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The Crystal and Molecular Structure of an Isomer of Chloro(1,5,8,11,14-pentaazacyclohexadecane)cobalt(III), Diperchlorate, [Co(16-[ane]-5)Cl]$(ClO_4)_2$

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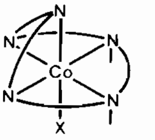
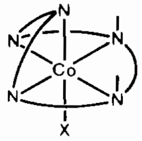
The structure of the title compound has been determined by counter data. The crystals are orthorhombic, space group $Pn2_1a$ *with* a = *14.317(7),* b = *13.484(7) and* c = *10.361(6) Å, Z = 4. The structure has been refined by full-matrix least-squares to a final conventional R value of 0.085 (Rw = 0.083). The geometry of the complex cation is a relatively undistorted octahedron with a chlorine atom* trans *to an 'angular' secondary nitrogen of the pentadentate 16-[ane]-5 ligand. Within the ligand the six-membered ring assumes a 'chair' conformation, while all five-membered rings are 'gauche'. Only one,* i.e., *the 'angular' N(1)* trans *to Cl(1) of the five secondary nitrogen atoms of 16-[ane]-5 does not exhibit chirality. The two 'flat' nitrogens have opposite chirality as do the two remaining 'angular' nitrogens. The* ClO_4 *anions assume a distorted tetrahedral configuration.*

Introduction

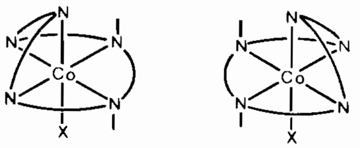
The study of the coordination chemistry of complexes with macrocyclic polyamine ligands has received much attention in recent years and the application of such complexes to a wide variety of problems of structure, bonding and mechanism are considerable. The major attention has been paid to quadridentate macrocycles but now, with the advent of new synthetic methods, interest has been extended to ligands of greater or smaller denticity. As a part of our interest in the mechanisms of the substitution reactions of acido-pentaaminecobalt(III) complexes, we have synthesised the complex [Co(16-[ane]-5)Cl]$(ClO_4)_2$ (16-[ane]-5 = 1,5,8,11,14-pentaazacyclohexadecane) and are investigating the other acido complexes of this series. A symmetrical pentadentate macrocycle can only be wrapped around an octahedron with one topology, although both chiralities of the 'flat' nitrogens [1] could be accommodated, thereby giving rise to three diastereomeric species, meso-syn *Ia*, meso-anti *Ib*, and the enantiomeric racemate *Ic*;



Ia meso-syn

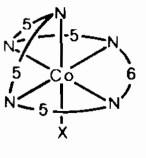


Ib meso-anti

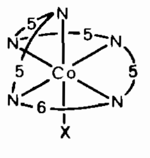


Ic racemate

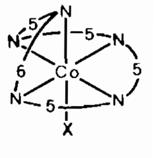
The unsymmetrical 16-[ane]-5 presents further scope for isomerism in the disposition of the 6-membered ring, *IIa, IIb, IIc,* two of which, *IIb* and *IIc,* have non-superimposable mirror images.



IIa



IIb



IIc

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The disadvantage of this extra complexity is outweighed by the ability of the six-membered ring, in certain of the isomers, to allow the 5-membered rings to take up their favoured gauche conformation while itself remaining in the chair form.

Until now we have only been able to characterise one isomeric form, and its preparation and structure are reported in this paper.

Experimental

1,5,8,11,14-Pentaazacyclohexadecane-pentahydrochloride

The pentatosylate was prepared by the method of Atkins *et al.* [2], and hydrolysed by sulphuric acid (144 h at 100 °C). The cooled solution was poured into excess diethylether and the amine sulphate precipitated. This was filtered off, dissolved in water and converted to the pentahydrochloride by ion exchange. 55% yield of white crystals. *Anal.* Found: C, 31.7; H, 7.53; N, 17.0; Cl, 42.5. $C_{11}H_{32}N_5Cl_5$ requires: C, 32.1; H, 7.83; N, 17.0, Cl, 43.1%. ^1H NMR (200 MHz) D_2O solvent, 2-methyl-2-propanol reference, δ = 1.2 ppm: δ 2.42 (quintet) (2H); 3.48 (triplet) (4H); 3.685 (16H). Amine protons exchange with solvent. ^{13}C NMR (50 MHz) (D_2O solvent, dioxan reference = δ 67.4 ppm) δ 22.22; 43.52; 44.00; 44.22; 44.76 ppm. Intensities in the ratio 1:4:2:2:2.

