Inorganica Chimica Acta, 75 (1983) 93–101

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]$(ClO_4)_2$ and that of an Isomer of Nitro[1,9-bis(2-pyridyl)2,5,8-triazanonane]cobalt(III), Perchlorate, [Co(*picdien*)-$(NO_2)](ClO_4)_2$

G. BOMBIERI

Dipartimento di Chimica Inorganica e Struttura Molecolare, University of Messina, Messina, Italy

E. FORSELLINI

Istituto di Chimica e Tecnologia dei Radioelementi del C.N.R., Padua, Italy

A. DEL PRA

Istituto Chimico Farmaceutico, Università di Milano, Viale Abruzzi 42, 20131 Milan, Italy

M. L. TOBE, C. CHATTERJEE and C. J. COOKSEY

University College, London, U.K.

Received March 25, 1983

The structure of an isomer of bromo [1,9-bis(2-pyridyl)2,5,8-triazanonane]cobalt(III), perchlorate, [Co(picdien)Br]$(ClO_4)_2$, (I) and that of an isomer of nitro [1,9-bis(2-pyridyl)2,5,8-triazanonane]cobalt-(III), perchlorate, [Co(picdien)$(NO_2)](ClO_4)_2$, (II), was determined by counter data. Crystal data are as follows: (I), $a = 21.242(9)$, $b = 21.732(9)$, 10.015(5) Å, orthorhombic,P b c a, $Z = 8$; (II), $a = 10.062(5)$, $b = 28.553(9)$, $c = 7.894(4)$ Å, $\beta = 97.9(1)°$, monoclinic, I c, $Z = 4$. Full matrix least-squares refinement converged at $R = 0.064$, (I), and $R = 0.068$, (II). The coordination geometry of both complex cations is near regular octahedral, with the pentadentate picdien ligand present in the α, β configuration. The absolute configuration of (I) can be designed as Δ-α, β-R (or Λ-α, β-S) whereas that of (II) is Δ-α, β-S (or Λ-α, β-R). The ClO_4 anions assume a distorted tetrahedral configuration.

Introduction

In the past few years we have been interested in complexes of cobalt(III) with pentadentate pyridyl containing ligands, especially 1,9-bis(2-pyridyl)2,5,8-triazanonane (*picdien*) and 1,11-bis-(2-pyridyl)2,6,10-triaza undecane (*picditn*) in connection with their unusual sensitivity towards base-catalysed solvolysis [1]. As part of this study it has been important to measure the rates of proton exchange at the amine nitrogens, and for this reason it was necessary to assign the various ^1H NMR signals and relate the chemical shifts and coupling constants found for the complex ion in solution (d_6-Me_2SO, D_2O) to the known structures in the crystalline solid [2]. In most cases of compounds of the type [Co(picdien)X]$^{2+}$ (X = Cl, Br, NO_2, NCS), the NMR spectra (^{13}C and ^1H) were consistent with the αβ arrangement of the ligand and the coupling between one of the methylene group and one adjacent NH could be used diagnostically to distinguish between the *syn*- and *anti*-forms of the αβ arrangement.

The search for other isomeric forms has, until now, been unsuccessful, but the ^1H NMR spectrum of the nitro complex suggested that the two pyridyl groups were much more equivalent than in the other αβ complexes. The single crystal X-ray determination of the structure was carried out to answer this question. In addition, we report the structure of another isomer of the [Co(picdien)Br]$^{2+}$ cation in order to compare the *trans* effects of NO_2 and Br. A preliminary communication of the crystallography of the [Co(picdien)$NO_2](ClO_4)_2$ complex has been presented [3]. After this work was completed a note appeared reporting the structure of a red form of the Co(picdien)NO_2^+ cation [4].

Experimental

Preparation

Syn-αβ (nitro(1,9-bis(pyridyl)-2,5,8-triazanonane)-cobalt(III) perchlorate was prepared by dissolving equimolar amounts of *syn*-αβ-chloro(1,9-bis pyridyl)-2,5,8-triazanonane)cobalt(III) perchlorate in the minimum amount of water at 90 °C and digesting the solution for 30 minutes. The colour rapidly changed from red to yellow-orange and yellow crystals separated on cooling to room temperature. These were filtered off, washed with cold water, ethanol and ether, and air dried. *Anal.* Found: C, 32.6; H, 3.96; N, 14.15. $C_{16}H_{23}N_6Cl_2CoO_{10}$ requires, C, 32.6; H, 3.93; N, 14.27.

Anti-$\alpha\beta$-bromo(1,9-bis pyridyl)2,5,8-triazanonane)cobalt(III) perchlorate was prepared by adding $\alpha\beta$-[Co(picdien)H_2O]$(ClO_4)_3$ (2 g, 3 mmol) to a solution of LiBr (2.61 g, 30 mmol) in the minimum amount of dimethylsulphoxide. The mixture was warmed on a water bath (80 °C) for 15 minutes and allowed to stand overnight and then filtered. Twice its volume of ice cold 1 *M* perchloric acid was added drop by drop and the solution set aside to crystallize at 5 °C for 12 hours. The dark red crystals that separated were filtered off, washed successively with 0.1 *M* perchloric acid, ethanol and ether, and dried in air. *Anal.* Found: C, 30.5; H, 3.60; N, 11.15. $C_{16}H_{23}N_5BrCl_2CoO_8$ requires C, 30.8; H, 3.72; N, 11.24.

X-Ray Structural Data

Suitable crystals for X-ray analysis of complexes (*I*) and (*II*) were selected from the above preparations.

