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Complexes of Binucleating Ligands. VIII. The Preparation, Structure and Properties of Some Mixed Valence Cobalt(II)–Cobalt(III) Complexes of a Macrocyclic Binucleating Ligand

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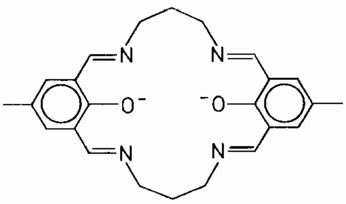
The complex $LCo_2Br_2 \cdot CH_3OH$ *has been isolated, where* LH_2 *represents the macrocyclic tetrakis-Schiff base obtained by condensation of two molecules each of 1,3-diaminopropane and 2-hydroxy-5-methylisophthalaldehyde and L represents the derived dianion which behaves as a macrocyclic binucleating ligand. By oxidation of* $LCo_2Br_2 \cdot CH_3OH$ *with bromine under a variety of conditions the following products were isolated:* $LCo_2Br_3 \cdot H_2O$*, two isomeric forms of* $LCo_2Br_3 \cdot 2H_2O$*,* $LCo_2Br_4 \cdot CH_3OH$*,* $LCo_2Br_5 \cdot 2CH_3OH$*,* $LCo_2Br_8 \cdot 4CH_3OH$*,* $(LH)CoBr_6 \cdot 2H_2O$ *and* $(LH_4)Br_6$*. Crystals of* $LCo_2Br_5 \cdot 2CH_3OH$ *have been shown by X-ray diffraction methods to consist of binuclear* $[LCo(II)Co(III)Br_2(CH_3OH)_2]^+$ *cations, in which both metal centres are essentially octahedral, and tribromide anions.* $LCo_2Br_3 \cdot H_2O$*, the two isomeric forms of* $LCo_2Br_3 \cdot 2H_2O$ *and* $LCo_2Br_4 \cdot CH_3OH$ *are assigned the binuclear Co(II)–Co(III) formulations,* $[LCo(II)Co(III)Br_2(H_2O)]^+Br^-$*,* $[LCo(II)Co(III)Br_2(H_2O)_2]^+Br^-$ *in two geometrically isomeric forms and* $\{[LCo(II)Co(III)Br_2(CH_3OH)]^+\}_2Br^-(Br_3^-)$ *respectively, in which the cobalt(III) centres are six coordinate and low spin and the cobalt(II) centres are high spin and either five or six coordinate.* $LCo_2Br_8 \cdot 4CH_3OH$ *is diamagnetic with a binuclear Co(III)–Co(III) structure and is unstable in the solid, liberating bromine and regenerating the paramagnetic Co(II)–Co(III) binuclear unit.* $(LH_4)Br_6$ *formulated as* $(LH_4^{2+})(Br_3^-)_2$*, is the first example of a metal-free derivative of the macrocycle and can now be isolated from a metal-free condensation reaction of the dialdehyde and diamine components.*

Crystals of $LCo_2Br_5 \cdot 2CH_3OH$ *are orthorhombic with cell dimensions* $a = 17.78$*,* $b = 37.74$ *and* $c = 19.79$ *Å, space group Pbca and* $Z = 16$*. Counter methods were used to collect 1993 reflections above background. Despite rapid decomposition of the crystal during data collection, the structural framework was ascertained readily and the structure refined to the limit of accuracy allowed by the quality of the data, using a least-squares method with isotropic temperature factors, to the somewhat high value of R 0.15.*

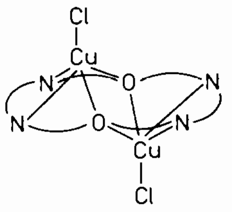
Introduction

The first example of a macrocyclic ligand capable of enclosing two metal ions was reported from this department,[1] the ligand being the dianion, L^{2-}, structure I, derived from the tetrakis-Schiff base, LH_2*, formally resulting from condensation of two molecules each of 2-hydroxy-5-methylisophthalaldehyde and 1,3-diaminopropane. A series of binuclear complexes of the type $LM_2Cl_2 \cdot$solvent was isolated where M is Mn(II), Fe(II), Co(II), Ni(II), Cu(II) and Zn(II) and on the basis of magnetic and spectral evidence the complexes were assigned structures in which the cations were in approximately square pyramidal environments.



I

An X-ray crystallographic analysis of $LCu_2Cl_2 \cdot 6H_2O$[2] confirmed the binucleating, macrocyclic nature of L which adopted a nearly planar configuration and showed that the copper ions were in the anticipated square pyramidal environment as in II.



II

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* Systematic name of LH_2: 11, 23-dimethyl-3,7,15,19-tetraazatricyclo[19.3.1.1^{9,13}]hexacosa-2,7,9,11,13(26),14,19,21(25),22,24-decaene-25,26-diol.

In view of the apparently general adoption of square pyramidal geometry for a range of cations and especially in view of the persistence, at least in some cases, of this geometry in aqueous solution, it was suggested[1] that, possibly, L allows no alternative to this arrangement for associated cations, in so far as unacceptable strain in the ligand may well accompany the incorporation of cations into the plane of the N_2O_2 donor sets, as is required for the alternative square planar or octahedral ligand arrangements.

With these considerations in mind we have attempted to use the ligand L to impose a square pyramidal environment upon a metal ion which normally has a very strong preference for octahedral geometry, namely Co(III), in the hope that the unusual geometry of the ligand set might lead to unusual electronic configurations and/or reactivity at the metal centre. The present report describes attempts to generate Co(III) bound to L by oxidation of binuclear Co(II) complexes, and studies on the products thereby obtained.

Results and Discussion

Binuclear Complexes

Attempts to generate binuclear Co(III) complexes of L by oxidation of the previously reported $LCo_2Cl_2 \cdot 2CH_3OH$ [1] with either molecular chlorine or with iodobenzene dichloride led to general disruption of L as indicated by the isolation of the hydrochloride of 1,3-diaminopropane. As a starting material for attempted oxidations using the weaker oxidant bromine, the corresponding bromo derivative was prepared as a brown crystalline solid of composition $LCo_2Br_2 \cdot CH_3OH$ by condensation of the diamine and dialdehyde in the presence of cobaltous bromide and cobaltous acetate in methanolic solution. $LCo_2Cl_2 \cdot 2CH_3OH$ and $LCo_2Br_2 \cdot CH_3OH$, in contrast to closely related cobalt(II) complexes of Schiff base ligands were completely stable to dioxygen, both in the solid state and in the solvents water, methanol and dichloromethane.

The diffuse reflectance electronic spectrum of $LCo_2Br_2 \cdot CH_3OH$, showing $d \leftrightarrow d$ bands at 9300, 14000 and 17500 cm^{-1} (the latter band appeared as a shoulder on the tail of an intense band of charge-transfer or $n \rightarrow \pi^*$ origin) was very similar to that of $LCo_2Cl_2 \cdot 2CH_3OH$ which has been discussed previously in terms of an approximately square pyramidal ligand field.[1] In particular, the band in both spectra near 14000 cm^{-1}, although weak, is difficult to reconcile with an octahedral cobalt(II) environment. The magnetic properties of $LCo_2Br_2 \cdot CH_3OH$ (Table I) also are very similar to those of the chloride, Curie–Weiss behaviour being observed in the temperature range 300–100° K with an effective magnetic moment per Co atom of 4.7 B.M. at room temperature. As discussed previously these properties are not inconsistent with a square pyramidal ligand field of low basal symmetry, but certainly do not exclude the possibility of an octahedral arrangement.

TABLE I. Magnetic Properties.

Compound	μ_{eff}[a] (B.M.)	Weiss Constant (° K)
$LCo_2Br_2 \cdot CH_3OH$	4.68[b] (304)	–55
$LCo_2Cl_2 \cdot 2CH_3OH$ [1]	4.61[b] (297)	–62
$LCo_2Br_2 \cdot H_2O$	4.53[b,d] (296)	
$LCo_2Br_3 \cdot H_2O$	4.76[c] (292)	–21
$LCo_2Br_4 \cdot CH_3OH$	4.64[c] (303)	–20
$LCo_2Br_5 \cdot 2CH_3OH$	4.46[c,d] (297)	

[a] Temperature (° K) in parentheses. Susceptibilities were corrected for diamagnetism using the diamagnetic susceptibility of L from the measured susceptibility of $LZn_2Cl_2 \cdot 2H_2O$ [1] and Pascal's constants. Measured by Gouy method except those with superscript d. [b] Moments calculated per Co atom. [c] Moments calculated assuming equal numbers of diamagnetic and paramagnetic Co atoms. [d] Measured at room temperature only on vibrating sample magnetometer.

