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Preparation and Crystal Structure of $K_3[Mo(NO)(C_2O_4)_3]\cdot 4H_2O$. On pentagonal Bipyramidal Complexes with $\{MoNO\}_4$ Configuration with Simple Ligands

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Introduction

The aqueous solution chemistry of mononuclear Mo complexes of the lower oxidation states is still poorly understood. We were able to show that nitrosyl complexes with $\{MoNO\}^n$ (n = 4, 5, 6) configuration [1] can be interconverted by redox reactions [2, 3]. Complexes with n = 5 (such as $[Mo(NO)(CN)_5]^{3-}$ [3]) and with n = 4 (such as $[Mo(NO)(Cl)_4]^-$ were obtainable by oxidation of $[Mo(NO)(CN)_5]^{4-}$ (n = 6). Whereas, it has been known for a long time that complexes with the configuration $\{MoNO\}^6$ could be prepared by nitrosylation of MoO_4^{2-} with NH_2OH in alkaline medium [1], we have now shown that the reduction in nearly neutral medium in the presence of several simple ligands yields complexes with $\{MoNO\}^4$ configuration. $[Mo(NO)(C_2O_4)_3]^{3-}$ as well as $[Mo_4(NO)_4S_{13}]^{4-}$ [4] and $[Mo(NO)(H_2NO)(NCS)_4]^{2-}$ [5] belong to this class of compounds. In this paper, we report the preparation and the crystal structure of $K_3[Mo(NO)(C_2O_4)_3]\cdot 4H_2O$. A remarkable feature of its structure and that of the other complexes is the seven coordination of Mo, which is rather seldom in the case of transition metal nitrosyl compounds [6]. (Regarding interesting complexes with larger ligands see papers of Wieghardt [7]).

Experimental

Crystals of $K_3[Mo(NO)(C_2O_4)_3]\cdot 4H_2O$ were obtained by reaction of an aqueous solution containing potassium molybdate with $NH_2OH\cdot HCl$ and $K_2C_2O_4\cdot H_2O$. The crystal structure was solved by direct methods and refined by full-matrix least squares to a final R value of 0.026 for 1285 independent reflections having $I > 1.96\sigma(I)$ (Syntex $P2_1$; see Table I). The final atomic coordinates and thermal parameters are given in Table II.

Results and Discussion

The unit cell contains four $K_3[Mo(NO)(C_2O_4)_3]\cdot 4H_2O$. An ORTEP plot of the molecular structure is given in Fig. 1. The structure can be described as a pentagonal bipyramid with the nitrosyl group in one of the apical positions.

Mo, O1, O4, O5, O8 and O12 lie nearly in one plane (sum of the angles: 359.2°) while the remaining oxygen atom (O9) is slightly non-linear with the

TABLE I. Summary of Crystal and Intensity Collection Data.

a	14.026(3) Å
b	7.871(1) Å
c	15.558(3) Å
β	91.77(2)°
V	1716.8 $Å^3$
Z	4
Density	2.24 g/cm^3 calcd.) 2.20 g/cm^3 (exptl.)
Space group	Cc-C_s^4 (monoclinic)
Crystal size	0.1 × 0.1 × 0.1 mm
Radiation	MoKα; $\lambda(K\alpha_1)$ 0.70926, $\lambda(K\alpha_2)$ 0.71354 Å, graphite monochromator
Absorption coefficient	15.6 cm^{-1}
Data collection	θ–2θ mode, range 3–54°, 2θ scan speed 2°···20°/min depending on intensity, background/scan time ratio 1:1, scan from 1.0° below $K\alpha_1$ to 1.0° above $K\alpha_2$ in 2θ; reference reflection every 50 reflections

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TABLE II. $K_3[Mo(NO)(C_2O_4)_3]\cdot4H_2O$: Atomic Coordinates and Thermal Parameters.[a]

