The crystal structure of the isomorphous $MnSO_3.3H_2O$ phase has been refined completely (Johansson & Lindqvist, 1979).

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The Crystal Structure of *fac*-Triamminetrinitrocobalt(III), *fac*-$[Co(NH_3)_3(NO_2)_3]$

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Abstract

fac-$[Co(NH_3)_3(NO_2)_3]$, monoclinic, $P2_1$, a = 7·051 (3), b = 10·264 (2), c = 10·819 (2) Å, β = 92·74 (2)°, Z = 4. The Co atoms are octahedrally coordinated by three NO_2 and three NH_3 ligands arranged facially. The structure was refined to R = 0·055 for 1165 independent reflections.

Introduction

$[Co(H_2O)_3(NH_3)_3]^{3+}$ (I) reacts with $NaNO_2$ primarily to give the trinitrito complex *fac*-$[Co(NH_3)_3(ONO)_3]$ (II). Spontaneous isomerization leads to the mixed nitrito–nitro complexes *fac*$[Co(NH_3)_3NO_2(ONO)_2]$ (III) and *fac*-$[Co(NH_3)_3(NO_2)_2(ONO)]$ (IV). From warm aqueous solutions of the latter compounds *fac*-$[Co(NH_3)_3(NO_2)_3]$ (V) is formed (Siebert, 1978). For a long time (V) has been the subject of investigations and communications but unlike its *mer* isomer (VI) (Laing,

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Bains & Sommerville, 1971), (V) had never been characterized unambiguously until recently (Siebert, 1978, and references therein). In this paper we describe the X-ray structure determination of (V) which confirms the facial arrangement.

Rotation and Weissenberg photographs (Cu $K\alpha$ radiation) showed the crystal to be monoclinic and provided approximate lattice constants. Exact lattice parameters were calculated by least squares (Berdesinski & Nuber, 1966) from diffractometrically determined θ values of 56 selected reflections. Intensity measurements were performed on a computer-controlled single-crystal diffractometer (AED Siemens, Mo $K\alpha$ radiation, θ–2θ scans, five-value method) up to $2\theta = 57{\cdot}98°$. Reflections with $I < 2{\cdot}58\sigma(I)$ were not considered. 1165 observed independent intensities remained for calculations. They were corrected for Lorentz and polarization factors only. Crystal data are listed in Table 1.

Positions of the two Co atoms were determined from the Patterson synthesis. The determination of the coordinates of the N and O atoms proved to be difficult, as the contributions of these atoms to the stronger reflections were very small; the coordinates could be obtained only by combining direct methods with Patterson and Fourier syntheses. Refinement with anisotropic temperature factors resulted in $R = 0{\cdot}059$, at which point a difference map allowed the location of only six H atoms. Even with the assistance of a model it was impossible to locate the remaining H atoms. The coordinates of the six located H atoms were refined independently ($B = 5$ Å^2). The final R was 0·055 and R_w was 0·062.*

All calculations were performed on Siemens 301 (Anorganisch-Chemisches Institut, Heidelberg) and IBM 370/168 (Universitätsrechenzentrum Heidelberg) computers with local versions of the XRAY system (Stewart, Kundell & Baldwin, 1970). Scattering factors were those of Hanson, Herman, Lea & Skillman (1964).

Coordinates of the non-hydrogen atoms are listed in Table 2, those of the H atoms in Table 3. The atom-numbering scheme is shown in Fig. 1. Data concerning least-squares planes are shown in Table 6, bond lengths and angles in Tables 4 and 5 respectively.

Table 1. *Crystal data*

$Co(NH_3)_3(NO_2)_3$, FW 248·04
Space group $P2_1$
λ(Mo $K\alpha$) = 0·7107 Å
a = 7·051 (3) Å
b = 10·264 (2)
c = 10·819 (2)
β = 92·74 (2)°
Systematic absences 0k0: $k = 2n + 1$
Crystal size 0·2 × 0·3 × 0·2 mm

$Z = 4$
V = 782·09 Å^3
D_o = 2·50 Mg m^{-3}
D_c = 2·498
$F(000) = 504$
μ(Mo $K\alpha$) = 2·73 mm^{-1}
Independent reflections 1165
Scan range 57·98 ≥ 2θ ≥ 5·47°

