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X-Ray Diffraction Study of Ammonium Octamolybdate

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Abstract—Ammonium isopolymolybdate $(NH_4)_4[Mo_8O_{26}]\cdot 4H_2O$ was prepared for the first time and studied by X-ray diffraction analysis.

Keywords: ammonium octamolybdate, polyanion, X-ray diffraction

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The iso- and heteropolycompounds form a vast group of polybasic acids and their salts containing a complex polyanion. Chemistry of such compounds has been developing over the last century, and the views on their structure and chemical properties have been changed several times. The related studies has been comprehensively reviewed in the literature [1–6].

The systematic investigation of preparation and properties of iso- and heteropolycompounds of vanadium, molybdenum, and tungsten with various complex forming species and the outer-sphere cations has extended the theoretical views on these compounds and the possibilities of their practical application, involving development of catalysts and electrochemical cell components [7, 8].

In this work we prepared ammonium octamolybdate $(NH_4)_4[Mo_8O_{26}]\cdot 4H_2O$ **I** and studied its structure by X-ray diffraction analysis.

Compound **I** was prepared by heating of saturated ammonium paramolybdate solution in the presence of nitric acid at 200°C in a pressure reactor. The product was a pale-yellow crystalline solid.

The basic unit building the crystal of compound **I** consisted of the $[Mo_8O_{26}]^{4-}$ polyanion, four ammonium cations, and four water molecules (Fig. 1). The isopolyanion was formed by eight distorted MoO_6 octahedrons, connected via the edges. The number of the multiple (the shortest) terminal metal–oxygen bonds was different for the MoO_6 octahedrons. The Mo^1 and Mo^{1A} were connected to one terminal oxygen each, and the Mo^2, Mo^3, Mo^4, Mo^{2A}, Mo^{3A}, and Mo^{4A} were bound to two terminal oxygen atoms each, with the average Mo=O distance of 1.70 Å. The six bridging fragments Mo–O–Mo in the anion structure were almost linear. Note the formation of the two molybdenum-oxygen bridges with coordination number of the O^1 and O^{1A} oxygen atoms equal to five and that of the O^2, O^{2A}, O^5, and O^{5A} atoms equal to three. The interatomic distances and the bond angles found in compound **I** are collected in Tables 1 and 2, respectively. The structure of the $[Mo_8O_{26}]^{4-}$ anion and the packing of the $(NH_4)_4[Mo_8O_{26}]\cdot 4H_2O$ units in the crystal are illustrated by Figs. 1 and 2, respectively. Schematic representation of the MoO_6 octahedrons constituting the $[Mo_8O_{26}]^{4-}$ polyanion is shown in Fig. 3.

EXPERIMENTAL

Ammonium octamolybdate I. 100 mL of ammonium paramolybdate solution (saturated at 80°C) acidified with nitric acid to pH 2 was heated in a pressure reactor at 200°C during 6 h. The cooled solution was then evaporated in a dessicator over P_2O_5. After several days, pale-yellow crystals appeared in the

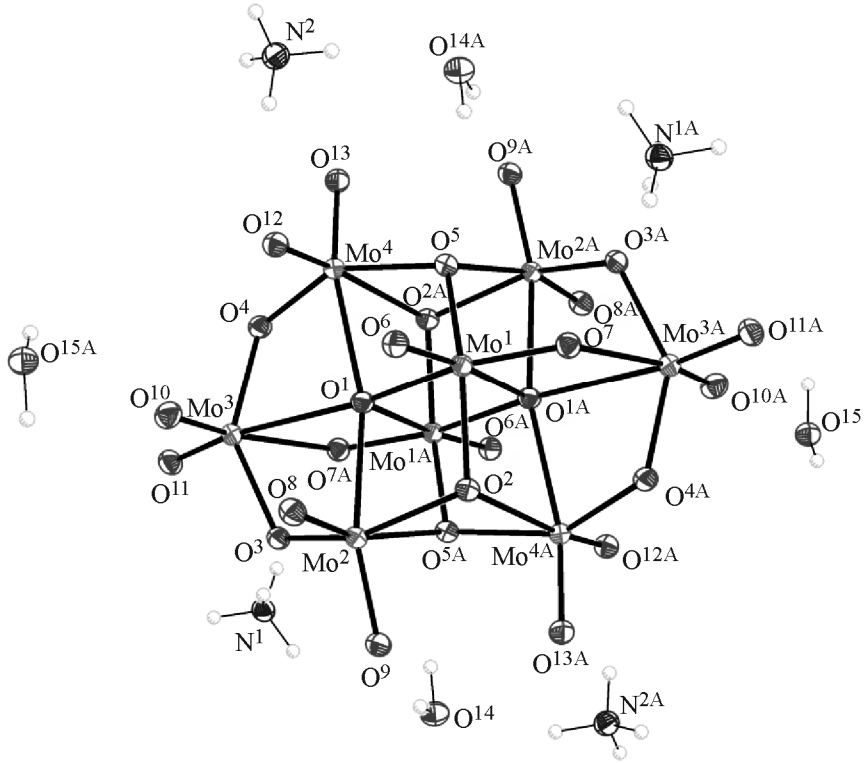

Fig. 1. Crystal structure of the $[Mo_8O_{26}]^{4-}$ anion.

