

Synthesis and Spectroscopic Studies of Cobalt(III) Complexes of the Chiral Pendant-arm Macrocyclic Ligand *N,N',N''*-Tris[(2*S*)-2-hydroxypropyl]-1,4,7-triazacyclononane (H_3L); Crystal Structure of the Hydrogen-bridged Dimer $[CoLH_3LCo][PF_6]_3$

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The preparation of the chiral macrocyclic ligand *N,N',N''*-tris[(2*S*)-2-hydroxypropyl]-1,4,7-triazacyclononane (H_3L) by reaction of (*S*)-propylene oxide with 1,4,7-triazacyclononane is described. The ligand forms a complex with Co^{III} whose spectroscopic properties are markedly pH dependent. The crystal structure of the $[PF_6]^-$ salt of the principal basic form of the complex has been determined and shows that the compound is a dimer, $[CoLH_3LCo][PF_6]_3$. The spectroscopic properties, including the circular dichroism, of the complex in neutral, acidic and basic non-aqueous media are discussed.

The 'small' macrocycle 1,4,7-triazacyclononane (tacn) has a rich chemistry. Unlike the more familiar tetra-aza macrocyclic ligands, such as 1,4,8,11-tetra-azacyclotetradecane (cyclam), tacn is too small to form equatorial complexes with transition-metal ions but must co-ordinate facially giving bis complexes such as $[Ni(tacn)_2]^{2+}$ which have a sandwich structure¹ or mono complexes such as $[Mo(tacn)(CO)_3]$ with a piano-stool structure.² A variety of ligands based on tacn have been prepared. These include the tris-N-methylated derivative *N,N',N''*-trimethyl-1,4,7-triazacyclononane³ and the C-methylated analogue (2*R*)-2-methyl-1,4,7-triazacyclononane [(*R*)-mtacn].⁴ It has also been used to prepare several pendant-arm ligands; the arms include $-CH_2CO_2H$,⁵ $-CH_2CH_2NH_2$ (taetacn),⁶ $-CH_2CH_2OH$,⁷ and (2*S*)- $CH_2CH(Me)OH$.⁸ Both the last two have the potential to be less than sexidentate and also to exhibit protonation-deprotonation equilibria at the alcoholic OH groups. The last (H_3L) has the additional advantages of chirality and of having a convenient n.m.r. 'tag' in the methyl group. The analogous pendant-arm macrocycle based on cyclam and having four hydroxyethyl arms has recently been prepared and the crystal structure of its nickel(II) complex reported.⁹ Equilibrium constants for the complexes of Cu^{2+} and Zn^{2+} with the CH_2CH_2OH derivative (thetacn) have been reported⁷ but, apart from our own work,¹⁰ no compounds with that ligand have been isolated.

We have reported the synthesis of $[Co(H_3L)Cl_3]$ in a preliminary communication.⁸ The complex exhibits remarkable acid-base equilibria in aqueous solution. It is stable from pH 1 to 13 but has quite different colours, electronic absorption, circular dichroism (c.d.), and ¹H n.m.r. spectra at the acidic and basic ends of this range. In an attempt to understand this behaviour, and to help interpret the optical activity of the complexes, we have determined the crystal structure of the $[PF_6]^-$ salt and investigated the spectra and reactions of this complex in non-aqueous solution.

Experimental

The ligands tacn and thetacn were prepared by literature methods.^{7,11}

Synthesis of $H_3L \cdot HCl$.—A solution of tacn in ethanol was prepared by dissolving tacn·3HCl (1.35 g, 0.006 mol) and

NaOH (0.72 g, 0.018 mol) in water (1 cm³), adding ethanol (5 cm³) and refrigerating overnight. The solution was filtered to remove NaCl, cooled in ice, and ice-cold (*S*)(-)-propylene oxide (1 g, 0.017 mol) was slowly added. The addition was sufficiently slow to ensure that none of the very volatile epoxide was lost during the addition. The mixture was left in a stoppered flask for 24 h (this is essential to allow the reaction to proceed to completion) after which the ethanol and water were removed to produce an oil containing traces of NaCl. The oil was purified by dissolving in the minimum volume of isopropyl alcohol, filtration, and removal of solvent. Yield of $H_3L \cdot HCl$ 1.29 g (71%) (Found: C, 53.1; H, 9.7; N, 12.4. Calc. for $C_{15}H_{33}N_3O_3 \cdot HCl$: C, 53.0; H, 9.8; N, 12.4%). N.m.r.: ¹H (CDCl₃), δ 3.9 (m, 3 H, CH), 3.4 (m, 1 H, NH), 2.4–2.9 (m, 18 H, CH₂), and 1.1 (d, 9 H, CH₃). *m/e* = 304 ($[H_4L]^+$).