Chloro(1,5,8,11,14-pentaazacyclohexadecane)cobalt(III) chloride perchlorate

Cobalt chloride hexahydrate (1.60 g) and 16-[ane]-N_5 5HCl (2.76 g) were dissolved by warming on a steam bath with water. Sodium hydroxide (1.22 g) dissolved in a little water was slowly added to deprotonate the ligand and air was bubbled through the solution for two hours. Concentrated hydrochloric acid (8 cm^3) was added and the solution warmed on a steam bath until the colour was clear orange-red. It was then cooled, treated with a saturated aqueous solution of lithium perchlorate and left overnight to crystallise. *Anal.* Found: C, 28.3; H, 6.00; N, 15.24. $C_{11}H_{27}N_5Cl_3O_4Co$ requires: C, 28.8; H, 5.93, N, 15.23%.

The diperchlorate was formed in well-developed crystals when lithium perchlorate solution was added to a saturated aqueous solution of the chloride-perchlorate.

X-ray Structure Analysis

Accurate unit cell dimensions and crystal orientation matrices, together with their estimated standard errors were obtained from least-squares refinement of the 2θ, ω, χ and ϕ values of 25 carefully centered high-angle reflections. Intensity data were collected from a crystal of approximate spherical shape (radius about 0.15 mm) on a Philips PW 1100 four-circle diffractometer operating in the $\theta/2\theta$ scan mode (scan width = 1.2°, scan speed = 0.05° s^{-1}) and by using graphite monochromatized MoK$\bar{\alpha}$ radiation. 1839 independent reflections up to $\theta = 23°$ were measured, of which 791 had $I \geqslant 2.5\sigma(I)$ being calculated from counting statistics. During the data collection two standard reflexions were measured every 120 min to check the stability of the crystal and the electronics. Intensities were corrected for Lorentz and polarization effects and put in an absolute scale by Wilson's method. An experimental absorption correction was applied [3].

Crystal Data

$C_{11}H_{27}N_5O_8Cl_3Co$, M = 416.3. Orthorhombic, space group $Pn2_1a$, a = 14.317(7), b = 13.484(7), c = 10.361(6) Å, U = 2000.2 $Å^3$, F(000) = 1060 e, D_o = 1.38, D_c = 1.39 g cm^{-3} for Z = 4, MoK$\bar{\alpha}$ radiation, λ = 0.71069 Å, μ(MoK$\bar{\alpha}$) = 12.8 cm^{-1}.

Structure Solution and Refinement

The molecular structure of the complex was solved by conventional Patterson and Fourier syntheses. The refinement of the structural model, which was by the method of full-matrix least-squares, was carried out allowing the cobalt atom to vibrate anisotropically while isotropic thermal parameters were applied to the remaining non-hydrogen atoms. Hydrogen atoms could not be located from electron density difference maps and therefore were included in the scattering model in calculated idealized positions (C–H = 0.95 Å), but not varied. The function minimized was $\Sigma w\Delta^2$, in which $w = 1.87 \cdot [\sigma^2(Fo) + 0.001414\ Fo^2]^{-1}$ and $\Delta = |Fo|-|Fc|$. Weighting scheme analyses showed no serious dependence of the mean $w\Delta^2$ on either |Fo| and $\lambda^{-1}\sin\theta$.

The final electron density difference map showed no unusual features. Atomic scatteting factors were taken from reference 4. Allowance was made for the anomalous scattering of cobalt and chlorine atoms, using values of $\Delta f'$ and $\Delta f''$ from reference 4.

The final conventional R values for the 791 observed reflections with $I \geqslant 2.5\sigma(I)$ was 0.085 (R_w = 0.083). Final atomic parameters and a selection of functions derived from them are presented in Tables I–V. All calculations were carried out on the CYBER 76 computer of the 'C.I.N.E.C.A.' with the SHELX-76 program for crystal structure determination [5].

