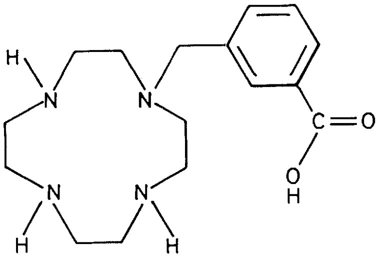
Structure of a Carboxylate-bridged Tetra-azamacrocyclic Complex of Cobalt(III)†

Theodore A. DelDonno, Naohide Matsumoto, and Daryle H. Busch *
Department of Chemistry, The Ohio State University, Columbus, Ohio 43210, U.S.A.
Nathaniel W. Alcock *
University of Warwick, Coventry CV4 7AL

A new macrocyclic ligand having a carefully selected pendant group has been synthesized and its cobalt(III) complex has been prepared and characterized by *X*-ray crystallography. 1,4,7,10-Tetra-azacyclododecane-*N*-*m*-toluic acid was prepared *via* the corresponding nitrile, from *m*-cyanobenzylbromide and the tetra-azamacrocycle, followed by formation of the cobalt(III) complex and then hydrolysis of the cyano group in the complex. The structure reveals a novel dinuclear structure in which the dangling carboxyl groups link the two metal ions. This is consistent with the molecular design since the pendant group was selected to prevent chelation of the carboxyl group to the same metal ion as the parent macrocycle. Crystal data: $[\{Co(C_{16}H_{25}N_4O_2)H_2O\}_2][ClO_4]_4\cdot6H_2O$: orthorhombic, space group *Pbcn*, $a = 25.346(7)$, $b = 15.722(2)$, $c = 25.720(4)$ Å, $Z = 8$ (dimers), and $R = 0.064$ for 2 806 unique observed $[I/\sigma(I) \geqslant 3.0]$ reflections. The crystal contains two independent but essentially identical dimers with two-fold symmetry, containing octahedral cobalt(III), *cis*-co-ordinated to four nitrogen atoms of the macrocycle, to a carboxylate oxygen, and to a water molecule.

It is well established that a major mode of activation of nucleophilic processes, both by metal complexes and by metal-containing enzymes, involves the polarization of the electrophilic centre by co-ordination to a metal atom throughout the course of nucleophilic attack at that electrophilic centre. At the active sites of such enzymes as carboxypeptidase A the nucleophile is precisely positioned to facilitate this bifunctional catalytic event.[1] It would seem to be a simple matter to add an extra nucleophile to a chelating ligand and provide the same dual role in relatively simple co-ordination compounds. The difficulty that must be overcome is the high probability that the putative nucleophile will also chelate to the metal ion. Clearly the solution to this simple problem requires careful consideration of the associated geometric relationships.

1,4,7,10-Tetra-azacyclododecane-*N*-*m*-toluic acid [HL, structure (**1**)] simultaneously conforms to the requisite geometric constraints described above and provides a readily synthesized example with which to test the proposed ligand type. The parent macrocycle, cyclen (1,4,7,10-tetra-azacyclododecane), can only chelate in a folded *cis* fashion to octahedral cobalt(III). This assures the presence of two unused *cis* sites in the co-ordination sphere of the metal ion for bidentate chelation to the substrate which would be an amino acid ester or amide, or a peptide. Again, it has been established that such chelation is required in order for a simple metal centre to bind and activate these carbonyl functions.[2] Further, the attachment of the putative nucleophile, the carboxyl group, at the *meta* position of the pendant benzyl moiety prevents the closure of a chelate ring and concomitant binding of the carboxyl group to the same metal atom. The present crystal structure determination shows that the undesirable chelation is indeed prevented, but that a dimer is formed in which the pendant carboxyl groups bind to other metal atoms.



(**1**)

Experimental

Synthesis of Complex (**7**).—The procedure is summarized in the Scheme. The 12-membered macrocycle, cyclen (**2**), was prepared by the method of Richman and Atkins.[3] *m*-Cyanobenzyl bromide (**3**) was prepared in excellent yield by reaction of *N*-bromosuccinimide (nbs) with *m*-cyanotoluene in carbon tetrachloride solution, using benzoyl peroxide as the initiator. Reaction between equimolar amounts of the macrocyclic tetramine and the α-bromo-*m*-toluonitrile in refluxing diethyl ether produces the desired product (**4**) which separates out as the insoluble hydrobromide salt in approximately 60% yield.