Approximate unit cell dimensions were obtained from preliminary Weissenberg and precession photographs. Systematic absences of the type 0kl (k = 2n + 1), h0l (l = 2n + 1) and hk0 (h = 2n + 1), observed in (*I*), uniquely define the centrosymmetric orthorhombic space group *P b c a* (D_{2h}^{15}, No. 61). Systematic absences of the type hkl (h + k + l = 2n + 1) and h0l (l = 2n + 1), observed in (*II*), led to the monoclinic space group I *c*, a non-standard setting of C *c* (C_s^4, No 9), with general equivalent positions: (0, 0, 0; 1/2, 1/2, 1/2) +; x, y, z; x, −y, 1/2 + z. The cell parameters in the standard setting and the transformation matrix are given in Table I.

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. Full details of the crystal data for both complexes are listed in Table I. Reflections data were collected on a Philips PW 1100 four-circle diffractometer. Intensities were corrected for Lorentz and polarization effects and put in an absolute scale by Wilson's method. An experimental absorption correction was applied [5]. Full details of the experimental conditions and data collection method used are given in Table II.

Structure Solution and Refinement

The structure of (*I*) was readily solved by conventional Patterson and Fourier methods, whereas that of (*II*) was initially solved by MULTAN direct methods [6] and subsequently by difference Fourier syntheses. The refinement of the structural models, which was by the method of full-matrix least-squares, was carried out for the complex (*I*) allowing the Co, Br, Cl and N atoms to vibrate anisotropically, while the oxygen and carbon atoms were assigned isotropic thermal parameters. In addition the population parameter was applied to the oxygen atoms of the perchlorate anions in order to take into account the disorder in this region of the crystal.

For (*II*) the oxygen atoms of the perchlorate anions were assigned isotropic thermal parameters and the remaining nonhydrogen atoms were allowed to vibrate anisotropically.

TABLE I. Crystal Data.

	Co(*picdien*)Br$(ClO_4)_3$, (*I*)	Co(*picdien*)$(NO_3)(ClO_4)_2$, (*II*)
Chemical formula	$C_{16}H_{23}N_5O_8Cl_2BrCo$	$C_{16}H_{23}N_6O_{10}Cl_2Co$
Formula wt	623.1	589.2
a (Å)	21.242(9)	10.062(5)[a]
b (Å)	21.732(9)	28.553(9)
c (Å)	10.015(5)	7.894(4)
β (°)		97.9(1)
Unit cell volume (Å^3)	4623.2	2246.6
Crystalline system	Orthorhombic	Monoclinic
Space group	*P b c a*	I *c*
F(000), (e)	2512	1208
ρ_{obsd} (g cm^{-3})	1.78	1.74
ρ_{calcd} (g cm^{-3})	1.79	1.75
Z	8	4
Absorption coeff. (cm^{-1})	27.0 (MoK$\bar{\alpha}$)	9.9 (MoK$\bar{\alpha}$)
Crystal dimensions (mm)	0.2 × 0.1 × 0.3	0.08 × 0.12 × 0.25
Colour	red	yellow-orange

[a] The standard lattice can be obtained by applying the following transformation matrix from Ic to Cc (−1, 0, −1); (0, 1, 0); (0, 0, 1) (*a* = 11.909, *b* = 28.553, *c* = 7.894 Å, β = 123.2°).

TABLE II. Details of Data Collection.

	[Co(*picdien*)Br](ClO$_4$)$_2$, (*I*)	[Co(*picdien*)(NO$_2$)](ClO$_4$)$_2$, (*II*)
Radiation	Mo-K$\bar{\alpha}$, λ 0.7107 Å	Mo-K$\bar{\alpha}$, λ 0.7107 Å
Monochromator	graphite crystal	graphite crystal
Scan method	$\vartheta-2\vartheta$	$\vartheta-2\vartheta$
Scan speed (° sec^{-1})	0.03	0.03
Scan width (°)	1.20	1.20
'Standard' reflections	2 every 120 min	2 every 120 min
2ϑ scan limit (°)	56	52
No. of data	5566	2376
No. of data with $I > 2.5\sigma(I)$	1920	1836

For both complexes hydrogen atoms could not be located from electron density difference maps and therefore were included in the scattering models in calculated idealized positions (C–H = 0.95 Å), but not varied. The function minimized was $\Sigma w\Delta^2$, ($\Delta = |Fo| - |Fc|$) and w were 2.01 $[\sigma^2(Fo) + 0.002\ Fo^2]^{-1}$, (*I*) and 1.93 $[\sigma^2(Fo) + 0.016\ Fo^2]^{-1}$, (*II*). Weighting-scheme analyses showed no significant dependence of the mean $w\Delta^2$ on either $|Fo|$ and λ^{-1} sinϑ. The final electron density difference maps showed no unusual features. Atomic scattering factors were taken from ref. 7. Allowance was made for the anomalous scattering of cobalt, bromine and chlorine atoms, using values of $\Delta f'$ and $\Delta f''$ from ref. 8. The final conventional R values for the observed reflections with $I \geqslant 2.5\sigma(I)$ were 0.064, (*I*) and 0.068, (*II*), [*R*w = 0.067, (*I*), *R*w = 0.073 (*II*)]. Final atomic parameters, and a selection of functions derived from them, are presented in Tables III–VI. Final atomic thermal parameters, hydrogen atom positions, and tables of structure factors are all available as supplementary material. 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 [9].

