SYNTHESIS AND CRYSTAL STRUCTURES

OF $[Pd(NH_3)_4]_2Mo_8O_{26}$ AND $Na_2[Pd(NH_3)_4]_2Mo_8O_{27}·5H_2O$

COMPLEX SALTS

A. S. Sukhikh[1], S. P. Khranenko[1], T. V. Basova[1], and S. A. Gromilov[1]*

$[Pd(NH_3)_4]_2Mo_8O_{26}$ (**I**) and $Na_2[Pd(NH_3)_4]_2Mo_8O_{27}·5H_2O$ (**II**) are synthesized and their crystal structures are determined. In the structure of **I**, isolated octamolybdate anions have a β-configuration; Mo atoms are bonded to 14 (6×2 + 2×1) terminal O atoms, the distances to which are in a range of 1.693-1.733 Å. The Mo–O distances with bridging O atoms connecting two Mo atoms range within 1.755-2.228 Å; with those connecting three Mo atoms it is 1.927-2.390 Å; and with those connecting five Mo atoms, it is 2.143-2.501 Å. The mutual arrangement of octamolybdate anions can be described in terms of a three-layer close packing: $a_T ≈ 9.5$ Å, $α_T ≈ 69.8°$. In the structure of **II**, octamolybdate anions form infinite chains $([Mo_8O_{27}]^{6-})_∞$. The Mo atoms are bonded to 16 (4×2 + 2×1 + 2×2.5) terminal O atoms, the distances to which are in a range of 1.705-1.901 Å. Some terminal O atoms are involved in the additional coordination of Na^+ cations, as a result of which, a complex 3D structure forms. The Mo–O distances with bridging O atoms connecting two Mo atoms range within 1.755-2.367 Å; with those connecting three Mo atoms it is 1.868-2.218 Å; with those connecting four Mo atoms it is 1.957-2.365 Å. The anions form pseudohexagonal layers ($a ≈ c ≈ 9.2$ Å, $∠β ≈ 120°$) perpendicular to the *Y* axis.

INTRODUCTION

Polyoxometalates are a large and very diverse group of compounds, and a large number of them have unique physicochemical properties [1-4]. Their major applications are analytical chemistry, medicine, biology, homogeneous and heterogeneous catalysis, and others. The structural diversity is based on the ability of metal oxo complexes (for the most part, of the fifth and sixth groups) to combine in different ways depending on the synthesis conditions. Polyanions formed mainly consist of MO_6 octahedra, but sometimes they also involve MO_5 (square pyramid) and MO_4 (tetrahedron). As a result, the number of possible configurations is truly enormous. In each such case, the polyanion has a certain charge, hence, the second aspect of the crystal structure diversity are the cation charge and structure. These factors open up great opportunities for the synthesis of more and more new crystal structures. This work considers two structures with octamolybdate anions (hereafter, OMA).

---

[1]Nikolaev Institute of Inorganic Chemistry, Siberian Branch, Russian Academy of Sciences, Novosibirsk, Russia; *grom@niic.nsc.ru. Original article submitted September 13, 2021; revised September 24, 2021; accepted September 25, 2021.

At present, the data on only few crystal structures of complex salts containing OMA and inorganic cations have been published. In their vast majority, hexaaqua cations of rare earth metals act as cations: $[Eu(H_2O)_6]_2Mo_8O_{27}\cdot6H_2O$ [5; No. 71216], $[Sm(H_2O)_6]_2Mo_8O_{27}\cdot6H_2O$ [5; No. 79725], $[Dy_2(H_2O)_{12}]Mo_8O_{27}\cdot8H_2O$ [5; Nos. 247333-247336]. There are much more complex salts containing OMA and organic cations [6].

