Cobalt(III) Complexes of 1,5,9-Triamino-5-methyl-3,7-diazanonane, L^1, a New Quinquedentate Polyamine Ligand. Crystal Structures of the Chlorocobalt(III) and μ-Superoxo-dicobalt(III) Complexes of L^1 †

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The polyamine 1,5,9-triamino-5-methyl-3,7-diazanonane (L^1) co-ordinates as a quinquedentate ligand to cobalt(III). The monomers $[Co(L^1)X]^{2+}$ ($X = Cl^-$, NCS^-, or NO_2^-) and the dimers $[(CoL^1)_2O_2]^{n+}$ (n = 4 or 5) were prepared and characterized spectroscopically. The complex $[Co(L^1)Cl]Cl[ClO_4]$ crystallizes in the monoclinic space group $P2_1/c$, a = 10.471(2), b = 11.878(3), c = 13.284(2) Å, and β = 97.70(1)°. The superoxo complex $[(CoL^1)_2O_2][ClO_4]_5 \cdot 4H_2O$ crystallizes in the triclinic space group $P\bar{1}$, a = 8.592(3), b = 9.792(3), c = 12.993(6) Å, α = 95.96(3), β = 97.70(1), and γ = 109.38(3)°. The cobalt–nitrogen bonds are unusually short in both structures, in the range 1.934—1.949(2) Å, and there is considerable strain in the molecules. The cobalt–chlorine bond in $[Co(L^1)Cl]Cl[ClO_4]$ is also short [2.261(1) Å] and the rate of base hydrolysis of this bond is slow. The Raman-active O_2 vibration in the peroxo-bridged dimer occurs *ca.* 40 cm^{-1} to lower wave number than for the deca-ammine analogue, indicative of a slightly longer O–O bond, whereas the O–O bond in the superoxo complex [1.294(14) Å] is shorter than that in the deca-ammine analogue.

There exists an extensive range of polyamine ligands which can act as quinquedentate ligands to cobalt(III), a number of which have been defined by crystal-structure analyses. These include simple linear molecules such as penten (L^2, 1,11-diamino-3,6,9-triazaundecane),[1] branched-chain molecules such as trenen [L^3, 1,8-diamino-3-(2-aminoethyl)-3,6-diazaoctane],[2] and macrocyclic ligands such as 1,4,7,10,13-penta-azacyclopentadecane (L^4).[3] Pendant-arm macrocycles can also act as quinquedentate ligands; the molecule diammac (L^5, 6,13-diamino-6,13-dimethyl-1,4,8,11-tetra-azacyclotetradecane) will adopt this role, where one primary amino group is protonated and hence unco-ordinated.[4] These ligands can yield a range of geometric and optical isomers when complexed with octahedral metal ions.

The polyamine 1,5,9-triamino-5-methyl-3,7-diazanonane (L^1) has been reported as its copper(II) complex along with the macrocyclic amine L^5.[5] These amines are products of zinc/acid reductions of the nitro precursors L^6 and L^7 which are formed readily from reaction of $[Cu(en)_2]^{2+}$ (en = ethane-1,2-diamine), nitroethane, and formaldehyde.[5]

The amine L^1 is based on the linear tetra-amine 2,3,2-tet (1,9-diamino-3,7-diazanonane) with a primary amino group, in addition to a methyl group, attached to the central carbon atom of the chain. It can also be considered as derived from 1,2,3-triaminopropane (L^8), with two (2-aminoethyl) arms attached to the 1- and 3-amino groups, and an additional methyl group on the central carbon of the chain. When co-ordinated as a quinquedentate L^1 may form two geometric isomers (**A**) and (**B**) with (**B**) being enantiomeric. Since short cobalt–nitrogen bonds have been observed with the related type of geometry found for six-co-ordination of L^5 to cobalt(III),[4] it was of interest to see if like bond 'compression' occurs when L^1 is complexed. The syntheses as well as spectroscopic properties of L^1 are reported here.

Experimental

Syntheses.—(1,9-*Diamino*-5-*methyl*-5-*nitro*-3,7-*diazanonane*)*copper*(II) *perchlorate*, $[CuL^6][ClO_4]_2$ was prepared exactly as previously described,[5] and characterized by spectroscopic comparisons with an authentic sample.

Chloro(1,5,9-*triamino*-5-*methyl*-3,7-*diazanonane*)*cobalt*(III)-*chloride perchlorate*, $[Co(L^1)Cl]Cl[ClO_4]$. A solution of $[CuL^6][ClO_4]_2$ (15 g) in distilled water (500 cm^3) was treated with granulated zinc (*ca.* 20 g) followed by hydrochloric acid (50 cm^3, 10 mol dm^{-3}) and the mixture was stirred at 60 °C for 1 h. Gravity filtration was employed to remove solids, then the pH of the filtrate was raised to *ca.* 6. Filtration removed precipitated zinc hydroxide; then an excess of cobalt(II) chloride hexahydrate (14 g) was added to the filtrate. To this solution was added hydrogen peroxide (4 cm^3, 32% w/w) and the red solution was stirred at 60 °C for 2 h. After dilution to *ca.* 3 dm^3, the solution was sorbed onto a column (3 × 20 cm) of SP Sephadex C-25 resin (Na^+ form). Washing with 0.1 mol dm^{-3} $NaClO_4$ solution removed unreacted Co^{2+}, and the product was eluted with 0.2 mol dm^{-3} $NaClO_4$. Rotary evaporation of the eluate to *ca.* 20 cm^3, followed by addition of HCl (5 cm^3, 10 mol dm^{-3}), afforded crimson crystals on standing. These were collected, washed with small volumes of ethanol and diethyl ether, and dried in a vacuum desiccator (3.6 g, 28%). The filtrate yielded further crops on standing for extended periods (Found: C, 23.1; H, 5.5; N, 16.5. Calc. for $C_8H_{23}Cl_3CoN_5O_4$: C, 23.0; H, 5.5; N, 16.7%). Electronic spectrum (in water): $\lambda_{max.}$ 518 (ε 87), 450(sh) (51), 357 (100), and 228 nm (5 900 dm^3 mol^{-1} cm^{-1}). N.m.r. (D_2O): ^1H, δ 1.32 (s, 3 H), 2.76 (m, 4 H), and 3.10 (m, 8 H); ^{13}C, δ 18.6, 43.5, 54.7, 59.9, and 66.2 p.p.m.

