The Crystal Structure of
Racemic *cis*(NO$_2$–NH$_3$)-*trans*(NH$_2$)-Nitrodiglycinatoamminecobalt(III) Monohydrate

By P. Vasić

Faculty of Science, University of Priština, Priština, Yugoslavia

R. Herak

Laboratory of Solid State Physics, 'Boris Kidrič' Institute, Belgrade, P.O. Box 522, Yugoslavia

and S. Djurić

Faculty of Mining, Geology and Metallurgy, University of Belgrade, Belgrade, Yugoslavia

Crystals of nitrodiglycinatoamminecobalt(III) monohydrate are monoclinic, space group $P2_1/a$, with $a = 10.553(6)$, $b = 12.912(6)$, $c = 7.950(4)$ Å, $\beta = 112.24(4)$, $Z = 4$. The data were collected by the ω scan technique on a Syntex P$\bar{1}$ diffractometer using Mo $K\alpha$ radiation. The structure was solved by the heavy-atom method and refined by conventional least-squares and Fourier techniques to a final R value of 0.068 for 1323 non-zero reflexions. The coordination around Co is slightly distorted octahedral. Two carboxylato O atoms are in the *cis* position, two amino N atoms are *trans* and N atoms from the nitro group and ammonia are *cis* to one another. The two glycine ligands form five-membered chelate rings using the amino N and carboxylato O atoms; chelate rings have an asymmetric envelope conformation. An extensive hydrogen-bonding network exists in the solid state.

Introduction

Compounds of the type CoNH$_3$(Am)$_2$NO$_2$, where Am is an aminoacidato residue, have been recently synthesized (Ćelap, Malinar & Janjić, 1974). When the ligand is glycine, the complex could appear in the form of six geometrical isomers: two *trans*(NO$_2$–NH$_3$) and four *cis*(NO$_2$–NH$_3$) (Fig. 1). The analysis of the electronic absorption spectrum of the isolated complex and the investigation of the optical activity of the corresponding complexes with higher amino acids have been carried out. On the basis of the number of the optical isomers obtained with optically active amino acids, the authors excluded the *trans*(NO$_2$–NH$_3$) isomer. In ad-

dition, on the basis of the electronic spectrum they consider that structures (IV) and (V) (Fig. 1) are less probable. The X-ray diffraction study reported here was undertaken to establish the correct structural isomerism of the nitrodiglycinatoamminecobalt(III) complex.

Experimental

Crystals of CoNH$_3$(gly)$_2$NO$_2$.H$_2$O suitable for X-ray diffraction measurements were kindly supplied by Professor M. B. Ćelap. Dark-red, lath-shaped crystals are elongated along the *a* axis. The unit-cell dimensions were initially determined from rotation and Weissenberg photographs and later adjusted by a least-squares refinement of a series of diffractometer-measured θ angles. From systematic absences, $h0l$ with h odd, and $0k0$ with k odd, the space group was uniquely defined as $P2_1/a$. The density of the crystal measured by the flotation method agrees very well with that calculated on the basis of four formula weights per unit cell. This places no restriction on the symmetry of the molecule, while the presence of a centre of symmetry in the crystal lattice ensures that both possible enantiomeric forms of this potentially asymmetric molecule will be present.

Crystal data

CoNH$_3$(NH$_2$CH$_2$COO)$_2$NO$_2$.H$_2$O, CoC$_4$H$_{13}$N$_4$O$_7$, $M = 288.2$. Monoclinic, $a = 10.553$ (6), $b = 12.912$ (6), $c = 7.950$ (4) Å, $\beta = 122.24$ (5)°, $V = 1000$ Å^3, $D_m = 1.88$, $Z = 4$, $D_x = 1.879$ g cm^{-3}. Space group $P2_1/a$. Mo $K\alpha$ radiation, $\lambda = 0.7107$ Å, μ(Mo $K\alpha$) = 20.1 cm^{-1}. All X-ray data were obtained from a crystal 0.04 × 0.17 × 0.64 mm on a Syntex P$\bar{1}$ four-circle diffractometer
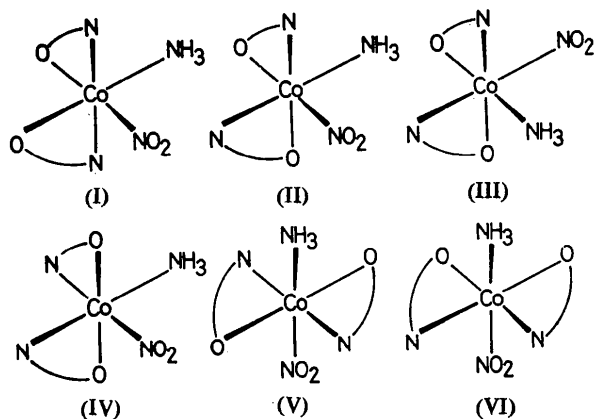

