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The Crystal and Molecular Structure of an Isomer of Bromo[1,9-bis(2-pyridyl)2,5,8-triazanonane]cobalt(III) Perchlorate, [Co(picdien)Br][ClO_4]$_2$

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The structure of an isomer of bromo[1,9-bis(2-pyridyl)2,5,8-triazanonane]cobalt(III) perchlorate, [Co(picdien)Br][ClO_4]$_2$ has been determined by counter data. The crystals are monoclinic, space group $P2_1/a$ with a = *10.263(5),* b = *27.845(9),* c = *7.888(4) Å, β = 97.4(1)°, Z = 4, D_o = 1.84, D_c = 1.85 g cm^{-3}. The structure has been refined by full-matrix least-squares to a final conventional R value of 0.073 (Rw = 0.075) for 1664 reflections with $I \geqslant 2.5\sigma(I)$. The coordination geometry of the complex cation is near regular octahedral, with the pentadentate picdien ligand present in the α, β configuration and with a Br* trans *to an 'angular' secondary nitrogen. Only two,* i.e., *one 'angular' and the 'flat' of the three secondary nitrogen atoms of the picdien ligand exhibit chirality and it is the same. The absolute configuration of the complex can be designed as Δ-α, β-S (and Λ-α, β-R). The ClO_4 anions assume a distorted tetrahedral configuration.*

Introduction

The acidopentammine complexes of the type, [Co(picdien)X]$^{2+}$ (X = Cl, Br, NO_3) are of special interest because of their sensitivity to base catalysed hydrolysis [1]. The inverse [H^+] dependence of the rate, which dominates the solvolysis, has been attributed to a hydroxide-catalysed pathway and the second-order rate constants are among the largest to be observed for the base hydrolysis of Co(III) amine complexes. Two isomers of the bromo complex have been isolated so far. Both have similar reactivity but are some ten times more labile than the chloro complex, which has been shown to have the 'anti'-αβ form [2]. In order to establish the isomeric form and test the conclusions drawn from the ^{1}H and ^{13}C n.m.r. [3] crystals of the diperchlorates were grown for X-ray analysis.

The structure of one of the isomers is reported in this paper.

Experimental

Preparation

$CoBr_2 \cdot 6H_2O$ (10 g) was dissolved in water (100 cm^3) and mixed with a solution of the ligand (picdien) (13 g) in water (250 cm^3). A vigorous stream of air was bubbled through the reaction mixture for 6 h and the orange solution was then heated on a water bath and treated with concentrated hydrobromic acid (60%; 4 cm^3). The solution changed the colour from orange to purple brown. Perchloric acid (60%; 10 cm^3) was added and the solution concentrated to a volume of 50 cm^3 by heating on a water bath while a gentle stream of air was blown over the surface. On cooling overnight dark purple crystals separated and were filtered off, washed with 0.1 *M* perchloric acid followed by ethanol and diethylether, and air dried. The crude product was then washed with warm 5 *M* hydrobromic acid (50 cm^3) followed by ethanol and diethylether and again air dried. Crystals suitable for X-ray analysis were obtained by dissolving the complex in the minimum volume of dimethylsulfoxide and adding, dropwise, twice the volume of ice cold 1 *M* perchloric acid. Crystals that separated after 12 h in the refrigerator were filtered off, washed with ice

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cold 0.1 *M* perchloric acid, ethanol and ether, and air dried.

Anal.: Found: C, 30.75; H, 3.69; N, 11.22. $C_{16}H_{23}N_5BrCl_2CoO_8$ requires, C, 30.83; H, 3.72; N, 11.24.

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 reflexions. Intensity data were collected at room temperature from a crystal of approximate dimensions 0.08 X 0.06 X 0.12 mm on a Philips PW 1100 four-circle diffractometer operating in the $\theta/2\theta$ scan mode (scan width = 1.2°, scan speed = $0.03°\ s^{-1}$) and by using graphite monochromatized MoK$\bar{\alpha}$ radiation. 3326 independent reflexions up to $\theta = 23°$ were measured, of which 1664 had $I \geqslant 2.5\sigma(I)$, $\sigma(I)$ 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 [4].