Isothiocyanato(1,5,9-*triamino*-5-*methyl*-3,7-*diazanonane*)-*cobalt*(III) *tetrachlorozincate dihydrate*, $[CoL^1(NCS)][ZnCl_4] \cdot 2H_2O$. Potassium thiocyanate (1 g) was added to a solution of $[Co(L^1)Cl]Cl[ClO_4]$ (0.2 g) in water (50 cm^3). The solution was heated at 60 °C for 30 min. Addition of saturated sodium chloride solution (2 cm^3) followed by zinc chloride hexahydrate

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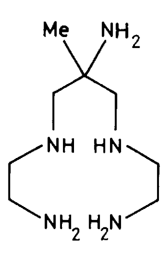
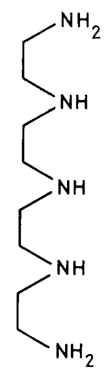
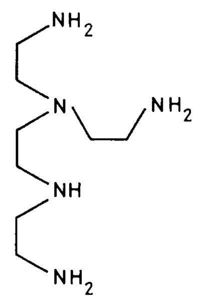
† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1990, Issue 1, pp. xix—xxii.



L^1



L^2



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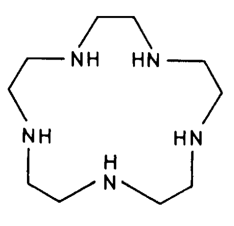
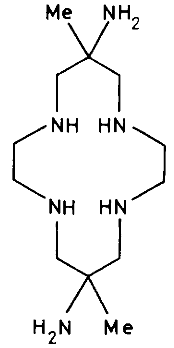


L^4



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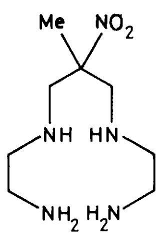
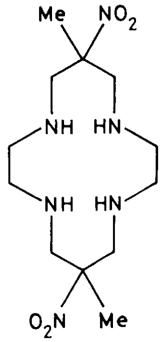
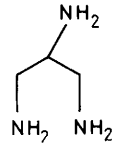


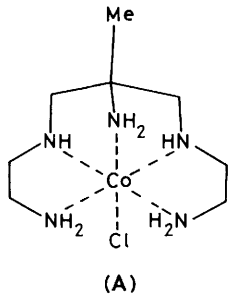
L^6



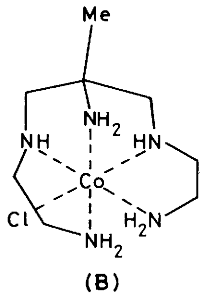
L^7



L^8



(A)



(B)

(0.5 g) and slow evaporation yielded the orange product, isolated as above (0.1 g, 38%) (Found: C, 19.65; H, 4.7; N, 15.2. Calc for $C_9H_{27}Cl_4CoN_6O_2SZn$: C, 19.7; H, 4.9; N, 15.2%). Electronic spectrum (in water): $\lambda_{max.}$ 480 (ε 130) and 294 nm (1 120 dm^3 mol^{-1} cm^{-1}). N.m.r. (D_2O): ^{1}H, δ 1.29 (s, 3 H) and 3.0 (m, 12 H); ^{13}C, δ 18.6, 43.5, 54.7, 60.6, 67.4, and 171.6 p.p.m.

$[Co(L^1 - H)(NO_2)][ClO_4]\cdot H_2O$. To a solution of $[Co(L^1)Cl]Cl[ClO_4]$ (0.5 g) in water (10 cm^3) was added sodium nitrate (0.5 g), and the solution was stirred at 80 °C for 2 h. Column chromatography (SP Sephadex C-25 resin) was employed, with the desired product eluted with 0.25 mol dm^{-3} $NaClO_4$ solution. The eluted solution was evaporated to *ca.* 20 cm^3 and on standing yielded yellow crystals which were collected, washed with small volumes of ethanol and diethyl ether, and dried in a vacuum desiccator (0.15 g, 31%) (Found: C, 23.4; H, 5.7; N, 20.3. Calc. for $C_8H_{24}ClCoN_6O_7$: C, 23.4; H, 5.9; N, 20.4%). Electronic spectrum (in water): $\lambda_{max.}$ 436 (ε 420), 326 (8 900), 239 (20 000), and 208 nm (33 000 dm^3 mol^{-1} cm^{-1}). N.m.r. (D_2O): ^{1}H, δ 2.08 (s, 3 H), 2.74 (m, 8 H), and 3.88 (s, br, 4 H); ^{13}C, δ 13.6, 36.7, 41.2, 42.9, 56.0, 57.7, 63.9, and 76.4 p.p.m.

μ-Peroxo-bis[(1,5,9-triamino-5-methyl-3,7-diazanonane)-cobalt(III)] perchlorate hydrate, $[(CoL^1)_2O_2][ClO_4]_4\cdot H_2O$. In the synthesis of $[Co(L^1)Cl]Cl[ClO_4]$ described above, a second slow-moving brown band was observed on the Sephadex chromatography column, and was eluted with 0.5 mol dm^{-3} $NaClO_4$ solution. Following rotary evaporation of the eluate to *ca.* 100 cm^3, the product precipitated as a brown powder and was isolated as above (2.5 g, 17%) (Found: C, 20.35; H, 5.1; N, 14.7. Calc. for $C_{16}H_{48}Cl_4Co_2N_{10}O_{19}$: C, 20.35; H, 5.1; N, 14.8%). Electronic spectrum (in water): $\lambda_{max.}$ 399 (ε 820), 294 (6 300), and 200 nm (13 000 dm^3 mol^{-1} cm^{-1}). N.m.r. (D_2O): ^{1}H, δ 1.28 (s, 6 H), 3.03 (q, 8 H), and 3.05 (m, 16 H); ^{13}C, δ 19.4, 43.5, 54.2, 59.4, and 64.3 p.p.m.

