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The Crystal Structure of *trans*-Dinitro(β-alaninato)(1,3-diaminopropane)cobalt(III)

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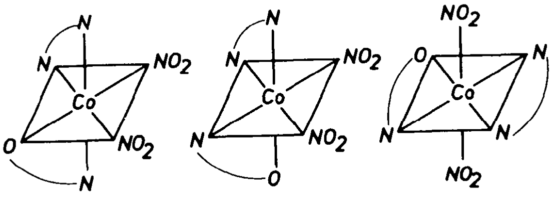
The crystal structure of *trans*-dinitro(β-alaninato)(1,3-diaminopropane)cobalt(III), $CoC_6H_{16}N_5O_6$, has been determined from three-dimensional X-ray diffraction data. Unit-cell dimensions are a = 12·928 (6), b = 11·177 (8), c = 8·174 (5) Å, β = 93·95 (4)°; the space group is $P2_1/a$, and Z = 4. In the analysis the intensities of 1280 independent non-zero reflexions, measured on a Syntex $P\bar{1}$ diffractometer, were used. The refinement with anisotropic thermal parameters for all non-hydrogen atoms converged at R = 0·057 and R_w = 0·046. The H atoms were included in the structure factor calculations, but their parameters were not refined. The crystal structure consists of discrete neutral molecules of the complex. The coordination around the Co atom is slightly distorted from octahedral, with angles between the adjacent coordinated atoms varying from 84·2 (2) to 94·4 (2)°. The β-alaninato ligand forms the six-membered chelate ring in a skew-boat conformation. The 1,3-diaminopropane six-membered ring has a chair conformation. The nitro groups are in the *trans* position, with Co—N distances of 1·912 (6) and 1·980 (6) Å.

Introduction

While studying the effects of the positions of the nitro groups and the size of the chelate ring on the electronic absorption maxima of Co^{III} complexes, Ćelap, Malinar & Janjić (1976) have recently described the preparation of dinitro(β-alaninato)(1,3-diaminopropane)cobalt(III). A complex compound of this type can theoretically be represented by three geometrical isomers (Fig. 1): two have the nitro group in the *cis* position, and one has it in the *trans* position. On the basis of electronic spectra and paper chromatography, they assumed that one of two isolated complexes had the *trans*-nitro configuration. To verify this and to study the conformation of the six-membered chelate rings, we have undertaken the X-ray diffraction analysis of *trans*-$[Co(tn)(\beta\text{-ala})(NO_2)_2]$, where (tn) = 1,3-diaminopropane.



(I) (II) (III)

Fig. 1. The three geometric isomers of dinitro(β-alaninato)(1,3-diaminopropane)cobalt(III).

Experimental

Crystal data

$CoC_6H_{16}N_5O_6$, M_r = 313·2, monoclinic, a = 12·928 (6), b = 11·177 (8), c = 8·174 (5) Å, β = 93·95 (4)°, V = 1178·3 Å^3, D_x = 1·766 g cm^{-3}, Z = 4; space group $P2_1/a$, Mo $K\alpha$ radiation, λ = 0·7107 Å, μ(Mo $K\alpha$) = 15·6 cm^{-1}.

The X-ray data were obtained from a prismatic crystal with dimensions 0·11 × 0·16 × 0·23 mm. Preliminary characterization of the material was undertaken with the Weissenberg technique. Unit-cell constants and their estimated standard deviations were derived from a least-squares refinement of the setting angles for 15 strong, general reflexions, measured on the Syntex $P\bar{1}$ diffractometer. From the systematic absences, $h0l$ with h odd, and $0k0$ with k odd, the space group was uniquely defined as $P2_1/a$. The intensity measurements were made by the ω-scan technique. Graphite-monochromated Mo $K\alpha$ radiation was used. The reference reflexion, monitored after every 25 measurement cycles, showed no significant variation in intensity during the collection of the data. All independent reflexions in the sphere $2\theta(\text{Mo } K\alpha) \leq 50°$ were measured, of which 1280 with $I \geq 2{\cdot}5\sigma(I)$ were included in the subsequent analysis. The integrated intensities and their standard deviations were corrected for Lorentz–polarization effects, but not for absorption.