Crystal data

$C_{16}H_{23}N_5O_8Cl_2BrCo$, M = 623.1, monoclinic, space group $P2_1/a$, (general equivalent positions: ± (x, y, z; 1/2 + x, 1/2 − y, z)) $a = 10.263(5)$, $b = 27.845(9)$, $c = 7.888(4)$ Å, $\beta = 97.4(1)°$, $U = 2235.4$ Å^3, F(000) = 1256 e, $D_o = 1.84$, (by flotation) $D_c = 1.85$ g cm^{-3} for $Z = 4$, MoK$\bar{\alpha}$ radiation, $\lambda = 0.71069$ Å, μ(MoK$\bar{\alpha}$) = 27.4 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 Co, Br, Cl and N atoms to vibrate anisotropically, while isotropic thermal parameters were applied to the oxygen and carbon 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 $w = 2.6616/|\sigma^2(F_o) + 0.100786\ F_o^2|$ and $\Delta = |F_o| - |F_c|$; discrepancy indices used are $R = (\Sigma||F_o| - |F_c||)/\Sigma|F_o|$ and $Rw = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$. Weighting scheme analyses showed no serious dependence of mean $w\Delta^2$ on either $|F_o|$ and $\lambda^{-1}\sin\theta$. The largest peaks on the final difference map were in proximity of the O atoms of the perchlorate groups (maximum value 0.8 e/Å^3). Atomic scattering factors were taken from reference 5. Allowance was made for the anomalous scattering of cobalt and chlorine atoms, using values of $\Delta f'$ and $\Delta f''$ from reference 5. The final conventional R value for the 1664 observed reflexions with $I \geqslant 2.5\sigma(I)$ was 0.073 (Rw = 0.075). Final atomic parameters and a selection of functions derived from them are presented in Table 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 [6].

TABLE I. Atomic Coordinates and Thermal Parameters.

a) Atomic coordinates (× 10^4, for hydrogen atoms × 10^3) with e.s.d. s in parentheses.

	x	y	z		x	y	z
Cl(1)	7810(4)	5836(2)	2335(6)				
O(11)	8760(13)	6212(5)	2396(18)				
O(21)	8384(20)	5711(7)	2937(28)				
O(31)	7065(20)	5781(7)	739(28)				
O(41)	6933(24)	5946(8)	3355(34)				
Cl(2)	8156(5)	2232(2)	3193(7)				
O(12)	8994(14)	2602(5)	3901(18)				
O(22)	7057(15)	2426(5)	2218(19)				
O(32)	7860(21)	1930(7)	4417(28)				
O(42)	8756(22)	1941(7)	2057(28)				
Co	8078(2)	3955(1)	11143(3)				
Br	8126(2)	4484(1)	8757(2)				
N(1)	7204(11)	3475(4)	9614(15)				
C(1)	5965(16)	3491(6)	8907(20)	H(1)	542	375	918
C(2)	5462(20)	3126(6)	7787(23)	H(2)	456	313	734
C(3)	6240(19)	2782(7)	7305(26)	H(3)	591	255	649
C(4)	7516(19)	2777(7)	8024(24)	H(4)	808	253	772

(continued on facing page)

TABLE I. *(continued)*

C(5)	7993(17)	3130(6)	9159(21)				
C(6)	9395(17)	3162(6)	9970(24)	H(61)	997	308	916
				H(62)	954	295	1092
N(2)	9641(12)	3650(5)	10513(17)	H(22)	990	378	950
C(7)	10770(16)	3756(5)	11852(21)	H(71)	1076	355	1280
				H(72)	1157	372	1138
C(8)	10642(18)	4255(6)	12383(24)	H(81)	1090	446	1153
				H(82)	1120	430	1342
N(3)	9235(11)	4368(4)	12659(17)	H(33)	914	470	1244
C(9)	8921(17)	4295(6)	14441(21)	H(91)	812	446	1456
				H(92)	960	442	1526
C(10)	8737(18)	3775(6)	14682(22)	H(101)	828	372	1564
				H(102)	958	363	1489
N(4)	7975(13)	3549(5)	13157(15)	H(44)	836	324	1306
C(11)	6549(16)	3495(6)	13314(23)	H(111)	644	340	1444
				H(112)	616	326	1252
N(5)	6502(12)	4246(4)	11893(16)				
C(12)	5923(15)	3972(5)	13001(20)				
C(13)	4869(16)	4133(6)	13735(22)	H(13)	443	393	1446
C(14)	4440(17)	4586(6)	13406(21)	H(14)	372	471	1393
C(15)	5035(15)	4884(6)	12361(20)	H(15)	474	520	1214
C(16)	6068(14)	4691(5)	11584(19)	H(16)	649	489	1085

b) Anisotropic and isotropic thermal parameters ($\times 10^3$) with e.s.d. s in parentheses.