Contrary to our assumption that L might effectively prevent the in-plane incorporation of metal ions, we eventually became convinced, in the face of evidence presented below, that cobalt(II) and cobalt(III) can indeed be accommodated within the N_2O_2 donor plane with additional monodentate ligands above and below the plane completing an essentially octahedral ligand field. This conclusion in turn led us to doubt our previous assignment of a square pyramidal ligand field in the cases of $LCo_2Cl_2 \cdot 2CH_3OH$ and $LCo_2Br_2 \cdot CH_3OH$, the only diagnostic evidence for which was the weak band near 14000 cm^{-1} in the electronic spectra. An X-ray crystallographic study of $LCo_2Br_2 \cdot CH_3OH$ was therefore undertaken, which dispelled these doubts and confirmed the initially predicted square pyramidal geometry in a structure closely analogous to II.[3] However, the situation is not quite as unequivocal as implied by II because the methanol molecules, which are disordered, are very weakly bonded (Co–O = 2.503(9)Å) in a random fashion to half the cobalt centres from the side of the N_2O_2 plane opposite to the coordinated bromine atom, whilst the remaining cobalt atoms are truly 5-coordinate. As in the case of $LCu_2Cl_2 \cdot 6H_2O$ the ligand is essentially planar except for the two central carbon atoms of the diaminopropane links.

Recrystallization of $LCo_2Br_2 \cdot CH_3OH$ from water yielded a presumably entirely analogous hydrate, $LCo_2Br_2 \cdot H_2O$, which showed ir and electronic spectra effectively identical to those of the methanolate (except for methanol bands in the ir spectrum of the latter) and which had a similar magnetic moment at room temperature (Table I). The ir spectra of $LCo_2Br_2 \cdot CH_3OH$, $LCo_2Br_2 \cdot H_2O$ and $LCo_2Cl_2 \cdot 2CH_3OH$ in the range 2000–600 cm^{-1} were identical in all details, except for the band which could be assigned with certainty, because of the otherwise identical pattern, to the C–O stretching mode of methanol at 1040 cm^{-1} in the chloride and 1023 cm^{-1} in the bromide.

Oxidation of $LCo_2Br_2 \cdot CH_3OH$ with molecular bromine yielded a number of products depending on reaction conditions. A species of composition $LCo_2Br_4 \cdot CH_3OH$ could be isolated by the following two different procedures. A methanolic solution at room temperature containing $LCo_2Br_2 \cdot CH_3OH$ and a large excess of Br_2 deposited a black amorphous precipitate which had a very high and variable bromine content and which liberated molecular bromine on exposure to the atmosphere. However, after being heated under vacuum at 60° C, during which molecular bromine was lost, the solid yielded quite reproducibly a residue of composition $LCo_2Br_4 \cdot CH_3OH$. Alternatively, a material identical in elemental composition and physical properties could be obtained by drying at 60° C under vacuum the black crystalline precipitate which separated upon evaporation at room temperature under vacuum of an equimolar mixture of $LCo_2Br_2 \cdot CH_3OH$ and molecular bromine in methanol. The black crystals after drying under vacuum at only room temperature showed an elemental composition close to $LCo_2Br_4 \cdot CH_3OH$ but invariably the bromine content was slightly high and heating to 60° C under vacuum was necessary to produce analytically pure $LCo_2Br_4 \cdot CH_3OH$.

A compound of stoichiometry $LCo_2Br_3 \cdot H_2O$ was obtained by drying at room temperature and atmospheric pressure the black crystals which separated upon cooling a boiling methanolic solution of equimolar proportions of $LCo_2Br_2 \cdot CH_3OH$ and Br_2. The appearance of a hydrate is surprising in view of the fact that $LCo_2Br_2 \cdot CH_3OH$ and $LCo_2Br_4 \cdot CH_3OH$ are obtained as methanolates from the same solvent. However, the methanol used, which was not especially dried, did contain approximately 0.5% water and analytical evidence on many independently prepared samples, together with the lack of any bands in the ir spectrum assignable to CH_3OH, support the hydrate formulation, which is confirmed by X-ray evidence discussed below.

$LCo_2Br_3 \cdot H_2O$ and $LCo_2Br_4 \cdot CH_3OH$ were moderately soluble with decomposition in water and methanol but in dichloromethane, in which they showed slight solubility, decomposition was sufficiently slow at room temperature to allow physical measurements.

The electronic spectra of $LCo_2Br_3 \cdot H_2O$ and $LCo_2Br_4 \cdot CH_3OH$ in dichloromethane solution and by diffuse reflectance were dominated by very intense bands, probably of charge-transfer or $n \rightarrow \pi^*$ origin, which obliterated any possibly diagnostically useful $d \leftrightarrow d$ bands. The ir spectra of the two compounds showed the same basic pattern of bands observed for all the $LM_2Cl_2 \cdot$solvent complexes,[1] suggesting that L had not undergone some gross change such as bromination. The C–O stretching band of the methanol in $LCo_2Br_4 \cdot CH_3OH$ was not so obvious as in the cases of $LCo_2Br_2 \cdot CH_3OH$ and $LCo_2Cl_2 \cdot 2CH_3OH$, appearing as a shoulder at approximately 1015 cm^{-1} on a ligand band located near 1000 cm^{-1} in all the L complexes. Pure 2-hydroxy-5-methylisophthalaldehyde was recovered from $LCo_2Br_3 \cdot H_2O$ and $LCo_2Br_4 \cdot CH_3OH$ in yields of 85% and 80% respectively upon heating with aqueous acid. Provided the unprecedented and unlikely bromination of the $-(CH_2)_3-$ chains of L can be excluded this mode of decomposition rules out the possibility that L has undergone bromination.

By voltammetry at a rotating platinum electrode in dichloromethane with $5 \times 10^{-2}M$ tetraethylammonium perchlorate as supporting electrolyte $LCo_2Br_3 \cdot H_2O$ and $LCo_2Br_4 \cdot CH_3OH$ (both at the same concentration of $5 \times 10^{-5}M$) showed reduction waves at $E_{1/2}$ +0.65 and +0.61 volts respectively relative to the silver-silver iodide electrode ($2.5 \times 10^{-2}M$ in iodide) with wave heights in the ratio 1:2. This appeared to support the oxidation state formulations suggested by the observed stoichiometries; namely that $LCo_2Br_3 \cdot H_2O$ contains binuclear Co(II)–Co(III) units and $LCo_2Br_4 \cdot CH_3OH$ contains binuclear Co(III)–Co(III) units.

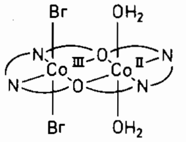
The magnetic properties of $LCo_2Br_3 \cdot H_2O$ and $LCo_2Br_4 \cdot CH_3OH$ are summarised in Table I. Curie–Weiss behaviour was observed in the temperature range 300–100° K in both cases. The observed susceptibilities for $LCo_2Br_3 \cdot H_2O$ are best interpreted in terms of one diamagnetic Co(III) per binuclear unit and one paramagnetic Co(II), for which the experimental data then require an effective moment of 4.8 B.M. at room temperature. The strong paramagnetism of $LCo_2Br_4 \cdot CH_3OH$ initially led us to believe we had achieved our objective of a cobalt(III) compound in an unusual electronic configuration. The experimental susceptibilities require either that both cobalt centres are paramagnetic, each with a moment of 3.3 B.M., or that one cobalt centre is diamagnetic and the other is paramagnetic with a moment of 4.6 B.M. We now believe the latter is the case and that the paramagnetic centre is cobalt(II) not cobalt(III) as initially anticipated and believed.

Repeated attempts to grow crystals suitable for X-ray studies by recrystallization of either $LCo_2Br_3 \cdot H_2O$ or $LCo_2Br_4 \cdot CH_3OH$ from methanol or dichloromethane uniformly failed, because of decomposition in solution in the case of methanol. The approach which ultimately proved successful was to allow crystals to grow from reaction solutions of

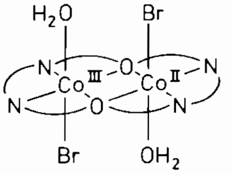
$LCo_2Br_2 \cdot CH_3OH$ and Br_2; however the materials isolated thereby, although related to $LCo_2Br_3 \cdot H_2O$ and $LCo_2Br_4 \cdot CH_3OH$ did not have exactly these compositions.