Octamolybdate anions form when eight distorted MoO_6 octahedra (in rare cases, together with MoO_4 tetrahedra) link through vertices and edges. The characteristics of the known OMA isomers with the composition Mo_8O_{26} are given in [7], but the list does not exhaust all possible variants of polyanions containing eight Mo atoms. For example, in the structure of $(NH_4)_4Mo_8O_{26}\cdot4H_2O$ [5; No. 427451] isolated OMA has a β-configuration; eight MoO_6 octahedra are involved in the organization. However, when the crystallization conditions change, the additional O atoms linking the neighboring OMA into infinite 1D chains can appear in the OMA composition; as a consequence, $(NH_4)_6Mo_8O_{27}\cdot4H_2O$ [5; No. 2017] salt forms where OMAs have other compositions and charges.

The terminal O atoms can be involved in the coordination environment of metal atoms belonging to the cations and, hence, form a variety of moieties: infinite 2D ribbons $\{[Co(H_2O)_4]_2Mo_8O_{27}\}_\infty$ [8]; $\{3D\text{-}[Cu(DIE)_2][1D\text{-}Mo_8O_{26}]_{0.5}\}$ (DIE is diimidazoloethane) [9]; $[Mo_8O_{26}(BiCl_3)_2)]^{4-}$ [10]. Some complexes based on OMA, the Ag^+ cation, and organic ligands are described in [11]. The list of different structural variants with OMA can be continued.

A special role in combining OMAs is played by monatomic cations, in particular Na^+. When infinite chains form, its coordination environment can include different number of O atoms from two neighboring anions: 4 + 4 [2; NEQPUV], 4 + 2 [2; NOKGEZ], etc.

This work is devoted to the synthesis and study of crystal structures containing OMA and Na^+ and $[Pd(NH_3)_4]^{2+}$ cations.

EXPERIMENTAL

In the synthesis, an aqueous $Na_6Mo_7O_{24}$ solution prepared according to the technique [12] by neutralization of a mixture of Na_2MoO_4 and Na_2CO_3 solutions (3:1 volume ratio) was used. The freshly prepared $Na_6Mo_7O_{24}$ solution (0.5 mmol in 35 mL of H_2O, pH ~ 5.5) was mixed with aqueous $[Pd(NH_3)_4](NO_3)_2$ and $NaNO_3$ solutions in the following ratio:

$$Na_6Mo_7O_{24} + 2[Pd(NH_3)_4](NO_3)_2 + 2NaNO_3.$$

A glass beaker with the reaction mixture was tightly covered with a film and left for crystallization. In four months, a fine crystalline white product formed on the bottom. It was filtered off, washed with acetone, and dried in the air (hereafter, product **A**). The product synthesized was a fine crystalline white powder. The mother liquor was left for further crystallization, and in two months a newly formed precipitate (hereafter, product **B**) was isolated in a similar way.

The single crystal XRD analysis was performed on a Bruker DUO diffractometer (MoK_α radiation, graphite monochromator, CCD detector). From product **A**, several crystals suitable for the XRD study were selected. All were $[Pd(NH_3)_4]_2Mo_8O_{26}$ (hereafter, **I**). The same crystals were found in product **B**, but along with them, single crystals with another faceting were extracted. These crystals were target complex salt $Na_2[Pd(NH_3)_4]_2Mo_8O_{27}\cdot5H_2O$ (hereafter, **II**). The additional syntheses aimed at obtaining **II** in its pure form (variations in the ratio of initial solutions and pH) were not successful.

The structures of **I** and **II** were determined using the SHELXT-2014/5 program [13] and refined in the anisotropic (isotropic for hydrogen atoms) approximation. The hydrogen atoms were calculated geometrically. The structure was refined using the SHELXL-2018/3 program [14]. The atomic coordinates and thermal parameters have been deposited with the Cambridge Crystallographic Data Centre_[2] and are available by request at the address: www.ccdc.cam.ac.uk/structures/. The crystallographic data, experimental conditions, and characteristics of the crystal structure refinement are listed in Table 1.

