The X-Ray Structure of the (+)$_{589}$-*cis*(O)*trans*(N_α)*cis*(N_δ)-Bis(L-ornithinato)cobalt(III) Complex

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(+)$_{589}$-Bis(L-ornithinato)cobalt(III) nitrate monohydrate was isolated by ion-exchange chromatography from a reaction mixture of trinitratotriamminecobalt(III) with L-ornithine at pH 9, and was assigned to the *cis*-(O)*trans*(N_α)*cis*(N_δ) isomer on the basis of the absorption and circular dichroism spectra. Then, the geometry of the complex was confirmed by X-ray structure analysis. The red crystal is orthorhombic, with these cell dimensions: $a=14.380$, $b=16.493$, and $c=6.787$ Å. The space group is $P2_12_12_1$, and $Z=4$. The crystal structure was solved by the Patterson and Fourier techniques and was refined by the least-squares method to R 0.099. The Co atom is surrounded by 2 O and 4 N atoms, the former being in *cis* positions. Each of the L-ornithinato ligands assumes the facial coordination, and the complex cation has an approximate two-fold axis by which the ligand are correlated.

The ornithinate ion, H_2N_δ–$(H_2C)_3$–$HC(H_2N_\alpha)$–COO^-, has three donor atoms ($O_{(carboxyl)}$, N_α, N_δ) and is capable of coordinating facially to a metal ion with octahedral stereochemistry,[1] while it acts as a bidentate ligand for the metal ion amenable to a square-planar or an elongated octahedral coordination.[2,3] We have prepared the bis(L-ornithinato)-cobalt(III) complex, $[Co(L\text{-}C_5H_{11}N_2O_2)_2]NO_3\cdot H_2O$, by the reaction of trinitratotriamminecobalt(III) with L-ornithine at pH 9. The complex cation may exist in three geometrical isomers, as is shown in Fig. 1. Actually,

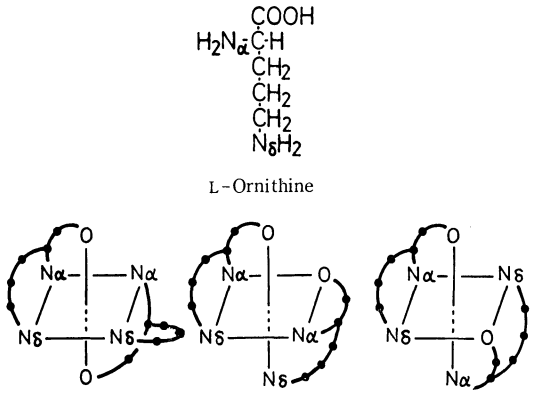


Fig. 1. Possible geometrical isomers of bis(L-ornithinato)-cobalt(III) ion.

the three bands could be separated from the reaction mixture by means of a cation-exchange column. The compound obtained from the most predominant band was inferred to be the *cis*(O)*trans*(N_α)*cis*(N_δ) isomer from its absorption and circular dichroism spectra. In order to confirm the geometry of the complex and in order to examine the conformational details of the chelate rings, the single crystal X-ray structure analysis was performed.

Experimental

Preparation of the Complex. From 1.5 g (0.009 mol) of L-ornithine hydrochloride and 1.5 g (0.009 mol) of silver nitrate, L-ornithine hydrogen nitrate was prepared as an aqueous solution of 40 ml, in which 1.3 g (0.0045 mol) of trinitratotriamminecobalt(III) was suspended. Then, 0.7 g (0.018 mol) of sodium hydroxide in 15 ml of water was added, and the solution was stirred at 50 °C for 5 h in the presence of activated charcoal. After the filtration of the charcoal and dilution to 100 ml, the reaction mixture was sorbed on the cation-exchange column (100—200 mesh Dowex 50W-X8 in the ammonium form). Three main bands developed upon elution with a 0.1 M NH_4NO_3 solution; the fastest band is red-violet in color, while the other two are red, the second band being overwhelmingly most abundant. Red, needle-like crystals were obtained by the slow evaporation of the solution from the second band; they were subsequently recrystallized from water.

Found: C, 29.69; H, 6.16; N, 17.34%; Calcd for $C_{10}H_{24}O_8N_5Co$: C, 29.93; H, 6.04; N, 17.45%.