Synthesis of $[CoLH_3LCo]Cl_3$.—To a solution of $CoCl_2 \cdot 6H_2O$ (0.24 g, 0.01 mol) in water (10 cm³) was added a second solution of $H_3L \cdot HCl$ (0.34 g, 0.01 mol) in water (5 cm³). Hydrogen peroxide (2 cm³ of 30 vol.) solution was then added and the mixture raised to 70 °C for 30 min to produce a purple solution which contains a mixture of the acid and basic forms of the cobalt(III) complex. If this solution is taken to dryness and the salt analysed the analysis corresponds approximately to equimolar quantities of the acid $[Co(H_3L)Cl_3]$ and the basic $[CoLH_3LCo]Cl_3$ forms of the complex. The best method of purification was as follows. The complex was converted into the purple basic form by addition of NaOH solution, solvent was removed, the residue extracted into ethanol and filtered, and the ethanol removed. Drying the resultant powder at 100 °C for 1 h produced 0.35 g (74%) of the chloride salt (Found: C, 41.7; H, 7.6; Cl, 13.2; N, 9.8. Calc. for $C_{30}H_{63}Cl_3Co_2N_6O_6$: C, 43.5; H, 7.7; Cl, 12.8; N, 10.2%).

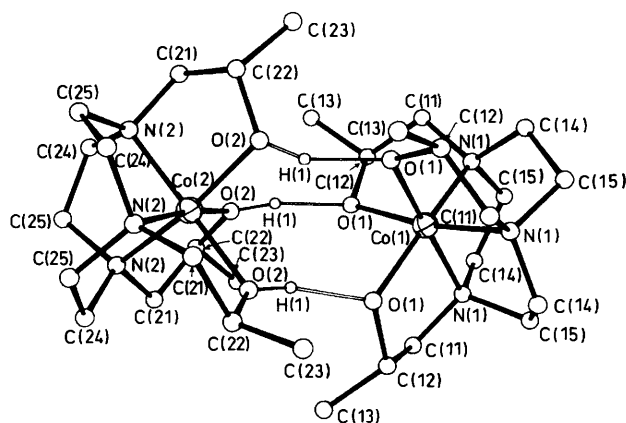
Synthesis of $[CoLH_3LCo][PF_6]_3$.—To $[CoLH_3LCo]Cl_3$ (0.2 g) in water (2 cm³) was added an aqueous solution (1 cm³) containing an excess of $[NH_4][PF_6]$. The precipitate, which formed immediately, was filtered off and washed with water before being air dried. The precipitate was washed with MeCN to remove a minor pink contaminant and recrystallised from dimethylformamide (dmf) to produce small truncated pyramidal blue-purple crystals (0.33 g, 88%) (Found: C, 30.8; H, 5.7; N, 7.3; P, 8.1. Calc. for $C_{30}H_{63}Co_2F_{18}N_6O_6P_3$: C, 31.2; H, 5.5; N, 7.3; P, 8.0%). A crystal of dimensions 0.3 × 0.32 × 0.3 mm was selected for X-ray structure analysis.

Table 1. Experimental data for the crystallographic study

Molecular formula	$C_{30}H_{63}Co_2F_{18}N_6O_6P_3$
<i>M</i>	1 156.62
Crystal system	Cubic
Space group	$P2_13$ (no. 198 T^4)
<i>a</i> /Å	16.277(3)
<i>U</i> /Å ³	4 312(1)
<i>Z</i>	4
<i>D_c</i> /g cm ³	1.78
<i>F</i> (000)	2 376
μ (Mo- <i>K_α</i>)/cm ⁻¹	10.0
<i>T</i> /K	298
Crystal size/mm	0.3 × 0.32 × 0.3
Scan mode	θ—2θ
2θ range/°	4 ≤ 2θ ≤ 50
Standards	$\bar{7} 3 2, \bar{8} 0 \bar{8}$
Measured every	2 h
Decay factor	1.2% in 10 000
Total no. of reflections	4 867
No. independent	1 704
No. used in refinement	950
Observability criterion, <i>n</i> in $I > n\sigma(I)$	2.5
No. of refined parameters	152 each cycle
<i>R</i> *	0.038
<i>R</i> '*	0.035
Largest remaining feature in electron-density map/e Å ⁻³	+0.30 (max.), -0.26 (min.)

