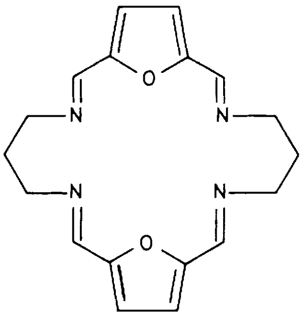
# Dicobalt(II) Complexes of a Macrocyclic Ligand containing Hydroxo-, Alkoxo-, Phenoxo-, Thiolato-, Halogeno-, and Pseudohalogeno-bridges: Structures and Magnetic Exchange Interactions †

**Michael G. B. Drew** *
*Department of Chemistry, The University, Reading RG6 2AD*
**Ferida S. Esho, Aidan Lavery, and S. Martin Nelson** *
*Department of Chemistry, Queen's University, Belfast BT5 5AG*

Two families of dicobalt(II) complex of a binucleating macrocyclic ligand (L), $C_{18}H_{20}N_4O_2$, derived from a cyclic [2 + 2] condensation of 2,5-diformylfuran with 1,3-diaminopropane, have been synthesised and characterised by analytical, spectroscopic, magnetic, and *X*-ray diffraction methods. They differ in the co-ordination geometry of the cobalt(II) ions (tetrahedral or trigonal bipyramidal) but are alike in that the metal ions are intramolecularly linked *via* two bridging ligands which may be the same or different. The co-ordination number of the metal ions is determined by the nature of the bridging groups which include $OH^-$, $OMe^-$, $OEt^-$, $OPr^{n-}$, $OPr^{i-}$, $OBu^{t-}$, $OPh^-$, $SEt^-$, $SPh^-$, $Cl^-$, $Br^-$, 1,1-$N_3^-$, and nitrogen atom-only $NCS^-$ and $NCSe^-$. Crystals of $[Co_2L(OEt)(NCS)_3]$ (1) are monoclinic with $a = 9.03(1)$, $b = 10.73(1)$, $c = 14.64(1)$ Å, $\beta = 99.0(1)°$, $Z = 2$, and space group $P2_1/c$. Crystals of $[Co_2L(OMe)(N_3)_3]$ (2) are monoclinic with $a = 8.381(7)$, $b = 10.09(1)$, $c = 14.185(11)$ Å, $\beta = 96.1(1)°$, $Z = 2$, and space group $P2_1/n$. For (1) and (2), 692 and 700 reflections above background were measured by diffractometer and refined by Fourier methods to $R$ 0.099 and 0.115, respectively. In both structures each cobalt(II) ion has a distorted trigonal-bipyramidal environment, being bonded to two nitrogen atoms of the macrocycle and a disordered N/O bridge atom in the equatorial plane. The two axial sites are occupied by a nitrogen atom of a terminal anion [$NCS^-$ in (1), $N_3^-$ in (2)] and the other disordered N/O bridge atom. The Co · · · Co separations are 3.119(6) and 3.195(6) Å, respectively. The structures are compared to those of other metal complexes of the same macrocycle. The magnetic moments of the five-co-ordinate complexes show little dependence on temperature although a small ferromagnetic interaction is apparent for the μ-azido-μ-methoxo-complex. All the tetrahedral complexes exhibit antiferromagnetic superexchange, the coupling constants $J$ (in $\hat{H} = -2J\hat{S}_1\hat{S}_2$) ranging from $-5.5$ cm$^{-1}$ for the di-μ-bromo-complex to $-90.5$ cm$^{-1}$ for the di-μ-thiophenolato-complex.

The synthesis of di- and poly-nuclear complexes in which the ligand maintains the metal centres in close proximity is an important current objective in transition-metal and bioinorganic chemistry.[1-4] Such systems allow the study of magnetic interactions [2,4,5] between the metal centres and they may also serve as models for metalloproteins containing di- or poly-nuclear active sites.[6] In many binuclear complexes the metal ions are permanently linked *via* bridging atoms or groups which are part of the organic ligand structures.[7-9] In others, lacking such fixed bridges, the metal ions, if co-ordinatively unsaturated, may bind small substrate molecules or ions between them.[2,4] Inclusion complexes of this kind are of particular interest because they permit a study of magnetic superexchange interactions as a function of the nature of the bridging substrate as well as of the nature of the metal ion and the structure of the binuclear unit. The most studied systems have been those containing two magnetically interacting copper(II) ions.[2,4,10,11] The interest here relates in large measure to the occurrence of the dicopper unit in Type 3 copper proteins.[10] By comparison, dicobalt(II) complexes [12-18] have received much less attention.

In the present paper we report the synthesis, properties, and structural characterisation of a series of dicobalt(II) complexes of the macrocycle L having a 20-membered inner large ring.



L

Earlier studies [19-21] on dicopper complexes have shown that this macrocycle is well adapted to the complexation of two transition-metal ions each bound to the macrocycle *via* two imino-nitrogen donor atoms and separated by about 3 Å. The metal ions are therefore well placed for the intramolecular binding of small bridging substrate molecules or ions particularly those presenting a single-atom bridge. The dicobalt(II) complexes described here vary in the co-ordination geometry about the metal ions (trigonal bipyramidal and tetrahedral), and in the nature of the bridging ligands which include $OH^-$, $OR^-$ (R = Me, Et, $Pr^n$, $Pr^i$, $Bu^t$, or Ph), $SR^-$ (R = Et or Ph), $Cl^-$, $Br^-$, $N_3^-$, $NCS^-$, and $NCSe^-$.

## Results and Discussion

*Synthesis of the Dicobalt*(II) *Complexes*.—The macrocycle L was synthesised as the barium(II) complex $BaL(ClO_4)_2{\cdot}EtOH$

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† *Supplementary data available* (No. SUP 23824, 13 pp.): thermal parameters, H-atom co-ordinates, structure factors. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1984, Issue 1, pp. xvii—xix.

*Non-S.I. units employed:* B.M. ≈ $9.27 \times 10^{-24}$ A m$^2$; mmHg ≈ 134 Pa; $\chi_{c.g.s.u.} = \chi_{S.I.} \times 10^6/4\pi$.

**Table 1.** Analytical, magnetic, and electrical conductance data for the dicobalt(II) complexes

| | | Analysis (%) | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | Found | | | Calc. | | | $\mu_{eff.}$ [a]/B.M. | | $\Lambda$ [b]/ S cm$^2$ mol$^{-1}$ |
| Complex | Colour | C | H | N | C | H | N | 293 K | 93 K | |
| $[Co_2LCl_2]Cl_2{\cdot}2H_2O$ | Blue | 34.8 | 3.9 | 8.9 | 34.9 | 3.9 | 9.0 | 4.46 | 3.80 | 248 |
| $[Co_2LBr_2]Br_2{\cdot}H_2O$ | Blue | 27.7 | 2.8 | 6.9 | 27.7 | 2.8 | 7.1 | 4.48 | 3.99 | 240 |
| $[Co_2L(OMe)(NCS)_3]$ | Red-brown | 40.6 | 3.6 | 15.0 | 40.8 | 3.6 | 15.1 | 5.10 | 4.88 | 101 |
| $[Co_2L(OEt)(NCS)_3]$ | Red-brown | 41.8 | 3.8 | 14.7 | 41.8 | 3.8 | 14.8 | 4.72 | 4.67 | 115 |
| $[Co_2L(OEt)(NCSe)_3]$ | Red-brown | 34.5 | 3.2 | 12.0 | 34.4 | 3.1 | 12.2 | 5.10 | 5.04 | 120 |
| $[Co_2L(OMe)(N_3)_3]$ | Red-brown | 38.1 | 3.9 | 30.4 | 38.1 | 3.9 | 30.4 | 5.11 | 5.31 | — |
| $[Co_2L(OH)_2][BPh_4]_2$ | Blue | 70.8 | 5.6 | 5.0 | 71.1 | 5.8 | 4.9 | 4.18 | 3.15 | 262 |
| $[Co_2L(OEt)_2][BPh_4]_2$ | Blue | 72.4 | 6.0 | 4.9 | 71.8 | 6.0 | 4.8 | 4.13 | 3.06 | 288 |
| $[Co_2L(OPr^n)_2][BPh_4]_2$ | Blue | 70.8 | 5.9 | 4.8 | 72.1 | 6.2 | 4.7 | 4.13 | 3.30 | 261 |
| $[Co_2L(OPr^i)_2][BPh_4]_2$ | Blue | 69.4 | 6.1 | 4.7 | 72.1 | 6.2 | 4.7 | 4.10 | 2.92 | |
| $[Co_2L(OBu^t)_2][BPh_4]_2$ | Blue | 72.4 | 6.5 | 4.5 | 72.4 | 6.4 | 4.6 | 4.07 | 2.88 | 260 |
| $[Co_2L(OH)_2(H_2O)_2][ClO_4]_2$ | Pink | 30.2 | 3.7 | 7.9 | 30.4 | 3.6 | 7.6 | 4.53 | 4.34 | 338 |
| $[Co_2L(OPh)_2(MeCN)_2][BPh_4]_2$ | Pink | 72.6 | 5.8 | 6.3 | 73.0 | 5.7 | 6.2 | 4.69 | 4.65 | 229 |
| $[Co_2L(SEt)_2][ClO_4]_2$ | Dark green | 34.8 | 4.0 | 7.4 | 34.6 | 4.0 | 7.3 | 3.20 | 2.12 | 282 |
| $[Co_2L(SPh)_2][ClO_4]_2$ | Dark green | 41.9 | 3.4 | 6.5 | 41.9 | 3.5 | 6.5 | 2.20 | 1.18 | 262 |

[a] Corrected for diamagnetism of ligands. [b] $10^{-3}$ mol dm$^{-3}$ in MeCN at 20 °C.

in *ca.* 60% yield *via* a $Ba^{2+}$ ion template method from 2,5-diformylfuran and 1,3-diaminopropane. The occurrence of the cyclic [2 + 2] Schiff-base condensation in the template synthesis has already been established [22] by means of the spectroscopic (i.r., $^1H$ n.m.r.) properties of this complex and by an *X*-ray structure determination of the derivative $[BaL_2(H_2O)_2][Co(NCS)_4]$ which contains two molecules of macrocyclic ligand per $Ba^{2+}$ ion. It was found that when solutions of $BaL(ClO_4)_2{\cdot}EtOH$ were treated with an excess of a cobalt(II) salt the single $Ba^{2+}$ ion in the precursor complex could be replaced by two cobalt(II) ions. By use of different cobalt(II) salts, different precipitating anions, different solvents, and different added substrates, a series of dicobalt(II) complexes all containing two bridging anionic ligands between the metal centres were prepared. Preparative details are given in the Experimental section.