Neutralization of the ligand salt in the presence of equimolar amounts of $CoCl_2\cdot6H_2O$ in methanol, followed by air oxidation, generates complex (**5**). The product is isolated in *ca.* 65% yield as a purple solid.

The final step in the ligand synthesis is carried out using the cobalt(III) complex prepared as described immediately above. The nitrile function is hydrolyzed in hot concentrated hydrochloric acid and the product (**6**) dissolved in water and reprecipitated by addition of perchlorate. This produces the target complex (**7**) as a crystalline blue-purple solid in 70% yield. Recrystallization from water gave the crystals of the dimeric species that were used for *X*-ray crystal structure analysis.

Crystal Structure Determination.—Crystal data. $[\{Co(C_{16}H_{25}N_4O_2)H_2O\}_2][ClO_4]_4\cdot6H_2O$: orthorhombic, space group

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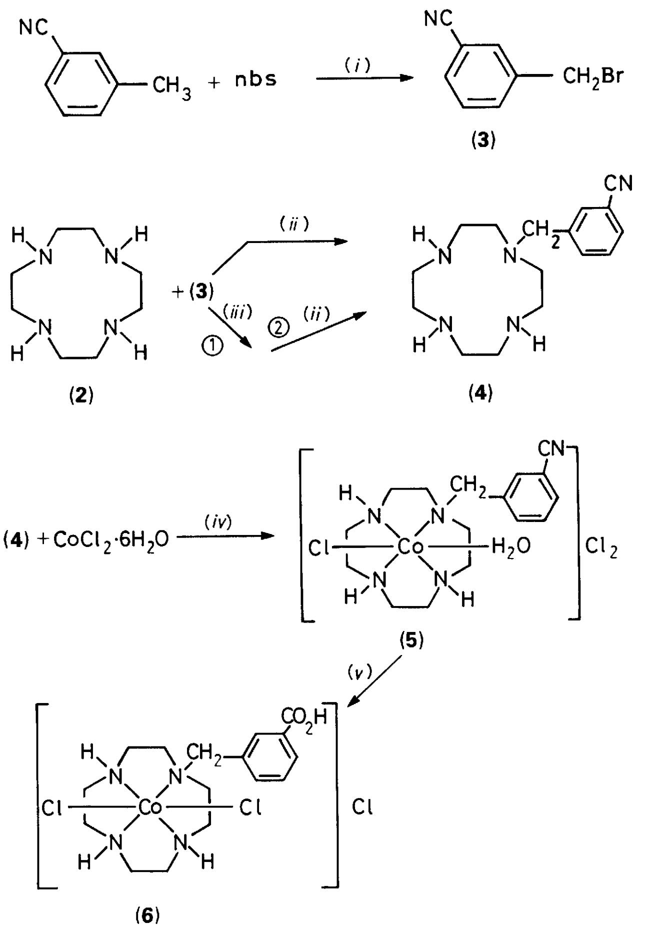
† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1990, Issue 1, pp. xix—xxii.



Scheme. (*i*) CCl_4, benzoyl peroxide; (*ii*) NEt_3, MeCN; (*iii*) Et_2O; (*iv*) MeOH; (*v*) concentrated HCl, heat

Pbcn, $M = 1\,270.5$, $a = 25.346(7)$, $b = 15.722(2)$, $c = 25.720(4)$, $U = 10\,249$ Å^3, $D_m = 1.64$ g cm^{-3}, $Z = 8$ (dimers), $D_c = 1.65$ g cm^{-3}, $\lambda(\text{Mo-}K_\alpha) = 0.710\,69$ Å, $\mu(\text{Mo-}K_\alpha) = 9.47$ cm^{-1}, T = 290 K. Data were collected with a Syntex $P2_1$ four-circle diffractometer. Maximum 2θ was 45°, with a scan range of ± 0.085 (2θ) around $K_{\alpha 1} - K_{\alpha 2}$, scan speed 1—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; *hkl* ranges 0—26, 0—16, 0—26. Monitored standard reflections showed no changes during data collection. Density was measured by flotation. Unit-cell dimensions and standard deviations were obtained by least-squares fit to 15 reflections ($20 < 2\theta < 25°$). A total of 7 259 reflections were processed of which 2 506 having $I/\sigma(I) \geqslant 3.0$ were used in refinement; reflections were corrected for Lorentz, polarization, and absorption effects, the last with ABSCOR;[4] maximum and minimum transmission factors, 0.92 and 0.81. Crystal dimensions were 0.29 × 0.27 × 0.17 mm. Systematic absences were $hk0, h + k \neq 2n$; $0kl, k \neq 2n$; $h0l, l \neq 2n$, indicating space group *Pbcn*.

