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The Crystal and Molecular Structure of Potassium *u-fac*-Bis(*N*-methyliminodiacetato)cobaltate(III) Sesquihydrate

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Synopsis. The crystal and molecular structure of the title complex has been determined by X-ray analysis. It has been found that the *cis*-N_2O_4 octahedron about the cobalt(III) has a large distortion caused by the steric compression between the two adjacent *N*-methyl groups.

Recently, the *u-fac* bis(*N*-methyliminodiacetato)cobaltate(III) complex, *u-fac*-[Co(mida)$_2$]$^-$, was newly prepared and characterized.[1] It was expected that the steric repulsion between the two adjacent *N*-methyl groups would result in the large distortion into the *cis*-N_2O_4 coordination geometry about the Co atom. Indeed, the first absorption-band maximum of the complex was observed at a considerably lower energy than those of the *u-fac*-[Co(ida)$_2$]$^-$,[2] [Co(edta)]$^-$, and [Co(1,3-pdta)]$^-$.[3] The *u-fac*-[Co(mida)$_2$]$^-$ decomposes easily in a basic aqueous solution, and the ligand decomposes.[1] In this note, we wish to report the results of the determination of the crystal and the molecular structure of the title compound. The highly strained *cis*-N_2O_4 geometry is compared with those related ones reported previously.

Experimental

Blue crystals were grown from an aqueous solution by adding methanol.[1] The cell dimensions and reflection intensities were measured on a SYNTEX-R3 diffractometer using Mo $K\alpha$ radiation(λ=0.7107 Å). The crystal data are as follows: $C_{10}H_{17}O_{9.5}N_2KCo$, M=415.3, monoclinic, a=29.057(3), b=7.144(1), c=15.783(2) Å, β=111.67(4)°, space group C2/c, D_m=1.80 g cm^{-3}, Z=8, D_c=1.81 g cm^{-3}. The intensity data were collected by the ω-scan technique up to 2θ=55°. The crystal used had approximate dimensions of 0.3×0.3×0.3 mm^3. A total of 2370 reflections were obtained, of which 2127 were non-zero reflections($|F_o|>3\sigma(F_o)$). No corrections for absorption and extinction were made(μ(Mo $K\alpha$)=15.0 cm^{-1}).

Structure Determination and Refinement

The structure was solved by the heavy-atom method and refined by the block-diagonal least-squares method. The R-value was finally reduced to 0.038 for 2127 reflections. The weighting scheme used was $w=(\sigma_{cs}^2+a|F_o|+b|F_o|^2)^{-1}$, where σ_{cs} is the standard deviation for each reflection; the a and b values were 0.2 and 0.0009. The final positional parameters and equivalent isotropic temperature factors for non-hydrogen atoms are listed in Table 1.[4]

Results and Discussion

Table 1. Positional ($\times 10^4$) and thermal parameters

ATOM	X	Y	Z	B_{eq}/Å^2	WG
O(W1)	5000(0)	-2435(6)	2500(0)	2.96(18)	0.50
O(W2)	2528(2)	-2852(8)	-1052(4)	11.86(38)	1.00
K	5199(0)	2463(1)	5854(1)	2.11(3)	1.00
CO	3853(0)	1245(1)	2035(0)	1.31(2)	1.00
O(1)	3301(1)	208(3)	1102(2)	2.13(11)	1.00
O(2)	4256(1)	122(3)	1476(2)	2.52(11)	1.00
O(3)	4391(1)	2397(4)	2935(2)	2.36(11)	1.00
O(4)	3969(1)	-944(3)	2745(2)	2.18(11)	1.00
N(1)	3803(1)	3381(4)	1185(2)	1.52(11)	1.00
N(2)	3439(1)	1945(4)	2737(2)	1.58(11)	1.00
C(ME1)	3818(2)	5340(5)	1515(3)	2.95(18)	1.00
C(ET1)	3340(1)	3084(5)	381(2)	2.10(15)	1.00
C(BX1)	3130(1)	1157(5)	366(2)	2.07(15)	1.00
O(XY1)	2795(1)	628(4)	-320(2)	3.00(13)	1.00
C(ET2)	4240(1)	3153(5)	925(3)	2.47(16)	1.00
C(BX2)	4361(1)	1104(5)	894(2)	2.11(16)	1.00
O(XY2)	4553(1)	497(4)	387(2)	3.29(13)	1.00
C(ME2)	3005(2)	3190(6)	2329(3)	3.28(19)	1.00
C(ET3)	3792(2)	2767(5)	3612(2)	2.55(17)	1.00
C(BX3)	4298(1)	3050(5)	3609(2)	2.00(15)	1.00
O(XY3)	4601(1)	3884(4)	4248(2)	2.95(13)	1.00
C(ET4)	3250(1)	127(5)	2931(2)	2.24(16)	1.00
C(BX4)	3652(1)	-1320(5)	3109(2)	2.07(15)	1.00
O(XY4)	3671(1)	-2724(4)	3559(2)	3.71(14)	1.00

$B_{eq}=8\pi^2(U_{11}+U_{22}+U_{33})/3$. The anisotropic thermal parameters have been preserved by the Chemical Society of Japan.