Single crystals of two isomeric forms, *A* and *B*, of a material of composition $LCo_2Br_3 \cdot 2H_2O$ were obtained. When a methanolic solution of $LCo_2Br_2 \cdot CH_3OH$ and bromine in equimolar proportions, which had been evaporated at the boiling point until solid just started to separate, was allowed to cool to room temperature a large proportion of the dissolved material separated in a form unsuitable for X-ray studies. Suitable crystals of isomer *A* (orthorhombic) were obtained by filtering off this initial precipitate and allowing the filtrate to evaporate slowly at room temperature overnight. If the crystals of isomer *A* were filtered off after slow evaporation for approximately one day, and the filtrate allowed to stand with slow evaporation at room temperature for a further period of two days, extensive decomposition occurred in solution and a few crystals of isomer *B* (monoclinic) were obtained.

Both forms of $LCo_2Br_3 \cdot 2H_2O$ were unstable with respect to loss of water on exposure to the atmosphere; in the case of isomer *A* complete loss of one molecule of water occurred rapidly, even at atmospheric pressure, yielding the $LCo_2Br_3 \cdot H_2O$ described above. The structures of the two isomers have been determined by X-ray methods using single crystals sealed in capillary tubes containing mother liquor.[3] Both consist of discrete $[LCo(II)Co(III)Br_2(H_2O)_2]^+$ cations and bromide anions, the cations existing in the geometrically isomeric forms III(isomer *A*) and IV (isomer *B*).



III

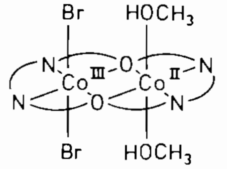


IV

In both cases the $N_2O_2N_2$ donor sets are very close to coplanar. In isomer *A* the macrocycle is bent so that the two benzene rings are at an angle of 21.6° to each other, whilst in isomer *B* the two benzene rings are almost coplanar with each other and with the $N_2O_2N_2$ donor set.

In view of the manner in which $LCo_2Br_3 \cdot H_2O$ is obtained from isomer *A* it seems most reasonable to propose that the two have very closely related structures, in which the cobalt(II) centre of the dihydrate, III, has simply lost one coordinated water molecule to achieve, in the monohydrate, the square pyramidal arrangement which it appears to prefer, as for example in $LCo_2Br_2 \cdot CH_3OH$. The properties of $LCo_2Br_3 \cdot H_2O$ are consistent with this formulation, but it is unfortunate that more direct electronic spectral evidence for the proposed 5-coordinate cobalt(II) is not available.

Attempts to grow crystals of $LCo_2Br_4 \cdot CH_3OH$ from methanolic reaction mixtures of $LCo_2Br_2 \cdot CH_3OH$ and bromine in equimolar proportions maintained at room temperature, in fact yielded crystals indicated by X-ray studies to have the composition $LCo_2Br_5 \cdot 2CH_3OH$. The structural determination, details of which are given below, showed that the crystal consisted of tribromide anions and two non-equivalent but very similar types of binuclear cation $[LCo(II)Co(III)Br_2(CH_3OH)_2]^+$, structure V, both of which closely resembled the binuclear cation of the isomeric *A* form of $LCo_2Br_3 \cdot 2H_2O$.



V

There is now no doubt that the initially precipitated solid in the above described approach to $LCo_2Br_4 \cdot CH_3OH$, involving the evaporation under vacuum at room temperature of a methanolic solution of $LCo_2Br_2 \cdot CH_3OH$ and an equimolar amount of bromine, is in fact $LCo_2Br_5 \cdot 2CH_3OH$. The latter can be obtained in bulk with the correct elemental composition provided vacuum, which leads to rapid bromine loss, is avoided in the drying procedure; this material, under vacuum at 60° C, then yields $LCo_2Br_4 \cdot CH_3OH$. These results leave no alternative but to formulate $LCo_2Br_4 \cdot CH_3OH$ as $\{[LCo(II)Co(III)Br_2(CH_3OH)]^+\}_2\ Br^-(Br_3^-)$ in which the cation is closely related to V except that the cobalt(II) has lost one methanol molecule to become square pyramidal, as in $LCo_2Br_2 \cdot CH_3OH$ and as proposed in $LCo_2Br_3 \cdot H_2O$. A mixed bromide-tribromide, analogous to the one proposed here, has been established by crystallography in the case of $[(CH_3)_3NH]Br_2$ whose true formulation is $[(CH_3)_3NH^+]_2Br^-(Br_3^-)$.[4] It is a little surprising that, in the solid phase, only half the tribromide ions of $LCo_2Br_5 \cdot 2CH_3OH$ lose bromine to yield bromide. However, the structural determination reveals that there are two non-identical tribromide ions present in equal numbers and, presumably because of some subtle solid state effect, one type degenerates more readily to bromide and the other type remains intact even at 60° C under vacuum. The physical properties of $LCo_2Br_4 \cdot CH_3OH$ are consistent with this formulation but, as in the case of $LCo_2Br_3 \cdot H_2O$, it is unfortunate that intense bands in the visible region mask $d \leftrightarrow d$ bands diagnostic of the proposed 5-coordinate cobalt(II).

Infra-red spectra of all the binuclear compounds of L isolated, including the earlier $LM_2Cl_2 \cdot$ solvent series,[1] although showing a common basic pattern, do show variability in detail, *e.g.* slight shifts in band positions, variations in relative intensities, in some cases additional shoulders. These fine details are no doubt linked to minor differences in ligand conformation and, in this context, it is significant that the details of the ir spectra of $LCo_2Br_3 \cdot H_2O$, $LCo_2Br_4 \cdot CH_3OH$ and $LCo_2Br_5 \cdot 2CH_3OH$ (except for 'solvent' bands) are effectively identical. It would appear therefore that the distinct twisting of L resulting in the benzene rings being of the order of 20° to each other, observed in isomer *A* of $LCo_2Br_3 \cdot 2H_2O$ and in $LCo_2Br_5 \cdot 2CH_3OH$, is also present in $LCo_2Br_3 \cdot H_2O$ and $LCo_2Br_4 \cdot CH_3OH$.

The structural data discussed above, indicating that the macrocycle can accommodate two metal ions within the $N_2O_2N_2$ plane (at least if one of them is cobalt(III)) with additional monodentate ligands completing "normal" pseudo-octahedral ligand fields, raise the question as to why the second cobalt atom is so reluctant to become cobalt(III), even in the presence of excess oxidant. It emerges that a binuclear Co(III)–Co(III) compound can in fact be generated but that this is very unstable reverting readily to Co(II)–Co(III). The initial black precipitate isolated in the approach to $LCo_2Br_4 \cdot CH_3OH$ involving a large excess of bromine, rapidly loses molecular bromine after isolation, but, if it is dried for only a short time at atmospheric pressure and then analysed immediately the composition corresponds closely to $LCo_2Br_8 \cdot 4CH_3OH$. It is significant that the freshly prepared material is effectively diamagnetic, rapidly becoming paramagnetic as molecular bromine is lost and achieving after a period of months at atmospheric pressure and room temperature a susceptibility of the order of that of $LCo_2Br_4 \cdot CH_3OH$. The initially formed compound is therefore assigned the oxidation state formulation $(L^{2-})(Co^{3+})_2(Br^-)_2(Br_3^-)_2$ with both metal centres in the normally preferred (for cobalt(III)) pseudo-octahedral, low spin state. It would appear that there is a very powerful driving force for one of the two cobalt(III) centres to become cobalt(II) even though the latter may remain pseudo-octahedral, and that, in the solid phase, the Co(III)–Co(III) species is a sufficiently strong oxidant to liberate bromine from bromide ion, formally the reverse of the process (in solution) whereby it was formed.

Whilst the cobalt(III) centre of the various Co(II)–Co(III) species isolated is less unstable than those in the above Co(III)–Co(III) compound, the general behaviour and the voltammetric data would suggest that it, also, is an oxidant comparable in strength with bromine, but somewhat weaker. In methanolic solution $LCo_2Br_3 \cdot H_2O$ is reduced after prolonged boiling (presumably either by bromide ion or by methanol) to $LCo_2Br_2 \cdot CH_3OH$.

