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Manganese(II) 9-Molybdomanganate(IV), $[Mn(H_2O)_4]_3 \cdot [MnMo_9O_{32}] \cdot 2H_2O$: Synthesis, Thermal Analysis, IR Spectra, and Crystal Structure

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Abstract—The $[Mn(H_2O)_4]_3 \cdot [MnMo_9O_{32}] \cdot 2H_2O$ complex was synthesized and studied by X-ray diffraction, thermogravimetry, powder X-ray diffraction, and IR spectroscopy. The crystals are trigonal: space group *R*32, $a = 14.811(2)$ Å, $c = 14.232(2)$ Å, $V = 2703.7(8)$ Å^3, $M = 1848.5$, $Z = 3$, ρ(calcd.) = 3.419 g/cm^3.

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Heteropoly compounds (**HPC**) constitute a large class of polyoxo compounds coordination compounds composed of metal–oxygen octahedra MO_6, which share vertices and edges to form a strong framework, i.e., heteropolyanion (**HPA**). Heteropoly compounds are widely used as homogeneous and heterogeneous, acid, and oxidating catalysts [1–4] and as model systems in studying fundamental catalysis problems [5, 6].

Today, heteropoly compounds are known with *p*-, *d*-, and *f* complex-forming elements; hydrogen, alkali, and alkaline earth metal and ammonium ions can serve as the cations [7, 8].

The first data on molybdomanganates (red crystals of the potassium and ammonium salts of the composition $5M_2O \cdot Mn_2O_3 \cdot 16MoO_3 \cdot 12H_2O$) were reported in [9]. Later, ruby-red crystals of $Na_2O \cdot MnO_2 \cdot 12MoO_3 \cdot nH_2O$ and $K_2O \cdot MnO_2 \cdot 12MoO_3 \cdot nH_2O$ [10] and the salts $3K_2O \cdot MnO_2 \cdot 8MoO_3 \cdot 5H_2O$ and $2(NH_4)_2O \cdot K_2O \cdot Mn_2O_3 \cdot 10MoO_3 \cdot 5H_2O$ [11] were synthesized. The preparation of potassium and ammonium molybdomanganates with different Mn : Mo ratio was described in [12].

Previously, we synthesized and studied ammonium 9-molybdomanganate [13]. It was of interest to synthesize and study by X-ray diffraction, powder X-ray diffraction, IR spectroscopy, and thermogravimetry $[Mn(H_2O)_4]_3 \cdot [MnMo_9O_{32}] \cdot 2H_2O$ (**I**).

EXPERIMENTAL

Compound **I** was synthesized using a known procedure [7] that was slightly modified. To a saturated ammonium molybdate solution acidified to pH 3 with nitric acid, a 30% solution of hydrogen peroxide (20 ml) was added with stirring and then, the Mn(II) sulfate solution. The mixture was heated on a water bath for 3.5 h. In 3 days, red-brown crystals were formed that were recrystallized from hot water and washed with an alcohol.

The elemental analysis for Mo, Mn was performed by a known procedure [14]. The composition of the synthesized compound **I** was confirmed by the mass spectrometry method.

For $[Mn(H_2O)_4]_3 \cdot [MnMo_9O_{32}] \cdot 2H_2O$

anal. calcd., %:	Mn 12.03;	Mo 46.71;	O 27.58;	H_2O 13.67
Found, %:	Mn 11.90;	Mo 46.74;	O 27.69;	H_2O 13.63

The powder X-ray diffraction analysis was performed on a STOE IP autodiffractometer, $2\theta = 5°–80°$. X-ray pictures were indexed with the Powder-2 program package. The comparison of X-ray picture obtained with the PCPDFWIN database showed that compound **I** is individual and does not contain impurities. The powder X-ray diffraction data are available from the authors (e-mail: gkaziev@mail.ru.).

TGA of **I** was carried out on a Paulik–Paulik–Erdey setup in the temperature range of 20–1000°C (heating rate 10 K/min, a 100 g sample) using calcined alumina as the reference.

IR spectra were recorded on a Perkin Elmer spectrophotometer at 400–4000 cm^{-1} (as KBr pellets).