TABLE 1. Crystallographic Characteristics and the Results of the Structure Refinement
for $[Pd(NH_3)_4]_2Mo_8O_{26}$ and $Na_2[Pd(NH_3)_4]_2Mo_8O_{27} \cdot 5H_2O$

Parameter	I	II
Formula	$H_{24}Mo_8N_8O_{26}Pd_2$	$H_{34}Mo_8N_8Na_2O_{32}Pd_2$
Weight of formula unit	1532.59	1684.65
T, K	150	298
a, b, c, Å	10.3990(4), 10.0947(3), 14.4229(5)	9.0291(4), 9.4473(4), 11.2543(5)
α, β, γ, deg	90, 107.851(2), 90	91.322(2), 113.426(2), 97.9410(10)
Space group	$P2_1/n$	$P\overline{1}$
Z	2	1
V, Å^3	1441.15(9)	869.20(7)
d_{calc}, g/cm^3	3.532	3.218
μ, mm^{-1}	4.682	3.931
2θ range, deg	5.76-72.65	3.96-61.14
$N_{refl.}$ / $N_{independent}$ / $N_{independent}$ $(I > 2\sigma(I))$	12751 / 6667 / 5910	10052 / 5229 / 3668
R_{int}	0.0335	0.0387
Completeness of data collection ($2\theta = 50°$), %	99.7	99.1
Refined parameters	204	247
S factor for F^2	1.059	0.977
R_1, wR_2 $(I > 2\sigma(I))$	0.0289, 0.0813	0.0408, 0.0767
R_1, wR_2 (all data)	0.0350, 0.0831	0.0722, 0.0879
CCDC No.	2077297	2077298

The XRD analysis of the obtained products was performed on a Bruker D8 Venture diffractometer (Incoatec IμS 3.0 microfocus tube, CuK_α radiation, three-circle goniometer, PHOTON III CPAD detector) using the Debye–Scherrer scheme at $T = 298$ K. The XRD pattern of product **A** (Fig. 1*a*) was indexed from the single crystal XRD data for $[Pd(NH_3)_4]_2Mo_8O_{26}$; the absence of "excess" reflections evidences that it is single phase. On the XRD pattern of **B** weak reflections from **II** were observed. The IR spectrum of product **A** (Fig. 1*b*) in a KBr pellet was recorded in a wavenumber range from 400 cm^{-1} to 4000 cm^{-1} on a Scimitar FTS 2000 IR Fourier spectrometer.
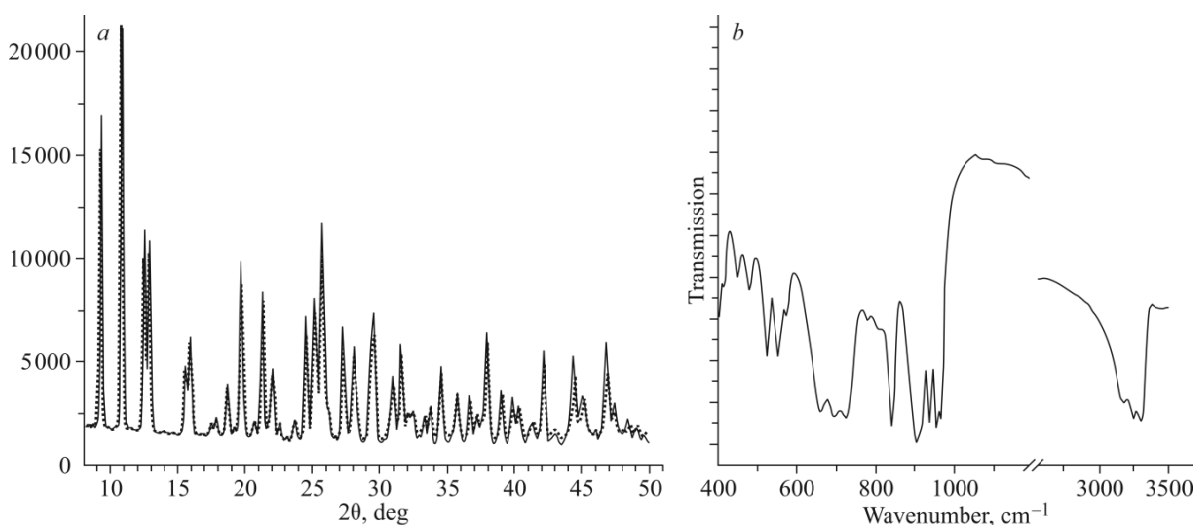

Fig. 1. Results for product **A**: the XRD pattern (the dashed line corresponds to the experimental curve, the solid line corresponds to the theoretical curve for $[Pd(NH_3)_4]_2Mo_8O_{26}$) (*a*); the IR spectrum (*b*).