The reasons why a square pyramidal cation geometry is preferred for divalent metals, and why cobalt (III) is so unstable when it is incorporated, especially when both metal centres are cobalt(III), probably are related to variations in some subtle form of strain in the macrocycle, the nature of which eludes us even with crystallographic data for five binuclear compounds of L at our disposal. The dimensions of the N_2O_2 cavities associated with cobalt(II) are, within the limits of experimental error, barely different in $LCo_2Br_2 \cdot CH_3OH$,[3] in which the cobalt(II) is 0.30 Å above the N_2O_2 plane, and in the three different Co (II)–Co(III) species in which the cobalt(II) is within the N_2O_2 plane. The only significant difference that does exist is in the O···O distances which, in the Co (II)–Co(III) compounds [2.34(5), 2.42(7), 2.44(2),[3] 2.48(2)[3] Å] are smaller than that in $LCo_2Br_2 \cdot CH_3OH$ [2.560(6) Å].[3] Clearly this O···O contraction occurs because these donor atoms are also attached to the smaller cobalt(III), which, as would be expected, appears to cause general contraction of its associated N_2O_2 set as compared with the set associated with cobalt(II). However, it remains a puzzle as to why the cobalt(II) in $LCo_2Br_2 \cdot CH_3OH$ prefers to locate itself 0.3 Å above the N_2O_2 set when the cavity available to it is somewhat larger than that into which it fits in-plane in the Co(II)–Co(III) compounds.

Mononuclear and metal-free derivatives

The reaction of $LCo_2Br_2 \cdot CH_3OH$ with a large excess of bromine in boiling methanol yielded a black crystalline precipitate, which slowly lost bromine at atmospheric pressure but which, immediately after isolation, was effectively diamagnetic (0.6 B.M.) with a composition consistent with the mononuclear formulation, $(LH^-)(Co^{3+})(Br_3^-)_2 \cdot 2H_2O$. Evaporation to small volume of the filtrate from the above reaction suspension yielded red crystals of the metal-free macrocyclic derivative $(LH_4^{2+})(Br_3^-)_2$ in very low yield. These results clearly point to competition between protons and metal ions for one or both of the two cavities provided by L, hydrogen bromide most probably arising from the secondary reaction of the excess bromine with methanol at its boiling point.

It is proposed that, in $(LH)Co(Br_3)_2 \cdot 2H_2O$, the macrocycle contains cobalt(III) in one cavity and one proton in the other. An analogous derivative with two protons in the second cavity, namely $(LH_2)Ni(ClO_4)_2 \cdot H_2O$, was described in the earlier report[1] and a similar species, (L′H)NiCl (where $L'H_2$ is the macrocycle analogous to LH_2 but with the diaminopropane links replaced by diaminoethane) has also been isolated.[5]

Many earlier attempts to isolate the metal-free macrocycle were unsuccessful.[1] The appearance of $(LH_4)(Br_3)_2$, albeit in very low yield, from the above reaction therefore suggested previously untried approaches to metal-free macrocyclic derivatives. Condensation of the diamine and dialdehyde in the presence of hydrogen bromide in methanol yielded a red solution from which LH_4Br_2, invariably contaminated with the hydrobromide of 1,3-diaminopropane, was isolated. Addition of excess bromine to the above red solution, however, precipitated $(LH_4)(Br_3)_2$ identical to that obtained in low yield from $LCo_2Br_2 \cdot CH_3OH$. It is proposed that in LH_4^{2+} the macrocycle contains two protons in both cavities.

Crystal Structure of $LCo_2Br_5 \cdot 2CH_3OH$

Crystal Data

Crystalline $LCo_2Br_5 \cdot 2CH_3OH$ was prepared by the method detailed in the Experimental section. The compound had a tendency to crystallize as clusters of many small crystallites, and it was only after repeated attempts that one single crystal large enough for intensity data collection was obtained. This crystal was far from ideal, being plate-like in shape, but was the best available. Preliminary photographic studies on other crystals showed that these decomposed rapidly, the diffraction pattern becoming obviously weaker over a period of several days. This decomposition was found to occur whether or not the crystals were sealed in Lindemann glass capillary tubes containing mother liquor. For all crystals examined, even those freshly prepared, reflections were streaked and diffuse, showing that the crystals at all times were significantly disordered. In spite of these limitations it was decided to proceed with the structure analysis in order to establish at least the overall structural features of $LCo_2Br_5 \cdot 2CH_3OH$, with the hope of resolving the problem of the structural nature of this and the related compound $LCo_2Br_4 \cdot CH_3OH$ reported here. Consequently the intensity data were collected as rapidly as possible, over a period of five days, the crystal being mounted in air at room temperature.

From oscillation and Weissenberg photographs taken with copper radiation [CuKα (nickel filtered), λ = 1.5418 Å] about the *b* and *c* axes ($h0l \rightarrow h1l$; $hk0 \rightarrow hk2$) the crystals were found to be orthorhombic with the systematic absences $hk0$ with h odd, $h0l$ with l odd and $0kl$ with k odd uniquely determining the space group to be *Pbca*. Because of the need to collect data quickly from the decomposing crystal, and because of limitations in the quality and extent of the diffraction pattern which did not extend much beyond $\Theta = 30°$, little time was spent on determining cell dimensions. These were determined on the diffractometer from the available $h00$, $0k0$ and $00l$ reflections and the reflection subsequently used as the check reflection (8, 12, 0). The calculated cell dimensions are a = 17.78, b = 37.74, c = 19.79 Å, V = 13279 Å^3. No estimate of the standard deviations was made. The calculated density of 1.969 g cm^{-3}, assuming Z = 16, is in agreement with the measured density of 1.96 g cm^{-3} determined by the flotation method using n-heptane and bromoform. This value of Z, in conjunction with the space group, requires two formula units, a total of 82 non-hydrogen atoms, per asymmetric unit.

Data Collection

The crystal used for data collection was a parallelepiped of dimensions 0.05 × 0.31 × 0.37 mm coincident with the *a, b* and *c* axes respectively. The crystal was mounted with the *c* axis coincident with the Φ diffractometer axis, and intensities were measured on a Siemens automatic single crystal diffractometer (AED) using CuKα radiation (nickel filtered, λ = 1.5418 Å) and the "five-values" $\Theta:2\Theta$ scan procedure detailed by Hoppe.[6]

The intensities of 4539 unique reflections were measured within the sphere $\Theta \leqq 40°$. On the basis of the 2σ criterion this gave 1993 statistically significant reflections. The overall intensity of a check reflection (8, 12, 0) measured after every 20 reflections, corrected for background, at the commencement of data collection was 3.4 times that of its intensity after the five days of counting, while the background counts remained essentially the same throughout. The decomposition was observed to be essentially isotropic, and the overall intensities were multiplied by a factor, varying from 1.0 to 3.4 depending on the variation of the check reflection throughout the data collection, to correct for the decrease in intensity. At the completion of the data collection, 62 of the observed reflections measured at the beginning of the collection were again measured, and corrected for decrease in intensity as described above. These 62 reflections were not used in the structure determination, but were used as a check on the accuracy of the method of correction for loss in intensity due to decomposition. A comparison of the structure amplitudes for the corrected 62 reflections with those for the analogous 62 collected at the beginning of the data collection yielded a conventional R-factor of 0.149.

The integrated intensities were also corrected for Lorentz and polarization effects and for absorption,[7] the linear absorption coefficient[8a] being 157.9 cm^{-1}.

Structure Determination and Refinement

Atomic scattering factor curves were taken from the compilations in *International Tables.*[8b] The scattering curves for Co^{2+}, Co^{3+}, and Br were modified for the real and imaginary anomalous dispersion corrections.[8c] All computations were performed on a CDC Cyber 73 computer.