Results and Discussion

The stereochemical arrangement of the complex cation is shown in Fig. 1, along with the atom nomenclature. The conformations and the helicities [6] adopted by the chelate rings are reported in Table IV. The torsion angles about the non-rigid bonds of the

TABLE I. Atomic Coordinates ($\times 10^4$) and Temperature Factors ($\times 10^3$) with e.s.d. s in Parentheses.

	x	y	z	U		x	y	z
Co[a]	6642(2)	5000	644(4)					
Cl(1)	5218(6)	5660(7)	916(8)	52(2)				
N(1)	7961(15)	4593(18)	431(21)	38(6)	H(1)	8049	3895	440
N(2)	6116(16)	4070(17)	−677(26)	39(6)	H(2)	5485	4080	−396
N(3)	7111(16)	5892(19)	2026(22)	39(6)	H(3)	6915	6556	1881
N(4)	6372(16)	4079(18)	2060(25)	36(7)	H(4)	5713	4135	2131
N(5)	6866(18)	5934(23)	−782(27)	63(9)	H(5)	6728	6593	−522
C(1)	6192(25)	4501(29)	−1908(41)	53(11)	H(11)	6791	4299	−2202
					H(12)	5726	4239	−2465
C(2)	6268(26)	5561(31)	−1919(42)	69(13)	H(21)	6488	5817	−2717
					H(22)	5642	5771	−1783
C(3)	7900(25)	5935(27)	−1148(35)	65(11)	H(31)	8233	6439	−701
					H(32)	7951	6042	−2051
C(4)	8276(20)	4966(33)	−813(27)	49(7)	H(41)	8074	4511	−1455
					H(42)	8939	4997	−811
C(5)	8509(21)	5009(34)	1537(29)	55(8)	H(51)	9136	5112	1269
					H(52)	8495	4535	2215
C(6)	8111(19)	5912(25)	2043(32)	49(9)	H(61)	8320	6016	2903
					H(62)	8325	6438	1509
C(7)	6711(25)	5504(29)	3312(41)	66(13)	H(71)	6081	5713	3403
					H(72)	7069	5747	4016
C(8)	6703(25)	4427(31)	3253(41)	62(13)	H(81)	6358	4149	3949
					H(82)	7333	4211	3301
C(9)	6585(22)	3032(25)	1830(33)	55(9)	H(91)	6448	2649	2576
					H(92)	7233	2991	1645
C(10)	6085(22)	2587(27)	704(30)	55(9)	H(101)	6177	1889	697
					H(102)	5443	2728	843
C(11)	6323(20)	3004(23)	−616(30)	44(8)	H(111)	5971	2670	−1261
					H(112)	6971	2905	−770
Cl(2)	3427(6)	3613(6)	−745(9)	48(2)				
O(1)	3011(17)	4572(18)	−736(25)	73(8)				
O(2)	3721(24)	3317(29)	400(39)	132(13)				
O(3)	9217(21)	3659(25)	6538(32)	107(10)				
O(4)	7773(22)	2984(25)	6130(27)	102(10)				
Cl(3)	407(6)	7485(7)	−364(8)	50(2)				
O(5)	3621(16)	2504(20)	4879(25)	78(3)				
O(6)	5054(30)	3110(35)	5453(40)	161(16)				
O(7)	9647(24)	2779(29)	1499(38)	136(13)				
O(8)	9939(19)	1512(22)	386(28)	97(11)				

[a]	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Co	22(2)	22(2)	34(2)	−8(3)	−1(2)	7(2)

in the form: $\exp[-2\pi^2\ \Sigma U_{ij} a_i a_j h_i h_j]$.

TABLE II. Interatomic Distances (Å) and Angles (°) with their e.s.d. s in Parentheses.

