a similar fashion from cadmium(II) bromide tetrahydrate (17.5 mg) and L (20.0 mg). This complex was quite insoluble in all solvents tested. $[ZnLCl_2]$ was also obtained in this way from zinc(II) chloride (7.0 mg) and L (20.0 mg); ^{13}C and ^1H n.m.r. spectra (latter at −10 °C) were recorded (Tables 2 and 3). Solutions of this complex turned yellow, and the complex decomposed when attempts were made to crystallise it. $[HgLCl_2]$ was prepared in the same way from mercury(II) chloride (13.5 mg) and L (20.0 mg); ^{13}C and ^1H n.m.r. spectra (latter at −20 °C) were recorded (Tables 2 and 3). Attempts at crystallisation resulted in decomposition.

Crystal Structure Analyses.—Complete details of the four crystal structure analyses are summarized in Table 4. Accurate cell parameters were obtained by a least-squares refinement of the setting angles of 25 reflections with 10 < θ < 15° measured

Table 7. Final fractional co-ordinates (× 10^4) for $[RhLCl_2]PF_6$ with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Rh(1)	0	0	0	C(21)	2 299(13)	−4 907(15)	−5 990(14)
Rh(2)	0	5 000	5 000	C(22)	−1 603(10)	−5 291(8)	−2 625(10)
Cl(1)	898(3)	1 615(2)	−153(3)	C(23)	493(10)	6 013(8)	2 446(11)
Cl(2)	547(3)	−3 253(2)	−4 393(3)	C(24)	−2 365(17)	−5 818(14)	−2 047(21)
S(1)	1 841(3)	−833(2)	1 379(3)	C(25)	−1 247(15)	−4 276(14)	−1 923(16)
N(1)	−416(8)	543(7)	1 692(7)	C(26)	−1 694(12)	6 411(10)	2 443(12)
C(11)	634(10)	934(8)	2 903(10)	C(27)	−2 871(10)	6 055(9)	2 458(11)
C(12)	1 622(9)	118(8)	3 635(9)	C(28)	−2 845(12)	5 350(15)	3 522(15)
C(13)	2 496(10)	−77(10)	2 888(10)	C(29)	−3 563(18)	5 532(17)	1 237(18)
C(14)	2 375(12)	623(10)	4 958(10)	C(210)	−3 629(16)	7 042(15)	2 458(24)
C(15)	1 098(11)	−909(9)	3 892(11)	P(1)	4 960(3)	2 523(3)	3 643(4)
C(16)	2 902(11)	−505(11)	589(11)	F(1)	3 604(7)	2 498(7)	3 502(11)
C(17)	2 673(11)	−1 095(10)	−700(11)	F(2)	6 283(7)	2 564(7)	3 739(11)
C(18)	1 368(14)	−1 334(13)	−1 375(12)	F(3)	4 951(8)	3 674(7)	4 018(13)
C(19)	3 112(18)	−476(14)	−1 597(15)	F(4)	4 997(9)	1 358(7)	3 406(15)
C(110)	3 355(16)	−2 163(14)	−419(16)	F(5)	5 378(10)	2 219(10)	5 084(9)
S*	9 340(4)	5 349(3)	2 720(4)	F(6)	4 528(11)	2 807(15)	2 244(11)
N*	−8 159(4)	−5 599(4)	−4 983(4)				

* Atoms S and N are mutually disordered. In the final rounds of anisotropic refinement atom S had an occupancy 0.76(S) and atom N had occupancy 0.68(S).