Heavy atoms were located by the Patterson interpretation section of SHELXTL and the light atoms were then found on successive Fourier syntheses, to reveal two dimers, each with crystallographic two-fold symmetry, together with six solvent (H_2O) molecules and two co-ordinated H_2O per asymmetric unit. Anisotropic thermal parameters were applied to all non-H atoms and hydrogen atoms were given fixed isotropic thermal parameters, $U = 0.07$ Å^2. The hydrogen atoms defined by the molecular geometry were inserted at calculated positions and not refined. The hydrogen atoms of the water molecules were not located. Final refinement of *F* was by cascaded least-squares methods. The largest positive and negative peaks on a final difference Fourier synthesis were of height +1.0 and −0.5 eÅ^{-3}. A weighting scheme of the form $w = 1/[\sigma^2(F) + gF^2]$ with $g = 0.003$ was used and shown to be satisfactory by a weighting analysis. Final $R = 0.064$ and $R' = 0.067$. Computations were with SHELXTL[5] on a Data General DG30, apart from absorption corrections which were on a Burroughs B6700. Scattering factors were in the analytical form and dispersion factors were taken from ref. 6. Final atomic co-ordinates are given in Table 1 and bond lengths and angles in Tables 2.

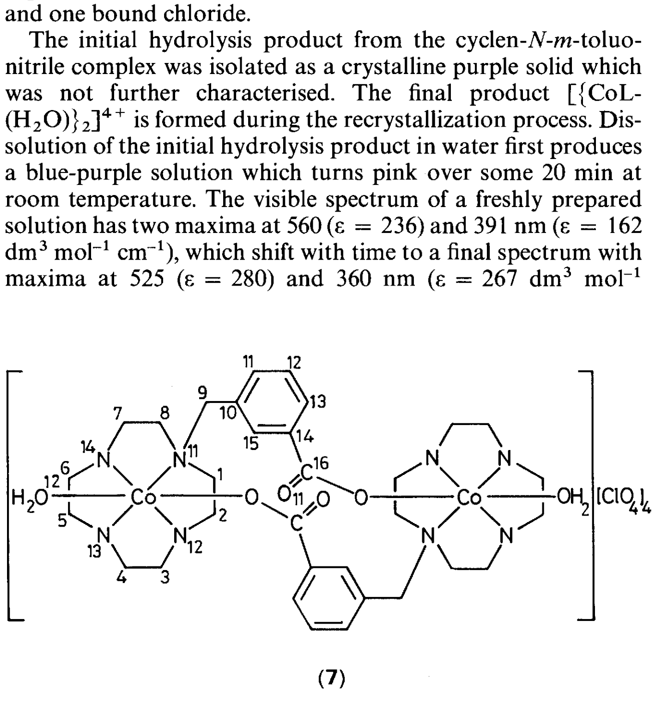
Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates and thermal parameters.

Discussion

Synthesis and Characterization.—The class of ligand sought in this study might be termed 'bimodal.' The target ligand molecule cyclen-*m*-toluic acid is designed to (1) chelate in a very specific way to a metal ion (*cis*-tetradentate) and (2) maintain an unencumbered nucleophilic function so positioned that it can readily attack an electrophilic centre located β to the metal centre (*e.g.* the carbonyl carbon of a bidentate chelated amino acid ester). As the Scheme shows, the synthesis of the target molecule is very straightforward but it enjoys the advantage of a final step that is a ligand reaction. The hydrolysis of the nitrile function within the metal complex is possible because of the great kinetic inertness of the cobalt(III) macrocyclic complex. The preceding steps are either routine organic chemistry or transition-metal co-ordination chemistry. A variety of alternative schemes were investigated but all encountered complexities when compared to this simple route.

The intermediate complex (**5**) was readily identified by the i.r. band of the nitrile group at 2 238 cm^{-1}. All other expected absorptions were also present. Conductivity measurements showed the compound to be a 2:1 electrolyte in aqueous solution, and the presence in the ^{13}C n.m.r. spectrum of eight distinct methylene carbon peaks attributable to the cyclen ring supported the formulation of the complex with one bound water and one bound chloride.

