Bridges in Polynuclear Complexes. II.† An X-Ray Investigation of the Coordination of Silver Ion to the μ-Peroxo Bridge of a Dinuclear Cobalt(III) Complex

Takashi SHIBAHARA,*,** Masayasu MORI, Keiji MATSUMOTO, and Shun'ichiro OOI

Department of Chemistry, Faculty of Science, Osaka City University, Sugimoto-cho, Sumiyoshi-ku, Osaka 558

(Received May 15, 1980)

The crystal structure of $[(en)_2Co(NH_2)(O_2)Co(en)_2](NO_3)_3 \cdot 15/8(AgNO_3) \cdot H_2O$ has been determined from X-ray diffraction data collected by the counter method. The crystal is monoclinic with the space group C2/c and with $a=8.710(3)$, $b=16.413(5)$, $c=20.024(8)$ Å, $\beta=90.30(4)°$, and $Z=4$. The structure was refined by the block-diagonal least-squares method to $R=0.107$ for 2157 independent reflections. It has been elucidated that the Ag atom is bound to each of the two peroxo oxygen atoms with the Ag–O bond length of 2.27(1) Å. Each Ag atom is also surrounded by two more oxygen atoms belonging to the nitrate anions and these Ag–O bond lengths are 2.45(2) and 2.50(2) Å. The central five-membered ring has a symmetric envelope conformation, with the peroxo O atom deviating from the Co, N, Co plane, by 0.38 Å. The crystals contain an equal amounts of the enantiomeric forms ($^{\delta}_{\delta}\Lambda\delta\Lambda^{\delta}_{\delta}$) and ($^{\lambda}_{\lambda}\Delta\lambda\Delta^{\lambda}_{\lambda}$). The formation constant of Ag^+ and $[(en)_2Co(NH_2)(O_2)Co(en)_2]^{3+}$ in aqueous solution was found to be less than 0.5.

The peroxo moiety of μ-amido-μ-peroxo dicobalt complex can be regarded as a Lewis base. The protonation to the peroxo moiety of the μ-amido-μ-peroxo dicobalt complex and subsequent isomerization was suggested by Mori and Weil from the analysis of kinetic data[1] and was confirmed by Thewalt by the X-ray structure analysis.[2]

Werner[3] reported the preparation of an addition compound, $[(en)_2Co(NH_2)(O_2)Co(en)_2](NO_3)_3 \cdot 5/3(AgNO_3)$. As the peroxo bridge of the complex is a Lewis base and the silver ion a Lewis acid, it seemed of interest to know whether a coordinate bond between the silver ion and the peroxo moiety is realized in this compound, and, if so, to determine the mode of coordination of the peroxo bridge to the cobalt atoms in connection with the isomerization scheme stated previously.

In the course of the study to elucidate this kind of problem, the addition compound obtained after Werner's description was shown by elemental analysis to have the composition $[(en)_2Co(NH_2)(O_2)Co(en)_2](NO_3)_3 \cdot 15/8(AgNO_3) \cdot H_2O$. The present paper reports the result of the X-ray structure analysis of this addition compound.

Experimental

Preparation of the Complex $[(en)_2Co(NH_2)(O_2)Co(en)_2](NO_3)_3 \cdot 15/8(AgNO_3) \cdot H_2O$. The addition compound of the above formula was prepared by Werner's method.[3] Recrystallization from water containing a large excess of silver nitrate gave deep red crystals suitable for the X-ray structure analysis.

Found: C, 10.38; H, 3.92; N, 21.27; NO_3^-, 32.58; Co, 12.53; Ag, 21.47; loss in wt over P_2O_5, in a vacuum, 1.71%. Calcd for $[Co_2C_8H_{34}N_9O_2](NO_3)_3 \cdot 15/8(AgNO_3) \cdot H_2O$: C, 10.34; H, 3.91; N, 20.92; NO_3^-, 32.54; Co, 12.69; Ag, 21.77; H_2O, 1.94%. The above composition appears to be maintained even when the amount of the silver nitrate was varied to some extent.