Results and Discussion

The stereochemical arrangements of the complex cations (*I*) and (*II*), along with the atom nomenclature, are shown in Figs 1 and 2. The coordination geometry of both cations is near regular octahedral, with the pentadentate *picdien* ligand present in the α,β configuration [10]. Two secondary nitrogens and the two pyridine nitrogen atoms of the *picdien* ligand are found to occupy one plane. The remaining secondary nitrogen of *picdien* and the bromine, (*I*), or NO$_2$, (*II*), 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. In the complex (*I*), the configuration of the 'flat' nitrogen N(2) is R, whereas that of the 'angular' N(4) is S [owing to the space group

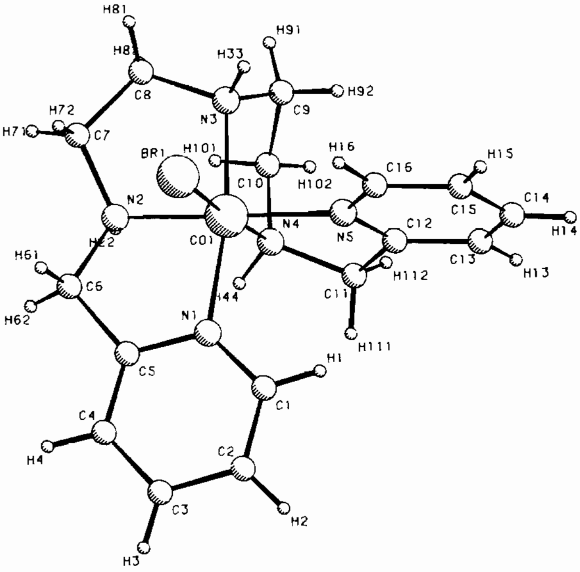

Fig. 1. Perspective view of the complex cation (*I*).

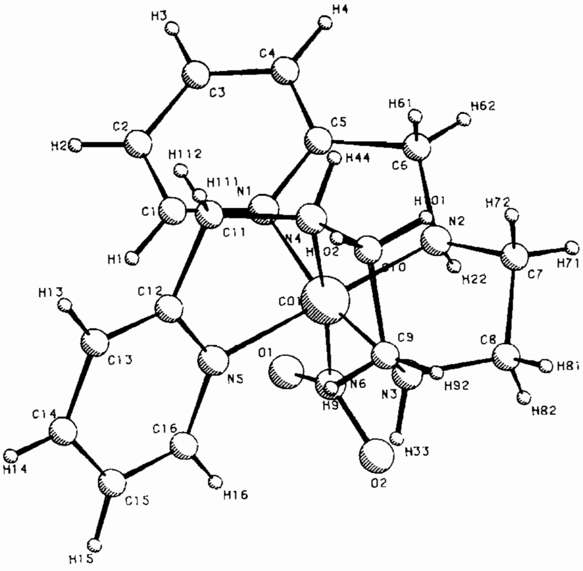

Fig. 2. View of the complex cation (*II*), down *c*.

TABLE III. Fractional Positional Parameters (×10^4) for Non-Hydrogen Atoms, with e.s.d.s in Parentheses.

(*I*) Atom	x/a (σ)	y/b (σ)	z/c (σ)	p.p.	(*II*) Atom	x/a (σ)	y/b (σ)	z/c (σ)
Co	8555(1)	1364(1)	9448(1)		Co	2128	1049(0)	5720
Br	8720(1)	2447(1)	9746(1)		N(1)	1277(11)	1512(4)	4226(14)
N(1)	7817(4)	1523(4)	8317(9)		N(2)	3737(10)	1337(3)	5208(14)
C(1)	7794(6)	1496(5)	6995(12)		N(3)	3280(10)	662(4)	7398(13)
C(2)	7239(6)	1598(6)	6322(14)		N(4)	1955(11)	1461(4)	7770(14)
C(3)	6696(7)	1743(6)	7054(14)		N(5)	502(10)	757(3)	6419(13)
C(4)	6748(6)	1784(6)	8418(14)		N(6)	2174(11)	621(4)	3920(14)
C(5)	7300(6)	1669(6)	9051(12)		O(1)	1545(18)	690(5)	2557(16)
C(6)	7384(6)	1695(6)	10525(11)		O(2)	2813(14)	252(4)	4140(18)
N(2)	7958(5)	1359(4)	10899(8)		C(1)	−34(14)	1517(6)	3504(21)
C(7)	8260(6)	1548(6)	12158(13)		C(2)	−503(16)	1859(6)	2323(20)
C(8)	8910(6)	1293(6)	12183(12)		C(3)	349(20)	2199(6)	1907(22)
N(3)	9178(4)	1190(4)	10828(9)		C(4)	1629(18)	2209(5)	2618(20)
C(9)	9398(5)	548(5)	10640(13)		C(5)	2082(16)	1855(5)	3796(19)
C(10)	8837(5)	156(6)	10307(14)		C(6)	3496(15)	1811(5)	4617(26)
N(4)	8474(4)	476(4)	9212(9)		C(7)	4865(13)	1247(6)	6551(20)
C(11)	8691(5)	303(5)	7868(12)		C(8)	4709(14)	741(5)	7152(19)
N(5)	9172(4)	1294(4)	7995(9)		C(9)	2968(15)	763(5)	9162(18)
C(12)	9181(5)	739(5)	7404(11)		C(10)	2761(17)	1298(5)	9306(17)
C(13)	9600(6)	603(7)	6367(14)		C(11)	495(14)	1495(5)	7868(21)
C(14)	10002(6)	1056(6)	5914(14)		C(12)	−117(12)	1026(5)	7482(18)
C(15)	9993(6)	1619(6)	6510(13)		C(13)	−1195(14)	863(5)	8169(18)
C(16)	9574(6)	1728(6)	7567(12)		C(14)	−1682(13)	415(5)	7770(20)
Cl(1)	8167(2)	32(1)	4237(3)		C(15)	−996(14)	148(5)	6720(18)
O(1)	8248(6)	645(6)	4756(13)	0.8	C(16)	46(13)	327(4)	6050(17)
O(2)	8751(7)	−211(8)	3836(17)	0.8	Cl(1)	7156(4)	7750(1)	2799(6)
O(3)	7804(7)	−261(7)	5218(15)	0.8	Cl(2)	6276(4)	9165(2)	−2537(5)
O(4)	7765(7)	114(7)	3092(14)	0.8	O(3)	8081(13)	7394(5)	3515(18)
O(11)	8525(23)	564(20)	4715(43)	0.2	O(4)	7792(23)	8067(8)	1788(32)
O(21)	8660(39)	−390(43)	4440(91)	0.2	O(5)	6053(15)	7548(5)	1892(20)
O(31)	8045(16)	−442(15)	5189(33)	0.2	O(6)	6897(22)	8071(8)	4032(31)
O(41)	7937(27)	−188(27)	3083(55)	0.2	O(7)	5328(20)	8830(6)	−2673(25)
Cl(2)	9196(2)	−1559(2)	8015(4)		O(8)	7154(26)	9155(8)	−1038(35)
O(5)	9552(9)	−1031(8)	7520(17)	0.7	O(9)	7062(36)	9109(10)	−3839(46)
O(6)	8588(9)	−1368(9)	8350(19)	0.7	O(10)	5901(31)	9562(10)	−3556(44)
O(7)	9197(8)	−1985(8)	6930(17)	0.7				
O(8)	9537(9)	−1803(10)	9091(21)	0.7				
O(51)	9633(26)	−2026(26)	8087(60)	0.3				
O(61)	8562(22)	−1722(23)	8208(46)	0.3				
O(71)	9316(19)	−1048(19)	7451(37)	0.3				
O(81)	9383(28)	−1384(30)	9469(64)	0.3				