The initial hydrolysis product from the cyclen-*N*-*m*-toluonitrile complex was isolated as a crystalline purple solid which was not further characterised. The final product $[\{CoL(H_2O)\}_2]^{4+}$ is formed during the recrystallization process. Dissolution of the initial hydrolysis product in water first produces a blue-purple solution which turns pink over some 20 min at room temperature. The visible spectrum of a freshly prepared solution has two maxima at 560 (ε = 236) and 391 nm (ε = 162 dm^3 mol^{-1} cm^{-1}), which shift with time to a final spectrum with maxima at 525 (ε = 280) and 360 nm (ε = 267 dm^3 mol^{-1}



(**7**)

Table 1. Atomic co-ordinates (× 10^4) for the complex $[\{CoL(H_2O)\}_2][ClO_4]_4\cdot6H_2O$

Atom	*x*	*y*	*z*
Co(1)	9 076(1)	4 827(1)	3 827(1)
Co(2)	8 747(1)	9 748(1)	1 431(1)
Cl(1)	4 626(2)	6 669(2)	1 434(2)
Cl(2)	2 504(2)	2 120(3)	2 036(2)
Cl(3)	2 831(2)	2 383(3)	14(2)
Cl(4)	9 314(2)	6 679(3)	1 570(2)
O(101)	4 080(5)	6 621(10)	1 494(5)
O(102)	4 892(4)	6 367(9)	1 873(5)
O(103)	4 768(5)	7 502(7)	1 312(6)
O(104)	4 782(6)	6 166(8)	1 007(5)
O(201)	2 751(7)	1 682(14)	2 413(7)
O(202)	2 777(5)	1 917(10)	1 570(5)
O(203)	2 520(8)	2 946(8)	2 139(11)
O(204)	2 000(6)	1 839(11)	2 059(7)
O(301)	3 368(5)	2 497(9)	−73(6)
O(302)	2 601(7)	3 077(10)	215(8)
O(303)	2 774(10)	1 739(13)	325(12)
O(304)	2 638(9)	2 221(24)	−416(9)
O(401)	9 506(6)	7 354(10)	1 300(8)
O(402)	9 665(5)	6 193(9)	1 831(7)
O(403)	8 889(6)	6 921(11)	1 845(6)
O(404)	9 081(17)	6 091(13)	1 180(11)
O(001)	7 497(6)	1 629(9)	1 525(5)
O(002)	6 455(6)	3 039(10)	346(5)
O(003)	5 776(5)	1 619(8)	14(4)
O(004)	5 030(5)	2 832(7)	−6(5)
O(005)	6 165(8)	4 081(15)	−325(7)
O(006)	3 067(7)	5 965(13)	924(9)
N(11)	8 811(4)	4 657(6)	3 089(4)
N(12)	9 263(4)	5 958(6)	3 622(4)
N(13)	9 227(4)	5 211(7)	4 537(4)
N(14)	8 343(4)	5 040(7)	4 004(4)
O(11)	10 230(3)	4 528(5)	1 390(3)
O(12)	8 972(3)	3 629(5)	4 033(3)
O(13)	9 817(4)	4 310(7)	641(3)
N(21)	8 682(3)	9 686(6)	2 222(4)
N(22)	7 998(4)	9 980(7)	1 434(4)
N(23)	8 697(4)	10 041(6)	688(4)
N(24)	8 990(4)	10 885(6)	1 529(4)
O(21)	10 527(3)	9 461(5)	3 519(3)
O(22)	8 587(3)	8 531(5)	1 306(4)
O(23)	10 344(4)	9 118(6)	4 342(3)
C(1)	9 035(5)	5 421(7)	2 796(4)
C(2)	9 002(6)	6 199(7)	3 130(5)
C(3)	9 241(6)	6 533(8)	4 059(5)
C(4)	9 487(6)	6 070(8)	4 502(5)
C(5)	8 719(5)	5 248(10)	4 853(6)
C(6)	8 271(5)	4 859(10)	4 551(5)
C(7)	8 021(5)	4 547(10)	3 645(6)
C(8)	8 224(5)	4 714(9)	3 108(5)
C(9)	8 980(5)	3 818(7)	2 859(4)
C(10)	8 947(5)	3 793(8)	2 275(5)
C(11)	8 499(5)	3 496(7)	2 012(5)
C(12)	8 486(5)	3 475(8)	1 474(5)
C(13)	8 919(5)	3 744(8)	1 183(5)
C(14)	9 369(4)	4 020(7)	1 444(5)
C(15)	9 373(5)	4 034(7)	1 977(4)
C(16)	9 823(5)	4 305(7)	1 114(5)
C(21)	8 100(4)	9 782(9)	2 347(5)
C(22)	7 773(5)	9 546(9)	1 892(5)
C(23)	7 777(5)	9 726(10)	927(5)
C(24)	8 123(5)	10 110(10)	519(5)
C(25)	8 979(6)	10 875(8)	610(5)
C(26)	8 873(5)	11 431(8)	1 073(5)
C(27)	8 864(6)	11 198(9)	2 058(5)
C(28)	8 972(5)	10 450(7)	2 415(5)
C(29)	8 898(4)	8 867(7)	2 456(5)
C(30)	9 010(5)	8 886(8)	3 019(5)
C(31)	8 629(5)	8 744(9)	3 396(5)
C(32)	8 755(5)	8 764(9)	3 901(5)
C(33)	9 254(5)	8 919(8)	4 074(5)
C(34)	9 643(5)	9 072(7)	3 713(5)
C(35)	9 531(5)	9 056(8)	3 180(5)
C(36)	10 202(5)	9 215(8)	3 886(5)