Spectroscopic Measurements. The AB and CD spectra were recorded at room temperature using a Hitachi EPS-3T Recording Spectrophotometer and a JASCO J-20 Automatic Recording Spectropolarimeter respectively.

X-Ray Data Measurement. Crystal Data: *cis*(O)*trans*-(N_α)*cis*(N_δ)-$[Co(L\text{-}C_5H_{11}O_2N_2)_2]NO_3\cdot H_2O$, $FW=401.32$, orthorhombic, $a=14.380(4)$, $b=16.493(3)$, $c=6.787(2)$ Å, $V=1609.7$ Å^3, $Z=4$, $D_m=1.66$ (flotation), $D_x=1.66$ g cm^{-3}, space group $P2_12_12_1$, $\mu(NiK_\alpha)=25.3$ cm^{-1}. The unit-cell dimensions were determined by the least-squares analysis of the θ values from 45 high-angle reflections on zero-level Weissenberg photographs calibrated with silicon powder.

Multiple-film equi-inclination Weissenberg photographs were taken about a (0—7kl) and c (hk0—6) axes with NiK_α radiation. Crystals with the dimensions of $0.20\times0.15\times0.15$ and $0.15\times0.17\times0.18$ mm were used for the intensity-data collections about the a and c axes respectively. The intensities were measured visually by the use of a calibrated intensity strip and were corrected for Lp factors, spot shape, and absorption. The structure amplitudes were placed on a common arbitrary scale by the least-squares method. A total of 1636 independent reflections was obtained; of those, the intensities of 172 reflections were too weak to be observed.

Determination and Refinement of Crystal Structure

The coordinate of the Co atom was derived from the three-dimensional Patterson synthesis. Approximate coordinates of the other non-hydrogen atoms were obtained from successive Fourier syntheses. The positional and thermal parameters were refined by the block-diagonal-matrix least-squares method, the function minimized being $w(F_o-|F_c|)^2$. Five cycles of refine-

TABLE 1. THE ATOMIC COORDINATES, TEMPERATURE FACTORS, AND THEIR e.s.d.'s.
Temperature factors are of the form
$\exp[-(h^2B_{11}+k^2B_{22}+l^2B_{33}+hkB_{12}+hlB_{13}+klB_{23})]$

Atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Co	0.4359(1)	0.4361(1)	−0.0661(3)	0.0011(1)	0.0012(1)	0.0055(4)	−0.0001(1)	0.0000(3)	−0.0006(3)
N(1)	0.4054(6)	0.3229(6)	−0.1283(15)	0.0011(4)	0.0012(3)	0.0089(22)	−0.0004(6)	0.0000(16)	0.0024(14)
N(2)	0.3958(8)	0.4312(7)	0.2100(15)	0.0026(5)	0.0025(4)	0.0066(20)	0.0000(9)	−0.0002(17)	−0.0013(17)
N′(1)	0.4584(7)	0.5522(6)	−0.0346(15)	0.0024(5)	0.0017(4)	0.0088(22)	0.0007(7)	−0.0048(17)	−0.0015(16)
N′(2)	0.5648(7)	0.4031(7)	−0.0024(15)	0.0008(4)	0.0028(4)	0.0072(20)	0.0007(8)	0.0016(17)	−0.0010(15)
O(1)	0.3117(6)	0.4605(4)	−0.1467(13)	0.0016(4)	0.0008(2)	0.0121(19)	−0.0003(5)	0.0042(15)	0.0014(12)
O(2)	0.1818(6)	0.4045(6)	−0.2689(16)	0.0019(4)	0.0023(3)	0.0229(27)	0.0006(7)	0.0081(19)	−0.0023(17)
O′(1)	0.4723(6)	0.4518(4)	−0.3372(12)	0.0025(4)	0.0008(3)	0.0082(17)	−0.0003(5)	−0.0017(15)	−0.0013(12)
O′(2)	0.5214(7)	0.5431(5)	−0.5525(13)	0.0044(5)	0.0020(3)	0.0086(19)	0.0017(7)	−0.0007(19)	0.0017(14)
C(1)	0.2606(8)	0.3986(7)	−0.1971(18)	0.0014(5)	0.0016(4)	0.0113(28)	−0.0018(8)	0.0017(20)	0.0018(19)
C(2)	0.3012(7)	0.3153(6)	−0.1517(18)	0.0011(5)	0.0009(4)	0.0117(25)	0.0004(7)	0.0006(19)	−0.0021(17)
C(3)	0.2565(9)	0.2811(7)	0.0332(20)	0.0023(6)	0.0017(4)	0.0117(30)	0.0011(8)	−0.0022(23)	0.0004(19)
C(4)	0.2558(9)	0.3398(9)	0.2148(20)	0.0027(6)	0.0027(5)	0.0103(28)	−0.0016(10)	−0.0018(23)	−0.0029(21)
C(5)	0.3505(10)	0.3609(8)	0.3030(17)	0.0031(7)	0.0026(5)	0.0039(24)	0.0009(10)	0.0007(22)	0.0001(18)
C′(1)	0.5000(8)	0.5241(8)	−0.3802(18)	0.0019(5)	0.0023(5)	0.0090(28)	0.0015(8)	−0.0010(20)	−0.0032(18)
C′(2)	0.5094(9)	0.5840(7)	−0.2138(18)	0.0033(7)	0.0018(4)	0.0089(27)	0.0018(9)	−0.0059(23)	−0.0036(18)
C′(3)	0.6105(10)	0.5965(9)	−0.1563(22)	0.0028(7)	0.0028(5)	0.0140(31)	0.0030(10)	−0.0042(26)	−0.0053(23)
C′(4)	0.6698(10)	0.5171(10)	−0.1206(24)	0.0017(6)	0.0037(6)	0.0204(40)	0.0013(10)	0.0001(25)	−0.0027(26)
C′(5)	0.6406(8)	0.4647(9)	0.0508(21)	0.0014(5)	0.0039(6)	0.0116(29)	0.0011(9)	0.0013(23)	−0.0009(24)
N(3)	0.6086(7)	0.3079(6)	0.5119(15)	0.0027(5)	0.0012(3)	0.0088(22)	−0.0031(7)	−0.0018(18)	0.0006(14)
O(3)	0.6277(12)	0.3111(10)	0.3371(18)	0.0105(11)	0.0064(7)	0.0126(27)	0.0004(17)	−0.0038(32)	0.0021(26)
O(4)	0.5455(10)	0.2669(7)	0.5802(28)	0.0074(9)	0.0031(5)	0.0559(62)	−0.0023(11)	−0.0258(44)	−0.0024(29)
O(5)	0.6628(10)	0.3430(9)	0.6343(22)	0.0056(8)	0.0060(7)	0.0309(41)	−0.0037(12)	0.0100(31)	−0.0144(30)
H_2O	0.4906(10)	0.2066(7)	0.1406(19)	0.0094(10)	0.0026(4)	0.0223(31)	−0.0053(11)	0.0142(32)	−0.0052(20)

ment ($w=1$ for all reflections) with isotropic temperature factors reduced R and R' ($=[\sum w(F_o-|F_c|)^2/\sum wF_o^2]^{1/2}$) to 0.116 and 0.152 respectively. In the subsequent refinements, the following weighting scheme was employed:

$$w = 0.3 \quad \text{for } F_o < F_{min}$$
$$w = 1.0 \quad \text{for } F_{min} \leq F_o \leq F_{max}$$
$$w = F_{max}/F_o \quad \text{for } F_{max} < F_o$$

F_{max} and F_{min} were varied as is indicated by F_o and $(\sin\theta/\lambda)$ analysis of $w(F_o-|F_c|)^2$. Moreover, four reflections (020, 080, 120, 200) thought to be suffering from extinction errors were omitted in the least-squares calculation. Anisotropic thermal parameters were introduced in the following step-by-step order: i) first, to the Co atom only; then, ii) to the O atoms of the water molecule and the nitrate ion, and finally, iii) to all the atoms. R' was thus improved in an order of 0.151, 0.143, and 0.133 ($R=0.099$). R'-ratio tests at each stage showed the introduction of thermal anisotropy to be significant at the 0.01 level of significance.[4] In the final cycle of the least-squares refinement, the shifts of the parameters were $<0.3\sigma$, F_{max} and F_{min} being 20.2 and 4.7 respectively. The absolute configuration of the complex cation was derived from the well-established configuration of the L-ornithine.