Pbca requirements N(2) can be also S, in which case N(4) is R]. Therefore the relative configuration of complex (*I*) can be designed as Δ-α, β-R (or Λ-α, β-S) [11]. In the complex (*II*), when N(2) is S, N(4) is R and therefore the relative configuration of the complex can be designed as Δ-α, β-S (or Λ-α, β-R).

In this isomer of the complex (*I*) the N(2)–H bond and the Co–Br bond lie on opposite sides of the Co, N(1), N(2), N(3), N(5) plane and we proposed to label this the '*anti*' isomer [12] as distinct from the '*syn*' isomer (Δ-α, β-S or Λ-α, β-R) [13]. '*Anti*' isomers have been already found in [Co(*picdien*)Cl]ZnCl$_4$, [8] and in [α,β-Co(*picditn*)Cl]-(CoCl$_4$)·1/2H$_2$O, [14]. '*Syn*' isomers, on the contrary, have been found in the present complex (*II*) and in the dioxygen bridged dimeric cobalt complexes with *picdien* and *picditn*, [LCoO$_2$CoL]$^{2+}$, which also have the α, β configuration [15, 16].

The conformations and the helicities [11] adopted by the chelate rings of (*I*) and (*II*) are reported in Table VII.

In both complexes the two pyridine rings are planar, within experimental error, and make an angle of about 80° with each other. Inspection of the Co–N bond distances in the *picdien*–cobalt moieties shows that some bonds to the terminal trigonal nitrogen atoms [Co–N(1) = Co–N(5) = 1.965(7) Å, (*I*) and Co–N(5) = 1.981(8) Å, (*II*)] are slightly

TABLE IV. Bond Lengths (Å) and Angles (°) in (*I*) and (*II*).

Distance	(*I*)	(*II*)
Co–Br(1)	2.398(1)	
Co–N(6)		1.880(8)
Co–N(1)	1.965(7)	1.896(9)
Co–N(2)	1.929(7)	1.906(8)
Co–N(3)	1.951(7)	1.976(8)
Co–N(4)	1.951(7)	2.025(8)
Co–N(5)	1.965(7)	1.981(8)
N(1)–C(1)	1.33(1)	1.36(1)
N(1)–C(5)	1.36(1)	1.34(1)
C(1)–C(2)	1.38(1)	1.39(2)
C(2)–C(3)	1.40(1)	1.36(2)
C(3)–C(4)	1.37(1)	1.33(2)
C(4)–C(5)	1.36(1)	1.41(2)
C(5)–C(6)	1.49(1)	1.49(2)
N(2)–C(6)	1.47(1)	1.44(1)
N(2)–C(7)	1.47(1)	1.47(1)
C(7)–C(8)	1.49(1)	1.54(2)
N(3)–C(8)	1.49(1)	1.49(1)
N(3)–C(9)	1.48(1)	1.50(1)
C(9)–C(10)	1.50(1)	1.55(2)
N(4)–C(10)	1.51(1)	1.44(1)
N(4)–C(11)	1.47(1)	1.48(1)
C(11)–C(12)	1.48(1)	1.49(2)
C(12)–C(13)	1.40(1)	1.36(1)
C(13)–C(14)	1.38(1)	1.39(2)
C(14)–C(15)	1.36(1)	1.38(2)
C(15)–C(16)	1.40(1)	1.34(2)
N(5)–C(12)	1.34(1)	1.35(1)
N(5)–C(16)	1.34(1)	1.33(1)
Cl(1)–O(1)	1.44(1)	
Cl(1)–O(2)	1.41(1)	
Cl(1)–O(3)	1.40(1)	1.44(1)
Cl(1)–O(4)	1.44(1)	1.42(2)
Cl(1)–O(5)		1.36(1)
Cl(1)–O(6)		1.39(2)
Cl(1)–O(11)	1.46(4)	
Cl(1)–O(21)	1.41(7)	
Cl(1)–O(31)	1.43(3)	
Cl(1)–O(41)	1.34(4)	
Cl(2)–O(5)	1.46(1)	
Cl(2)–O(6)	1.40(2)	
Cl(2)–O(7)	1.43(1)	1.35(2)
Cl(2)–O(8)	1.40(2)	1.38(2)
Cl(2)–O(9)		1.39(3)
Cl(2)–O(10)		1.41(3)
Cl(2)–O(51)	1.38(4)	
Cl(2)–O(61)	1.40(4)	
Cl(2)–O(71)	1.27(3)	
Cl(2)–O(81)	1.56(5)	
N(6)–O(1)		1.19(1)
N(6)–O(2)		1.23(1)

