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PHYSICAL METHODS OF INVESTIGATION

Synthesis and Study of Ammonium Decamolybdodimetallates

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Abstract—Ammonium decamolybdodimetallates $(NH_4)_n[M_2Mo_{10}O_{34}(OH)_4] \cdot 7H_2O$, where M = Cr^{3+} ($n = 6$), Cu^{2+} ($n = 8$), or Ni^{2+} ($n = 8$), were synthesized for the first time and studied by X-ray diffraction, thermogravimetry, and IR spectroscopy. The compounds crystallize in the triclinic system with the following unit cell parameters: $a = 10.68(2)$ Å, $b = 9.46(2)$ Å, $c = 7.97(2)$ Å, $\alpha = 75.12(3)°$, $\beta = 96.82(3)°$, $\gamma = 102.21(3)°$, $V = 754.4(3)$ Å^3, $\rho_{calcd} = 4.05$ g/cm^3, $Z = 1$ for the chromium compound; and $a = 10.57(2)$ Å, $b = 9.29(2)$ Å, $c = 8.47(2)$ Å, $\alpha = 73.91(3)°$, $\beta = 96.05(3)°$, $\gamma = 104.71(3)°$, $V = 854.3(3)$ Å^3, $\rho_{calcd} = 3.68$ g/cm^3, $Z = 1$ (for the copper compound); and $a = 10.96(2)$ Å, $b = 8.95(2)$ Å, $c = 7.40(2)$ Å, $\alpha = 71.76(3)°$, $\beta = 97.04(3)°$, $\gamma = 102.91(3)°$, $V = 875.3(3)$Å^3, $\rho_{calcd} = 3.65$ g/cm$_3$, $Z = 1$ for the nickel compound.

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Heteropoly compounds (HPC) are rather complex and theoretically interesting representatives of inorganic compounds, which are finding wide use in various fields of science and engineering. They are polyoxo derivatives built of metal–oxygen octahedra MO_6, which share vertices and edges to form a stable framework, the heteropolyanion (HPA). The center of the HPA is occupied by one or several heteroatoms. Complex cobalt molybdates were first described by N.S. Kurnakov in 1900 [1]. Later, ammonium and potassium HPC salts were studied by Friedheim and Keller [2]. The dimeric nature of the complex HPA in these compounds was demonstrated by Tsigdinos [3]. The synthesis and physicochemical properties of alkali metal and ammonium decamolybdodicobaltates were also reported [4, 5]. Detailed descriptions of structural data for HPC are documented in a review [6] and publications [7–9].

This work is devoted to the synthesis and properties of ammonium decamolybdodimetallates $(NH_4)_n[M_2Mo_{10}O_{34}(OH)_4] \cdot 7H_2O$, where M = Cr^{3+} ($n = 6$) (**I**), Cu^{2+} ($n = 8$) (**II**), Ni^{2+} ($n = 8$) (**III**).

EXPERIMENTAL

The compounds were synthesized by a modification of a reported method [5]. An equivalent amount of a solution of chromium nitrate (copper or nickel acetate, respectively) were added to a 0.2 M solution of ammonium molybdate (400 mL) acidified by nitric acid to pH 3 and preheated to 70°C on a water bath. Activated carbon (15 g) was added to the resulting mixture. The solution was brought to boiling, and 30% hydrogen peroxide (50 mL) was added dropwise with continuous stirring. After oxygen evolution ceased, the mixture was filtered to remove activated carbon. After several days, crystals precipitated (dark lilac for compound **I**, blue for compound **II**, and green for compound **III**). The crystals were filtered off, recrystallized from hot water, washed with ethanol, and dried.

The chemical composition of the compounds was determined by mass spectroscopy, and crystal water was quantified by thermogravimetry. The results of analyses are presented below.

For $(NH_4)_6[Cr_2Mo_{10}O_{34}(OH)_4] \cdot 7H_2O$ anal. calcd. (%): $(NH_4)_2O$, 8.16; Cr_2O_3, 7.95; MoO_3, 75.39; H_2O, 8.48.

Found (%): $(NH_4)_2O$, 8.21; Cr_2O_3, 7.90; MoO_3, 75.45; H_2O, 8.42.