For comparison, the calculated values for two other different formulae are given. Calculated for $[Co_2C_8H_{34}N_9O_2](NO_3)_3 \cdot 2(AgNO_3)$: C, 10.31; H, 3.68; N, 21.04; Co, 12.65; Ag, 23.15; NO_3^-, 33.06%. Calcd for $[Co_2C_8H_{34}N_9O_2](NO_3)_3 \cdot 5/3(AgNO_3)$ (Werner's formula); C, 10.89; H, 3.91; N, 21.87; Co, 13.46; Ag, 20.54; NO_3^-, 33.06%.

X-Ray Data Collection. The specimen employed for data collection had a shape of an approximate sphere and its diameter was 0.23 mm. The Laue symmetry, space group, and approximate unit-cell dimensions were determined from oscillation and Weissenberg photographs taken with Cu Kα radiation. Crystal Data: $[Co_2C_8H_{34}N_9O_2](NO_3)_3 \cdot 15/8(AgNO_3) \cdot H_2O$, $M=929.12$, monoclinic, $a=8.710(3)$, $b=16.413(5)$, $c=20.024(8)$ Å, $\beta=90.30(4)°$, $V=2862.6(15)$ Å^3, $Z=4$, $D_m=2.15$, $D_c=2.16$ g·cm^{-3}, space group C2/c, λ(Mo Kα)$=0.7101$ Å, μ(Mo Kα)$=25.2$ cm^{-1}. Both the structure refinement and piezoelectric test suggest that the centrosymmetric space group C2/c is the correct choice. The unit-cell dimensions were refined by the least-squares analysis of the 36θ values measured on a Philips PW1100 automated diffractometer. The intensity data with $2\theta \leqq 55°$ were collected at room temperature by the use of graphite-monochromated Mo Kα radiation. The ω-2θ scan technique was employed. The scan range was $(0.9+0.2\tan\theta)°$, and the scan speed, 1°/min in ω: the background was counted for half of the scan time at each end of the scan. The three standard reflections, 200, 080, and 006, monitored every 180 min, showed no appreciable decay. A total of 2159 intensities with $F^2 \geqq 3\sigma(F^2)$ were observed and used for the structure analysis. A spherical absorption correction was applied.[4]

Structure Determination and Refinement. The structure was solved by the heavy-atom technique. The parameters were refined by the block-diagonal least-squares method using isotropic temperature factor for each atom. The R factor was 0.16. Further refinement, based on the anisotropic temperature factores for the Co and Ag atoms, resulted in $R=0.107$ and the refinement was terminated at this point. When the anisotropic temperature factors were applied to all non-hydrogen atoms, the R-factor decreased to 0.085. There is some doubt, however, as to the meaning of this value, since all the nitrate anions and water of crystallization were found to be disordered. The minimized function was $\sum w(F_o - |F_c|)^2$ and weighting scheme, $w=(24.7/F_o)^2$ for $F_o > 24.7$, $w=1$ for $24.7 \geqq F_o \geqq 16.5$, $w=0.9$ for $F_o < 16.5$ was used.

† Part I: S. Kubo, T. Shibahara, and M. Mori, *Bull. Chem. Soc. Jpn.*, **52**, 101 (1979).

** Present address: Department of Chemistry, Okayama University of Science, 1-1 Ridai-cho, Okayama 700.

Full occupation of the general position in the C2/c system suggests the formula $[(en)_2Co(NH_2)(O_2)Co(en)_2](NO_3)_3 \cdot 2AgNO_3 \cdot H_2O$, but the actual composition was $[(en)_2Co(NH_2)(O_2)(Co(en)_2](NO_3)_3 \cdot 15/8(AgNO_3) \cdot H_2O$. In order to accomodate this descrepancy, the occupation factor of 0.938 (15/16) was used for the Ag ions. For the nitrate ions, the occupation factor of 0.975 based on an equal partition of the nitrate shortage (0.125) over all the five nitrate positions was adopted, because it has been difficult to determine the extent of lattice defect to each nitrate position. Application of the occupation factors different from unity as above, however, did not produce any significant difference of structural parameters. In the final cycle of the refinement, all the parameter shifts were less than their standard deviations. The large peaks in the final difference synthesis were 3.5 and 2.2 $eÅ^{-3}$ in the vicinity of the Ag atom and H_2O molecules, respectively. No attempt was made to locate the hydrogen atoms. The atomic scattering factors of the Ag, Co, O, N, and C atoms were taken from Ref. 5. The real part of the anormalous dispersion correction were applied for the Co and Ag atoms.[5] A complete list of the F_o and F_c tables is preserved by the Chemical Society of Japan (Document No. 8112). All the computation were carried out by the FACOM 230-60 computer at Osaka City University. The programs used included a local version of the UNICS.[6]

Measurement of Ag^+ activity in the Aqueous Solution. The activity of Ag^+ in the presence of Co complexes was measured by using a Horiba CN^- ion electrode 8001 and a Horiba ion meter N-7 ⟨ION⟩.

