Preparation and Characterisation of Organocobalt(III) Complexes of Tetraaza Macrocyclic Ligands. Crystal Structures of Ethyl- and Propyl-cobalt(III) Complexes of 3,7,11,17-Tetraazabicyclo[11.3.1]heptadeca-1(17),13,15-triene†

Hadi A. A. Omar, Peter Moore* and Nathaniel W. Alcock
Department of Chemistry, University of Warwick, Coventry CV4 7AL, UK

Several organocobalt(III) complexes of general formula *trans*-$[\mathrm{CoR(L)(OH_2)}][\mathrm{ClO_4}]_2$ have been prepared in moderate yield using a photochemical route (L = a tetraaza macrocycle; R = Me, Et, Pr or Bu). The complexes have been isolated and characterised by microanalyses, ^{1}H, ^{13}C and ^{59}Co NMR spectroscopies, and fast atom bombardment (FAB) mass spectrometry. Crystal structures of two of the complexes, *trans*-$[\mathrm{CoR(L)(OH_2)}][\mathrm{ClO_4}]_2$ (L = 3,7,11,17-tetraazabicyclo[11.3.1]heptadeca-1(17),13,15-triene; R = Et or Pr) establish the *trans*-geometry, with relatively long Co–O bond lengths of 2.121(3) and 2.29(3) Å respectively, showing the *trans* influence of the alkyl groups.

Interest in the synthesis and investigation of organocobalt(III) complexes was stimulated by the discovery that the naturally occurring vitamin B_{12} co-enzyme contains a Co–C bond.[1] It is well established that visible light causes homolysis of $\mathrm{Co^{III}}$–C bonds, giving alkyl radicals and reduction of cobalt(III) to the 2+ oxidation state [equation (1)].[2,3] These homolytic reactions

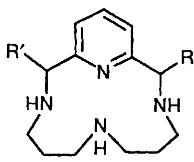
$$\mathrm{Co^{III}\text{–}R} \xrightarrow{h\nu} \mathrm{Co^{II}} + \mathrm{R^{\bullet}} \tag{1}$$

are reversible, but in the presence of activated alkenes they can initiate C–C bond formation, and polymerisation.[4] Our interest is in the utilisation of such species as photopolymerisation catalysts.

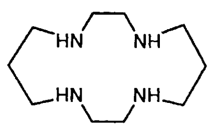
In most of the organocobalt(III) complexes reported, cobalt(III) is co-ordinated to unsaturated ligands such as porphyrins, bis(dimethylglyoximate) ion and Schiff-base macrocycles (*e.g.* L^4). Only a few organocobalt(III) complexes of saturated tetraaza macrocycles have been described.[3,5]

We have used the previously reported photochemical synthetic route[3] to obtain organocobalt(III) complexes of the tetraaza macrocycles L^1–L^3. Whereas some organocobalt(III) complexes such as *trans*-$[\mathrm{CoR(Hdmg)_2L}]$ [Hdmg = dimethylglyoximate(1 −), L = unidentate ligand such as pyridine, R = alkyl] are readily obtained by the oxidative addition of alkyl halides to the reduced cobalt(I) complexes under anaerobic conditions, the inaccessibility of the $\mathrm{Co^I}$ state for the cobalt complexes of the macrocycles studied here necessitates a different synthetic strategy. The synthetic photochemical method relies on the relative acid inertness of aza macrocyclic cobalt(II) complexes and the acid lability of bis[dimethylglyoximato(1 −)]cobalt(II) species, and involves transfer of an alkyl group from an organocobaloxime to an aza macrocyclic cobalt(II) complex [reactions (2)–(4); R = alkyl group, py = pyridine, L = tetraaza macrocycle].[3,5] Hence, the bis[dimethylglyoximato(1 −)]cobalt(II) produced by photolysis [reaction (2)] undergoes rapid acid-catalysed hydrolysis [reaction (3)], leaving the acid tolerant aza macrocyclic cobalt(II) complex to capture the alkyl radical [reaction (4)].

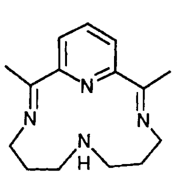
$$trans\text{-}[\mathrm{CoR(Hdmg)_2(py)}] \xrightarrow{h\nu\,(\mathrm{H_2O})} [\mathrm{Co(Hdmg)_2(OH_2)_2}] + \mathrm{py} + \mathrm{R^{\bullet}} \tag{2}$$



L^1 R′ = H
L^2 R′ = CH_3



L^3



L^4

$$[\mathrm{Co(Hdmg)_2(OH_2)_2}] + 2\,\mathrm{H^+} \xrightarrow{(\mathrm{H_2O})} [\mathrm{Co(OH_2)_6}]^{2+} + 2\,\mathrm{H_2dmg} \tag{3}$$

$$[\mathrm{Co(L)(OH_2)}]^{2+} + \mathrm{R^{\bullet}} \longrightarrow trans\text{-}[\mathrm{CoR(L)(OH_2)}]^{2+} \tag{4}$$

Experimental

Materials and Methods.—All chemicals were of the highest available purity and were not purified further. NMR spectra were recorded with a Bruker WH400 FTNMR spectrometer, mass spectra with a Kratos MS80 instrument, and UV/VIS spectra with a Shimadzu 365 spectrometer. Microanalyses were obtained commercially, and gel-permeation chromatography was carried out by the analytical department of ICI Paints.