Fig. 1. The six geometric isomers of nitrodiglycinatoamminecobalt(III).

using graphite-monochromatized Mo $K\alpha$ radiation. The ω scanning mode was used. Intensities for 1974 reflexions in a quarter of the molybdenum sphere in reciprocal space, $2\theta \le 50°$ were measured. 1323 reflexions for which the net intensity was greater than $2\sigma(I)$ were considered observed. A standard reflexion was remeasured after every 25 reflexions, but no significant change in its value was observed. The integrated intensities and their standard deviations were corrected for Lorentz–polarization effects, but not for absorption.

The structure was solved by the heavy-atom method. A three-dimensional Patterson function revealed the position of the Co atom. The subsequent difference synthesis, interspersed with least-squares refinement, gave the positions of all the remaining non-hydrogen atoms. The atomic parameters were refined by full-matrix least-squares calculations. The function minimized was $\sum w\Delta^2$, where $w = 1/\sigma^2$, $\Delta = |F_o| - |F_c|$ and F_o and are the observed and calculated structure amplitudes. Refinement of the positional and isotropic thermal parameters of all non-hydrogen atoms converged at $R = 0.068$, $R_w = 0.074$. As the crystal had an unsuitable shape and we were not able to make a proper absorption correction, no allowance for the anisotropic vibrations of the atoms was made. In the last cycle of the refinement all parameters shifted by $< 0.1\sigma$. The highest function value in the final difference synthesis was 1·0 and the minimum peak height for a C atom in the final electron density synthesis was 7·9 e $Å^{-3}$.

All atoms were assumed to be uncharged. The scattering factor for Co was taken from Cromer & Waber (1965) and for the remaining atoms from *International Tables for X-ray Crystallography* (1962). The anomalous scattering was accounted for using Cromer's (1965) values of $\Delta f'$ and $\Delta f''$ for Co. H atoms were neither located nor included in the structure-factor calculations.

The final atomic parameters are given in Table 1.*

The computer programs used were Zalkin's *FORDAP* Fourier program, Ibers's *NUCLS* least-squares, Baur's *SADIANA* for the calculation of the interatomic distances and angles, and the function and error program *ORFFE* of Busing & Levy, on the CDC-3600 computer.

Discussion

The crystal structure of nitrodiglycinatoamminecobalt(III) monohydrate (Figs. 2 and 3) consists of discrete molecules of the complex enantiomers and molecules of water, linked together by a three-dimensional arrangement of hydrogen bonds. The coordination around Co is slightly distorted octahedral. Both glycine ligands are bidentate and bonded to the metal atom through carboxylato O in the *cis* position and

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31136 (12 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

amino N atoms in the *trans* position. The ammonia and nitro groups are nitrogen-bound and are in the *cis* position to one another. Hence, the configuration