$$* R = \frac{\sum |F_o| - |F_c|}{\sum |F_o|}, R' = \left[\frac{\sum w(|F_o| - |F_c|)^2}{\sum w F_o^2} \right]^{1/2}$$

Crystal Structure Determination.—Details of the data-collection procedures and structural refinements are given in Table 1. Crystals of $[CoLH_3LCo][PF_6]_3$ grew as well formed truncated pyramids. Data were collected at ambient temperature on an Enraf-Nonius CAD4F automated diffractometer with graphite-monochromated *X*-radiation ($\lambda = 0.710 69$ Å). The unit-cell length *a* was determined by refinement of the setting angles ($\theta \geq 12^\circ$) of 25 reflections. Standards were measured every 2 h during data collection and no significant decay was observed. Systematic absences were consistent with the cubic space groups $P2_13$ or $P4_232$. Laue symmetry indicated that the point group was 23 and therefore that the correct space group was $P2_13$. The structure was solved by direct methods (MITHRIL¹²) and subsequent refinement by full-matrix least squares. The structure is pseudo-centrosymmetric, with systematic weaknesses in reflections $0kl$, $k = 2n + 1$ (and cyclic permutations) corresponding to the space group $Pa\bar{3}$. Anisotropic thermal parameters were used for all non-H atoms. Hydrogen atoms were included at fixed calculated positions (C–H 1.073 Å) with fixed isotropic ($U = 0.05$ Å²) thermal parameters, except for the O–H hydrogen which was located in a Fourier difference map. The $[PF_6]^-$ group, at *ca.* 0.5, 0.5, 0.5 (a site of $\bar{3}$ symmetry in $Pa\bar{3}$), was disordered and the roughly spherical electron density was modelled by two sets of F atoms with occupancies 0.667 and 0.333. Refinement converged at $R(R') = 0.038$ (0.035). The correctness of the chosen enantiomer was confirmed by refining the coefficient of the imaginary component of the anomalous scattering,¹³ η [0.8(2)]. In addition refinement using the inverted configuration resulted in significantly higher residuals $R(R')$ of 0.43 (0.041). The function minimised was $\sum w(|F_o| - |F_c|)^2$ with the weighting function $w = [\sigma^2(F_o)]^{-1}$ used and judged satisfactory. Neutral atom scattering factors were taken from ref. 14, with corrections applied for anomalous dispersion. All calculations were carried out on a Gould-SEL 32/27 mini-computer using the GX suit of programs.¹⁵

**Figure 1.** View of the $[CoLH_3LCo]^{3+}$ cation

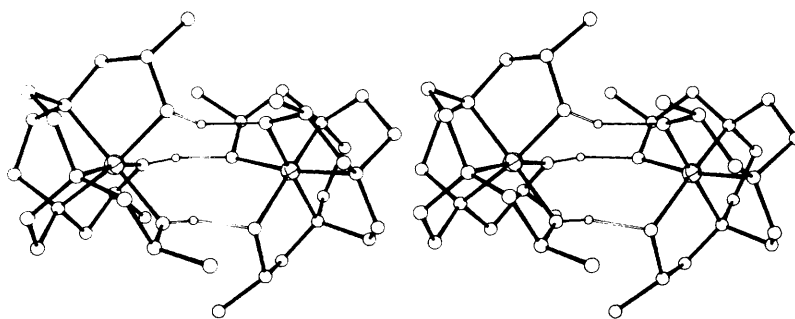
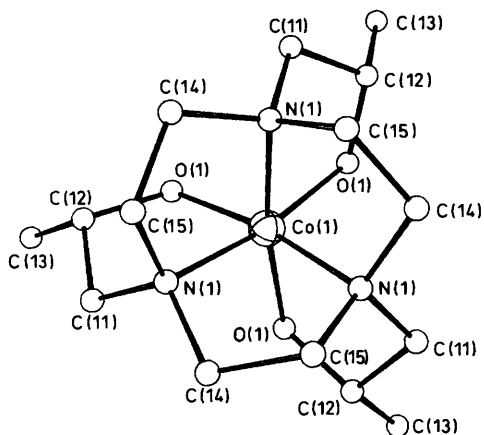
Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates, thermal parameters and remaining bond lengths and angles.