Angles	(*I*)	(*II*)
N(1)–Co–N(2)	84.9(3)	83.8(4)
N(2)–Co–N(3)	84.9(3)	86.9(4)
N(3)–Co–N(5)	93.2(3)	90.5(3)
N(5)–Co–N(1)	96.9(3)	98.5(4)
Br–Co–N(1)	90.9(2)	
Br–Co–N(2)	90.5(2)	
Br–Co–N(3)	90.1(2)	
Br–Co–N(5)	94.1(2)	
N(6)–Co–N(1)		92.2(4)
N(6)–Co–N(2)		90.6(4)
N(6)–Co–N(3)		94.0(4)
N(6)–Co–N(4)		173.9(4)
N(6)–Co–N(5)		92.5(3)
N(4)–Co–N(1)	91.9(3)	90.7(4)
N(4)–Co–N(2)	91.5(3)	95.1(4)
N(4)–Co–N(3)	87.4(3)	84.0(3)
N(4)–Co–N(5)	83.8(3)	81.8(3)
O(1)–N(6)–O(2)		118.2(9)
O(1)–N(6)–Co		120.7(8)
O(2)–N(6)–Co		121.0(8)
C(1)–N(1)–Co	127(1)	126(1)
C(5)–N(1)–Co	112(1)	115(1)
C(1)–N(1)–C(5)	121(1)	118(1)
N(1)–C(1)–C(2)	121(1)	120(1)
C(1)–C(2)–C(3)	119(1)	120(1)
C(2)–C(3)–C(4)	118(1)	121(1)
C(3)–C(4)–C(5)	122(1)	118(1)
C(4)–C(5)–N(1)	119(1)	123(1)
N(1)–C(5)–C(6)	117(1)	114(1)
C(4)–C(5)–C(6)	124(1)	124(1)
C(5)–C(6)–N(2)	110(1)	109(1)
C(6)–N(2)–Co	110(1)	111(1)
C(7)–N(2)–Co	111(1)	112(1)
C(6)–N(2)–C(7)	116(1)	118(1)
N(2)–C(7)–C(8)	108(1)	107(1)
C(7)–C(8)–N(3)	113(1)	109(1)
C(8)–N(3)–Co	111(1)	108(1)
C(9)–N(3)–Co	108(1)	110(1)
C(8)–N(3)–C(9)	112(1)	115(1)
N(3)–C(9)–C(10)	108(1)	108(1)
C(9)–C(10)–N(4)	108(1)	109(1)
C(10)–N(4)–Co	109(1)	113(1)
C(11)–N(4)–Co	110(1)	106(1)
C(10)–N(4)–C(11)	113(1)	115(1)
N(4)–C(11)–C(12)	110(1)	108(1)
C(11)–C(12)–N(5)	115(1)	115(1)
C(13)–C(12)–N(5)	121(1)	121(1)
C(11)–C(12)–C(13)	123(1)	124(1)
C(12)–C(13)–C(14)	119(1)	120(1)
C(13)–C(14)–C(15)	119(1)	117(1)
C(14)–C(15)–C(16)	119(1)	121(1)
C(15)–C(16)–N(5)	122(1)	122(1)
C(12)–N(5)–Co	114(1)	114(1)
C(16)–N(5)–Co	127(1)	127(1)
C(12)–N(5)–C(16)	119(1)	119(1)
O(1)–Cl(1)–O(2)	110(1)	
O(1)–Cl(1)–O(3)	104(1)	
O(1)–Cl(1)–O(4)	104(1)	
O(2)–Cl(1)–O(3)	121(1)	
O(2)–Cl(1)–O(4)	110(1)	
O(3)–Cl(1)–O(4)	107(1)	111(1)
O(3)–Cl(1)–O(5)		110(1)
O(3)–Cl(1)–O(6)		111(1)

(continued overleaf)