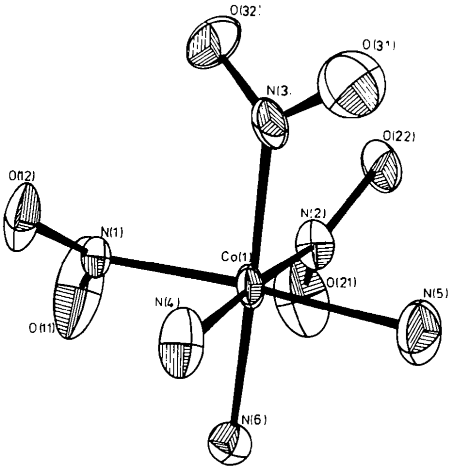

Fig. 1. *ORTEP* drawing (Johnson, 1965) of one of the two independent molecules in the unit cell of the complex *fac*-[$Co(NH_3)_3(NO_2)_3$]. 50% probability ellipsoids are displayed.

Table 2. *Final atomic fractional coordinates of the non-hydrogen atoms* (× 10^4)

	x	y	z		x	y	z
Co(1)	2641 (3)	2500	−39 (2)	Co(2)	7681 (3)	2608 (3)	4949 (2)
N(1)	−98 (18)	7884 (15)	716 (15)	N(7)	5000 (17)	2591 (21)	4387 (11)
N(2)	3863 (18)	3237 (15)	8594 (11)	N(8)	8268 (24)	1312 (21)	3749 (16)
N(3)	2783 (18)	4149 (16)	772 (14)	N(9)	8261 (22)	3953 (17)	3850 (15)
N(4)	1533 (20)	1679 (20)	1443 (15)	N(10)	7138 (24)	3894 (19)	6181 (16)
N(5)	5234 (20)	1971 (19)	646 (15)	N(11)	7087 (23)	1178 (17)	6114 (17)
N(6)	2416 (20)	781 (20)	9089 (15)	N(12)	378 (14)	2542 (21)	5527 (11)
O(11)	9710 (16)	2683 (27)	8188 (11)	O(71)	4322 (17)	1617 (15)	3851 (15)
O(12)	1102 (15)	8184 (15)	−1 (14)	O(72)	4029 (17)	3553 (14)	4585 (14)
O(21)	3777 (18)	2720 (22)	7554 (12)	O(81)	2169 (18)	6446 (16)	7360 (11)
O(22)	4931 (16)	4190 (14)	8746 (13)	O(82)	791 (19)	5342 (15)	5910 (13)
O(31)	3864 (21)	4311 (16)	1698 (15)	O(91)	9715 (17)	3905 (16)	3209 (13)
O(32)	1854 (18)	5086 (14)	399 (16)	O(92)	2654 (18)	−22 (14)	6237 (14)

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34183 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 3. *Final atomic fractional coordinates* (× 10^3) *of some hydrogen atoms*

	x	*y*	*z*		*x*	*y*	*z*
H(51)	571 (24)	270 (23)	100 (16)	H(101)	265 (29)	920 (22)	342 (19)
H(52)	493 (26)	186 (20)	180 (17)	H(102)	342 (29)	843 (22)	336 (19)
H(53)	449 (26)	576 (21)	915 (18)	H(103)	365 (30)	954 (21)	382 (18)

Table 4. *Bond lengths* (Å)

Co(1)–N(1)	1·945 (13)	Co(1)–N(4)	2·002 (17)	Co(2)–N(7)	1·958 (12)	Co(2)–N(10)	1·927 (19)
–N(2)	1·904 (14)	–N(5)	2·014 (15)	–N(8)	1·918 (20)	–N(11)	1·992 (18)
–N(3)	1·907 (16)	–N(6)	2·004 (18)	–N(9)	1·880 (17)	–N(12)	1·974 (10)
N(1)–O(11)	1·221 (20)	N(5)–H(51)	0·90 (22)	N(7)–O(71)	1·240 (24)	N(10)–H(101)	0·55 (22)
–O(12)	1·214 (20)	–H(52)	1·29 (19)	–O(72)	1·227 (23)	–H(102)	0·80 (22)
N(2)–O(21)	1·243 (20)	–H(53)	1·27 (22)	N(8)–O(81)	1·232 (21)	–H(103)	0·87 (22)
–O(22)	1·241 (20)			–O(82)	1·243 (24)		
N(3)–O(31)	1·241 (21)			N(9)–O(91)	1·266 (21)		
–O(32)	1·223 (21)			–O(92)	1·235 (22)		