---

† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1994, Issue 1, pp. xxiii–xxviii.

Table 1 Microanalytical data (calculated values in parentheses) and synthetic yields for the organocobalt(III) complexes of L^1–L^3

			Analysis (%)		
Complex	Yield (%)	Formula	C	H	N
$[CoMe(L^1)(OH_2)][ClO_4]_2$	19	$C_{14}H_{27}Cl_2CoN_4O_9$	32.25 (32.00)	5.25 (5.20)	10.80 (10.65)
$[CoMe(L^1)(OH_2)][PF_6]_2$	33	$C_{14}H_{27}CoF_{12}N_4OP_2$	27.45 (27.30)	4.50 (4.40)	9.15 (9.10)
$[CoEt(L^1)(OH_2)][ClO_4]_2$	20	$C_{15}H_{29}Cl_2CoN_4O_9$	33.15 (33.40)	5.35 (5.40)	10.25 (10.40)
$[CoPr(L^1)(OH_2)][ClO_4]_2$	15	$C_{16}H_{31}Cl_2CoN_4O_9$	34.85 (34.75)	5.55 (5.65)	10.20 (10.15)
$[CoBu(L^1)(OH_2)][ClO_4]_2 \cdot H_2O$	10	$C_{17}H_{35}Cl_2CoN_4O_{10}$	34.40 (34.90)	5.90 (6.05)	9.40 (9.55)
$[CoPr(L^2)(OH_2)][ClO_4]_2 \cdot H_2O$	22	$C_{18}H_{37}Cl_2CoN_4O_{10}$	35.65 (36.05)	6.30 (6.20)	9.30 (9.35)
$[CoBu(L^3)(OH_2)][ClO_4]_2 \cdot H_2O$	19	$C_{14}H_{37}Cl_2CoN_4O_{10}$	30.65 (30.50)	6.10 (6.75)	10.70 (10.15)

Table 2 Proton decoupled ^{13}C NMR chemical shifts [δ relative to $SiMe_4$ (δ 0); relative populations in parentheses] of the macrocycles L^1 and L^2, and organocobalt(III) complexes of L^1–L^3, in CD_3NO_2 solution at 298 K unless specified

	py						
Compound	*ortho*	*para*	*meta*	py–CH_2–N	N–CH_2–C	C–CH_2–C	CH–CH_3
L^1	161.29(2)	137.56(1)	121.41(2)	55.23(2)	48.66(2), 47.54(2)	30.35(2)	
$L^{1\,a}$	160.83(2)	137.16(1)	121.05(2)	55.10(2)	48.49(2), 47.34(2)	30.05(2)	
L^2 (isomer 1, 60%)	165.11(2)	137.98(1)	120.03(2)	59.57(2)	49.35(2), 46.88(2)	30.28(2)	21.14(2)
L^2 (isomer 2, 40%)	166.13(2)	137.43(1)	121.84(2)	60.23(2)	46.88(2), 45.14(2)	29.89(2)	23.93(2)
$[CoMe(L^1)(OH_2)][ClO_4]_2{}^b$	162.41(2)	141.47(1)	120.69(2)	61.28(2)	53.03(2), 51.55(2)	28.08(2)	
$[CoEt(L^1)(OH_2)][ClO_4]_2{}^{a,c}$	161.10(2)	140.70(1)	119.98(2)	60.91(2)	52.43(2), 51.31(2)	27.30(2)	
$[CoPr(L^1)(OH_2)][ClO_4]_2{}^d$	161.08(2)	140.42(1)	119.81(2)	60.05(2)	52.03(2), 50.64(2)	26.69(2)	
$[CoBu(L^1)(OH_2)][ClO_4]_2{}^{a,b,e}$	161.69(2)	140.31(1)	120.16(2)	60.49(2)	52.12(2), 50.91(2)	26.96(2)	
$[CoPr(L^2)(OH_2)][ClO_4]_2{}^f$	165.82(2)	142.00(1)	121.67(2)	68.15(2)	53.25(2), 50.27(2)	27.59(2)	17.36(2)
$[CoPr(L^2)(OH_2)][ClO_4]_2{}^g$	168.19(1), 165.35(1)	141.88(1)	121.91(1), 121.54(1)	67.94(1), 66.32(1)	53.25(1), 53.09(1), 49.87(1), 47.17(1)	27.41(1), 26.60(1)	19.46(1), 17.26(1)
$[CoBu(L^3)(OH_2)][ClO_4]_2{}^{b,h}$					53.06(2), 52.90(2), 50.71(2), 46.89(2)	28.17(1), 28.04(1)	