Table 1. *The final atomic parameters (with standard deviations in parentheses)*

|	x	y	z	B
Co	0·6064 (1)	0·33133 (8)	0·2382 (1)	1·62 (2)
O(1)	0·6519 (5)	0·4736 (4)	0·2417 (7)	2·3 (1)
O(3)	0·7438 (5)	0·3061 (4)	0·1383 (7)	2·2 (1)
O(2)	0·8049 (6)	0·5910 (5)	0·3939 (8)	3·5 (1)
O(4)	0·7789 (6)	0·3183 (5)	0·8832 (8)	3·4 (1)
O(5)	0·4656 (6)	0·3117 (5)	0·4591 (8)	3·2 (1)
O(6)	0·3822 (7)	0·4255 (6)	0·2543 (9)	4·3 (1)
O(W)	0·8899 (10)	0·5598 (9)	0·0679 (13)	7·8 (2)
N(1)	0·7479 (6)	0·3231 (5)	0·4834 (8)	2·0 (1)
N(2)	0·5672 (7)	0·1835 (5)	0·2367 (9)	2·5 (1)
N(3)	0·4785 (6)	0·3447 (5)	0·9893 (8)	1·8 (1)
N(4)	0·4696 (7)	0·3600 (5)	0·3283 (9)	2·3 (1)
C(1)	0·7545 (8)	0·5041 (6)	0·3813 (11)	2·1 (1)
C(2)	0·8128 (10)	0·4261 (7)	0·5310 (12)	3·2 (2)
C(3)	0·7013 (8)	0·3182 (6)	0·9660 (11)	2·3 (1)
C(4)	0·5492 (9)	0·3255 (7)	0·8620 (11)	2·8 (2)
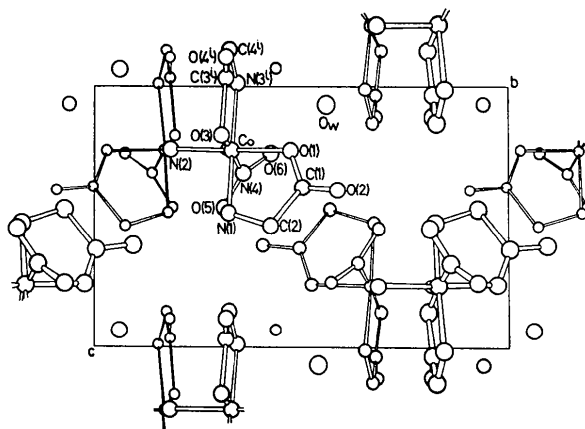
Fig. 2. The crystal structure viewed down the a axis. The labelling of atoms in the asymmetric unit is shown. The significance of the roman superscript is the same as in Table 3.
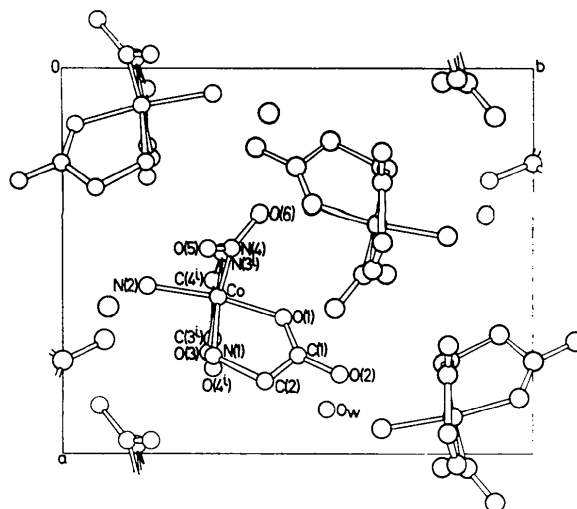

Fig. 3. The crystal structure viewed down the c axis.

of the complex molecule is cis(NO₂-NH₃)-trans(NH₂)-cis(O), in accordance with the prediction of Ćelap et al. (1974) that the complex should be one of the cis(NO₂-NH₃)-cis(O) isomers.

The glycine ligands form five-membered chelate rings. The bond lengths and angles in the glycine rings (Table 2) are in the range of the values reported for a number of compounds containing five-membered amino acids chelate rings (Freeman, 1967; Watson, Johnson, Ćelap & Kamberi, 1972; Svetich, Voge, Brushmiller & Berends; 1972, Herak, Prelesnik, Manojlović-Muir & Muir, 1974; Herak & Prelesnik, 1973). The equation of the least-squares plane fitted to the glycine ligand containing atoms Co, O(1), C(1), C(2) and N(1) is $9\cdot35x - 3\cdot09y - 5\cdot59z = -0\cdot45$. The displacements from this plane are 0·001 (1), -0·031 (6), 0·054 (8), 0·003 (10) and -0·020 (6) Å respectively. Hence, the conformation of the chelate ring is an asymmetric envelope, and C(2) is puckered away from the nitro group. Viewed along C(1)–C(2), the C(2)–N(1) and C(1)–O(1) bonds define a right-handed helix, with a torsion angle of 5·0 (1·1)°. The equation of the plane defined by Co, O(3), C(3), C(4) and N(3) is 1·88x +

$12\cdot7y - 0\cdot30z = 3\cdot39$, and the atoms are displaced from this plane by 0·001 (1), -0·032 (5), 0·094 (8), -0·069 (9) and 0·004 (6) Å, respectively. The conformation of the chelate ring is also an asymmetric envelope. The torsion angle down C(3)–C(4) is 15·0 (1·0)°, and viewed along this bond, the C(4)–N(3) and C(3)–O(3) define a left-handed helix. C(4) is slightly puckered to the ammonia. The enantiomers, consequently, exhibit the opposite chirality of the corresponding chelate rings.