Table 8. Final fractional co-ordinates (× 10^4) for $[CuLCl_2]{\cdot}0.5C_7H_8$ with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Cu(1)	1 260(2)	1 536(1)	2 780(3)	Cl(22)	7 008(4)	7 508(2)	1 427(5)
S(11)[a]	338(4)	2 527(3)	3 045(5)	N(21)	4 207(10)	7 726(6)	69(12)
S(12)[a]	2 259(5)	556(3)	2 563(5)	N(22)	6 137(11)	6 066(6)	1 374(13)
Cl(11)	3 168(4)	1 957(2)	3 729(4)	C(21)	4 982(16)	7 900(8)	2 910(17)
Cl(12)	−888(4)	1 036(2)	1 681(5)	C(22)	3 881(14)	8 254(8)	2 105(18)
N(11)[a]	1 127(9)	1 212(5)	4 651(9)	C(23)	3 387(15)	7 906(8)	743(17)
N(12)[a]	945(9)	1 760(4)	674(11)	C(24)	2 969(17)	8 320(10)	2 791(19)
C(11)	−592(12)	2 317(7)	3 800(15)	C(25)	4 142(18)	8 893(10)	1 867(22)
C(12)	115(12)	2 222(8)	5 295(16)	C(26)	3 597(14)	7 747(8)	−1 373(16)
C(13)	1 293(12)	1 863(7)	5 521(16)	C(27)	4 385(12)	7 878(8)	−2 166(16)
C(14)	303(17)	2 850(9)	5 951(20)	C(28)	5 495(14)	7 441(7)	−1 785(16)
C(15)	−605(14)	1 858(11)	5 840(16)	C(29)	3 685(16)	7 790(10)	−3 641(16)
C(16)	2 414(13)	853(8)	5 331(15)	C(210)	4 653(14)	8 547(8)	−1 927(18)
C(17)	2 331(20)	190(10)	4 871(23)	C(211)	6 702(13)	6 332(7)	−925(17)
C(18)	1 687(15)	109(8)	3 391(19)	C(212)	6 794(15)	5 650(8)	−512(18)
C(19)	3 549(21)	−130(11)	5 216(25)	C(213)	6 003(15)	5 572(8)	291(18)
C(110)	1 553(26)	−131(13)	5 515(26)	C(214)	6 374(17)	5 247(9)	−1 729(19)
C(111)	1 473(14)	384(7)	924(15)	C(215)	8 008(15)	5 427(9)	246(20)
C(112)	1 856(13)	729(8)	−16(15)	C(216)	5 941(15)	5 814(8)	2 480(18)
C(113)	2 031(12)	1 398(7)	423(15)	C(217)	6 482(15)	6 100(10)	3 813(19)
C(114)	2 943(21)	406(9)	−121(24)	C(218)	6 322(14)	6 835(8)	3 823(18)
C(115)	831(20)	722(10)	−1 407(19)	C(219)	6 009(20)	5 849(11)	4 781(20)
C(116)	1 144(11)	2 468(7)	783(16)	C(220)	7 795(17)	5 952(9)	4 358(22)
C(117)	4(16)	2 846(9)	594(19)	C(1)	8 989(14)	4 359(8)	5 442(29)
C(118)	−660(11)	2 620(8)	1 457(14)	C(2)	8 389(14)	4 214(8)	4 159(29)
C(119)	245(19)	3 524(9)	994(31)	C(3)	7 374(14)	3 982(8)	3 879(29)
C(120)	−789(16)	2 752(12)	−870(19)	C(4)	6 958(14)	3 895(8)	4 882(29)
Cu(2)	5 028(2)	6 862(1)	666(2)	C(5)	7 558(14)	4 040(8)	6 165(29)
S(21)	4 884(4)	7 080(2)	2 789(5)	C(6)	8 573(14)	4 272(8)	6 445(29)
S(22)	5 274(4)	6 686(2)	−1 432(4)	C(7)[b]	8 809(32)	4 267(18)	3 381(40)
Cl(21)	3 305(3)	6 302(2)	−32(5)	C(7′)[b]	9 212(53)	4 441(28)	7 391(64)

[a] Atoms S(11), N(11), and S(12), N(12) are mutually disordered. In the final cycles of refinement, S(11) and S(12) had occupancies 0.82(S) and N(11) and N(12) 0.62(S). [b] The toluene of solvation is disordered over two sites: C(7) and C(7′) appear as *para*-methyl groups and were included with 0.5 occupancy.

on a CAD4 diffractometer. All data sets were corrected for Lorentz and polarization effects. The structures were solved by the heavy-atom method and refined by full-matrix[32] and block-diagonal[33] least-squares calculations. Hydrogen atoms were allowed for, where appropriate, in geometrically idealized positions. Final difference maps at the conclusion of the refinements showed no chemically significant maxima.