The positions of two of the bromine atoms were obtained from a three-dimensional Patterson synthesis. Two Fourier syntheses then gave the positions of the remaining 12 heavy atoms, and a set of scaled structure factors calculated using these 14 atomic positions and an arbitrarily assigned overall isotropic temperature factor with $B = 5.0 \text{Å}^2$ gave an R-factor, defined as $\Sigma \Delta F/\Sigma |F_o|$ where $\Delta F = | |F_o|-|F_c| |$, of 0.47. Due to the limitations in the accuracy of the data, some of the light atoms were poorly defined, and a number of further Fourier syntheses were necessary to give the positions of all non-hydrogen atoms, excepting the four carbon atoms of the terminal methanol groups. The atomic coordinates of the methanol oxygen atoms were not refined, as when this was done these atoms shifted to positions intermediate between the true oxygen and carbon positions ot the methanol molecules. After several least-squares cycles it was clear that the isotropic temperature factors of the non-methanol carbon atoms and the methanol oxygen atoms, many of which were poorly resolved in the electron density maps, could not be refined, converging at unreasonable values. On the basis of these calculations the mean values of $B = 3.5$ and 2.6Å^2 were assigned to each of the non-methanol carbon and methanol oxygen atoms and held constant for the remainder of the refinement procedure. Least-squares refinement on all atomic coordinates (except those of the methanol atoms),

TABLE II. Final Atomic Parameter for $LCo_2Br_5 \cdot 2CH_3OH$[a, b]

Atom	x	y	z	*B*(Iso)	Atom	x	y	z	*B*(Iso)
Co1	.3672(6)	.0799(3)	.0134(6)	2.9(.3)	Co3	.1585(7	–.1197(3)	.0909(6)	4.0(.3)
Co2	.4037(6)	.1618(3)	.0146(6)	3.3(.3)	Co4	.1886(6)	–.1179(3)	–.0642(6)	3.4(3)
Br1	.6230(6)	.2406(2)	.2430(5)	6.9(.3)	Br4	.1579(7)	.0113(3)	.2682(6)	8.7(.3)
Br2	.4789(5)	.2443(2)	.2637(4)	4.8(.2)	Br5	.2900(5)	–.0115(2)	.2533(5)	5.1(2)
Br3	.3392(6)	.2449(2)	.2759(5)	6.6(.3)	Br6	.4272(6)	–.0328(3)	.2490(6)	7.3(.3)
Br7	.2621(5)	.0860(2)	.0893(4)	4.5(.2)	Br9	.0313(6)	–.1430(2)	.0750(5)	5.6(.2)
Br8	.4690(5)	.0691(2)	–.0646(5)	5.0(.2)	Br10	.2825(5)	–.0965(2)	.1174(5)	5.5(.2)
O1	.342(3)	.123(1)	–.030(2)	2.8(1.0)	O5	.147(2)	–.088(1)	.013(2)	2.5(1.0)
O2	.426(2)	.115(1)	.064(2)	3.2(1.1)	O6	.197(2)	–.145(1)	.016(2)	1.6(.9)
O3	.305	.168	.084	2.6	O7	.072	–.141	–.077	2.6
O4	.499	.154	–.051	2.6	O8	.304	–.097	–.045	2.6
N1	.308(4)	.053(1)	–.046(3)	4.2(1.5)	N5	.123(4)	–.083(2)	.151(3)	5.2(1.6)
N2	.368(3)	.203(1)	–.042(3)	3.4(1.4)	N6	.162(3)	–.080(1)	–.136(3)	2.7(1.3)
N3	.468(3)	.190(1)	.074(2)	1.7(1.1)	N7	.233(3)	–.154(1)	–.122(2)	1.8(1.1)
N4	.399(3)	.042(1)	.068(3)	4.3(1.5)	N8	.175(3)	–.155(1)	.159(3)	4.5(1.5)
C1	.289(4)	.132(2)	–.071(4)	3.5	C27	.125(4)	–.052(2)	.013(4)	3.5
C2	.249(4)	.102(2)	–.101(4)	3.5	C28	.116(4)	–.035(2)	.070(4)	3.5
C3	.182(4)	.109(2)	–.147(4)	3.5	C29	.093(4)	–.001(2)	.064(4)	3.5
C4	.165(4)	.142(2)	–.170(4)	3.5	C30	.086(4)	.018(2)	.004(4)	3.5
C5	.204(4)	.175(2)	–.134(4)	3.5	C31	.103(4)	.001(2)	–.062(4)	3.5
C6	.267(4)	.166(2)	–.094(4)	3.5	C32	.124(4)	–.037(2)	–.054(4)	3.5
C7	.108(4)	.151(2)	–.226(3)	3.5	C33	.068(4)	.058(2)	–.006(4)	3.5
C8	.258(4)	.065(2)	–.084(4)	3.5	C34	.099(4)	–.052(2)	.131(4)	3.5
C9	.301(4)	.201(2)	–.075(4)	3.5	C35	.140(4)	–.051(2)	–.118(4)	3.5
C10	.458(4)	.109(2)	.121(4)	3.5	C36	.237(4)	–.173(2)	.019(4)	3.5
C11	.458(4)	.077(2)	.148(4)	3.5	C37	.255(4)	–.194(2)	.076(4)	3.5
C12	.499(4)	.074(2)	.213(4)	3.5	C38	.289(4)	–.226(2)	.098(3)	3.5
C13	.537(4)	.102(2)	.251(4)	3.5	C39	.321(4)	–.245(2)	.043(4)	3.5
C14	.532(4)	.136(2)	.222(3)	3.5	C40	.317(4)	–.227(2)	–.017(4)	3.5
C15	.498(4)	.142(2)	.159(4)	3.5	C41	.273(4)	–.194(2)	–.030(4)	3.5
C16	.577(4)	.100(2)	.324(4)	3.5	C42	.373(4)	–.277(2)	.043(3)	3.5
C17	.440(4)	.045(2)	.115(4)	3.5	C43	.218(4)	–.185(2)	.151(3)	3.5
C18	.500(4)	.176(2)	.124(4)	3.5	C44	.274(4)	–.183(2)	–.104(3)	3.5
C19	.380(4)	.002(2)	.048(3)	3.5	C45	.141(4)	–.157(2)	.231(4)	3.5
C20	.303(4)	–.004(2)	.023(4)	3.5	C46	.133(4)	–.123(2)	.256(4)	3.5
C21	.308(4)	.011(2)	–.044(4)	3.5	C47	.104(4)	–.094(2)	.235(4)	3.5
C22	.493(4)	.229(2)	.061(4)	3.5	C48	.243(4)	–.151(2)	–.200(4)	3.5
C23	.426(4)	.246(2)	.051(4)	3.5	C49	.247(4)	–.117(2)	–.219(3)	3.5
C24	.398(4)	.242(2)	–.031(3)	3.5	C50	.174(4)	–.092(2)	–.207(4)	3.5
C25	.289	.184	.145	6.5	C51	.058	–.171	–.115	6.5
C26	.533	.173	–.104	6.5	C52	.366	–.085	–.082	6.5

[a] Estimated standard deviations, where applicable, are given in parentheses in units of the least significant digits.

[b] Isotropic thermal parameters, in units of Å^2, are defined by $T = \text{Exp}[-B(\text{iso})(\sin\Theta/\lambda)^2]$.

scale factor, and individual isotropic temperature factors of non-carbon atoms was performed using a locally modified ORFLS[9] program. The function minimized was $\Sigma w\,\Delta F^2$ where w is the weight assigned on the basis of the $|F_0|$ values. Only the 1993 observed reflections were used in the refinement and R-factor calculations, and these were weighted according to the straight-line scheme $w = (660 + 1.33\,|F_0|)^{-1}$, for $|F_0|$ on absolute scale. There was found to be some poor consistency in apparently chemically equivalent bond lengths, and an inspection of the observed and calculated structure factors found some reflections with high ΔF values. Towards the end of the refinement 95 reflections with the highest ΔF values [greater than 80.0 (absolute scale)] were downweighted ($w = 10^{-4}$), resulting in a more internally consistent set of molecular parameters. Because of the inherent crystal disorder and decomposition, discrepancies of this magnitude in the ΔF values are not unexpected.

After several cycles the R-factor was reduced to 0.16. From a difference Fourier synthesis the positions of the remaining four methanol carbon atoms were then determined, all of which were very poorly defined and showed disorder. Each of these carbon atoms was arbitrarily assigned an isotropic temperature factor with $B = 6.5$ Å^2. The best positions for the four carbon and four oxygen atoms of the methanol groups were determined by difference Fourier syntheses, and the atomic coordinates and temperature factors of these eight atoms were held constant for two further least-squares cycles on the positional coordinates, and on those isotropic temperature factors not held constant, of the remaining 74 atoms, at which stage convergence was obtained. The final R-factor was 0.150, with an R_w of 0.159 where $R_w = (\Sigma w\Delta F^2/\Sigma w|F_0|^2)^{1/2}$. A final difference Fourier synthesis was free of detail except for regions of electron density in the vicinity of the methanol groups and some relatively large peaks, up to a maximum of $|2.0|\,e\text{Å}^{-3}$, close to the bromine atoms. The final parameters and their e.s.d.'s are reported in Table II and a Table of the observed and calculated structure factors is available from the Editor upon request.