Table 1. Selected bond lengths and bond angles in $[Mn(H_2O)_4]_3 \cdot [MnMo_9O_{32}] \cdot 2H_2O$*

Bond	*d*, Å	Bond	*d*, Å
Mo(1)–O(4)	1.707(2)	Mo(2)–O(1d)	2.206(2)
Mo(1)–O(3b)	1.967(2)	Mo(2)–O(1a)	2.240(2)
Mo(1)–O(1b)	2.229(2)	Mo(2)–O(1a)	1.889(2)
Mo(2)–O(5)	1.700(2)	Mn(2)–O(1*w*a)	1.931(2)
Mo(2)–O(6)	1.715(2)	Mn(2)–O(2*w*)	1.999(4)
Mo(2)–O(3)	1.881(2)	Mn(2)–O(6)	2.232(2)
Mo(2)–O(2)	2.076(1)	Mn(2)–O(1*w*b)	2.060(2)
Angle	**ω, deg**	**Angle**	**ω, deg**
O(4a)Mo(1)O(4)	106.19(1)	Mo(2e)O(2)Mo(2)	107.99(9)
O(4a)Mo(1)O(3b)	96.67(1)	Mo(2)O(3)Mo(1e)	112.34(1)
O(4)Mo(1)O(3b)	100.17(1)	O(1a)Mn(1)O(1)	101.29(1)
O(3b)Mo(1)O(3c)	151.80(1)	O(1a)Mn(1)O(1)	86.61(9)
O(4a)Mo(1)O(1b)	91.76(1)	O(1b)Mn(1)O(1)	169.23(1)
O(4)Mo(1)O(1b)	161.22(1)	O(1*w*ae)Mn(2)O(1*w*a)	73.60(1)
O(3b)Mo(1)O(1b)	82.77(9)	O(1*w*ae)Mn(2)O(2*w*)	170.10(5)
O(3c)Mo(1)O(1b)	74.29(8)	O(1*w*a)Mn(2)O(2*w*)	98.50(7)
O(1b)Mo(1)O(1c)	71.03(1)	O(2*w*)Mn(2)O(2*w*e)	90.00(3)
O(5)Mo(2)O(6)	105.74(1)	O(1*w*ae)Mn(2)O(1*w*b)	91.80(8)
O(5)Mo(2)O(3)	102.10(1)	O(2*w*)Mn(2)O(1*w*b)	80.40(6)
O(6)Mo(2)O(3)	102.42(1)	O(2*w*e)Mn(2)O(1*w*b)	167.90(7)
O(5)Mo(2)O(2)	90.10(1)	O(1*w*be)Mn(2)O(1*w*b)	110.00(3)
O(6)Mo(2)O(2)	101.48(1)	O(1*w*af)Mn(2)O(6)	85.50(5)
O(3)Mo(2)O(2)	148.97(1)	O(1*w*a)Mn(2)O(6)	89.90(5)
O(5)Mo(2)O(1d)	95.70(1)	O(2*w*)Mn(2)O(6)	88.63(1)
O(6)Mo(2)O(1d)	158.16(1)	O(2*w*f)Mn(2)O(6)	95.44(4)
O(3)Mo(2)O(1d)	76.48(8)	O(1*w*bf)Mn(2)O(6)	84.90(6)
O(2)Mo(2)O(1d)	73.96(8)	O(1*w*b)Mn(2)O(6)	91.80(6)
O(5)Mo(2)O(1d)	160.98(1)	O(6f)Mn(2)O(6)	174.26(1)
O(6)Mo(2)O(1a)	86.90(1)	Mn(1)O(1)Mo(2d)	101.31(1)
O(3)Mo(2)O(1a)	88.60(9)	Mn(1)O(1)Mo(1e)	101.20(8)
O(2)Mo(2)O(1a)	73.22(9)	Mo(2d)O(1)Mo(1e)	92.26(7)
O(1d)Mo(2)O(1a)	71.30(1)	Mn(1)O(1)Mo(2a)	100.06(8)
Mo(2d)O(1)Mo(2a)	98.13(7)	Mo(2)O(6)Mn(2)	158.16(1)
Mo(1e)O(1)Mo(2a)	153.96(1)		

* The coordinates of symmetrically equivalent atoms: (a) $-x, -x + y, -z + 1$; (b) $y, x, -z + 1$; (c) $-y, -y, z$; (d) $-y, -y, -z + 1$; (e) $-x + y, -x, z$; (f) $-y - 1/3, -y - 2/3, -z + 1/3$.