TABLE IV *(continued)*

Angles	*(I)*	*(II)*
O(4)–Cl(1)–O(5)		112(1)
O(4)–Cl(1)–O(6)		97(1)
O(5)–Cl(1)–O(6)		115(1)
O(11)–Cl(1)–O(21)	95(3)	
O(11)–Cl(1)–O(31)	116(2)	
O(11)–Cl(1)–O(41)	139(2)	
O(21)–Cl(1)–O(31)	64(3)	
O(21)–Cl(1)–O(41)	99(4)	
O(31)–Cl(1)–O(41)	105(2)	
O(5)–Cl(2)–O(6)	109(1)	
O(5)–Cl(2)–O(7)	104(1)	
O(5)–Cl(2)–O(8)	107(1)	
O(6)–Cl(2)–O(7)	112(1)	
O(6)–Cl(2)–O(8)	114(1)	
O(7)–Cl(2)–O(8)	110(1)	115(1)
O(7)–Cl(2)–O(9)		109(1)
O(7)–Cl(2)–O(10)		113(1)
O(8)–Cl(2)–O(9)		106(2)
O(8)–Cl(2)–O(10)		127(1)
O(9)–Cl(2)–O(10)		79(1)
O(51)–Cl(2)–O(61)	117(2)	
O(51)–Cl(2)–O(71)	122(2)	
O(51)–Cl(2)–O(81)	88(2)	
O(61)–Cl(2)–O(71)	118(2)	
O(61)–Cl(2)–O(81)	100(2)	
O(71)–Cl(2)–O(81)	99(2)	

longer than predicted from radii-sum rules 1.92 Å [17], although similar values have been already found in crystal structures of other Co(III) complexes with linear pentadentate *picdien* and *picditn* ligands [12, 16]. The bonds to the 'flat' N(2) and 'angular' N(4) secondary nitrogens lie in the range of observed Co–N(tetrahedral) lengths (1.89 to 2.06 Å) [12–16, 18], 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 [12, 13, 19].

Another geometrical feature of the 'flat' secondary nitrogen N(2), common to all the structures examined [12, 13, 19] is the expansion of the C(6)–N(2)–C(7) bond angle [116(1)°, *(I)* and 118(1)°, *(II)*]. The Co–N(2) bond length is reduced relative to the other Co–N bond distances in order to reduce angular 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 angular distortions in the polyamine skeletons. In fact, within the *picdien* chelates, 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

TABLE V. Some Mean Planes and Dihedral Angles of *(I)* and *(II)*.

1) *(I)*

a) 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) −0.009, C(1) 0.010, C(2) −0.001, C(3) −0.010, C(4) 0.012, C(5) −0.003]	4.89504	21.09807	−0.66332	6.49688
Plane 2 N(5), C(12), C(13), C(14), C(15), C(16) [N(5) −0.003, C(12) −0.007, C(13) 0.011, C(14) −0.006, C(15) −0.004 C(16) 0.009]	14.57614	−6.71853	6.59441	17.77533
Plane 3 Co, N(1), N(2), N(3),N(5) [Co 0.040, N(1) 0.016, N(2) −0.038, N(3) 0.017, N(5) −0.035]	3.46303	21.34029	0.95780	6.73811
Plane 4 Co, N(2), Br, N(5), N(4) [Co −0.031, N(2) −0.002, Br 0.016, N(5) −0.002, N(4) 0.020]	15.56510	−3.74475	6.59306	19.06543
Plane 5 Co, Br, N(1), N(4), N(3) [Co 0.055, Br 0.081, N(1) −0.117, N(4) 0.102, N(3) −0.122]	13.94483	0.19979	−7.55424	4.76491
Plane 6 Co, N(1), N(2) [C(5) 0.258, C(6) 0.515]	2.75679	21.38819	1.20796	6.41706

(continued on facing page)

TABLE V *(continued)*

	P	Q	R	S
Plane 7 Co, N(2), N(3) [C(7) 0.660, C(8) 0.317]	3.02991	21.31820	1.32009	6.74711
Plane 8 Co, N(3), N(4) [C(9) 0.441, C(10 −0.210]	15.39680	0.42847	−6.89681	6.71430
Plane 9 Co, N(4), N(5) [C(11) −0.512, C(12) −0.206]	15.44918	−3.19362	6.71414	19.12469

b) Dihedral angles (°) between the planes.

1−2	79.3
3−1	10.1
3−2	82.6

2) (*II*)

a) 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) −0.009, C(1) 0.009, C(2) −0.003, C(3) −0.005, C(4) 0.005, C(5) 0.002]	−3.49149	16.26937	6.19985	4.64294
Plane 2 N(5), C(12), C(13), C(14), C(15), C(16) [N(5) 0.003, C(12) −0.005, C(13) −0.004, C(14) 0.015, C(15) −0.017, C(16) 0.008]	−5.09937	10.10371	−5.60004	−3.08898
Plane 3 Co, N(1), N(2), N(3), N(5) [Co −0.064, N(1) 0.045, N(2) −0.016, N(3) 0.043, N(5) −0.008]	−1.23653	19.04475	5.87912	5.16154
Plane 4 Co, N(2), N(6), N(5), N(4) [Co 0.030, N(2) −0.009, N(3) −0.007, N(5) −0.008, N(4) −0.006]	−4.82965	18.10535	−4.22258	−1.57405
Plane 5 Co, N(6), N(1), N(4), N(3) [Co −0.026, N(6) −0.119, N(1) 0.134, N(4) −0.123, N(3) 0.134]	8.88325	12.55262	−2.24516	1.94938
Plane 6 Co, N(1), N(2) [C(5) 0.245, C(6) 0.504]	−1.20702	17.73897	6.18490	5.14173
Plane 7 Co, N(2), N(3) [C(7) 0.400, C(8) −0.171]	−1.70284	19.64747	5.70036	4.95926
Plane 8 Co, N(3), N(4) [C(9) −0.516, C(10) 0.078]	8.37761	14.96389	−2.30037	2.03666
Plane 9 Co, N(4), N(5) [C(11) 0.754, C(12) 0.366]	−5.01144	18.15799	−4.07221	−1.49097
Plane 10 N(6), O(1), O(2)	8.47901	12.73533	−3.26809	1.35310

b) Dihedral angles (°) between the planes.

