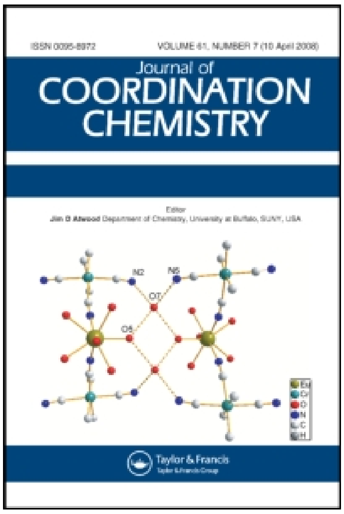

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CHIRAL METAL COMPLEXES. 30 THE CRYSTAL AND MOLECULAR STRUCTURES OF A-β-[DINITRO{*N,N'*-BIS(2-PICOLYL)-lR,2R-DIAMINOCY CLOHEXANE}COBALT(III)] PERCHLORATE MONOHYDRATE, AND α-β-*EXO*-[DINITRO{ 3*R*-METHYL-1,6-BIS(2-PYRIDYL)-2,5-DIAZAHEXANE}COBALT(III)] PERCHLORATE MONOHYDRATE

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CHIRAL METAL COMPLEXES. 30* THE CRYSTAL AND MOLECULAR STRUCTURES OF Λ-β-[DINITRO{*N,N'*-BIS(2-PICOLYL)-1*R*,2*R*-DIAMINOCYCLOHEXANE}COBALT(III)] PERCHLORATE MONOHYDRATE, AND Δ-β-*EXO*-[DINITRO{3*R*-METHYL-1,6-BIS(2-PYRIDYL)-2,5-DIAZAHEXANE}COBALT(III)] PERCHLORATE MONOHYDRATE

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The structures of two Co(III) complexes containing *N*-bonded nitrite ions and one of the N_4 tetradentate ligands *R,R*-picchxn (*N,N'*-bis(2-picolyl)-1*R*,2*R*-diaminocyclohexane) or *R*-picpn (3*R*-methyl-1,6-bis(2-pyridyl)-2,5-diazahexane) have been determined by X-ray analyses. Λ-β-[Co(*R,R*-picchxn)$(NO_2)_2$]$ClO_4.H_2O$ is triclinic, space group $P1$, with $a = 8.611(2)$, $b = 9.188(1)$, $c = 8.576(1)$ Å, $\alpha = 117.60(1)$, $\beta = 96.40(1)$, $\gamma = 73.69(1)^\circ$ and $Z = 1$. The structure was refined by full-matrix least-squares methods to $R = 0.035$ for 2712 non-zero reflexions. Δ-β-*exo*-[Co(*R*-picpn)$(NO_2)_2$]$ClO_4.H_2O$ is orthorhombic, space group $P2_12_12_1$, with $a = 7.664(1)$, $b = 15.121(3)$, $c = 18.429(4)$ Å and $Z = 4$. The structure was refined as above to $R = 0.040$ for 2063 non-zero reflexions. In the *R,R*-picchxn complex both amine nitrogen atoms of the tetradentate have the same relative configuration, whereas in the *R*-picpn diastereoisomer their relative configurations are opposite. In the latter complex this permits the *exo* methyl group substituent to adopt a nearly ideal equatorial position in the central chelate ring. Hydrogen bonding networks in the two structures, which link the complex cations to the perchlorate ions and lattice water molecules, are apparent.

Keywords: cobalt(III), complexes, chiral, structures, x-ray

INTRODUCTION

It is now well established that substitution on the backbone of linear nitrogenous tetradentates and their congeners can influence the mode of coordination of these ligands,[1] and this is exemplified in ternary Co(III) complexes which contain analogues of the ligand 1,6-bis(2-pyridyl)-2,5-diazahexane (picen). The related chiral ligand *N,N'*-bis(2-picolyl)-1*R*,2*R*-diaminocyclohexane (*R,R*-picchxn) displays a remarkable degree of stereospecificity in such complexes. In a large number of substitution reactions of the complex cation Λ-β-[Co(*R,R*-picchxn)Cl_2]$^+$ the Λ-β geometry is retained. Under certain synthetic conditions small amounts of Δ-α

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ternary intermediates incorporating bidentate aminoacidates have been identified in this system, but these are quite unstable with respect to the Λ-β diastereoisomers and as a result inversion-isomerisation of Δ-α to Λ-β topology may be observed.[2] These topological changes occur spontaneously in dimethylsulfoxide solutions.