The geometry of the coordinated nitro group in the present compound is closely similar to that found in related complexes (Table 2). The Co–N(4) distance is 1·875 (7) Å. Values ranging from 1·87 to 1·98 Å are reported for the Co–N(NO₂) distance in a variety of nitro complexes of Co(III) (Watson et al., 1972; Herak & Prelesnik, 1973; Kent Murman & Schlemper, 1973; Herak et al., 1974). The N–O distances are also in the range of values reported in the literature. In this compound the Co–N(NH₃) distance is longer than Co–N(NO₂), as was observed in a number of nitroammine-cobalt(III) complexes (Oonishi, Fujimaki, Muto & Komiyama, 1970).

In the crystal structure of nitrodiglycinatoamino-cobalt(III) monohydrate there exists an extensive hydrogen-bonding network. The water O atoms and N atoms from ammonia and amino groups make many contacts short enough to permit hydrogen bonding of the type O–H···O and N–H···O. Table 3 lists distances and angles for most probable hydrogen-bonded atoms. All of them are intermolecular.

Table 2. *Interatomic distances and angles in the cis-(NO₂-NH₃)-trans(NH₂)-nitrodiglycinatoamminecobalt-(III) monohydrate*

(a) Bond lengths (Å)

Co—O(1)	1·897 (6)	N(1)—C(2)	1·478 (11)
Co—O(3)	1·927 (5)	C(2)—C(1)	1·502 (12)
Co—N(1)	1·959 (6)	C(1)—O(2)	1·229 (10)
Co—N(3ⁱ)	1·935 (6)	C(1)—O(1)	1·284 (9)
Co—N(2)	1·952 (7)	N(3ⁱ)—C(4)	1·488 (11)
Co—N(4)	1·875 (7)	C(4)—C(3)	1·505 (12)
N(4)—O(5)	1·226 (9)	C(3)—O(4)	1·230 (10)
N(4)—O(6)	1·225 (9)	C(3ⁱ)—O(3)	1·280 (9)

(b) Bond angles (°)

O(1)—Co—O(3)	86·8 (2)	Co—N(1)—C(2)	108·1 (5)
O(1)—Co—N(1)	86·8 (3)	N(1)—C(2)—C(1)	112·9 (7)
O(1)—Co—N(3ⁱ)	90·2 (2)	C(2)—C(1)—O(1)	116·0 (7)
O(1)—Co—N(2)	177·7 (3)	C(2)—C(1)—O(2)	120·8 (7)
O(1)—Co—N(4)	91·8 (3)	O(1)—C(1)—O(2)	123·1 (8)
O(3)—Co—N(1)	89·5 (2)	C(1)—O(1)—Co	115·8 (5)
O(3)—Co—N(3ⁱ)	86·3 (2)	Co—N(3ⁱ)-C(4ⁱ)	110·2 (5)
O(3)—Co—N(2)	91·3 (2)	N(3)—C(4)—C(3)	110·0 (6)
O(3)—Co—N(4)	177·7 (3)	C(4ⁱ)-C(3ⁱ)—O(3)	117·7 (7)
N(1)—Co—N(3ⁱ)	175·0 (3)	C(4)—C(3)—O(4)	119·6 (7)
N(1)—Co—N(2)	91·9 (3)	O(3)—C(3ⁱ)—O(4ⁱ)	122·6 (7)
N(1)—Co—N(4)	92·1 (3)	C(3)—O(3ⁱ)—Co	114·0 (5)
N(3ⁱ)—Co—N(2)	91·0 (3)	Co—N(4)—O(5)	120·2 (6)
N(3ⁱ)—Co—N(4)	91·9 (3)	Co—N(4)—O(6)	120·0 (6)
N(2)—Co—N(4)	90·2 (3)	O(5)—N(4)—O(6)	119·8 (7)

(c) Non-bonded contacts (Å)

O(1)—O(3)	2·626 (8)	O(3)—N(2)	2·774 (9)
O(1)—N(1)	2·650 (8)	N(1)—N(2)	2·810 (9)
O(1)—N(3ⁱ)	2·714 (8)	N(1)—N(4)	2·762 (9)
O(1)—N(4)	2·708 (8)	N(3ⁱ)—N(2)	2·772 (9)
O(3)—N(1)	2·736 (8)	N(3ⁱ)—N(4)	2·739 (9)
O(3)—N(3ⁱ)	2·642 (8)	N(2)—N(4)	2·710 (10)

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

Table 3. *Distances and angles between potential hydrogen-bonded atoms*

The superscripts refer to the following transformation of the atomic coordinates x,y,z.