Results and Discussion

The ligand H_3L is prepared by treating (*S*)-propylene oxide with a solution of free tacn. Attack is at the less hindered carbon atom of the epoxide and so the absolute configuration at the C–Me carbon is conserved. The attack is shown to be 100% regiospecific by the n.m.r. spectrum of the ligand and the structure and chirality, *S*, of H_3L is confirmed by the crystal structure of the cobalt(III) complex (see below). The ligand is obtained as the mono-HCl adduct (as is the analogous thctacn⁷); the parent ion in the mass spectrum has a *m/e* of 304 corresponding to $[H_4L]^+$.

Synthesis of Cobalt(III) Complexes of H_3L .—Reaction of equimolar quantities of H_3L and $CoCl_2 \cdot 6H_2O$ followed by H_2O_2 oxidation produces a red-purple solution which can be separated on cation SP-Sephadex ion-exchange resin into two fractions. The first eluted fraction is blue-purple and is stable in strongly basic solution (the 'basic form' of the complex); the second eluted form is red and is stable in acidic solution (the 'acid form' of the complex). The two forms can be interconverted in aqueous solution by the addition of acid or base. Discussion of their spectroscopic properties will be deferred until the crystal structure and properties of the $[PF_6]^-$ salt have been described. The $[PF_6]^-$ salt is precipitated from aqueous solution by addition of $[NH_4][PF_6]$ and recrystallised from dmf to give crystals of crystallographic quality. Analysis shows that there are 1.5 $[PF_6]^-$ ions per $Co(H_3L)$ unit.

Crystal Structure of $[CoLH_3LCo][PF_6]_3$.—The most striking aspect of the structure is that the molecule is a dimer (Figure 1, Tables 2 and 3). One species CoL [designated Co(1)] has lost three protons and is joined to a $CoLH_3$ ion [designated Co(2)] by three asymmetric hydrogen bonds connecting the six oxygen atoms. A stereoscopic view of the dimer is provided in Figure 2. A view of one of the half units looking down the Co–Co axis is shown in Figure 3 and illustrates the C_3 symmetry of the complex. The absolute configurations of the half units (which are necessarily the same) were shown to be Δ (as defined by the exocyclic chelate rings). In both half units the ligators are twisted from the ideal octahedral positions. The upper donor set of the cobalt ion (N_3) is twisted in the clockwise direction relative to the lower set (O_3) when viewed down the C_3 axis (Figure 3). The twist is 10.2° for the Co(1) ion and 11.2°

Figure 2. Stereoview of the $[\text{CoLH}_3\text{LCo}]^{3+}$ cationFigure 3. View of one half of the $[\text{CoLH}_3\text{LCo}]^{3+}$ cation (*i.e.* the CoL unit) looking down the C_3 axis

for the Co(2) ion. In terms of the definition proposed in refs. 16 and 17, the angle is respectively $+49.8$ and $+48.8^\circ$ for the absolute configuration of the Co(1) and Co(2) half units. Thus both the absolute configuration and the sense of twist of Δ - $[\text{CoLH}_3\text{LCo}][\text{PF}_6]_3$ are the same as those of Δ - $[\text{Co}(\text{en})_3]^{3+}$ (en = ethylenediamine).¹⁶ The geometries of the two half units of Δ - $[\text{CoLH}_3\text{LCo}][\text{PF}_6]_3$ are very similar. In addition to the twist angles mentioned above the extent of trigonal compression and expansion is very similar. In both halves of the dimer the angle between the C_3 axis and the Co–N bond is less than half the tetrahedral angle indicating trigonal elongation, while that between the C_3 axis and the Co–O bond is greater than half the tetrahedral angle indicating trigonal compression. Thus the ‘tacn’ half of the molecule is trigonally elongated while the ‘hydroxypropyl’ part is trigonally compressed. The endocyclic chelate rings are all in the λ conformation while the exocyclic chelate rings adopt the δ conformation with equatorial methyl groups. The overall chirality description of the complex (using the nomenclature of Taylor *et al.*¹⁸) is therefore $[\Delta(\lambda\delta)]$. Table 4 gives a comparison of the relevant geometric parameters for Δ - $[\text{CoLH}_3\text{LCo}][\text{PF}_6]_3$, Δ - $[\text{Co}(\text{taetacn})]^{3+}$,¹⁸ and $[\text{Co}\{\text{(R)-mtacn}\}]^{3+}$.¹⁹ The bridging hydrogen atoms were directly located. The $\text{O}(1)\cdots\text{O}(2)$ distance is $2.481(8)$ Å and the $\text{O}(1)\cdots\text{H}(1)\cdots\text{O}(2)$ angle is $157.7(6.3)^\circ$.