1−2	78.0
3−1	14.0
3−2	73.8
3−10	88.4

TABLE VI. Torsion Angles (°) of *(I)* and *(II)*.

	(I)	*(II)*
N(1)–C(5)–C(6)–N(2)[a]	–19	19
C(5)–C(6)–N(2)–C(7)	155	–159
C(6)–N(2)–C(7)–C(8)	–164	169
N(2)–C(7)–C(8)–N(3)	27	–46
C(7)–C(8)–N(3)–C(9)	–125	–91
C(8)–N(3)–C(9)–C(10)	81	82
N(3)–C(9)–C(10)–N(4)	49	43
C(9)–C(10)–N(4)–C(11)	89	96
C(10)–N(4)–C(11)–C(12)	–92	–86
N(4)–C(11)–C(12)–N(5)	–23	–27

[a] The torsion angle W(IJKL) is defined as the angle between the vector JI and the vector KL when viewed down JK. The sign of W is positive if JI is to be rotated clockwise into KL and negative if anticlockwise.

TABLE VII. Helicity of the Conformation for All Chelate Rings of *(I)* and *(II)*.

Ring	Conformation		Helicity	
	(I)	*(II)*	*(I)*	*(II)*
N(1)–Co–N(2)	envelope	envelope	δ	δ
N(2)–Co–N(3)	envelope	half-chair	λ	λ
N(3)–Co–N(4)	half-chair	envelope	λ	λ
N(4)–Co–N(5)	envelope	envelope	δ	λ

compounds [12, 14, 15]. All C–C and C–N distances are reasonably close to their usual values [17]. In the complex cation *(I)* the Co–Br(1) bond distance, 2.398(1) Å, is slightly larger than the sum of appropriate covalent radii, 2.36 Å [17], but is very close to the value of 2.396(3) Å found in the '*syn*' isomer [13] where a partial ionic character is suggested for this bond.

In the complex *(II)*, the Co–N(nitro) bond distance, of 1.880(8) Å, is in agreement with those found in other nitro complexes, where values ranging from 1.87(2) to 1.982(3) Å are reported [20].

The Co–NO_2 distance is significantly shorter than the Co–NH_2 distances. This difference is also apparent in a number of Co nitro-complexes recently investigated and may give some evidence for the π-bonding character of the Co–NO_2 bond [21]. In our laboratory the $[Co(\textit{picdien})X]^{2+}$ complexes (X = Cl, Br, NO_2), where the ligand X is *trans* to the secondary angular nitrogen N(4) have been examined [12, 13]. The Co–N(4) bond distances are 1.951(7) and 1.96(1) Å, when X is bromine [13]. Values of 1.97(2) and 2.025(8) Å are found for chlorine and nitro-group respectively. Although the rationalization of the *trans*-influence in $[Co(\textit{picdien})X]^{2+}$ complexes solely on the basis of the Co–N(4) distances is probably an oversimplification, we conclude from the above data that the *trans* influence increases along this series: Br $\simeq$ Cl $<$ NO_2. In the perchlorate anions of both compounds a distorted tetrahedral arrangement of oxygen atoms about the central chlorine atom is observed (Table V). In *(II)* the mean Cl–O bond distance is 1.39(2) Å, which is slightly shorter than the average Cl–O bond distance of 1.43 Å found in $HClO_4 \cdot H_2O$ [22]. This difference may be attributed to error introduced by the high correlation of the positional parameters with the large thermal motion of these oxygen atoms. Nevertheless, comparable values have been found in structures containing the perchlorate anion [19, 23, 24]. In the compound *(I)* the high values of the e.s.d.'s and the unusual values of some Cl–O bond lengths, caused mainly by the presence of disorder in the crystal, mean that the precise values of bond lengths and angles within the perchlorate anions do not warrant further discussion.

In both crystals (Figs. 3 and 4) the packing is mainly due to coulombic and van der Waals forces and all intermolecular contacts are as expected for standard van der Waals values.

Martell *et al.* [4] report the formation of red and yellow crystalline products from the reaction between the decomposed dioxygen dimer $\{[Co(\textit{picdien})]_2O_2\}I_4$ and sodium nitrite, and have determined the structure of the perchlorate of the red form. The complex has the same *syn*-$\alpha\beta$ arrangement of the ligand as our yellow species with a minor difference in its conformation, due to a different inclination of one of the pyridyl ring with respect to the dimethylene containing 5 membered ring. The main difference is found in the N–Co distance (2.104(5) Å as against 1.880(8) Å in this work) and the geometry of the nitro group with an unusually large O–N–O angle 135.3(8)° and small Co–N–O angle

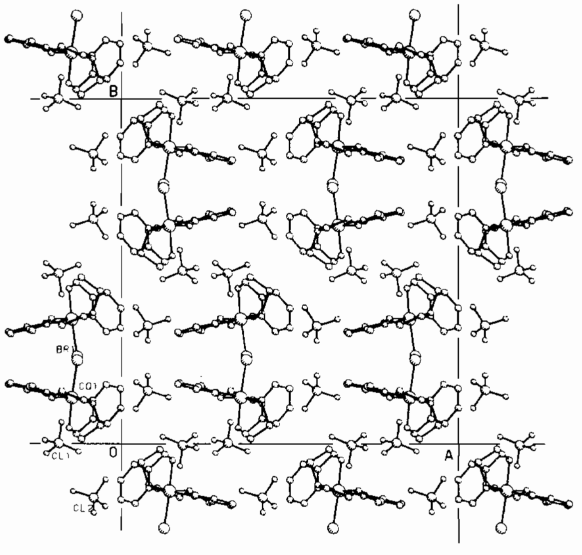

Fig. 3. The crystal packing of *(I)* down *c*.