The atomic scattering factors for C, N, O, and neutral Co atoms were employed from Ref. 5. The real part of the anomalous dispersion was taken into account for the Co atom. The final atomic coordinates and thermal parameters are listed in Table 1. The atomic coordinates correspond exactly to the absolute crystal structure. A complete list of the F_o and $|F_c|$ values is preserved by the Chemical Society of Japan (Document No. 7608). All the computations were carried out by means of the FACOM 270-30 computer at Osaka City University. The computer programs used were RSSFR-4 (Fourier synthesis) and HBLS-IV (least-squares calculation).

Results and Discussion

The AB and CD spectra are shown in Fig. 2, and they are summarized in Table 2. The pattern of the first absorption band (Band I) indicates that the present complex has two O atoms in the *cis* positions. In the figure, the CD curves for the bis(L-2,3-diaminopropionato)cobalt(III) and bis(L-2,4-diaminobutyrato)-cobalt(III) ions are also shown as references.[6,7] In these ions, the amino acidato ligand has the facial coordination *via* 2 N and O atoms and forms a 5-membered ring composed of the carboxyl and α-amino groups as well as a 5- or 6-membered chelate ring involving α- and β- or γ-amino groups. These two complexes have been assigned to the *cis*(O)*trans*(N_α)*cis*(N_β or N_γ) isomers by Liu *et al.*[6,7] The three complexes in Fig. 2 show similar Cotton effects in the Band I region. This

TABLE 2. DATA OF THE ABSORPTION AND CIRCULAR DICHROISM SPECTRA

	$\tilde{\nu}_{max}$ [a]	ε_{max}	$\tilde{\nu}_{ext}$ [a]	$\Delta\varepsilon_{ext}$
Band I	20.3	121	18.3	+1.27
			20.3	−0.32
Band II	28.0	172	27.7	−0.44

a) $\tilde{\nu}$ in $cm^{-1}\times 10^{-3}$.

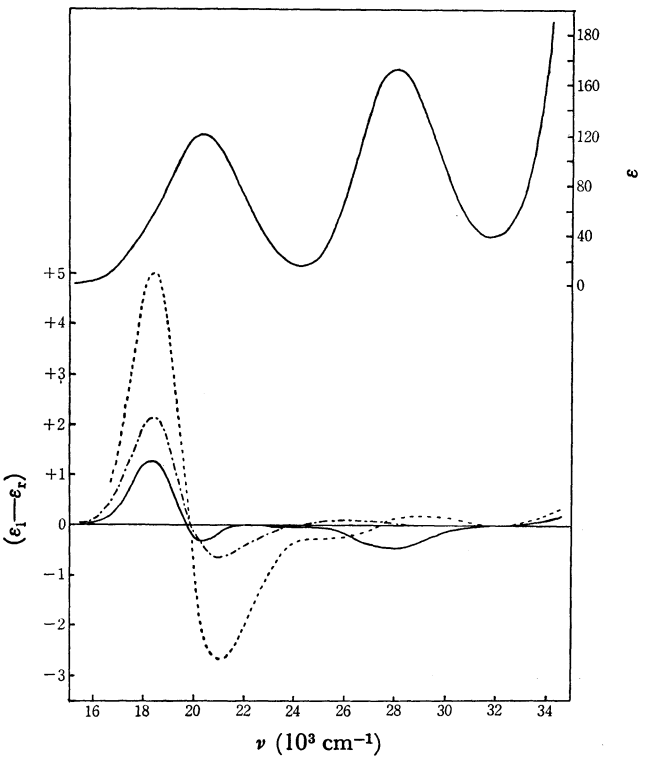


Fig. 2. AB and CD spectra (—) of the present bis(L-ornithinato)cobalt(III) ion, and CD spectra of: (···) *cis*(O)*trans*(N_α)*cis*(N_β) isomer of bis(L-2,3-diaminopropionato)cobalt(III) ion; (-·-) *cis*(O)*trans*(N_α)*cis*(N_γ) isomer of bis(L-2,4-diaminobutyrato)cobalt(III) ion.

implies that the present complex can be assigned to the *cis*(O)*trans*(N_α)*cis*(N_δ) isomer, though the sign of the CD band in the second absorption-band region (Band II) is opposite to the signs of the complexes cited for comparison. However, since the correlation between the CD spectrum and the absolute configuration of the Co(III) chelate of the tridentate α-amino acidato ligand has not yet been established, X-ray structure analysis was undertaken in order to establish the stereochemistry of the present complex.