Table 2. The coordinates of atoms (×10^4) and their equivalent thermal parameters (×10^3) for $[Mn(H_2O)_4]_3 \cdot [MnMo_9O_{32}] \cdot 2H_2O$

Atom	x	y	z	U_{eq}, Å^2
Mo(1)	0	2154(1)	5000	18(1)
Mo(2)	617(1)	–887(1)	3235(1)	17(1)
Mn(1)	0	0	50000	12(1)
Mn(2)	–912(1)	–3333	1667	31(1)
O(1)	699(2)	–459(2)	5810(1)	15(1)
O(2)	0	0	2715(2)	17(1)
O(3)	1217(2)	–1227(2)	4242(2)	19(1)
O(4)	636(2)	3164(2)	5769(2)	29(1)
O(5)	1632(2)	–296(2)	2472(2)	30(1)
O(6)	–213(2)	–2086(2)	2757(2)	29(1)
O(1*w*a)	–202(14)	–4000(20)	2213(10)	77(6)
O(1*w*b)	–605(18)	–4320(20)	2457(14)	102(8)
O(2*w*)	–2215(3)	–4031(4)	2435(3)	73(2)
O(3*w*)	364(14)	–283(15)	779(10)	82(4)

X-ray diffraction analysis was carried out on automated Enraf-Nonius CAD-4 (MoK_α radiation, λ = 0.71073 Å) at room temperature.

The crystals are trigonal: a = 14.811(2), c = 14.232(2) Å, V = 2703.7(8) Å^3, M = 1855.5, Z = 3, ρ(calcd.) = 3.419 g/cm^3, space group $R32$.

The red-brown single crystal 0.32 × 0.32 × 0.26 mm in size was used. Three control reflections measured every 100 min showed constant intensities to within 0.4%. Altogether 2790 reflections were recorded, including 1751 independent reflections ($I > 2\sigma(I)$) in the θ range of 2.14°–29.98° (R_{int} = 0.0191). The structure was solved by the direct method and refined by the full-matrix least-squares method in the anisotropic approximation for non-hydrogen atoms. An absorption correction was applied (μ = 4.505 mm^{-1}) by ψ-scanning, T_{min} = 0.326, T_{max} = 0.387. The range of indices: $0 \le h \le 20$, $-20 \le k \le 18$, $0 \le l \le 19$. The value Δ_{max} = 0.427 e Å^{-3}, Δ_{min} = –0.474 e Å^{-3}. The final values R_1 = 0.0168, wR_2 = 0.0422 (for $I > 2\sigma(I)$), R_1 = 0.0182, wR_2 = 0.0425 (for all), GOOF = 1.136, extinction coefficient 0.00238(8). The calculations were carried out with the SHELX-97 program package [15]. The bond lengths and bond angles are listed in Table 1, the coordinates of the atoms and the thermal parameters are given in Table 2.

RESULTS AND DISCUSSION

The structure of the HPA $[MnMo_9O_{32}]^{6-}$ can be represented as a result of removal of three out of the six octahedra lying in the plane perpendicular to the C_3 axis of the hypothetical anion $[MnO_4Mo_{12}O_{36}]^{4-}$containing twelve MoO_6 octahedra [16, 17].

Symmetrically equivalent octahedral with the atoms Mo(2), Mo(2a), Mo(2b), Mo(2c), Mo(2d), Mo(2e) each contain two terminal atoms O(5) and O(6) of the *cis*-MoO_2 groups (Mo=O_{term} 1.700 and 1.715 Å, respectively), the bridging atom μ_2-O(3) (Mo(2)–O(3) 1.881 Å), the bridging atom μ_3-O(2), linking three Mo atoms in the triplet Mo_3O_{13} (Mo(2)–O(2) 2.076 Å), and two atoms μ_4-O(1a) and μ_4-O(1b), linking three Mo atoms in the triplet Mo_3O_{13} with the central heteroatom Mn(1) (Mo(2)–O(1d) 2.206, Mo(2)–O(1a) 2.240 Å).

The HPA also contains three Mo(1)O(6) octahedral that are not bonded with the complex cation $[Mn(H_2O)_4]^{2+}$ and each contain two terminal O(4) and O(4a) atoms (Mo(1)=O(4) 1.707 Å), two atoms O(3) and O(3a) forming the bridging bond with the Mo atoms of two different triplet groups Mo_3O_6 (Mo(1)–O(3) 1.967 Å) and two atoms O(1) and O(1b), bonding three Mo atoms and a central atom Mn(1) (Mo(1)–O(1) 2.229 Å).

The Mn(1) heteroatom has a regular octahedral surrounding of the O atoms (Mn(1)–O 1.889 Å).

The outer-sphere hydrated complex cation forms an octahedron containing four O atoms of water molecules $[Mn(H_2O)_4]^{2+}$ (Mn(2)–O(1*w*) 1.999, Mn(2)–O(2*w*) 1.931 Å), two O(6) atoms (Mn(2)–O(6) 2.232 Å). The O(6) atoms of dioxo group *cis*-MoO_2 act as the bridging bonds between the HPA and the outer-sphere cations in the HPC.

