

Table 2. Distances (Å) and angles (°) involved in hydrogen bonds

A	B	C	A-B	B-C	∠A-B-C	A-C
O(1)...	H(W)-O(W)		1.76 (1)	0.95 (1)	171.0 (1)	2.692 (4)
O(2)...	H'(W)-O(W)		1.79 (1)	0.95 (1)	173.0 (1)	2.731 (4)
O(1)...	H(N)-N		2.10 (1)	1.00 (1)	162.0 (1)	3.053 (6)

their amine nitrogens and O(2) oxygens of their carboxylate groups. The resulting coordination polyhedron is in a distorted octahedral configuration.

The O-C distances in the carboxylate group are somewhat different, as expected. It is interesting to note, however, that the interplay among these distances and the bond angles around C(1) is by no means arbitrary but follows closely the four systematic relationships described by Borthwick (1980).

The crystal structure is strongly stabilized by a net of hydrogen bonds. As pointed out by Stosick (1945) each of the water molecules of the complex forms two strong hydrogen bonds: one with oxygen O(1) of a neighboring complex and another with oxygen O(2) of a different neighboring complex. Also, one amine nitrogen forms a weaker hydrogen bond with oxygen O(1) of a neighboring molecule while the other one is close to O(1) of another neighbor molecule. As pointed out by Freeman & Guss (1968) this contact probably does not qualify as a potential hydrogen bond because of the unfavorable O-N distance [3.130 (5) Å] and N-H-O angle [137 (1)°]. Fig. 1 is a stereoscopic

projection down the mid-point of the unit cell, along a direction which minimizes overlap of the central molecule with its neighbors, showing the different types of hydrogen bonds formed by this molecule, including the short N-O contact which is probably not a hydrogen bond. For clarity not all hydrogen atoms and hydrogen bonds are displayed. Distances and angles about protons involved in hydrogen bonding are given in Table 2.

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## Structure of (-)<sub>589</sub>-*fac*-Triammineglycinatonitrocobalt(III) Perchlorate

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**Abstract.** [Co(C<sub>2</sub>H<sub>4</sub>NO<sub>2</sub>)(NH<sub>3</sub>)<sub>3</sub>(NO<sub>2</sub>)]ClO<sub>4</sub>·C<sub>2</sub>H<sub>13</sub>Co-N<sub>5</sub>O<sub>4</sub><sup>+</sup>·ClO<sub>4</sub><sup>-</sup>, *M<sub>r</sub>* = 329.5, monoclinic, *P*2<sub>1</sub>, *a* = 10.734 (2), *b* = 8.441 (1), *c* = 6.080 (1) Å, β = 95.39 (1)°, *V* = 548.5 (1) Å<sup>3</sup>, *Z* = 2, *D<sub>x</sub>* = 1.99 Mg m<sup>-3</sup>, λ(Mo *K*α) = 0.7107 Å, μ(Mo *K*α) = 1.91 mm<sup>-1</sup>. The structure was solved by Patterson-Fourier methods and refined to a final *R* value of 0.032 for 1955 observed reflections. The absolute configuration

of the complex ion can be designated as *abc*-triammine-*ed*-glycinato-*f*-nitrocobalt(III).

**Introduction.** Three isomers of a new complex ion, [Co(gly)(NH<sub>3</sub>)<sub>3</sub>(NO<sub>2</sub>)]<sup>+</sup> (gly: glycinate), were prepared and characterized by Fujinami & Shibata (1981). The optical resolution of the *fac*(NH<sub>3</sub>) isomer was achieved by column chromatography and the last-eluted (-)<sub>589</sub>-

isomer has been subjected to X-ray crystal-structure analysis in order to determine its absolute configuration and to establish the relationship between the CD spectra and the absolute configurations.