Similarly, replacement of the chloride donors in the precursor complex by nitrite ions produces Λ-β-[Co(*R*,*R*-picchxn)$(NO_2)_2]^+$ stereospecifically,[3] as evidenced by chiroptical and nmr measurements. In contrast the chiral tetradentate 3*R*-methyl-1,6-bis(2-pyridyl)-2,5-diazahexane (*R*-picpn) lacks stereospecificity in its coordination to Co(III). Spectral and synthetic studies[4] have shown that Λ-α-[Co(*R*-picpn)$Cl_2]^+$ reacts with nitrite ions in aqueous solution to yield predominantly Δ-β-*exo*-[Co(*R*-picpn)$(NO_2)_2]^+$. The small quantity of Λ-α dinitro isomer which also forms is seen to invert completely to the Δ-β-*exo* form in dmso at room temperature.

TABLE I
Summary of Crystal Data, Data Collection and Structure Refinements.

Compound[a]	{I}	{II}
Crystal Data		
Formula	$C_{18}H_{26}N_6O_9ClCo$	$C_{15}H_{22}N_6O_9ClCo$
Mr	564.8	524.8
System	triclinic	orthorhombic
Space Group	*P*1 (No. 1)	$P2_12_12_1$ (No. 19)
a (Å)	8.611(2)	7.644(1)
b	9.188(1)	15.121(3)
c	8.576(1)	18.429(4)
α (°)	117.60(1)	
β	96.40(1)	
γ	73.69(1)	
U (Å³)	577.0	2135.7
Z	1	4
Dc ($g\,cm^{-3}$)	1.700	1.632
μ-MoKα (cm^{-1})	10.0	10.2
F(000)	292	1040
Data Collection		
Crystal size (mm)	0.3 × 0.3 × 0.3	0.13 × 0.15 × 0.5
Radiation	Mo-Kα	
2θ° (min, max)	2.0, 56.0	2.0, 52.0
Absorption corr.	empirical	
Transmission factors (min, max)	0.963, 0.999	0.979, 0.999
Total reflexions	2753	2402
No. $I > 3\sigma(I)$	2712	2063
Refinement		
Anisotropic	all non-hydrogen atoms	
H atoms	parameters included but not refined	
R	0.035	0.040
R' ($[\Sigma w\Delta^2/\Sigma w\lvert F_o\rvert^2]^{\frac{1}{2}}$)	0.039	0.035
$(\Delta/\sigma)_{max}$	0.1	0.1
Final Δ map (ρ eÅ^{-3})	<|0.5|	<|0.5|

[a] {I}: Λ-β-[Co(*R*,*R*-picchxn)$(NO_2)_2]ClO_4.H_2O$; {II}: Δ-β-*exo*-[Co(*R*-picpn)$(NO_2)_2]ClO_4.H_2O$.

Reaction of Λ-α-[Co(*R*-picpn)Cl_2]$^+$ with chiral α-aminoacids yields a variety of ternary species.[5] These include β_1 and β_2 species in both Δ and Λ absolute configurations and with *exo* and *endo* disposition of the methyl substituent on the central tetradentate chelate ring. Nevertheless, Δ-β-*exo*-[Co(*R*-picpn)$(NO_2)_2$]$^+$ appears to be the only stable species formed on nitrite ion substitution.

In order to confirm our structural conclusions concerning the nature of the dinitro products obtained with these two tetradentates we have determined their molecular structures using single crystal X-ray diffraction methods, the results of which are reported below.

TABLE II
Final Atomic Coordinates (fractional × 10^4) for Non-hydrogen Atoms with Estimated Standard Deviations in Parentheses (picchxn complex).