Results and Discussion

Figure 1 gives two projections of the complex ion which show the coordination mode of the Ag atom to the peroxo oxygen atom. Figure 2 shows the crystal structure viewed down the a axis. The nearest neighbor to the Ag atom is the oxygen atom of the peroxo moiety of the complex ion (Fig. 2). The Ag–O(1) bond distance of 2.27(1) Å, indicating the presence of a coordinate bond between the Ag and O(1)$(1/2-x, -1/2+y, 1/2-z)$ atoms, is somewhat longer than the strongest Ag–O bond length (2.17 Å) in $Ag_2C_2O_4$.[7] The OA(2) and OA(4) atoms of the nitrate anions lies at a slightly greater distance than that between Ag and O(1). The Ag–OA(2) and Ag–OA(4) bond distances are 2.47(2)

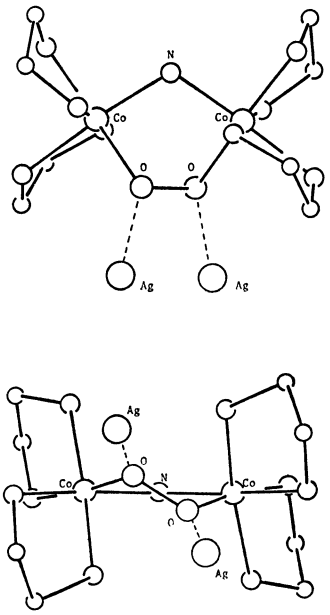

Fig. 1. Perspective drawing of complex ion.

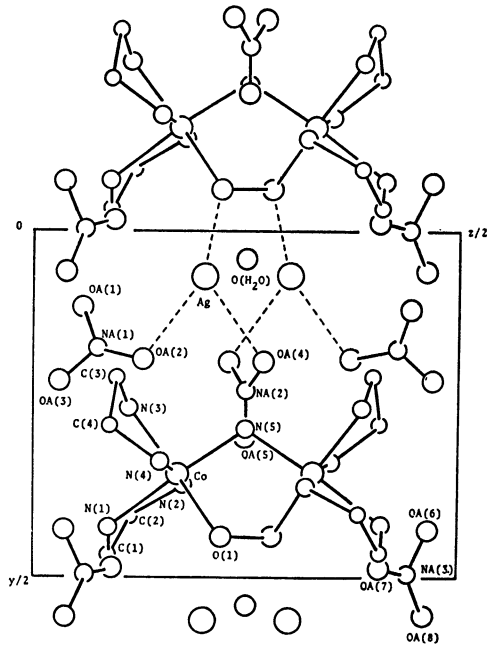

Fig. 2. The crystal structure viewed down the a axis. The dotted lines indicate possible Silver–Oxygen bonds.

Table 1. Positional and thermal parameters

Atom	$10^3 \times x$	$10^3 \times y$	$10^3 \times z$	$10 \times B$
Co	498.6(0.2)	351.3(0.1)	167.9(0.1)	a)
Ag	152.1(0.2)	67.0(0.1)	201.4(0.1)	a)
N(1)	482(2)	426(1)	90(0.5)	31(2)
N(2)	275(2)	369(1)	177(0.5)	32(2)
N(3)	470(2)	252(1)	112(0.5)	34(2)
N(4)	719(2)	337(1)	151(0.5)	32(2)
N(5)	500(0)	287(1)	250(0)	26(2)
C(1)	334(2)	471(1)	95(1)	49(3)
C(2)	212(2)	412(1)	117(1)	50(3)
C(3)	626(2)	210(1)	100(1)	45(3)
C(4)	742(2)	281(1)	92(1)	43(3)
O(1)	544(1)	444(0.5)	220(0.5)	25(1)
NA(1)	106(1)	171(1)	74(0.5)	34(2)
NA(2)	0(0)	231(1)	250(0)	32(3)
NA(3)	139(4)	493(2)	441(2)	113(8)
OA(1)	35(2)	113(1)	57(1)	76(4)
OA(2)	152(2)	188(1)	128(1)	64(3)
OA(3)	100(3)	217(2)	31(1)	119(7)
OA(4)	120(2)	193(1)	269(1)	59(3)
OA(5)	0(0)	301(1)	250(0)	44(3)
OA(6)	127(6)	432(3)	462(3)	230(19)
OA(7)	179(4)	481(2)	409(2)	136(9)
OA(8)	43(4)	552(2)	460(2)	148(10)
$O(H_2O)$	500(0)	46(2)	250(0)	70(5)