*Characterisation of the Complexes.*—The complexes studied are listed in Table 1 along with analytical and selected physical data pertaining to them. The crystalline complexes may be divided into two groups on the basis of colour and other properties. One group of complexes are intense blue or green while the second group are mauve or pink. It will be shown that the former complexes contain tetrahedrally co-ordinated $Co^{II}$ while the latter contain five-co-ordinate $Co^{II}$. For the most part the complexes have low to moderate solubility in polar organic solvents, frequently with colour change (see below).

*Infrared spectra.* A common feature in the i.r. spectra of all the complexes was a strong band at *ca.* 1 625 cm$^{-1}$ attributable to the ν(C=N) stretching vibration. No absorption at *ca.* 1 700 cm$^{-1}$ characteristic of ν(C=O) was apparent in any of the spectra. The presence of $H_2O$ or of co-ordinated MeCN indicated by the analytical data was confirmed by absorption at 3 300—3 500 cm$^{-1}$ or by a low-intensity doublet between 2 260 and 2 300 cm$^{-1}$. The complexes formulated as containing bridging $OH^-$ exhibited a fairly sharp ν(OH) absorption at 3 500—3 600 cm$^{-1}$.

Early in the investigation it was noticed that the colours and properties of some of the alkoxo-bridged complexes were dependent on the conditions of the preparation and isolation. As described in the Experimental section, the $[Co_2L(OR)_2][BPh_4]_2$ complexes were obtained by replacement of $Ba^{2+}$ in $BaL(ClO_4)_2{\cdot}EtOH$ by two cobalt(II) ions in a dry ROH–MeCN (2 : 1) solvent mixture. For the cases of R = Et, $Pr^i$, and $Bu^t$ the products separated as stable blue-green microcrystalline powders. For R = Me or $Pr^n$, on the other hand, the products were red or pink crystalline solids. On exposure to the atmosphere the latter complexes changed colour to blue solids within a period of a few minutes. Infrared spectra, run as hexachlorobutadiene mulls, taken at intervals during the colour transformation established that the colour change was accompanied by three changing features in the i.r. spectra. For both complexes the doublet at 2 262 and 2 292 cm$^{-1}$ assigned to co-ordinated MeCN diminished in intensity while a fairly sharp band at *ca.* 3 540 cm$^{-1}$ grew in intensity. In addition, a band of weak to moderate intensity at 2 790 cm$^{-1}$ (R = Me) or 2 840 cm$^{-1}$ (R = $Pr^n$), assigned to the symmetric ν(C–H) stretch of the α-$CH_3$ (or $CH_2$) group of the alkoxide, also diminished with time paralleling the growth of the ν(OH) absorption. We attribute these spectral changes to loss of MeCN from the five-co-ordinate cobalt(II) ion in red $[Co_2L(OR)_2(MeCN)_2][BPh_4]_2$ with accompanying exchange of $OR^-$ by $OH^-$ in moist air. Proof of this formulation for the initially isolated red crystals is lacking because they were insufficiently stable for analysis. However, it corresponds to that of the stable complex $[Co_2L(OPh)_2(MeCN)_2][BPh_4]_2$ (see below). When the initially formed red complexes were protected from the atmosphere and the co-ordinated MeCN removed by evacuation at low pressure, the product for R = $Pr^n$ was blue-green rather than blue, although still blue for R = Me. Infrared spectra of the blue-green material showed the presence of the $OPr^n$ group and absence of OH. Attempts to isolate $[Co_2L(OMe)_2][BPh_4]_2$ in a pure form were not wholly successful. It is interesting that $[Co_2L(OPr^n)_2][BPh_4]_2$ prepared in this way appeared less susceptible to exchange of $OR^-$ by $OH^-$ in moist air. The implication is that the five-co-ordinate complex may exchange co-ordinated MeCN for co-ordinated $H_2O$ before reorganisation to a tetrahedral structure with, presumably, loss of ROH. In the spectra of the perchlorate complexes the asymmetric O–Cl–O stretching and bending modes appeared as unsplit bands at *ca.* 1 090 and *ca.* 625 cm$^{-1}$, respectively, in agreement with their formulation as perchlorate salts. All the diperchlorate and bis(tetraphenylborate) complexes are 1 : 2 electrolytes in MeCN.

In the i.r. spectra of the pseudohalide complexes $[Co_2L(OR)X_3]$ (X = NCS, NCSe, or $N_3$) the asymmetric stretch of the $NCS^-$, $NCSe^-$, and $N_3^-$ ions appeared as two strong

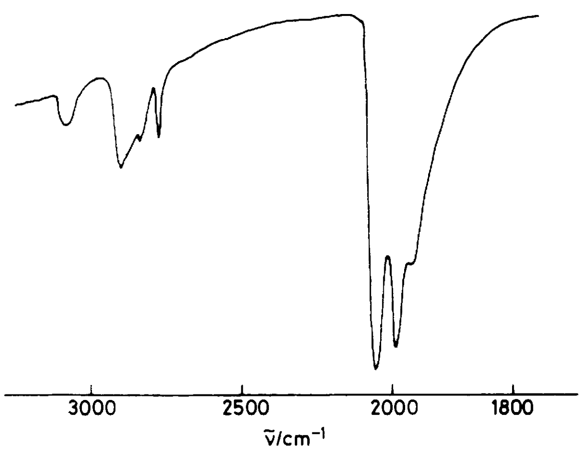
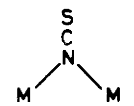


**Figure 1.** Part of the i.r. spectrum (KBr disc) of $[Co_2L(OMe)(NCS)_3]$ showing the asymmetric stretch of the nitrogen atom-only bridging $NCS^-$ group (1 995 $cm^{-1}$) and the symmetric (C–H) stretch of the bridging methoxo-group (2 785 $cm^{-1}$)

bands in the 1 950—2 100 $cm^{-1}$ region (Figure 1). For the thiocyanate and selenocyanate complexes the higher-energy band at *ca.* 2 070 $cm^{-1}$ is consistent with terminal N-bonding.[23] The lower-energy, somewhat less intense, band occurred at 1 995 $cm^{-1}$ with a shoulder (*ca.* 1 970 $cm^{-1}$) on the low-energy side. These low values for $\nu_{asym}$ of $NCS^-$ and $NCSe^-$ are most unusual. As will be shown below from the results of a single-crystal *X*-ray structure determination of $[Co_2L(OEt)(NCS)_3]$, they can be associated with a bridging co-ordination mode [structure (I)] which uses the nitrogen atom only. Two previous examples of nitrogen atom-only bridging thiocyanate have been reported for both of which $\nu_{asym}$ occurs at energies below 2 000 $cm^{-1}$. One is the mixed-valence dinuclear anion $[Re_2(NCS)_{10}]^{3-}$ in which the two metal atoms are bridged *via* the nitrogen atoms of two of the thiocyanate ions.[24] Nitrogen atom-only bridges also occur in the complex $[\{Cd_2(NCS)_4(btrz)_3\}_\infty]$ (btrz = 4-t-butyl-1,2,3-triazole) which consists of chains of cadmium(II) ions linked alternately by triazole and N(CS) bridges.[25,*] The complex $[Co_2L(OEt)(NCSe)_3]$ is the first example of nitrogen atom-only bridging of the selenocyanate ion. For the azido-complex $[Co_2L(OMe)(N_3)_3]$, $\nu_{asym}$ of the $N_3^-$ occurs as a doublet at 2 045 and 2 068 $cm^{-1}$. Again, the *X*-ray structure determination of this complex (see below) shows that two of the azide ions are terminally co-ordinated and one is bridging *via* a single nitrogen atom (μ-1,1 bridging mode). We are uncertain as to which i.r. band is to be associated with the bridging mode in this case. It is noteworthy that both the methoxide-bridged complexes showed a medium-intensity band at 2 785 $cm^{-1}$. As noted above, and previously,[26] we assign this to $\nu_{sym}$ (C–H) of the bridging methoxide group. For the ethoxide complexes $\nu_{sym}$(C–H) occurs at somewhat higher energy (*ca.* 2 840 $cm^{-1}$).[26]



(I)

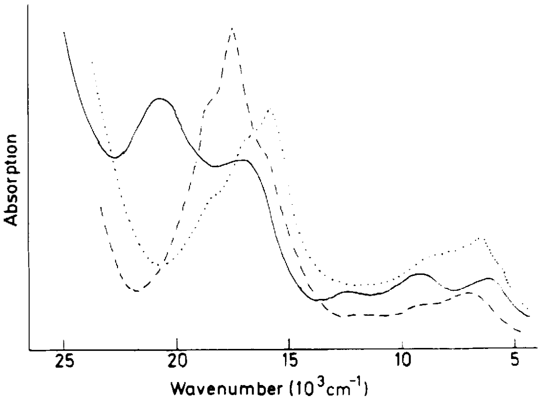


**Figure 2.** Electronic spectra of solid $[Co_2L(OH)_2(H_2O)_2][ClO_4]_2$ (——), solid $[Co_2L(OBu^t)_2][BPh_4]_2$ (· · ·), and $[Co_2L(OBu^t)_2][BPh_4]_2$ in MeCN (— — —)

*Electronic spectra.* Electronic spectra of the solid complexes and of their solutions in MeCN and $MeNO_2$ were recorded in in the range 25 000—5 000 $cm^{-1}$ (Table 2). The complexes may be divided into two classes on the basis of their solid-state spectra, and, indeed, of their colours. All of the blue, blue-green, and green complexes have spectra typical of tetrahedrally co-ordinated $Co^{II}$, consisting of a fairly intense multicomponent absorption centred around 16 000 $cm^{-1}$ and another less-intense region of absorption between 6 000 and 10 000 $cm^{-1}$.[27] The higher-energy absorption is assigned to the transition $^4A_2 \longrightarrow {}^4T_1(P)$ (in $T_d$ symmetry) split by spin–orbit coupling, while the lower-energy absorption is assigned to the transition $^4A_2 \longrightarrow {}^4T_1(F)$. The multicomponent nature of this band having an overall band width of 3 000—4 000 $cm^{-1}$ is a commonly noted feature of tetrahedral cobalt(II) complexes and is usually attributed to low-symmetry effects.[28] It should be noted that the complexes under discussion cannot have a symmetry higher than $C_{2v}$. The variations in colour (blue, blue-green, and green) among the tetrahedral hydroxo-, alkoxo- and thiolato-complexes are determined not so much by the energy of the visible $^4A_2 \longrightarrow {}^4T_1$ $(P)$ transition as by the energy of a more-intense absorption occurring between 20 000 and 30 000 $cm^{-1}$. This may be attributed to a bridging ligand-to-metal charge transfer, for which the energy varies in the order $OH^- > OR^- > SR^-$.