Atom	*x*/*a*	*y*/*b*	*z*/*c*
Co	5000	5000	5000
N(11)	4197(5)	2965(5)	3740(6)
N(1)	2825(5)	6147(5)	4566(5)
N(2)	5403(5)	7268(6)	6112(6)
N(21)	5956(5)	4824(6)	2935(6)
N(3)	7102(6)	3850(7)	5487(7)
N(4)	4292(5)	5339(6)	7239(6)
O(31)	8329(6)	4061(7)	5267(9)
O(32)	7111(5)	2790(7)	5995(6)
O(41)	4570(5)	6548(5)	8601(5)
O(42)	3602(6)	4410(6)	7358(5)
C(11)	5074(6)	1354(6)	3029(6)
C(12)	4370(7)	14(6)	2144(7)
C(13)	2699(8)	382(7)	1985(7)
C(14)	1795(7)	2026(7)	2703(7)
C(15)	2576(5)	3314(6)	3591(6)
C(16)	1686(6)	5146(6)	4441(7)
C(1)	2432(5)	7924(5)	5947(6)
C(2)	3908(6)	8530(6)	5993(6)
C(3)	3758(7)	10330(7)	7479(7)
C(4)	2233(8)	11533(7)	7246(8)
C(5)	724(7)	10907(7)	7143(8)
C(6)	912(6)	9097(6)	5654(7)
C(26)	6798(6)	7239(7)	5195(7)
C(25)	6782(5)	5991(7)	3287(7)
C(24)	7605(6)	5996(7)	2003(7)
C(23)	7614(7)	4743(8)	269(7)
C(22)	6788(7)	3540(7)	−87(7)
C(21)	5953(7)	3630(7)	1248(7)
Cl	8811(2)	8653(2)	9822(2)
O(1)	9163(8)	8662(12)	11423(9)
O(2)	9974(9)	7810(15)	8606(10)
O(3)	7285(7)	8538(14)	9362(8)
O(4)	8730(15)	10280(15)	10314(26)
O(w)	2426(6)	6070(6)	11168(5)

EXPERIMENTAL

Both dinitro cations were synthesised following published procedures.[3,4] It has become evident that their perchlorate salts exist in a number of hydrated forms.

Suitable crystals of the monohydrates of both complexes were grown by slow evaporation of dilute aqueous solutions of Λ-β-[Co(*R*,*R*-picchxn)$(NO_2)_2$]$ClO_4 \cdot 3H_2O$ [3] and Δ-β-*exo*-[Co(*R*-picpn)$(NO_2)_2$]ClO_4.[4] The ^1H nmr spectra of the cations were identical to those reported previously.[3,4]

TABLE III
Final Atomic Coordinates (fractional × 10^4) for Non-hydrogen Atoms with Estimated Standard Deviations in Parentheses (picpn complex).

Atom	x/a	y/b	z/c
Co	3889.0(9)	5090.5(4)	1366.6(4)
N(11)	2681(6)	5843(3)	672(2)
N(1)	2111(6)	5545(3)	2021(3)
N(2)	4638(6)	4355(3)	2180(3)
N(21)	2513(6)	4026(3)	1091(3)
N(3)	5658(7)	4643(3)	739(3)
N(4)	5438(6)	6040(3)	1631(3)
O(31)	5378(6)	4493(3)	101(2)
O(32)	7124(6)	4479(4)	990(3)
O(41)	5794(7)	6182(3)	2257(3)
O(42)	6052(7)	6501(3)	1156(2)
C(11)	3289(8)	6138(4)	41(3)
C(12)	2223(9)	6612(4)	−434(3)
C(13)	524(9)	6766(4)	−247(4)
C(14)	−60(8)	6490(4)	404(4)
C(15)	1013(8)	6028(3)	867(3)
C(16)	494(7)	5701(4)	1604(3)
C(1)	1911(7)	4959(4)	2656(3)
C(m)	1023(11)	5424(4)	3277(3)
C(2)	3759(10)	4663(4)	2847(3)
C(26)	4326(9)	3396(4)	2020(4)
C(25)	2942(8)	3296(4)	1478(3)
C(24)	2180(9)	2490(4)	1325(4)
C(23)	990(12)	2419(4)	771(4)
C(22)	605(10)	3166(4)	372(4)
C(21)	1374(10)	3954(4)	545(4)
Cl	1474(2)	8178(1)	1920(1)
O(1)	1816(7)	8882(4)	2365(4)
O(2)	2578(8)	7484(4)	2042(5)
O(3)	−273(7)	7926(4)	1952(4)
O(4)	1713(13)	8448(6)	1200(4)
O(w)	8519(10)	4651(4)	−818(4)

