X-ray powder diffraction data for three new 3-ethylanilinium molybdates

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X-ray powder diffraction data for new metal-organic compounds: tetrakis(3-ethylanilinium) octamolybdate $Mo_8O_{26}(C_8H_{12}N)_4$ [$a = 10.682(4)$, $b = 16.589(5)$, $c = 7.307(2)$ Å, $\alpha = 92.79(2)°$, $\beta = 97.99(3)°$, $\gamma = 103.89(3)°$, $V = 1240.27$ Å^3, $Z = 1$, space group $P-1$]; tetrakis(3-ethylanilinium) octamolybdate tetrahydrate $Mo_8O_{26}(C_8H_{12}N)_4 \cdot (H_2O)_4$ [$a = 18.801(7)$, $b = 17.943(6)$, $c = 7.334(3)$ Å, $\beta = 98.50(5)°$, $V = 2446.99$ Å^3, $Z = 2$, space group $P2_1/m$] and bis(3-ethylanilinium) pentamolybdate $Mo_5O_{16}(C_8H_{12}N)_2$ [$a = 34.643(6)$, $b = 5.5796(7)$, $c = 14.200(3)$ Å, $\beta = 96.20(2)°$, $V = 2728.69$ Å^3, $Z = 4$, space group $I2/a$] are reported in this paper. The investigated compounds were synthesized from molybdic acid and 3-ethylaniline in acidic solution. In the first two cases, we obtained octamolybdates, while the last compound crystallized as pentamolybdate. © *2020 International Centre for Diffraction Data*. [doi:10.1017/S0885715620000123]

Key words: metal-organic compounds, X-ray powder diffraction, inorganic–organic synthesis

I. INTRODUCTION

Molybdic acid mixed with aniline and its derivatives in acidic solutions forms polymeric trimolybdates, layered penta- and octamolybdates which can form isolated clusters. The compounds we synthesized have promising catalytic properties and can be applied in numerous industrial processes (Bożek *et al*., 2018). The investigated molybdates are frequently applied in catalysis, medicine and chemistry of new materials. Like many layered or polymeric compounds, molybdates can also be used as ion exchangers. Moreover, they can be applied in the production of valuable catalysts for oxidation processes in organic chemistry and petroleum industry.

Starting from the same reactants, changing the time of the synthesis, or using various agents to obtain an acidic environment, the chemical synthesis can result in new compounds with unexpected compositions and promising properties. The compounds we synthesized and investigated are new, obtained for the first time, and there is a lack of information about them in the chemical and crystallographic databases (neither crystallographic data nor analytical and spectroscopic data are reported).