The spectra of the solid red or mauve complexes consist of strong broad absorption at 18 000—20 000 $cm^{-1}$ together with several low-intensity bands between 15 000 and 5 000 $cm^{-1}$. Distinctive differences between these spectra and those of the tetrahedral complexes (Figure 2) are the higher energy of the visible absorption and the presence of a band at 13 000—14 000 $cm^{-1}$. The spectra are, in fact, closely similar to those of authentic trigonal-bipyramidal cobalt(II) complexes.[29] As described below, confirmation of this geometry is provided by the *X*-ray structure determination of two members of the series.

The spectral behaviour of the complexes in MeCN solution was variable. For the chloride and bromide there was an excellent correspondence of the spectra in the two phases, so we may conclude that the complexes dissolve without alteration in structure. Both complexes are 1 : 2 electrolytes in MeCN so they may be formulated as halide salts of the dinuclear tetrahedral cations $[Co_2LX_2]^{2+}$.

For the four pseudohalide complexes $[Co_2L(OR)X_3]$ (R = Me or Et; X = NCS, NCSe, or $N_3$) there were marked spectral changes on dissolution in MeCN. While the solutions are violet in colour rather than blue, the spectra (Table 2 and

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[*] A related trinuclear nickel(II) complex containing nitrogen atom-only $NCS^-$ bridges has also been prepared recently (J. Reedijk, personal communication).

**Table 2.** Electronic spectra of the dicobalt(II) complexes

| Complex | State | Band positions ($cm^{-1} \times 10^3$), $\varepsilon$ ($dm^3\ mol^{-1}\ cm^{-1}$) in parentheses |
|---|---|---|
| $[Co_2LCl_2]Cl_2\cdot2H_2O$ | Solid | 18.5 (sh), 17.2, 15.8, 10.6, 7.5 |
| | $MeNO_2$ | 18.0 (sh), 17.0 (220), 15.8 (160), 10.2 (30), 7.4 (40) |
| | MeCN | 18.2 (sh), 17.2 (350), 15.4 (190), 10.8 (25), 7.3 (45) |
| $[Co_2LBr_2]Br_2\cdot H_2O$ | Solid | 18.4, 16.7, 14.3, 10.2, 7.2 |
| | $MeNO_2$ | 18.2 (200), 16.9 (370), 15.2 (210), 10.0 (10), 7.0 (41) |
| | MeCN | 18.2 (270), 16.8 (530), 14.6 (290), 10.4 (20), 7.1 (55) |
| $[Co_2L(OMe)(NCS)_3]$ | Solid | 20.2, 18.4, 16.2, 13.2, 10.4, 6.7 |
| | MeCN | 18.6 (sh), 17.4 (415), 16.3 (410), 10.6 (sh), 8.0 (80) |
| $[Co_2L(OEt)(NCS)_3]$ | Solid | 20.2, 18.4, 16.3, 13.3, 10.4, 6.7 |
| | MeCN | 18.4 (sh), 17.4 (440), 16.3 (410), 10.6 (sh), 8.0 (80) |
| $[Co_2L(OEt)(NCSe)_3]$ | Solid | 20.3, 18.1, 16.6, 13.1, 10.2, 6.8 |
| | MeCN | 18.6 (sh), 17.5 (270), 16.5 (sh), 10.4 (sh), 7.6 (70) |
| $[Co_2L(OMe)(N_3)_3]$ | Solid | 19.5, 17.0, 15.9, 12.5, 9.6, 6.2 |
| $[Co_2L(OH)_2][BPh_4]_2$ | Solid | 18.2 (sh), 17.0 (sh), 16.4, *ca.* 9.0 (sh), 6.6 |
| | $MeNO_2$ | 19.6 (sh), 17.2 (445), 16.4 (sh), 10.9 (sh), 9.6 (sh), 7.5 (94) |
| | MeCN | 19.2 (150), 17.6 (195), 16.6 (sh), *ca.* 10.2 (sh), 8.4 (sh), 7.6 (50) |
| $[Co_2L(OEt)_2][BPh_4]_2$ | Solid | 18.4 (sh), 17.2 (sh), 15.8, *ca.* 9.5 (sh), 8.2, 6.4 |
| | $MeNO_2$ | 18.8 (sh), 17.5 (414), 16.2 (sh), *ca.* 10.5 (sh), 8.2 (70) |
| | MeCN | 18.9 (sh), 17.6 (203), 16.2 (sh), *ca.* 9.6 (sh), 8.0 (30) |
| $[Co_2L(OPr^n)_2][BPh_4]_2$ | Solid | 18.4 (sh), 17.2 (sh), 16.2, 8.8 (sh), 7.4 |
| | $MeNO_2$ | 18.6 (sh), 17.2 (391), 16.3 (sh), 10.4 (sh), 7.9 (36) |
| | MeCN | 19.0 (sh), 17.8 (135), 16.6 (sh), 9.4 (sh), 8.2 (sh), 6.6 (38) |
| $[Co_2L(OPr^i)_2][BPh_4]_2$ | Solid | 18.6, 17.1, 15.8, *ca.* 8.9, 6.6 |
| | $MeNO_2$ | 18.4 (sh), 17.4 (280), 16.5 (sh), *ca.* 10.2 (sh), 8.2 (42), 6.2 (sh) |
| | MeCN | 19.2 (146), 17.7 (176), 16.6 (sh), 9.6 (20), 7.2 (25) |
| $[Co_2L(OBu^t)_2][BPh_4]_2$ | Solid | 18.6, 17.1, 15.8, *ca.* 8.9, 6.6 |
| | $MeNO_2$ | 18.6, 17.4 (425), 16.4 (sh), 10.4 (30), 7.8 (50) |
| | MeCN | 19.2 (165), 17.7 (210), 16.5 (sh), 9.4 (sh), 7.6 (43) |
| $[Co_2L(OH)_2(H_2O)_2][ClO_4]_2$ | Solid | 21.0, 17.7, 12.6, 9.4, 6.8 |
| | $MeNO_2$ | 18.6 (sh), 17.5 (460), 16.5 (sh), 10.4 (sh), 8.7 (sh), 7.5 (90) |
| | MeCN | 19.0 (sh), 17.6 (450), 16.6 (sh), 10.4 (sh), 8.4 (30), 7.3 (35) |
| $[Co_2L(OPh)_2(MeCN)_2][BPh_4]_2$ | Solid | 19.8, 19.0, 18.1, 14.0, 10.4, 6.4 |
| | MeCN | 19.9 (sh), 19.0 (sh), 18.0 (70), *ca.* 14.2, 10.2 (10), 6.3 (15) |
| $[Co_2L(SEt)_2][ClO_4]_2$ | Solid | 20.6, 16.8, 15.1, 9.8, 8.0, 6.8 |
| | $MeNO_2$ | 21.5 (sh), 17.3 (490), 16.6 (500), 15.5 (430), 10.2 (46), 8.4 (50), 6.6 (85) |
| | MeCN | 20.0 (sh), 16.3 (340), 15.0 (380), 10.0 (55), 8.2 (65), 6.6 (100) |
| $[Co_2L(SPh)_2][ClO_4]_2$ | Solid | 25.5 (sh), 20.0 (sh), 16.3 (sh), 15.0, 10.0, 8.0 (sh), 6.5 |
| | $MeNO_2$ | 20.2 (sh), 17.5 (sh), 16.0 (410), 14.9 (430), 10.2 (46), 8.4 (50), 6.2 (85) |
| | MeCN | 19.8 (sh), 16.7 (355), 15.0 (380), 9.8 (50), 5.6 (75) |

Figure 2) leave no doubt that the solution species contain tetrahedrally co-ordinated $Co^{II}$, although with the baricentres of the two absorption envelopes occurring at slightly higher energies than often found with tetrahedral cobalt(II) complexes. These solutions show 1 : 1 electrolyte behaviour in MeCN so presumably one of the two bridging ligands has dissociated. It is not possible, on the available evidence, to decide whether this is the alkoxo-bridge or the pseudohalide bridge.

The solution spectrum of the phenoxo-bridged complex $[Co_2L(OPh)_2(MeCN)_2][BPh_4]_2$ is closely similar to that of the solid. This shows that the complex retains the trigonal-bipyramidal structure on dissolution. In contrast, the five-co-ordinate di-μ-hydroxo-complex $[Co_2L(OH)_2(H_2O)_2][ClO_4]_2$ dissociates, presumably by loss of $H_2O$, to give a spectrum typical of tetrahedral $Co^{II}$.

The solution spectra of the tetrahedral alkoxo- and thiolato-bridged complexes depend on the solvent. Spectra of the latter complexes in MeCN agreed well with the solid-state spectra, while in $MeNO_2$ decomposition set in as evidenced by a time-dependent colour change from green to yellow. For the alkoxo-bridged complexes in $MeNO_2$ no decomposition was apparent and there was a fair correspondence with the solid-state spectra although with certain changes in profile of the multicomponent bands. In MeCN, however, there were more noticeable changes. These solutions were violet in colour, reminiscent of five-co-ordinate species. Despite the colour, inspection of the spectra clearly revealed that the absorbing species are tetrahedral, the change in colour being due simply to a shift of the visible absorption to higher energies (Figure 2). Evidently there is a change in the nature of the tetrahedral field on dissolving these complexes in this potentially co-ordinating solvent. Since the electrical conductances indicate, for the most part, 1 : 2 species we suggest that in MeCN the $OR^-$ bridges are cleaved but the $OR^-$ groups are still co-ordinated, one to each metal atom, the vacant tetrahedral sites now being occupied by the stronger field MeCN molecules. Gatteschi and co-workers[30] have previously drawn attention to the occurrence of high-energy bands for pseudotetrahedral cobalt(II) complexes.