The position of the Co atom was found from a three-dimensional Patterson synthesis and was used to phase the F_o values for a three-dimensional difference synthesis. From the first map all the remaining non-hydrogen atoms were located. The refinement of positional and isotropic thermal parameters by full-matrix least squares gave $R = 0{\cdot}079$. The function minimized was $\Sigma\, w\Delta^2$, where $w = 1/\sigma^2$, $\Delta = |F_o| - |F_c|$ and F_o and F_c are the observed and calculated structure amplitudes. Full-matrix least-squares refinement with all non-hydrogen atoms anisotropic reduced R to 0·065 and R_w to 0·060. At this stage a low-angle difference synthesis was calculated from which all 16 H atoms were found and included in the subsequent refinement at calculated, fixed positions with fixed isotropic temperature factors. The refinement resulted in $R = 0{\cdot}057$ and $R_w = 0{\cdot}046$.

All atoms were assumed to be uncharged. The atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1962), except those for Co (Cromer & Waber, 1965) and H (Stewart, Davidson & Simpson, 1965). The anomalous dispersion was accounted for in the structure factor calculations, taking the values of f' and f'' for Co from Cromer (1965).

Table 1. *Final positional parameters* (*with standard deviations in parentheses*)

	x	y	z
Co	0·59476 (7)	0·28029 (9)	0·0366 (1)
O(1)	0·4707 (4)	0·3431 (4)	0·9281 (6)
O(2)	0·3249 (4)	0·3460 (5)	0·7760 (7)
O(3)	0·5267 (4)	0·0675 (5)	0·1570 (7)
O(4)	0·4377 (4)	0·2130 (5)	0·2329 (7)
O(5)	0·7654 (4)	0·4241 (5)	0·9804 (8)
O(6)	0·6452 (5)	0·4439 (6)	0·7910 (7)
N(1)	0·6133 (4)	0·1565 (5)	0·8709 (7)
N(2)	0·7174 (4)	0·2148 (6)	0·1591 (7)
N(3)	0·5759 (4)	0·4090 (5)	0·1957 (7)
N(4)	0·5099 (5)	0·1762 (6)	0·1561 (8)
N(5)	0·6793 (5)	0·3957 (5)	0·9195 (8)
C(1)	0·4099 (6)	0·2992 (6)	0·8145 (9)
C(2)	0·4426 (6)	0·1894 (7)	0·7231 (9)
C(3)	0·5565 (6)	0·1744 (7)	0·7108 (9)
C(4)	0·7257 (5)	0·2217 (8)	0·3408 (9)
C(5)	0·7119 (6)	0·3489 (8)	0·4036 (9)
C(6)	0·6043 (6)	0·3962 (7)	0·3719 (9)
H(1)	0·588	0·074	0·917
H(2)	0·693	0·148	0·853
H(3)	0·571	0·106	0·635
H(4)	0·585	0·250	0·659
H(5)	0·416	0·117	0·780
H(6)	0·406	0·192	0·608
H(7)	0·783	0·261	0·120
H(8)	0·724	0·124	0·125
H(9)	0·794	0·186	0·384
H(10)	0·669	0·168	0·383
H(11)	0·761	0·403	0·347
H(12)	0·733	0·351	0·526
H(13)	0·597	0·475	0·431
H(14)	0·554	0·337	0·421
H(15)	0·619	0·480	0·160
H(16)	0·501	0·433	0·184

A Fourier synthesis with the observed structure factor magnitudes and phases from the last cycle of calculated structure factors showed that the smallest peak density for a C atom was 7·3 e Å^{-3}. A final difference Fourier map revealed no electron density greater than 0·7 e Å^{-3}. The final positional parameters are given in Table 1.*

All calculations were performed on the CDC-3600 computer using the following programs: *FORDAP* (Zalkin, 1965), *NUCLS* (least squares, J. A. Ibers) and *ORFFE* (Busing & Levy, 1964).