The coordination of the outer-sphere cation brings about some changes in the bond lengths of the HPA in accordance with the regularities discovered in [17–19]. It was found that the complex formation leads to some elongation of one Mo=O_{term} bond in the Mo(2)O(6) octahedron of the triplet group Mo_3O_{13} from 1.707 to 1.715 Å and shortening of the other bond from 1.707 to 1.700 Å (Fig. 2).

The water molecules in compound **I** have partially occupied positions.

The TGA of the title compound **I** (Fig. 3) revealed three endotherms, the first (at 125°C) corresponding to dehydration of the compound with removal of two crystallization water molecules. The second endotherm at 330°C corresponds to removal of 12 water molecules of the outer-sphere complex cation and decomposition of the HPC with the formation of the brown mixture $4MnO_2 + 9MoO_3$. The third endotherm (at 700°C) refers to removal of nine MoO_3 molecules. The scheme of the thermal decomposition is as follows:

$$[Mn(H_2O)_4]_3 \cdot [MnMo_9O_{32}] \cdot 2H_2O$$

$$\xrightarrow[125°C]{-2H_2O} [Mn(H_2O)_4]_3 \cdot [MnMo_9O_{32}]$$

$$\xrightarrow[330°C]{-12H_2O,\ 3/2O_2} 4MnO_2 + 9MoO_3 \xrightarrow[700°C]{-9MoO_3} 4MnO_2.$$

IR spectra of the HPC are sufficiently characteristic for the compounds of this class belonging to different

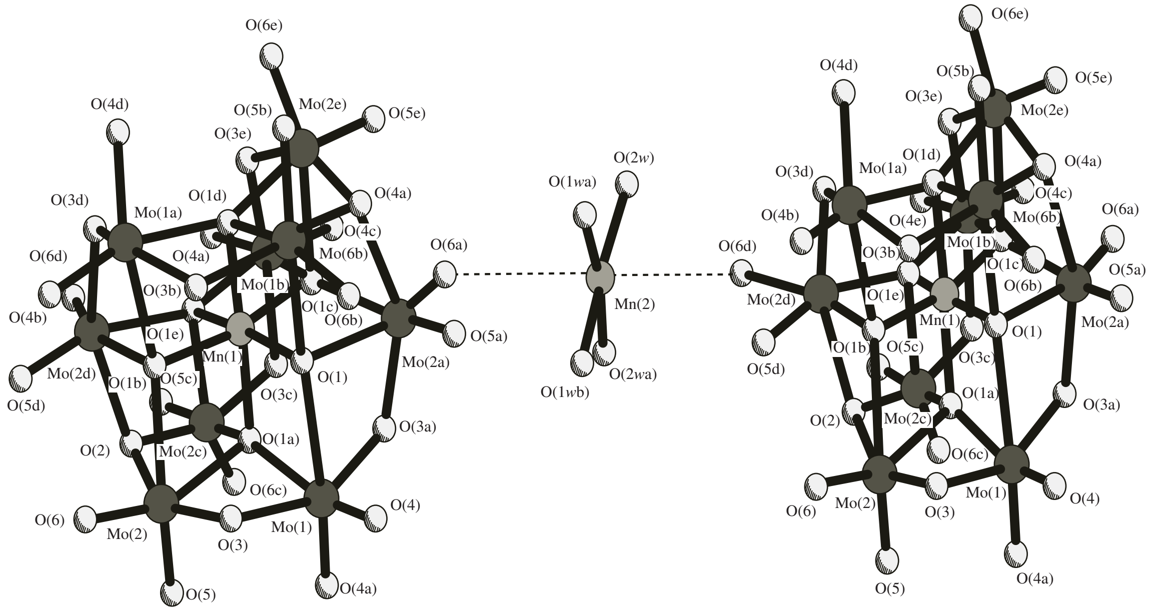

Fig. 1. The structure of HPA $[MnMo_9O_{32}]^{6-}$.