*The Structures of* $[Co_2L(OEt)(NCS)_3]$ (1) *and* $[Co_2L(OMe)(N_3)_3]$ (2).—A short preliminary report of these two structures has appeared.[31] Experimental details relating to the solution and refinement of the structures are given in the Experimental section. The structures of complexes (1) and (2) are illustrated in Figures 3—5, together with the atomic numbering schemes. Both molecules have disordered centrosymmetric structures with the two cobalt(II) ions encompassed within the macrocycle. In the Figures we show one possible orientation of an ordered molecule. Figure 3 is a general view of (1) while Figures 4 and 5 are views of the molecules down the plane of the macrocycle which more clearly illustrate the bridging groups. Molecular dimensions in the co-ordination sphere are given in Table 3. Because of the disorder and the rather poor quality of the data, it is difficult to assess the accuracy of the dimensions, particularly those in the bridge. However, the geometry of the metal atoms is quite unambiguous. In both structures the cobalt atoms are five-co-ordinate with distorted trigonal-bipyramidal environments. Each metal atom is bonded to two nitrogen atoms of the macrocycle [2.09(2) and 2.15(2) Å in (1); 2.07(2), and 2.12(2) Å in (2)] which form part of the equatorial plane of the trigonal bipyramid. In one axial position is a nitrogen atom of a terminally bound pseudohalide ion [$NCS^-$ in (1), $N_3^-$ in (2)] at distances of 2.03(2) and 2.04(2) Å, respectively. The other axial position is occupied by a disordered bridging N/O atom at 2.09(2) and 2.14(2) Å in complex (1) and (2), respectively. The equatorial plane is completed by the second disordered N/O bridge atom at 1.97(2) Å in (1) and 2.01(2) Å in (2). Despite the disorder it seems clear that the equatorial bridge bonds are significantly shorter than the axial bridge bonds. The Co · · · Co separations are 3.119(6) and 3.195(6) Å in complexes (1) and (2), respectively; it is clear that there can be little significant direct metal–metal bonding. In common with previously studied dicopper complexes [19–21] of this macrocycle, but in contrast to [BaL$_2$(H$_2$O)$_2$][Co(NCS)$_4$],[22] and presumably all other mononuclear alkaline-earth-metal and lead(II) complexes,[22] the furan oxygen atoms are not co-ordinated (Co · · · O *ca.* 3.0 Å).

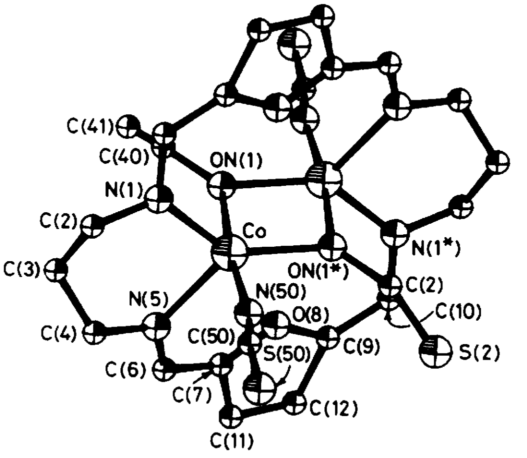


**Figure 3.** The structure of an ordered molecule of [Co$_2$L(OEt)(NCS)$_3$] (1)

As shown clearly in Figures 4 and 5 the macrocycle, atoms C(3) and C(3*) excepted, in both complexes is fairly planar. The metal atoms, however, are displaced to either side of the macrocycle plane; in (1) by 0.57 and −0.57 Å; in (2) by 0.60 and −0.60 Å.

Because of the centre of symmetry, the Co–O/N–Co* angles

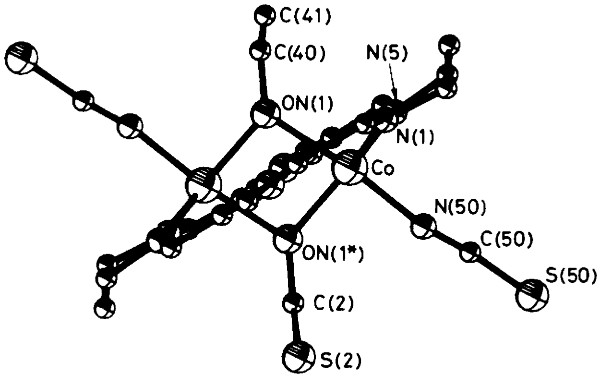


**Figure 4.** An ordered molecule of [Co$_2$L(OEt)(NCS)$_3$] (1) viewed down the plane of the macrocycle

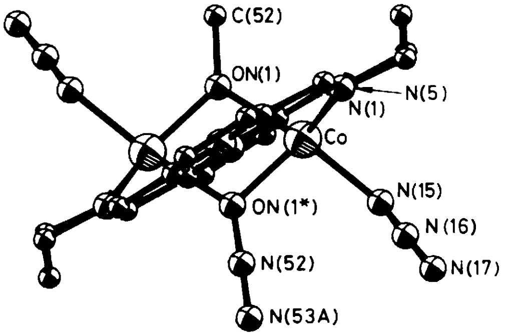


**Figure 5.** An ordered molecule of [Co$_2$L(OMe)(N$_3$)$_3$] (2) viewed down the plane of the macrocycle

**Table 3.** Dimensions (distances in Å, angles in °) in the co-ordination sphere for complexes (1) and (2) †

| Complex (1) | | Complex (2) | |
|---|---|---|---|
| Co(1)–N(50) | 2.031(21) | Co(1)–N(1) | 2.075(18) |
| Co(1)–N(1) | 2.093(23) | Co(1)–N(5) | 2.123(16) |
| Co(1)–N(5) | 2.152(21) | Co(1)–ON(1) | 2.143(19) |
| Co(1)–ON(1) | 2.092(17) | Co(1)–N(15) | 2.037(23) |
| Co(1)–ON(1*) | 1.972(17) | Co(1)–ON(1*) | 2.011(23) |
| Co(1) · · · Co(1*) | 3.119(6) | Co(1) · · · Co(1*) | 3.195(6) |
| N(50)–Co(1)–N(1) | 87.8(8) | N(1)–Co(1)–N(5) | 100.1(6) |
| N(50)–Co(1)–N(5) | 92.1(8) | N(1)–Co(1)–ON(1) | 91.9(7) |
| N(1)–Co(1)–N(5) | 97.6(8) | N(5)–Co(1)–ON(1) | 91.9(6) |
| N(50)–Co(1)–ON(1) | 173.6(7) | N(1)–Co(1)–N(15) | 88.9(8) |
| N(1)–Co(1)–ON(1) | 94.4(7) | N(1)–Co(1)–ON(1*) | 131.8(7) |
| N(5)–Co(1)–ON(1) | 93.6(7) | N(5)–Co(1)–ON(1*) | 127.3(7) |
| N(50)–Co(1)–ON(1*) | 94.5(7) | N(5)–Co(1)–N(15) | 93.6(7) |
| N(1)–Co(1)–ON(1*) | 135.8(8) | ON(1)–Co(1)–N(15) | 174.2(8) |
| N(5)–Co(1)–ON(1) | 126.3(8) | ON(1*)–Co(1)–N(15) | 95.7(9) |
| ON(1)–Co(1)–ON(1*) | 79.7(7) | ON(1)–Co(1)–ON(1*) | 79.5(8) |

† Atoms marked * are related by a centre of symmetry to those given in Tables 7 and 8. They have co-ordinates $-x$, $-y$, $-z$ (1) and $-x$, $-y$, $1 - z$ (2).

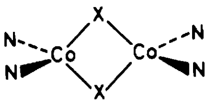
[100.3(8) and 100.5(8)°] are related to the O/N–Co–O/N* angles [79.7(7) and 79.5(8)°]. The $L_{ax}$–Co–$L_{ax}$ and $L_{ax}$–Co–$L_{eq}$ angles are within 11° of the ideal (trigonal-bipyramidal) values in both structures, with the O/N–Co–O/N* angles giving rise to the largest deviations. On the contrary, the $L_{eq}$–Co–$L_{eq}$ angles deviate considerably from 120°. Because of the restrictions imposed by the macrocycle, the N(1)–Co–N(5) angles are less than 100°. To maintain a planar equatorial grouping, the N–Co–O/N* angles are increased to 130—135°.

The disorder in complex (1) also manifests itself in the macrocycle. In the saturated (propane) segment atoms C(2) and C(3) are disordered and two positions, *ca.* 0.8 Å apart, were refined. It is interesting to speculate whether one particular orientation of the macrocycle is matched with one bridging group (OEt or $NCS^-$) but intramolecular distances proved inconclusive. In complex (2) the macrocycle appears ordered. In neither structure are there any intermolecular contacts of significance.

*General Discussion of the Structures of the Dicobalt*(II) *and Related Complexes.*—It is useful at this stage to summarise the structural conclusions relating to the dicobalt(II) complexes gained from the i.r. and ligand-field spectra and the two *X*-ray structure determinations, and to compare them with those for previously determined structures of other metal complexes of the same macrocycle.[19–22]

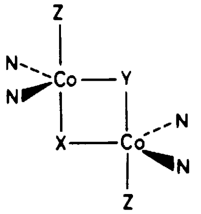
The solid complexes have been shown to contain two cobalt(II) ions within the macrocycle. In one category the metal ions are tetrahedrally co-ordinated while in the second category they have a distorted trigonal-bipyramidal geometry. In all the complexes the cobalt(II) ions are intramolecularly linked *via* two single-atom bridging anions which may be the same or different. The choice of structure is determined primarily by the nature of the bridging ligand but also, to some extent, by the nature of the non-co-ordinating counter ion. The structural results may conveniently be summarised diagrammatically, below.