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cl(1)	40(3)	68(3)	40(3)	2(2)	11(2)	3(2)
O(11)	77(4)					
O(21)	131(7)					
O(31)	147(8)					
O(41)	181(9)					
Cl(2)	52(3)	46(3)	71(3)	3(2)	−6(3)	6(2)
O(12)	81(4)					
O(22)	87(4)					
O(32)	147(7)					
O(42)	145(7)					
Co	30(1)	37(1)	32(1)	3(1)	7(1)	1(1)
Br	48(1)	53(1)	37(1)	9(1)	14(1)	6(1)
N(1)	26(7)	37(8)	33(7)	1(6)	−1(6)	3(6)
C(1)	43(4)					
C(2)	64(6)					
C(3)	58(5)					
C(4)	62(5)					
C(5)	45(4)					
C(6)	56(5)					
N(2)	22(8)	63(10)	45(9)	−2(7)	3(7)	−1(7)
C(7)	44(4)					
C(8)	55(5)					
N(3)	27(8)	42(8)	46(8)	2(6)	9(6)	−14(6)
C(9)	46(4)					
C(10)	55(5)					
N(4)	55(9)	44(8)	26(7)	6(7)	4(7)	5(6)
C(11)	55(5)					
N(5)	33(8)	33(8)	38(8)	1(6)	1(7)	4(6)
C(12)	36(4)					
C(13)	45(4)					
C(14)	45(5)					
C(15)	46(4)					
C(16)	33(4)					

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

Co–Br	2.396(3)	C(9)–C(10)	1.48(2)
Co–N(1)	1.94(1)	N(4)–C(10)	1.49(2)
Co–N(2)	1.94(1)	N(4)–C(11)	1.49(2)
Co–N(3)	1.95(1)	C(11)–C(12)	1.48(2)
Co–N(4)	1.96(1)	C(12)–C(13)	1.37(2)
Co–N(5)	1.97(1)	C(13)–C(14)	1.35(2)
N(1)–C(1)	1.32(2)	C(14)–C(15)	1.37(2)
N(1)–C(5)	1.34(2)	C(15)–C(16)	1.40(2)
C(1)–C(2)	1.40(2)	N(5)–C(12)	1.35(2)
C(2)–C(3)	1.33(3)	N(5)–C(16)	1.33(2)
C(3)–C(4)	1.36(3)	Cl(1)–O(11)	1.43(2)
C(4)–C(5)	1.38(2)	Cl(1)–O(21)	1.38(2)
C(5)–C(6)	1.50(2)	Cl(1)–O(31)	1.39(2)
N(2)–C(6)	1.44(2)	Cl(1)–O(41)	1.32(3)
N(2)–C(7)	1.49(2)	Cl(2)–O(12)	1.41(1)
C(7)–C(8)	1.46(2)	Cl(2)–O(22)	1.39(2)
N(3)–C(8)	1.52(2)	Cl(2)–O(32)	1.34(2)
N(3)–C(9)	1.50(2)	Cl(2)–O(42)	1.41(2)
N(1)–Co–N(2)	82.5(5)	C(7)–N(2)–Co	109(1)
N(2)–Co–N(3)	87.5(5)	C(6)–N(2)–C(7)	119(1)
N(3)–Co–N(5)	91.8(5)	N(2)–C(7)–C(8)	107(1)
N(5)–Co–N(1)	98.0(5)	C(7)–C(8)–N(3)	111(1)
Br–Co–N(1)	89.4(4)	C(8)–N(3)–Co	108(1)
Br–Co–N(2)	88.1(4)	C(9)–N(3)–Co	108(1)
Br–Co–N(3)	92.7(4)	C(8)–N(3)–C(9)	115(1)
Br–Co–N(5)	94.8(4)	N(3)–C(9)–C(10)	108(1)
N(4)–Co–N(1)	92.2(5)	C(9)–C(10)–N(4)	112(1)
N(4)–Co–N(2)	95.0(6)	C(10)–N(4)–Co	109(1)
N(4)–Co–N(3)	86.3(5)	C(11)–N(4)–Co	106(1)
N(4)–Co–N(5)	82.1(5)	C(10)–N(4)–C(11)	113(1)
Co–N(1)–C(1)	126(1)	N(4)–C(11)–C(12)	108(1)
Co–N(1)–C(5)	114(1)	C(11)–C(12)–N(5)	113(1)
C(1)–N(1)–C(5)	120(2)	C(13)–C(12)–N(5)	122(1)
N(1)–C(1)–C(2)	120(2)	C(11)–C(12)–C(13)	125(1)
C(1)–C(2)–C(3)	121(2)	C(12)–C(13)–C(14)	119(2)
C(2)–C(3)–C(4)	118(2)	C(13)–C(14)–C(15)	122(2)
C(3)–C(4)–C(5)	120(1)	C(14)–C(15)–C(16)	117(1)
C(4)–C(5)–N(1)	121(2)	C(15)–C(16)–N(5)	122(1)
N(1)–C(5)–C(6)	115(1)	C(12)–N(5)–Co	114(1)
C(4)–C(5)–C(6)	124(2)	C(16)–N(5)–Co	127(1)
C(5)–C(6)–N(2)	108(1)	C(12)–N(5)–C(16)	119(1)
C(6)–N(2)–Co	112(1)		
O(11)–Cl(1)–O(21)	111(1)	O(12)–Cl(2)–O(22)	110(1)
O(11)–Cl(1)–O(31)	114(1)	O(12)–Cl(2)–O(32)	111(1)
O(11)–Cl(1)–O(41)	109(1)	O(12)–Cl(2)–O(42)	112(1)
O(21)–Cl(1)–O(31)	112(1)	O(22)–Cl(2)–O(32)	113(1)
O(21)–Cl(1)–O(41)	106(1)	O(22)–Cl(2)–O(42)	105(1)
O(31)–Cl(1)–O(41)	104(1)	O(32)–Cl(2)–O(42)	105(1)