Discussion

A projection of the structure viewed down the *c* axis (with the atom-numbering scheme) is shown in Fig. 2.

The crystal structure consists of discrete neutral octahedral molecules of the complex arranged in sheets parallel to the (001) plane. The geometry of the molecule is given in Table 2.

The coordination around the Co atom is distorted octahedral. Two nitro groups are coordinated *via* N atoms in the *trans* position. The average nitro N—O distance (1·232 Å) and O—N—O angle (118·6°) agree very well with those in other nitro complexes. The best

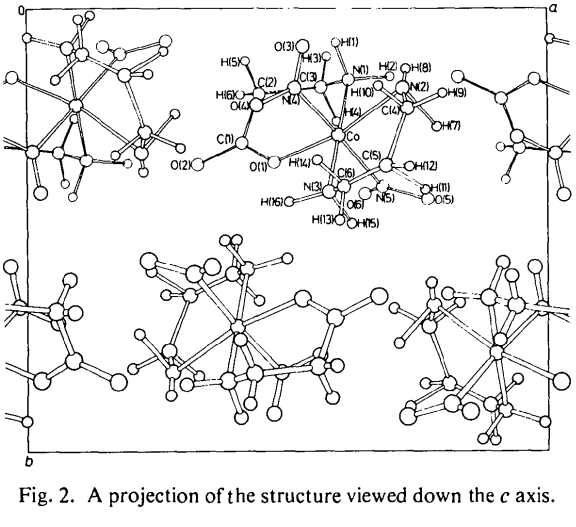


Fig. 2. A projection of the structure viewed down the *c* axis.

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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 32688 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 2. *Molecular geometry of trans*-[Co(tn)(β-ala)-$(NO_2)_2$]

The superscript refers to the *x,y,z* − 1 transformation of the coordinates *x,y,z*.

(*a*) Bond lengths (Å)

Co—O(1^i)	1·912 (5)	C(1)—O(1)	1·272 (8)
Co—N(1^i)	1·962 (6)	C(1)—O(2)	1·238 (8)
Co—N(2)	1·958 (6)	C(1)—C(2)	1·513 (10)
Co—N(3)	1·966 (6)	C(2)—C(3)	1·492 (10)
Co—N(4)	1·912 (6)	C(3)—N(1)	1·469 (9)
Co—N(5^i)	1·980 (6)	N(2)—C(4)	1·484 (9)
N(4)—O(3)	1·235 (7)	C(4)—C(5)	1·526 (11)
N(4)—O(4)	1·231 (7)	C(5)—C(6)	1·494 (10)
N(5)—O(5)	1·229 (8)	C(6)—N(3)	1·469 (9)
N(5)—O(6)	1·234 (8)		

(*b*) Bond angles (°)

O(1^i)—Co—N(1^i)	94·4 (2)	N(3)—C(6)—C(5)	111·8 (6)
O(1^i)—Co—N(2)	176·7 (2)	C(6)—C(5)—C(4)	113·6 (7)
O(1^i)—Co—N(3)	84·2 (2)	C(5)—C(4)—N(2)	112·5 (6)
O(1^i)—Co—N(4)	88·2 (3)	C(4)—N(2)—Co	119·5 (5)
O(1^i)—Co—N(5)	90·6 (3)	Co—N(1^i)—C(3^i)	116·2 (5)
N(1^i)—Co—N(2)	87·5 (2)	N(1)—C(3)—C(2)	113·0 (6)
N(1^i)—Co—N(3)	178·8 (2)	C(3)—C(2)—C(1)	115·8 (6)
N(1^i)—Co—N(4)	91·4 (3)	C(2)—C(1)—O(1)	119·6 (6)
N(1^i)—Co—N(5^i)	91·6 (2)	C(1^i)—O(1)—Co	130·8 (5)
N(2)—Co—N(3)	93·9 (3)	O(1)—C(1)—O(2)	121·0 (7)
N(2)—Co—N(4)	89·1 (3)	C(2)—C(1)—O(2)	119·4 (7)
N(2)—Co—N(5^i)	92·1 (3)	Co—N(4)—O(3)	119·7 (5)
N(3)—Co—N(4)	90·3 (3)	Co—N(4)—O(4)	122·6 (5)
N(3)—Co—N(5^i)	86·6 (2)	O(3)—N(4)—O(4)	117·7 (7)
N(4)—Co—N(5^i)	176·8 (3)	Co—N(5^i)—O(5^i)	119·1 (5)
Co—N(3)—C(6)	122·9 (5)	Co—N(5^i)—O(6^i)	121·3 (5)
		O(5)—N(5)—O(6)	119·5 (6)

