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The Meridional Isomer of (Diethylenetriamine)trinitrocobalt(III), *mer*-[Co(dien)$(NO_2)_3$]

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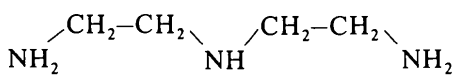
Abstract. [Co$(C_4H_{13}N_3)(NO_2)_3$], orthorhombic, *Pbca*, $Z = 8$, $a = 12{\cdot}710\,(2)$, $b = 13{\cdot}199\,(2)$, $c = 13{\cdot}024\,(2)$ Å, $V = 2184{\cdot}8\,(7)$ Å^3, $D_c = 1{\cdot}824$ Mg m^{-3}, $M_r = 300{\cdot}12$, μ(Mo $K\alpha$) = 1·595 mm^{-1}. Final $R_1 = 3{\cdot}4\%$ for 1320 reflections with $F_o > \sigma(F_o)$. The Co^{III} ion has a slightly distorted octahedral coordination geometry; the dien ligand occupies meridional sites, with Co–N(4) = 1·948 (3), Co–N(5) = 1·950 (3), and Co–N(6) = 1·946 (4) Å; the Co–NO_2 linkages range from 1·916 (3) to 1·997 (3) Å in length.

Introduction. The title compound was studied as part of a program to identify isomers of (dien)Co^{III} complexes [dien = diethylenetriamine (I)]. The complex was synthesized *via* the method of Crayton & Mattern (1960) and slowly crystallized as orange-red brick-shaped crystals from aqueous solution (20 d at room temperature).



(I)

Cell dimensions and intensities were measured at 297 K with a Syntex $P2_1$ diffractometer (Churchill, Lashewycz & Rotella, 1977) using Mo $K\alpha$ radiation ($\bar{\lambda} = 0{\cdot}71073$ Å) and a crystal of size 0·25 × 0·30 × 0·35 mm. The systematic absences $0kl$ for $k = 2n + 1$, $h0l$ for $l = 2n + 1$ and $hk0$ for $h = 2n + 1$ indicated the space group *Pbca*. Data with $2\theta = 3$–45° for $+h$, $+k$, $\pm l$ (2798 total) were corrected for Lorentz, polarization and absorption effects; equivalent pairs of data were averaged ($R_{Av} = 2{\cdot}1\%$), yielding 1437 independent data. The structure was solved using Patterson and difference-Fourier techniques and refined *via* full-matrix least squares to $R_1 = 3{\cdot}4\%$ and $R_2 = 3{\cdot}3\%$ for 1320 reflections with $F_o > \sigma(F_o)$ ($R_1 = 4{\cdot}1\%$, $R_2 = 3{\cdot}3\%$ for all 1437 data). The largest peak on a final difference-Fourier synthesis (height 0·56 e Å^{-3}) was close to the position of the Co atom; the structure is thus complete. All calculations were performed on a Nova 1200 minicomputer using a locally modified version of the Syntex *XTL* program package. Analytical scattering factors for neutral atoms from *International Tables for X-ray Crystallography* (1974) were corrected for both f' and f'' terms. The function minimized during least-squares refinement was $\sum w(|F_o| - |F_c|)^2$ where $w = \{[\sigma(F_o)]^2 + (0{\cdot}01F_o)^2\}^{-1}$.

The F_o values were corrected for secondary extinction using the formula $F_{o,cor.} = F_{o,uncor.}\,(1{\cdot}0 + kI_o)$; the resulting value for k was $6{\cdot}6 \times 10^{-8}$.

Atomic coordinates are given in Table 1.*

* Lists of structure factor amplitudes and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35792 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Positional parameters for* [Co(dien)$(NO_2)_3$]