μ-Hyperoxo-bis[(1,5,9-triamino-5-methyl-3,7-diazanonane)-cobalt(III)] perchlorate tetrahydrate, $[(CoL^1)_2O_2][ClO_4]_5\cdot 4H_2O$. A solution of $[CuL^1][ClO_4]_2$ (7 g) was treated with granulated zinc and HCl as described above. After removal of zinc hydroxide, cobalt(II) chloride hexahydrate (5 g) was added to the filtrate. Aeration of the solution with a bubbler for 1 h was followed by the addition of hydrochloric acid (30 cm^3, 10 mol dm^{-3}). The solution was stirred and heated at 60 °C for 1 h, diluted to *ca.* 3 dm^3, and sorbed onto a column (3 × 15 cm) of Dowex 50W × 2 cation-exchange resin (H^+ form). Washing with 1 mol dm^{-3} HCl removed monomeric species (isolated as before) and the desired product was subsequently eluted with 3 mol dm^{-3} acid. This eluate was concentrated to *ca.* 50 cm^3 by rotary evaporation and perchloric acid (20 cm^3, 5 mol dm^{-3}) was added. Upon standing, lustrous green crystals of crystallographic quality formed and were collected, washed with small volumes of ethanol and diethyl ether, and dried in a vacuum desiccator (0.5 g, 7%) (Found: C, 17.45; H, 5.1; N, 12.65. Calc. for $C_{16}H_{54}Cl_5Co_2N_{10}O_{26}$: C, 17.5; H, 5.0; N, 12.75%). Electronic spectrum (in water): $\lambda_{max.}$ 701 (ε 1 760), 464 (630), 303 (7 400), and 214 nm (9 800 dm^3 mol^{-1} cm^{-1}).

Physical Methods.—Electronic spectra were recorded using an Hitachi 150-20 spectrophotometer, i.r. spectra of compounds dispersed in KBr discs on a Nicolet MX-1 FT-IR spectrometer. N.m.r. spectra were recorded using a JEOL FX90Q FT spectrometer, using sodium trimethylsilylpropionate and 1,4-dioxane as internal standards for ^{1}H and ^{13}C respectively, although ^{13}C chemical shifts are cited *versus* tetramethylsilane. Voltammetry experiments were performed with a BAS model CV-27 controller and a conventional three-electrode configuration comprising a glassy carbon working electrode, a platinum auxiliary electrode, and a Ag–AgCl reference electrode. Direct current (d.c.) polarography employed an AMEL model 457 analyser and a PAR model 303 dropping mercury working electrode, with other electrodes as above. All solutions were 0.1 mol dm^{-3} in sodium perchlorate, and were purged with nitrogen before measurement. Raman spectra were measured with a Spex Ramalog 5 laser spectrophotometer using argon-ion excitation generally at 5 145 Å over the region 700—1 200 cm^{-1}. The sample as either a disc or aqueous solution (typically 5 × 10^{-3}

mol dm^{-3}) was spun at approximately 1 200 revolutions min^{-1} in a rotating disc holder or glass solution cell, respectively, to minimize decomposition by the laser beam.

Table 1. Positional parameters ($\times 10^4$) for [Co(L^1)Cl]Cl[ClO$_4$]

Atom	*x*	*y*	*z*
Co	1 703(1)	2 953(1)	3 660(1)
Cl(1)	981(1)	3 674(1)	2 113(1)
N(1)	3 228(2)	2 346(2)	3 165(2)
N(2)	808(2)	1 548(2)	3 312(2)
N(3)	2 378(2)	2 191(2)	4 913(2)
N(4)	2 701(3)	4 303(2)	4 028(2)
N(5)	166(2)	3 451(2)	4 208(2)
C(1)	3 680(3)	1 349(3)	3 791(2)
C(2)	2 706(3)	1 068(2)	4 513(2)
C(3)	1 432(3)	639(2)	3 966(2)
C(4)	4 180(3)	3 274(3)	3 143(3)
C(5)	4 074(3)	4 059(3)	4 002(3)
C(6)	−593(3)	1 738(3)	3 370(3)
C(7)	−709(3)	2 476(3)	4 262(3)
C(8)	3 273(3)	249(3)	5 341(2)
Cl(2)	1 840(1)	4 389(1)	6 320(1)
Cl(3)	3 677(1)	7 283(1)	3 586(1)
O(1)	6 545(3)	1 492(2)	2 200(2)
O(2)	6 877(5)	1 873(4)	582(4)
O(3)	4 969(3)	2 343(4)	1 155(3)
O(4)	6 792(8)	3 351(5)	1 776(5)
O(1′)	7 384(39)	3 153(33)	1 471(33)
O(2′)	6 854(37)	3 201(33)	2 099(31)
O(3′)	6 266(37)	3 405(40)	1 503(38)
O(4′)	6 499(31)	2 453(29)	273(24)

Table 2. Positional parameters ($\times 10^4$) for [(CoL^1)$_2$O$_2$][ClO$_4$]$_5$·4H$_2$O