[a] In $(CD_3)_2CO$. [b] The Co–C resonance is very broad (undetected). [c] Methyl resonance of ethyl group at δ 17.59. [d] Broad Co–C resonance detected at 203 K, δ 28.80; other propyl group resonances at δ 25.26 and 13.25. [e] Other butyl group resonances at δ 34.64, 22.03 and 13.54. [f] Symmetric isomer; Co–C at δ 30.41; other propyl group resonances at δ 27.51 and 12.86. [g] Asymmetric isomer; Co–C at δ 30.41; other propyl group resonances at δ 27.41 and 12.77. [h] Other butyl group resonances at δ 37.12, 22.98 and 14.01.

Ligand Syntheses.—The compounds L^1 and L^3 were prepared as described;[6,7] L^2 was obtained in 70% yield using the template method reported for L^1, starting from 2,6-diacetylpyridine and 1,7-diamino-4-azaheptane.[6]

Preparation of Alkylcobaloximes.—The complex *trans*-$[CoMe(Hdmg)_2(py)]$ was prepared by the literature method.[8] The analogous ethyl, propyl and butyl derivatives were obtained in 60–70% yields using the following procedure (described for the ethyl derivative). A solution of pyridine (2.4 g) in methanol (100 cm^3) was deoxygenated by bubbling dry N_2 for 1 h; keeping the solution under N_2, dimethylglyoxime (6.96 g) and $CoCl_2 \cdot 6H_2O$ (7.11 g) were added with vigorous stirring. Then a deoxygenated solution of NaOH (4.8 g) in water (7 cm^3) was added, followed by ethyl bromide (3.5 g). The solution changed from dark green to orange-red, and an orange solid precipitated. The mixture was stirred for 10 min, then transferred to a separating funnel and extracted with chloroform (5 x 100 cm^3). The combined chloroform extracts were dried with anhydrous $MgSO_4$, filtered, and the chloroform removed with a rotary evaporator to leave the product, *trans*-$[CoEt(Hdmg)_2(py)]$ (8.33 g, 70%), as an orange-red solid. ^1H NMR ($CDCl_3$): δ 0.36 (t, 3 H), 1.72 (q, 2 H), 2.16 (s, 12 H), 7.20 (d, 2 H), 7.80 (t, 1 H), 8.68 (d, 2 H) and 18.40 (br, 2 H).

Preparation of Organocobalt(III) *Complexes of* L^1–L^3.—A photochemical route very similar to the published method was used [equations (2)–(4)].[3] A typical procedure is described here for *trans*-$[CoMe(L^1)(OH_2)][ClO_4]_2$. To a deoxygenated solution of L^1 (234 mg, 1 mmol) in water (100 cm^3) in a 250 cm^3 round bottom flask, was added under N_2 an aliquot of deoxygenated aqueous cobalt(II) perchlorate (0.54 mol dm^{-3}, 1.86 cm^3, 1 mmol). The deep red solution was stirred for 15 min under N_2, and *trans*-$[CoMe(Hdmg)_2(py)]$ (380 mg, 1 mmol) added. The suspension was stirred under N_2 whilst cooling to 0 °C, and dinitrogen-scrubbed 5.3 mol dm^{-3} $HClO_4$ (1 cm^3) was then added. The mixture was irradiated with a 300 W sun lamp at a distance of 30 cm for 2.5 h. During this time the solution changed from red to orange-yellow, and solid dimethylglyoxime precipitated. The solid was removed by filtration, and the solution loaded onto a column (20 x 2.5 cm) of Sephadex SP-C25. A yellow band containing unreacted organocobaloxime was eluted first by washing the column with water (100 cm^3), and the required product was then eluted as an orange-red band using 0.2 mol dm^{-3} $NaClO_4$ containing 0.05 mol dm^{-3} $HClO_4$ (200 cm^3). The eluent was concentrated in a desiccator under vacuum over dry silica gel. The red crystals were collected by filtration, and washed with a small amount of ice-cold water to give the product, *trans*-$[CoMe(L^1)(OH_2)][ClO_4]_2$ (100 mg, 19%). The analogous ethyl, propyl and butyl complexes were obtained in the same way starting from the corresponding organocobaloximes, using irradiation times of 120, 110 and 100 min, and giving yields of 20, 15 and 10% respectively. An improved yield of *trans*-$[CoMe(L^1)(OH_2)]^{2+}$ was obtained by adding $NaPF_6$ (1.5 g) to the red solution eluted from the Sephadex column, which after concentration as described above gave *trans*-$[CoMe(L^1)(OH_2)][PF_6]_2$ (200 mg, 33%). The purity of the products was established by elemental analyses (Table 1), ^1H and ^{13}C NMR spectroscopy (Table 2) and fast atom bombardment (FAB) mass spectra (Table 3). Visible spectra are in Table 4 and ^{59}Co NMR chemical shifts in Table 5. The structures of *trans*-$[CoR(L^1)(OH_2)][ClO_4]_2$ (R = Et or Pr) were established by X-ray crystallography.