solution; they were filtered off, washed with ethanol, and dried. The product chemical composition was determined by mass spectrometry. The presence of hydrate water was confirmed by thermogravimetry.

X-ray study. Parameters of the unit cell and the reflections intensities of compound **I** were measured using the Bruker SMART APEX-II CCD automated diffractometer (100 K, MoK_α radiation, graphite mono-

Table 1. Interatomic distances in compound **I**

Bond	*d*, Å	Bond	*d*, Å	Bond	*d*, Å
Mo^1–O^6	1.7007(17)	Mo^3–O^{11}	1.6997(18)	O^{14}–H^{14A}	0.9001
Mo^1–O^7	1.7473(17)	Mo^3–O^{10}	1.7008(19)	O^{14}–H^{14B}	0.9000
Mo^1–O^5	1.9432(17)	Mo^3–O^4	1.9388(17)	O^{15}–H^{15A}	0.9000
Mo^1–O^2	1.9502(17)	Mo^3–O^3	1.9432(17)	O^{15}–H^{15B}	0.9000
Mo^1–O^1	2.1825(17)	Mo^3–$O^{7\#1}$	2.3144(18)	N^1–H^{1A}	0.8999
Mo^1–$O^{1\#1}$	2.3470(17)	Mo^3–O^1	2.4842(17)	N^1–H^{1B}	0.9001
Mo^2–O^8	1.7110(18)	Mo^4–O^{13}	1.7048(17)	N^1–H^{1C}	0.9000
Mo^2–O^9	1.7162(18)	Mo^4–O^{12}	1.7153(17)	N^1–H^{1D}	0.9000
Mo^2–O^3	1.8940(17)	Mo^4–O^4	1.8956(17)	N^2–H^{2A}	0.9000
Mo^2–O^2	2.0051(16)	Mo^4–O^5	2.0114(17)	N^2–H^{2B}	0.9000
Mo^2–O^1	2.3049(16)	Mo^4–O^1	2.3076(16)	N^2–H^{2C}	0.9000
Mo^2–$O^{5\#1}$	2.3130(17)	Mo^4–$O^{2\#1}$	2.3178(17)	N^2–H^{2D}	0.9000

