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Crystal Structure of the Tetramethylammonium Salt of trans-Dinitro-bis(dimethylglyoximato)cobalt(III), $[N(CH_3)_4][Co(C_4H_7N_2O_2)_2(NO_2)_2]$

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Crystal structure of the tetramethylammonium salt of trans-dinitrobis(dimethylglyoximato)cobalt(III), $NMe_4[Co(dmgH)_2(NO_2)_2]$, is reported. The results of X-ray diffraction analysis reveal that the difference in the stretching frequency mode between IR spectrum of $NMe_4[Co(dmgH)_2(NO_2)_2]$ and that of $Na[Co(dmgH)_2(NO_2)_2]\cdot 2H_2O$ results from the difference in the coordination mode of the equatorial ligand dmgH and in the orientation of axial NO_2^- and Co-N(NO_2) distance.

Recently the interest in the axial-equatorial interactions in octahedral cobalt(III) dimethylglyoximato complexes has been considerably increased from the view point of electronic,[1] NMR,[2] and IR[3] spectra, X-ray structural analyses,[4] and the acid-dissociation behavior[5] and the rates of recombination with OH^- ion of OH···O proton.[6] The strength of the intramolecular OH···O hydrogen bond in solution reflecting in the acid-dissociation constants and the rates of recombination with OH^- ion is primarily controlled by the basicity, the charge type, and the π-back donation of the axial ligand.[5,6] The stretching frequency of the OH···O bond, $\nu_{OH\cdots O}$, a parameter of the strength of the intramolecular OH···O hydrogen bond in solid, is determined primarily by the nature of the axial ligand. However, the value of $\nu_{OH\cdots O}$ observed for $NMe_4[Co(dmgH)_2(NO_2)_2]$ was found to be quite different from that for $Na[Co(dmgH)_2(NO_2)_2]\cdot 2H_2O$.[7] The axial-equatorial interactions in the complex anion, $[Co(dmgH)_2(NO_2)_2]^-$, of a series of solid complex salts with various counter cations are affected also by the nature of the environment immediate to the complex anion.

In the present communication, we report the characteristic difference in the crystal structures between the tetramethylammonium salt, $NMe_4[Co(dmgH)_2(NO_2)_2]$, **1**, and the sodium salt,[8] $Na[Co(dmgH)_2(NO_2)_2]\cdot 2H_2O$, **2**.

The title complex **1** was prepared in the same manner as described in the synthesis of $NH_4[Co(dmgH)_2(NO_2)_2]$.[9] After the solution had been kept standing at room temperature for two weeks, dark brown columnar crystals appeared. The crystallographic data for **1** were as follows: $[N(CH_3)_4][Co(C_4H_7N_2O_2)_2(NO_2)_2]$,

Table 1. Comparison of Bond Lengths (Å) for **1** and **2**[a)]

Complex		Co-N(NO_2)	Co-N(dmgH)	N-O	N=C	=C-CH_3	=C-C=	O-H
$NMe_4[Co(dmgH)_2(NO_2)_2]$, **1**		1.974(3)	1.885(2)	1.350(4)	1.292(4)	1.489(5)	1.465(4)	0.79(7)
			1.901(2)	1.328(3)	1.295(4)	1.497(5)		
$Na[Co(dmgH_2)(dmg)(NO_2)_2]\cdot 2H_2O$	b)	1.949	1.918(2)	1.371(4)	1.295	1.496	1.494	0.98
			1.918(2)	1.366(3)	1.297	1.496		0.82
2	c)	1.943	1.902(2)	1.353(3)	1.301	1.497	1.482	
			1.903(2)	1.350(4)	1.297	1.507		

a) Ref. 8. b) Bond lengths for $dmgH_2$. c) Bond lengths for dmg. d) Values in parentheses represent the estimated standard deviations (e.s.d.). The values of e.s.d. for N=C, =C-CH_3, =C-C=, and O-H for **2** were not specified in Ref. 8.

monoclinic, space group C2/c, a = 11.334(3), b = 12.263(4), c = 14.987(4) Å, β = 102.38(4)°, V = 2034.6 $Å^3$, Z = 4, D_c = 1.486 g cm^{-3}. The intensities of 1910 independent reflections with 2θ < 55° were measured on a Rigaku four-circle diffractometer with graphite-monochromated MoKα radiation, using the ω-2θ scanning mode. The intensity measurements were performed at the High Brilliance X-ray Laboratory of the Hokkaido University. The structure was solved by the heavy-atom method, and refined by the block-diagonal least-squares method with anisotropic temperature factors. After all hydrogen atoms had been located in a difference Fourier map, full-matrix least-squares refinements were carried out including the hydrogen atoms. The final R value was 0.048($|F_o| \gtrsim 3\sigma(|F_o|)$).