Table 3 Fast atom bombardment (FAB) mass spectral data for *trans*-$[CoR(L)(OH_2)][ClO_4]_2$ with relative heights in parentheses

	m/*z*	
	Found	Calc.
R = Me, L = L^1	407 (100), 408 (27), 409 (41), 410 (8)	407 (100), 408 (18), 409 (34), 410 (6)
R = Et, L = L^1	421 (100), 422 (12), 423 (20)	421 (100), 422 (19), 423 (34)
R = Pr, L = L^1	435 (100), 436 (26), 437 (36)	435 (100), 436 (20), 437 (35)
R = Bu, L = L^1	449 (100), 450 (33), 451 (30)	449 (100), 450 (21), 451 (35)
R = Pr, L = L^2	463 (100), 464 (23), 465 (35)	463 (100), 464 (22), 465 (35)
R = Bu, L = L^3	415 (100), 416 (0), 417 (42)	415 (100), 416 (18), 417 (34)

Table 4 Visible spectra of *trans*-$[CoR(L)(OH_2)][ClO_4]_2$ in aqueous solution

R	L	λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1})
Me*	L^1	477 (161), 360 (sh)
Et	L^1	490 (271), 365 (sh)
Pr	L^1	483 (172), 370 (sh)
Bu	L^1	485 (218), 370 (sh)
Pr	L^2	490 (221), 376 (sh)
Bu	L^3	490 (92), 380 (sh)

* *trans*-$[CoMe(L^1)(OH_2)][PF_6]_2$ has λ_{max} = 477 nm (ε = 180 dm^3 mol^{-1} cm^{-1}).

Crystal Structures.—Crystal data for *trans*-$[CoR(L^1)(OH_2)][ClO_4]_2$ (R = Et **1** or Pr **2**), are given in Table 6. Reflections were measured with a Nicolet R3M four-circle diffractometer in the ω–2θ mode. Data were measured over the stated range around the Kα1–Kα2 angles, with scan speed 3–29° min^{-1} depending on the intensity of a 2 s pre-scan; backgrounds were measured at each end of the scan for 0.25 of the scan time. Three standard reflections were monitored every 200 reflections, and showed a slight change (R = Pr) or no change (R = Et) during the data collection; the data were rescaled to correct for this in the former case. Unit-cell dimensions and standard deviations were obtained by a least-squares fit to 15 reflections ($25 < 2\theta < 28°$ when R = Et and $20 < 2\theta < 22°$ when R = Pr). Reflections were processed using profile analysis, and those with $I/\sigma(I) > 2.0$ were used in the refinement; they were corrected for Lorentz, polarisation and absorption effects (for **1** only), the latter by the Gaussian method. Heavy atoms were located by the Patterson interpretation section of SHELXTL, and light atoms then found on successive Fourier syntheses. Final refinement was on *F* by least-squares methods. A weighting scheme of the form $w = 1/[\sigma^2(F) + gF^2]$ (for *g* see Table 6) was used and found to be satisfactory by a weight analysis. Scattering factors in the analytical form and anomalous dispersion factors were taken from ref. 9. Computing was with SHELXTL PLUS on a DEC Microvax II.[10] Hydrogen atoms were given fixed isotropic thermal parameters, $U = 0.07$ Å^2, and except in the case of those attached to O(1) of complex **1**, were inserted at calculated positions and not refined; methyl groups were treated as rigid CH_3 units, with their initial orientation taken from the strongest H-atom peak on a Fourier-difference synthesis. The H-atoms attached to O(1) of complex **1** were located on Fourier-difference syntheses, and the O–H bond lengths were fixed at 0.85 Å.

For complex **1** crystals (red plates) were obtained by slow evaporation of an aqueous solution kept in the dark. Anisotropic thermal parameters were used for all atoms other than hydrogen. Systematic absences (Table 6) indicated space group $P2_1/c$. One ClO_4^- group was refined as disordered around a Cl–O axis. Maximum shift/error in the final cycle was 0.41.

For **2** crystals (small brown blocks) were obtained by slow diffusion of diethyl ether into a nitromethane solution of the complex. Systematic absences (Table 6) indicated space group $P2_12_12_1$. The crystals scattered weakly with broad diffuse peaks, and the ClO_4^- groups were severely disordered. It was possible to solve the structure, but refinement could not be carried out to the normal limit. It is considered that the overall structure has been satisfactorily established, but the detailed dimensions remain somewhat uncertain. Anisotropic thermal parameters were used for Co, Cl, O (major positions) and N. One ClO_4^- group was modelled with two sets of O atoms with constrained Cl–O distances. Unit weights were used with no absorption correction and hydrogen atoms were not included.