Tetrahedral



X = Cl, Br, OH, OR (R = Et, Pr$^n$, Pr$^i$, or Bu$^t$), or SR (S = Et or Ph)

Trigonal bipyramidal



| X | Y | Z |
|---|---|---|
| OH | OH | $H_2O$ |
| OPh | OPh | MeCN |
| OMe | N(CS) | NCS |
| OEt | N(CS) | NCS |
| OEt | N(CSe) | NCSe |
| OMe | N(NN) | $N_3$ |

The choice of co-ordination number may be accounted for qualitatively in terms of Pauling's electroneutrality principle [32] which states that charge tends to get distributed so that no atom in a complex accumulates a charge greater than about ±1 unit. Thus, we may expect lower-co-ordination numbers in a complex composed of polarisable donor atoms and higher co-ordination numbers for complexes composed of ' hard ' or electronegative ligands. The results are in excellent accord with this simple idea. Thus, four-co-ordinate structures are obtained when the bridging ligands are the polarisable chloride, bromide, and thiolate anions or the strongly electron-donating alkoxide ions. When the electron-donating power of the $OR^-$ group is reduced as in $OPh^-$ the positive charge on the cobalt(II) ions is insufficiently neutralised, and the co-ordination number increases to five by binding of a further ligand (MeCN). The $OH^-$ ion appears to have an intermediate effect since both four- and five-co-ordinate di-μ-hydroxo-complexes have been isolated depending on the nature of the counter anion. The five-co-ordinate structures found for the pseudohalide complexes are also fully consistent with these ideas. Earlier studies [33] on the thermodynamics of tetrahedral $\rightleftharpoons$ octahedral equilibria in solutions of cobalt(II) complexes have clearly established that the effect of $NCS^-$ and $NCSe^-$ as ligands, compared to *e.g.* $Cl^-$, is to shift the equilibrium in favour of the higher co-ordination number. What is not understood in the present study is why there should be two different bridging groups in the pseudohalide complexes.

An interesting feature of the results is the occurrence in $[Co_2L(OEt)(NCS)_3]$ of a nitrogen atom-only thiocyanate bridge between the metal centres. As noted above the present complex represents only the third structurally defined example of this bridging mode in μ-thiocyanato-complexes which contrasts with the many hundreds (thousands?) of end-to-end thiocyanate bridges which use both the nitrogen and sulphur atoms.[23] The nitrogen atom-only thiocyanate bridging mode in the present complex and in the $[Re_2(NCS)_{10}]^{3-}$ anion described by Cotton *et al.*[24] may reasonably be associated with the imposed close proximity of the metal centres which precludes the formation of the more common lengthways bridge. In $[Re_2(NCS)_{10}]^{3-}$ the metal ions are held together by a metal–metal bond (*ca.* 2.61 Å), while in $[Co_2L(OEt)(NCS)_3]$, and in the analogous selenocyanate and azide, it is the small cavity size of the macrocycle that is responsible for the small metal $\cdots$ metal separation. It is also significant in the context of the present discussion to recall that in the dicopper(I) complex $[Cu_2L(SCN)_2]$ of the same macrocycle the copper(I) ions, 2.80 Å apart, are bridged by the sulphur atoms only of the two $NCS^-$ ions, this being the only case of this bridging mode so far known.[19] The choice of bridging atom, nitrogen *vs.* sulphur, in these complexes therefore appears to be determined by the ' hard ' or ' soft ' nature of the metal ion. The reason for the occurrence of the single-atom thiocyanate bridge between cadmium(II) ions in the polymeric structure described by Reedijk and co-workers [25] is less clear and may simply be a consequence of crystal-packing requirements.

It is of interest to compare the structures of the dicobalt(II) complexes described here with those of previously investigated complexes of the same macrocycle with other metal ions. As noted above the macrocycle is synthesised as its complex with $Ca^{II}$, $Sr^{II}$, $Ba^{II}$, or $Pb^{II}$ *via* a template method. All of these complexes are mononuclear, and have a 1 : 1 metal : macrocycle stoicheiometry except for $Ba^{II}$ which forms both 1 : 1 and 1 : 2 complexes (*i.e.* containing two macrocyclic ligands per metal atom).[22] The single alkaline-earth-metal ion in the macrocycle maybe replaced by two $Cu^I$ or $Cu^{II}$ [19–22] or, as described above, by two $Co^{II}$. It seems clear that the mononuclear *vs.* dinuclear nature of the complexes is governed principally by the size of the metal ion in relation to the

**Table 4.** Comparison of the macrocycle conformations in complexes (1) and (2) with those in other metal complexes of the same macrocycle

| Complex | M · · · M separation (Å) | ' $N_4$ ' planar to within (Å) | Distance (Å) of M from ' $N_4$ ' plane | Distance (Å) of O from ' $N_4$ ' plane | θ [a]/° | ' Hole ' size [b]/Å | Ref. |
|---|---|---|---|---|---|---|---|
| (1) $[Co_2L(OEt)(NCS)_3]$ | 3.119 | 0.00 | 0.57, −0.57 | 0.02, −0.02 | 5.6, 5.6 | 6.27 | This work |
| (2) $[Co_2L(OMe)(N_3)_3]$ | 3.195 | 0.00 | 0.60, −0.60 | 0.00, −0.00 | 7.1, 7.1 | 6.26 | This work |
| $[Cu_2L(MeCN)_2]^{2+}$ | 3.394 | 0.00 | 0.55, −0.55 | 0.06, 0.06 | 10.1, 10.1 | 6.21 | 21 |
| $[Cu_2L(SCN)_2]$ | 2.80 | 0.00 | 0.07, −0.07 | 0.05, −0.05 | 6.0, 6.0 | 6.23 | 19 |
| $[Cu_4L_2(CCPh)]^{3+}$ (ring A) | 2.95 | 0.08 | 0.77, 0.82 | −0.81, −0.88 | 28.9, 51.5 | 5.97 | 20 |
| (ring B) | 2.88 | 0.12 | 0.62, 0.79 | −0.76, −0.75 | 41.3, 37.7 | 6.17 | 20 |
| $[BaL_2(H_2O)_2]^{2+}$ (ring A) [c] | — | 0.03 | 0.79 | −0.78, −0.70 | 48.1, 35.3 | 5.61 [d] | 22 |
| (ring B) [e] | — | 0.03 | 1.69 | −1.05, −1.12 | 80.4, 87.8 | — | 22 |

[a] Angle between the furan rings and the ' $N_4$ ' plane. [b] Based on the four nitrogen atoms only, except where otherwise indicated. [c] Ring A is co-ordinated *via* four nitrogen and two oxygen atoms. [d] Based on four nitrogen and two oxygen atoms. [e] Ring B is co-ordinated *via* two nitrogen and one oxygen atom.

' hole ' size of the macrocycle inner large ring, the $Ca^{2+}$, $Sr^{2+}$, $Ba^{2+}$, and $Pb^{2+}$ ions being too large to form dinuclear complexes and the transition-metal ions too small to form mononuclear complexes. However, because of the non-rigid nature of the macrocycle arising from the saturated ' propane ' segments, it is not possible to define a single ' hole ' size for the macrocycle. Moreover, since the furan oxygen atoms are co-ordinated in some cases (the alkaline-earth-metal complexes [22]) but not in others (the transition-metal complexes [19-21]) the effective hole size also depends on this factor.

Including the two dicobalt(II) complexes described above the structures of six complexes of this macrocycle have so far been determined (Table 4). Four of these contain discrete molecules or cations containing two metal ions within a single macrocycle. In $[BaL_2(H_2O)_2]^{2+}$ the single $Ba^{II}$ is bonded to all six heteroatoms (' $N_4O_2$ ' ) of one macrocycle (A) but only three (' $N_2O$ ') of the second (B).[22] The complex cation $[Cu_4L(CCPh)]^{3+}$ also contains two macrocycles; in this case all four copper(I) ions are co-ordinated (*via* both σ and π bonds) to the acetylide ion.[20] Clearly, the macrocycle must adopt a variety of conformations so as to accommodate to such differing structures. The principal variations in the structures are summarised by the data in Table 4 which includes values for the hole size defined [34] as twice the mean distance of the donor atoms from their centroid. For five of the complexes in Table 4, the calculation is based on the four imino-nitrogens only. For the barium(II) complex the two furan oxygen atoms are included.

In the present structures, and in $[Cu_2L(MeCN)_2]^{2+}$,[21] the metal atoms are positioned either side (*ca.* 0.6, and −0.6 Å) of the $N_4$ plane with the two furan rings lying close to the plane. In $[Cu_2L(SCN)_2]$ the metal atoms as well as the furan rings are close to the $N_4$ plane.[19] In $[Cu_4L_2(CCPh)]^{3+}$ the two metal atoms of a given macrocycle are displaced (*ca.* 0.7 Å) on the same side of the ' $N_4$ ' plane while the furan oxygen atoms are displaced (*ca.* 0.75 Å) to the other side, giving rise to a tilt of the furan rings with respect to the $N_4$ plane (angles of intersection, 28.9—51.5°).[20] In $[BaL_2(H_2O)_2]^{2+}$ the metal sits 0.79 Å above the $N_4$ plane of macrocycle A while the furan oxygens are −0.74 Å on the other side with tilt angles of 35.3 and 48.1°. For macrocycle B (co-ordinated only by three donor atoms) a more extreme displacement (1.69 Å) of the metal from the $N_4$ plane is seen, and the furan tilt angles are also significantly larger.[22]

These examples illustrate the versatility of the macrocycle L as a ligand. The ' hole ' size, and thus its mononucleating *vs.* binucleating capabilities, are controlled both by the macrocycle conformation and the use or otherwise of the furan-oxygen atoms as donors. Thus, with large ' hard ' metal ions such as $Ca^{2+}$, $Sr^{2+}$, or $Ba^{2+}$ ($Mg^{2+}$ being too small does not form complexes) it will form mononuclear complexes, while with the smaller transition-metal ions of ' softer ' character, with little tendency to bond to the weakly basic furan oxygens, binuclear complexes are readily prepared. The close proximity of the metal centres, within the range 2.8—3.4 Å, dictates that they can best attain a co-ordination number greater than three by use of bridging ligands, preferably single-atom bridges. The nature of the binuclear complexes is determined also by the electronic configuration of the metal ion. Molecular models suggest that the preferred macrocycle conformation is that in which all the atoms except C(3),C(3*) lie close to a single plane. This means that for binuclear complexes of metal ions which do not co-ordinate to the furan groups the least strained co-ordination geometry about the metal is tetrahedral. In this way steric interaction of bridging ligands with the furan-oxygen atoms is minimised. While the detailed structures are unknown this is believed to be the arrangement occurring in the tetrahedral cobalt(II) complexes described in this paper. It is certainly the case in the dicopper(I) complex $[Cu_2L(SCN)_2]$.[19] Where the electronic configuration of the metal ion, *e.g.* $Cu^{II}$ or $Co^{II}$ with electronegative bridging ligands, renders higher co-ordination numbers desirable, the complexes adopt a trigonal-bipyramidal geometry. However, this is achieved only at the expense of some bond-angle strain about the imino-groups. Indeed, this is very probably the reason for the facile reduction to dicopper(I) observed in the dicopper(II) system.[19-21]