Crystal Structure Analyses

Unit cell parameters were determined initially from single-crystal precession photographs. Accurate cell parameters were obtained from a least-squares fit to diffractometer data. Intensities were collected on an Enraf-Nonius CAD4 diffractometer by Dr M.B. Hursthouse at Queen Mary College, London. These were corrected for Lorentz, polarisation and absorption effects. A summary of crystal data and refinement parameters for the two structures is given in Table I.

Both structures were solved by the heavy-atom method and refined by full-matrix least-squares technique in which the function minimised was $\Sigma w\Delta^2$. Weights used were obtained from counting statistics. After isotropic refinement hydrogen atoms were located from difference maps. Their positions were optimised assuming C–H, N–H and O–H to be 1.0 Å, and refinement was continued with H atoms held in these positions. Thermal parameters of $B = 2.0$ Å were assigned to H atoms in both structures. Anisotropic refinement was continued for all other atoms.

All calculations were carried out on a UNIVAC 1106 computer using programmes written by F.S.S. Neutral-atom scattering factors were taken from International Tables for X-ray Crystallography[6] with corrections being applied for anomalous dispersion.[6] The final coordinates for the heavy atoms in the two structures are given in Tables II and III.

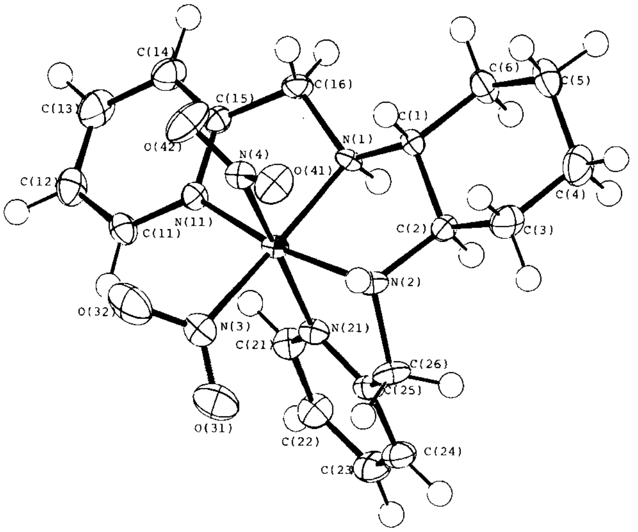

FIGURE 1 A perspective view [8] of the cation Λ-β-[Co(*R*,*R*-picchxn)$(NO_2)_2]^+$ showing the atomic numbering scheme. Thermal ellipsoids are scaled to include 35% probability.

RESULTS AND DISCUSSION

Λ-β-[Co(R,R-picchxn)$(NO_2)_2]ClO_4.H_2O$

A perspective view of the complex cation with the atom numbering scheme is shown in Figure 1, and a list of bond lengths and angles is given in Table IV. As expected, the nitrite ligands are *N*-coordinated in the *cis* positions of the coordination sphere. There are no unusual features apparent in the geometry of the cation, whose absolute configuration is as predicted from spectral studies.[3] Geometrical constraints imposed by the central cyclohexane ring of the tetradentate ligand enforce an *S* configuration at both internal amine nitrogen atoms. This is not the case in the related complexes of *R*-picpn (*vide infra*), and it would seem that this feature in *R*,*R*-picchxn may be largely responsible for the coordination stereospecificity observed in its complexes with Co(III).