The structure of the complex anion of **1** is shown in Fig. 1. The cobalt atom, lying on a center of symmetry, is very nearly coplanar with the atoms in the dimethylglyoximato groups. In Table 1, the lengths of the corresponding bonds in **1** and **2**[8)] are compared with each other. The bond length of OH···O in **1** (2.480(3) Å) is shorter than that in **2** (2.491 and 2.544 Å). A difference in the structural feature between **1** and **2** is observed both in the coordination mode of the equatorial ligands and in the orientation of the axial ligands, NO_2^-. The complex **1** is found to be formulated as $NMe_4[Co(dmgH)_2(NO_2)_2]$ containing two monoanionic dmgH ligands, whereas the complex **2** to be $Na[Co(dmgH_2)(dmg)(NO_2)_2]$[10)] as containing one neutral dimethylglyoxime ligand, $dmgH_2$, and one dianionic ligand, dmg.[8)] The N-O, Co-N(NO_2), and O-H bond lengths are quite

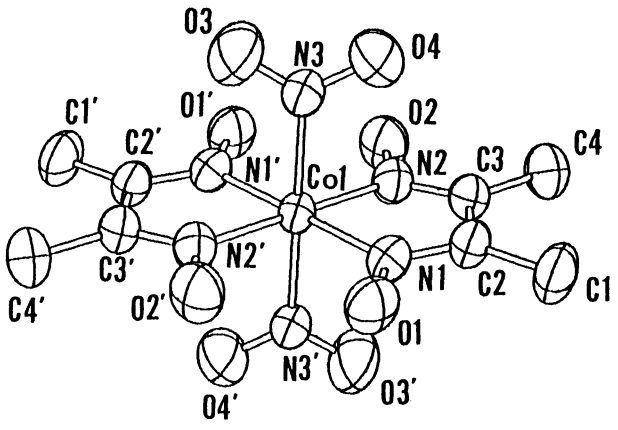

Fig. 1. Structure of the complex anion of **1**. Hydrogen atoms are omitted for clarity.

different between **1** and **2**; the other bond lengths (C-Me and C=N) are almost the same. The two axial ligands of **2** are disposed nearly parallel to each other, the dihedral angle between the planes passing through Co, N3, O3, O4, and Co, N3', O3', O4' atoms being 12.3°.[8] The planes of the nitro groups contain the line separating two dimethylglyoxime groups which is perpendicular to the O3-N3-O4 line in Fig. 2. On the other hand, the planes of the nitro groups of the complex **1** almost dissect the two dmgH ligands in such an unusual conformation[11] as shown in Fig. 2. This difference in the orientation of the axial ligands leads to the appreciably longer Co-N(NO_2) bond of **1** (1.974 Å) than that of **2** (av. 1.946 Å) and that of $[Co(NO_2)_2(NH_3)_4]NO_3 \cdot H_2O$[12] (av. 1.935 Å). These differences observed both in the orientation of the axial ligands and in the Co-N(NO_2) bond length would be attributed to the difference in the interaction of the complex anion with the counter cation. The sodium ion in fact interacts with the O4 and O3' atoms of NO_2^- ($Na^+ \cdots O$: 2.433 and 2.445 Å), the apical O1 atom of the dmg group (2.433 Å) and the oxygen atoms of two water molecules (2.358 and 2.292 Å),[8] while the tetramethylammonium cation does not interact with the particular oxygen atoms of the complex anion of **1**, as judged by the interatomic distances depicted in Fig. 3.