The orange-red crystals are plate-like and elongated along *b*. Crystallographic data were measured on a spherically shaped specimen 0.37 mm in diameter using a Rigaku automated four-circle diffractometer with graphite-monochromated Mo *K*α radiation. Preliminary Weissenberg photographs showed the crystal to be monoclinic, and the space group was determined to be *P*2<sub>1</sub> by the systematic absences *0k0* for *k* odd. The cell parameters were obtained by least-squares methods from the 2θ values of 20 independent reflections measured with Mo *K*α radiation (20 < 2θ < 30°, λ = 0.7107 Å). The intensity measurements (the ±*h* + *k* + *l* set) were performed in the θ–2θ scan mode (2θ<sub>max</sub> = 55°) at a speed of 2° min<sup>-1</sup> in θ and with a scan width of (1.2 + 0.5 tan θ)°. The intensities of the ±*h* – *k* + *l* set were also measured up to a 2θ value of 40°. 1965 intensities with |*F*<sub>o</sub>| > 3σ(|*F*<sub>o</sub>|) were considered as observed. Corrections were applied for Lorentz and polarization effects but not for absorption (μ<sub>r</sub> = 0.35).

Table 1. Positional parameters (×10<sup>4</sup>; for H ×10<sup>3</sup>) and equivalent isotropic temperature factors

$$B_{\text{eq}} = \frac{1}{3}(a^2 \beta_{11} + 2ab \cos \gamma \beta_{12} + \dots).$$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> <sub>eq</sub> (Å <sup>2</sup> )
Co	2571 (1)	5000	2702 (1)	1.1 (0.1)
N(1)	3436 (4)	3045 (5)	3579 (7)	2.1 (0.1)
N(2)	3463 (4)	5163 (9)	56 (6)	2.7 (0.1)
N(3)	1207 (4)	3776 (5)	1061 (7)	2.1 (0.1)
N(4)	1635 (4)	6963 (5)	2077 (7)	1.8 (0.1)
C(1)	745 (6)	7213 (7)	3729 (9)	2.4 (0.1)
C(2)	1013 (5)	6108 (6)	5665 (8)	1.6 (0.1)
O(1)	1749 (3)	4887 (6)	5367 (5)	1.6 (0.1)
O(2)	529 (4)	6323 (5)	7391 (6)	2.6 (0.1)
N(5)	3885 (4)	6219 (6)	4261 (7)	2.0 (0.1)
O(3)	4132 (4)	7567 (5)	3554 (7)	3.3 (0.1)
O(4)	4471 (4)	5680 (5)	5910 (6)	2.7 (0.1)
Cl	2724 (1)	189 (2)	8282 (2)	2.9 (0.1)
O(5)	2176 (6)	351 (11)	6011 (9)	8.0 (0.2)
O(6)	1782 (5)	140 (10)	9782 (9)	7.3 (0.2)
O(7)	3500 (6)	1560 (7)	8768 (9)	5.9 (0.2)
O(8)	3440 (7)	-1207 (7)	8507 (10)	6.6 (0.2)
H(N1)1	299 (6)	259 (8)	394 (10)	3.5 (1.4)
H(N1)2	357 (5)	242 (7)	248 (10)	2.9 (1.3)
H(N1)3	436 (7)	294 (9)	436 (13)	5.9 (1.9)
H(N2)1	343 (7)	642 (9)	-58 (11)	5.6 (1.9)
H(N2)2	426 (6)	471 (10)	7 (10)	6.6 (2.0)
H(N2)3	301 (6)	465 (9)	-117 (10)	6.3 (1.9)
H(N3)1	60 (5)	328 (6)	166 (9)	2.5 (1.3)
H(N3)2	148 (6)	306 (7)	52 (10)	3.5 (1.5)
H(N3)3	91 (5)	396 (7)	30 (9)	2.2 (1.2)
H(N4)1	221 (5)	786 (6)	216 (9)	2.4 (1.2)
H(N4)2	145 (9)	770 (12)	71 (16)	9.4 (2.7)
H(C1)1	-17 (5)	726 (6)	304 (9)	2.5 (1.2)
H(C1)2	63 (6)	813 (7)	407 (10)	3.8 (1.5)