Final atomic coordinates for complex **1** are given in Table 7, and selected bond lengths and angles in Table 8.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles for complex **1** and atomic coordinates, thermal parameters and bond lengths and angles for complex **2**.

Results and Discussion

The photochemical synthetic method [reactions (2)–(4)] was found to be very effective for the synthesis of alkylcobalt(III) complexes of the macrocycles L^1–L^3 in modest yields (Table 1). Since the products are photolabile, irradiation times were adjusted to maximise the yield of product.

The complex *trans*-$[CoMe(L^1)(OH_2)]^{2+}$ was isolated as the hexafluorophosphate and perchlorate salts; both have identical ^1H NMR spectra in CD_3NO_2 solution, with the CH_3–Co resonance at δ 2.2, and visible spectra with λ_{max} = 477 nm. All of the alkylcobalt(III) complexes are characterised by a visible peak in the range 477–490 nm (Table 4). The FAB mass spectrum of *trans*-$[CoMe(L^1)(OH_2)][ClO_4]_2$ shows clusters of peaks centred at *m*/*z* 407 and 392 as calculated for $[Co^{III}Me(L^1)(ClO_4)]^+$ and $[Co^{II}(L^1)(ClO_4)]^+$ respectively [the latter ion indicating that reaction (1) occurs in the mass spectrometer]; loss of $HClO_4$ from $[Co^{II}(L^1)(ClO_4)]^+$ gives $[Co^{II}(L^1 - H)]^+$ (*m*/*z* 292). The ^{13}C NMR spectrum (Table 2) indicates that a single symmetric isomer predominates in solution, but small amounts (in total *ca.* 4%) of two further isomers were detected in the ^{59}Co NMR spectrum (Table 5). These are attributed to the *N*-configurational isomers (four isomers are possible for such systems).[11] The use of ^{59}Co NMR spectroscopy to detect small amounts of such species is an advantage due to the enhanced sensitivity over ^{13}C NMR. The *trans* geometry of $[CoMe(L^1)(OH_2)]^{2+}$ is inferred by analogy with the crystal structures of the ethyl and propyl complexes.

The complex *trans*-$[CoEt(L^1)(OH_2)][ClO_4]_2$ was isolated in 20% yield, and showed characteristic ^1H NMR resonances for the ethyl group at δ −0.2 (t, 3 H) and +3.5 (q, 2 H). The ^{13}C NMR spectrum shows the Co–C resonance to be very broad due to relaxation effects from the quadrupolar ^{59}Co nucleus ($I = \frac{7}{2}$), with the methyl of the ethyl group sharp at δ 17.59. Similar behaviour was observed for all of the alkylcobalt(III) complexes, with the resonance of the carbon atom bonded to cobalt always broad. Predominantly two isomers (in the ratio 84:15) were detected in the ^{59}Co NMR spectrum of *trans*-$[CoEt(L^1)(OH_2)][ClO_4]_2$, with a trace (< 1%) of a third isomer. The FAB mass spectrum is analogous to that of the methyl complex, with a parent ion at *m*/*z* 421 as expected for $[CoEt(L^1)(ClO_4)]^+$. The

Table 5 Cobalt-59 NMR chemical shifts {δ relative to external [Co(acac)$_3$] (acac = acetylacetonate) (δ 0; 298 K)}

Complex	
[CoMe(L^1)(OH$_2$)][ClO$_4$]$_2$ ^{a}	6977 (3%), 6837 (96%), 6412 (< 2%)
[CoEt(L^1)(OH$_2$)][ClO$_4$]$_2$ ^{b}	6919 (84%), 6561 (15%), 6477 (< 1%)
[CoPr(L^1)(OH$_2$)][ClO$_4$]$_2$ ^{a}	6950 (84%), 6531 (12%), 6322 (4%)
[CoBu(L^1)(OH$_2$)][ClO$_4$]$_2$·H$_2$O ^{b}	6964 (94%), 6542 (4%), 6327 (2%)
[CoPr(L^2)(OH$_2$)][ClO$_4$]$_2$·H$_2$O ^{a}	6996 (76%), 6620 (7%), 6572 (14%), 6353 (3%)
[CoBu(L^3)(OH$_2$)][ClO$_4$]$_2$ ^{a}	6918 (81%), 6350 (15%), 5983 (4%)

[a] In CD$_3$NO$_2$. [b] In (CD$_3$)$_2$CO.