Spectroscopic Properties of $[\text{CoLH}_3\text{LCo}][\text{PF}_6]_3$.—The two CoL units are not crystallographically equivalent nor are they chemically equivalent because of the asymmetric hydrogen bridge. In solution on the n.m.r. time-scale, however, the hydrogen bridge is evidently symmetric. With this difference, the ^1H n.m.r. spectrum of $[\text{CoLH}_3\text{LCo}][\text{PF}_6]_3$ in CD_3CN is compatible with the solid-state structure. The bridging

Table 2. Final positional parameters (fractional co-ordinates) with estimated standard deviations for the complex $[\text{CoLH}_3\text{LCo}][\text{PF}_6]_3$ in parentheses

Atom	X/a	Y/b	Z/c
Co(1)	−0.081 26(6)	−0.081 26	−0.081 26
Co(2)	0.083 31(7)	0.083 31	0.083 31
C(11)	−0.218 8(5)	0.016 6(5)	−0.072 4(5)
C(12)	−0.200 3(5)	0.002 3(5)	0.016 8(5)
C(13)	−0.209 6(5)	0.079 0(5)	0.067 3(5)
C(14)	−0.184 1(5)	−0.040 4(6)	−0.208 6(5)
C(15)	−0.247 7(5)	−0.128 4(5)	−0.103 7(5)
C(21)	0.224 2(5)	0.061 1(5)	−0.005 0(6)
C(22)	0.016 4(5)	0.199 4(5)	−0.028 6(5)
C(23)	0.212 3(5)	−0.079 2(6)	−0.058 2(5)
C(24)	0.198 5(5)	0.202 8(5)	0.040 1(6)
C(25)	0.247 3(6)	0.098 2(6)	0.140 4(6)
N(1)	−0.191 9(4)	−0.055 4(4)	−0.118 2(4)
N(2)	0.197 7(4)	0.114 5(4)	0.064 4(4)
O(1)	−0.116 9(3)	−0.030 4(3)	0.020 4(3)
O(2)	0.042 2(4)	0.116 5(4)	−0.023 5(4)
P(1)	0.305 1(2)	0.3051	0.3051
P(2)	−0.301 17(19)	−0.301 17	−0.301 17
P(3)	0.497 3(4)	0.4973	0.4973
F(1)	0.332 9(4)	0.283 2(4)	0.395 6(4)
F(2)	0.215 0(4)	0.276 2(5)	0.326 7(5)
F(3)	−0.394 5(4)	−0.321 0(4)	−0.283 5(4)
F(4)	−0.205 9(4)	−0.281 5(4)	−0.316 5(4)
F(5A)	0.444 9(14)	0.545 4(16)	0.560 2(17)
F(5B)	0.573 7(19)	0.505 4(23)	0.558 0(25)
F(6A)	0.466(3)	0.432(2)	0.552(2)
F(6B)	0.483(3)	0.418(3)	0.451(5)
H(1)	−0.051(4)	0.024(4)	0.072(4)

Table 3. Selected bond lengths (Å) and angles ($^\circ$) for the complex $[\text{CoLH}_3\text{LCo}][\text{PF}_6]_3$

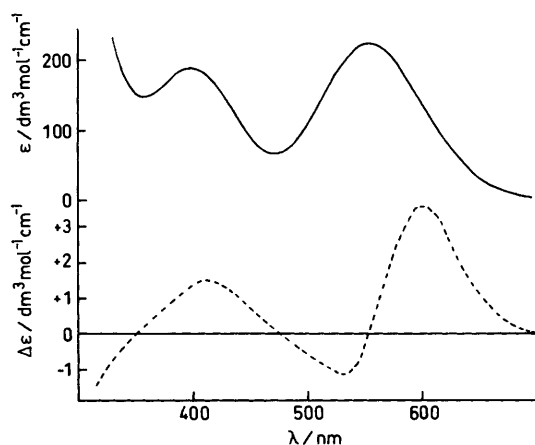
Co(1)–N(1)	1.944(7)	Co(2)–N(2)	1.954(8)
Co(1)–O(1)	1.939(6)	Co(2)–O(2)	1.939(7)
N(1)–C(11)	1.456(11)	N(2)–C(21)	1.490(12)
C(11)–C(12)	1.501(12)	C(21)–C(22)	1.553(12)
O(1)–C(12)	1.461(9)	O(2)–C(22)	1.416(11)
C(12)–C(13)	1.501(12)	C(22)–C(23)	1.482(12)
N(1)–C(15)	1.513(11)	N(2)–C(25)	1.501(12)
C(14)–C(15)	1.514(13)	C(24)–C(25)	1.521(14)
N(1)–C(14)	1.497(12)	N(2)–C(24)	1.492(12)
O(1)–H(1)	1.62(7)	O(2)–H(1)	0.90(7)
N(1)–Co(1)–N(1)	88.9(3)	N(2)–Co(2)–N(2)	86.7(3)
O(1)–Co(1)–O(1)	91.0(3)	O(2)–Co(2)–O(2)	92.1(3)
N(1)–Co(1)–O(1)	84.0(3)	N(2)–Co(2)–O(2)	85.0(3)