(i)	−x −y 1−z
(ii)	½+x ½−y z
(iii)	−x −y −z
(iv)	½−x ½+y 1−z
(v)	½−x ½+y −z

Donor D	Acceptor A	Distance (Å) D···A	Angle (Å) A–D–A
O(W)	O(2)	3·07	102·6
	O(6ⁱ)	3·04	
N(1)	O(4)	3·07	106·1
	O(5ⁱⁱ)	2·95	
N(2)	O(Wⁱᵛ)	3·08 } 114·9 }	
	O(2ᵛ)	2·98 }	107·0
	O(3ⁱⁱ)	3·20 } 114·0 }	
N(3)	O(4ⁱⁱ)	2·87	106·4
	O(1ⁱⁱⁱ)	2·73	

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A Powder Neutron Diffraction Study of Lanthanum and Cerium Trifluorides

BY A. K. CHEETHAM AND B. E. F. FENDER

Inorganic Chemistry Department, University of Oxford, England

AND H. FUESS AND A. F. WRIGHT

Institut Laue–Langevin, B.P. 156, 38042 Grenoble Cedex, France

The structures of LaF_3 and CeF_3 have been re-examined by neutron powder diffraction by the profile analysis method in order to decide between the three space groups proposed for the tysonite structure ($P\bar{3}c1$, $P6_3/mcm$ and $P6_3mc$). The refinement of positional and thermal parameters gave strong support for $P\bar{3}c1$. The rare-earth atoms have an 11-fold coordination of F atoms with distances between 2·421 and 2·999 Å (LaF_3) and 2·400 and 2·974 Å (CeF_3). It is shown that a high intensity/low resolution instrument gives results equivalent to those from a high resolution/medium intensity instrument.

Introduction

The trifluorides of the early lanthanides, La, Ce, Pr, Nd, adopt the structure of the natural mineral tysonite (a lanthanum cerium fluoride). Pure LaF_3 in particular has been extensively studied but the structure is still disputed. Single-crystal studies by Mansmann (1965) and Zalkin, Templeton & Hopkins (1966) indicate the space group $P\bar{3}c1$, a result supported by Raman measurements (Bauman & Porto, 1967). On the other hand the X-ray and neutron measurements of de Rango, Tsoucaris & Zelwer (1966) have been interpreted in $P6_3cm$, while from recent n.m.r. results on CeF_3, PrF_3 and NdF_3 Afanasiev, Habuda & Lundin (1972) favour $P6_3/mcm$ (the same space group is implied for LaF_3). The alternatives are summarized in Table 1.

We have re-examined the structure of LaF_3 by neutron diffraction because of its importance as a host crystal for the spectroscopic investigation of paramagnetic lanthanide ions, with particular relevance to crystal-field calculations (*e.g.* Newman & Curtis, 1969). Results for CeF_3 are also presented. Finally, as part of a programme to assess the value of profile analysis techniques, we compare the merits of the LaF_3 data which were collected on an instrument with modest resolution and a restricted angular 2θ range but high intensity, with the CeF_3 data collected on a high-resolution diffractometer.

Experimental

Powder neutron diffraction experiments were carried out on LaF_3 (supplied as 'Optran' quality by BDH Ltd., England) at room temperature with the D2 diffractometer on the High Flux Beam Reactor at the ILL, Grenoble. Data were collected over a period of about 6 h from 5° to 61° (in 2θ) in steps of 0·1°. The neutron beam was monochromated by the 200 planes of a Cu crystal with a take-off angle of about 14° in 2θ. The wavelength was not determined independently, but with the Zalkin *et al.* (1966) cell parameters $a = 7·185$, $c = 7·351$ Å it was deduced to be 1·085 Å. Absorption effects were negligible and no correction was applied.

The CeF_3 was supplied from the Cerac range of materials by Cambrian Chemicals Ltd., England and the experiment was performed at room temperature on the high-resolution D1A diffractometer at the ILL. Data were collected with neutrons of mean wavelength