Co–Cl(1)	2.242(9)	Co–N(3)	1.99(2)
Co–N(1)	1.98(2)	Co–N(4)	1.96(2)
Co–N(2)	2.00(2)	Co–N(5)	1.97(3)
N(1)–C(4)	1.46(3)	N(1)–C(5)	1.50(4)
C(3)–C(4)	1.46(5)	C(5)–C(6)	1.44(5)
N(5)–C(3)	1.53(4)	N(3)–C(6)	1.43(3)
N(5)–C(2)	1.54(4)	N(3)–C(7)	1.54(4)
C(1)–C(2)	1.43(4)	C(7)–C(8)	1.45(4)

(continued overleaf)

TABLE II. *(continued)*

N(2)–C(1)	1.41(4)	N(4)–C(8)	1.40(4)
N(2)–C(11)	1.47(3)	N(4)–C(9)	1.46(4)
C(10)–C(11)	1.52(4)	C(9)–C(10)	1.50(4)
Cl(2)–O(1)	1.42(3)	Cl(3)–O(5)	1.41(2)
Cl(2)–O(2)	1.32(4)	Cl(3)–O(6)	1.36(4)
Cl(2)–O(3)	1.40(3)	Cl(3)–O(7)	1.24(4)
Cl(2)–O(4)	1.32(3)	Cl(3)–O(8)	1.40(3)
N(1)–Co–Cl(1)	173(1)	N(4)–Co–N(1)	96(1)
N(2)–Co–Cl(1)	90(1)	N(4)–Co–N(2)	92(1)
N(2)–Co–N(1)	96(1)	N(5)–Co–Cl(1)	89(1)
N(3)–Co–Cl(1)	89(1)	N(5)–Co–N(1)	86(1)
N(3)–Co–N(1)	86(1)	N(5)–Co–N(2)	87(1)
N(3)–Co–N(2)	177(1)	N(5)–Co–N(4)	178(1)
N(4)–Co–Cl(1)	89(1)	N(5)–Co–N(3)	96(1)
O(1)–Cl(2)–O(2)	114(2)	O(5)–Cl(3)–O(6)	111(2)
O(1)–Cl(2)–O(3)	108(2)	O(5)–Cl(3)–O(7)	103(2)
O(1)–Cl(2)–O(4)	107(2)	O(5)–Cl(3)–O(8)	112(2)
O(2)–Cl(2)–O(3)	106(2)	O(6)–Cl(3)–O(7)	111(3)
O(2)–Cl(2)–O(4)	108(2)	O(6)–Cl(3)–O(8)	115(2)
O(3)–Cl(2)–O(4)	115(2)	O(7)–Cl(3)–O(8)	105(2)

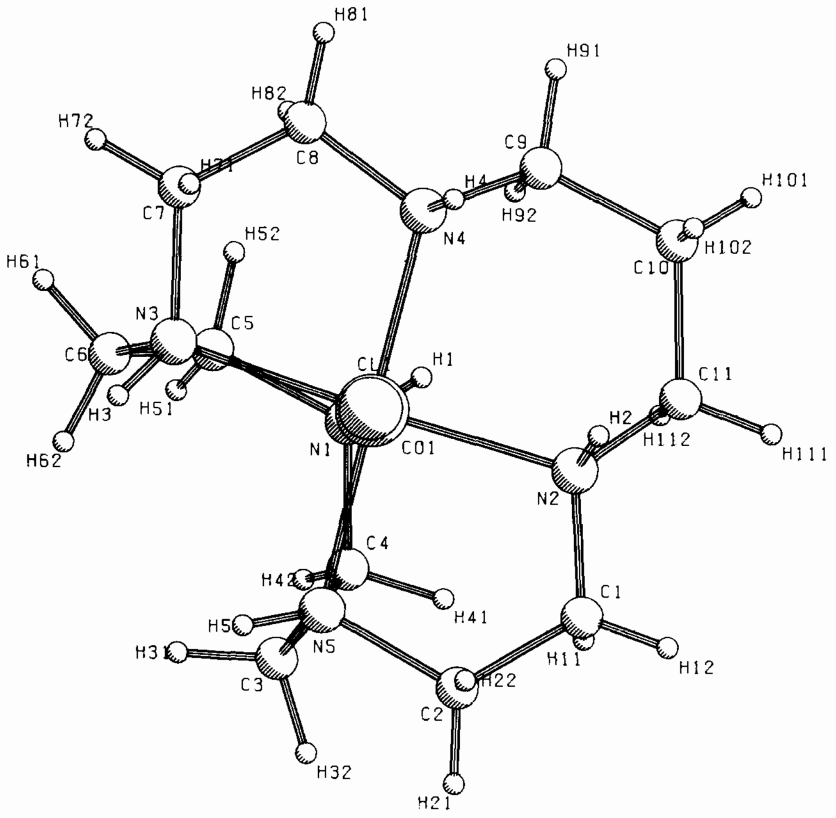

Fig. 1. View of the complex cation.