Crystal structure of [Pd(NH₃)₄]₂Mo₈O₂₆. The structure of $[Mo_8O_{26}]^{4-}$ OMA is shown in Fig. 2a. According to the nomenclature [7], OMA is a β-isomer. It has such a configuration in many structures, for example, $(NH_4)_4Mo_8O_{26}\cdot 4H_2O$

Mo1...Mo3   3.439
Mo1...Mo2   3.528
Mo1...Mo4   3.266
Mo3...Mo2   3.529
Mo3...Mo4   3.275
Mo2...Mo4   3.437
Mo2...Mo2   3.597

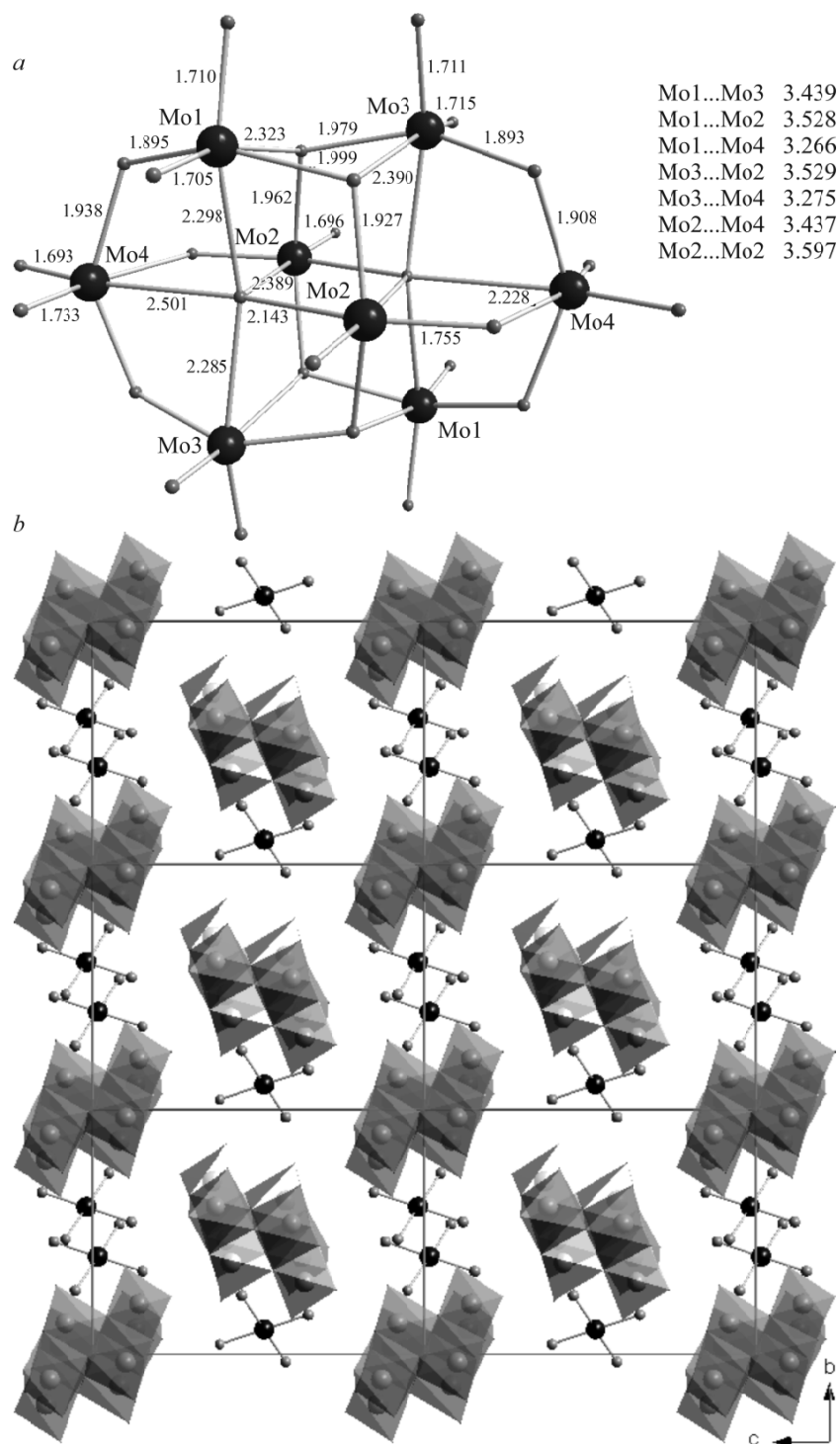**Fig. 2.** Fragments of the crystal structure of $[Pd(NH_3)_4]_2Mo_8O_{26}$: the OMA structure at 150 K, the interatomic distances are given in Å (a); the anion packing motif (b).