hydrogens are seen as a singlet at δ 14.60, the methyl resonance is a doublet [$^3J(\text{H}–\text{H}) = 6.21$ Hz] at 1.49, the methine resonance is a complex multiplet at 4.6, and the remaining six

Table 4. A comparison of selected geometrical parameters of $[\text{CoLH}_3\text{LCo}][\text{PF}_6]_3$ with those of related complexes

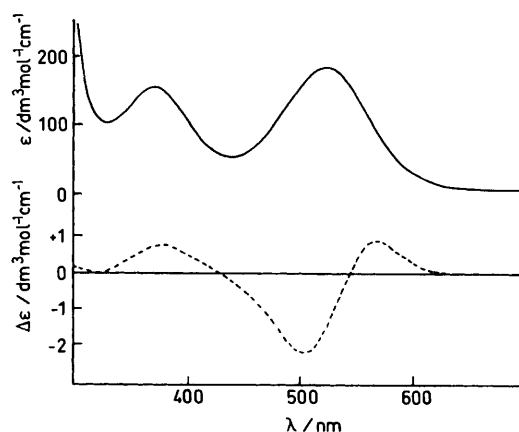
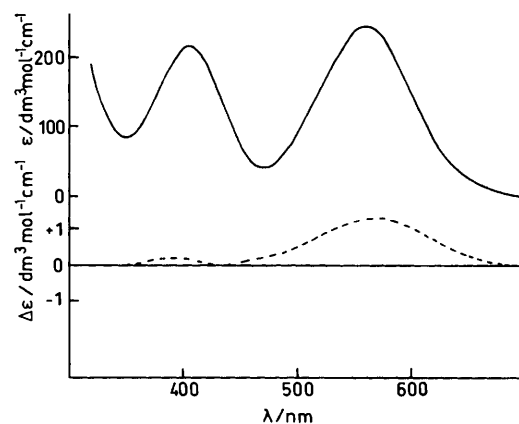
Complex	Co-N/Å	$\theta_1^a/^\circ$	$\theta_2^b/^\circ$	$\omega^c/^\circ$	Ref.
$\Delta\text{-}[\text{CoLH}_3\text{LCo}]^{3+}$ [Co(1) unit]	1.944	54.0	55.5	+49.8	This work
[Co(2) unit]	1.954	52.5	56.2	+48.8	This work
$\Delta\text{-}[\text{Co}(\text{taetacn})]^{3+}$	1.963	52.9	55.4	+48.9	18
$[\text{Co}\{\text{(R)}(\text{mtacn})\}]^{3+}$	1.974	51.3		+52.4	19
Regular octahedron		54.74	54.74	60.0	

^a The polar angle between the C_3 axis and the Co-N(tacn) bond. ^b The polar angle between the C_3 axis and the Co-OH or Co-NH₂ bond. ^c The twist angle between the two sets of ligands (see text and ref. 16).

**Figure 4.** Absorption (upper) and c.d. (lower) spectra of a 10^{-2} mol dm^{-3} solution of $[\text{CoLH}_3\text{LCo}][\text{PF}_6]_3$ in MeCN

methylene resonances (which are all non-equivalent) are seen between 2.5 and 3.8. Addition of a drop of $\text{CF}_3\text{CO}_2\text{H}$ changes the colour of the solution from blue to pink. The bridging proton resonances are lost, the single methyl resonance shifts slightly to δ 1.38 [d, $^3J(\text{H-H}) = 6.26$ Hz], the methine resonance moves downfield to 4.8, and the remaining six methylene resonances are found between 2.7 and 4.1. Thus addition of acid in non-aqueous media leads to cleavage of the hydrogen-bridged dimer and the formation of the $[\text{Co}(\text{H}_3\text{L})]^{3+}$ cation.