Results and Discussion

The stereochemical arrangement of the complex cation is shown in Fig. 1, along with the atom nomenclature.

The coordination geometry of the cation is near regular octahedral, with the pentadentate picdien ligand present in the α,β configuration [7]. Two secondary nitrogens and the two pyridine nitrogen atoms of the picdien ligand are found to occupy one plane. The bromine and the remaining secondary nitrogen of picdien complete the coordination about the cobalt atom. Only two, *i.e.*, N(2) and N(4) of the three secondary nitrogen atoms of the picdien ligand exhibit chirality; the configuration of the 'flat' nitrogen N(2) and that of the 'angular' N(4) is S (owing to the space group symmetry requirements N(2) and N(4) can be also R). Therefore the absolute con-

TABLE III. Least-squares Planes with Deviations (Å) 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 N(1), C(1), C(2), C(3), C(4), C(5) [N(1) –0.014, C(1) 0.023, C(2) –0.022, C(3) 0.012, C(4) –0.003, C(5) 0.004]	3.46773	15.62949	–6.25310	1.93219
Plane 2 N(5), C(12), C(13), C(14), C(15), C(16) [N(5) –0.011, C(12) 0.022, C(13) –0.011, C(14) –0.011, C(15) 0.021, C(16) –0.010]	5.55407	9.24834	5.49325	14.08247
Plane 3 Co, N(1), N(2), N(3), N(5) [Co 0.038, N(1) –0.008, N(2) –0.011, N(3) –0.007, N(5) –0.012]	0.86541	18.30223	–5.94400	1.27652
Plane 4 Co, N(2), Br, N(5), N(4) [Co –0.012, N(2) –0.004, Br 0.009, N(5) –0.004, N(4) 0.011]	5.16401	17.93976	3.99437	15.72954
Plane 5 Co, Br, N(1), N(4), N(3) [Co 0.045, Br 0.090, N(1) –0.124, N(4) 0.114, N(3) –0.126]	–8.99206	12.34585	2.36956	0.21397
Plane 6 Co, N(1), N(2) [C(5) –0.254, C(6) –0.554]	0.98384	17.64594	–6.10193	0.97433
Plane 7 Co, N(2), N(3) [C(7) –0.463, C(8) 0.124]	1.19950	18.38147	–5.92304	1.63878
Plane 8 Co, N(3), N(4) [C(9) 0.605, C(10) 0.065]	–8.47296	14.55618	2.50102	1.69940
Plane 9 Co, N(4), N(5) [C(11) –0.778, C(12) –0.363]	5.20385	18.09555	3.91398	15.72181

Angles (°) between planes

1–2	77.6
3–1	15.6
3–2	71.7

figuration of the complex can be designated as Δ-α, β-S (and Λ-α,β-R) [8].