a) Anisotropic temperature factores ($\times 10^5$) in the forms

$\exp[-(B_{11}h^2+B_{22}k^2+B_{33}l^2+B_{12}hk+B_{13}hl+B_{23}kl)]$

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Co	671(17)	248(6)	98(3)	−2(16)	−16(11)	9(9)
Ag	1896(25)	267(5)	496(6)	−251(16)	47(20)	60(8)

Table 2. Interatomic distances and bond angles[a)]

Bond lengths(l/Å)			
Co–N(5)	1.95(1)	Co–O(1)	1.88(1)
Co–N(1)	1.99(1)	Co–N(2)	1.98(1)
Co–N(3)	1.99(1)	Co–N(4)	1.97(1)
O(1)–O(1)(II)	1.43(3)	N(1)–C(1)	1.49(2)
N(2)–C(2)	1.50(2)	N(3)–C(3)	1.55(3)
N(4)–C(4)	1.50(2)	C(1)–C(2)	1.50(3)
C(3)–C(4)	1.56(3)	Ag–O(1)(VI)	2.27(1)
Ag–OA(4)(I)	2.49(2)	Ag–OA(2)(I)	2.47(2)
Ag···OA(1)(I)	3.15(2)	Ag···OA(7)(V)	3.02(3)
Ag···O(H_2O)(I)	3.20(2)	Ag···O(1)(V)	3.08(1)
Bond angles(ϕ/°)			
O(1)–Co–N(5)	88.2(5)	N(1)–Co–N(2)	85.2(5)
N(3)–Co–N(4)	85.6(5)	Co–N(1)–C(1)	108(1)
Co–N(2)–C(2)	110(1)	Co–N(3)–C(3)	180(1)
Co–N(4)–C(4)	110(1)	N(1)–C(1)–C(2)	109(1.4)
N(2)–C(1)–C(2)	106(1.4)	N(3)–C(3)–C(4)	105(1.3)
N(4)–C(4)–C(3)	107(1.3)	Co–O(1)–O(1)(II)	110.9(4)
Co–N(5)–Co(II)	114.6(7)		

Possible hydrogen bonds (l/Å) and bond angles(ϕ/°)[b)]

	H···O	N···O	N–H···O
N(1)–H···OA(1)(III)	2.11	3.02	151
N(2)–H···OA(5)(IV)	2.39	3.02	120
N(3)–H···OA(3)(III)	2.01	2.98	160
N(4)–H···OA(7)(II)	1.85	2.80	157

a) Symmetry code, (I): (x, y, z), (II): ($1-x$, y, $1/2-z$), (III): ($1/2-x$, $1/2-y$, $-z$) (IV): ($-x$, y, $1/2-z$), (V): ($1/2-x$, $-1/2+y$, $1/2-z$), (VI): ($-1/2+x$, $-1/2+y$, z). b) The coordinates of the H atoms were calculated on the assumption that the N–H distance is 1.00 Å.

and 2.49(2) Å, respectively, which are generally considered as weak Ag–O bonds.[8)] More than 3 Å apart from the Ag atom are the OA(1), OA(7)($1/2-x$, $-1/2+y$, $1/2-z$), O(H_2O), and O(1)($1-x$, y, $1/2-z$) atoms. In case that the last four oxygen atoms are excluded from the coordination sphere, the Ag atom can be regarded as coordinated to three O atoms.

Table 2 gives the interatomic bond distances and angles. The complex ion has a crystallographically imposed two-fold axis of rotation, which passes through the bridging N(NH_2) atom and the center of the O–O bond of the peroxo group. The central five-membered ring is of a symmetric envelope conformation (Fig. 1).