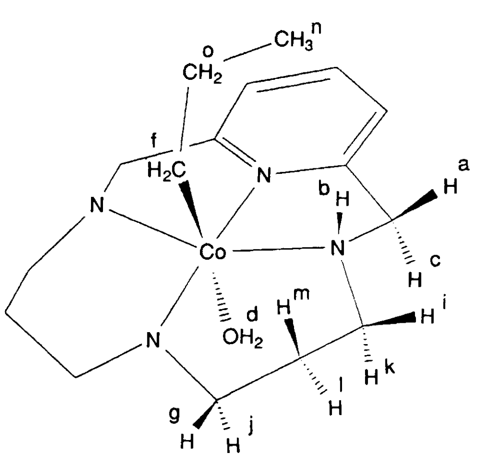
Table 6 Crystal data for *trans*-[CoR(L^1)(OH$_2$)][ClO$_4$]$_2$ (R = Et **1** or Pr **2**)[a]

Compound	**1**	**2**
Formula	$C_{15}H_{29}Cl_2CoN_4O_9$	$C_{16}H_{31}Cl_2CoN_4O_9$
M	539.26	553.28
System	Monoclinic	Orthorhombic
Crystal dimensions/mm	0.5 × 0.8 × 0.3	—
Space group	$P2_1/c$	$P2_12_12_1$
a/Å	8.628(3)	9.9601(14)
b/Å	14.947(7)	12.8155(9)
c/Å	17.665(8)	17.6696(17)
β/°	97.85(3)	90
U/Å^3	2256.9	2255(3)
D_c/g cm^{-3}	1.59	1.65
F(000)	1120	1184
Absences	$h0l, l \neq 2n + 1$ $0k0, k \neq 2n + 1$	$h00, h \neq 2n + 1$ $0k0, k \neq 2n + 1$ $00l, l \neq 2n + 1$
Total reflections	4007	1698
Reflections used in refinement	3254	1384
$2\theta_{max}$/°	50	45
Range (2θ) about Kα1 − Kα2/°	−0.5 to +0.65	±0.5
Scan speed/° min^{-1}	8–29	1.5–29
Index ranges, *hkl*	0–0, −22 to 11, 18–22	0–0, 0 to 11, 14–20
Max. (min.) transmission factors	0.84 (0.71)	—
Parameters refined	310	175
Final *R* (*R′*)[b]	0.051 (0.058)	0.16 (0.16)
Weighting factor, *g*	0.000 969	Unit weights
Largest difference peaks on *F* map/e Å^3	+0.7 and −0.5	+2.4 and −2.3

[a] Details in common: *Z* = 4; Mo-Kα radiation (λ 0.710 69 Å, μ 10.5 cm^{-1}). [b] $R = \Sigma|\Delta|/\Sigma|F_o|$; $R' = (\Sigma w\Delta^2/F_o^2)^{\frac{1}{2}}$; $\Delta = F_o - F_c$.

Table 7 Atomic coordinates (× 10^4) for *trans*-[CoEt(L^1)(OH$_2$)][ClO$_4$]$_2$ **1**, with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*
Co	2 595.1(6)	2 823.6(3)	6 545.0(3)
Cl(1)	372.1(15)	1 060.0(8)	8 790.6(6)
Cl(2)	6 579.3(15)	738.1(8)	13 867.6(8)
O(11)	900(7)	808(3)	8 103(3)
O(12)	130(9)	315(3)	9 206(3)
O(13)	1 428(9)	1 593(5)	9 197(3)
O(14)	−979(10)	1 461(7)	8 636(6)
O(21)	5 453(6)	1 407(3)	13 680(3)
O(22)	5 699(19)	−30(10)	13 893(12)
O(23)	6 654(22)	562(13)	14 710(7)
O(24)	7 667(26)	929(13)	14 396(13)
O(25)	8 016(22)	1 075(20)	13 891(22)
O(26)	7 202(15)	638(14)	13 155(8)
O(27)	6 333(34)	−37(11)	13 510(13)
O(1)	1 059(4)	3 618(2)	5 781(2)
N(1)	4 219(4)	3 208(2)	6 019(2)
N(2)	3 298(4)	3 865(2)	7 214(2)
N(3)	736(4)	2 473(3)	7 034(2)
N(4)	2 500(4)	1 797(2)	5 819(2)
C(1)	4 584(5)	2 725(3)	5 420(3)
C(2)	5 781(6)	3 007(4)	5 028(3)
C(3)	6 542(7)	3 793(4)	5 240(3)
C(4)	6 112(6)	4 296(3)	5 832(3)
C(5)	4 920(5)	3 998(3)	6 206(3)
C(6)	4 184(6)	4 493(3)	6 796(3)
C(7)	2 168(6)	4 348(3)	7 634(3)
C(8)	1 171(6)	3 714(3)	8 011(3)
C(9)	29(6)	3 208(4)	7 445(3)
C(10)	−533(5)	2 030(4)	6 516(3)
C(11)	−40(6)	1 238(4)	6 090(3)
C(12)	943(6)	1 453(3)	5 477(3)
C(13)	3 539(6)	1 937(3)	5 227(3)
C(14)	3 891(5)	2 043(3)	7 310(3)
C(15)	5 600(5)	1 965(3)	7 243(3)