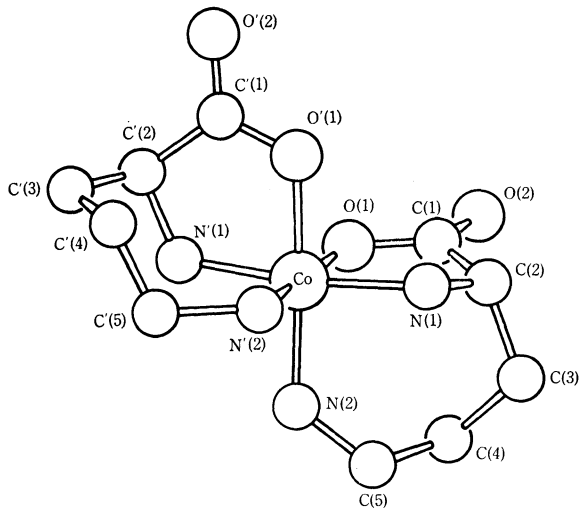


Fig. 3. Absolute configuration of *cis*(O)*trans*(N_α)*cis*(N_δ) isomer of bis(L-ornithinato)cobalt(III) cation.

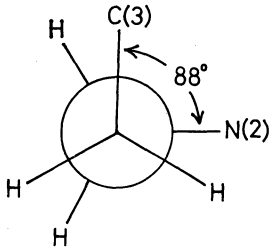
Table 3. Bond lengths and angles

Co–N(1)	1.96(1)Å	N(1)–Co–N'(2)	89.7(4)°
Co–N(2)	1.96(1)	N'(1)–Co–N(2)	89.1(5)
Co–N'(1)	1.95(1)	N(1)–Co–O'(1)	89.1(4)
Co–N'(2)	1.98(1)	N'(1)–Co–O(1)	88.8(4)
Co–O(1)	1.91(1)	N(2)–Co–N'(2)	93.2(5)
Co–O'(1)	1.93(1)	O(1)–Co–O'(1)	87.2(4)
N(1)–C(2)	1.51(2)	Co–N(1)–C(2)	109(1)
C(2)–C(3)	1.52(2)	N(1)–C(2)–C(3)	111(1)
C(3)–C(4)	1.57(2)	C(2)–C(3)–C(4)	115(1)
C(4)–C(5)	1.53(2)	C(3)–C(4)–C(5)	116(1)
C(5)–N(2)	1.47(2)	C(4)–C(5)–N(2)	114(1)
C(1)–C(2)	1.53(2)	C(5)–N(2)–Co	125(1)
C(1)–O(1)	1.30(2)	C(1)–C(2)–C(3)	110(1)
C(1)–O(2)	1.24(2)	C(1)–C(2)–N(1)	109(1)
		O(1)–C(1)–C(2)	116(1)
N'(1)–C'(2)	1.51(2)	O(2)–C(1)–C(2)	120(1)
C'(2)–C'(3)	1.52(2)	O(1)–C(1)–O(2)	124(2)
C'(3)–C'(4)	1.58(2)		
C'(4)–C'(5)	1.51(2)	Co–N'(1)–C'(2)	109(1)
C'(5)–N'(2)	1.53(2)	N'(1)–C'(2)–C'(3)	108(1)
C'(1)–C'(2)	1.51(2)	C'(2)–C'(3)–C'(4)	116(1)
C'(1)–O'(1)	1.29(2)	C'(3)–C'(4)–C'(5)	116(1)
C'(1)–O'(2)	1.25(2)	C'(4)–C'(5)'–N'(2)	113(1)
		C'(5)–N'(2)–Co	122(1)
N(3)–O(3)	1.22(2)	C'(1)–C'(2)–C'(3)	112(1)
N(3)–O(4)	1.22(2)	C'(1)–C'(2)–N'(1)	109(1)
N(3)–O(5)	1.28(2)	O'(1)–C'(1)–C'(2)	118(1)
		O'(2)–C'(1)–C'(2)	121(1)
N(1)–Co–N(2)	95.8(5)°	O'(1)–C'(1)–O'(2)	121(1)
N(1)–Co–O(1)	86.0(4)		
N(2)–Co–O(1)	90.4(4)	O(3)–N(3)–O(4)	124(2)
N'(1)–Co–N'(2)	95.2(4)	O(4)–N(3)–O(5)	117(1)
N'(1)–Co–O'(1)	85.9(4)	O(5)–N(3)–O(3)	118(1)
N'(2)–Co–O'(1)	89.5(4)		

Figure 3 shows the absolute configuration of the complex cation. This has a pseudo two-fold axis which passes through the Co atom and bisects N(2)–Co–N'(2) bond angle. This axis correlates the primed and unprimed atoms in Fig. 3. In the bond lengths and angles (Table 3), those related by the two-fold axis are in good agreement within the limits of experimental error.