(*c*) Torsional angles (°)

O(1)—Co—N(1)—C(3)	18·5 (5)
Co—N(1)—C(3)—C(2)	55·8 (8)
N(1)—C(3)—C(2)—C(1)	64·3 (9)
C(3)—C(2)—C(1)—O(1)	28·9 (1·0)
C(2)—C(1)—O(1)—Co	11·6 (1·0)
C(1)—O(1)—Co—N(1)	15·7 (6)
N(2)—Co—N(3)—C(6)	31·4 (6)
Co—N(3)—C(6)—C(5)	49·8 (8)
N(3)—C(6)—C(5)—C(4)	64·9 (9)
C(6)—C(5)—C(4)—N(2)	68·4 (8)
C(5)—C(4)—N(2)—Co	53·9 (8)
C(4)—N(2)—Co—N(3)	32·7 (6)

least-squares plane containing the Co atom and the corresponding nitro group (Table 3) shows that both groups are planar, the angle between the planes being 75·5°. The two Co—N(NO_2) bond lengths are significantly different, 1·912 (6) and 1·980 (6) Å. Values ranging from 1·87 (2) to 1·982 (3) Å are reported for the Co—N(NO_2) distance in a variety of nitro complexes of Co^{III} (Herak, Prelesnik, Manojlović-Muir & Muir, 1974; Kent Murmann & Schlemper, 1973; Ito, Marumo & Saito, 1972*a*,*b*; Jensen, Soling & Thorup, 1970; Herak & Prelesnik, 1976; Vasić, Herak & Djurić, 1976). However, most of the data are between 1·91 and 1·94 Å; *e.g.* the average Co—N(NO_2) distance in potassium trinitroglycinatoammine-cobalt(III) monohydrate is 1·913 (7) Å (Herak & Prelesnik, 1976); in trinitroammine(ethylendiamine)-cobalt(III) this average is 1·933 (7) Å (Jensen, Soling & Thorup, 1970). In the crystal structure of *trans*-dinitro(β-alaninato)(1,3-diaminopropane)cobalt(III) the nitro group with the longer Co—N distance is directed toward the carboxyl group of the β-alaninato ligand. Thus, the elongation of the Co—N(5) bond might be a consequence of the repulsive interactions between nitro O and carbonyl O atoms.

The β-alaninato ligand is bidentate and bonded to the metal atom through the carboxylato O and amino N atoms forming a six-membered chelate ring. The bond lengths and angles in the ring are closely similar to the values found in the crystal structures of the few Co

Table 3. *Equations of least-squares mean planes through selected atoms*

The equation of the plane is expressed as $AX + BY + CZ - D = 0$, where *X*, *Y* and *Z* are the monoclinic coordinates.