TABLE IV
Bond Lengths and Angles with Estimated Standard Deviations in Parentheses for Λ-β-[Co(*R*,*R*-picchxn)$(NO_2)_2$]$ClO_4.H_2O$.

a) *Distances* (Å)

	n = 1	n = 2		n = 1	n = 2
Co (n1)	1.956(4)	1.956(4)	Co–N(3)	1.932(5)	
Co–N(n)	1.964(4)	1.966(4)	Co–N(4)	1.938(5)	
N(n1)–C(n1)	1.331(6)	1.352(7)	N(3)–O(3n)	1.176(7)	1.235(6)
N(n1)–C(n5)	1.347(6)	1.352(6)	N(4)–O(4n)	1.241(6)	1.213(6)
C(n1)–C(n2)	1.382(7)	1.377(7)	C(1)–C(2)	1.514(6)	
C(n2)–C(n3)	1.389(8)	1.378(7)	C(2)–C(3)	1.529(6)	
C(n3)–C(n4)	1.361(8)	1.395(7)	C(3)–C(4)	1.522(8)	
C(n4)–C(n5)	1.389(6)	1.377(6)	C(4)–C(5)	1.541(8)	
C(n5)–C(n6)	1.489(6)	1.502(7)	C(5)–C(6)	1.533(7)	
C(n6)–N(n)	1.486(6)	1.495(6)	C(6)–C(1)	1.524(6)	
N(n)–C(n)	1.473(6)	1.502(6)			
Cl–O(1)	1.369(6)		Cl–O(3)	1.349(5)	
Cl–O(2)	1.318(6)		Cl–O(4)	1.334(10)	

b) *Angles* (°)

N(11)–Co–N(1)	83.2(2)	N(21)–Co–N(2)	82.7(2)
N(11)–Co–N(3)	95.9(2)	N(21)–Co–N(3)	88.8(2)
N(11)–Co–N(4)	91.3(2)	N(21)–Co–N(4)	171.6(2)
N(1)–Co–N(3)	177.7(2)	N(2)–Co–N(3)	95.5(2)
N(1)–Co–N(4)	91.5(2)	N(2)–Co–N(4)	90.9(2)
N(11) C) N(21)	96.1(2)	N(2)–Co–N(1)	85.5(2)
N(11)–Co–N(2)	168.5(2)	N(21)–Co–N(1)	93.3(2)
N(3)–Co–N(4)	86.5(2)		

	n = 1	n = 2		
Co–N(3)–O(3n)	124.1(5)	115.9(4)	O(31)–N(3)–O(32)	120.0(6)
Co–N(4)–O(4n)	118.4(4)	122.5(4)	O(41)–N(4)–O(42)	119.0(5)
Co–N(n)–C(n)	107.9(2)	109.0(3)	N(1)–C(1)–C(2)	104.4(3)
Co–N(n)–C(n6)	108.6(3)	109.6(3)	N(1)–C(1)–C(6)	115.4(4)
C(n)–N(n)–C(n6)	115.6(4)	110.2(4)	C(2)–C(1)–C(6)	110.5(4)
Co–N(n1)–C(n1)	127.1(4)	127.5(4)	N(2)–C(2)–C(1)	109.5(3)
Co–N(n1)–C(n5)	113.4(3)	114.8(3)	N(2)–C(2)–C(3)	112.8(4)
C(n1)–N(n1)–C(n5)	119.5(4)	117.6(4)	C(1)–C(2)–C(3)	111.2(4)
N(n1)–C(n1)–C(n2)	121.9(5)	122.6(5)	C(2)–C(3)–C(4)	109.5(4)
C(n1)–C(n2)–C(n3)	118.3(5)	119.7(5)	C(3)–C(4)–C(5)	111.2(5)
C(n2)–C(n3)–C(n4)	120.1(5)	118.1(5)	C(4)–C(5)–C(6)	111.0(4)
C(n3)–C(n4)–C(n5)	118.7(5)	119.4(5)	C(5)–C(6)–C(1)	109.0(4)
C(n4)–C(n5)–N(n1)	121.4(5)	122.5(5)	O(1)–Cl–O(2)	117.0(5)
C(n4)–C(n5)–C(n6)	122.5(4)	122.3(5)	O(1)–Cl–O(3)	111.2(4)
N(n1)–C(n5)–C(n6)	116.0(4)	115.1(4)	O(1)–Cl–O(4)	98.1(9)
C(n5)–C(n6)–N(n)	107.8(4)	108.0(4)	O(2)–Cl–O(3)	119.2(5)
O(3)–Cl–O(4)	103.8(7)		O(2)–Cl–O(4)	103.6(7)

Figure 2 shows the orientation of the ions and the lattice water molecule in the triclinic unit cell. A hydrogen bonding network links these three components together, and details are listed in Table V. Both internal amine groups in the tetradentate are hydrogen bonded to oxygen atoms, one to a water molecule and the other to a perchlorate ion. The water molecule acts as a hydrogen-bond donor to one of the oxygen atoms of the coordinated nitro groups and to an oxygen of the perchlorate ion. Hence its position in the lattice is well defined.

