Crystal and Molecular Structure of the Dicobalt(III) Complex Containing Bridging Di-μ-hydroxo Ligands, [(gly)(en)Co(μ-OH)$_2$Co(gly)(en)]$^{2+}$

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Synopsis. The molecular and crystal structure of the title compound has been determined by the X-ray method. The cation structure consists of well-separated dimeric pairs of the octahedrally coordinated cobalt(III) atom linked by two μ-hydroxo bridges. There are two intramolecular N-H···O hydrogen bonds bridging the two chromophores.

There have been many reports on the preparation and characterization of dicobalt(III) complexes containing two bridging hydroxo ligands.[1] The complexes of this type are fundamental in the study of the polynuclear complexes, and a comparative study of the geometrical isomers of the (μ-OH)$_2$ complexes is important in clarifying the factor stabilizing the polynuclear structure. Recently, three isomers of the [(gly)(en)Co(μ-OH)$_2$Co(gly)(en)]$^{2+}$ complex ion were synthesized by one of the present authors.[2] However, there are so many possible isomers (theoretically 20 isomers) in the complex ion that it is necessary to confirm the structure of the synthesized isomers by the X-ray method.

Experimental

[(en)(gly)Co(μ-OH)$_2$Co(en)(gly)]·2ClO$_4$ was prepared by the method reported previously[2] and then recrystallized from a water-ethanol solution. A wine-red crystal with approximate dimensions of 0.30×0.18×0.15 mm^3 was used for the X-ray measurement. The unit-cell parameters and reflection intensities were measured on a Rigaku AFC-4 automatic four-circle diffractometer with graphite-momochromated Mo$K\alpha$ radiation (λ=0.71073 Å). Independent reflections with the range of $2\theta<55°$ were collected by the 2θ-ω scan technique. The scan width, scan rate, and background counting time at both ends of scan were $\Delta\omega=(1.2+0.35\tan\theta)°$, 4°($2\theta$)min^{-1}, and 4 s respectively. Three standard reflections were measured after every 100 reflections; they showed no decay during the intensity measurement. The Lorentz and polarization effects were corrected, but no corrections for absorption and extinction were applied. 2116 independent reflections with $F_o>3\sigma$ (F_o) were used for the structure analysis. The structure was solved by the direct method (MULTAN 78)[3] and refined by the block-diagonal least-squares procedure (HBLS-V),[4] with anisotropic thermal parameters for nonhydrogen atoms. The function minimized was $\sum w(|F_o|-|F_c|)^2$, where a unit weight was applied throughout the refinement. All the hydrogen atoms were found in the difference Fourier map and included in the refinements with isotropic thermal parameters. The final R-value was 0.051 (R_w=0.056). The final atomic parameters are listed in Table 1.[5] The atomic-scattering factors were taken from International Tables for X-ray Crystallography.[7] The computations were carried out on an IBM-3081 computer at the Information Processing Center of Shimane University.

Crystal data: $C_8H_{26}N_6O_6Co_2$ $2ClO_4$ $2H_2O$, $F.W.$=655.11, Monoclinic, $P2_1/n$, a=15.982(2), b=11.732(2), c=6.086(1) Å, β=94.51(1)°, Z=2, D_x=1.912 Mg m^{-3}, D_m=1.913(3) Mg m^{-3}, μ=1.84 mm^{-1}, $F(0\,0\,0)$=672.

Table 1. Final Atomic Coordinates (×10^5 for Co and Cl, ×10^4 for C, N, and O), with Estimated Standard Deviations in Parentheses, and Their Equivalent Isotropic Thermal Parameters

Atom	x	y	z	B_{eq}/Å^2 [6]
Co	−1818(4)	11767(5)	4148(9)	1.4
Cl	12628(8)	56596(11)	53719(25)	2.9
C(1)	−1806(3)	1602(5)	1612(8)	2.2
C(2)	−1311(3)	1045(4)	3564(8)	2.0
C(3)	1002(3)	2335(5)	−1870(8)	2.5
C(4)	822(4)	3144(4)	−39(9)	2.8
N(1)	−1222(2)	2041(3)	23(6)	1.9
N(2)	230(2)	1637(3)	−2327(6)	1.8
N(3)	484(2)	2440(3)	1730(6)	1.9
O(1)	−542(2)	801(3)	3279(5)	1.9
O(2)	−1639(2)	817(4)	5275(6)	3.1
O(3)	−747(2)	−142(3)	−786(5)	1.6
O(4)	2141(3)	5914(5)	5492(10)	5.7
O(5)	1111(4)	4554(4)	4559(10)	5.6
O(6)	977(4)	5710(6)	7568(11)	4.1
O(7)	826(4)	6506(6)	4172(15)	9.8
O(w)	2147(3)	1500(4)	3706(7)	4.0