[1; No. 427451]. Mo2 atoms related by the symmetry element have one terminal O atom at a distance of 1.696 Å, the other six Mo atoms have two terminal O atoms; the Mo–O$_{term}$ distances are in a range of 1.693-1.733 Å (Table 2). Six O atoms are the inner bridges for the pairs of Mo atoms (Mo2–Mo4, Mo3–Mo4, Mo1–Mo4) and symmetrical to them pairs; the Mo–O$_{\mu2}$ range is 1.755-2.228 Å. Four O atoms link three Mo atoms each (Mo–O$_{\mu3}$ of 1.927-2.390 Å), the other two link five Mo atoms each (Mo–O$_{\mu5}$ of 2.143-2.501 Å). Note that the presence of O$_{\mu5}$ atoms is the distinguishing feature of the Mo$_8$O$_{26}$ β-configuration among ten others currently known.

Similar to the previously studied IR spectra of polymolybdates [15-18], the bands in a range of 935-970 cm^{-1} refer to ν(Mo=O) stretching vibrations (Fig. 1b). A band at 905 cm^{-1} corresponds to ν(O–Mo–O) vibrations; and two bands at 725 am^{-1} and 695 cm^{-1} correspond to ν(Mo–O–Mo) vibrations where the O atom is connected with three Mo atoms. The δ(O–Mo–O) bending vibrations occur at 552 cm^{-1}, whereas δ(Mo–O$_\mu$–Mo), in which the O$_\mu$ atom is connected with two of three Mo atoms, is at 522 cm^{-1}. In the IR spectra, the vibrations corresponding to the [Pd(NH$_3$)]$^{2+}$ cation are also observed: ν(N–H) in a range of 3300-3180 cm^{-1}, δ(NH$_3$) at 1626 cm^{-1}, 1340 cm^{-1}, 1312 cm^{-1}, ρ(NH$_3$) at 842 cm^{-1} and 807 cm^{-1}, and Pd–N at 479 cm^{-1} [15]. The geometry of the complex cation is fairly standard: the Pd–N distances are 2.04 Å, the ∠N–Pd–N angle is 90°.

The general motif of the crystal structure was identified by the method described in [19, 20]. Given that [Pd(NH$_3$)$_4$]$^{2+}$ cations are much lighter than OMAs, we focused on the search for their mutual arrangement. To this end, the XRD pattern was calculated with regard to the positions of only Mo atoms. This approach was previously employed in the analysis of packings of some structures, for example, in [21] for [CoEn$_3$]$_2$W$_7$O$_{24}$·6H$_2$O. The most symmetrical sublattice was chosen using the software [22], which takes into account symmetry-related planes. Eventually, the anion sublattice (the centers of gravity of OMAs should correspond to its nodes) is formed by the intersection of the families of {1 0 –1}, {0 1 1}, {0 –1 1} planes and is spanned by the vectors $a_\tau = a$, $b_\tau = a/2 + b/2 + c/2$, $c_\tau = a/2 – b/2 + c/2$. The subcell metrics ($a_t = 10.40$, $b_t = c_t = 9.03$ Å, $\alpha_t = 67.97$, $\beta_t = \gamma_t = 70.67°$) allow us to consider the mutual arrangement of anions in terms of the three-layer close packing based on a distorted rhombohedron: $a_T \approx 9.5$ Å, $\alpha_T \approx 69.8°$. Fig. 2b depicts one of the planes forming the anion sublattice.