Table 3. Dimensions of the ethylenediamine molecules

Torsion angles(ϕ/°)			
Co–N(1)–C(1)–C(2)	41	Co–N(2)–C(2)–C(1)	36
Co–N(3)–C(3)–C(4)	38	Co–N(4)–C(4)–C(3)	43
N(1)–C(1)–C(2)–N(2)	50	N(3)–C(3)–C(4)–N(4)	51

Deviations of the C(1), C(2), C(3), and C(4) atoms from the [N Co N] planes

C(1), −0.40; C(2), 0.26; C(3), 0.31; C(4), −0.42 Å

The dihedral angles between the [N Co N] and [C Co C] planes

27° in the [Co, N(1), N(2), C(1), C(2)] chelate ring

28° in the [Co, N(3), N(4), C(3), C(4)] chelate ring

The deviation of the O(1) atom from the Co, N(5), Co plane is 0.38 Å and the Co–O–O–Co torsion angle 61°. The O(1)–O(1)($1-x$, y, $1/2-z$) distance of 1.43(3) Å is essentially identical with the value (1.46 Å) found in DL-[$(en)_2Co(NH_2)(O_2)Co(en)_2$]$(NCS)_3 \cdot H_2O$.[2)] The Co–O and Co–N bond lengths of the central ring are 1.88(1) and 1.95(1) Å, respectively, and are in good agreement with the corresponding lengths in other peroxo and amido bridged Co(III) complexes.[2,9)] The dimensions of the Co-en chelate rings are identical with those previously reported[2)] (Table 3).

The complex ion shown in Fig. 1 can be described by the symbol $(^{\delta}_{\delta}\Lambda\delta\Lambda^{\delta}_{\delta})$. The enantiomeric form of the complex ion is also present in the crystal and its configuration is denoted by the symbol $(^{\lambda}_{\lambda}\Delta\lambda\Delta^{\lambda}_{\lambda})$.

Possible hydrogen bonds are summarized in Table 2. One of the N-bonded hydrogen atoms of ethylenediamine molecules participates in the N–H···O hydrogen bonding. The hydrogen bonds range from 2.80 to 3.02 Å. These hydrogen bonds seem rather weak because some of the donor···acceptor(H···O) distances are long and the N–H···O angles deviate considerably from 180°.

The activities of $AgNO_3$ in the presence of 0.01—0.1 mol/l of [$(en)_2Co(NH_2)(O_2)Co(en)_2$]$(NO_3)_3$ as measured with an AgCN electrode coincided within the experimental error with those in the presence of the same concentration of [$Co(NH_3)_6$]$(NO_3)_3$, so that the formation constant in aqueous media should be less than 0.5. The coordinate bond between Ag^+ and O_2 in the addition compound is thus concluded to be to a large extent lattice-stabilized.

The observed ratio of Ag : Co_2 (15 : 8) in various preparations suggests the special stability of the crystal lattice with a certain amount of defect of Ag^+ ion. However, it has not been possible to elucidate the nature of this defect by the refinement of the crystal structure.

The authors are grateful to Mr. J. Goda for the analyses of carbon, hydrogen, and nitrogen.

References

1) M. Mori and J. A. Weil, *J. Am. Chem. Soc.*, **89**, 3732 (1967).
2) U. Thewalt, *Z. Anorg. Allg. Chem.*, **393**, 1 (1972).
3) A. Werner, *Ann. Chem.*, **375**, 75 (1910).
4) J. Hornstra and B. Stubbe, PW1100 Data Processing Programs, Philips Research Laboratories, Findhoven, Holland.
5) "International Tables for X-Ray Crystallography," Kynoch Press, Birmingham (1974), Vol. IV, pp. 71, 148.
6) "The Universal Crystallographic Computation Program System," The Crystallographic Society of Japan (1969).
7) L. E. Sutton, "Interatomic Distances," The Chemical Society, London (1958).
8) L. Helmholz and R. Levine, *J. Am. Chem. Soc.*, **64**, 354 (1942); P. F. Lindley and P. W. Woodward, *J. Chem. Soc.*, **1966**, 123; D. Britton and J. D. Dunitz, *Acta Crystallogr.*, **19**, 815 (1965).
9) U. Thewalt and R. Marsh, *J. Am. Chem. Soc.*, **89**, 6364 (1967).