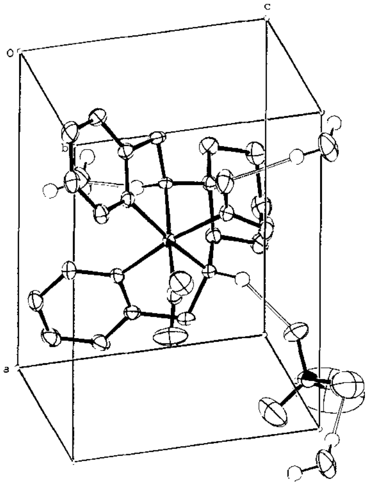

FIGURE 2 The packing of Λ-β-[Co(*R*,*R*-picchxn)$(NO_2)_2$]ClO_4·H_2O in the triclinic unit cell. Hydrogen bonds are unfilled.

TABLE V
Dimensions of Proposed Hydrogen Bonds (Å) with Estimated Standard Deviations in Parentheses.[a]

*Λ-β-[Co(*R,R*-picchxn)$(NO_2)_2$]ClO_4.H_2O*	
N(1)H(N1) - - - *O*(W^{I})	2.865(5)
N(2)H(N2) - - - *O*(3)	2.966(7)
O(W)H(W2) - - - *O*(42)	3.047(6)
O(W)H(W1) - - - *O*(1^{II})	3.084(9)
Δ-β-exo-*[Co(*R*-picpn)$(NO_2)_2$]ClO_4.H_2O*	
N(2)H(N2) - - - *O*(1^{III})	2.933(7)
N(1)H(N1) - - - *O*(2)	2.953(7)
O(W)H(W1) - - - *O*(31)	2.953(8)
O(W)H(W2) - - - *O*(4^{IV})	3.267(11)

[a] Superscripts refer to positions relative to *x*, *y*, *z*.
I: $x, y, z-1$; II: $x-1, y, z$; III: $1-x, y-\frac{1}{2}, \frac{1}{2}-z$; IV: $\frac{1}{2}+x, \frac{3}{2}-y, -z$.

Δ-β-exo-*[Co(*R*-picpn)$(NO_2)_2$]ClO_4.H_2O*

Figure 3 shows a perspective view of the cation together with the numbering scheme for the non-hydrogen atoms. Both nitrite ligands are *N*-coordinated, the tetradentate being coordinated in the Δ-β fashion and the *R*-picpn methyl substituent being disposed *exo* to the fold of the ligand. The geometry of the complex contains no unexpected features. In these respects the nature of the complex is as predicted from CD, ^1H nmr and infrared spectral studies.[4] A list of bond lengths and angles is given in Table VI.

On the basis of those original results, though, it had been suggested that the *S*(N),*R*(N) isomer (ignoring the methyl substituent*) would be somewhat more strained than the corresponding *S*(N),*S*(N) form. The structure as determined proves

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* In this isomer both internal amine nitrogen atoms in fact possess the *S* configuration as defined by the Cahn-Ingold-Prelog rules.

unequivocally that the unique isomer which forms is in fact the *S*(N),*R*(N) species, with the tetradentate locked in a rigid conformation. The almost *trans* and *gauche* relative dispositions observed for the hydrogen atoms of the central ethyl bridge are consistent with the interpretation of the ^{1}H nmr spectrum[4] of the complex with respect to chemical shift and coupling constant assignments.