In this isomer the N(2)–H(22) bond and the Co–Br(1) bond lie on the same side of the Co, N(1), N(2), N(3), N(5) plane and we propose to label this the 'syn' isomer [2], as distinct from the 'anti' isomer (Δ-α, β-R or Λ-α, β-S). (The H(22)···Br contact distance is 2.68 Å).

'Anti' isomers have already been found in [Co(picdien)Cl] [ZnCl$_4$] [2], and in (α,β-Co(picditn)Cl-[CoCl$_4$·$\frac{1}{2}$H$_2$O] [9]. 'Syn' isomers, on the contrary, have been found in the dioxygen bridged dimeric cobalt complexes with picdien and picditn, [LCoO$_2$CoL]$^{++}$, which also have the α,β configuration [10, 11].

Inspection of the Co–N bond distances in the

TABLE IV. Torsion Angles (°)*.

N(1)–C(5)–C(6)–N(2)	−22
C(7)–N(2)–C(6)–C(5)	160
C(6)–N(2)–C(7)–C(8)	−169
N(2)–C(7)–C(8)–N(3)	45
C(9)–N(3)–C(8)–C(7)	92
C(8)–N(3)–C(9)–C(10)	−78
N(3)–C(9)–C(10)–N(4)	−42
C(11)–N(4)–C(10)–C(9)	−97
C(10)–N(4)–C(11)–C(12)	77
N(4)–C(11)–C(12)–N(5)	31

*The torsion angle w(IJKL) is defined as the angle between the vector KL when viewed down JK. It is positive if clockwise and negative if counter-clockwise.

TABLE V. Helicity of the Conformation [8] for all Chelate Rings.

Ring	Conformation	Helicity
N(1)–Co–N(2)	envelope	λ
N(2)–Co–N(3)	envelope	δ
N(3)–Co–N(4)	envelope	λ
N(4)–Co–N(5)	envelope	δ

picdien–cobalt moiety shows that the bonds to the terminal trigonal nitrogen atoms [Co–N(1) = 1.94(1), Co–N(5) = 1.97(1) Å] are slightly longer than predicted from radii-sum rules, 1.92 Å [12], although similar values have been already found in crystal structures of other Co(III) complexes with linear pentadentate picdien and picditn ligands [9, 10]. The bonds to the 'flat' and 'angular' secondary nitrogens [Co–N(2) = 1.94(1), Co–N(3) = 1.95(1), Co–N(4) = 1.96(1) Å] lie in the middle of the range of observed Co–N (tetrahedral) lengths (1.89 to 2.06 Å) [9–11, 13], the bond to the 'flat' secondary nitrogen N(2) being slightly shorter than the other Co–N bonds, as has been found in the structures of a number of cobalt(III) complexes containing trien, coordinated in the β configuration or picdien in the α,β configuration [2, 14].

Another geometrical feature of the 'flat' secondary nitrogen N(2) atom, common to all the structures examined [2, 14], is the expansion of the C(6)–N(2)–C(7) bond angle [119(1)°]. The Co–N(2) bond length is reduced relative to the other Co–N bond distances in order to reduce strain at this centre. By comparison there is less distortion in the angles about the 'angular' secondary N(3) and N(4) atoms. Likewise there are no other significant intra-ligand