For $(NH_4)_8[Cu_2Mo_{10}O_{34}(OH)_4] \cdot 7H_2O$ anal. calcd. (%): $(NH_4)_2O$, 10.56; CuO, 8.08; MoO_3, 73.12; H_2O, 8.22.

Found (%): $(NH_4)_2O$, 10.60; CuO, 8.04; MoO_3, 73.15; H_2O, 8.19.

For $(NH_4)_8[Ni_2Mo_{10}O_{34}(OH)_4] \cdot 7H_2O$ anal. calcd. (%): $(NH_4)_2O$, 10.56; NiO, 7.62; MoO_3, 73.12; H_2O, 8.69.

Table 1. X-Ray powder diffraction data for $(NH_4)_6[Cr_2Mo_{10}O_{34}(OH)_4] \cdot 7H_2O$ (**I**)

2θ, deg	*d*, Å	*I*	*h*	*k*	*l*
8.485	10.4124	100	1	0	0
9.834	8.9871	42.87	0	1	0
11.578	7.6371	5.12	0	0	1
15.046	5.8835	3.21	1	0	1
16.858	5.2551	46.37	0	1	$\bar{1}$
17.352	5.1064	1.91	1	1	1
18.127	4.8899	5.61	2	$\bar{1}$	0
19.575	4.5312	21.71	2	0	$\bar{1}$
20.515	4.3256	2.45	0	2	1
21.294	4.1692	2.13	2	1	0

Table 2. X-Ray powder diffraction data for $(NH_4)_8[Cu_2Mo_{10}O_{34}(OH)_4] \cdot 7H_2O$ (**II**)

2θ, deg	*d*, Å	*I*	*h*	*k*	*l*
8.8581	9.9748	100	1	0	0
10.3218	8.5633	12.73	0	1	0
11.1800	7.9134	44.60	0	1	1
17.8635	4.9422	7.31	2	1	$\bar{1}$
18.8475	4.7005	5.78	2	$\bar{1}$	0
20.3903	4.3582	9.82	2	$\bar{1}$	$\bar{2}$
22.2484	3.9999	8.50	0	1	$\bar{2}$
24.3409	3.6490	5.43	0	1	3
26.9107	3.3098	13.07	3	$\bar{1}$	0
28.9267	3.0833	6.25	1	$\bar{3}$	$\bar{1}$
29.7172	3.0036	7.36	3	0	$\bar{1}$
31.1586	2.8688	8.72	1	$\bar{1}$	$\bar{4}$
33.0246	2.6971	0.01	1	3	1
36.0770	2.4860	2.61	4	$\bar{2}$	$\bar{1}$
37.0256	2.4259	2.53	1	0	4
37.7536	2.3815	2.66	3	2	1
39.1917	2.2969	2.94	1	$\bar{4}$	$\bar{1}$
50.3953	1.8091	1.81	4	0	$\bar{5}$
52.0703	1.7549	0.72	5	1	$\bar{3}$

Table 3. X-Ray powder diffraction data for $(NH_4)_8[Ni_2Mo_{10}O_{34}(OH)_4] \cdot 7H_2O$ (**III**)

2θ, deg	*d*, Å	*I*	*h*	*k*	*l*
9.35	9.4484	100	1	0	0
11.50	7.6862	27.98	0	1	0
13.46	6.5687	3.95	1	$\bar{1}$	$\bar{2}$
15.48	5.7164	16.99	0	1	2
17.26	5.1325	30.26	2	$\bar{1}$	$\bar{2}$
18.43	4.809	29.89	1	1	$\bar{1}$
18.69	4.4734	57.77	2	0	0
20.21	4.3887	6.56	1	$\bar{2}$	$\bar{2}$
21.61	4.1080	6.71	1	0	$\bar{3}$
23.14	3.8405	7.36	0	2	0
24.12	3.6863	11.75	2	1	0
24.60	3.6149	5.97	2	1	$\bar{1}$
26.44	3.3677	21.74	1	2	1
27.70	3.2178	15.35	1	0	3
29.09	3.0671	10.90	1	1	$\bar{3}$
31.97	2.7969	55.47	1	2	3
32.92	2.7184	5.53	0	3	1
34.2	2.6135	11.33	0	3	3
34.48	2.5988	16.70	2	0	3
36.54	2.4568	7.08	1	0	$\bar{5}$

Found (%): $(NH_4)_2O$, 10.51; NiO, 7.67; MoO_3, 73.15; H_2O, 8.66.