TABLE VI
Bond Lengths and Angles with Estimated Standard Deviations in Parentheses for Δ-β-*exo*-[Co(*R*-picpn)$(NO_2)_2$]$ClO_4.H_2O$.

a) *Distances (Å)*

	n = 1	n = 2		
Co–N(n1)	1.947(4)	1.990(5)	Co–N(3)	1.906(5)
Co–N(n)	1.946(5)	1.952(4)	Co–N(4)	1.926(5)
N(n1)–C(n1)	1.330(7)	1.338(8)	C(1)–C(2)	1.526(9)
N(n1)–C(n5)	1.357(8)	1.354(7)	C(1)–C(m)	1.504(8)
C(n1)–C(n2)	1.395(8)	1.367(8)	Cl–O(1)	1.369(5)
C(n2)–C(n3)	1.367(9)	1.378(9)	Cl–O(2)	1.367(6)
C(n3)–C(n4)	1.346(9)	1.374(10)	Cl–O(3)	1.393(5)
C(n4)–C(n5)	1.376(8)	1.381(8)	Cl–O(4)	1.399(8)
C(n5)–C(n6)	1.500(8)	1.464(8)		
C(n6)–N(n)	1.477(7)	1.498(7)		
N(n)–C(n)	1.476(7)	1.477(7)		
N(3)–O(3n)	1.218(6)	1.240(6)		
N(4)–O(4n)	1.204(6)	1.213(6)		

b) *Angles (°)*

N(11)–Co–N(1)	82.4(2)	N(21)–Co–N(2)	83.7(2)
N(11)–Co–N(3)	98.5(2)	N(21)–Co–N(3)	86.3(2)
N(11)–Co–N(4)	91.3(2)	N(21)–Co–N(4)	173.9(2)
N(1)–Co–N(3)	179.0(2)	N(2)–Co–N(3)	93.1(2)
N(1)–Co–N(4)	90.6(2)	N(2)–Co–N(4)	92.8(2)
N(11)–Co–N(21)	93.0(2)	N(2)–Co–N(1)	86.1(2)
N(11)–Co–N(2)	167.8(2)	N(21)–Co–N(1)	94.2(2)
N(3)–Co–N(4)	88.8		

	n = 1	n = 2		
Co–N(3)–O(3n)	121.8(4)	119.3(4)	O(31)–N(3)–O(32)	118.8(5)
Co–N(4)–O(4n)	120.9(4)	119.0(4)	O(41)–N(4)–O(42)	120.1(5)
Co–N(n)–C(n)	110.6(4)	108.9(4)	N(1)–C(1)–C(2)	105.1(4)
Co–N(n)–C(n6)	108.7(3)	110.7(4)	N(1)–C(1)–C(m)	111.7(5)
C(n)–N(n)–C(n6)	114.9(4)	113.3(5)	C(2)–C(1)–C(m)	112.4(5)
Co–N(n1)–C(n1)	127.2(4)	127.1(4)	N(2)–C(2)–C(1)	108.9(5)
Co–N(n1)–C(n5)	113.2(4)	113.4(4)	O(1)–Cl–O(2)	112.3(4)
C(n1)–N(n1)–C(n5)	119.5(5)	119.2(5)	O(1)–Cl–O(3)	111.7(4)
N(n1)–C(n1)–C(n2)	121.1(5)	121.8(6)	O(1)–Cl–O(4)	108.4(5)
C(n1)–C(n2)–C(n3)	119.1(6)	119.9(6)	O(2)–Cl–O(3)	112.2(4)
C(n2)–C(n3)–C(n4)	119.3(6)	118.3(6)	O(2)–Cl–O(4)	107.4(5)
C(n3)–C(n4)–C(n5)	120.7(6)	120.1(6)	O(3)–Cl–O(4)	104.3(5)
C(n4)–C(n5)–N(n1)	120.3(6)	120.6(6)		
C(n4)–C(n5)–C(n6)	124.8(6)	122.5(6)		
N(n1)–C(n5)–C(n6)	114.9(5)	116.8(5)		
C(n5)–C(n6)–N(n)	107.5(4)	110.4(5)		