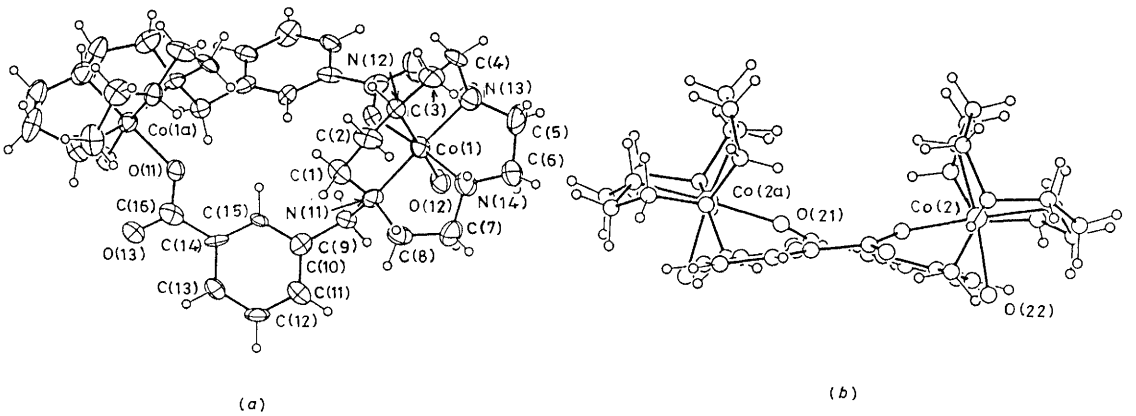


Figure. Structure of the dimeric complex cation $[\{Co(cyclen\text{-}N\text{-}m\text{-}toluato)(H_2O)\}_2]^{4+}$: (*a*) view of cation (**I**) showing the atomic numbering, emphasising the bridges and co-ordination spheres, (*b*) view of cation (**II**) looking along the planes of the benzene rings, emphasising the orientation of the chelate rings

cm^{-1}). Conductimetric measurements under the same conditions show values ranging from those typical of 1:1 electrolytes to those typical of 3:1 electrolytes for fresh and aged solutions, respectively. These results identify the aquation reactions that must accompany formation of the final product if the initial hydrolysis product is $[Co(HL)Cl_2]Cl$ (**6**). Preliminary kinetic experiments show rates for the successive aquation of the co-ordinated chlorides of 1.5×10^{-3} and 6.7×10^{-5} s^{-1}, respectively, values that are consistent with the suggestion.

The crystal contains two independent dimers, each with crystallographic two-fold symmetry [see structure (**7**) and the Figure]. Each cobalt ion has a distorted octahedral environment, made up of four *cis*-nitrogen atoms, a water oxygen, and the oxygen of the carboxylate group of the other

Table 2. Bond lengths (Å) and angles (°)