The distinct difference between **1** and **2**[13] observed in the stretching frequencies, $\nu_{OH\cdots O'}$ $\nu_{C=N'}$ and $\nu_{N-O'}$ could be attributed to the difference in the coordination mode of the equatorial dmgH and in the orientation of the axial ligands; the larger Co-N(NO_2) distance is closely related to the coordination mode of the equatorial dmgH. Thus, the remarkable differences in the structural feature between **1** and **2** are consequently correlated with the difference in the interaction of Na^+ and NMe_4^+ cation with the oxygen atoms in the complex anion. In aqueous solutions, the acid-dissociation constant (K_a) and the rate constants for recombination with OH^- ion are quite similar to each other in **1** and **2**.[14]

The present results demonstrate that in solid the several factors such as the nature of the counter ion, degree of hydration, and crystal packing should be crucial to control the axial-equatorial interactions in the series of the inert complexes of $[Co(dmgH)_2(NO_2)_2]^-$ anion.

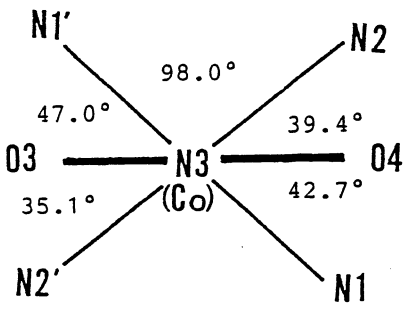

Fig. 2. The orientation of the axial ligands, NO_2^-, relative to the dmgH moiety with bond angles of interest for **1**.

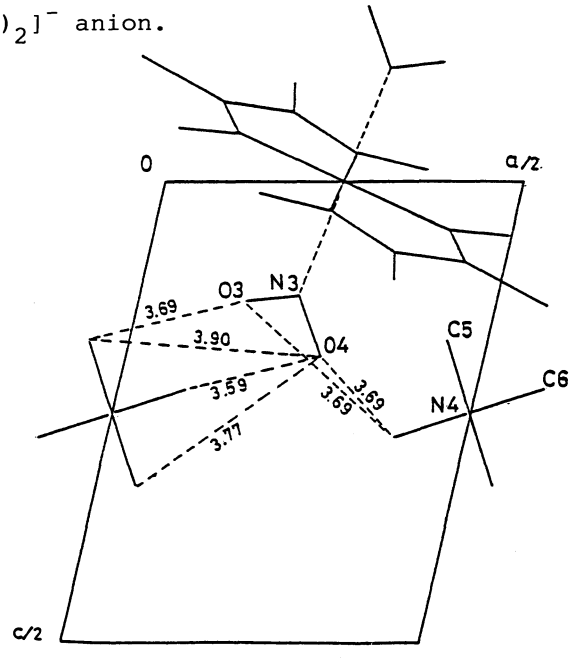

Fig. 3. A side view of the structure of **1** along the b axis. Interatomic distances between NMe_4^+ cation and the complex anion of **1** are also reported.

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11) The most unusual structural feature in the complex **1** is the orientation of the two axial NO_2^- ligands in that those are positioned over the five-membered chelate rings in the dmgH moiety. In the complex **2**, two NO_2^- ligands lie over the pseudo six-membered chelate rings with the OH···O bonds (a usual conformation).
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13) IR(KBr): $\nu_{OH\cdots O}$, 1770 (1744), $\nu_{C=N}$, 1578 (1558), and ν_{N-O}, 1242, 1096 cm^{-1} (1236, 1092 cm^{-1}) for **1** (**2**).
14) The values of pK_a (= $-\log(K_a/\text{mol dm}^{-3})$) of **1** and **2** in aqueous solutions are determined to be 11.88 and 11.80, respectively at I = 0.1 mol dm^{-3} ($NaClO_4$) and 25 °C. The rate constants, k_f (k_b), for the following recombination with OH^- ion are determined to be 1.2 x 10^5 mol^{-1} dm^3 s^{-1} (1.0 x 10^5 mol^{-1} dm^3 s^{-1}) and 890 s^{-1} (900 s^{-1}) for **1** (**2**) from the temperature-jump experiments. $[Co(dmgH)_2(NO_2)_2]^+ + OH^- \rightleftharpoons [Co(dmgH)(dmg)(NO_2)_2] + H_2O$; k_f, k_b.

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