Table 5. *Bond angles* (°)

N(1)–Co(1)–N(2)	94·0 (6)	N(2)–Co(1)–N(3)	89·4 (7)	N(3)–Co(1)–N(5)	92·5 (7)
N(1)–Co(1)–N(3)	91·2 (6)	N(2)–Co(1)–N(4)	176·0 (6)	N(3)–Co(1)–N(6)	178·4 (6)
N(1)–Co(1)–N(4)	90·0 (6)	N(2)–Co(1)–N(5)	87·5 (6)	N(4)–Co(1)–N(5)	88·5 (6)
N(1)–Co(1)–N(5)	176·0 (9)	N(2)–Co(1)–N(6)	90·7 (7)	N(4)–Co(1)–N(6)	88·9 (8)
N(1)–Co(1)–N(6)	87·1 (6)	N(3)–Co(1)–N(4)	91·1 (7)	N(5)–Co(1)–N(6)	89·2 (7)
O(11)–N(1)–O(12)	122·2 (14)	Co(1)–N(1)–O(11)	119·5 (12)	Co(1)–N(1)–O(12)	117·9 (12)
O(21)–N(2)–O(22)	117·4 (15)	Co(1)–N(2)–O(21)	122·0 (13)	Co(1)–N(2)–O(22)	120·3 (11)
O(31)–N(3)–O(31)	117·5 (17)	O(31)–N(3)–Co(1)	120·5 (13)	O(32)–N(3)–Co(1)	122·0 (12)
N(7)–Co(2)–N(8)	91·1 (7)	N(8)–Co(2)–N(9)	91·2 (8)	N(9)–Co(2)–N(11)	179·6 (9)
N(7)–Co(2)–N(9)	92·6 (7)	N(8)–Co(2)–N(10)	178·7 (7)	N(9)–Co(2)–N(12)	89·4 (7)
N(7)–Co(2)–N(10)	90·0 (7)	N(8)–Co(2)–N(11)	88·6 (8)	N(10)–Co(2)–N(11)	90·7 (8)
N(7)–Co(2)–N(11)	87·8 (7)	N(8)–Co(2)–N(12)	87·4 (7)	N(10)–Co(2)–N(12)	91·4 (7)
N(7)–Co(2)–N(12)	177·5 (9)	N(9)–Co(2)–N(10)	89·5 (8)	N(11)–Co(2)–N(12)	90·2 (7)
O(71)–N(7)–O(72)	121·7 (13)	O(71)–N(7)–Co(2)	119·8 (13)	O(72)–N(7)–Co(2)	118·5 (13)
O(81)–N(8)–O(82)	119·0 (18)	O(81)–N(8)–Co(2)	122·0 (15)	O(82)–N(8)–Co(2)	119·0 (18)
O(91)–N(9)–O(92)	115·2 (16)	O(91)–N(9)–Co(2)	121·6 (13)	O(92)–N(9)–Co(2)	123·0 (13)

Table 6. *Data of some least-squares planes*

Atoms defining the planes and their distances from them (Å) (e.s.d.'s in parentheses)

A	N(1) 0·01 (1), N(3) –0·01 (1), N(6) –0·01 (1), N(5) 0·01 (1)
B	N(2) 0·05 (6), N(3) –0·05 (6), N(4) 0·05 (6), N(6) –0·05 (6)
C	N(1) –0·03 (3), N(2) 0·03 (3), N(5) –0·03 (3), N(4) 0·03 (3)
D	N(1), O(11), O(12)
E	N(3), O(31), O(32)
F	N(2), O(21), O(22)
A'	N(7) –0·01 (1), N(9) 0·01 (1), N(11) 0·01 (1), N(12) –0·01 (1)
B'	N(7) –0·01 (1), N(8) 0·01 (1), N(10) 0·01 (1), N(12) –0·01 (1)
C'	N(8) 0·01 (1), N(9) –0·01 (1), N(10) 0·01 (1), N(11) –0·01 (1)
D'	N(7), O(71), O(72)
E'	N(8), O(81), O(82)
F'	N(9), O(91), O(92)

Angles between planes (°)

AB 88·83, *AC* 89·13, *BC* 89·79, *AD* 51·80, *BD* 80·12, *CD* 40·48, *AE* 23·89, *BE* 67·28, *CE* 88·58, *DE* 60·40, *AF* 81·49, *BF* 23·36, *CF* 67·90, *DF* 58·30, *EF* 76·18