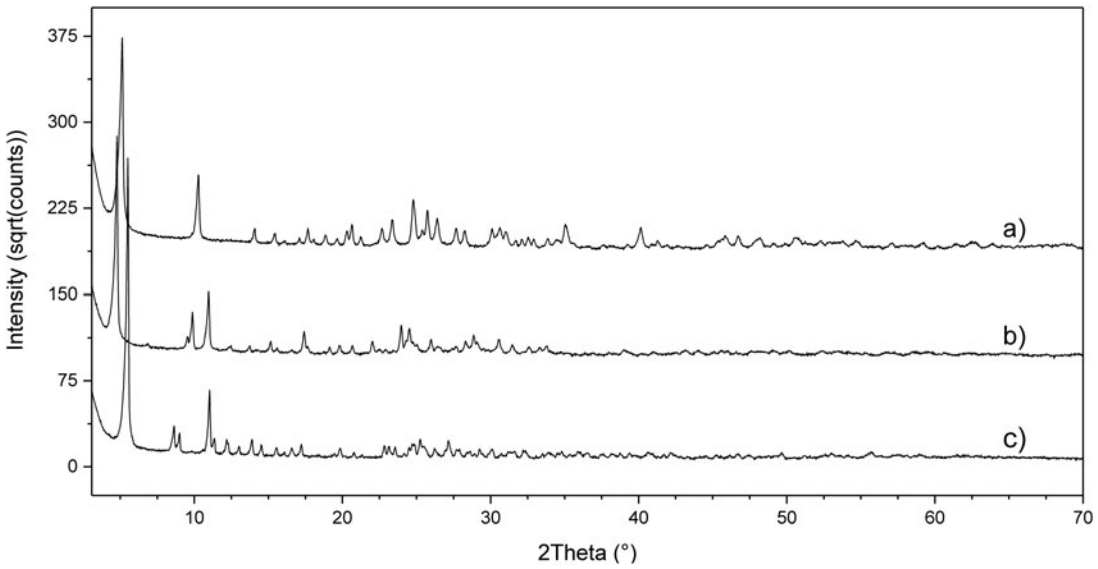

Figure 1. Experimental powder diffraction patterns of the investigated molybdates: tetrakis(3-ethylanilinium) octamolybdate (a), tetrakis(3-ethylanilinium) octamolybdate tetrahydrate (b) and bis(3-ethylanilinium) pentamolybdate (c). Axes in the figure: $x - 2\theta$ (°) and y – square root of the number of counts.

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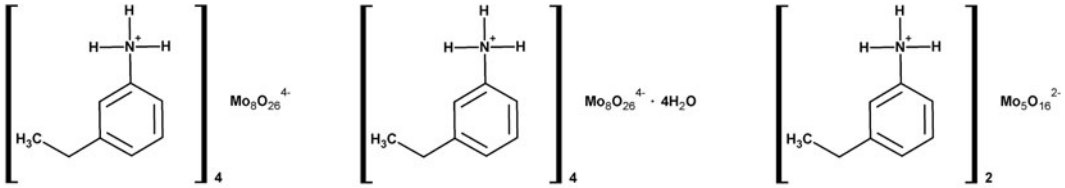

Figure 2. Molecular diagram of the investigated compounds.

TABLE I. XPRD data of tetrakis(3-ethylanilinium) ctamolybdate $Mo_8O_{26}(C_8H_{12}N)_4$.

$2\theta_{obs}$ (°)	d_{obs} (Å)	I_{obs} [a]	h	k	l	$2\theta_{cal}$ (°)	d_{cal} (Å)	$\Delta 2\theta$
5.517	16.0193	1000	0	1	0	5.508	16.0448	0.009
8.634	10.2418	15	1	0	0	8.632	10.2438	0.002
9.012	9.8131	10	−1	1	0	9.009	9.8168	0.003
11.032	8.0204	65	0	2	0	11.029	8.0224	0.003
11.351	7.7957	8	1	1	0	11.350	7.7965	0.001
12.191	7.2604	7	−1	2	0	12.198	7.2561	−0.007
12.290	7.2021	5	0	0	1	12.276	7.2100	0.013
13.030	6.7947	3	0	−1	1	13.026	6.7968	0.004
13.908	6.3677	7	−1	0	1M	13.879	6.3811	0.029
			0	1	1M	13.889	6.3764	0.019
14.529	6.0969	4	−1	1	1	14.523	6.0993	0.006
15.590	5.6842	3	1	2	0	15.639	5.6666	−0.049
16.088	5.5094	1	1	0	1	16.095	5.5070	−0.007
16.568	5.3508	3	0	3	0	16.576	5.3483	−0.008
17.226	5.1479	5	0	2	1	17.223	5.1487	0.002
19.463	4.5610	1	2	1	0M	19.464	4.5607	−0.002
			−2	1	1M	19.494	4.5537	−0.032
19.846	4.4738	3	0	−3	1	19.808	4.4823	0.038
20.727	4.2856	1	1	−3	1	20.718	4.2875	0.009
20.785	4.2738	2	−1	3	1M	20.801	4.2706	−0.016
			−2	3	0M	20.805	4.2696	−0.021
22.823	3.8965	4	2	0	1M	22.807	3.8993	0.016
			2	2	0M	22.813	3.8982	0.010
23.553	3.7774	4	−2	3	1	23.556	3.7769	−0.003
24.501	3.6333	3	0	−4	1M	24.458	3.6396	0.042
			−2	4	0M	24.537	3.6281	−0.037
24.701	3.6044	5	0	0	2M	24.697	3.6050	0.004
			1	−4	1M	24.718	3.6019	−0.018
			2	1	1M	24.739	3.5990	−0.038
24.840	3.5845	5	0	−1	2M	24.849	3.5833	−0.009
			−1	0	2M	24.878	3.5792	−0.038
			2	−3	1M	24.881	3.5787	−0.042
25.260	3.5259	6	−1	4	1M	25.263	3.5254	−0.004
			−3	1	0M	25.276	3.5237	−0.017
26.221	3.3988	3	0	−2	2	26.224	3.3984	−0.004
27.140	3.2858	7	−3	0	1M	27.104	3.2901	0.036
			−3	2	1M	27.143	3.2854	−0.003
			−2	4	1M	27.150	3.2846	−0.010
27.701	3.2205	3	2	2	1	27.699	3.2207	0.001
27.897	3.1983	3	−2	−3	1M	27.889	3.1993	0.008
			2	−4	1M	27.892	3.1989	0.005
28.616	3.1195	2	0	−3	2	28.659	3.1150	−0.044
28.917	3.0878	1	1	1	2M	28.900	3.0896	0.017
			−2	5	0M	28.913	3.0882	0.003
29.239	3.0545	3	−2	2	2M	29.286	3.0497	−0.048
			1	−5	1M	29.287	3.0496	−0.049
30.056	2.9733	3	−1	3	2M	30.007	2.9780	0.048
			1	4	1M	30.064	2.9726	−0.008
			−1	−3	2M	30.079	2.9710	−0.024
30.116	2.9674	3	−1	5	1	30.157	2.9636	−0.040
32.198	2.7801	3	2	−2	2M	32.200	2.7801	−0.001
			−1	−5	1M	32.212	2.7790	−0.014
			−2	−4	1M	32.213	2.7789	−0.015