Description of Structure

The obvious limitations in the accuracy of the data, due to the crystal disorder and decomposition and the limited diffraction pattern which, even with the best crystal, was observable only for Θ less than 40°, are evident in the high R-factor, the large e.s.d.'s of the atomic coordinates and the large differences observed between chemically similar bond distances and angles. It must be emphasized that the structure refinement has been taken to the limit of accuracy allowed by the quality of the data available. Although the structure analysis has not afforded precise geometry it has been more than sufficient to define the overall structural features and thereby resolve the essential question concerning the nature of $LCo_2Br_5\cdot 2CH_3OH$ and the derived compound $LCo_2Br_4\cdot CH_3OH$. The correctness of these gross features is beyond doubt because all the non-hydrogen atoms, except those of the disordered methanol groups, were clearly discernible in the electron density maps and because of the very close similarity (discussed below) of the binuclear cation observed in $LCo_2Br_5\cdot 2CH_3OH$ to that found for isomer *A* of $LCo_2Br_3\cdot 2H_2O$ (structure III), the structure of which has been accurately determined (R 0.074).[3]

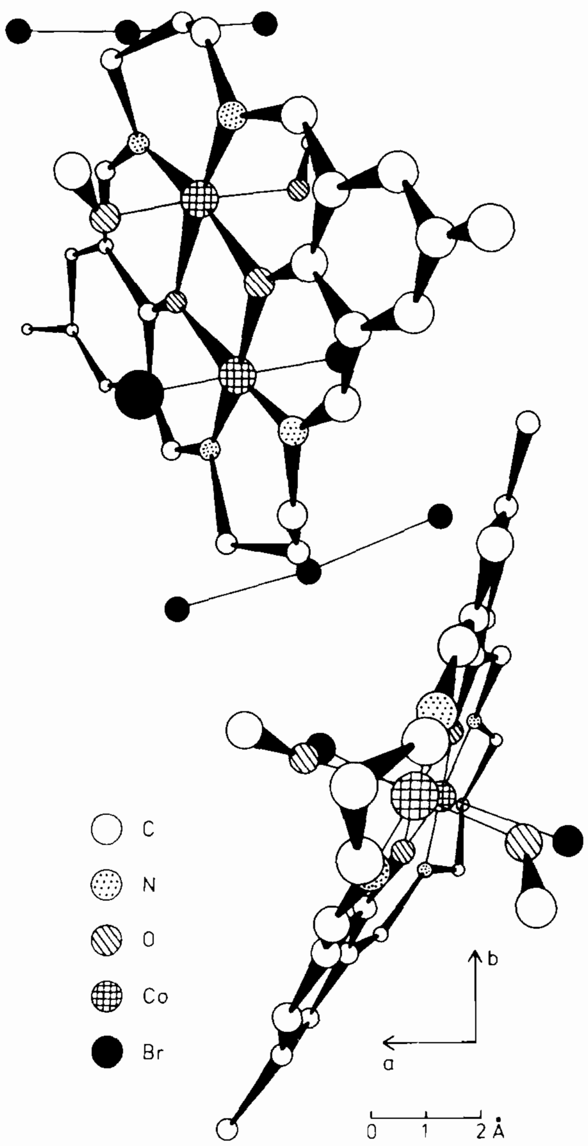


Figure 1. Configuration of the asymmetric unit of $LCo_2Br_5\cdot 2CH_3OH$.

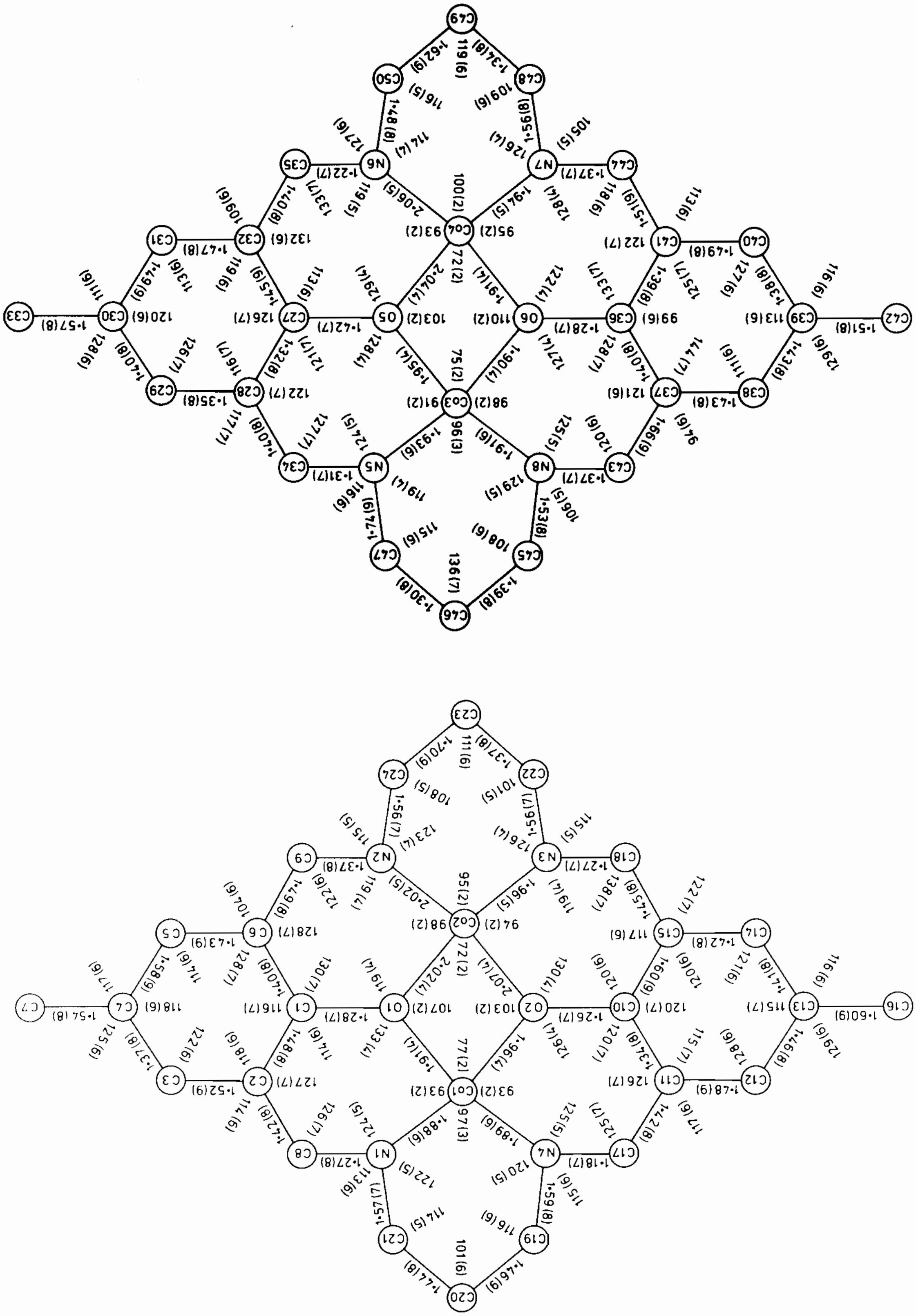


Figure 2a. Numbering of atoms and bond lengths (Å) and angles (Degrees) in the ligand planes of $LCo_2Br_5 \cdot 2CH_3OH$.

The two unique formula units which comprise the asymmetric unit are basically identical, and each consists of a tribromide anion and a discrete binuclear cation of formulation $[LCo(II)Co(III)Br_2(CH_3OH)_2]^+$ (structure V) with Co···Co distances in each of 3.16(1) and 3.12(2) Å. For convenience, in the following discussion the N_2O_2 donor plane around each octahedral cobalt will be referred to as the 'equatorial' plane, and the two coordination sites perpendicular to the N_2O_2 donor plane as the 'apical' positions. The relation between the two complex cations and two tribromide anions within the asymmetric unit is shown in Figure 1.