Crystal structure of Na$_2$[Pd(NH$_3$)$_4$]$_2$Mo$_8$O$_{27}$·5H$_2$O. The Na$_2$[Pd(NH$_3$)$_4$]$_2$Mo$_8$O$_{27}$·5H$_2$O crystals formed in a very small amount during the crystallization of the mother liquor remained after the extraction of product **A**. We conducted a number of additional syntheses which led only to a slight increase in the fraction of **II** rather than the formation of a single-phase product.

The structure of the polyanion is shown in Fig. 3a; previously, such a configuration was observed in the structures of (NH$_4$)$_6$Mo$_8$O$_{27}$·4H$_2$O [5; No. 2017], [Eu(H$_2$O)$_6$]$_2$Mo$_8$O$_{27}$·6H$_2$O [5; No. 71216], [Sm(H$_2$O)$_6$]$_2$Mo$_8$O$_{27}$·6H$_2$O [5; No. 79725], (NH$_4$)$_4$(Mo$_8$O$_{24}$(O$_2$)$_2$(H$_2$O)$_2$)·4H$_2$O [5; No. 403077], [Dy$_2$(H$_2$O)$_{12}$]Mo$_8$O$_{27}$·8H$_2$O [5; Nos. 247333-247336]. In all cases, OMAs form ([Mo$_8$O$_{27}$]$^{6-}$)$_\infty$ chains. In the structure of **II**, Mo atoms are in total bonded to 16 (4×2 + 2×1 + 2×2.5) terminal O atoms, the distances to which are in a range of 1.705-1.901 Å. The distance ranges of Mo–O with bridging O atoms

TABLE 2. Characteristics of OMAs in the Structures of [Pd(NH$_3$)$_4$]$_2$Mo$_8$O$_{26}$ and Na$_2$[Pd(NH$_3$)$_4$]$_2$Mo$_8$O$_{27}$·5H$_2$O

Parameter	[Pd(NH$_3$)$_4$]$_2$Mo$_8$O$_{26}$ (**I**)		Na$_2$[Pd(NH$_3$)$_4$]$_2$Mo$_8$O$_{27}$·5H$_2$O (**II**)	
Anion	[β-Mo$_8$O$_{26}$]$^{4-}$		[Mo$_8$O$_{27}$]$^{6-}$	
Number / Distance	N	Mo–O, Å	N	Mo–O, Å
O$_{term}$	14	1.693-1.733	16	1.705-1.901
O$_{\mu2}$	6	1.755-2.228	6	1.755-2.367
O$_{\mu3}$	4	1.927-2.390	4	1.868-2.350
O$_{\mu4}$	0	-	2	1.957-2.365
O$_{\mu5}$	2	2.143-2.501	0	-

Mo1...Mo2	3.299
Mo1...Mo4	3.363
Mo1...Mo3	4.002
Mo2...Mo4	3.472
Mo4...Mo3	3.256
Mo4'...Mo2	3.993
Mo4...Mo4'	3.445
Mo4'...Mo3	3.597
Mo4'...Mo2	3.472
Mo2...Mo3	3.250

Fig. 3. Fragments of the crystal structure of $Na_2[Pd(NH_3)_4]_2Mo_8O_{27}·5H_2O$: the OMA structure, interatomic distances are given in Å (*a*); the packing motif (*b*).

connecting two, three, and four Mo atoms are given in Table 2. No O atoms bonding five Mo atoms, as in the case of **I**, have been identified.