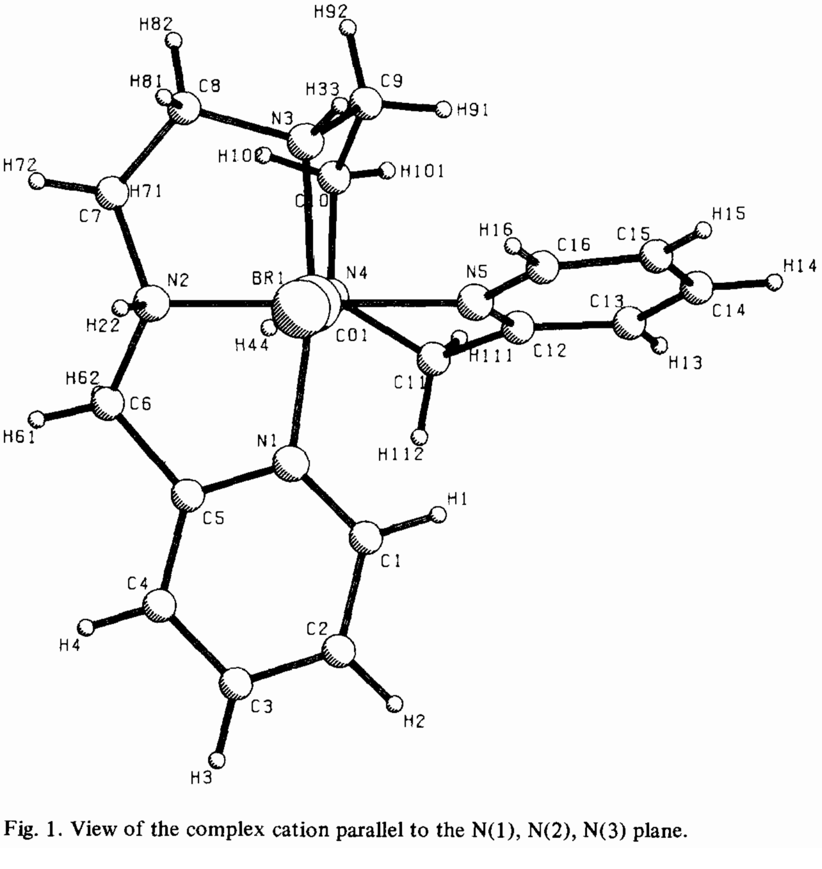

Fig. 1. View of the complex cation parallel to the N(1), N(2), N(3) plane.

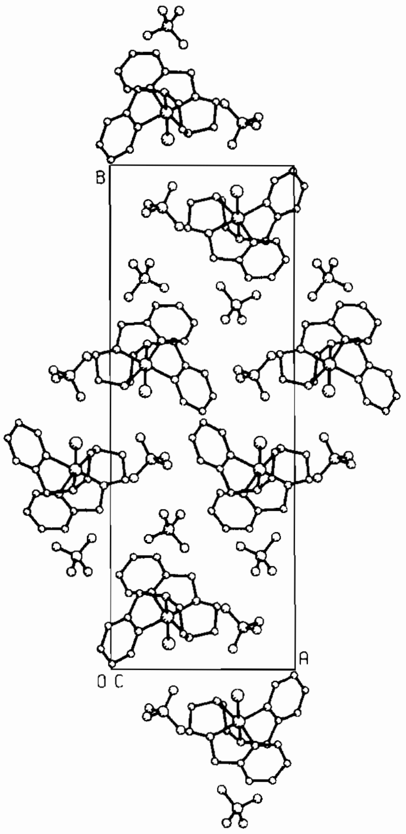

Fig. 2. The crystal packing down *c*.

angular distortions in the polyamine skeleton. In fact, within the picdien chelate, all internal angles at C and N are close to the regular tetrahedral value. The angles subtended by the chelate rings at the metal ion are similar and compare well with the values found in analogous compounds [9, 14]. All C–C and C–N distances are reasonably close to their usual values [12]. The conformations and the helicities [8] adopted by the chelate ring are reported in Table V.

The two pyridine rings in this complex are planar within experimental error and make an angle of 77.6° each other.

The Co–Br(1) bond distance of 2.396(3) Å, which is slightly larger than the sum of appropriate covalent radii 2.36 Å [12] suggests a partial ionic character for this bond. This distance is, to our knowledge, among the shortest that have been recorded for octahedral Co^{III} complexes with bromine, where the bond lengths are in the range, 2.33–2.49 Å, [15].

In both perchlorate anions a distorted tetrahedral arrangement of oxygen atom about the central chlorine atom is observed (Table II) with mean Cl–O bond distance of 1.38(2) Å. This value is significantly shorter than the average Cl–O bond distance of 1.43 Å found in $HClO_4 \cdot H_2O$ [16]. 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 [14, 17].

The crystal packing which is presented in Fig. 2, is mainly due to Coulombic and van der Waals forces and all intermolecular contacts are as expected for standard van der Waals values.

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