[a] I_{obs} is in the range of 1–1000, FWHM for a single, well-resolved line is in the range of 0.11–0.19 (°) 2θ.

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TABLE II. XPRD data of tetrakis(3-ethylanilinium) octamolybdate tetrahydrate $Mo_8O_{26}(C_8H_{12}N)_4 \cdot (H_2O)_4$.

$2\theta_{obs}$ (°)	d_{obs} (Å)	I_{obs}[a]	h	k	l	$2\theta_{cal}$ (°)	d_{cal} (Å)	$\Delta 2\theta$
4.775	18.5064	1000	1	0	0	4.752	18.5945	0.023
6.834	12.9346	4	1	1	0	6.846	12.9117	−0.012
9.515	9.2952	12	2	0	0	9.513	9.2972	0.002
9.868	8.9635	56	0	2	0	9.860	8.9713	0.008
10.951	8.0794	112	1	2	0	10.950	8.0801	0.001
12.217	7.2448	2	0	0	1	12.202	7.2538	0.015
12.426	7.1234	8	−1	0	1	12.426	7.1236	.000
13.690	6.4685	5	2	2	0	13.717	6.4558	−0.027
14.268	6.2077	2	3	0	0	14.290	6.1982	−0.022
15.147	5.8494	12	3	1	0M	15.124	5.8585	0.023
			−2	1	1M	15.166	5.8422	−0.019
15.569	5.6918	3	1	3	0	15.564	5.6936	0.005
16.567	5.3511	3	2	0	1	16.575	5.3486	−0.008
17.407	5.0947	24	3	2	0M	17.391	5.0995	0.016
			−3	0	1M	17.393	5.0989	0.014
			−2	2	1M	17.428	5.0887	−0.021
17.627	5.0316	6	−2	3	0	17.633	5.0300	−0.006
19.125	4.6407	6	4	0	0	19.093	4.6486	0.032
19.804	4.4831	8	0	4	0	19.793	4.4857	0.011
20.663	4.2987	8	3	3	0M	20.638	4.3039	0.025
			−2	3	1M	20.669	4.2974	−0.006
22.003	4.0398	14	2	4	0	22.002	4.0400	0.001
23.942	3.7168	37	5	0	0	23.929	3.7189	0.013
24.302	3.6626	5	−1	0	2	24.300	3.6630	0.002
24.501	3.6333	45	−3	4	0M	24.498	3.6339	0.003
			−2	4	1M	24.524	3.6300	−0.023
			0	0	2M	24.545	3.6269	−0.044
24.721	3.6015	8	4	1	1	24.730	3.6003	−0.009
25.000	3.5619	7	−2	0	2	25.001	3.5618	−0.001
25.257	3.5262	2	−5	0	1M	25.247	3.5277	0.010
			−1	5	0M	25.277	3.5235	−0.020
25.960	3.4323	14	2	4	1M	25.925	3.4370	0.035
			5	2	0M	25.937	3.4354	0.023
26.450	3.3699	9	−3	4	1	26.466	3.3679	−0.016
27.638	3.2276	8	1	2	2M	27.598	3.2322	0.040
			4	4	0M	27.636	3.2279	0.002
28.278	3.1560	14	5	3	0	28.259	3.1582	0.019
28.837	3.0961	20	6	0	0	28.809	3.0991	0.028
29.099	3.0688	15	−4	4	1	29.104	3.0683	−0.005
30.536	2.9276	19	6	2	0M	30.519	2.9292	0.017
			−3	3	2M	30.561	2.9253	−0.025