Table 2. Bond angles in compound **I**

Angle	ω, deg	Angle	ω, deg	Angle	ω, deg
$O^{6}Mo^{1}O^{7}$	105.49(9)	$O^{11}Mo^{3}O^{4}$	103.73(8)	$Mo^{2}O^{1}Mo^{4}$	163.25(8)
$O^{6}Mo^{1}O^{5}$	101.91(8)	$O^{10}Mo^{3}O^{4}$	99.09(8)	$Mo^{1}O^{1}Mo^{1\#1}$	104.26(7)
$O^{7}Mo^{1}O^{5}$	98.24(8)	$O^{11}Mo^{3}O^{3}$	102.19(8)	$Mo^{2}O^{1}Mo^{1\#1}$	97.41(6)
$O^{6}Mo^{1}O^{2}$	99.92(8)	$O^{10}Mo^{3}O^{3}$	99.35(8)	$Mo^{4}O^{1}Mo^{1\#1}$	97.42(6)
$O^{7}Mo^{1}O^{2}$	96.62(8)	$O^{4}Mo^{3}O^{3}$	142.52(7)	$Mo^{1}O^{1}Mo^{3}$	163.84(8)
$O^{5}Mo^{1}O^{2}$	149.15(7)	$O^{11}Mo^{3}O^{7\#1}$	90.47(8)	$Mo^{2}O^{1}Mo^{3}$	85.62(5)
$O^{6}Mo^{1}O^{1}$	96.68(8)	$O^{10}Mo^{3}O^{7\#1}$	163.71(8)	$Mo^{4}O^{1}Mo^{3}$	86.14(5)
$O^{7}Mo^{1}O^{1}$	157.78(7)	$O^{4}Mo^{3}O^{7\#1}$	76.81(7)	$Mo^{1\#1}O^{1}Mo^{3}$	91.90(6)
$O^{5}Mo^{1}O^{1}$	78.26(7)	$O^{3}Mo^{3}O^{7\#1}$	76.38(7)	$Mo^{1}O^{2}Mo^{2}$	109.59(8)
$O^{2}Mo^{1}O^{1}$	77.79(7)	$O^{11}Mo^{3}O^{1}$	159.58(8)	$Mo^{1}O^{2}Mo^{4\#1}$	109.76(7)
$O^{6}Mo^{1}O^{1\#1}$	172.37(7)	$O^{10}Mo^{3}O^{1}$	94.59(8)	$Mo^{2}O^{2}Mo^{4\#1}$	104.20(7)
$O^{7}Mo^{1}O^{1\#1}$	82.06(7)	$O^{4}Mo^{3}O^{1}$	73.18(6)	$Mo^{2}O^{3}Mo^{3}$	116.16(9)
$O^{5}Mo^{1}O^{1\#1}$	77.67(6)	$O^{3}Mo^{3}O^{1}$	73.05(6)	$Mo^{4}O^{4}Mo^{3}$	117.32(9)
$O^{2}Mo^{1}O^{1\#1}$	77.82(6)	$O^{7\#1}Mo^{3}O^{1}$	69.12(6)	$Mo^{1}O^{5}Mo^{4}$	109.24(8)
$O^{1}Mo^{1}O^{1\#1}$	75.74(7)	$O^{13}Mo^{4}O^{12}$	104.38(9)	$Mo^{1}O^{5}Mo^{2\#1}$	110.10(8)
$O^{8}Mo^{2}O^{9}$	106.04(9)	$O^{13}Mo^{4}O^{4}$	100.58(8)	$Mo^{4}O^{5}Mo^{2\#1}$	104.16(7)
$O^{8}Mo^{2}O^{3}$	102.43(8)	$O^{12}Mo^{4}O^{4}$	102.04(8)	$Mo^{1}O^{7}Mo^{3\#1}$	116.89(9)
$O^{9}Mo^{2}O^{3}$	101.03(8)	$O^{13}Mo^{4}O^{5}$	100.26(8)	$H^{14A}O^{14}14B$	109.5
$O^{8}Mo^{2}O^{2}$	97.17(8)	$O^{12}Mo^{4}O^{5}$	95.88(8)	$H^{15A}O^{15}15B$	108.7
$O^{9}Mo^{2}O^{2}$	98.94(8)	$O^{4}Mo^{4}O^{5}$	148.06(7)	$H^{1A}N^{1}H^{1B}$	114.0
$O^{3}Mo^{2}O^{2}$	146.78(7)	$O^{13}Mo^{4}O^{1}$	160.49(7)	$H^{1A}N^{1}H^{1C}$	104.4
$O^{8}Mo^{2}O^{1}$	93.62(7)	$O^{12}Mo^{4}O^{1}$	94.83(7)	$H^{1B}N^{1}H^{1C}$	114.0
$O^{9}Mo^{2}O^{1}$	159.88(8)	$O^{4}Mo^{4}O^{1}$	78.29(7)	$H^{1A}N^{1}H^{1D}$	104.4
$O^{3}Mo^{2}O^{1}$	78.33(7)	$O^{5}Mo^{4}O^{1}$	74.01(6)	$H^{1B}N^{1}H^{1D}$	114.0
$O^{2}Mo^{2}O^{1}$	73.87(6)	$O^{13}Mo^{4}O^{2\#1}$	88.56(7)	$H^{1C}N^{1}H^{1D}$	105.1
$O^{8}Mo^{2}O^{5\#1}$	163.48(7)	$O^{12}Mo^{4}O^{2\#1}$	163.58(7)	$H^{2A}N^{2}H^{2B}$	111.0
$O^{9}Mo^{2}O^{5\#1}$	88.10(7)	$O^{4}Mo^{4}O^{2\#1}$	85.11(7)	$H^{2A}N^{2}H^{2C}$	103.9
$O^{3}Mo^{2}O^{5\#1}$	82.67(7)	$O^{5}Mo^{4}O^{2\#1}$	71.51(6)	$H^{2B}N^{2}H^{2C}$	107.2
$O^{2}Mo^{2}O^{5\#1}$	71.71(6)	$O^{1}Mo^{4}O^{2\#1}$	71.93(6)	$H^{2A}N^{2}H^{2D}$	111.5
$O^{1}Mo^{2}O^{5\#1}$	71.82(6)	$Mo^{1}O^{1}Mo^{2}$	92.11(6)	$H^{2B}N^{2}H^{2D}$	111.5
$O^{11}Mo^{3}O^{10}$	105.82(9)	$Mo^{1}O^{1}Mo^{4}$	91.76(6)	$H^{2C}N^{2}H^{2D}$	111.5

chromator, φ and ω-scanning). The extinction of X-ray radiation was accounted for using the SADABS software [9]. The principal crystal structure parameters are collected in Table 3. The structure was solved by the direct method and refined by the full-matrix least-squares method under the anisotropic approximation for the non-hydrogen atoms.