The overall geometry, numbering of the atoms, interatomic distances, angles, and correlated e.s.d.'s[10] (in parentheses, in units of the least significant digits) are shown for the asymmetric unit; for the ligand planes in Figure 2a, for the 'apical' atoms in Figure 2b, for the N_4O_2 donor sets in Figure 2c, and for the tribromide anions in Figure 2d. The Co–Br distances of 2.41(1), 2.41(2), 2.43(2), and 2.45(2) Å are within the range reported for octahedral Co(III)–Br distances of 2.44,[11] 2.45,[12] and 2.49Å [13] and, in the two isomers of $LCo_2Br_3·2H_2O$,[3] 2.380(4), 2.415(3) and 2.426(3) Å. These distances are all considerably less than the octahedral Co(II)–Br distance of 2.647(5)Å found in isomer *B* of $LCo_2Br_3·2H_2O$. The structure of each of the two unique binuclear cations closely resembles the structure of the binuclear cationic unit $[LCo(II)Co(III)Br_2(H_2O)_2]^+$ in isomer *A* of $LCo_2Br_3·2H_2O$ (structure III).[3] Here the cobalt atoms have been found, in an accurate X-ray study, to be in octahedral environments with the cobalt(III) atom bonded in the 'apical' positions to two bromine atoms and the cobalt(II) atom similarly bonded to two water molecules. By analogy, in the present structure determination, it is proposed that Co1 and Co3 are the trivalent cobalt cations, with each coordinated to two bromine atoms. This is electrostatically favoured over the alternative situation with the two bromine atoms coordinated to the divalent cobalt cation. Although the bond distances between the cobalt atoms and oxygen and nitrogen atoms have large e.s.d.'s, the 'equatorial' Co–O distances about Co1 and Co3 [1.90(4), 1.91(4), 1.95(4), 1.96(4)Å] are generally shorter than those about Co2 and Co4 [1.91(4), 2.02(4), 2.04(4), 2.07(4)Å]. This suggested trend can also be found in the Co–N distances, which about Co1 and Co3 [1.88(6), 1.89(6), 1.91(6), 1.93(6)Å] are shorter than those about Co2 and Co4 [1.94(5), 1.96(5), 2.02(5), 2.06(5)Å]. The suggestion of shorter Co–O and Co–N bonds about the cobalt(III) cation than about the cobalt(II) is in agreement with the results of other structural studies on mixed valence cobalt(II)–cobalt(III) compounds.[3,14,15]

Within the macrocyclic ligands, large differences are observed in bond lengths and angles between appar-

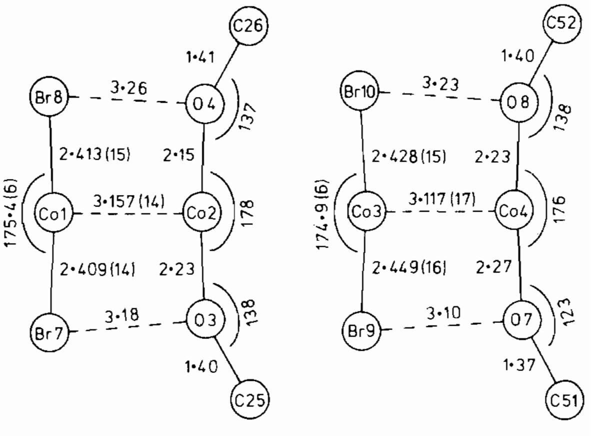


Figure 2b. Numbering of the 'apical' atoms and corresponding interatomic distances (Å) and angles (Degrees) in $LCo_2Br_5·2CH_3OH$.

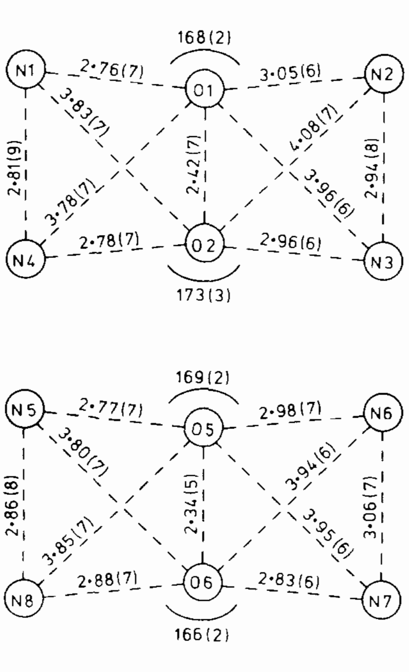


Figure 2c. Some interatomic distances (Å) and angles (Degrees) associated with the N_4O_2 donor sets of $LCo_2Br_5·2CH_3OH$.

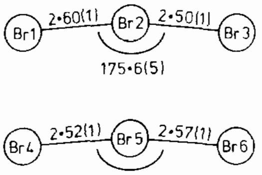


Figure 2d. Numbering of atoms and bond lengths (Å) and angles (Degrees) in the tribromide anions of $LCo_2Br_5·2CH_3OH$.

ently chemically similar atoms. These differences are evidence of the poor accuracy of the structure due to the limitations in the accuracy and extent of the intensity data, as too are the large e.s.d.'s of the bond lengths and angles. There is no evidence for disorder or partial occupancy within the macrocyclic ligands, as was found in the structure of $LCo_2Br_2 \cdot CH_3OH$[3] about the central carbon atom of each diaminopropane residue.

The bond lengths and angles found within the tribromide anions (Figure 2d) indicate that the anions are almost linear, and are slightly asymmetrical. It is presumably the loss of molecular bromine from the tribromide anions which results in the decomposition observed during data collection.

The non-bonded interatomic distances within the N_4O_2 donor sets (Figure 2c) are essentially the same as those found in the structures of the two isomers of $LCo_2Br_3 \cdot 2H_2O$,[3] each of which contains octahedral cobalt(II) and cobalt(III) atoms.

Mean plane equations were calculated by the method of Blow,[16] and each of the four cobalt atoms in the asymmetric unit is found to be effectively within the plane of its N_2O_2 donor set. Adjacent N_2O_2 sets are essentially coplanar. The six carbon atoms and one oxygen atom of each of the four unique phenoxy groups lie on a plane, with dihedral angles of 22.7° and 17.3° between the two phenoxy planes of each of the two unique binuclear units, the ligand in each binuclear unit being bent considerably about the N...O...N axes as seen in Figure 3. This situation is similar to that found in the structure of isomer *A* of $LCo_2Br_3 \cdot 2H_2O$,[3] where the analogous dihedral angle is 21.6°. However in isomer *B* where the analogous dihedral angle is 0.6°, the two phenoxy groups are essentially coplanar with each other and with the $N_2O_2N_2$ donor set. In two other structural determinations on the ligand L, in the complexes $LCo_2Br_2 \cdot CH_3OH$[3] and $LCu_2Cl_2 \cdot 6H_2O$,[2] both of which contain metal cations in square pyramidal environments, the two phenoxy groups are essentially coplanar, the analogous dihedral angles being 0.0° and 4.1° respectively.

The displacements of the central carbon atoms of the diaminopropane residues from the N_2O_2 donor planes are in the same direction as the displacements of the phenoxy group atoms from these planes (Figure 3). The same configuration was observed in the structure of isomer *A* of $LCo_2Br_3 \cdot 2H_2O$.[3]

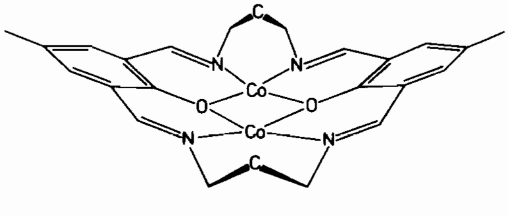


Figure 3. Representation of the macrocyclic ligand geometry in $LCo_2Br_5 \cdot 2CH_3OH$.