Atom	*x*	*y*	*z*
Co(1)	373(1)	1 750(1)	1 497(1)
O(1)	−251(5)	557(7)	123(4)
O(1′)	−423(15)	62(27)	387(17)
N(1)	−313(2)	158(2)	2 287(2)
N(2)	2 613(2)	1 684(2)	1 558(2)
N(3)	1 003(3)	3 009(2)	2 859(2)
N(4)	−1 882(2)	1 770(2)	1 544(2)
N(5)	1 255(3)	3 436(2)	789(2)
C(1)	568(3)	700(3)	3 349(2)
C(2)	1 883(3)	2 194(2)	3 386(2)
C(3)	3 272(3)	2 117(3)	2 675(2)
C(4)	−2 166(3)	−392(3)	2 276(2)
C(5)	−2 742(3)	908(3)	2 333(2)
C(6)	3 608(3)	2 625(3)	842(2)
C(7)	3 082(3)	3 946(3)	902(2)
C(8)	2 550(5)	2 960(4)	4 487(2)
Cl(1)	5 000(1)	0(1)	5 000(1)
O(2)	5 413(7)	1 355(7)	4 576(6)
O(3)	3 066(6)	−474(7)	4 951(5)
O(4)	4 731(9)	1 098(8)	5 731(6)
O(5)	5 480(10)	191(11)	5 963(4)
Cl(2)	7 002(1)	2 062(1)	8 898(1)
O(6)	5 761(3)	2 487(2)	8 463(2)
O(7)	6 236(2)	847(2)	9 430(2)
O(8)	7 881(3)	1 549(2)	8 081(2)
O(9)	8 080(3)	3 263(2)	9 620(2)
Cl(3)	1 759(1)	4 110(1)	7 652(1)
O(10)	955(3)	2 923(2)	6 837(2)
O(11)	678(4)	4 953(3)	7 890(2)
O(12)	1 965(4)	3 523(3)	8 543(2)
O(13)	3 221(4)	4 979(4)	7 311(3)
O(14)	1 286(4)	6 266(4)	5 615(2)
O(15)	2 474(5)	6 226(3)	3 464(3)
O(15′)	6 479(21)	3 971(15)	6 587(11)

Structure Determination.—Crystal data. [Co(L^1)Cl]Cl[ClO$_4$] (**1**), $C_8H_{23}Cl_3CoN_5O_4$, M = 418.6, monoclinic, space group $P2_1/c$, a = 10.471(2), b = 11.878(3), c = 13.284(2) Å, β = 97.70(1)°, U = 1 637.3(5) Å^3, D_c (Z = 4) = 1.698 g cm^{-3}, F(000) = 864, μ(Mo-K_α) = 14.99 cm^{-1}. Specimen: crimson needles, 0.25 × 0.20 × 0.08 mm. $A^*_{\text{min.,max.}}$ 0.84, 0.76. N = 2 729, N_o = 2 474, range of hkl 0—12, 0—14, −15 to 15, merging R = 0.014, R = 0.029, R' = 0.034, residual extrema ± 0.5 e Å^{-3}.

[(CoL^1)$_2$O$_2$][ClO$_4$]$_5$·4H$_2$O (**2**), $C_{16}H_{54}Cl_5Co_2N_{10}O_{26}$, M = 1 093.8, triclinic, space group $P\bar{1}$, a = 8.592(3), b = 9.792(3), c = 12.993(6) Å, α = 95.96(3), β = 97.70(1), γ = 109.38(3)°, U = 1 013.4(5) Å^3, D_c (Z = 1) = 1.792 g cm^{-3}, F(000) = 563, μ(Mo-K_α) = 11.91 cm^{-1}. Specimen: dark green prisms, 0.40 × 0.38 × 0.24 mm. $A^*_{\text{min.,max.}}$ 0.76, 0.72. N = 3 521, N_o = 3 360, range of hkl 0—10, −11 to 11, −15 to 15, merging R = 0.008, R = 0.031, R' = 0.037, residual extrema ± 0.4 e Å^{-3}.

Cell constants were determined by a least-squares fit to the setting parameters of 25 independent reflections. Data were measured on an Enraf-Nonius CAD4-F diffractometer within the limit $2\theta_{\text{max.}}$ = 50°, with Mo-K_α radiation, λ = 0.710 69 Å, graphite monochromator, and operating in the ω—1.33θ mode. Independent reflections with $I > 2.5\,\sigma\,(I)$ were considered observed and used for solution of structures. Data were reduced and Lorentz, polarization, and decomposition corrections were applied using a local data reduction program. Structure (**1**) was solved by Patterson and Fourier synthesis techniques, and was refined by full-matrix least-squares analysis with SHELX 76.[6] The perchlorate anion was found to be rotationally disordered over two sites. All non-hydrogen atoms with the exception of the minor contributors to the perchlorate were refined anisotropically. Hydrogen atoms were refined with isotropic thermal parameters. Structure (**2**) was solved using the automatic Patterson methods of SHELX 86,[7] and was refined using SHELX 76.[6] The superoxide group and one water molecule were found to be disordered over two sites [both 85(2):15(2)]. Non-hydrogen atoms with the exception of minor contributors to disordered sites were refined anisotropically. Hydrogen atoms were refined with individual isotropic thermal parameters. Hydrogen atoms were not located for the disordered water molecule. Residuals on $|f|$ at convergence are conventional R,R', $w = g/(\sigma F_o = kF_o{}^2)$ where g, k are 2.10, 1.6×10^{-4} for structure (**1**) and 5.23, 8.3×10^{-5} for structure (**2**) respectively. Scattering factors and anomalous dispersion corrections for Co were taken from ref. 8, and for all others the values supplied in SHELX 76 were used. The absorption correction was made by numerical integration.[9] Non-hydrogen atom co-ordinates are listed in Tables 1 and 2. The atomic nomenclature is defined in ORTEP drawings[10] in Figures 1 and 2.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates and thermal parameters.

Results

Reaction of the multidentate amine L^1 with Co^{2+}(aq) and air or peroxide yielded cobalt(III) products with cobalt:ligand ratios of 1:1 and the ligand co-ordinated as a quinquedentate. Complexes isolated as μ-peroxo-dicobalt and μ-superoxo-dicobalt species both have the common ligand geometry depicted in (**A**), from crystallographic and n.m.r. evidence. The superoxo dimer was characterized by a crystal-structure analysis (see below), whereas the peroxo analogue exhibited only five resonances in the proton-decoupled ^{13}C n.m.r. spectrum arising from the unique methyl and tertiary carbons plus the three sets of methylene carbons, each pair being symmetry related to its partner by a mirror plane bisecting the metal, tertiary carbon, and methyl carbon atoms. The [Co(L^1)Cl]$^{2+}$ ion displayed a