The intrinsic symmetry of the $[Mo_8O_{26}]^{4-}$ polyanion was of *C*2*h* (2/*m*), and it occupied the partial position

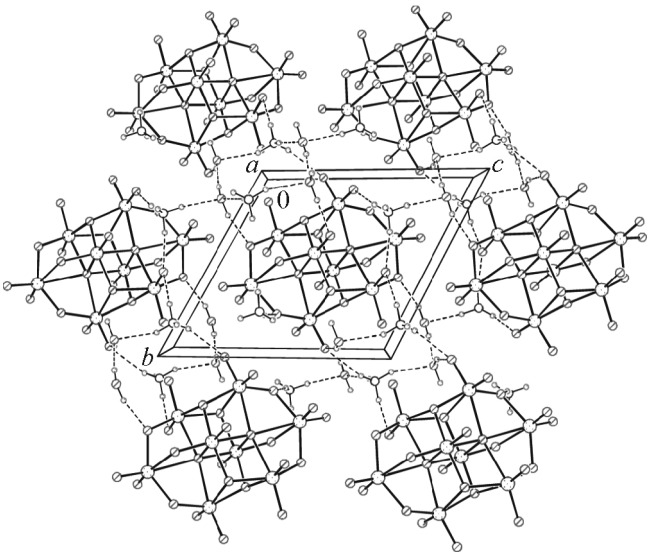

Fig. 2. Packing of the units in the $(NH_4)_4[Mo_8O_{26}]\cdot 4H_2O$ crystal.

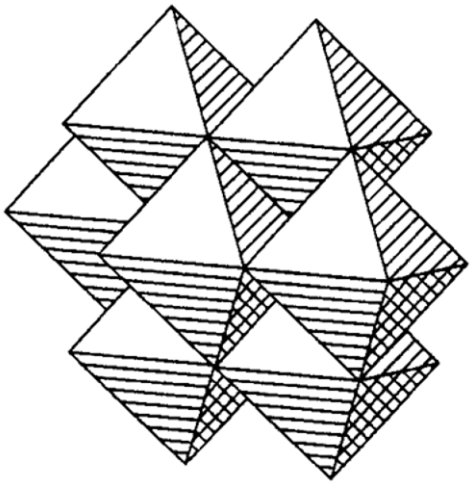

Fig. 3. Schematic representation of the MoO_6 octahedrons, the building blocks of the $[Mo_8O_{26}]^{4-}$ anion. One of the octahedrons is completely hidden by the other seven octahedrons.

in the inversion center. The crystal contained two solvate water molecules in the independent part of the unit cell. Hydrogen atoms of ammonium cations and water molecules were found via the differential Fourier synthesis and included into the refinement with the fixed position (the *rider* model) and thermal [U_{iso}(H) = 1.5U_{eq}(O,N)] parameters. All the calculations were performed using the SHELXTL software package [10]. The tables of atomic coordinates, bond lengths, bond angles, and anisotropic temperature parameters of compound **I** were deposited at the Crystal Structure Depot (Karlsruhe, Germany) under CSD 427451.

Table 3. X-ray diffraction data and parameters of compound **I** structure refinement

Parameter	Value	Parameter	Value
Empirical formula	$H_{24}Mo_8N_4O_{30}$	V, Å^3	693.85(4)
M	1327.75	d_{calc}, g/cm^3	3.178
T, K	100(2)	F(000)	628
Crystal size, mm	0.25×0.20×0.20	μ, mm^{-1}	3.613
Crystal shape	Prism	$2\theta_{max}$, deg	64
λ, Å	0.71073	Number of measured reflections	10245
Crystal system	Triclinic	Number of independent reflections	4777
Space group	P-1	Number of reflections with $I > 2\sigma(I)$	4517
Z	1	Number of refined parameters	191
a, Å	7.8217(3)	$R_1[I > 2\sigma(I)]$	0.0239
b, Å	10.0403(3)	wR_2 (all data)	0.0579
c, Å	10.5817(3)	GOF	1.002
α, deg	113.495(1)	T_{min}; T_{max}	0.465 / 0.532
β, deg	100.803(1)		
γ, deg	105.275(1)		

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