	A	*B*	*C*	*D*
Plane 1: Co, N(4), O(3), O(4)	7·38	1·22	6·32	4·96
Plane 2: Co, N(5), O(5), O(6)	5·55	−8·35	−4·38	0·80
Plane 3: O(1), C(1), O(2), C(2)	6·07	6·48	−5·69	−0·21
Plane 4: N(2), N(3), C(4), C(6)	9·83	7·23	−0·90	8·45

Distances of atoms from the planes (Å)

Plane						
1	Co	0·0,	N(4)	0·002,	O(3)	−0·001,
	O(4)	−0·001				
2	Co	0·0,	N(5)	0·018,	O(5)	−0·008,
	O(6)	−0·009				
3	O(1)	0·001,	C(1)	−0·006,	O(2)	0·001,
	C(2)	0·002				
4	N(2)	0·010,	N(3)	−0·009,	C(4)	−0·022,
	C(6)	0·020,	Co	−0·613,	C(5)	0·708

Table 4. *Interatomic distances* (Å) *and angles* (°) *involving hydrogen atoms*

A—H···*B*	*A*—*B*	*A*—H	H···*B*	∠*A*—H···*B*
N(1) H(1)···O(3^i)	2·841	1·064	2·163	119·4
N(1)—H(1)···O(3^{ii})	3·088	1·064	2·215	137·8
N(1)—H(2)···O(2^{iii})	2·895	1·057	1·856	166·2
N(2)—H(7)···O(4^{iii})	2·982	1·060	2·164	132·2
N(2)—H(7)···O(5^{iv})	2·849	1·060	2·154	121·0
N(3)—H(15)···O(2^v)	3·027	1·023	2·131	145·0
N(3)—H(15)···O(1^v)	2·996	1·023	2·375	118·4
N(3)—H(16)···O(1^{iv})	2·601	1·002	2·331	94·0

Symmetry code (the superscripts refer to transformations of the coordinates *x,y,z*)

(i)	$x, y, 1 + z$	(iv)	$x, y, z - 1$
(ii)	$1 - x, -y, 1 - z$	(v)	$1 - x, 1 - y, 1 - z$
(iii)	$\frac{1}{2} + x, \frac{1}{2} - y, z$		

complexes with β-alanine so far investigated (Prelesnik, Ćelap & Herak, 1973; Herak, Jeremić & Ćelap, 1975) as well as in Cu β-alanine (Bryan, Poljak & Tomita, 1961; Mitsui, Iitaka & Sakaguchi, 1976) and Ni β-alanine complexes (Jose, Pant & Biswas, 1964). The torsional angles in the ring are given in Table 2. The six-membered chelate ring has a skew-boat conformation, as was found in the other β-alaninato complexes. The mean plane defined by the atoms O(1), C(1), O(2) and C(2) (Table 3) indicates that the carboxylato group is planar.

The 1,3-diaminopropane ligand is coordinated to the Co atom through the amino N atoms, also forming the six-membered ring which has a chair conformation. The equation of the plane through N(2), N(3), C(5) and C(6) and the displacements of the relevant atoms out of this plane are given in Table 3. The torsional angles in the ring are given in Table 2. The geometry of this chair conforms to the general geometric trends observed in other chair structures (Geue & Snow, 1971; Jurnak & Raymond, 1974). The flattening of the ring is, however, more pronounced than the Co—NH_2 distances of 1·958 and 1·966 Å would require. Jurnak & Raymond (1974) suggested a correlation between the M—N bond length and the dihedral angle D_1 (between the N—Co—N and N—C—C—N planes), on the assumption that the least flattened chairs are the rings with the shortest M—N bond lengths. The Co—NH_2 distances noted belong to the lower values found in related compounds, but the dihedral angle of 27·3° is still one of the lowest reported values. The dihedral angle D_2, between the N—C—C—N and C—C—C planes, is 58·9°, very near to the ideal value of 60°.

Interatomic distances involving the H atoms are listed in Table 4. The amino groups from the β-alanine and 1,3-diaminopropane ligands have many contacts with O atoms and form normal and bifurcated N—H···O hydrogen bonds. The positional parameters of the H atoms are not of sufficient accuracy and have not been refined, thus a detailed discussion on the geometry of the hydrogen bonds is not justified. Table 4 indicates that hydrogen bonds only connect molecules in a sheet; there are no hydrogen-bond contacts between sheets.

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