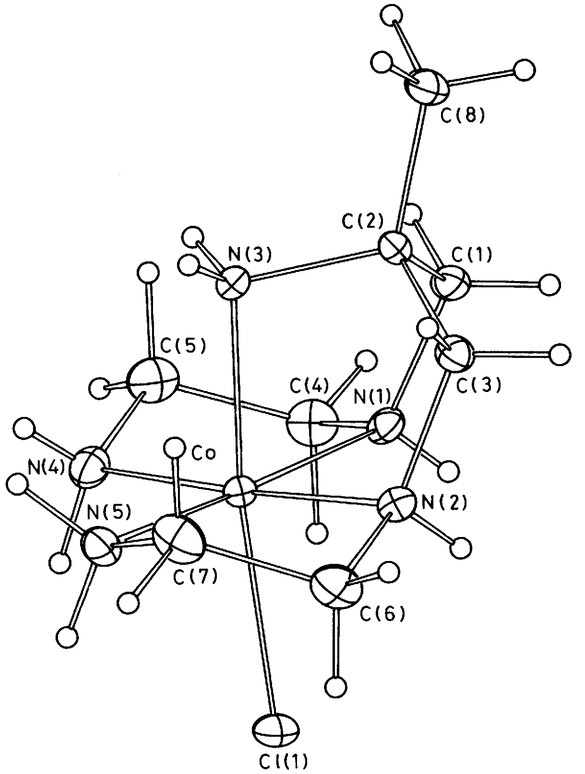


Figure 1. View of the cation $[Co(L^1)Cl]^{2+}$

Table 3. Bond distances (Å) and angles (°) for $[Co(L^1)Cl]Cl[ClO_4]$

Cl(1)–Co	2.261(1)	N(1)–Co	1.945(2)
N(2)–Co	1.939(2)	N(3)–Co	1.944(2)
N(4)–Co	1.941(3)	N(5)–Co	1.945(2)
C(1)–N(1)	1.487(4)	C(4)–N(1)	1.490(4)
C(3)–N(2)	1.482(3)	C(6)–N(2)	1.497(4)
C(2)–N(3)	1.493(3)	C(5)–N(4)	1.472(4)
C(7)–N(5)	1.486(4)	C(2)–C(1)	1.528(4)
C(3)–C(2)	1.519(4)	C(8)–C(2)	1.527(4)
C(5)–C(4)	1.489(5)	C(7)–C(6)	1.491(5)
N(1)–Co–Cl(1)	91.3(1)	N(2)–Co–Cl(1)	91.0(1)
N(2)–Co–N(1)	89.6(1)	N(3)–Co–Cl(1)	173.8(1)
N(3)–Co–N(1)	84.0(1)	N(3)–Co–N(2)	84.9(1)
N(4)–Co–Cl(1)	91.1(1)	N(4)–Co–N(1)	87.3(1)
N(4)–Co–N(2)	176.3(1)	N(4)–Co–N(3)	92.7(1)
N(5)–Co–Cl(1)	91.8(1)	N(5)–Co–N(1)	175.6(1)
N(5)–Co–N(2)	87.3(1)	N(5)–Co–N(3)	92.6(1)
N(5)–Co–N(4)	95.7(1)	C(1)–N(1)–Co	108.7(2)
C(4)–N(1)–Co	108.3(2)	C(4)–N(1)–C(1)	115.8(2)
C(3)–N(2)–Co	109.1(2)	C(6)–N(2)–Co	107.7(2)
C(6)–N(2)–C(3)	116.0(2)	C(2)–N(3)–Co	100.7(1)
C(5)–N(4)–Co	109.0(2)	C(7)–N(5)–Co	109.2(2)
C(2)–C(1)–N(1)	109.6(2)	C(1)–C(2)–N(3)	103.5(2)
C(3)–C(2)–N(3)	103.9(2)	C(3)–C(2)–C(1)	113.0(2)
C(8)–C(2)–N(3)	113.4(2)	C(8)–C(2)–C(1)	111.3(2)
C(8)–C(2)–C(3)	111.3(2)	C(2)–C(3)–N(2)	109.0(2)
C(5)–C(4)–N(1)	109.3(3)	C(4)–C(5)–N(4)	108.4(3)
C(7)–C(6)–N(2)	108.3(2)	C(6)–C(7)–N(5)	107.6(3)

similar ^{13}C n.m.r. spectrum, and the crystal structure confirmed the symmetry of the complex to be C_s. No other geometric isomers were detected chromatographically or following crystallization of products.

The co-ordinated chloro ligand was replaced by thiocyanate ion without alteration of the cation symmetry. The ^{13}C n.m.r. spectrum of the thiocyanato derivative replicates that of the chloro species, with the exception of the additional resonance, at low field, from the co-ordinated anion itself. The i.r. spectrum of the thiocyanato derivative displays, in addition to amine resonances, peaks at 2 120 and 846 cm^{-1} which are assigned as C–N and C–S vibrations respectively in an N-bound thicyanato ligand. Also, the electronic maximum at low energy (480 nm) is more consistent with a CoN_6 chromophore than a CoN_5S species. The nitro derivative, however, displayed the low-symmetry *cis*-type geometry depicted in (**B**). The i.r. spectrum showed a distinct splitting of the H–N–H bending vibration into two peaks at 1 596 and 1 570 cm^{-1}. The proton-decoupled ^{13}C n.m.r. spectrum confirmed this assignment by displaying eight resonances, with no two carbons remaining chemically equivalent. The NO_2^- ion was assigned as N-bound from the characteristic nitro vibrations at 1 396, 1 332, and 828 cm^{-1} in the i.r. spectrum, reinforced by the low-energy maximum in the electronic spectrum appearing at 436 nm, clearly consistent with a CoN_6 chromophore. The isomerization is most probably a function of the strong *trans*-labilizing effect of the nitro ligand in comparison with chloride and thiocyanate ions. The isolation of the chromatographically pure nitro complex as an apparently monodeprotonated species from neutral solution may also be related to this effect.