In the 7-membered chelate ring composed of $N_\alpha(1)$, $C_\alpha(2)$, $C_\beta(3)$, $C_\gamma(4)$, $C_\delta(5)$, $N_\delta(2)$, and Co atoms, the N_α–Co–N_δ bond angle is larger than 90°, the average value being 95.5°; this can be ascribed to the repulsion between two confronting H atoms—H($N_\alpha H_2$) and H($C_\delta H_2$). This value is comparable to that (92°—95°) in the 6-membered ring formed by the trimethylenediamine molecule (tn) and the Co atom.[8,9] The bond angle of Co–N_α–C_α is close to the tetrahedral angle, while that of Co–N_δ–C_δ is much greater than 109.5°, but compares with the corresponding one in the tn ring. The C–C–C and N–C–C angles range from 108° to 116°. They are also similar to those in the tn ring of $[Co(tn)_3]^{3+}$ and the 7-membered ring found in bis(L-ornithinato)palladium(II), but are larger by 2°—5° than those in the L-ornithine hydrochloride[10] and hydrobromide.[11]

The $-CH-CH_2-CH_2-CH_2-$, $-CH_2-CH_2-CH_2-NH_2-$ and $-CH_2-CH_2-NH_2-Co-$ fragments in the 7-membered ring assume a *gauche* conformation. However, the $-H_2C(3)-H_2C(4)-H_2C(5)-H_2N(2)-$ fragment and the corresponding one composed of the primed atoms are somewhat close to the eclipsed conformation; the torsional angles between the two terminal bonds about the central C–C bond are 88° for the unprimed fragment and 87° for the primed one. These values agree well within the limits of experimental error (88° on the average).



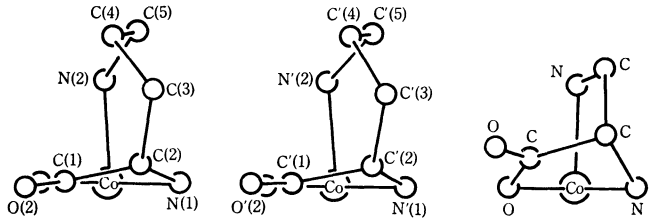


Fig. 4. Elevation of the chelate ring in: (a) and (b), bis(L-ornithinato)cobalt(III) nitrate monohydrate; (c), *cis* (O) *trans* (N_a) *cis* (N_β)-bis (L-2,3-diaminopropionato)-cobalt(III) bromide. Numbers in parentheses indicate the deviation (Å) of the C_α atoms in 5-membered glycinato ring from the (Co, N_α, O) planes.

The elevation of the 5-membered rings (or glycinato rings) formed by the N_α, C_α, $C_{(carboxyl)}$, O, and Co atoms are shown in Fig. 4, where the glycinato ring in bis(L-2,3-diaminopropionato)cobalt(III) bromide is also drawn for comparison.[12] Although the bond lengths and angles in the glycinato ring of the present complex are in good harmony with those in the planar chelate ring made by a glycinate ion and a Co atom,[13] the C(2) and C'(2) atoms are pulled upward from the $Co\langle^{N(1)}_{O(1)}$ and $Co\langle^{N'(1)}_{O'(1)}$ planes by the wing composed of C_α, C_β, C_γ, C_δ, N_δ, and Co atoms. In the glycinato ring of tridentate α-amino acid, the deviation of the C_α atom from the (Co, N_α, O) plane appears to be reduced as the members of the wings are increased.

TABLE 4. PLANES DEFINED BY THE O, Co, AND N_α ATOMS
Deviations(Å) of atoms from the plane are given in square brackets.