Co(1)–N(11)	2.032(9)	Co(1)–N(12)	1.914(9)	O(11)–Co(1a)	1.904(8)	O(13)–C(16)	1.218(16)
Co(1)–N(13)	1.960(10)	Co(1)–N(14)	1.940(10)	N(21)–C(21)	1.518(14)	N(21)–C(28)	1.493(15)
Co(1)–O(12)	1.975(8)	Co(1)–O(11a)	1.905(8)	N(21)–C(29)	1.525(15)	N(22)–C(22)	1.477(17)
Co(2)–N(21)	2.042(9)	Co(2)–N(22)	1.932(10)	N(22)–C(23)	1.473(17)	N(23)–C(24)	1.520(16)
Co(2)–N(23)	1.970(10)	Co(2)–N(24)	1.907(9)	N(23)–C(25)	1.507(17)	N(24)–C(26)	1.484(16)
Co(2)–O(22)	1.982(8)	Co(2)–O(21a)	1.899(7)	N(24)–C(27)	1.481(16)	O(21)–C(36)	1.311(15)
Cl(1)–O(101)	1.395(13)	Cl(1)–O(102)	1.397(13)	O(21)–Co(2a)	1.899(8)	O(23)–C(36)	1.238(15)
Cl(1)–O(103)	1.393(12)	Cl(1)–O(104)	1.409(14)	C(1)–C(2)	1.497(16)	C(3)–C(4)	1.490(18)
Cl(2)–O(201)	1.345(19)	Cl(2)–O(202)	1.420(14)	C(5)–C(6)	1.505(20)	C(7)–C(8)	1.497(20)
Cl(2)–O(203)	1.327(15)	Cl(2)–O(204)	1.353(16)	C(9)–C(10)	1.503(17)	C(10)–C(11)	1.403(18)
Cl(3)–O(301)	1.392(15)	Cl(3)–O(302)	1.341(17)	C(10)–C(15)	1.377(17)	C(11)–C(12)	1.382(18)
Cl(3)–O(303)	1.298(25)	Cl(3)–O(304)	1.234(24)	C(12)–C(13)	1.396(18)	C(13)–C(14)	1.394(17)
Cl(4)–O(401)	1.358(18)	Cl(4)–O(402)	1.352(16)	C(14)–C(15)	1.372(17)	C(14)–C(16)	1.497(17)
Cl(4)–O(403)	1.342(16)	Cl(4)–O(404)	1.487(29)	C(21)–C(22)	1.480(18)	C(23)–C(24)	1.495(19)
N(11)–C(1)	1.527(15)	N(11)–C(8)	1.491(15)	C(25)–C(26)	1.502(18)	C(27)–C(28)	1.517(17)
N(11)–C(9)	1.507(15)	N(12)–C(2)	1.477(16)	C(29)–C(30)	1.473(18)	C(30)–C(31)	1.385(18)
N(12)–C(3)	1.444(16)	N(13)–C(4)	1.505(17)	C(30)–C(35)	1.412(18)	C(31)–C(32)	1.338(19)
N(13)–C(5)	1.525(18)	N(14)–C(6)	1.449(16)	C(32)–C(33)	1.364(19)	C(33)–C(34)	1.376(18)
N(14)–C(7)	1.455(18)	O(11)–C(16)	1.300(15)	C(34)–C(35)	1.399(18)	C(34)–C(36)	1.501(17)
N(11)–Co(1)–N(12)	86.9(4)	N(11)–Co(1)–N(13)	167.3(4)	Co(1)–N(14)–C(6)	108.3(8)	Co(1)–N(14)–C(7)	107.3(8)
N(12)–Co(1)–N(13)	85.6(4)	N(11)–Co(1)–N(14)	85.7(4)	C(6)–N(14)–C(7)	116.2(11)	C(16)–O(11)–Co(1a)	129.7(8)
N(12)–Co(1)–N(14)	98.2(4)	N(13)–Co(1)–N(14)	85.2(4)	Co(2)–N(21)–C(21)	106.5(7)	Co(2)–N(21)–C(28)	104.8(7)
N(11)–Co(1)–O(12)	94.7(4)	N(12)–Co(1)–O(12)	173.3(4)	C(21)–N(21)–C(28)	109.2(9)	Co(2)–N(21)–C(29)	114.0(7)
N(13)–Co(1)–O(12)	94.0(4)	N(14)–Co(1)–O(12)	88.5(4)	C(21)–N(21)–C(29)	110.4(9)	C(28)–N(21)–C(29)	111.7(9)
N(11)–Co(1)–O(11a)	89.9(3)	N(12)–Co(1)–O(11a)	85.3(4)	Co(2)–N(22)–C(22)	107.1(8)	Co(2)–N(22)–C(23)	108.6(8)
N(13)–Co(1)–O(11a)	99.7(4)	N(14)–Co(1)–O(11a)	174.2(4)	C(22)–N(22)–C(23)	115.8(10)	Co(2)–N(23)–C(24)	110.8(7)
O(12)–Co(1)–O(11a)	88.1(3)	N(21)–Co(2)–N(22)	85.8(4)	Co(2)–N(23)–C(25)	107.6(7)	C(24)–N(23)–C(25)	110.7(10)
N(21)–Co(2)–N(23)	166.4(4)	N(22)–Co(2)–N(23)	84.0(4)	Co(2)–N(24)–C(26)	111.9(7)	Co(2)–N(24)–C(27)	111.3(8)