TABLE III. Least-squares Planes with Deviations (A) of the Relevant Atoms in Square Brackets. The Equation of a Plane in the Direct Space is Given by PX + QY + RZ = S.

	P	Q	R	S
Plane 1 Co, N(5), N(2), N(4), N(3) [Co 0.025; N(5) –0.008; N(2) –0.005; N(4) –0.007; N(3) –0.005].	13.0446	–5.3292	–1.2101	5.8963
Plane 2 Co, N(4), Cl(1), N(5), N(1) [Co –0.041; N(4) –0.047, Cl(1) 0.066; N(5) –0.052; N(1) 0.073].	4.7778	9.1212	6.8025	8.2128
Plane 3 Co, Cl(1), N(3), N(1), N(2) [Co –0.015; Cl(1) 0.066; N(3) –0.066; N(1) 0.073; N(2) –0.058].	2.3964	9.3833	–7.2358	5.8326
Plane 4 Co, N(5), N(1) [C(3) 0.166; C(4) –0.369].	4.0109	9.4347	6.8095	7.8199
Plane 5 Co, N(1), N(3) [C(5) –0.259; C(6) 0.198].	1.9001	9.8084	–6.9755	5.7170
Plane 6 Co, N(3), N(4) [C(7) –0.442; C(8) 0.129].	13.0726	–5.3470	–0.9852	5.9459
Plane 7 Co, N(4), N(2) [C(9) 0.890; C(10) 0.628; C(11) 0.859].	12.9129	–5.6140	–1.1893	5.6932
Plane 8 Co, N(2), N(5) [C(1) 0.047; C(2) –0.416].	13.0072	–5.3146	–1.4377	5.8895
Plane 9 Co, Cl(1), N(1), C(10) [Co –0.013; Cl(1) 0.006; N(1) 0.006 C(10) 0.000; N(2) –1.444; N(4) 1.415; H(1) 0.045].	1.7425	–0.2008	10.2828	1.7318

TABLE IV. Helicity of the Conformation for all Chelate Rings.

Ring	Conformation	Helicity
N(1)–Co–N(5)	envelope (or gauche)	λ
N(5)–Co–N(2)	envelope	λ
N(2)–Co–N(4)	chair	non-helical
N(4)–Co–N(3)	envelope	δ
N(3)–Co–N(1)	envelope	δ

16-[ane]-5 ligand are presented in Table V. The coordination geometry of the cation is a relatively undistorted octahedron with the pentadentate 16-[ane]-5 ligand present in the previously quoted *IIa* configuration.

Four secondary nitrogen atoms, two 'flat' and two 'angular' of the pentadentate ligand are found to occupy one plane. The chlorine and the remaining 'angular' nitrogen of 16-[ane]-5 complete the coordination about the cobalt atom. Only one, *i.e.*, the 'angular' N(1), *trans* to Cl(1) of the five secondary nitrogen atoms of 16-[ane]-5 does not exhibit chirality. The two 'flat' N(2) and N(4) have opposite chirality, as do the two remaining 'angular' N(5) and N(3).