The structure of $[Co(L^1)Cl]Cl[ClO_4]$ consists of a dipositive cation and chloride and perchlorate anions, with hydrogen bonds between the amine hydrogen atoms and the anions helping to stabilize the structure. Quinquedentate co-ordination of L^1 is confirmed, with the chloro ligand occupying the site *trans* to the nitrogen atom 'pendant' to the 2,3,2-tet backbone (Figure 1). Overall, the symmetry of the complex approaches C_s. Thus, the two five-membered chelate rings in the equatorial plane have opposite chiralities. Co-ordination of the 'pendant' nitrogen forces the six-membered ring defined by Co(1), N(1), N(2), and C(1)—C(3) into a near-perfect boat conformation and results in considerable strain in the complex. This is most evident in the bond angles Co–N(3)–C(2) 100.7(1), C(1)–N(1)–C(4) 115.8(2), and C(3)–N(2)–C(6) 116.0°. Despite this strain, or perhaps because of it, the cobalt–nitrogen bond lengths are unusually short at between 1.939(2) and 1.945(2) Å compared with hexakis(amine)cobalt(III) complexes such as $[Co(en)_3]^{3+}$ at 1.964 Å (average over 27 structures obtained from the Cambridge Crystallographic Data Base files). Similarly short lengths have been observed for the sexidentate complex $[CoL^5]Cl_2[ClO_4]$.[4] In that case similar distortions of angles were found and bond lengths in the range 1.938(2)—1.946(2) Å were reported. Evidently, expansion of the ligands would increase the intra-ligand strain which results from co-ordination of the 'pendant' nitrogen and the formation of the boat conformation. Somewhat surprisingly, the cobalt–chlorine bond length is also unusually short at 2.261(1) Å. This can be compared with the equivalent distance of 2.286(1) Å for $[Co(NH_3)_5Cl]Cl_2$.[11] Bond distances and angles appear in Table 3.

Both μ-peroxo-dicobalt(III) and μ-superoxo-dicobalt(III) complexes of L^1 were isolated in addition to monomers. They exhibit the typically brown and green colours, respectively, anticipated for these ions. Further, the two ions exhibit equivalent reversible, one-electron redox couples associated with the superoxo/peroxo system ($E_{\frac{1}{2}}$ 0.56 V *versus* Ag–AgCl, glassy carbon working electrode, ΔE 70 mV, i_c/i_a 1.0 at scan rate 100 mV s^{-1}). An irreversible couple ($E_{\frac{1}{2}}$ −0.73 V) for the simultaneous two Co^{III}–Co^{II} reductions is also observed for these dimers, whereas a quasi-reversible Co^{III}–Co^{II} couple observed for $[Co(L^1)Cl]^{2+}$ occurs at −0.40 V (*versus* Ag–AgCl, hanging mercury drop working electrode, ΔE 130 mV, i_c/i_a 1.0 at scan rate 100 mV s^{-1}). The common ligand geometry of these

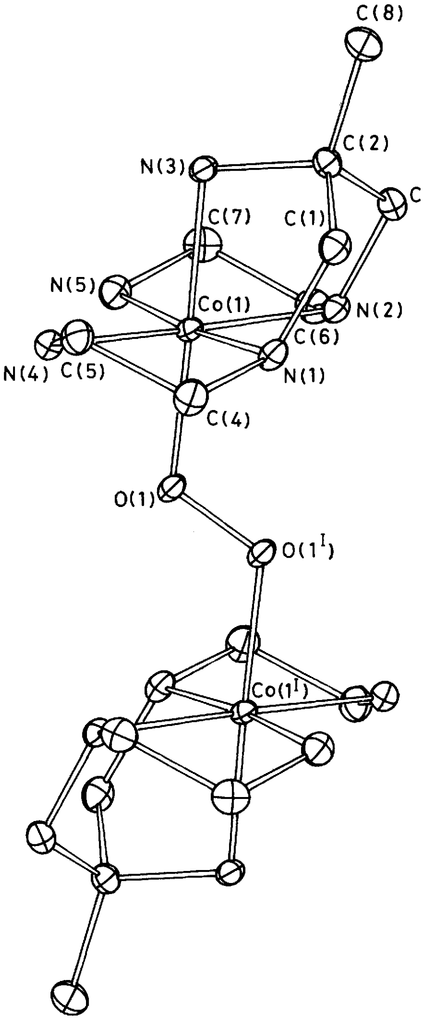


Figure 2. View of the cation $[(CoL^1)_2O_2]^{5+}$

Table 4. Bond distances (Å) and angles (°) for $[(CoL^1)_2O_2][ClO_4]_5 \cdot 4H_2O$

O(1)–Co(1)	1.922(5)	O(1′)–Co(1)	1.922(21)
N(1)–Co(1)	1.944(2)	N(2)–Co(1)	1.949(2)
N(3)–Co(1)	1.934(2)	N(4)–Co(1)	1.947(2)
N(5)–Co(1)	1.962(2)	O(1)–O(1^{I})	1.294(14)
O(1′)–O(1′^{I})	1.258(39)	C(1)–N(1)	1.494(3)
C(4)–N(1)	1.501(3)	C(3)–N(2)	1.493(3)
C(6)–N(2)	1.492(3)	C(2)–N(3)	1.504(4)
C(5)–N(4)	1.484(4)	C(7)–N(5)	1.480(4)
C(2)–C(1)	1.516(3)	C(3)–C(2)	1.526(4)
C(8)–C(2)	1.508(4)	C(5)–C(4)	1.502(4)
C(7)–C(6)	1.496(5)		
N(1)–Co(1)–O(1)	97.3(2)	N(1)–Co(1)–O(1′)	78.8(8)
N(2)–Co(1)–O(1)	95.4(2)	N(2)–Co(1)–O(1′)	94.1(5)
N(2)–Co(1)–N(1)	89.2(1)	N(3)–Co(1)–O(1)	178.0(2)
N(3)–Co(1)–O(1′)	163.3(8)	N(3)–Co(1)–N(1)	84.6(1)
N(3)–Co(1)–N(2)	85.2(1)	N(4)–Co(1)–O(1)	87.5(2)
N(4)–Co(1)–O(1′)	87.6(5)	N(4)–Co(1)–N(1)	87.0(1)
N(4)–Co(1)–N(2)	175.5(1)	N(4)–Co(1)–N(3)	92.0(1)
N(5)–Co(1)–O(1)	86.6(2)	N(5)–Co(1)–O(1′)	105.0(7)
N(5)–Co(1)–N(1)	174.6(1)	N(5)–Co(1)–N(2)	86.8(1)
N(5)–Co(1)–N(3)	91.5(1)	N(5)–Co(1)–N(4)	96.9(1)
Co(1)–O(1)–O(1^{I})	118.5(5)	Co(1)–O(1′)–O(1′^{I})	120.0(20)
Co(1)–N(1)–C(1)	108.4(1)	C(4)–N(1)–Co(1)	108.7(2)
C(4)–N(1)–C(1)	115.3(2)	C(3)–N(2)–Co(1)	108.4(2)
C(6)–N(2)–Co(1)	108.6(2)	C(6)–N(2)–C(3)	114.9(2)
C(2)–N(3)–Co(1)	101.1(1)	C(5)–N(4)–Co(1)	109.3(2)
C(7)–N(5)–Co(1)	108.8(2)	C(2)–C(1)–N(1)	109.9(2)
C(1)–C(2)–N(3)	103.2(2)	C(3)–C(2)–N(3)	103.8(2)
C(3)–C(2)–C(1)	112.4(2)	C(8)–C(2)–N(3)	112.8(2)
C(8)–C(2)–C(1)	112.6(2)	C(8)–C(2)–C(3)	111.5(2)
C(2)–C(3)–N(2)	109.7(2)	C(5)–C(4)–N(1)	107.9(2)
C(4)–C(5)–N(4)	107.6(2)	C(7)–C(6)–N(2)	108.2(2)
C(6)–C(7)–N(5)	108.2(2)		