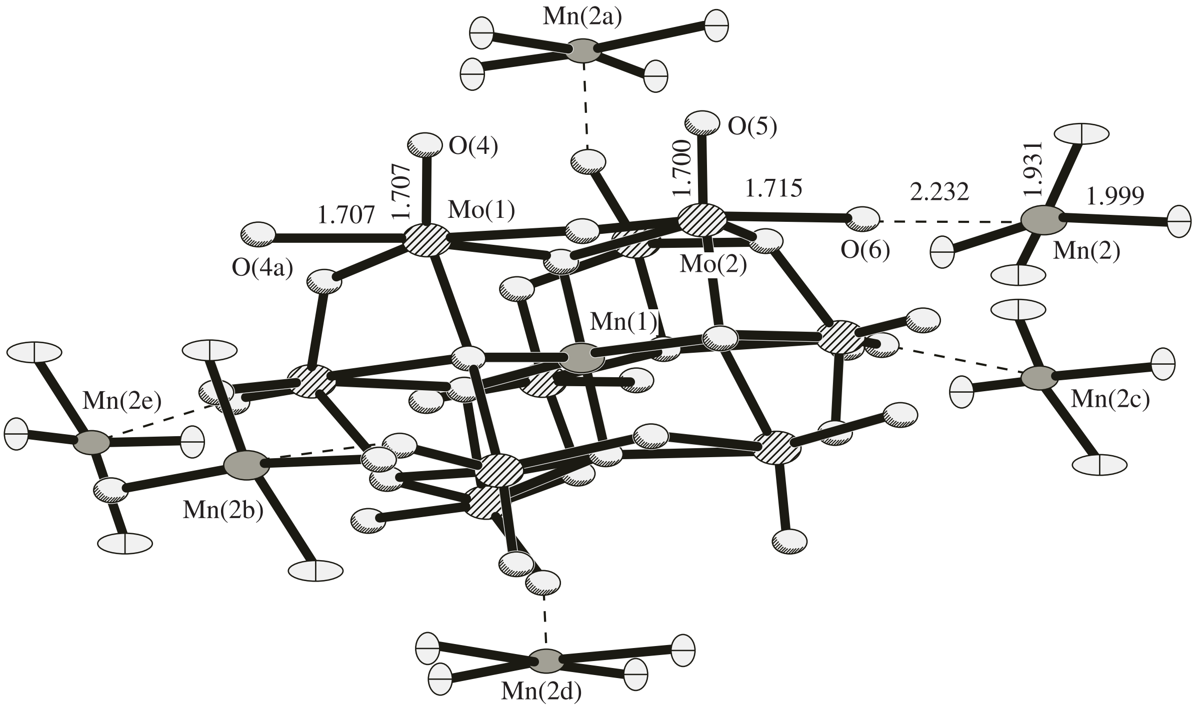

Fig. 2. The structure of HPC **I**.

structural types. The IR spectrum of compound **I** contains several sets of the bands due to vibrations of the terminal and bridging bonds metal–oxygen. As follows from the literature data [19, 20], the vibrations of the terminal (multiple) bonds $Mo=O_{term}$ appear as a doublet at 900–1000 cm^{-1}. However, in addition to two remaining bonds at 900 (ν_s) and 935 (ν_{as}) cm^{-1} due to the vibrations of the *cis*-MoO_2 groups and not participation

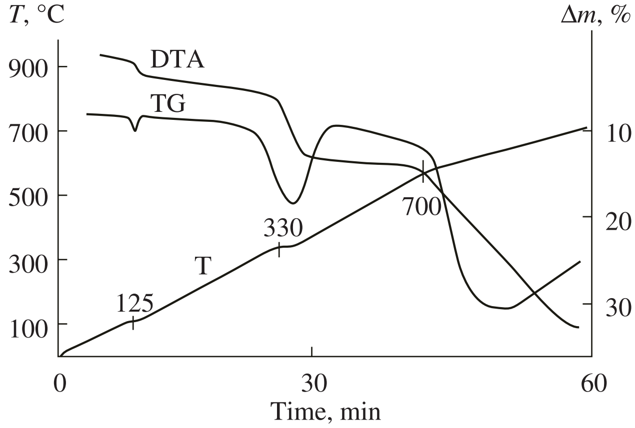

Fig. 3. Thermogravimetric pattern of compound **I**.

in the complex formation, the spectrum also contains a band, at 875 cm^{-1}, which appears due to a new coordination Mo(2)–O$_{\text{term}}$–Mn(2).

The IR spectrum of compound **I** also exhibits the intense absorption bands at 500–700 cm^{-1} (493, 592, 656, 692) corresponding to different vibrations of the bridging bonds Mo–O–Mo. The intense band at 542 cm^{-1} should be assigned to the vibrations of Mn(1)–O of a central octahedron of the HPA, whereas the band in the form of a doublet at 425, 435 cm^{-1} corresponds to the Mn(2)–O vibrations of the outer-sphere hydrated cation $[Mn(H_2O)_4]^{2+}$.

The bands at 1620 and 3000–3650 cm^{-1} are due to vibrations of the crystallization water molecules.

The X-ray diffraction and IR study confirm the hexadentate function of a macroligand $[MnMo_9O_{32}]^{6-}$ due to two triplet groups Mo_3O_{13} with six active terminal O atoms of the *cis*-MoO_2 groups capable of coordinating with the central metal atom.

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