	x	*y*	*z*	*B* (Å^2)
Co	0·10851 (3)	0·18733 (3)	0·10319 (3)	1·89*
N(1)	0·2163 (2)	0·2480 (2)	0·1963 (2)	2·8
N(2)	0·0002 (2)	0·1387 (2)	0·0112 (2)	3·0
N(3)	0·0698 (2)	0·3210 (2)	0·0600 (3)	3·4
N(4)	0·2180 (3)	0·1720 (2)	−0·0003 (2)	2·7
N(5)	0·1429 (2)	0·0484 (2)	0·1415 (2)	2·2
N(6)	0·0112 (3)	0·1828 (3)	0·2184 (3)	3·6
O(1*A*)	0·3060 (2)	0·2514 (2)	0·1735 (3)	6·0
O(1*B*)	0·1855 (3)	0·2912 (3)	0·2711 (3)	9·0
O(2*A*)	0·0228 (2)	0·1012 (2)	−0·0708 (2)	5·2
O(2*B*)	−0·0926 (2)	0·1439 (2)	0·0357 (3)	5·9
O(3*A*)	0·1066 (3)	0·3559 (2)	−0·0180 (3)	5·7
O(3*B*)	0·0100 (3)	0·3712 (2)	0·1099 (3)	8·3
C(1)	0·2624 (4)	0·0676 (3)	0·0009 (4)	3·5
C(2)	0·2517 (3)	0·0256 (3)	0·1086 (3)	3·1
C(3)	0·1172 (3)	0·0333 (3)	0·2511 (3)	3·3
C(4)	0·0097 (3)	0·0795 (3)	0·2653 (3)	3·6
H(41)	0·190 (3)	0·183 (3)	−0·062 (3)	4·5 (10)
H(42)	0·263 (3)	0·215 (2)	0·017 (3)	2·7 (9)
H(5)	0·105 (3)	0·010 (2)	0·105 (3)	3·2 (9)
H(61)	0·039 (3)	0·224 (2)	0·264 (3)	3·1 (9)
H(62)	−0·048 (3)	0·197 (3)	0·198 (3)	4·9 (12)
H(1*A*)	0·338 (3)	0·071 (2)	−0·014 (3)	3·9 (8)
H(1*B*)	0·221 (3)	0·028 (3)	−0·046 (3)	3·6 (9)
H(2*A*)	0·297 (2)	0·066 (2)	0·159 (3)	3·1 (8)
H(2*B*)	0·268 (2)	−0·040 (2)	0·109 (2)	3·0 (8)
H(3*A*)	0·177 (2)	0·070 (2)	0·291 (2)	2·8 (7)
H(3*B*)	0·117 (2)	−0·036 (2)	0·270 (2)	2·8 (8)
H(4*A*)	−0·042 (2)	0·044 (2)	0·226 (3)	2·6 (8)
H(4*B*)	−0·012 (3)	0·083 (2)	0·337 (3)	3·4 (8)

* Equivalent isotropic thermal parameters are given for non-hydrogen atoms. These are calculated as $B_{eq} = \frac{1}{3}(B_{11} + B_{22} + B_{33})$.

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Discussion. The labeling of non-hydrogen atoms is shown in Fig. 1; a stereoscopic view of the molecule appears as Fig. 2. Bond distances and angles are collected in Table 2.

The completed analysis shows the complex reported by Crayton & Mattern (1960) to be the meridional (*mer*), rather than the facial (*fac*), isomer.

The Co^{III} ion is in a slightly distorted octahedral environment with a dien ligand occupying a meridional belt of coordination sites. The dien ligand has a $\lambda\delta$ conformation (Purcell & Kotz, 1977) and is coordinated to the Co^{III} ion *via* three equivalent linkages,

Table 2. *Bond distances* (Å) *and selected angles* (°)

Co–N(1)	1·997 (3)	Co–N(4)	1·948 (3)
Co–N(2)	1·935 (3)	Co–N(5)	1·950 (3)
Co–N(3)	1·916 (3)	Co–N(6)	1·946 (4)
N(1)–O(1*A*)	1·179 (4)	N(2)–O(2*B*)	1·225 (4)
N(1)–O(1*B*)	1·195 (5)	N(3)–O(3*A*)	1·209 (5)
N(2)–O(2*A*)	1·211 (4)	N(3)–O(3*B*)	1·200 (5)
N(4)–C(1)	1·489 (5)	N(5)–C(3)	1·478 (5)
C(1)–C(2)	1·514 (6)	C(3)–C(4)	1·506 (6)
C(2)–N(5)	1·480 (5)	C(4)–N(6)	1·494 (6)
N–H	0·82 (4)–0·89 (4); average = 0·85 (3)		
C–H	0·89 (3)–1·04 (3); average = 0·97 (5)		
N(1)–Co–N(2)	175·74 (13)	N(2)–Co–N(6)	90·89 (14)
N(1)–Co–N(3)	89·17 (13)	N(3)–Co–N(4)	94·36 (14)
N(1)–Co–N(4)	88·36 (13)	N(3)–Co–N(5)	176·90 (13)
N(1)–Co–N(5)	93·90 (12)	N(3)–Co–N(6)	95·27 (15)
N(1)–Co–N(6)	88·87 (14)	N(4)–Co–N(5)	85·35 (13)
N(2)–Co–N(3)	86·61 (13)	N(4)–Co–N(6)	169·94 (15)
N(2)–Co–N(4)	92·58 (13)	N(5)–Co–N(6)	85·18 (14)
N(2)–Co–N(5)	90·32 (12)		
Co–N(1)–O(1*A*)	121·8 (3)	O(2*A*)–N(2)–O(2*B*)	118·8 (3)
Co–N(1)–O(1*B*)	117·5 (3)	Co–N(3)–O(3*A*)	119·9 (3)
O(1*A*)–N(1)–O(1*B*)	120·2 (4)	Co–N(3)–O(3*B*)	120·8 (3)
Co–N(2)–O(2*A*)	120·9 (2)	O(3*A*)–N(3)–O(3*B*)	119·3 (4)
Co–N(2)–O(2*B*)	120·3 (2)		
Co–N(4)–C(1)	111·1 (2)	Co–N(5)–C(3)	108·9 (2)
N(4)–C(1)–C(2)	108·3 (3)	N(5)–C(3)–C(4)	105·3 (3)
C(1)–C(2)–N(5)	106·1 (3)	C(3)–C(4)–N(6)	107·9 (3)
C(2)–N(5)–Co	109·1 (2)	C(4)–N(6)–Co	110·6 (3)
C(2)–N(5)–C(3)	117·3 (3)		