It is worthy of note that in this Δ-β-*exo*-dinitro diastereoisomer the tetradentate has exactly the same stereochemistry as has been determined crystallographically for the related Δ-β_1-*exo*-[Co(*R*-picpn)(*S*-pro)]$^{2+}$ complex, where *S*-pro is the *S*-prolinate anion.[5] Hence it would appear that this internal nitrogen stereochemistry is specific for any Δ-β diastereoisomer containing the *R* enantiomer of picpn, and with *exo* disposition of the methyl group. The crystal structures of complex cations containing *R*-picpn coordinated to Co(III) with both Λ-β-*exo* and Λ-β-*endo* geometries also have been reported.[7] In these structures the amine nitrogen atom configurations are each *R*(N),*R*(N), again if the methyl substituent on the central chelate ring is ignored. Subtle differences in discriminating forces ultimately are responsible for the stereochemistries observed. In the structure of the Δ-β-*exo* diastereoisomer reported here the observed nitrogen configurations permit the *R*-picpn methyl substituent to lie in an almost ideal equatorial position. The energetic preference for this arrangement must outweigh the apparent extra rigidity imposed on the tetradentate by the adoption by N(1) of a configuration opposite to that which necessarily would be enforced in a Λ-α isomer.

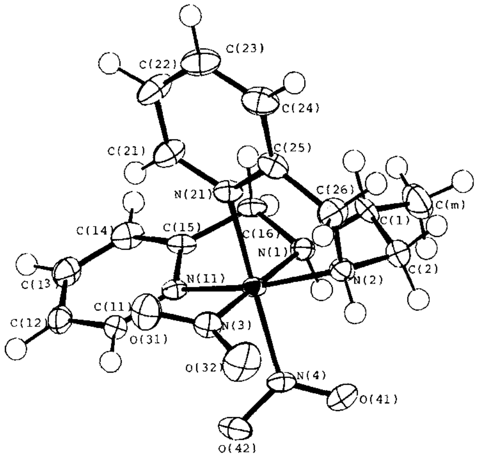

FIGURE 3 A perspective view [8] of the cation Δ-β-*exo*-[Co(*R*-picpn)$(NO_2)_2]^+$ showing the atomic numbering scheme. Thermal ellipsoids are scaled to include 35% probability.

Finally, it has been found here that in the crystal structure of this *R*-picpn complex the individual ions and water molecules again are linked in a hydrogen bonding network. However, unlike the scheme found in the *R*,*R*-picchxn analogue, the amine hydrogen atoms hydrogen bond only to perchlorate oxygen atoms. The water molecule again is associated with one perchlorate oxygen atom and an oxygen atom of one of the coordinated nitro groups. The dimensions of this proposed hydrogen bonding scheme are given in Table V, and a view of the unit cell contents showing these bonds is given in Figure 4.

SUPPLEMENTARY MATERIAL

Lists of hydrogen atomic coordinates, anisotropic thermal parameters and observed and calculated structure factors are available from the Editor upon request.

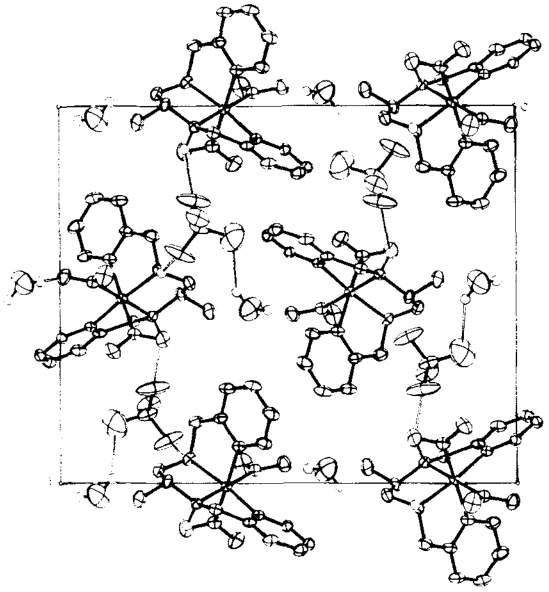

FIGURE 4 The packing of Δ-β-*exo*-[Co(*R*-picpn)$(NO_2)_2$]$ClO_4 \cdot H_2O$ in the unit cell. Hydrogen bonds are unfilled.

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