	x/a	y/b	z/c	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
K1	−0.0407(1)	0.1027(2)	0.2059(1)	4.40(9)	2.72(8)	2.12(6)	0.80(8)	0.03(6)	−0.31(6)
K2	−0.2536(1)	0.4389(2)	0.1501(1)	2.25(7)	3.66(9)	3.69(8)	0.18(7)	0.29(6)	1.29(7)
K3	0.2509(1)	0.2787(2)	−0.0991(1)	2.40(8)	3.79(9)	5.70(11)	0.24(7)	−0.02(7)	−1.76(8)
Mo	0.0[b]	0.41059(6)	0.0[b]	1.71(2)	1.41(2)	1.45(2)	−0.08(3)	0.21(1)	0.03(3)
O1	−0.0054(4)	0.1977(6)	−0.0851(3)	3.2(2)	2.3(2)	2.0(2)	−0.2(2)	0.5(2)	−0.3(2)
O2	−0.0765(5)	−0.0433(7)	−0.1216(4)	5.8(3)	3.4(3)	3.1(3)	1.5(3)	1.3(2)	1.6(2)
O3	−0.1876(4)	0.0070(7)	0.0238(3)	5.0(3)	2.5(2)	3.6(3)	−1.9(2)	1.7(2)	−0.6(2)
O4	−0.1040(3)	0.2447(6)	0.0445(3)	2.6(2)	1.8(2)	1.7(2)	−0.5(2)	0.4(2)	−0.1(2)
O5	−0.0712(3)	0.5250(6)	0.1006(3)	2.2(2)	1.7(2)	2.5(2)	−0.8(2)	0.4(2)	−0.1(2)
O6	−0.0910(4)	0.7503(7)	0.1850(3)	4.1(3)	2.9(2)	3.4(3)	−0.4(2)	2.0(2)	−0.7(2)
O7	0.0474(4)	0.9080(6)	0.0827(3)	4.1(3)	1.9(2)	3.6(2)	−0.4(2)	0.9(2)	−1.0(2)
O8	0.0575(3)	0.6597(6)	0.0160(3)	2.4(2)	2.0(2)	2.4(2)	−0.5(2)	0.6(2)	−0.1(2)
O9	−0.1009(3)	0.5213(6)	−0.0849(3)	1.5(2)	2.5(2)	2.1(2)	0.2(2)	0.5(2)	0.5(2)
O10	−0.1200(4)	0.6275(6)	−0.2163(3)	2.8(2)	2.2(2)	1.8(2)	0.3(2)	−0.6(2)	0.2(2)
O11	0.0767(4)	0.5914(8)	−0.2338(3)	2.7(2)	5.2(3)	2.1(2)	−0.1(2)	1.1(2)	1.3(2)
O12	0.0829(3)	0.4638(6)	−0.1060(3)	1.8(2)	1.9(2)	1.8(2)	0.3(2)	0.6(2)	0.0(2)
N	0.0953(4)	0.3185(7)	0.0622(3)	2.3(3)	1.4(2)	1.4(2)	0.0(2)	−0.2(2)	0.3(2)
O	0.1621(4)	0.2573(6)	0.0994(3)	2.5(2)	2.5(2)	3.7(3)	0.5(2)	−0.9(2)	0.0(2)
C1	−0.0665(5)	0.0814(9)	−0.0749(4)	3.2(4)	2.0(3)	2.3(3)	−0.2(3)	0.3(3)	0.1(3)
C2	−0.1259(5)	0.1073(9)	0.0029(4)	2.7(3)	2.1(3)	2.4(3)	−0.3(3)	−0.2(3)	0.1(3)
C3	−0.0531(5)	0.6779(9)	0.1265(5)	2.3(3)	2.1(3)	2.6(3)	0.0(3)	0.0(3)	0.3(3)
C4	0.0239(5)	0.7606(9)	0.0734(4)	2.7(3)	2.1(3)	1.8(3)	0.0(3)	0.1(2)	0.3(3)
C5	−0.0716(5)	0.5669(8)	−0.1586(4)	2.4(3)	1.1(3)	1.8(3)	−0.2(2)	0.4(2)	0.6(2)
C6	0.0389(5)	0.5415(9)	−0.1700(4)	2.0(3)	1.9(3)	2.5(3)	0.2(3)	0.3(3)	0.4(2)
(H2O)1	−0.2632(4)	0.0943(7)	0.1861(4)	4.3(3)	3.8(3)	4.6(3)	1.0(3)	0.4(2)	0.8(3)
(H2O)2	−0.3760(4)	0.4272(9)	0.2877(4)	3.1(3)	6.1(4)	3.9(3)	−1.1(3)	0.9(2)	−0.8(3)
(H2O)3	0.2595(5)	0.2400(11)	0.3075(5)	5.4(4)	9.9(6)	6.9(5)	2.2(4)	1.0(3)	3.6(4)
(H2O)4	−0.3016(5)	0.4466(9)	−0.0411(5)	3.8(3)	6.6(4)	7.1(4)	−0.1(3)	1.9(3)	−0.8(3)

[a] Anisotropic temperature factor is defined by $\exp[-\frac{1}{4}(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*]$ with the B_{ij}s in A^2. [b] Hled fixed to define the origin.

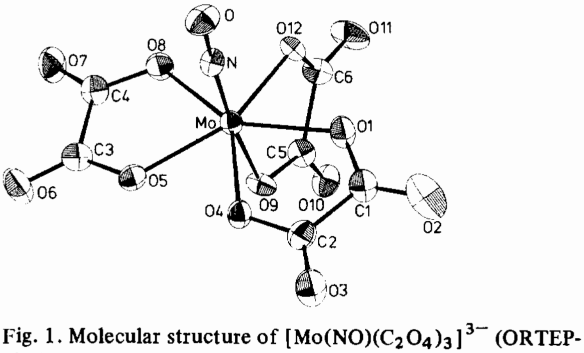

Fig. 1. Molecular structure of $[Mo(NO)(C_2O_4)_3]^{3-}$ (ORTEP-plot).

Mo–N-group (O9–Mo–N: 173.3(2)°). The Mo–O distances, with the exception of Mo–O1 and Mo–O8 are almost identical (average: 2.091 Å). The other 2 Mo–O distances (average: 2.134 Å) are slightly larger. The Mo–N and N–O bond distances (1.780(5) Å and 1.188(7) Å) and the MoNO angle (176.0(5)°) also show good agreement with the corresponding values in other compounds with $\{MoNO\}^4$ configuration, as for instance $(NH_4)_4[Mo_4(NO)_4S_{13}]\cdot2H_2O$, in which all Mo atoms have the coordination number 7, too (see also [6]).

Whereas complexes with $\{MoNO\}^6$ configuration can be prepared by nitrosylation of MoO_4^{2-} with NH_2OH in strong alkaline medium like $K_4[Mo(NO)(CN)_5]$ [1], the corresponding reaction in nearly neutral medium gives yellow solutions containing complexes with $\{MoNO\}^4$ configuration. Depending on the pH value and the type of other ligands, interesting complexes like $[Mo_4(NO)_4S_{13}]^{4-}$ [4] (a tetranuclear complex with five S_2^{2-} ligands), $[Mo(NO)(H_2NO)(NCS)_4]^{2-}$ [5] or $[Mo(NO)(CH_3)_2CNO(NCS)_4]^{2-}$ [8] (oximato (O,N) complex) can be isolated. All compounds have a pentagonal bipyramidal structure, which seems to be characteristic for the $\{MoNO\}^4$ configuration type complexes containing at least one bidentate ligand (see also [8]).

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