[a]I_{obs} is in the range of 1–1000, FWHM for a single, well-resolved line is in the range of 0.13–0.22 (°) 2θ.

II. EXPERIMENTAL

A. Sample preparation

1. Synthesis of tetrakis(3-ethylanilinium) octamolybdate $Mo_8O_{26}(C_8H_{12}N)_4$

Molybdic acid (1.8 g) was dissolved in boiling water (150 ml) under reflux. To this solution, the mixture of 3-ethylaniline (1.3 ml) with acetic acid (50 ml) was added and heated for 2 h, then filtered off and left for crystallization. After 1 day, the obtained crystals (white, very small, not suitable for single-crystal study) were separated, dried in air and investigated by an X-ray powder diffraction (XRPD) technique. Chemical analysis: C 23.15% (calc. 22.98%), H 2.938% (calc. 2.89%) and N 3.36% (calc. 3.35%). The elemental (C, N and O) analysis was performed using a Euro Vector EA 300 for all investigated samples.

2. Synthesis of tetrakis(3-ethylanilinium) octamolybdate tetrahydrate $Mo_8O_{26}(C_8H_{12}N)_4 \cdot (H_2O)_4$

Molybdic acid (1.8 g) was dissolved in boiling water (150 ml) under reflux. To this solution, the mixture of 3-ethylaniline (1.3 ml) with hydrochloric acid (10 ml of 1 m) was added and heated for 2 h. The obtained precipitate (white, very fine powder) was filtered off, dried in air and investigated by an XRPD technique. Chemical analysis: C 22.13% (calc. 22.03%), H 3.274% (calc. 3.24%) and N 3.24% (calc. 3.21%).

3. Synthesis of bis(3-ethylanilinium) pentamolybdate $Mo_5O_{16}(C_8H_{12}N)_2$

Molybdic acid (1.8 g) was dissolved in boiling water (150 ml) under reflux. To this solution, the mixture of

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TABLE III. XPRD data of bis(3-ethylanilinium) pentamolybdate $Mo_5O_{16}(C_8H_{12}N)_2$.