*Magnetic Properties of the Dicobalt*(II) *Complexes.*— Measurements of magnetic susceptibility were made by the Gouy method in the temperature range 80—300 K. There is a clear distinction in magnetic properties according to the structures of the complexes. For the five-co-ordinate complexes the moments (Table 1) fall in the range 4.5—5.1 B.M. and show little dependence on temperature in the available range, although for the μ-azido-μ-methoxo-complex a small ferromagnetic effect is apparent. In contrast, the magnetic moments of the tetrahedral complexes decrease with falling temperature to an extent dependent on the nature of the bridging ligand, clearly indicating the occurrence of antiferromagnetic superexchange coupling. Since tetrahedral $Co^{II}$ has an orbital singlet ground state the estimation of antiferromagnetic exchange is uncomplicated by spin–orbit coupling effects. The experimental molar susceptibility *vs.* temperature

**Table 5.** Derived magnetic parameters for the 'tetrahedral' dicobalt(II) complexes

| Complex | $-J$/cm$^{-1}$ | $g$ | $N(\alpha)$ */ $10^6$ c.g.s. units |
|---|---|---|---|
| $[Co_2LCl_2]Cl_2 \cdot 2H_2O$ | 7.2 | 2.34 | 200 |
| $[Co_2LBr_2]Br_2 \cdot H_2O$ | 5.5 | 2.34 | 200 |
| $[Co_2L(OH)_2][BPh_4]_2$ | 14.5 | 2.31 | 200 |
| $[Co_2L(OEt)_2][BPh_4]_2$ | 15.5 | 2.33 | 150 |
| $[Co_2L(OPr^n)_2][BPh_4]_2$ | 12.3 | 2.28 | 10 |
| $[Co_2L(OPr^i)_2][BPh_4]_2$ | 16.6 | 2.29 | 200 |
| $[Co_2L(OBu^t)_2][BPh_4]_2$ | 17.5 | 2.30 | 50 |
| $[Co_2L(SEt)_2][ClO_4]_2$ | 66.5 | 2.32 | 80 |
| $[Co_2L(SPh)_2][ClO_4]_2$ | 90.5 | 2.30 | 0 |

* Per cobalt(II) ion.

data were therefore fitted by the theoretical equation [35] for isotropic antiferromagnetic exchange in the spin Hamiltonian $\hat{H} = -2J\hat{S}_1\hat{S}_2$ where $J$ is the exchange coupling constant. For dicobalt(II) complexes where $S_1 = S_2 = \frac{3}{2}$ the temperature variation of the molar susceptibility per $Co^{II}$ is given by equation (i) where the symbols have their usual meanings. Fitting the experimental $\chi_M$ *vs.* $T$ data by the equation gave the values of $J$, $g$, and $N(\alpha)$ given in Table 5. Figure 6 compares the experimental and calculated $\chi_M$ *vs.* $T$ curves for a selection of the complexes. The agreement is reasonably satisfactory in all cases, but because of the limited temperature range available the uncertainty in the derived values of $J$ may be as high as *ca.* 5% in some cases.

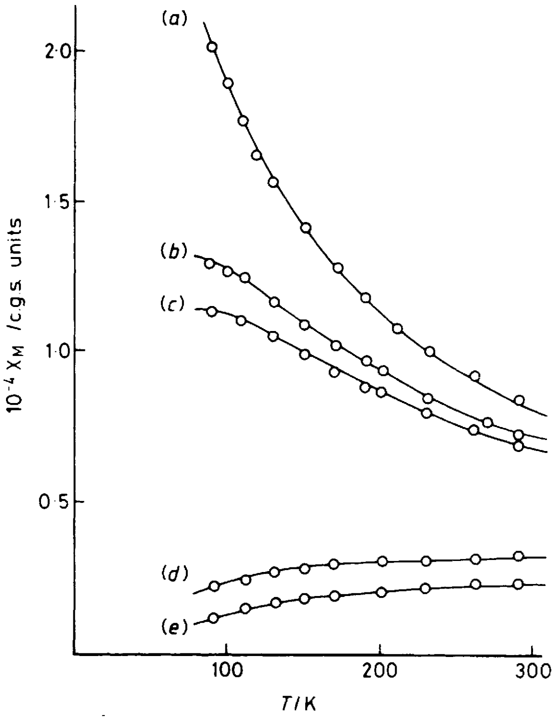


**Figure 6.** Variation with temperature of the molar susceptibility (per $Co^{II}$) of (*a*) $[Co_2LCl_2]Cl_2 \cdot 2H_2O$, (*b*) $[Co_2L(OEt)_2][BPh_4]_2$, (*c*) $[Co_2L(OBu^t)_2][BPh_4]_2$, (*d*) $[Co_2L(SEt)_2][ClO_4]_2$, and (*e*) $[Co_2L(SPh)_2][ClO_4]_2$. The circles are experimental points and the full lines are calculated from equation (i) for values of the parameters given in Table 5

$$\chi_M = \frac{Ng^2\beta^2}{kT} \cdot \left[\frac{14 + 5\exp(-6J/kT) + \exp(-10J/kT)}{7 + 5\exp(-6J/kT) + 3\exp(-10J/kT) + \exp(-12J/kT)}\right] + N(\alpha) \qquad \text{(i)}$$

There is a definite correlation of the magnitude of the coupling constant $J$ with the nature of the bridges between the cobalt(II) ions, the antiferromagnetic interaction increasing as the bridging atom changes in the order $Br^- < Cl^- < OR^- \ll SR^-$. Moreover, within the series of $OR^-$-bridged complexes (R = H, Et, $Pr^i$, or $Bu^t$) there is a small but definite increase in $-J$ with increasing substitution of the α-carbon atom. Without a detailed knowledge of the structures it is impossible to decide how far this increase might be due to small variations in structural parameters such as the Co–O(R)–Co bond angle. However, the trend observed is that predicted on theoretical grounds,[36] *i.e.* an increase in electron density on the bridge atom should lead to increased coupling. The coupling constant for the n-propoxo-bridged complex appears anomalously low. Possibly, some $OPr^{n-}$–$OH^-$ exchange occurred before the measurements were made although precautions were taken to avoid this. Alternatively, the smaller coupling may result from some (relatively minor) structural difference in this case. We have noted above that this complex (and the methoxo-bridged analogue) is also anomalous with respect to its formation of a five-co-ordinate adduct with acetonitrile in the solid state and the ease of exchange of $OPr^{n-}$ bridges for $OH^-$ bridges.

The $-J$ values for all the alkoxo-bridged complexes are substantially larger than those found by Hendrickson and co-workers [14,15] for square-pyramidal ($-J$ = 9.3 cm$^{-1}$) and pseudo-octahedral ($-J$ = 4.1 cm$^{-1}$) dicobalt(II) complexes of the binucleating macrocycle derived from the condensation of 2 mol of 2,6-diformyl-4-methylphenol with 2 mol of 1,3-diaminopropane. In these structures the cobalt(II) ions are bridged by the phenolate oxygen atoms of the macrocycle. A somewhat larger coupling ($J = -19$ cm$^{-1}$) has recently been reported by Gatteschi and co-workers [16] for the monohydroxo-bridged complex $[Co_2(tren)_2(OH)][ClO_4]_3 \cdot H_2O$ [tren = tris(2-aminoethyl)amine]. The greatest antiferromagnetic coupling in the present series of complexes occurs in the $SEt^-$- and $SPh^-$-bridged complexes ($J = -66.5$ and $-90.5$ cm$^{-1}$, respectively). As far as we are aware this is the largest interaction yet reported for dicobalt(II) complexes. The superiority of $SR^-$ compared to $OR^-$ in transmitting superexchange can be related, as pointed out by Kahn,[5] to the lower electronegativity of the sulphur atom together with the greater diffuseness of the sulphur 3*p* orbitals.

The present results demonstrate a very clear dependence of the magnitude of $J$ on the co-ordination geometry (trigonal bipyramidal *vs.* tetrahedral) of the interacting cobalt(II) ions. It is generally accepted that antiferromagnetic superexchange arises from an overlap of the metal *d* orbitals containing the unpaired spins with filled *s* and *p* orbitals of the bridging atom or group.[5,37] However, when the magnetic orbitals are orthogonal a ferromagnetic interaction should apply. This latter situation is approximated in the two structurally defined trigonal-bipyramidal complexes (and presumably also in the other complexes of this co-ordination number) where the bridging atoms link axial and equatorial sites. The Co–O/N–Co bridge angles [100.3(8) and 100.5(8) for complexes (1) and (2), respectively] are relatively close to 90° so the antiferromagnetic effect might be expected to be small. In addition, ferromagnetic pathways are available and indeed a net ferromagnetism is apparent in the μ-azido-μ-methoxo-derivative.

For the tetrahedral complexes the orthogonality is absent and antiferromagnetic exchange is now expected. It is interesting to note that the Co–X–Co bridge angles are likely to be <90° in these systems. In the di-tetrahedral copper(I) complex $[Cu_2L(SCN)_2]$ the Cu–S–Cu bridge angle is 71.9°.[19]

The strong coupling observed for the di-μ-$SR^-$ dicobalt(II) complexes is of interest in relation to the possible structure of the active site of cytochrome c oxidase, the terminal redox enzyme responsible for the catalytic reduction of $O_2$ to $H_2O$ with release of energy.[38] For the oxidised resting form of the enzyme it has been shown that the $O_2$-binding site comprises an iron(III) ($S = \frac{5}{2}$) centre antiferromagnetically coupled to a (e.s.r. non-detectable) copper(II) ($S = \frac{1}{2}$) ion with a coupling constant $-J = \geqslant 200$ cm$^{-1}$, leading to a resultant $S = 2$ ground state for the spin-coupled [Fe–X–Cu] dimer.[39] However, the nature of the bridging group X is still a matter of debate. Several candidates for X have been considered, including an imidazolato-group [39,40] (from a histidine residue of the protein), an oxo- (or hydroxo-) bridge [41–43] (derived from $O_2$ itself), and a thiolato-group [44] (from cysteine). A weakness of the imidazolate-bridged theory has been that this bridge does not usually mediate strong antiferromagnetic coupling (however, see ref. 40). A μ-oxo-model system recently reported by Wilson and co-workers [43] does provide for strong coupling, although with generation of an $S = 1$ rather than an $S = 2$ spin-coupled ground state. While the results presented in the present work say nothing about the active site of cytochrome c oxidase, they do clearly show that an interaction at least as large as $-J \geqslant 200$ cm$^{-1}$ can be expected for thiolate-bridged $S = \frac{5}{2}$, $S = \frac{1}{2}$ systems.