symmetric *trans* geometry of the dominant isomer was established by means of a crystal structure determination (Fig. 1). The N–H groups all point in the direction of the Co–Et group. The Co atom is displaced very slightly out of the plane of the 4 N atoms in the direction of the ethyl group. The Co–C bond length [2.006(4) Å] is similar to that reported in the analogous *trans*-[CoEt(L^3)(OH$_2$)]$^{2+}$ (Co–C 1.99 Å).[3] Due to the *trans* influence of the ethyl group, the Co–O bond length [2.121(3) Å] is longer than that in *trans*-[Co(L^3)(OH$_2$)$_2$]$^{3+}$ (1.91 Å),[12] but somewhat shorter than that found in *trans*-[CoEt(L^3)(OH$_2$)]$^{2+}$ (2.20 Å). The Co–N bond lengths to the aliphatic N atoms are all similar (average 1.995 Å), with that to the pyridine N atom shorter [Co–N(1) 1.874(4) Å] as found in analogous systems.[6,11] The bond angles are close to those expected for a *trans*-octahedral geometry, with C(14)–Co–O(1) 175.2(2) and N(1)–Co–N(3) 174.9(1)°, but distortions due primarily to the shorter Co–N(1) bond length result in a N(2)–Co–N(4) angle of only 164.2(2)°.

The complex *trans*-[CoPr(L^1)(OH$_2$)][ClO$_4$]$_2$ was obtained in 15% yield, and found to have ^{1}H NMR resonances from the propyl group at δ 0.6 (m, 2 H), 0.9 (t, 3 H) and 3.3 (t, 2 H), and the expected ^{13}C NMR resonances for a predominantly symmetric *trans* geometry (Table 2). The FAB mass spectrum shows the expected peaks at *m*/*z* 435 {[CoPr(L^1)(ClO$_4$)]$^+$} and 392 {[Co(L^1)(ClO$_4$)]$^+$}.

The solution conformation of this complex was investigated by means of ^{1}H nuclear Overhauser difference spectroscopy.

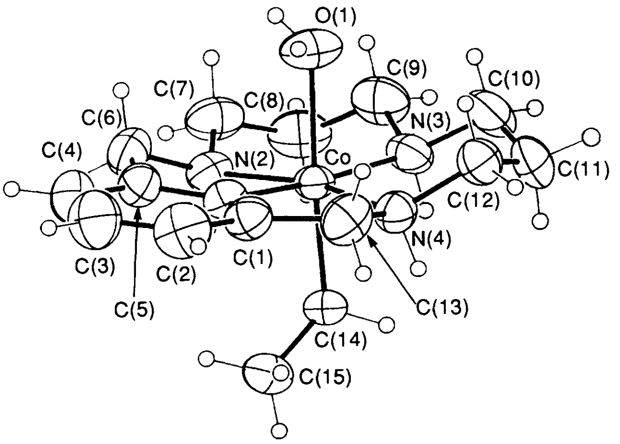


Fig. 1 Crystal structure of the $[\mathrm{CoEt}(\mathrm{L}^1)(\mathrm{OH}_2)]^{2+}$ cation of **1** showing the atomic numbering

Table 8 Selected bond lengths (Å) and angles (°) in *trans*-$[\mathrm{CoEt}(\mathrm{L}^1)(\mathrm{OH}_2)]^{2+}$

Co–O(1)	2.121(3)	Co–N(1)	1.874(4)
Co–N(2)	1.998(3)	Co–N(3)	1.993(4)
Co–N(4)	1.994(4)	Co–C(14)	2.006(4)
O(1)–Co–N(1)	87.6(1)	O(1)–Co–N(2)	93.0(1)
N(1)–Co–N(2)	87.4(1)	O(1)–Co–N(3)	87.3(1)
N(1)–Co–N(3)	174.9(1)	N(2)–Co–N(3)	98.4(2)
O(1)–Co–N(4)	93.1(1)	N(1)–Co–N(4)	83.4(1)
N(2)–Co–N(4)	164.2(2)	N(3)–Co–N(4)	96.4(2)
O(1)–Co–C(14)	175.2(2)	N(1)–Co–C(14)	97.3(2)
N(2)–Co–C(14)	87.7(1)	N(3)–Co–C(14)	87.9(2)
N(4)–Co–C(14)	87.5(2)		

Proton NMR spectra were recorded with irradiation of the proton resonances from a, c, f, j, m, n and o. This revealed proximal protons as follows (irradiated resonance given first, followed by enhanced resonances): a (i, b, f, g, m); c (k, d, l, j); f (a, i, m, g, b); j (m, d, k, c); m (d, i, j, c); n (a, i, l, k); o (a, i, c, l, g). The *trans* geometry is consistent with these observations; for example, irradiation of a enhances f and i, and irradiation of d or k enhances the resonance from c. The ^{59}Co NMR spectrum shows the presence of three isomers in nitromethane solution, in the ratio 84:12:4.