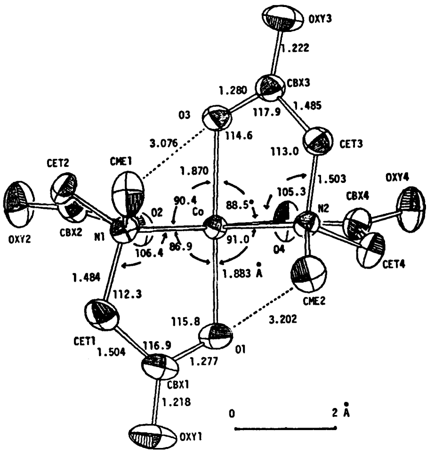

Fig. 1. The projected structure viewed down the pseudo two-fold axis of the complex molecule. Hydrogen atoms are omitted for clarity.

The structure viewed down the pseudo-two-fold axis of the complex molecule is shown in Fig. 1 (ORTEP program[5]), while that projected on the N_2O_2 plane is shown in Fig. 2, along with the selected bond distances and angles.[6] In the complex molecule, both *N*-methyliminodiacetato groups act as terdentate ligands and form a distorted *cis*-N_2O_4-type octahedron about the cobalt atom. The nonbonded short contact between the two adjacent methyl groups is 3.438(7) Å. This value is comparable with the intramolecular nonbonded $-CH_3\cdots H_3C-$ contact, 3.466(8) Å, observed in [Co(NH$_2$CH$_3$)$_5$Cl](NO$_3$)$_2$.[7] Recently, the nonbonded short contact of the $-CH_3$ group has aroused some interest in relation to the CH/π interactions.[8] The present result indicates that the minimum radius

Table 2. The geometrical parameters and absorption maxima of the first band for *cis*-$[CoN_2O_4]$-type complexes with (edta)-like ligands

Complex	Bond distance Co-N(av)	l/Å Co-O(av)	Bond angle N-Co-N	ϕ/° O-Co-O	λ/nm
$NH_4[Co(edta)]\cdot 2H_2O$[a)]	1.93(1)	1.92(3)	89.7(7)	104.0(6)	537[e)]
$K[Co(1,3\text{-pdta})]\cdot 2H_2O$[b)]	1.966(9)	1.904(9)	99.0(3)	92.6(3)	553[f)]
$K[Co(ida)_2]\cdot 2.5H_2O$[c)]	1.942(4)	1.899(4)	98.5(2)	90.0(2)	561.5[g)]
$K[Co(mida)_2]\cdot 1.5H_2O$[d)]	1.990(4)	1.880(4)	105.9(2)	88.5(2)	580.0[h)]

a) Ref. 9. b) Ref. 10. c) Ref. 11. d) This work. e) Ref. 3. f) Ref. 3. g) Ref. 2. h) Ref. 1.

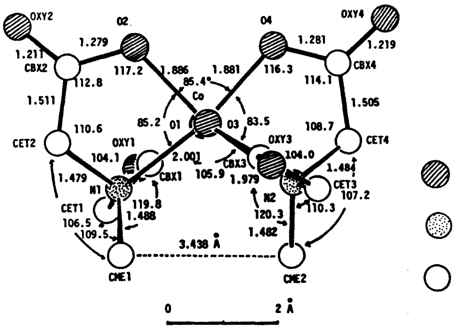

Fig. 2. The molecular structure projected on the N_2O_2 plane.

of the $-CH_3$ group in side contact is 1.72 Å. The Co–N–C(methyl) angles, 119.8(3)° for N1 and 120.3 (3)° for N2, are considerably larger than the tetrahedral value. If the tetrahedral angle around the nitrogen atoms is assumed (109.5°), the CME1···CME2 contact falls at 3.16 Å. Therefore, the relaxation of CME1···CME2 steric repulsion comes from three factors: (1) the elongation of the Co–N bonds, (2) the increase in the N–Co–N angle, and (3) the increase in the Co–N–C(methyl) angles.

The geometrical parameters of the N_2O_2 plane(N1, N2, O2, and O4) are listed in Table 2, along with the previously reported values of the related complexes: $NH_4[Co(edta)]\cdot 2H_2O$,[9)] $K[Co(1,3\text{-pdta})]\cdot 2H_2O$,[10)] and *u-fac*-$K[Co(ida)_2]\cdot 2.5H_2O$.[11)] The values of the first absorption maxima of these complexes are also listed in Table 2. In the equatorial N_2O_2 plane, a gradual increase in the N–Co–N angle and a gradual decrease in the O–Co–O angle are observed in these *cis*-N_2O_4-type structures. The observed red shift in the first absorption maximum from $[Co(edta)]^-$ to *u-fac*-$[Co(mida)_2]^-$ reflects the distortion about the cobalt atom.

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4) Tables of the atomic parameters for the hydrogen atoms, the anisotropic temperature factors, the structure factors, and the projected figure of the crystal structure are kept in the Office of the Chemical Society of Japan (Document No. 8334).

5) All computations were carried out using a HITAC-M-180 computer at the Hiroshima University Information Processing Center, using UNICS programs of The Crystallographic Society of Japan with slight modifications.

6) The estimated standard deviations are as follows: Co–N 0.003; Co–O 0.003; C–O, C–N, and C–C 0.006~7 Å; N–Co–N, O–Co–O, and N–Co–O 0.2°; Co–O–C and Co–N–C 0.3°; N–C–C, O–C–C, and O–C–O 0.4°, respectively.

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