## Experimental

*Preparation of the Complexes.*—The starting material for the preparation of all the dicobalt(II) complexes was the complex $BaL(ClO_4)_2\cdot EtOH$ described previously.[22]

$[Co_2LCl_2]Cl_2\cdot 2H_2O$ and $[Co_2LBr_2]Br_2\cdot H_2O$. Hydrated cobalt(II) halide was dissolved in the minimum quantity of hot EtOH and filtered into a gently refluxing solution of $BaL(ClO_4)_2\cdot EtOH$ (0.0015 mol) in EtOH–MeCN (2 : 1, 150 cm$^3$). After reflux for *ca.* 10 min the mixture was filtered to remove barium(II) halide. The filtrate was refluxed for a further hour and concentrated to about half volume by rotary evaporation. The blue microcrystalline products separated, on standing, in 55% (chloride) and 82% (bromide) yield.

$[Co_2L(OMe)(NCS)_3]$ *and* $[Co_2L(OEt)(NCS)_3]$. Sodium thiocyanate (0.005 mol) dissolved in a little MeOH (or EtOH) was filtered into a solution of $[Co_2LBr_2]Br_2\cdot H_2O$ (0.001 mol) in hot MeOH–MeCN (or EtOH–MeCN) (1 : 3, 400 cm$^3$). Heating was maintained for 15 min and the red-brown products separated in 70—80% yield on cooling. The complex $[Co_2L(OEt)(NCSe)_3]$ was prepared similarly using KNCSe instead of NaNCS. After mixing the reactants the mixture was filtered to remove any precipitated KBr. The red-brown product separated soon afterwards in *ca.* 50% yield.

$[Co_2L(OMe)(N_3)_3]$. Sodium azide (0.005 mol) dissolved in the minimum quantity of MeOH was filtered into a hot stirred solution of $[Co_2LBr_2]Br_2\cdot H_2O$ (0.001 mol) in MeOH–MeCN (1 : 3, 400 cm$^3$). The red-brown product separated in *ca.* 80% yield within minutes.

$[Co_2L(OH)_2(H_2O)_2][ClO_4]_2$. A warm solution of $Co(ClO_4)_2\cdot 6H_2O$ (0.003 mol) in EtOH (20 cm$^3$) was added with stirring to a hot solution of $BaL(ClO_4)_2\cdot EtOH$ (0.001 mol) in EtOH–MeCN (2 : 1, 90 cm$^3$) to give a deep violet solution. On reducing the volume to *ca.* 30 cm$^3$ by rotary evaporation a crystalline blue solid separated. On isolation the blue crystal quickly changed to pink in air. Yield 66%.

$[Co_2L(OPh)_2(MeCN)_2][BPh_4]_2$. The complex $BaL(ClO_4)_2\cdot EtOH$ (0.001 mol) was dissolved in MeCN (80 cm$^3$). To this solution phenol (0.01 mol) was added, followed by $Co(ClO_4)_2\cdot 6H_2O$ (0.003 mol). The resulting mauve solution was refluxed for 15 min at which stage $Na[BPh_4]$ (0.004 mol) in MeCN (10 cm$^3$) was added. The mixture was gently refluxed for a further 30 min and allowed to cool to give a pink crystalline solid in 46% yield.

$[Co_2L(OR)_2][BPh_4]_2$ (R = Et, Pr$^i$, *or* Bu$^t$). The salt $Co(ClO_4)_2\cdot 6H_2O$ (0.003 mol) was added as the solid to a hot solution of $BaL(ClO_4)_2\cdot EtOH$ (0.001 mol) in dry MeCN (30 cm$^3$) and dry ROH (60 cm$^3$). The resulting deep blue solution was stirred and heated at *ca.* 70 °C for 15 min. A solution of $Na[BPh_4]$ (0.0026 mol) in MeCN (100 cm$^3$) was slowly added. Heating was continued for 1 h before reducing the volume to *ca.* 30 cm$^3$ by rotary evaporation. The blue-green products were isolated in 55% (R = Et), 65% (R = Pr$^i$), and 45% (R = Bu$^t$) yield.

When attempts were made to prepare the di-μ-methoxo- and di-μ-n-propoxo-derivatives in this way the products were mauve or pink in colour. On isolation the pink crystals (believed to contain co-ordinated MeCN) changed to blue in air. As discussed in the Results and Discussion section the blue products are thought to be the di-μ-hydroxo-complex. The di-μ-n-propoxo-complex was finally prepared under anhydrous conditions under $N_2$. The solution of $Co(ClO_4)_2\cdot 6H_2O$ was pre-dried by reflux with 2,2-dimethoxypropane. The mauve product so obtained was quickly transferred to a vacuum line and pumped at $10^{-2}$ mmHg for 10 h to yield the blue-green product. Application of this method to the preparation of $[Co_2L(OMe)_2][BPh_4]_2$ appeared not to give a completely pure product, rapid exchange of OMe for OH occurring on exposure to air.

The blue complex $[Co_2L(OH)_2][BPh_4]_2$ was prepared in a 'wet' MeOH–MeCN solvent mixture as described above. Alternatively, it could be prepared by triturating the blue-green complex $[Co_2L(OPr^n)_2][BPh_4]_2$ with 'wet' acetone.

$[Co_2L(SEt)_2][ClO_4]_2$ *and* $[Co_2L(SPh)_2][ClO_4]_2$. The salt $Co(ClO_4)_2\cdot 6H_2O$ (0.003 mol) was added as a solid to a hot stirred solution of $BaL(ClO_4)_2\cdot EtOH$ (0.001 mol) in MeCN (30 cm$^3$) containing 0.005 mol EtSH or PhSH. The resulting dark green solutions were gently refluxed for 1 h. The dark green products separated on cooling in 90% (SEt) and 76% (SPh) yield.

*Structure Determinations.*—Crystal data for $[Co_2L(OEt)(NCS)_3]$ (1) and $[Co_2L(OMe)(N_3)_3]$ (2) are given in Table 6. Both crystals were rather small and gave weak diffraction patterns. Despite considerable effort we were unable to grow larger crystals and therefore the structure determinations are of limited accuracy, particularly as both showed disorder. Fortunately we were able to establish clearly the main features of the two structures.

The two crystals were mounted in turn on a Stoe STADI2 diffractometer and data were collected *via* a variable-width ω scan. Background counts were 20 s and a scan rate of 0.033° s$^{-1}$ was applied to a width of (1.5 +sin μ/tan θ). Absorption and extinction corrections were not applied. Both structures were solved by the Patterson method and the positions of non-hydrogen atoms found from the Fourier syntheses.

In complex (1) there was disorder in the bridging atoms and part of the macrocycle. In the bridge the two different groups OEt and NCS were each given 50% occupancy. The bridging atom itself was given a scattering factor of $0.5(f_O + f_N)$. Two distinct positions were observed for the two carbons bonded to this atom and these were refined with 50% occupancy as were the terminal $CH_3$ and S moieties. It proved necessary to constrain the O–C and N–C distances. Perhaps as a consequence

**Table 6.** Crystal data and refinement details for complexes (1) and (2)

| | (1) | (2) |
|---|---|---|
| Formula | $C_{23}H_{25}Co_2N_7O_3S_3$ | $C_{19}H_{23}Co_2N_{13}O_3$ |
| *M* | 661.2 | 599.0 |
| Space group | $P2_1/c$ | $P2_1/n$ |
| Absences | 0*k*0, $k = 2n + 1$<br>*h*0*l*, $l = 2n + 1$ | 0*k*0, $k = 2n + 1$<br>*h*0*l*, $h + l = 2n + 1$ |
| *a*/Å | 9.03(1) | 8.381(7) |
| *b*/Å | 10.73(1) | 10.09(1) |
| *c*/Å | 14.64(1) | 14.185(11) |
| β/° | 99.0(1) | 96.1(1) |
| *U*/Å$^3$ | 1 401.0 | 1 192.7 |
| *F*(000) | 676 | 612 |
| μ/cm$^{-1}$ | 14.87 | 15.03 |
| $D_m$/g cm$^{-3}$ | 1.57 | 1.67 |
| $D_c$/g cm$^{-3}$ | 1.57 | 1.67 |
| λ/Å | 0.7107 | 0.7107 |
| Crystal size (mm) | 0.3 × 0.3 × 0.3 | 0.2 × 0.3 × 0.4 |
| Rotation axis | *c* | *b* |
| No. of data | 1 369 | 1 334 |
| No. of data used in refinement | 692 | 700 |
| No. of parameters | 108 | 98 |
| *R* | 0.099 | 0.115 |
| *R'* | 0.102 | 0.121 |

Information common to both complexes: crystal class, monoclinic; $Z = 2$; $2\theta_{max.} = 40°$; criterion for data inclusion, $I > 1.5\sigma(I)$.