Experimental

Preparation of Compounds

$LCo_2Br_2 \cdot CH_3OH$

Solutions of 2-hydroxy-5-methylisophthalaldehyde (10.6 g) and of cobalt bromide hexahydrate (11.0 g) and cobalt acetate tetrahydrate (8.0 g) in the minimum volumes of methanol were mixed, and to the mixture was added 1,3-diaminopropane (5.5 cm^3). The resulting solution was heated under reflux for 2 hours, at which stage methanol was removed by boiling at atmospheric pressure until precipitation had just commenced. Upon cooling, a brown solid was obtained. The crude solid was recrystallized from hot methanol yielding dark brown crystals which were collected, washed with a little methanol, and dried in vacuum over silica gel at room temperature. *Anal.* Calcd. for $C_{25}H_{30}N_4Co_2Br_2O_3$: C, 42.2; H, 4.2; N, 7.9; Co, 16.5; Br, 22.4. Found: C, 42.3; H, 4.4; N, 7.8; Co, 16.3; Br, 22.8.

$LCo_2Br_2 \cdot H_2O$

Recrystallization of $LCo_2Br_2 \cdot CH_3OH$ from aqueous solution yielded the pale brown microcrystalline complex $LCo_2Br_2 \cdot H_2O$. The solid was dried in vacuum over silica gel at room temperature. *Anal.* Calcd. for $C_{24}H_{28}N_4Co_2Br_2O_3$: C, 41.3; H, 4.0; N, 8.0; Co, 16.9; Br, 22.9. Found: C, 41.0; H, 4.1; N, 8.1; Co, 16.7; Br, 22.8.

$LCo_2Br_3 \cdot H_2O$

To the red solution of $LCo_2Br_2 \cdot CH_3OH$ (1.5 g, 0.002 mol) in methanol at room temperature (500 cm^3) was added bromine (0.1 cm^3, 0.002 mol). The resulting black solution was boiled at atmospheric pressure to remove methanol, until precipitation had just commenced. Upon cooling, a black crystalline solid was obtained, washed with a little methanol, and dried at atmospheric pressure over silica gel at room temperature. *Anal.* Calcd. for $C_{24}H_{28}N_4Co_2Br_3O_3$: C, 37.0; H, 3.6; N, 7.2; Co, 15.1; Br, 30.8. Found: C, 37.0; H, 3.6; N, 7.3; Co, 14.8; Br, 30.9.

$LCo_2Br_4 \cdot CH_3OH$

Two different methods of preparation were found to yield this compound. Neither method could be adapted to yield crystals suitable for X-ray diffraction analysis.

Method a: To a solution of $LCo_2Br_2 \cdot CH_3OH$ (1.5 g, 0.002 mol) in methanol (500 cm^3) at room temperature was added bromine (0.1 cm^3, 0.002 mol). The resulting black solution was evaporated to approximately 100 cm^3 under vacuum at room temperature, and the black crystalline precipitate collected, washed with a little methanol, and dried at 60° C under vacuum for 14 hours to remove any excess bromine present in the form of tribromide anions. *Anal.* Calcd. for $C_{25}H_{30}N_4Co_2Br_4O_3$: C, 34.4; H, 3.5; N, 6.4; Co, 13.5; Br, 36.7. Found: C, 34.3; H, 3.4; N, 6.5; Co, 13.2; Br, 36.5.

Method b: To a solution of $LCo_2Br_2 \cdot CH_3OH$ (1 g) in methanol at room temperature was added excess bromine (4 cm^3). The resultant black solution was allowed to stand at room temperature for 15 minutes, during which a black, non-crystalline solid separated. This was collected and washed with a little methanol (if this material was dried at room temperature and atmospheric pressure for a short time over silica gel, a distinct odour of molecular bromine was evident from the dried solid. This solid was analysed almost immediately and found to approximate the formulation $LCo_2Br_8 \cdot 4CH_3OH$. *Anal.* Calcd. for $C_{28}H_{42}N_4Co_2Br_8O_6$: C, 26.1; H, 3.3; N, 4.4; Co, 9.2; Br, 49.6. Found: C, 25.0; H, 2.8; N, 4.2; Co, 9.0; Br, 49.1). The black solid was then dried at 60° C under vacuum for 20 hours, during which a large amount of molecular bromine was removed from the compound, which was then analysed. *Anal.* Calcd. for $C_{25}H_{30}N_4Co_2Br_4O_3$: C, 34.4; H, 3.5; N, 6.4; Co, 13.5; Br, 36.7. Found: C, 34.0; H, 3.3; N, 6.3; Co, 13.2; Br, 37.0.

$LCo_2Br_5 \cdot 2CH_3OH$

To a solution of $LCo_2Br_2 \cdot CH_3OH$ (0.5 g) in methanol at room temperature was added bromine (0.05 cm^3). Methanol was removed under vacuum at room temperature until precipitation had just commenced. The solution was left standing overnight, during which a black, crystalline solid precipitated. The solid was washed with a little methanol and dried at room temperature and atmospheric pressure over silica gel. *Anal.* Calcd. for $C_{26}H_{34}N_4Co_2Br_5O_4$: C, 31.7; H, 3.5; N, 5.7; Co, 12.0; Br, 40.6. Found: C, 31.7; H, 3.4; N, 5.5; Co, 11.9; Br, 40.8.

$(LH)CoBr_6 \cdot 2H_2O$ and $(LH_4)Br_6$ from $LCo_2Br_2 \cdot CH_3OH$

A solution in methanol (350 cm^3) of $LCo_2Br_2 \cdot CH_3OH$ (1 g) and excess bromine (1 cm^3) was heated at the boiling point for 10 minutes and then allowed to cool during which a black crystalline solid separated. The crystals were collected, washed with methanol and dried over silica gel at room temperature, yielding $(LH)CoBr_6 \cdot 2H_2O$. *Anal.* Calcd. for $C_{24}H_{31}N_4CoBr_6O_4$: C, 29.5; H, 3.2; N, 5.7; Co, 6.0; Br, 49.0. Found: C, 29.7; H, 3.2; N, 5.5; Co, 6.1; Br, 49.4.

The red filtrate from the above preparation of $(LH)CoBr_6 \cdot 2H_2O$ was boiled down to 50 cm^3 and upon cooling $(LH_4)Br_6$ separated as red needles. The crystals were collected, washed with a little methanol, and dried in vacuum at room temperature. The tribromide appeared to be very much more stable towards loss of bromine than in the tribromide compounds described above. *Anal.* Calcd. for $C_{24}H_{30}N_4Br_6O_2$: C, 32.5; H, 3.4; N, 6.3; Br, 54.1. Found: C, 32.2; H, 3.4; N, 6.4; Br, 54.7.

LH_4^{2+} salts from direct condensation of diamine and dialdehyde

To a solution of 1,3-diaminopropane (0.12 g) and 2-hydroxy-5-methylisophthalaldehyde (0.27 g) in ethanol (10 cm^3) was added concentrated hydrobromic acid (0.2 cm^3 of 48% solution) and the mixture was boiled to give a clear red solution. On cooling the solution deposited an orange solid which, after being washed with ethanol and dried under vacuum, showed an ir spectrum which was a composite of the patterns shown by $(LH_4)(Br_3)_2$ and the hydrobromide of 1,3-diaminopropane.

Concentrated hydrobromic acid (0.2 cm^3 of 48% solution) was added to a solution of 1,3-diaminopropane (0.12 g) and 2-hydroxy-5-methylisophthalaldehyde (0.27 g) in methanol (40 cm^3) and the mixture heated to boiling yielding a clear red solution. The solution was cooled to room temperature and bromine (1 cm^3) was added, whereupon $(LH_4)(Br_3)_2$ separated immediately as an orange solid which, after it had been washed with methanol and dried under vacuum, showed an ir spectrum identical to that of the analytically pure material above.

Physical Measurements

The infrared, diffuse reflectance and solution spectra were recorded on a Perkin–Elmer 457 grating spectrophotometer, a Beckman DK-2A spectrophotometer and a Hitachi EPS-3T spectrophotometer respectively. Magnetic susceptibilities over the temperature range 100–300° K were measured by the Gouy method for all compounds except $LCo_2Br_2 \cdot H_2O$, $LCo_2Br_5 \cdot 2CH_3OH$, $LCo_2Br_8 \cdot 4CH_3OH$ and $(LH)CoBr_6 \cdot 2H_2O$; in these cases susceptibilities were measured at room temperature only on a PAR vibrating sample magnetometer, model 155. Fresh mercury tetrathiocyanatocobaltate(II) was used as calibrant.

Analyses

C, H, N, Co (as an ash) and Br were determined by the Australian Microanalytical Service, Melbourne.

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