The absorption and c.d. spectra of $[\text{CoLH}_3\text{LCo}][\text{PF}_6]_3$ and $[\text{Co}(\text{H}_3\text{L})]^{3+}$ in MeCN solution (produced as described above by addition of $\text{CF}_3\text{CO}_2\text{H}$) are shown in Figures 4 and 5. The spectra of $[\text{CoLH}_3\text{LCo}][\text{PF}_6]_3$ in MeCN are identical to those obtained from crystals of $[\text{CoLH}_3\text{LCo}][\text{PF}_6]_3$ dispersed in a KCl disc and confirm that the structure of the complex in the non-aqueous solvent is identical to that in the crystal on the time-scale of electronic transitions. Addition of methanolic NaOH to a dmf solution of $[\text{CoLH}_3\text{LCo}][\text{PF}_6]_3$ produces the spectra shown in Figure 6. We have no independent evidence for the nature of the species produced but it seems reasonable to assume that we have deprotonated the H_3L ligand entirely to give $[\text{CoL}]$. The ligand-field parameters for the three species (given in the order acidic MeCN solution, neutral MeCN solution, and basic dmf solution) are: $10Dq/\text{cm}^{-1} = 17\,225$, $16\,230$, and $15\,850$; $B/\text{cm}^{-1} = 480$, 440 , and 420 . Thus the ligand-field splitting decreases and the extent of covalency increases as the OH groups are progressively deprotonated. It is quite clear from Figures 4–6 that the c.d. spectrum

**Figure 5.** Absorption (upper) and c.d. (lower) spectra of a 10^{-2} mol dm^{-3} solution of $[\text{CoLH}_3\text{LCo}][\text{PF}_6]_3$ in MeCN with the addition of two drops of $\text{CF}_3\text{CO}_2\text{H}$ **Figure 6.** Absorption (upper) and c.d. (lower) spectra of a 10^{-2} mol dm^{-3} solution of $[\text{CoLH}_3\text{LCo}][\text{PF}_6]_3$ in dmf with the addition of an excess of methanolic NaOH solution

of $[\text{CoLH}_3\text{LCo}]^{3+}$ is not the sum of the c.d. spectra of $[\text{Co}(\text{H}_3\text{L})]^{3+}$ and $[\text{CoL}]$. Presumably the hydrogen bridge, which persists in solution, imposes a geometry on the two halves of the dimer which is slightly different from the geometries of free $[\text{Co}(\text{H}_3\text{L})]^{3+}$ and $[\text{CoL}]$.

The C.D. Spectra.—The visible absorption spectrum of a cobalt(III) complex of C_3 symmetry consists of two broad bands: $^1A(^1A_{1g}) \rightarrow ^1(A,E)(^1T_{1g})$ at lower and $^1A(^1A_{1g}) \rightarrow ^1(A,E)(^1T_{2g})$ at higher energy, where the octahedral symmetry labels are given in parentheses. Within each band the $^1A \rightarrow ^1A$ and $^1A \rightarrow ^1E$ transitions must have oppositely signed c.d. Unfortunately there is no easy method of deciding the energy order of the 1A and 1E components produced by the C_3 perturbation of the octahedral $^1T_{1g}$ and $^1T_{2g}$ states. The only unambiguous method, polarised c.d. spectroscopy, is not available in this case since the complex $[\text{CoLH}_3\text{LCo}][\text{PF}_6]_3$ crystallises in a cubic space group. An empirical rule,¹⁶ derived from the c.d. spectra of a variety of complexes whose structures are known, is that an elongation of the complex along the trigonal axis results in the $^1A(^1T_{1g})$ component having lower energy than the $^1E(^1T_{1g})$ component and *vice versa*. This rule has been proposed from considering the spectra and structures of D_3 molecules, where both sets of ligands are identical and in which the $^1A_1(^1T_{2g})$ and $^1A_2(^1T_{1g})$ states cannot mix. It is not

at all clear whether the splitting (which in any case is usually rather small) should be in the same sense in strongly distorted C_3 complexes.