**Table 7.** Atomic co-ordinates (× 10$^4$) for complex (1) with estimated standard deviations in parentheses

| Atom | *x* | *y* | *z* | Atom | *x* | *y* | *z* |
|---|---|---|---|---|---|---|---|
| Co(1) | 856(3) | 789(3) | 810(2) | C(7) | 3 266(33) | 860(29) | −739(19) |
| S(50) | 3 736(10) | 83(9) | 3 776(6) | O(8) | 2 275(18) | −98(16) | −848(11) |
| N(50) | 2 121(22) | 413(19) | 2 053(14) | C(9) | 2 549(28) | −1 011(25) | −1 439(17) |
| C(50) | 2 799(27) | 261(22) | 2 767(18) | C(10) | 1 651(37) | −1 995(30) | −1 680(20) |
| N(1) | −288(27) | 2 111(20) | 1 487(14) | C(11) | 4 313(35) | 543(29) | −1 308(19) |
| C(2A) | 541(51) | 3 497(50) | 1 559(46) | C(12) | 3 939(35) | −548(29) | −1 686(20) |
| C(2B) | 512(48) | 3 076(48) | 2 083(44) | S(2) | −2 758(24) | 3 007(17) | −862(13) |
| C(3A) | 1 212(75) | 3 836(58) | 985(53) | C(2) | −1 661(56) | 1 952(45) | −711(28) |
| C(3B) | 1 770(96) | 3 706(65) | 1 423(49) | ON(1) | −0 554(18) | 0 978(18) | −0 459(11) |
| C(4) | 2 744(37) | 3 127(31) | 1 008(23) | C(41) | −1 791(105) | 2 861(87) | −977(59) |
| N(5) | 2 539(23) | 2 013(20) | 421(16) | C(40) | −742(77) | 1 911(65) | −866(43) |
| C(6) | 3 381(32) | 1 827(28) | −152(19) | | | | |

**Table 8.** Atomic co-ordinates (× 10$^4$) for complex (2) with estimated standard deviations in parentheses

| Atom | *x* | *y* | *z* | Atom | *x* | *y* | *z* |
|---|---|---|---|---|---|---|---|
| Co(1) | 129(4) | 967(3) | 4 120(2) | C(12) | −5 422(27) | −455(22) | 3 723(16) |
| N(1) | 1 510(20) | 2 658(18) | 4 388(13) | C(13) | −5 213(26) | −1 741(25) | 4 157(16) |
| C(2) | 983(29) | 3 782(26) | 3 793(18) | ON(1) | −0 541(20) | 0 945(20) | 5 536(13) |
| C(3) | −809(29) | 3 997(26) | 3 744(18) | N(52) | −630(84) | 1 834(67) | 6 076(58) |
| C(4) | −1 851(29) | 3 080(23) | 3 126(17) | C(52) | −604(94) | 2 117(90) | 6 088(76) |
| N(5) | −2 088(19) | 1 839(18) | 3 583(11) | N(53A) | −478(66) | 2 831(54) | 6 482(37) |
| C(6) | −3 482(25) | 1 415(22) | 3 537(15) | N(53B) | −1 248(92) | 2 718(69) | 6 519(49) |
| C(7) | −3 990(26) | 126(23) | 3 873(15) | N(15) | 939(25) | 848(23) | 2 819(16) |
| O(8) | −2 896(16) | −657(14) | 4 354(10) | N(16) | 499(24) | 370(21) | 2 095(17) |
| C(9) | −3 616(26) | −1 824(24) | 4 530(16) | N(17) | 16(30) | −65(27) | 1 364(20) |
| C(10) | −2 906(26) | −2 815(25) | 5 120(15) | | | | |

of this bridge disorder, two positions were also observed for C(3) and C(4). These were given occupancy factors of *x* and 1 − *x* but *x* refined to 0.5. Other atoms in the macrocycle also had high thermal parameters and it may be that they are disordered, but no reasonable model could be refined.

In complex (2) the disordered bridging groups are NNN and OMe. As in (1) we could not see any disorder in the bridging atom position and this refined with occupancy $0.5(f_O + f_N)$. The second atom when refined as one atom converged at a position 1.32(3) Å from the bridging atom, a distance which is approximately halfway between a O–C and N–N bond. We then separated this peak into two, constraining the bond lengths, and this model was refined. The third atom position should have an electron density proportional to half a nitrogen atom but its peak was very elongated. We separated it into two and refined each position with an occupancy of $\frac{1}{4}f_N$. This complete model converged successfully. In this molecule, at least, the macrocyclic ring seemed ordered.

For both structures, hydrogen atoms were included in calculated positions and a common thermal parameter was

**Table 9.** Dimensions in the anionic ligands and macrocycle (distances in Å, angles in °)

Complex (1)

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| S(50)–C(50) | 1.595(27) | C(3A)–C(4) | 1.57(6) | C(7)–C(11) | 1.40(3) | S(2)–C(2) | 1.50(5) |
| N(50)–C(50) | 1.138(26) | C(3B)–C(4) | 1.30(7) | O(8)–C(9) | 1.356(24) | C(2)–ON(1) | 1.45(5) |
| N(1)–C(2A) | 1.66(5) | C(4)–N(5) | 1.47(3) | C(9)–C(10) | 1.34(3) | ON(1)–C(40) | 1.16(6) |
| N(1)–C(2B) | 1.47(4) | N(5)–C(6) | 1.233(28) | C(9)–C(12) | 1.45(3) | C(40)–C(41) | 1.38(9) |
| C(2A)–C(3A) | 1.17(7) | C(6)–C(7) | 1.34(3) | N(1*)–C(10) | 1.31(4) | | |
| C(2B)–C(3B) | 1.74(10) | C(7)–O(8) | 1.355(29) | C(11)–C(12) | 1.32(3) | | |

| | | | | | |
|---|---|---|---|---|---|
| Co(1)–N(50)–C(50) | 176.2(21) | C(3A)–C(4)–N(5) | 111(3) | C(10)–C(9)–C(12) | 136(3) |
| S(50)–C(50)–N(50) | 178.5(25) | C(3B)–C(4)–N(5) | 129(4) | C(9)–C(10)–N(1*) | 124.5(29) |
| Co(1)–ON(1)–Co(1*) | 100.3(8) | Co(1)–N(5)–C(4) | 111.8(18) | C(7)–C(11)–C(12) | 108(3) |
| Co(1)–N(1)–C(2A) | 112.7(20) | Co(1)–N(5)–C(6) | 128.1(22) | C(9)–C(12)–C(11) | 112.1(28) |
| Co(1)–N(1)–C(2B) | 121.7(22) | C(4)–N(5)–C(6) | 119.7(26) | S(2)–C(2)–ON(1) | 174(3) |
| Co(1)–N(1)–C(10*) | 125.9(20) | N(5)–C(6)–C(7) | 125(3) | Co(1)–ON(1)–C(2) | 126.5(18) |
| C(10*)–N(1)–C(2A) | 120.0(28) | C(6)–C(7)–O(8) | 130.2(28) | Co(1*)–ON(1)–C(2) | 124.3(20) |
| C(10*)–N(1)–C(2B) | 109.2(29) | C(6)–C(7)–C(11) | 125(3) | Co(1)–ON(1)–C(40) | 124(3) |
| N(1)–C(2A)–C(3A) | 121(4) | O(8)–C(7)–C(11) | 104.0(27) | Co(1*)–ON(1)–C(40) | 134(3) |
| N(1)–C(2B)–C(3B) | 104(3) | C(7)–O(8)–C(9) | 116.1(21) | ON(1)–C(40)–C(41) | 137(7) |
| C(2A)–C(3A)–C(4) | 113(5) | O(8)–C(9)–C(10) | 124.9(26) | | |
| C(2B)–C(3B)–C(4) | 128(5) | O(8)–C(9)–C(12) | 99.4(23) | | |

Complex (2)

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| N(1)–C(2) | 1.454(27) | C(6)–C(7) | 1.46(3) | C(9)–C(13) | 1.39(3) | N(52)–N(53A) | 1.16(10) |
| C(2)–C(3) | 1.51(3) | C(7)–O(8) | 1.341(23) | C(10)–N(1*) | 1.306(27) | N(52)–N(53B) | 1.24(10) |
| C(3)–C(4) | 1.49(3) | C(7)–C(12) | 1.332(29) | C(12)–C(13) | 1.44(3) | N(15)–N(16) | 1.158(25) |
| C(4)–N(5) | 1.434(26) | O(8)–C(9) | 1.358(25) | ON(1)–N(52) | 1.19(7) | N(16)–N(17) | 1.159(28) |
| N(5)–C(6) | 1.239(23) | C(9)–C(10) | 1.396(29) | ON(1)–C(52) | 1.42(10) | | |

| | | | | | |
|---|---|---|---|---|---|
| Co(1)–ON(1)–Co(1*) | 100.5(8) | N(5)–C(6)–C(7) | 126.5(20) | C(9)–C(13)–C(12) | 106.6(21) |
| Co(1)–N(1)–C(2) | 113.9(14) | C(6)–C(7)–O(8) | 118.8(18) | Co(1)–ON(1)–N(52) | 130(3) |
| Co(1)–N(1)–C(10*) | 130.4(16) | C(6)–C(7)–C(12) | 128.9(21) | Co(1*)–ON(1)–N(52) | 126(4) |
| C(10*)–N(1)–C(2) | 114.5(19) | O(8)–C(7)–C(12) | 112.2(20) | Co(1)–ON(1)–C(52) | 122(3) |
| N(1)–C(2)–C(3) | 112.2(21) | C(7)–O(8)–C(9) | 108.1(16) | Co(1*)–ON(1)–C(52) | 133(4) |
| C(2)–C(3)–C(4) | 117.1(23) | O(8)–C(9)–C(10) | 124.2(20) | ON(1)–N(52)–N(53A) | 165(7) |
| C(3)–C(4)–N(5) | 112.1(19) | O(8)–C(9)–C(13) | 107.9(20) | ON(1)–N(52)–N(53B) | 159(7) |
| Co(1)–N(5)–C(4) | 111.5(13) | C(10)–C(9)–C(13) | 127.1(23) | Co(1)–N(15)–N(16) | 136.2(18) |
| Co(1)–N(5)–C(6) | 131.3(16) | C(9)–C(10)–N(1*) | 122.2(22) | N(15)–N(16)–N(17) | 177.1(28) |
| C(4)–N(5)–C(6) | 117.0(19) | C(7)–C(12)–C(13) | 105.2(19) | | |

refined. Only the cobalt and sulphur atoms were refined anisotropically. Parameters were obtained by full-matrix least squares with a weighting scheme $w = 1/[\sigma^2(F) + 0.003F^2]$. Final $R$ values were 0.099 and 0.115 respectively. Calculations were carried out using SHELX 76[45] at the University of Manchester Computing Centre. Atomic scattering factors and dispersion corrections were taken from ref. 46. Atomic parameters are given in Tables 7 and 8, macrocycle and anion dimensions in Table 9.

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