Table 2. Bond Lengths and Angles, with Estimated Standard Deviations in Parentheses

(a) Bond lengths (Å)

Co-O(1)	1.929(3)	Co-O(3)	1.908(3)	Co-O[a]	1.917(3)
Co-N(1)	1.946(4)	Co-N(2)	1.919(4)	Co-N(3)	1.958(4)
N(1)-C(1)	1.488(7)	C(1)-C(2)	1.522(7)	C(2)-O(1)	1.287(6)
C(2)-O(2)	1.231(6)	N(2)-C(3)	1.489(7)	C(3)-C(4)	1.509(8)
C(4)-N(3)	1.491(7)	Cl-O(4)	1.431(6)	Cl-O(5)	1.403(6)
Cl-O(6)	1.447(7)	Cl-O(7)	1.388(10)		

(b) Bond angles (°)

O(1)-Co-O(3)	89.7(1)	O(1)-Co-N(1)	85.2(2)
O(1)-Co-N(2)	175.7(2)	O(1)-Co-N(3)	89.7(2)
O(3)-Co-N(1)	90.1(2)	O(3)-Co-N(2)	94.6(2)
O(3)-Co-N(2)	174.8(2)	N(1)-Co-N(2)	95.5(2)
N(1)-Co-N(3)	95.0(2)	N(2)-Co-N(3)	86.0(2)
O(3)-Co-O(3)[a]	82.6(1)	Co-O(3)-Co[a]	97.4(2)
Co-O(1)-C(2)	115.3(3)	Co-N(1)-C(1)	108.3(3)
Co-N(2)-C(3)	109.2(3)	Co-N(3)-C(4)	109.9(4)
N(1)-C(1)-C(2)	110.0(5)	C(1)-C(2)-O(1)	115.7(5)
C(1)-C(2)-O(2)	121.6(5)	O(1)-C(2)-O(2)	122.7(5)
N(2)-C(3)-C(4)	106.3(3)	C(3)-C(4)-N(3)	106.6(3)
O(4)-Cl-O(5)	110.7(4)	O(4)-Cl-O(6)	108.9(4)
O(4)-Cl-O(7)	109.2(5)	O(5)-Cl-O(6)	107.8(4)
O(5)-Cl-O(7)	114.2(5)	O(6)-Cl-O(7)	105.9(5)

a) $-x, -y, -z$.

Results and Discussion

The crystal structure consists of well-separated dimeric cations, perchlorate ions, and H_2O molecules. The bond distances and angles of the complex are listed in Table 2. A perspective view of the complex cation is shown in Fig. 1. The complex cation has an inversion center at the middle of the dimer. The coordination of Co(III) is roughly octahedral, and the bridging unit, Co-O-Co-O, is strictly planar. The Co-Co and O-O separations in the bridging unit are 2.874 (1) and 2.524 (4) Å respectively. The two independent bridging Co-O bond lengths are essentially the same (1.917 (3) and 1.908 (3) Å). The Co-O-Co and O-Co-O angles are 97.4 (2)° and 82.6 (1)° respectively. The geometry of the Co-O-Co-O bridging unit is similar to that of the Cr-O-Cr-O unit found in $[Cr(gly)_2(OH)_2]$[9] and $[Cr(L\text{-}Pro)_2(OH)_2]$.[10] There are two intramolecular hydrogen bonds formed between the N(2)-H ethylenediamine ligating to one of the two cobalt atoms and the O(1) of glycinate coordinated to the other cobalt atom, whose N(2)···O(1) length is 2.968(5) Å. The hydrogen bonds significantly contribute to stabilizing the dinuclear structure. The ethylenediamine-chelate ring adopts a gauche conformation, where C(3) and C(4) are 0.482(8) and −0.203(8) Å, from the plane of the three remaining atoms (Co, N(2), and N(3)). On the other hand, the glycinate-chelate ring adopts an envelope conformation, where C(1) and C(2) are 0.491(7) and 0.252(7) Å, from the plane of the remaining atoms (Co, N(1), and O(1)). As shown in Fig. 2, the O(2) and N(3) form intermolecular hydrogen bonds with the water molecules, and the lengths of O(2)···O(w) ($-x$, $-y$, $1-z$) and N(3)···O(w) (x, y, z) are 2.918(6) and 3.037(6) Å respectively. The N(2) forms an intermolecular hydrogen bond with the O(7) of the perchlorate ion, and