N(21)–Co(2)–N(24)	86.5(4)	N(22)–Co(2)–N(24)	98.1(4)	C(26)–N(24)–C(27)	119.5(9)	C(36)–O(21)–Co(2a)	129.1(8)
N(23)–Co(2)–N(24)	86.0(4)	N(21)–Co(2)–O(22)	95.7(4)	N(11)–C(1)–C(2)	109.9(9)	N(12)–C(2)–C(1)	104.8(9)
N(22)–Co(2)–O(22)	88.9(4)	N(23)–Co(2)–O(22)	93.1(4)	N(12)–C(3)–C(4)	105.9(10)	N(13)–C(4)–C(3)	107.5(10)
N(24)–Co(2)–O(22)	172.8(4)	N(21)–Co(2)–O(21a)	89.9(4)	N(13)–C(5)–C(6)	110.2(11)	N(14)–C(6)–C(5)	109.1(11)
N(22)–Co(2)–O(21a)	175.0(4)	N(23)–Co(2)–O(21a)	100.5(4)	N(14)–C(7)–C(8)	107.4(11)	N(11)–C(8)–C(7)	111.2(10)
N(24)–Co(2)–O(21a)	84.3(4)	O(22)–Co(2)–O(21a)	88.8(3)	N(11)–C(9)–C(10)	113.5(9)	C(9)–C(10)–C(11)	122.4(11)
O(101)–Cl(1)–O(102)	111.7(8)	O(101)–Cl(1)–O(103)	109.3(9)	C(9)–C(10)–C(15)	120.5(11)	C(11)–C(10)–C(15)	117.1(11)
O(102)–Cl(1)–O(103)	112.1(9)	O(101)–Cl(1)–O(104)	109.5(9)	C(10)–C(11)–C(12)	120.8(12)	C(11)–C(12)–C(13)	120.7(12)
O(102)–Cl(1)–O(104)	107.7(8)	O(103)–Cl(1)–O(104)	106.3(8)	C(12)–C(13)–C(14)	118.7(11)	C(13)–C(14)–C(15)	119.4(11)
O(201)–Cl(2)–O(202)	105.4(10)	O(201)–Cl(2)–O(203)	110.0(15)	C(13)–C(14)–C(16)	116.8(11)	C(15)–C(14)–C(16)	123.8(11)
O(202)–Cl(2)–O(203)	111.9(13)	O(201)–Cl(2)–O(204)	103.9(11)	C(10)–C(15)–C(14)	123.3(11)	O(11)–C(16)–O(13)	123.6(12)
O(202)–Cl(2)–O(204)	115.2(10)	O(203)–Cl(2)–O(204)	109.9(12)	O(11)–C(16)–C(14)	112.4(11)	O(13)–C(16)–C(14)	123.9(12)
O(301)–Cl(3)–O(302)	112.4(10)	O(301)–Cl(3)–O(303)	107.9(13)	N(21)–C(21)–C(22)	110.7(10)	N(22)–C(22)–C(21)	107.3(11)
O(302)–Cl(3)–O(303)	110.5(15)	O(301)–Cl(3)–O(304)	105.7(13)	N(22)–C(23)–C(24)	106.8(11)	N(23)–C(24)–C(23)	109.4(11)
O(302)–Cl(3)–O(304)	110.0(18)	O(303)–Cl(3)–O(304)	110.3(21)	N(23)–C(25)–C(26)	108.4(11)	N(24)–C(26)–C(25)	104.8(10)
O(401)–Cl(4)–O(402)	117.4(10)	O(401)–Cl(4)–O(403)	109.7(11)	N(24)–C(27)–C(28)	105.1(10)	N(21)–C(28)–C(27)	109.3(10)
O(402)–Cl(4)–O(403)	115.2(10)	O(401)–Cl(4)–O(404)	106.5(14)	N(21)–C(29)–C(30)	116.1(10)	C(29)–C(30)–C(31)	123.4(11)
O(402)–Cl(4)–O(404)	104.1(14)	O(403)–Cl(4)–O(404)	102.3(18)	C(29)–C(30)–C(35)	118.1(11)	C(31)–C(30)–C(35)	118.5(11)
Co(1)–N(11)–C(1)	103.5(7)	Co(1)–N(11)–C(8)	106.9(7)	C(30)–C(31)–C(32)	120.7(12)	C(31)–C(32)–C(33)	122.9(13)
C(1)–N(11)–C(8)	109.9(9)	Co(1)–N(11)–C(9)	112.8(7)	C(32)–C(33)–C(34)	118.4(12)	C(33)–C(34)–C(35)	120.9(11)
C(1)–N(11)–C(9)	113.0(9)	C(8)–N(11)–C(9)	110.4(9)	C(33)–C(34)–C(36)	120.1(11)	C(35)–C(34)–C(36)	118.9(11)
Co(1)–N(12)–C(2)	111.3(7)	Co(1)–N(12)–C(3)	110.9(7)	C(30)–C(35)–C(34)	118.8(11)	O(21)–C(36)–O(23)	122.4(11)
C(2)–N(12)–C(3)	119.2(9)	Co(1)–N(13)–C(4)	107.9(7)	O(21)–C(36)–C(34)	115.1(11)	O(23)–C(36)–C(34)	122.5(11)
Co(1)–N(13)–C(5)	110.1(8)	C(4)–N(13)–C(5)	111.5(10)				