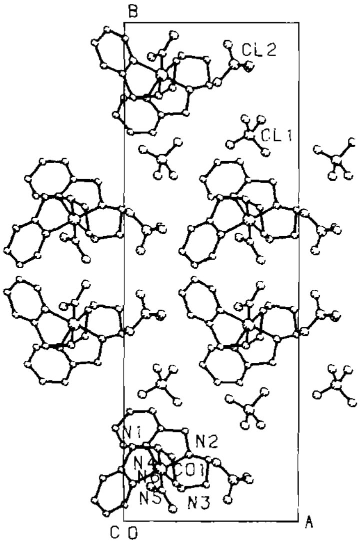

Fig. 4. The crystal packing of *(II)* down *c*.

(112.3(5)°) (the short O–N distance 1.054(10) Å could be connected with the high thermal motion of the oxygens). This is unlikely to be a new form of isomerism and the red colour of the sample could suggest that it is initially (at least) a nitrito rather than a nitro complex, undergoing isomerization during irradiation in the solid state with nearly complete retention of crystallinity.

The effect would appear as the superposition of contribution from a nitro and nitrito groups in the appropriate coordination site. The nitrito group may be disordered.

Reactions of this type have recently been reported for *trans*-$[Co(en)_2NCS(ONO)]^+$ (en = 1,2-diaminoethane) [25]. The only effect observed on the crystallinity was some disordering of the perchlorate group (this is also found in the structure of the red 'nitro' complexes). A disordered nitrito group in place of the nitro group cannot be completely ruled out as an alternative explanation. The angle Co–N–O (112.3°) reported for the red species agrees well with the value for Co–O–N (115°) found in *trans*-$[Co(en)_2(NCS)(ONO)]ClO_4$ [25].

Acknowledgements

We thank Mrs M. Magnabosco for technical assistance, C. C. and M. L. T. thank the Science and Engineering Research Council for a Research Grant.

References

1 M. Humanes, C. Chatterjee and M. L. Tobe, to be submitted.
2 C. J. Chatterjee, C. J. Cooksey and M. L. Tobe, to be submitted.
3 G. Bombieri, E. Forsellini, F. Benetollo and A. Del Pra, *Acta Cryst., A 37*, SUPP. 09-4-35 (1981).
4 E. C. Niederhoffer, C. J. Raleigh, A. E. Martell, P. Rudolf and A. Clearfield, *Cryst. Struct. Comm., 11*, 1163 (1982).
5 A. C. T. North, D. C. Phillips and F. Mathews, *Acta Cryst., A24*, 351 (1968).
6 P. Main 'MULTAN 80', University of York, England (1980).
7 International Tables for X-Ray Crystallography, Vol. IV, 3rd Ed., 99, Kynoch Press, Birmingham (1974).
8 International Tables for X-ray Crystallography, vol. IV, 3rd Ed. 149, Kynoch Press, Birmingham (1974).
9 G. M. Sheldrick, 'SHELX-76-Program for Crystal Structure Determination', Univ. of Cambridge (1976).
10 M. R. Snow, *J. Chem. Soc. Dalton*, 1627 (1972).
11 IUPAC, 'Nomenclature of Inorganic Chemistry', 2nd ed., pp. 75–83, Butterworths, London (1970).
12 G. Bombieri, E. Forsellini, A. Del Pra and M. L. Tobe, *Inorg. Chim. Acta, 51*, 177 (1981).
13 G. Bombieri, E. Forsellini, A. Del Pra, M. L. Tobe and C. Chatterjee, *Inorg. Chim. Acta, 68*, 205 (1983).
14 G. Bombieri, E. Forsellini, A. Del Pra and M. L. Tobe, *Inorg. Chim. Acta, 40*, 71 (1980).
15 J. H. Timmons, A. Clearfield, A. E. Martell and R. H. Niswander, *Inorg. Chem., 18*, 1042 (1979).
16 J. H. Timmons, R. H. Niswander, A. Clearfield and A. E. Martell, *Inorg. Chem., 18*, 2977 (1979).
17 L. Pauling 'The Nature of the Chemical Bond', 3rd Ed., Cornell University Press, Ithaca, New York (1966).
18 P. A. Tucker, *Acta Cryst., B35*, 67 (1979).
19 G. Bombieri, E. Forsellini, A. Del Pra, M. L. Tobe and R. Henderson, *Gazz. Chim. It., 109*, 207 (1979).
20 R. M. Herak, M. P. Celap and I. Krstanovic, *Acta Cryst., B33*, 3368 (1977).
21 G. Srdanov, R. Herak and B. Prelesnik, *Inorg. Chim. Acta, 33*, 23 (1979).
22 S. Lee and G. B. Carpenter, *J. Phys. Chem., 63*, 279 (1959).
23 F. A. Jurnak, D. R. Greig and K. N. Raymond, *Inorg. Chem., 14*, 2585 (1975).
24 G. Bombieri, E. Forsellini, A. Del Pra, C. J. Cooksey, H. Humanes and M. L. Tobe, *Inorg. Chim. Acta, 61*, 43 (1982).
25 I. Grenthe and E. Nordin, *Inorg. Chem., 18*, 1109 (1979).