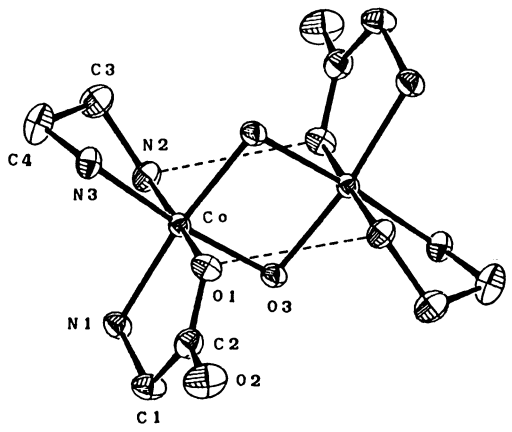

Fig. 1. A perspective view of the $[(gly)(en)Co(\mu\text{-}OH)_2Co(gly)(en)]^{+2}$ drawn by a ORTEP.[8] Thermal ellipsoids are drawn at the 50% probability. Hydrogen bonds are indicated by broken lines.

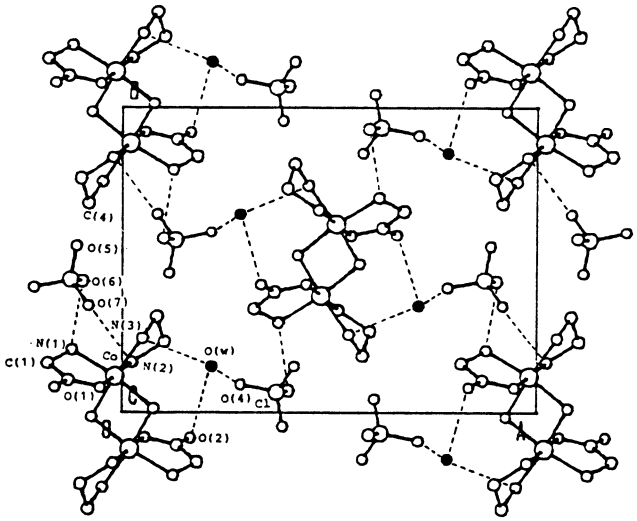

Fig. 2. A crystal structure of the complex along c-axis. Water molecules are drawn in solid circles. Hydrogen bonds are indicated by broken lines.

the length of N(2)···O(7) ($-x$, $1-y$, $-z$) is 2.925(10) Å. The N(1) also forms a hydrogen bond with the O(6), whose N(1)···O(6) ($-x$, $1-y$, $1-z$) length is 3.029(8) Å. The water molecule also forms an intermolecular hydrogen bond with O(4) of the perchlorate ion, O(w)···O(4) ($1/2-x$, $-1/2+y$, $1/2-z$) being 2.958(8) Å.

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References

1) T. Ama, H. Kawaguchi, and T. Yasui, *Bull. Chem. Soc. Jpn.*, **60**, 1183 (1987).
2) T. Ama, A. Mukai, K. Miyauchi, H. Kawaguchi, and T. Yasui, *Mem. Fac. Sci. Kochi Univ., Ser. C*, **7**, 1 (1986).
3) P. Main, S. E. Hull, L. Lessinger, G. Germain, J.-P. Declercq, and M. M. Woolfson, MULTAN 78 "A System Computer Program for the Automatic Solution of Crystal Structures from X-ray Diffraction Data," Univs. of York, England, and Louvain, Belgium, 1978.
4) T. Ashida, HBLS V, "The Universal Crystallographic Computing System-Osaka," The Computation Center, Osaka University, 1979.
5) Tables of the observed and calculated structure factors, the anisotropic thermal parameters for nonhydrogen atoms, and the atomic parameters for hydrogen atoms are deposited at the Chemical Society of Japan as Document No. 8862.
6) W. C. Hamilton, *Acta Crystallogr.*, **12**, 609 (1959).
7) "International Tables for X-ray Crystallography," Kynoch Press, Birmingham, England (1974), Vol. IV, p. 71.
8) C. K. Jonson, ORTEP II, Report ORNL-5138, Oak Ridge National Laboratory, Tennessee, 1976.
9) J. T. Veal, W. Hatfield, D. Y. Jeter, J. C. Hempel, and D. J. Hodgson, *Inorg. Chem.*, **12**, 342 (1973).
10) H. Oki and H. Yoneda, *Inorg. Chem.*, **20**, 3875 (1981).