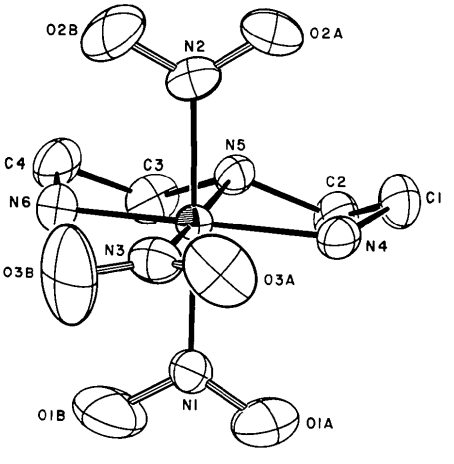

Fig. 1. Labeling of non-hydrogen atoms in $Co(dien)(NO_2)_3$.

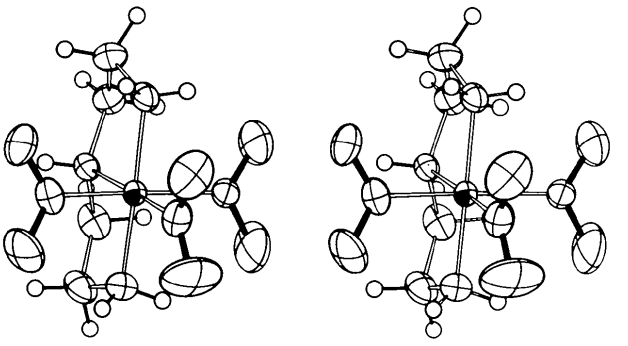

Fig. 2. Stereoscopic view of the $[Co(dien)(NO_2)_3]$ molecule, including H atoms.

Table 3. *Deviations* (*in* Å) *of atoms from planes*

Plane	Atom, with deviation
N(4)–Co–N(5)	C(1), 0·073 (4); C(2), −0·559 (4)
N(5)–Co–N(6)	C(3), −0·564 (4); C(4), 0·102 (4)
O(1*A*)–N(1)–O(1*B*)	Co, 0·2504 (4)
O(2*A*)–N(2)–O(2*B*)	Co, −0·0305 (4)
O(3*A*)–N(3)–O(3*B*)	Co, −0·0206 (4)

with Co–N(av.) = 1·948 (2) Å. The Co–NO_2 linkages range from 1·916 (3) to 1·997 (3) Å, while N–O distances vary from 1·179 (4) to 1·225 (4) Å. The most weakly bound NO_2 group [that centered on N(1)] is not coplanar with the Co^{III} ion (see Table 3). This anomalous nitro group is tipped away from the dien system and participates in two intramolecular hydrogen bonds *viz.* O(1*B*)···N(6) = 2·725 (5) Å and ∠O(1*B*)···H(61)–N(6) = 131 (3)°; O(1*A*)···N(4) = 2·734 (5) Å and ∠O(1*A*)···H(42)–N(4) = 125 (3)°. These are the two shortest hydrogen bonds (either intra- or intermolecular) in the system.

Bond distances and angles agree generally with those reported for *mer*-$[Co(NH_3)_3(NO_2)_3]$ (Laing, Baines & Sommerville, 1971) and *fac*-$[Co(dien)(NO_2)_3]$ (Kushi, Watanabe & Kuroya, 1967), but are of greater precision.

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