Symmetry equivalent position: I $-x, -y, -z$.

complexes was confirmed by a crystal-structure analysis of the superoxo complex, supported by n.m.r. spectroscopy of the peroxo complex.

The structure of the superoxo complex consists of a dimeric cation situated at a centre of symmetry, one perchlorate anion, with oxygens disordered over two inversion-related sites, at a centre of symmetry, two perchlorates at general sites, and three water molecules one of which is disordered over two sites. There are numerous hydrogen bonds between the amine groups, perchlorate anions, and water molecules. The complex cation (Figure 2) comprises two CoL^1 units bridged by a superoxide anion. The ligand geometry and the cobalt–nitrogen distances are similar to those observed in the chloro structure. The cobalt–oxygen distance [1.922(5) Å] is longer than that in the superoxo-bridged complex $[\{Co(NH_3)_5\}_2O_2]^{5+}$ [1.895(3) Å],[12] but the oxygen–oxygen bond length in this work [1.294(14) Å] is shorter than the equivalent length in the ammine complex [1.317(10) Å]. The Co–O–O angles in the two structures are similar; 117.6° in the ammine dimer and 118.5(5)° in the present structure. The Co–O–O–Co assembly is perfectly planar since it lies about a centre of symmetry, consistent with the formulation of the O–O group as a superoxide. Bond distances and angles appear in Table 4. The disorder of the O–O group results from a movement of the oxygen atom towards N(1) and away from N(5). The geometry about the minor contributor to the O–O group is also consistent with a superoxo group. This disorder appears to be correlated with the disorder of the water molecule O(15) which is hydrogen bonded to the NH_2 group *trans* to O(1). It is not obvious which disorder causes which, if indeed the two are correlated.

A Raman spectrum of the μ-peroxo-dicobalt(III) complex of L^1 was measured to determine exclusively the frequency of the O–O stretching vibration. The spectrum in a disc with KBr displayed two bands, at 768 and 789 cm^{-1}. Both are characteristic of an O–O stretch in a peroxo-bridged dicobalt(III) complex. Although one should expect a single band, a similar observation has been reported during an extensive study of related complexes,[13] and was attributed to interaction between the dispersant and the complex. We were unable to obtain a satisfactory spectrum of the superoxo complex in either the solid or solution, possibly because of an inherently lower intensity and masking by a perchlorate resonance which arises in the same region.

Hydrolysis of the $[Co(L^1)Cl]^{2+}$ ion in aqueous base was investigated briefly, and proceeds in a single step to the hydroxo analogue. Rate constants were measured at various pH values at 25 °C [$10^5\, k_{obs.}/s^{-1}$ (pH): 1.65 (8.77), 5.50 (9.25), 10.7 (9.53), 12.0 (9.62), and 16.2 (9.74)]; the values were essentially independent of the buffer concentration or choice of buffer. These data yielded a second-order rate constant of 2.4(1) $dm^3\, mol^{-1}\, s^{-1}$. This rate is slow in comparison with data for a range of chloropentaminecobalt(III) ions[14] (see Table 5) and probably reflects the shorter than normal Co–Cl bond in the complex.

Table 5. Comparative physical properties of chloropentaminecobalt(III) complexes

Complex	Electronic spectrum $\lambda_{max.}$/nm (ε/dm^3 mol^{-1} cm^{-1})	Average bond lengths/Å Co–N	Co–Cl	Base hydrolysis rate constant, at 25 °C k_{OH}/dm^3 mol^{-1} s^{-1}
$[Co(NH_3)_5Cl]^{2+}$[a]	534 (50), 364 (47)	1.973	2.286	1.6
χ-$[Co(en)(dien)Cl]^{2+}$[b]	518 (86), 488 (84), 366 (88)	1.960	2.268	3 000
π-$[Co(en)(dien)Cl]^{2+}$[b]	525 (67), 475 (44), 361 (71)	1.968	2.249	27
αβ-$[Co(L^2)Cl]^{2+}$[c]	525 (99), 480 (101), 360 (107)	1.97	2.271	3 500
s-$[Co(L^3)Cl]^{2+}$[d]	510 (154), 367 (138)			880
$[Co(HL^5)Cl]^{2+}$[e]	518 (81), 470 (83), 347 (170)			160
$[Co(L^1)Cl]^{2+}$[f]	518 (87), 450 (51), 357 (100)	1.943	2.261	2.4

[a] Ref. 11 and 14. [b] A. R. Gainsford, D. A. House, and W. T. Robinson, *Inorg. Chim. Acta*, 1971, **5**, 595. (dien = 3-azapentane-1,5-diamine.) [c] Ref. 1. [d] Ref. 2. [e] Ref. 4; P. V. Bernhardt, unpublished work. [f] This work.