Compounds **I–III** were studied by powder X-ray diffraction, thermogravimetric analysis (**TGA**), and IR spectroscopy. The powder X-ray diffraction study was carried out on a Stoe IP automated diffractometer; 2θ = 10° – 70°. The X-ray diffraction patterns were indexed using the Powder-2 program package. The TGA was carried out on a Paulik-Paulik-Erdey unit in the temperature range from 20 to 1000°C (heating rate, 10 K/min; sample size, 400 g; reference calcined alumina). The IR spectra of compounds **I–III** were measured on a Perkin-Elmer spectrophotometer in the 200–4000 cm^{-1} range. The samples were prepared as mineral oil mulls and placed between KBr plates.

RESULTS AND DISCUSSION

Powder X- ray diffraction analysis was carried out to verify the purity and individuality of the HPC and to determine their crystal characteristics (Tables 1–3,

Table 4. Crystal data for compounds **I–III**

Compouny	System	*a*, Å	*b*, Å	*c*, Å	α, deg	β, deg	γ, deg	*V*, Å^3	ρ, g/cm^3	*Z*
I	Triclinic	10.68	9.42	7.97	75.12	96.82	102.2	754.4	4.05	1
II	The same	10.57	9.29	8.47	73.91	96.05	104.7	854.3	3.68	1
III	The same	10.96	8.95	7.40	71.76	97.04	102.9	875.3	3.65	1

Table 5. Vibration frequencies and band assignment in the IR spectra of $(NH_4)_6[Cr_2Mo_{10}O_{34}(OH)_4] \cdot 7H_2O$ (**I**)

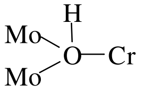
Band assignment	ν cm^{-1}	Band assignment	ν cm^{-1}
		820	ν(Cr–O)
320	terminal *cis*-MoO_2	850	$\nu_s(MoO_2)$
380	ν terminal *cis*-MoO_2	900	$\nu_{as}(MoO_2)$
400	ν terminal *cis*-MoO_2	950	$\nu_{as}(MoO_2)$
440	ν_s(Mo–O–Mo)	1400	$\nu(NH_3)$
550	ν(Mo–O^H–Mo)	1600	$\nu(NH_3)$
580	ν_{as}(Mo–O^H–Mo)	1640	$\nu(OH^-)$
650	ν_{as}(Mo–O–Mo)	3000–3650	$\nu(H_2O + \nu(NH_3)$

Table 6. TGA data of compounds **I–III**

Compound	Endotherms			
I	120°C	260°C	360°C	770°C
II	130°C	270°C	370°C	780°C
III	120°C	270°C	375°C	770°C

Fig. 1). Comparison of the measured X-ray diffraction patterns with the PCPDFWIN database led to the conclusion that compounds **I–III** are individual and crystallize in the triclinic system. The X-ray diffraction patterns were indexed by selecting isostructural compounds. The number of formula units was determined by measuring the densities of the compounds by the pycnometer method [10]. X-Ray diffraction data are displayed in Table 4.

It can be seen in the IR spectra of compound **I** (Table 5) that the complexity of the dimeric HPA$[M_2Mo_{10}O_{34}(OH)_4]^{n-}$ is reflected as numerous bands caused by various stretching vibrations. The bands can be assigned by comparing the IR spectrum of compound **I** with the IR spectra of analogous HPC studied previously [11–13]. Consider the spectrum of ammonium decamolybdodichromate as an example.

The fundamental vibrations of the terminal *cis*-MoO_2 groups and the bridging Mo–O–Mo groups appear in the region of 1000–300 cm^{-1}. In our case, these are two bands: an intense doublet at 900–950 cm^{-1} (ν_{as}) and a weak band at 850 cm^{-1} (ν_s). These bands are, in some cases, superimposed by the vibration of the whole HPA. The IR spectrum also exhibits two strong bands at 650 (ν_{as}) and 440 cm^{-1} (ν_s) associated with the stretching vibrations of three peripheral Mo–O–Mo bridging bonds. The bands at 580 and 550 cm^{-1} can be assigned to the asymmetric and symmetric Mo–O vibrations in the  $Mo_2\overset{H}{O}{-}Cr$ fragment, respectively. The band at 820 cm^{-1} in compound^{-1} corresponds to Cr–O vibrations. The bands below 400 cm^{-1} are due to the bending vibrations of both the *cis*-MoO_2 and Mo–O–Mo groups.