Table 2. Determination of the absolute configuration

<i>h k l</i>	<i>F</i> ( <i>hkl</i> )  –   <i>F</i> ( <i>h<math>\bar{k}</math>l</i> )		<i>h k l</i>	<i>F</i> ( <i>hkl</i> )  –   <i>F</i> ( <i>h<math>\bar{k}</math>l</i> )	
	obs.	calc.		obs.	calc.
130	-2.2	-2.1	172	1.8	2.1
550	-2.6	-1.8	463	-1.4	-1.1
121	-3.5	-3.1	614	1.9	1.6
231	3.8	3.4	534	2.3	2.3
831	1.9	1.5	644	2.2	1.8
341	-3.1	-2.6	215	2.0	2.3
841	-0.9	-1.1	045	-2.3	-1.6
712	-1.8	-1.8			

The structure was solved by Patterson–Fourier methods and refined by block-diagonal least squares with anisotropic thermal parameters for all non-H atoms. The H atoms were found on a difference map and included in the refinement. Ten low-angle reflection data affected by secondary extinction were removed from the refinement. The function minimized was  $\sum w ||F_o| - |F_c||^2$ ; weights were assigned as *w* = 1.0 for |*F*<sub>o</sub>| < 15 and *w* = 0.25 for |*F*<sub>o</sub>| ≥ 15. The final *R* (=  $\sum ||F_o| - |F_c|| / \sum |F_o|$ ) was 0.032 and *R*<sub>w</sub> [( $\sum w ||F_o| - |F_c||^2 / \sum w |F_o|^2$ )<sup>1/2</sup>] = 0.036 for 1955 reflections. Complex neutral-atom scattering factors were used (*International Tables for X-ray Crystallography*, 1974). The calculations were carried out on a FACOM M-160F computer at the Institute for Solid State Physics, The University of Tokyo, with the *Universal Crystallographic Computation Program UNICS III* (Sakurai & Kobayashi, 1979). The final atomic parameters are listed in Table 1.\*

The absolute structure was determined by an anomalous-scattering technique. The observed and calculated intensity differences, |*F*(*hkl*)| – |*F*(*h $\bar{k}$ l*)|,

\* Lists of structure factors, anisotropic thermal parameters and mean-square displacement tensors have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36625 (15 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

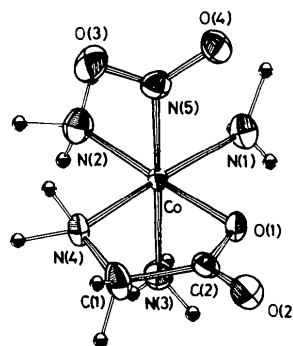


Fig. 1. An ORTEP drawing of the complex cation with thermal ellipsoids scaled at the 50% probability level (Johnson, 1965). H atoms are represented by circles of radius 0.08 Å.

for which  $|F_o(hkl)|$  and  $|F_o(h\bar{k}l)|$  differed by more than 15%, are compared in Table 2. The concordance in this table indicates that the absolute crystal structure listed in Table 1 is correct.

**Discussion.** An *ORTEP* drawing (Johnson, 1965) is shown in Fig. 1. The Co atom is surrounded octahedrally by six ligating atoms. A set of the facial coordination sites is occupied by the N atoms of the three ammonia molecules. The remaining sites are occupied by the N atom of a nitrite ion and by the N and one of the O atoms of the glycinate ion. The absolute configuration of the complex cation is designated as *abc*-triammine-*ed*-glycinato-*f*-nitroco-balt(III), according to the IUPAC (1970) convention.

Bond lengths and angles within the complex cation are listed in Tables 3 and 4. One of the three Co—NH<sub>3</sub> bonds that is in the *trans* position with respect to the nitro group is significantly longer than the other Co—NH<sub>3</sub> bonds. The Co—N(3) bond is 1.983 (4) Å; the mean value of the Co—N(1) and Co—N(2) bonds is 1.948 (4) Å. This observation may be explained by a *trans* influence of the nitro group. The Co—NO<sub>2</sub> bond is 1.922 (4) Å, 0.03 Å shorter than the value of 1.952 (1) Å observed for the [Co(NO<sub>2</sub>)<sub>6</sub>]<sup>3-</sup> ion (Ohba, Toriumi, Sato & Saito, 1978). The octahedral angle in the five-membered chelate ring formed by the glycinato moiety is 86.4 (2)°. The torsion angles Co—N(4)—C(1)—C(2) and N(4)—C(1)—C(2)—O(1) are 12.6 (5) and -15.9 (6)° respectively, suggesting that the glycinato chelate ring is nearly planar as was found for the (-)<sub>589</sub>-[Co(gly)(NH<sub>3</sub>)(tacn)]<sup>2+</sup> ion (tacn: 1,4,7-triazacyclononane; Sato, Ohba, Shimba, Fujinami, Shibata & Saito, 1980). The present complex ion, (-)<sub>589</sub>-*fac*-[Co(gly)(NH<sub>3</sub>)<sub>3</sub>(NO<sub>2</sub>)]<sup>+</sup> ion, and the (-)<sub>589</sub>-[Co(gly)(NO<sub>2</sub>)(tacn)]<sup>+</sup> ion have the same absolute configuration with respect to the arrangement of the three facial N atoms, glycinato and nitro groups. This result does not agree with the prediction based on the