Since the structure of **II** is triclinic and $Z = 1$, the anion subcell coincides with the unit cell. Pseudohexagonal anion layers ($a \approx c \approx 9.2$ Å, $\angle\beta \approx 120°$) are perpendicular to the *Y* axis. The Na^+ cations and the crystallization water molecules occupy the cavities between them (Fig. 3*b*). Some terminal O atoms are involved in the coordination of Na^+ cations, as a result of which, a complex 3D structure forms. The Na^+ coordination polyhedron is a distorted octahedron; the Na…O distances are in a range of 2.315-2.693 Å.

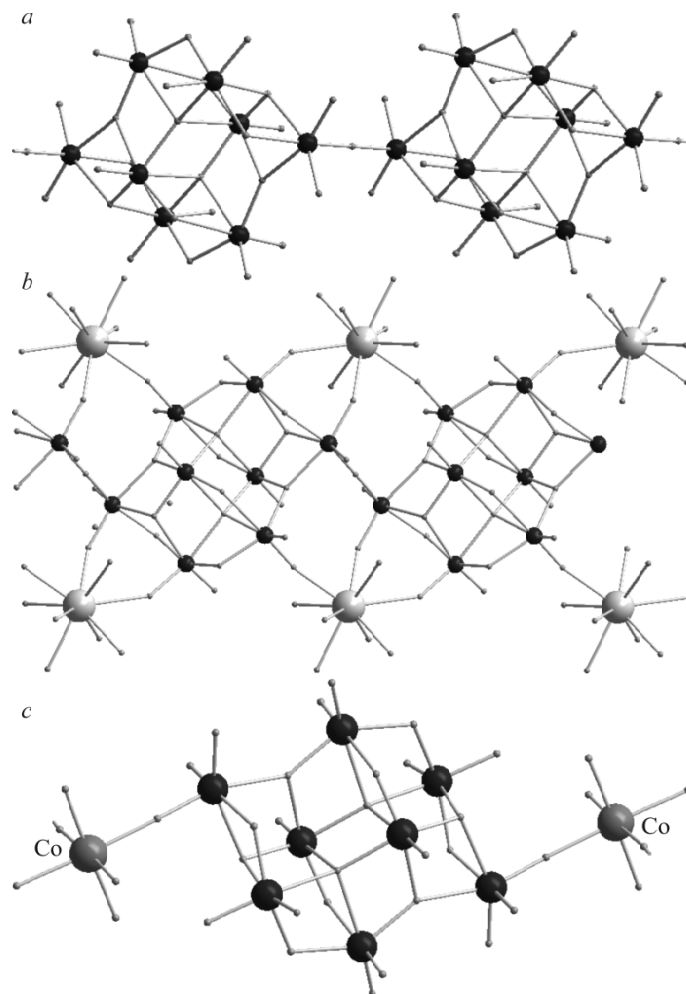**Fig. 4.** Fragments of the crystal structures of $(NH_4)_6Mo_8O_{27} \cdot 4H_2O$ [5; No. 2017] (*a*), $[Eu(H_2O)_6]_2Mo_8O_{27} \cdot \cdot 6H_2O)$ [5; No. 71216] (*b*); $(NH_4)_2[Co(H_2O)_4]_2Mo_8O_{27} \cdot 6H_2O$ [8] (*c*).

Thus, in this work, it is shown that fractional crystallization from a mixture of aqueous $Na_6Mo_7O_{24}$, $[Pd(NH_3)_4](NO_3)_2$ and $NaNO_3$ solutions results in the formation of two new complex salts containing OMAs with fundamentally different structures: $[Mo_8O_{26}]^{4-}$ and $([Mo_8O_{27}]^{6-})_\infty$.

FUNDING

CONFLICT OF INTERESTS

The authors declare that they have no conflict of interests.

REFERENCES

1. M. S. Pope. Hetepoly and Isopoly Oxometallates. Berlin, Heidelberg, New York, Tokyo: Springer-Verlag, **1983**.
2. M. A. Porai-Koshits and L. O. Atovmyan. *Adv. Sci. Tech.*, *Ser.: Cryst. Chem.*, **1984**, *18*, 49.