The geometry of *trans*-$[\mathrm{CoPr}(\mathrm{L}^1)(\mathrm{OH}_2)][\mathrm{ClO}_4]_2$ was also investigated by structural analysis. Its crystals were found to be weakly diffracting with a severely disordered perchlorate group. As a result, only the chemical nature of the complex and its general conformation as the *trans* isomer could be established; it appears that the Co–O bond is exceptionally long [2.29(3) Å], but this cannot be taken as highly reliable.

As expected, *trans*-$[\mathrm{CoPr}(\mathrm{L}^2)(\mathrm{OH}_2)][\mathrm{ClO}_4]_2$ is similar to the analogous complex of L^1. It was obtained in 22% yield, and the ^{13}C NMR spectrum in nitromethane solution shows the presence of symmetric and asymmetric isomers. There is evidence from the ^{59}Co NMR spectrum of small amounts of two further isomers (Table 5).

The ^{59}Co NMR spectra of the butylcobalt(III) complexes, *trans*-$[\mathrm{CoBu}(\mathrm{L})(\mathrm{OH}_2)][\mathrm{ClO}_4]_2$ (L = L^1 or L^3) show the presence of predominantly two isomers, one major species (94% for L^1 and 81% for L^3), the second of abundance 4% and 15%, and a minor species of abundance 2% and 4% respectively. The analytical data, FAB mass spectra, and solution NMR spectra confirm the proposed formulations.

Polymerisation Experiments.—Preliminary results confirm that all of these alkylcobalt(III) complexes are potent catalysts for the photopolymerisation of vinyl monomers such as ethyl acrylate, methyl methacrylate and acrylonitrile in tetrahydrofuran solution. Polymerisations were carried out using degassed solutions containing 1–10 mg of catalyst, 2 g of monomer, and 20 g of tetrahydrofuran, with continuous irradiation in a glass vessel with a 300 W sun lamp positioned 10 cm away. Gel-permeation chromatography analyses show the polymers obtained in this way have average molecular weights in the range 6000–30 000 depending on the precise conditions used. We shall report more fully on these polymerisation experiments at a later date.

Acknowledgements

We thank ICI for support of this work through their strategic research fund, the SERC for provision of X-ray and NMR facilities, and Drs. E. Nield and J. Mathews of ICI Paints for helpful discussions.

References

1 P. G. Lenhert and D. C. Hodgkin, *Nature*, 1961, **192**, 937; *B12*, ed. D. Dolphin, Wiley Interscience, New York, 1982, vols 1 and 2; P. J. Toscano and L. G. Marzilli, *Prog. Inorg. Chem.*, 1984, **31**, 105; J. M. Pratt, *Chem. Soc. Rev.*, 1985, **14**, 161; J. Halpern, *Science*, 1985, **227**, 869; M. N. Hughes, *Comprehensive Co-ordination Chemistry*, eds. G. Wilkinson, R. D. Gillard and J. A. McCleverty, Pergamon, Oxford, 1987, vol. 6, ch. 62.1, p. 637; B. D. Gupta and S. Roy, *Inorg. Chim. Acta*, 1988, **146**, 209.
2 J. K. Kochi, *Organometallic Mechanisms and Catalysis*, Academic Press, New York, 1978.
3 A. Bakac, and J. H. Espenson, *Inorg. Chem.*, 1987, **26**, 4353; 1989, **28**, 3901, 4319.
4 G. Pattenden, *Chem. Soc. Rev.*, 1988, **17**, 361.
5 T. S. Roche and J. F. Endicott, *J. Am. Chem. Soc.*, 1972, **94**, 8622; *Inorg. Chem.*, 1974, **13**, 1575.
6 K. P. Balakrishnan, H. A. A. Omar, P. Moore, N. W. Alcock and G. A. Pike, *J. Chem. Soc., Dalton Trans.*, 1990, 2965.
7 E. K. Barefield, F. Wagner, A. W. Herlinger and A. R. Dahl, *Inorg. Synth.*, 1976, **16**, 220.
8 G. N. Schrauzer, *Inorg. Synth.*, 1968, **11**, 65.
9 *International Tables for X-Ray Crystallography*, Kynoch Press, Birmingham, 1974, vol. 4.
10 G. M. Sheldrick, SHELXTL PLUS User Manual, Nicolet Instrument Co., Madison, WI, 1986.
11 N. W. Alcock, P. Moore and H. A. A. Omar, *J. Chem. Soc., Dalton Trans.*, 1987, 1107.
12 J. F. Endicott, B. Durham, M. D. Glick, T. J. Anderson, T. M. Kusza, W. G. Schmonsees and K. P. Balakrishnan, *J. Am. Chem. Soc.*, 1981, **103**, 1431.

Received 14*th March* 1994; *Paper* 4/01491J