Table 3. Bond lengths (Å)

Co—N(1)	1.943 (4)	N(4)—C(1)	1.465 (8)
Co—N(2)	1.952 (4)	C(1)—C(2)	1.509 (8)
Co—N(3)	1.983 (4)	C(2)—O(1)	1.321 (7)
Co—N(4)	1.956 (4)	C(2)—O(2)	1.227 (6)
Co—O(1)	1.919 (3)	N(5)—O(3)	1.254 (6)
Co—N(5)	1.922 (4)	N(5)—O(4)	1.221 (6)

Table 4. Bond angles (°)

N(1)—Co—N(2)	91.6 (2)	N(4)—Co—O(1)	86.4 (2)
N(1)—Co—N(3)	90.4 (2)	N(4)—Co—N(5)	89.0 (2)
N(1)—Co—N(4)	174.8 (2)	O(1)—Co—N(5)	89.1 (2)
N(1)—Co—O(1)	88.4 (2)	Co—N(4)—C(1)	110.2 (3)
N(1)—Co—N(5)	90.6 (2)	N(4)—C(1)—C(2)	110.9 (5)
N(2)—Co—N(3)	91.0 (2)	C(1)—C(2)—O(1)	116.6 (4)
N(2)—Co—N(4)	93.6 (2)	C(1)—C(2)—O(2)	120.7 (5)
N(2)—Co—O(1)	177.7 (2)	O(1)—C(2)—O(2)	122.6 (5)
N(2)—Co—N(5)	88.6 (2)	Co—O(1)—C(2)	113.9 (3)
N(3)—Co—N(4)	90.1 (2)	Co—N(5)—O(3)	119.1 (3)
N(3)—Co—O(1)	91.3 (2)	Co—N(5)—O(4)	120.2 (4)
N(3)—Co—N(5)	179.0 (2)	O(3)—N(5)—O(4)	120.7 (4)

order of elution in column chromatography (Fujinami & Shibata, 1981). In fact, the order of elution in column chromatography is reversed when the tacn molecule in the [Co(gly)(NO<sub>2</sub>)(tacn)]<sup>+</sup> ion is substituted for three NH<sub>3</sub> molecules. The CD spectrum of the present complex ion shows two peaks of opposite sign in the region of the first absorption band [ $\nu = 20.2 \times 10^2 \text{ mm}^{-1}$ ,  $\Delta\epsilon = -0.92$  and  $\nu = 23.5 \times 10^2 \text{ mm}^{-1}$ ,  $\Delta\epsilon = +0.09$ ; Fujinami & Shibata (1981)]. It differs from that of the (-)<sub>589</sub>-[Co(gly)(NO<sub>2</sub>)(tacn)]<sup>+</sup> ion which exhibits three Cotton peaks [ $\nu = 19.8 \times 10^2 \text{ mm}^{-1}$ ,  $\Delta\epsilon = -0.32$ ;  $\nu = 21.3 \times 10^2 \text{ mm}^{-1}$ ,  $\Delta\epsilon = +0.15$  and  $\nu = 23.6 \times 10^2 \text{ mm}^{-1}$ ,  $\Delta\epsilon = -0.66$ ; Shimba, Fujinami & Shibata (1980)]. These differences seem to be mainly due to the presence of -NH—CH<sub>2</sub>—CH<sub>2</sub>—NH— moieties in the tacn molecule.

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