Discussion

The ligand L^1 represents a new type of multidentate, non-cyclic ligand. Because of its structure, with both secondary amino groups and the 'pendant' primary amino group required to occupy an octahedral face, L^1 may form but two geometric isomers around an octahedral metal ion (**A**) and (**B**). We have observed both, although the symmetric structure appears to be preferred. More importantly, at least when bound to cobalt(III), the metal–nitrogen bond lengths are uniformly unusually short, an observation which has not been reported previously for non-cyclic saturated amine ligands. Although short bonds have been observed in a range of structures, they are generally compensated by long Co–N bonds elsewhere in the molecule. This may be seen by comparing averaged Co–N distances for a range of complex cations (Table 5), where the value for $[Co(L^1)Cl]^{2+}$ is shorter than others by *ca.* 2 pm.

The structural unit of the molecule which appears to govern the structural and physical properties of complexes comprising L^1 (or L^5 likewise) is the co-ordinated 'pendant' primary amino group in combination with the adjacent secondary amino groups. The closest relative of L^1 in this sense is the tridentate amine L^8, which has the same arrangement of donors on an octahedral face, but with all primary amine donors. The central (or 'pendant') amine donor in the $[CoL^8{}_2]^{3+}$ complex also forces a boat conformation when co-ordinated and the Co–N distance in that case is only 1.942(2) Å compared with 1.939(2) Å in the L^1 complex.[15,16] The other donors in L^8, however, unconstrained by another chelate ring and terminal donors, form significantly longer bonds [1.961(2) and 1.964(2) Å][15] compared with distances in $[Co(L^1)Cl]^{2+}$ *ca.* 2 pm shorter [1.944(2) and 1.945(2) Å]. Clearly, the co-ordination of the aminoethyl arms in L^1 plays a role in constraining the two secondary donors and shortening these distances, with the two primary amine donors subsequently constrained to approach the metal ion more closely. The central 'pendant' primary amino group locks the six-membered chelate it is attached to into a rigid boat conformation. Elongation of this axial Co–N bond would also require lateral displacement, so the ligand may 'require' the shorter bonds. Nevertheless, it is debatable whether these bonds are compressed or are more optimal than unusual. Molecular mechanics modelling of these structures, in which the unstrained bond length is taken to be 1.905 Å, reproduces the observed bond lengths.[4] We believe that the present ligand does not stretch the Co–N bonds as much as other pentamine ligands. The short Co–Cl bond length in $[Co(L^1)Cl]^{2+}$ may be a corollary of this, with the contracted co-ordination sphere of the complex allowing a closer approach by the chloro ligand.

However one argues for the shorter bond lengths, it appears that the physical properties of the complexes are influenced when they occur.[4] Shorter Co–N bond lengths can be tied to higher energy maxima in the electronic spectrum. In the spectra of chlorocobalt(III) complexes of quinquedentate amines this is best demonstrated by comparisons of the energies of the higher-energy spin-allowed transition $[{}^1T_{2g} \longrightarrow {}^1A_{1g}\ (O_h)]$ since the low-energy transition is split under the influence of the local C_{4v} symmetry; data in Table 5 place the maxima for L^1 at highest energy of those listed. Further, the Co^{III}–Co^{II} redox couple in $[Co(L^1)Cl]^{2+}$ occurs at a quite negative potential in comparison with other complexes of this type. This has also been observed in the electrochemistry of the related sexidentate in $[CoL^5]^{3+}$ which displays the most negative Co^{III}–Co^{II} redox couple of any hexaminecobalt(III) ion.[4] The surprisingly high degree of reversibility observed in this couple for $[Co(L^1)Cl]^{2+}$ is probably a function of the short bonds, both Co–N and Co–Cl, which result in the co-ordination sphere remaining intact, on a voltammetric scale, even when reduced to the labile cobalt(II) state. Base hydrolysis of the cobalt–chlorine bond in $[Co(L^1)Cl]^{2+}$ is slow in comparison with other systems (see Table 5), and is consistent with the short, and presumably more stable, bond if ground-state control of hydrolysis is important.

From dioxygen through superoxide to peroxide there is a decrease in bond order and hence an increase in bond length.[17] For O_2 (bond order 2), its stretching frequency occurs at 1 580 cm^{-1}, compared with 1 097 cm^{-1} for $O_2{}^-$ (bond order 1.5) and 802 cm^{-1} for $O_2{}^{2-}$ (bond order 1) in simple salts. Further, the bond lengths vary from 1.21 (O_2) to 1.33 (KO_2) to 1.49 Å (BaO_2). For ionic binuclear cobalt(III) dioxygen complexes average bond lengths are 1.32 (μ-superoxo-dicobalt) and 1.47 Å (μ-peroxo-dicobalt). The short Co–N bonds observed in $[Co(L^1)Cl]^{2+}$ are duplicated in the superoxo-bridged complex. Moreover, the cobalt–oxygen bonds are longer and the dioxygen bond shorter than in the simple deca-ammine analogue. The Raman-active O_2 vibration in the peroxo-bridged complex occurs *ca.* 40 cm^{-1} to lower wave number than reported for the deca-ammine and other polyamine complexes.[13] Although structural information is not available, it seems reasonable to assume that the relatively low energy of the O–O vibration in the peroxo dimer observed here is a result of a longer than average O–O bond, in contrast to the relatively short O–O bond defined by a crystal structure of the superoxo analogue. Reasons for this apparent inversion are not immediately obvious, but presumably relate to the change in charge and bonding to the metal ion from superoxo to peroxo.

It is apparent that the type of chemistry recently reported[4] for the amino-substituted macrocycle L^5 is largely replicated with the open-chain relative L^1, since comparable bond 'compression' and related influences on physical properties operate. Although this comparison applies to date only for cobalt(III) chemistry, the observation of unusual properties for complexes of L^5 with a range of transition-metal ions[18] suggests that the chemistry of L^1 with other metal ions deserves investigation.

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