A'B' 89·02, *A'C'* 88·70, *B'C'* 88·58, *A'D'* 65·27, *B'D'* 23·79, *C'D'* 87·09, *A'E'* 85·96, *B'E'* 50·33, *C'E'* 41·32, *D'E'* 57·54, *A'F'* 47·11, *B'F'* 84·04, *C'F'* 41·92, *D'F'* 67·51, *E'F'* 56·97

Discussion

fac-$[Co(NH_3)_3(NO_2)_3]$ (V) is formed by isomerization of the nitrito complexes (III) and (IV). The structure determination shows the NO_2 groups to be bound *via* the N atoms, as was already indicated by spectroscopic data (Siebert, 1978). The cell contains two crystallographically independent molecules. Bond lengths and angles of the two octahedra are identical within the e.s.d.'s. The meridional isomer [(VI)] of (V) has also been characterized by X-ray structure determination (Laing, Bains & Sommerville, 1971). As with (VI) the difference in the Co–NH_3 and Co–NO_2 lengths in (V) is barely significant, although the Co–NO_2 lengths seem to be shorter (average: Co–NO_2 1·919 Å, Co–NH_3 1·986 Å). In terms of the back-bonding concept this seems to be reasonable. The 12 N–O distances of both octahedra agree within 1σ; they can be compared with the data for species like (VI) and $[Co(NH_3)_2(NO_2)_4]^-$ (VII) (Komiyama, 1957).

Angular distortions from the ideal octahedral arrangement are minor (Table 5) and do not seem to follow any particular pattern. The planes defined by the six nitro groups of the two octahedra are twisted with respect to those defined by four N atoms lying in a plane. Thus the nitro group O(11)—N(1)—O(12) (plane *D*) is twisted 51·8, 80·1 and 40·5° from the planes N(1), N(3), N(6), N(5) (*A*), N(2), N(3), N(4), N(6) (*B*) and N(1), N(2), N(5), N(4) (*C*) respectively. The nitro groups themselves form angles of 60·4, 58·3 and 76·2° with each other in one octahedron and 57·5, 57·0 and 67·5° in the second.

Siebert (1978) reported that the solubility of the facial isomer in various solvents is much lower than that of the meridional. This might be due to intra- and intermolecular hydrogen bonding. This could be confirmed by some short intra- and intermolecular N(ammonia)···O(nitro) distances ranging from 2·7–3·0 Å (intramolecular) and 3·0–3·3 Å (intermolecular) respectively. These data fall well within the range given for O—H—N interactions (Wells, 1975). The argument for hydrogen bonding is also supported by relatively short O···H distances, the shortest being 1·7 Å (intramolecular) and 2·2 Å (intermolecular) respectively.

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X-ray Structure of Ammonium Perchlorate.
I. X-ray Data Collection and Estimation of Variances of the Intensities

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Abstract

X-ray diffraction data have been collected at 295 K for a single crystal of ammonium perchlorate, NH_4ClO_4. Intensities for 5560 reflexions, excluding test reflexions, were recorded on a Stoe–Philips four-circle diffractometer up to $\sin\theta/\lambda = 0{\cdot}86$ Å^{-1}. On average, five symmetry-related reflexions within a form were measured on the orthorhombic crystal, space group *Pnma*. Variances for the observed intensities were calculated from Poisson counting statistics together with the information obtained from the repeated recording of twelve test reflexions. An analysis of the scatter observed among symmetry-related reflexions after absorption correction gave no indication of anisotropic systematic errors in the data set. It suggested, moreover, that the estimation of the variances was reasonable. The agreement among symmetry-related reflexions, $R_w = [\sum w(F_o^2 - \bar{F}_o^2)^2/\sum wF_o^4]^{1/2}$, was 0·018.

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Introduction

In an X-ray redetermination of the crystal structure of ammonium perchlorate, Peyronel & Pignedoli (1975) described the structure in terms of the non-centrosymmetric space group *Pna*2_1. This result was in conflict with earlier reported two-dimensional (Smith & Levy, 1962) and three-dimensional (Choi, Prask & Prince, 1974) neutron diffraction studies, in which the structure was reported to crystallize in the centrosymmetric space group *Pnma*.