$2\theta_{obs}$ (°)	d_{obs} (Å)	I_{obs}[a]	h	k	L	$2\theta_{cal}$ (°)	d_{cal} (Å)	$\Delta 2\theta$
5.133	17.2165	1000	2	0	0	5.132	17.2199	0.001
10.270	8.6135	140	4	0	0	10.274	8.6099	−0.005
14.068	6.2955	17	2	0	2	14.066	6.2967	0.002
15.445	5.7372	14	6	0	0	15.438	5.7400	0.007
17.086	5.1897	6	4	0	2M	17.083	5.1905	0.003
			0	1	1M	17.089	5.1890	−0.003
17.647	5.0259	15	−2	1	1M	17.655	5.0237	−0.008
			−3	1	0M	17.675	5.0183	−0.028
18.046	4.9157	3	2	1	1	18.050	4.9147	−0.004
18.845	4.7091	6	−6	0	2	18.844	4.7094	0.001
19.642	4.5197	2	−4	1	1	19.622	4.5244	0.020
20.284	4.3781	10	−1	1	2	20.280	4.3791	0.004
20.623	4.3069	20	1	1	2M	20.626	4.3063	−0.003
			8	0	0M	20.633	4.3050	−0.010
21.205	4.1900	6	−3	1	2	21.234	4.1844	−0.029
22.643	3.9271	19	−6	1	1	22.640	3.9276	0.003
23.324	3.8139	33	−5	1	2	23.338	3.8118	−0.014
24.761	3.5957	75	0	1	3	24.751	3.5972	0.010
25.361	3.5120	17	8	0	2	25.372	3.5106	−0.011
25.719	3.4639	49	2	1	3	25.716	3.4643	0.003
26.360	3.3811	33	2	0	4M	26.321	3.3862	0.039
			−7	1	2M	26.331	3.3848	0.029
			−8	1	1M	26.371	3.3798	−0.011
27.658	3.2253	16	4	1	3	27.655	3.2257	0.003
28.257	3.1583	12	−6	0	4M	28.217	3.1628	0.040
			−9	1	0M	28.281	3.1558	−0.024
30.076	2.9713	15	10	0	2	30.077	2.9712	−0.001
30.596	2.9220	17	−10	1	1	30.581	2.9235	0.015
30.976	2.8870	13	−8	0	4	30.982	2.8865	−0.006
31.675	2.8249	5	3	1	4	31.677	2.8247	−0.003
32.075	2.7905	7	9	1	2M	32.085	2.7898	−0.010
			0	2	0M	32.085	2.7898	−0.010
32.514	2.7539	10	2	2	0	32.514	2.7539	.000
32.874	2.7245	8	1	2	1	32.884	2.7238	−0.010
33.833	2.6495	10	5	1	4M	33.824	2.6502	0.009
			3	2	1M	33.830	2.6498	0.003
35.033	2.5614	26	12	0	2M	35.001	2.5637	0.032
			−5	2	1M	35.027	2.5619	0.007
40.107	2.2483	17	14	0	2M	40.101	2.2487	0.006
			−9	2	1M	40.104	2.2485	0.003
41.228	2.1897	4	−2	2	4M	41.232	2.1896	−0.004
			14	1	1M	41.234	2.1894	−0.006
			0	2	4M	41.251	2.1886	−0.023
45.803	1.9811	11	−3	2	5M	45.809	1.9809	−0.006
			15	1	2M	45.845	1.9794	−0.042
46.702	1.9450	9	−5	2	5M	46.662	1.9466	0.040
			10	1	5M	46.682	1.9459	0.020

[a]I_{obs} is in the range of 1–1000, FWHM for a single, well-resolved line is in the range of 0.12–0.21 (°) 2θ.

3-ethylaniline (1.3 ml) with hydrochloric acid (10 ml of 1 m) was added and heated for 16 h. The obtained precipitate (white, very fine powder) was filtered off, dried in air and investigated by an XRPD technique. Chemical analysis: C 19.56% (calc. 19.61%), H 2.51% (calc. 2.47%) and N 2.84% (calc. 2.86%).

B. XRPD measurements and crystallographic studies

Before the measurements, each sample was thoroughly powdered (using agate mortar and pestle; particle size after grinding ∼1 μm) and back-loaded into a sample holder to avoid preferred orientation. The XPRD measurements were performed at the Faculty of Chemistry Jagiellonian University using an X'Pert PRO MPD diffractometer, a diffracted-beam graphite monochromator, and with a PIXcel 1D detector and Cu$K\alpha$ radiation (generator setting: 40 kV and 30 mA) at 298 K. The diffraction data were collected over the angular range from 3° to 70° 2θ with a step size of 0.02° (time of diffraction measurement ∼1 h). The divergence of the incident X-ray beam was 0.25°.