half of the dimer. The co-ordination is significantly distorted, as seen most clearly in the angles N(*n*1)–Co(*n*)–N(*n*3) of 166.9(4)°, average. This indicates that the 12-membered macrocycle is somewhat too small to fit around the cobalt. The Co–N bond distances show a systematic variation that is much greater than experimental error, with the longest bonds being to the nitrogen carrying the carboxylate [2.032(9) and 2.042(9) Å in dimers I and II]. Next in length are those to the nitrogens *trans* to the last [1.960(10), 1.970(10) Å], then those *trans* to the carboxylate oxygens [1.940(10), 1.932(10) Å], and shortest, those *trans* to water [1.914(9) and 1.907(9) Å]. These variations are probably due to a combination of steric and electronic effects, but their magnitude is surprising. The Co–O bonds also vary, but in a more predictable fashion, with the bonds to H_2O [1.975(8), 1.982(8) Å] longer than the presumably stronger bonds to the negatively charged carboxylate oxygens [1.905(8), 1.899(7) Å]. Other dimensions are standard.

The dihedral angles of the four chelate rings comprising the macrocycle are all intermediate between ideal values for the eclipsed and *gauche* conformations. Three of them, including the two chelate rings adjacent to the substituent [N(11)C(1)C(2)N(12) 54.1, N(14)C(7)C(8)N(11) 46.3°] and one of the other chelate rings [N(12)C(3)C(4)N(13) 50.7°], have typical *gauche* conformations while the fourth Co–N(13)–C(5)–C(6)–N(14)– chelate ring has a dihedral angle of only 34.5°. The chiralities of the rings adjacent to the appended group are both λ and the other two are both δ. This pattern is the same as that found for $[Co(cyclen)(NO_2)_2]Cl$[7] and $[Co(cyclen)(CO_3)]ClO_4 \cdot H_2O$.[8]

A network of hydrogen bonds is formed in the crystal

Table 3. Probable hydrogen bonds

Atom 1	Atom 2 (transformed by)	Length (Å)
O(001) ···	N(22) $(x, y - 1, z)$	2.90(2)
···	O(201) $(1 - x, y, 0.5 - z)$	2.81(2)
O(002) ···	O(22) $(1.5 - x, y - 0.5, z)$	2.59(2)
···	O(005) (x, y, z)	2.49(2)
O(003) ···	O(004) (x, y, z)	2.69(2)
···	O(12) $(1.5 - x, 0.5 - y, z - 0.5)$	2.63(2)
O(004) ···	O(23) $(x - 0.5, y - 0.5, 0.5 - z)$	2.76(2)
O(006) ···	O(303) $(0.5 - x, 0.5 + y, z)$	2.90(2)
O(12) ···	O(103) $(0.5 + x, 1.5 - y, z)$	2.83(2)

involving the solvent water molecules, some of the perchlorate oxygen atoms, and the dimers (Table 3). Possible hydrogen bonds are also indicated within the dimers, between the free C=O groups [O(13) and O(23)] of the carboxylate and the symmetry-related nitrogen atoms [N(13a) and N(23a)] and also the water molecule O(12) in the dimer **I**. However, the hydrogen atoms attached to N(13) and N(23) have calculated positions very far from the O–N line, while O(12) has two much more probable external hydrogen bonds. These internal contacts are therefore not likely to be significant.

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