The fundamental vibrations of the NH_3 groups in the complexes are ν_1 = 3040, ν_2 = 1600, ν_3 = 3149, and ν_4 = 1400 cm^{-1} [14]. Of them, only ν_2 and ν_4 should be IR-active. The IR spectra of compounds **I–III** exhibit two strong bands at ~1600 and 1400 cm^{-1}. In addition, the IR spectrum exhibits bands at 1640 and 3000–3650 cm^{-1} due to the water molecules and the hydroxide groups, which overlap the bands ν_1 = 3040 and ν_3 = 3149 cm^{-1}.

Thermogravimetric analysis of compounds **I–III** shows several endo- and exotherms (Table 6, Fig. 2). Seven water molecules of crystallization are removed in the temperature range from 120 to 140°C, which is accompanied by an endotherm [15]. Ammonia is evolved from 200 to 280°C; this is accompanied by an endotherm at 260–270°C. The endotherm at 360–380°C is due to the removal of five inner-sphere water molecules and the complete destruction of HPA. The endotherm at 770–780°C corresponds to the removal of ten molybdenum oxide molecules.

The schemes of thermal decomposition of compounds **I–III** can be represented as follows:

for compound **I**,

$$(NH_4)_6[Cr_2Mo_{10}O_{34}(OH)_4] \cdot 7H_2O \xrightleftharpoons[120\text{–}130°C]{-7H_2O} (NH_4)_6[Cr_2Mo_{10}O_{34}(OH)_4] \xrightleftharpoons[260\text{–}270°C]{-6NH_3} 6H \cdot [Cr_2Mo_{10}O_{34}(OH)_4] \xrightleftharpoons[360\text{–}370°C]{-5H_2O} Cr_2O_3 \cdot 10MoO_3 \xrightleftharpoons[770\text{–}780°C]{-10MoO_3} Cr_2O_3;$$

and for compounds **II** and **III**,

$$(NH_4)_8[M_2Mo_{10}O_{34}(OH)_4] \cdot 7H_2O \xrightleftharpoons[120\text{–}130°C]{-7H_2O} (NH_4)_8[M_2Mo_{10}O_{34}(OH)_4] \xrightleftharpoons[260\text{–}270°C]{-8NH_3} 8H \cdot [M_2Mo_{10}O_{34}(OH)_4] \xrightleftharpoons[360\text{–}370°C]{-6H_2O} 2MO \cdot 10MoO_3 \xrightleftharpoons[770\text{–}780°C]{-10MoO_3} 2MO.$$