III. RESULTS AND DISCUSSION

The obtained powder diffraction data were analyzed using the Data Viewer and HighScore – X'Pert PRO diffractometer software (peak search, detection of α_2 lines and phase analysis). To test the purity of the sample (looking for impurity

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TABLE IV. X-ray crystal structure data for the investigated compounds.

Compound	$Mo_8O_{26}(C_8H_{12}N)_4$	$Mo_8O_{26}(C_8H_{12}N)_4 \cdot (H_2O)_4$	$Mo_5O_{16}(C_8H_{12}N)_2$
System	Triclinic	Monoclinic	Monoclinic
Space group	$P-1$	$P2_1/m$	$I2/a$
Z	1	2	4
D_{calc} (g cm^{-3})	2.24	2.37	2.38
a (Å)	10.682(4)	18.801(7)	34.643(6)
b (Å)	16.589(5)	17.943(6)	5.5796(7)
c (Å)	7.307(2)	7.334(3)	14.200(3)
α (°)	92.79(2)		
β (°)	97.99(3)	98.50(5)	96.20(2)
γ (°)	103.89		
V (Å^3)	1240.27	2446.99	2728.69
$M(30)$	10.65(0.00005,92)	9.39(0.00005,103)	16.73(0.00005,130)
$F(30)$	30.26(0.01078,92)	25.13(0.01159,103)	31.11(0.0742,130)

phases, similar compounds, etc.) PDF-4+ (Gates-Rector and Blanton, 2019), database was used. Then, the PROSZKI package was used to index the patterns (Lasocha and Lewinski, 1994). Experimental powder diffraction patterns are depicted in Figure 1. XRPD data of the investigated compounds are shown in Tables I–III. The intensity of the diffraction lines (heights) and their positions were determined using the program of Sonneveld and Visser (1975). For lattice parameters refinement, the least-squares program by Appleman *et al.* (1966) was used. The crystallographic characteristic and indexing figures of merit (de Wolff, 1968; Smith and Snyder, 1979) for all three compounds are reported in Table IV. Figure 2 presents the molecular diagrams of the investigated compounds.

Diffraction patterns of polyoxometalates usually contain one (or few) very strong low-angle diffraction lines, while the other lines are weak or very weak which can hinder the phase analysis process, indexing and space group determination. Such patterns are very common in the case of low symmetry, complicated organic or hybrid inorganic–organic materials. The preferred orientation effect (strong in the case of layered compounds measured applying Bragg–Brentano geometry) may additionally increase the problems with the analysis of such compounds by powder diffraction techniques.

IV. CONCLUSION

Molybdic acid reacting with 3-ethylaniline forms different compounds depending on the time of reaction and the acid used to obtain an acidic environment. Interestingly, using 3-ethylaniline, we managed to obtain two different types of polyoxometalates: octamolybdate of the type of an isolated cluster and a layered pentamolybdate. The resulting pentamolybdate extends the group of known layered pentamolybdates of aromatic amines.

Practical importance of the investigated compounds is connected with the fact that the catalysts based on Mo, W or V derivatives are produced in amounts of hundred tons every year. The investigated polyoxometalates can be applied to crystal engineering of complex hybrid inorganic–organic materials with tailored properties. As we reported earlier (Bożek *et al.*, 2018, Szymańska *et al.*, 2016), pentamolybdates are very promising catalysts in reactions of oxidation of cyclic hydrocarbons and their epoxidation. The investigated pentamolybdates are thermally stable and also stable under the conditions of chemical reactions. Moreover, their synthesis is efficient, relatively simple and inexpensive.

V. DEPOSITED DATA

CIF and/or RAW data files were deposited with ICDD. You may request this data from ICDD at info@icdd.com.

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