The correlation between the sign of the c.d. spectrum and the geometry of the complex is rather better established. Provided the ligands are saturated, the ${}^1A \longrightarrow {}^1E({}^1T_{1g})$ transition will have a negative c.d. for a positive value of ω (clockwise rotation of the top set of ligands with respect to the bottom set). This correlation has been established¹⁶ for a wide range of D_3 complexes and is also calculated^{20,21} from the ligand polarisation model. This then establishes the lowest-energy c.d. band in the spectra of Δ -[CoLH₃LCO][PF₆]₃ and Δ -[Co(H₃L)]³⁺ as the ${}^1A \longrightarrow {}^1E({}^1T_{1g})$ transition. Hammershoi and Sargeson⁶ came to the same conclusion for the assignment of the c.d. spectrum of Δ -[Co(taetacn)]³⁺ (which has the same sign of twist angle and the same overall chirality¹⁸ as Δ -[CoLH₃LCO]-[PF₆]₃) assigning the lowest-energy, positive, c.d. band to the ${}^1A \longrightarrow {}^1E({}^1T_{1g})$ transition. This energy order is in contrast to that of the D_3 tris(chelates) with five-membered chelate rings, such as [Co(en)₃]³⁺, where the ${}^1A \longrightarrow {}^1E({}^1T_{1g})$ transition is of lowest energy, and to the trigonally elongated complexes [Co(tacn)₂]³⁺ (ref. 10) and [Co{(R)-mtacn}₂]³⁺ (ref. 22) where single-crystal studies show that the A_2 and E components have the same energy within experimental error.

The most obvious qualitative aspect of the c.d. spectrum of a cobalt(III) species, the relative intensity of the ${}^1A \longrightarrow {}^1E({}^1T_{1g})$ and ${}^1A \longrightarrow {}^1A({}^1T_{1g})$ transitions, is unfortunately the least easy to relate to any geometric property of the complex. Tris(chelate) complexes such as [Co(en)₃]³⁺ (including those with unsaturated ligands) invariably have a more intense ${}^1A \longrightarrow {}^1E({}^1T_{1g})$ transition. The complex [Co(tacn)₂]³⁺ (ref. 10) and 'capped' complexes such as [CoL]³⁺ (L = 1,3,6,8,10,13,16,19-octa-azabicyclo[6.6.6]icosane, sepulchrate),⁶ on the other hand, have dominant ${}^1A \longrightarrow {}^1A_2({}^1T_{1g})$ transitions. The major difference between the two types of complex is that in the former the major chiral perturbation is located in the equatorial region and in the latter it is located in the polar or axial region with respect to the C_3 axis. In the cobalt(III) complexes of H₃L and of taetacn the ligands impose both equatorial (the exocyclic chelate rings) and polar (the tacn moiety) perturbations. The rotational strength of the A component, $R(A)$, is greater than that of the E component, $R(E)$, for [CoLH₃LCO]³⁺ and is even more dominant in the deprotonated [CoL], while $R(E)$ is greater than $R(A)$ for the protonated [Co(H₃L)]³⁺ and [Co(taetacn)]³⁺. It appears therefore that the polar perturbation dominates in the former pair of complexes but not in the latter.

Behaviour of the Complexes in Aqueous Solution.—Our interest in the cobalt(III) complexes of H₃L was aroused by the spectroscopic changes seen in aqueous solution, and in particular by the n.m.r. spectrum of the complex in acidic aqueous media. As described in our preliminary communication, the acid form of the complex has two different methyl signals: δ 1.2 (relative intensity 2) and 1.45 (relative intensity 1). Both resonances have the same coupling constant ${}^3J(\text{H-H}) = 6.2$ Hz.

From the spectra in non-aqueous solvents we know that the following species are present in acidic, basic, and neutral solutions [Co(H₃L)]³⁺ $\xrightleftharpoons{3\text{H}^+}$ [CoLH₃LCO]³⁺ $\xrightleftharpoons{3\text{H}^+}$ [CoL]. The first two have been established unequivocally by absorption, c.d., and n.m.r. measurements, the last being a reasonable inference. There is no evidence that in MeCN solution it is possible to protonate further [Co(H₃L)]³⁺.

The species in aqueous basic solution is probably a mixture of [CoLH₃LCO]³⁺ and [CoL] (and possible intermediate species) depending on the exact pH. The purple species formed in the initial reaction is likely to be the former since it is adsorbed on ion-exchange resin. The red aqueous acidic solution species cannot be simply [Co(H₃L)]³⁺ since it has two inequivalent types of methyl group. The two most obvious possibilities are [CoH₂LHLH₂Co]⁵⁺ or [Co(H₄L)]⁴⁺. The former complex, in which one of the hydrogen bridges is still intact, seems a strong possibility in aqueous acid solution.

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