Crystals of $[CoLCl_2]$ and $[CoLBr_2]$ are isomorphous, and the molecules have inversion symmetry, with the Co atoms occupying the inversion site. The $[CoLBr_2]$ structure also has the S and N atoms mutually disordered and this was allowed for by appropriate scattering factor curves.

In the structure of $[RhLCl_2]PF_6$, there are two independent centrosymmetric half-cations and one PF_6 anion in the

Table 9. Bond angles (°) at the metal atoms[a] in [CoLCl$_2$], [CoLBr$_2$], and [RhLCl$_2$]PF$_6$ with estimated standard deviations in parentheses

			[RhLCl$_2$]PF$_6$	
Angle[b]	[CoLCl$_2$]	[CoLBr$_2$]	Molecule 1	Molecule 2
X–M–S	93.8(1)	94.8(1)	93.8(1)	85.3(2)
X–M–N	89.4(1)	88.7(3)	91.9(3)	96.6(2)
S–M–N	87.2(1)	87.8(2)	92.2(2)	88.8(2)

[a] In these molecules the metal atoms lie on crystallographic inversion centres.[b] X = Cl or Br, M = Co or Rh.

Table 10. Bond angles (°) at Cu in [CuLCl$_2$]·0.5C$_7$H$_8$ with estimated standard deviations in parentheses

	Molecule 1	Molecule 2
S(1)–Cu–S(2)	176.6(2)	176.1(2)
S(1)–Cu–Cl(1)	89.9(2)	92.2(2)
S(1)–Cu–Cl(2)	91.2(2)	88.7(2)
S(1)–Cu–N(1)	91.2(3)	89.7(4)
S(1)–Cu–N(2)	88.9(3)	90.3(4)
S(2)–Cu–Cl(1)	87.7(2)	91.7(2)
S(2)–Cu–Cl(2)	91.2(2)	87.4(2)
S(2)–Cu–N(1)	88.8(3)	89.4(4)
S(2)–Cu–N(2)	91.7(3)	89.9(4)
Cl(1)–Cu–Cl(2)	178.8(2)	179.1(2)
Cl(1)–Cu–N(1)	98.6(3)	96.6(4)
Cl(1)–Cu–N(2)	96.9(3)	94.2(4)
Cl(2)–Cu–N(1)	81.6(3)	83.1(4)
Cl(2)–Cu–N(2)	82.8(3)	86.0(4)
N(1)–Cu–N(2)	164.4(4)	169.2(5)

asymmetric unit. One of the cations has the S and N atoms mutually disordered, as found for [CoLBr$_2$].

In the structure of [CuLCl$_2$] one of the cations has the S and N atoms disordered. A toluene molecule of solvation (with the CH$_3$ group disordered over two sites) is also present. The crystals did not diffract well and no allowance was made for H-atom contributions in the calculations.

In the refinement cycles, weights were based on counting statistics. Scattering factors used in the structure factor calculations, for the above four structures, were taken from refs. 34 and 35 and allowance was made for anomalous dispersion.[36] The final fractional co-ordinates and standard deviations for [CoLCl$_2$], [CoLBr$_2$], [RhLCl$_2$]PF$_6$, and [CuLCl$_2$]·0.5C$_7$H$_8$ are in Tables 5—8. Selected bond lengths are in Table 1. Selected bond angles for [CoLCl$_2$], [CoLBr$_2$], and [RhLCl$_2$]PF$_6$ are in Table 9. Selected bond angles for [CuLCl$_2$]·0.5C$_7$H$_8$ are in Table 10.

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