In this isomer the N–H bonds, involving N(5), N(2), N(4) and N(3) and the Co–Cl bond lie on the same side of the Co, N(5), N(2), N(4), N(3) plane,

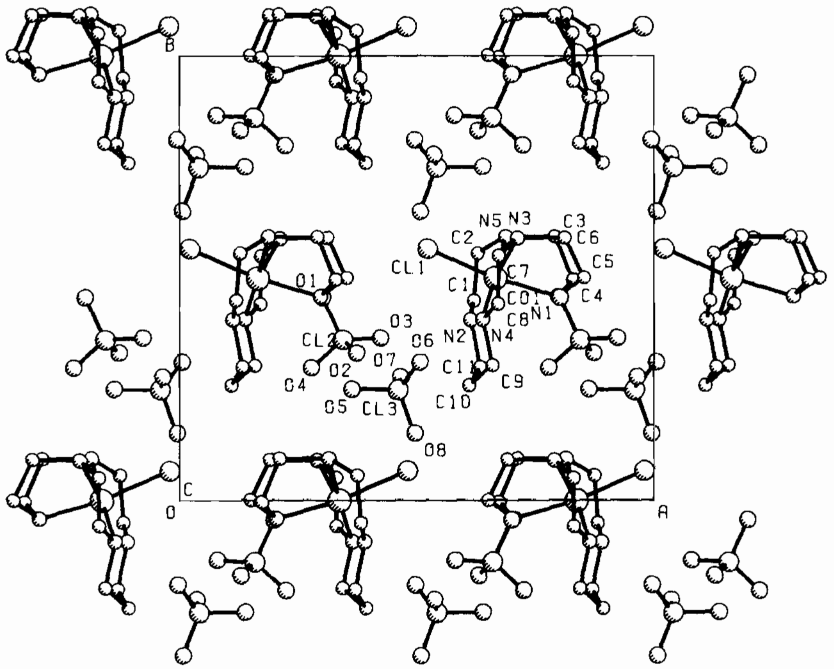

Fig. 2. Crystal packing diagram as viewed down *c* axis.

TABLE V. Torsion Angles (°)[a].

C(5)–N(1)–C(4)–C(3)	–82.0
C(4)–N(1)–C(5)–C(6)	90.2
C(11)–N(2)–C(1)–C(2)	–162.3
C(1)–N(2)–C(11)–C(10)	–171.6
C(7)–N(3)–C(6)–C(5)	92.4
C(6)–N(3)–C(7)–C(8)	–84.5
C(9)–N(4)–C(8)–C(7)	164.5
C(8)–N(4)–C(9)–C(10)	168.4
C(3)–N(5)–C(2)–C(1)	86.7
C(2)–N(5)–C(3)–C(4)	–89.4
N(2)–C(1)–C(2)–N(5)	37.4
N(5)–C(3)–C(4)–N(1)	–42.6
N(1)–C(5)–C(6)–N(3)	36.7
N(3)–C(7)–C(8)–N(4)	–43.9
N(4)–C(9)–C(10)–C(11)	64.6
C(9)–C(10)–C(11)–N(2)	–59.6

[a] The torsion angle w(IJKL) is defined as the angle between the vector KL when viewed down JK. It is positive if counterclockwise and negative if clockwise.

and we propose to label this the 'syn' isomer. In addition because the N(1)–H bond lies approximately on the Co, Cl(1), N(1), C(10) plane and the pentatomic chelate rings have opposite helicity [6] with respect to this plane (Table IV), it seems that the present complex cation can be divided in two enantiomaric parts mirrored by the Co, Cl(1), N(1), C(10) plane.

The bonds to the 'flat' and 'angular' secondary nitrogens lie in the middle of the range of observed Co–N(tetrahedral) lengths (1.89 to 2.06) [7]. The Co–Cl(1) bond distance, 2.242(9) Å, is slightly longer than the sum of appropriate covalent radii, 2.21 Å [8], but agrees with the Co–Cl bonds in several Co^{III} complexes [7, 9–11].

In both perchlorate anions a distorted tetrahedral arrangement of oxygen atoms about the central chlorine atom is observed (Table II), with a mean Cl–O bond distance of 1.36(3) Å. This value is shorter than the average Cl–O bond distance of 1.43 Å found in $HClO_4 \cdot H_2O$ [12]. This difference may be attributed to error introduced by the high correlation of the positional parameters with the large motion of these oxygen atoms. Nevertheless, comparable values have been found in structures containing the perchlorate anion [9, 13, 14].

The crystal packing, which is presented in Fig. 2, is mainly determined by Coulombic and van der Waals forces and all intermolecular contacts agree with those predicted from radii-sum rules.

Acknowledgements

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