(O(1), Co, $N_\alpha(1)$) plane
$-0.318X-0.317Y+0.938Z=-3.40$
[C(1) 0.05, $C_\alpha(2)$ 0.35]
(O'(1), Co, $N'_\alpha(1)$) plane
$-0.951X+0.188Y-0.244Z=-4.50$
[C'(1) 0.08, $C'_\alpha(2)$ 0.30]

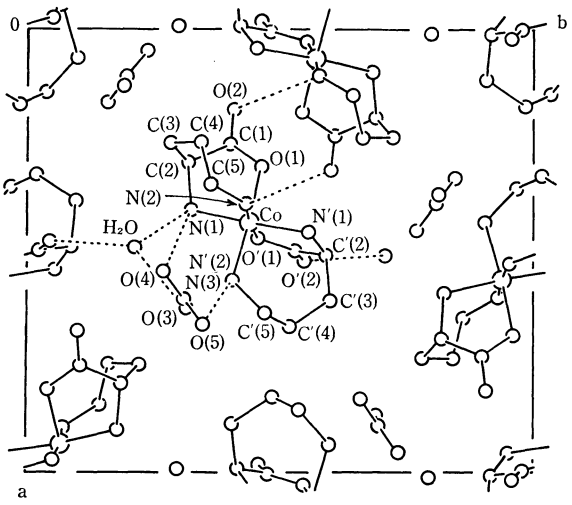


Fig. 5. Crystal structure viewed down the c axis. Broken lines indicate the hydrogen bonds.

TABLE 5. DATA OF THE HYDROGEN BONDS

A–H···B		A···B	H···B	A–H···B	Positions[a] of A	B
N(1)	H_2O	2.92(2)Å	1.91Å	165°	1	1
N(1)	O(4)	2.97(2)	2.01	155	1	3
N(2)	O(2)	2.94(2)	1.98	153	1	4
N(2)	O'(2)	3.05(2)	2.19	139	1	2
N'(1)	O(2)	2.80(2)	2.05	128	1	4
N'(2)	O(3)	2.90(2)	1.99	146	1	1
N'(2)	O(5)	3.01(2)	2.02	161	1	3
H_2O	O(3)	2.94(2)			1	1
H_2O	O'(2)	2.77(2)			1	5

a) Numerals refer to the following equivalent positions:
1 x, y, z 2 $x, y, 1+z$ 3 $x, y, -1+z$
4 $1/2-x, 1-y, 1/2+z$ 5 $1-x, -1/2+y, -1/2-z$

The crystal structure viewed down the c axis is depicted in Fig. 5. There are N–H···O and O–H···O hydrogen bonds in the crystal (Table 5), though they are rather weak in view of the distance between the proton donor and the acceptor. The positions of the H atoms of the amino groups are calculated on the assumption that the N–H distance is 1.03 Å. Both of the H atoms in the $N(1)H_2$ group and in the water molecule, and one of those in the $N(2)H_2$ and $N'(2)H_2$ groups participate in the hydrogen bonding, while none of those in $N'(1)H_2$ groups do.

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References

1) M. Watabe and S. Yoshikawa, Proceeding of the 28th Meeting of the Chemical Society of Japan, I (1973), p. 554.
2) Y. Nakayama, K. Matsumoto, S. Ooi, and H. Kuroya, *Chem. Commun.*, **1973**, 170.

3) S. Guha and N. Saha, *Acta Crystallogr.*, **B26**, 2073 (1970).
4) W. C. Hamilton, *ibid.*, **18**, 502 (1965).
5) "International Tables for X-Ray Crystallography," Vol. III, Kynoch Press, Birmingham (1962).
6) W. A. Freeman and C. F. Liu, *Inorg. Chem.*, **7**, 764 (1968).
7) W. A. Freeman and C. F. Liu, *ibid.*, **9**, 1191 (1970).
8) R. Nagao, F. Marumo, and Y. Saito, *Acta Crystallogr.*, **B29**, 2438 (1973).
9) K. Matsumoto, H. Kawaguchi, H. Kuroya, and S. Kawaguchi, This Bulletin, **46**, 2424 (1973).
10) S. Guha, S. K. Mazumdar, and N. N. Saha, *Z. Kristallogr.*, **129**, 84 (1969).
11) R. Schaffrin and J. Trotter, *J. Chem. Soc., A*, **1970**, 25.
12) C. F. Liu and J. A. Ibers, *Inorg. Chem.* **8**, 1911 (1969).
13) S. Yamaguchi, S. Ooi, and H. Kuroya, unpublished work.