3. V. S. Sergienko and M. A. Porai-Koshits. *Adv. Sci. Tech.*, *Ser.: Cryst. Chem.*, **1985**, *19*, 79.

4. M. T. Pope and A. Muller. *Angew. Chem.*, *Int. Ed. Engl.*, **1991**, *30*, 34-48. https://doi.org/10.1002/anie.199100341

5. Inorganic Crystal Structure Database. ICSD. Karlsruhe, Germany: Fashinformationszentrum, **2021**.

6. F. H. Allen. *Acta Crystallogr.*, *Sect. B*, **2002**, *58*, 380-388. https://doi.org/10.1107/S0108768102003890

7. X. L. Wang, J. Y. Zhang, Z. H. Chang, Z. Zhang, X. Wang, H. Y. Lin, and Z. W. Cui. *Inorg. Chem.*, **2021**, *60*, 3331-3337. https://doi.org/10.1021/acs.inorgchem.0c03738

8. G. Z. Kaziev, S. Holguin Quinones, A. F. Stepanova, V. N. Khrustalev, A. De Ita, and N. A. Panurin. *J. Struct. Chem.*, **2015**, 56(5), 912-918. https://doi.org/10.1134/S0022476615050133

9. H.-J. Du, Z.-Z. Shu, Y.-Y. Niu, L.-S. Song, and Y. Zhu. *J. Solid. State Chem.*, **2012**, 190, 2350-2357. https://doi.org/10.1016/j.jssc.2012.02.050

10. S. A. Adonin, E. V. Peresypkina, M. N. Sokolov, I. V. Korolkov, and V. P. Fedin. *Inorg. Chem.*, **2014**, *53*, 6886-6892. https://doi.org/10.1021/ic500710t

11. A. V. Chupina, A. A. Mukhacheva, P. A. Abramov, and M. N. Sokolov. *J. Struct. Chem.*, **2020**, *61*(2), 299-308. https://doi.org/10.1134/S0022476620020158

12. K. G. Burtseva, L. A. Kochubei, L. A. Voropanova, and B. X. Gorbatkova. *Russ. J. Inorg. Chem.*, **1981**, *26*(8), 2121-2123.

13. G. M. Sheldrick. *Acta Crystallogr.*, *Sect. A*, **2015**, *71*, 3-8. https://doi.org/10.1107/S2053273314026370

14. G. M. Sheldrick. *Acta Crystallogr.*, *Sect. C*, **2015**, *71*, 3-8. https://doi.org/10.1107/S2053229614024218

15. G. Guzman, B. Yebka, J. Livage, and C. Julien. *Solid State Ionics*, **1996**, *86*, 407-413. https://doi.org/10.1016/0167-2738(96)00338-4

16. W. Dong and B. Dunn. *J. Non-Cryst. Solids*, **1998**, *225*, 135-140. https://doi.org/10.1016/S0022-3093(98)00018-0

17. X.-D. Du, C.-H. Li, Y. Zhang, S. Liu, Y. Ma, and X.-Z. You. *CrystEngComm*, **2011**, *13*, 2350-2357. https://doi.org/10.1039/c0ce00517g

18. S. T. Thompson, H. H. Lamb, B. Delley, and S. Franzen. *Spectrochim. Acta*, *Part A*, **2017**, *173*, 618-624. https://doi.org/10.1016/j.saa.2016.10.011

19. S. V. Borisov. *J. Struct. Chem.*, **1986**, *27*(3), 164-167. https://doi.org/10.1093/screen/27.3-4.164

20. S. A. Gromilov and S. V. Borisov. *J. Struct. Chem.*, **2003**, *44*(4), 664-680. https://doi.org/10.1023/B:JORY.00000 17943.51537.b7

21. N. V. Kuratieva, I. O. Tereshkin, S. P. Khranenko, and S. A. Gromilov. *J. Struct. Chem.*, **2013**, *54*(6), 1133-1136. https://doi.org/10.1134/S0022476613060188

22. S. A. Gromilov, E. A. Bykova, and S. V. Borisov. *Crystallogr. Rep.*, **2011**, *56*(6), 947-952. https://doi.org/10.1134/S1063774511060101