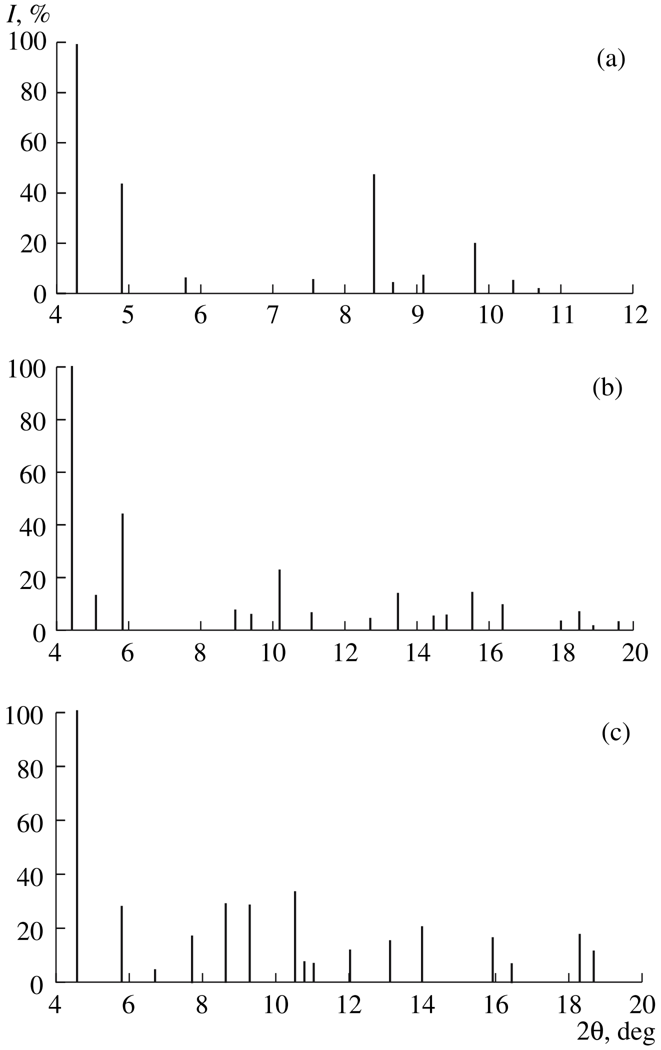


Fig. 1. Line X-ray diffraction patterns for compounds$(NH_4)_n[M_2Mo_{10}O_{34}(OH)_4] \cdot 7H_2O$, where (a) M = Cr^{3+}, $n = 6$; (b) M = Cu^{2+}, $n = 8$; and (c) Ni^{2+}, $n = 8$.

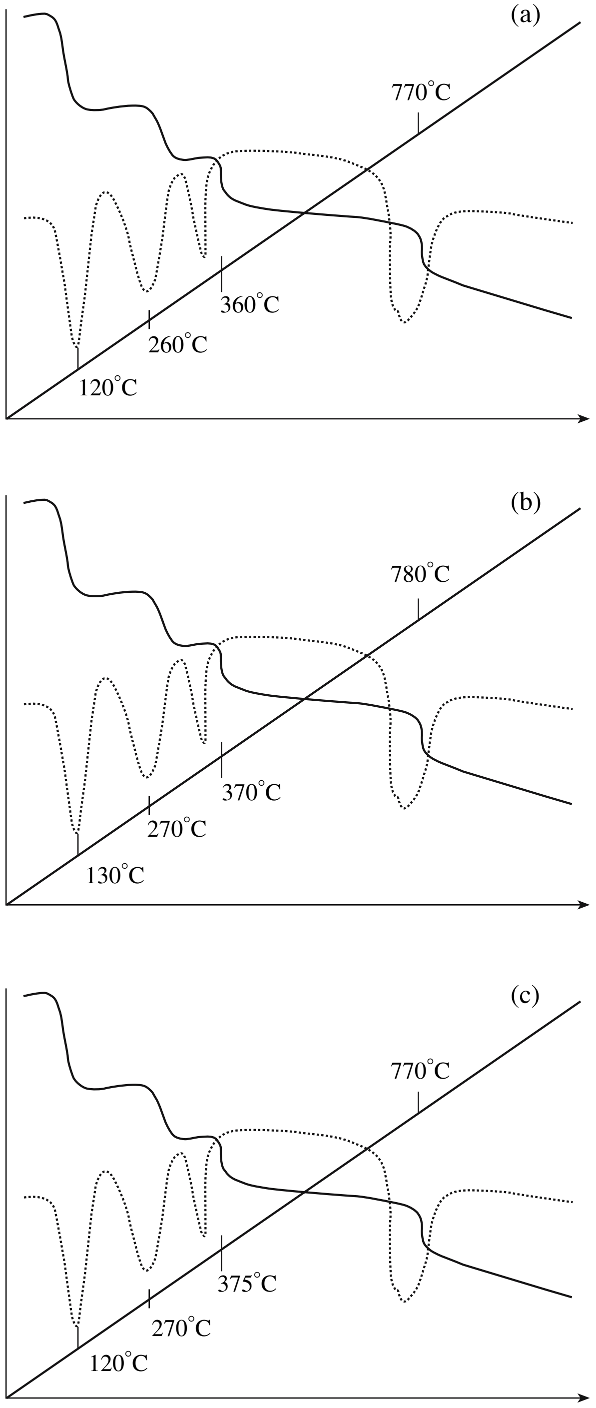


Fig. 2. Thermoanalytical curves for compounds $(NH_4)_n[M_2Mo_{10}O_{34}(OH)_4] \cdot 7H_2O$, where (a) M = Cr^{3+}, $n = 6$; (b) Cu^{2+}, $n = 8$; and (c) Ni^{2+}, $n = 8$.

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