

Tetraammonium Diglycyl-octamolybdate(VI) Dihydrate, $(\text{NH}_4)_4[(\text{NH}_3\text{CH}_2\text{CO})_2(\text{Mo}_8\text{O}_{28})] \cdot 2\text{H}_2\text{O}$

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Abstract. The reaction of ammonium heptamolybdate with hydrazine sulfate in an aqueous solution of glycine at room temperature yielded colorless crystals of $(\text{NH}_4)_4[(\text{NH}_3\text{CH}_2\text{CO})_2(\text{Mo}_8\text{O}_{28})] \cdot 2\text{H}_2\text{O}$. The crystal is monoclinic, space group C2/c (no. 15), $a = 17.234 \text{ \AA}$, $b = 10.6892 \text{ \AA}$, $c = 18.598 \text{ \AA}$, $\beta = 108.280^\circ$, $V = 3253.2 \text{ \AA}^3$, $Z = 4$. The crystal

structure contains ammonium cations and isolated octamolybdate(4-) anions, $[(\text{NH}_3\text{CH}_2\text{CO})_2(\text{Mo}_8\text{O}_{28})]^{4-}$, with two zwitterionic glycine molecules as ligands.

Keywords: Molybdenum; Molybdate; Glycine; Crystal structure; Photosensitivity

Tetraammonium-diglycyl-octamolybdate(VI)-Dihydrat, $(\text{NH}_4)_4[(\text{NH}_3\text{CH}_2\text{CO})_2(\text{Mo}_8\text{O}_{28})] \cdot 2\text{H}_2\text{O}$

Inhaltsübersicht. Die Reaktion von Ammoniumheptamolybdat mit Hydrazin in einer wässrigen Lösung von Glykokoll bei Raumtemperatur ergibt farblose Kristalle von $(\text{NH}_4)_4[(\text{NH}_3\text{CH}_2\text{CO})_2(\text{Mo}_8\text{O}_{28})] \cdot 2\text{H}_2\text{O}$. Die Kristalle sind monoklin, Raumgruppe C2/c (Nr. 15), $a = 17,234 \text{ \AA}$, $b = 10,6892 \text{ \AA}$,

$c = 18,598 \text{ \AA}$, $\beta = 108,280^\circ$, $V = 3253,2 \text{ \AA}^3$, $Z = 4$. Die Kristallstruktur enthält Ammoniumkationen und isolierte Okta-molybdat(4-) Anionen, $[(\text{NH}_3\text{CH}_2\text{CO})_2(\text{Mo}_8\text{O}_{28})]^4$, mit zwei zwitterionischen Glykokoll-Molekülen als Liganden.

1 Introduction

Polyoxomolybdate chemistry has been actively pursued owing to its various applications in fields such as catalysis, electric conductivity, magnetism, nonlinear optical properties and medicine [1]. Octamolybdates with the description $[\text{Mo}_8\text{O}_{26}\text{X}_2]^{2n-4}$ (n is the normal charge of the coordinating ligand X) are a large family containing various structures, such as the α -, β -, γ -, α - β -, α - γ -, β - γ - $[\text{Mo}_8\text{O}_{26}]^{6-}$ isomers [2–4]. Some of them (for X = H, HCOO) have been studied in great details for their interesting optical properties, showing a color change from colorless to reddish violet or red-brown on exposure to ultraviolet rays, and being bleached again on heating [5, 6]. Although it has already been known that the selectivity of ternary groups 5 A and 6 A transition metal oxides as catalysts for the partial oxidation of hydrocarbons appears to depend upon the ease with which surface carboxylates are formed, carboxylated octamolybdate anion like $[(\text{HCO})_2(\text{Mo}_8\text{O}_{28})]^{6-}$ reported by Adams and his

group [6] are rather limited in the literature. In this article, we report a new octamolybdate, $(\text{NH}_4)_4[(\text{NH}_3\text{CH}_2\text{CO})_2(\text{Mo}_8\text{O}_{28})] \cdot 2\text{H}_2\text{O}$, in which two zwitterionic glycine molecules act as ligands.

2 Experimental

2.1 Synthesis

All chemicals were analysis pure as received from commercial sources.

0.20 g (1.5 mmol) $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{SO}_4$ was added into a colorless solution of 0.70 g (0.57 mmol) $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ and 3.04 g (40.5 mmol) $\text{NH}_2\text{CH}_2\text{COOH}$ in 60 ml water. The solution was stirred at room temperature for 10 minutes with a color change from green to dark blue. 0.54 g (10 mmol) NH_4Cl was added and then the solution was stood without disturbance for half a month. Colorless prismatic crystals were isolated from the red-brown precipitation but the color of the crystals changes gradually to red-brown in the air.

2.2 Structure Determination

A 0.35 mm \times 0.10 mm \times 0.10 mm single crystal was selected and mounted on the goniometer of Rigaku R-AXIS RAPID imaging plate diffractometer. Diffraction data was collected at 173 K with graphite monochromated $\text{MoK}\alpha$ radiation ($\lambda = 0.071073 \text{ nm}$) operating at 50 kV and 40 mA. Indexing was performed from two oscillation images that were

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Table 1 Positional and displacement parameters U_{ij}/pm^2

Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Mo1	0.11700(2)	0.91463(3)	0.109093(18)	161.6(18)	114.4(16)	137.9(17)	-7.2(12)	83.3(13)	8.8(12)
Mo2	0.04789(2)	0.73341(3)	-0.036970(18)	154.1(18)	114.2(15)	143.6(17)	-6.6(12)	73.5(13)	-0.4(13)
Mo3	0.16672(2)	0.53693(3)	-0.086873(18)	160.9(18)	105.1(15)	155.2(18)	-16.3(12)	83.2(13)	-7.6(12)
Mo4	0.24595(2)	0.69306(3)	0.085539(18)	155.2(18)	94.4(15)	129.9(17)	3.9(12)	82.1(13)	4.3(12)
O1	0.12966(18)	1.0732(3)	0.11998(16)	215(15)	159(13)	216(15)	-29(12)	97(12)	0(12)
O2	0.03537(17)	0.8781(3)	0.13841(15)	207(15)	167(13)	170(14)	-14(11)	88(12)	-8(12)
O3	0.13506(17)	0.7151(2)	0.08290(15)	180(14)	121(12)	177(14)	19(11)	99(11)	4(11)
O4	1.19918(17)	0.8728(3)	0.21678(15)	191(14)	226(14)	129(13)	22(11)	82(11)	39(12)
O5	0.23270(17)	0.8912(2)	0.09038(15)	187(14)	104(12)	172(14)	4(10)	93(11)	-3(11)
O6	0.29872(17)	0.6649(2)	0.17779(15)	227(15)	154(13)	158(13)	2(11)	87(11)	27(12)
O7	0.23834(17)	0.5456(2)	0.04373(15)	197(14)	108(12)	177(14)	2(10)	85(11)	-9(11)
O8	0.17252(17)	0.7365(2)	-0.04666(15)	173(14)	122(12)	148(13)	-7(11)	84(11)	-1(11)
O9	0.018988(18)	0.3797(3)	-0.07357(17)	213(15)	149(13)	262(15)	-39(12)	147(12)	-15(12)
O10	0.11164(18)	0.5505(3)	-0.17997(16)	199(15)	241(15)	209(15)	-35(12)	89(12)	-32(12)
O11	0.07109(17)	0.9048(2)	0.00214(15)	194(15)	109(12)	150(13)	-1(10)	85(11)	-5(11)
O12	-0.03614(18)	0.7009(2)	-0.00921(16)	242(15)	152(13)	195(14)	24(11)	115(12)	28(12)
O13	0.00798(17)	0.7747(3)	-0.13047(15)	192(14)	154(13)	185(14)	-4(11)	67(11)	-11(12)
O14	0.07774(17)	0.5612(2)	-0.04584(15)	198(15)	119(12)	140(13)	-25(10)	92(11)	0(11)
O15	0.13296(17)	0.8728(3)	0.30357(15)	201(15)	191(13)	156(13)	17(11)	91(11)	21(12)
O16	0.06238(18)	0.5435(3)	0.14664(16)	208(15)	206(14)	206(15)	25(12)	97(12)	-18(12)
N1	0.3435(2)	0.8224(3)	0.31214(18)	165(17)	157(15)	144(16)	-11(13)	56(13)	14(14)
N2	-0.1361(2)	0.8698(3)	0.04080(18)	190(18)	152(15)	167(16)	-10(13)	84(13)	23(14)
N3	0.0000	0.3242(5)	-0.2500	210(30)	182(20)	310(30)	0	130(20)	0
N4	0.0000	0.9455(4)	-0.2500	220(30)	180(20)	130(20)	0	88(19)	0
C1	0.1943(2)	0.8602(3)	0.2833(2)	190(20)	113(16)	168(19)	3(15)	101(16)	-3(15)
C2	0.2746(3)	0.8229(4)	0.3426(2)	220(20)	170(18)	155(19)	17(15)	106(16)	9(16)

Table 2 Selected bond lengths d/ \AA

Bond	d/ \AA	Bond	d/ \AA	Bond	d/ \AA
Mo1–O2	1.706(3)	Mo2–O8	2.211(3)	Mo4–O3	1.911(3)
Mo1–O1	1.713(3)	Mo2–O3	2.272(3)	Mo4–O8 ^a	1.924(3)
Mo1–O11	1.899(3)	Mo3–O10	1.700(3)	Mo4–O5	2.135(3)
Mo1–O4	2.107(3)	Mo3–O9	1.727(3)	Mo4–O8	2.431(3)
Mo1–O5	2.144(3)	Mo3–O5 ^a	1.916(3)	O4–C1	1.273(4)
Mo1–O3	2.231(3)	Mo3–O14	1.933(2)	O15–C1	1.236(4)
Mo2–O13	1.715(3)	Mo3–O8	2.253(3)	N1–C2	1.467(5)
Mo2–O12	1.719(3)	Mo3–O7	2.356(3)	C1–C2	1.528(5)
Mo2–O14	1.933(3)	Mo4–O6	1.698(3)		
Mo2–O11	1.966(3)	Mo4–O7	1.745(3)		

^a) symmetric code 7565: +x, 1 - y, -0.5 + z.

exposed for 5 min. The detector swing angle was 5.00°. The crystal-to-detector distance was 127.4 mm. Readout was performed in the 0.100 mm pixel mode. Absorption corrections were applied by correlation of symmetry-equivalent reflections using the ABSCOR program. Data reduction was performed by teXsan for Windows version 1.06 (MSC, 1997–1999). The structures were solved by direct method and difference Fourier map using SHELXS97 (Sheldrick, 1997) and refined on F^2 by full-matrix least-squares techniques using SHELXL97 (Sheldrick, 1997).

The crystal is monoclinic, space group C2/c (no. 15), $a = 17.234(1)$ \AA , $b = 10.6892(8)$ \AA , $c = 18.598(2)$ \AA , $\beta = 108.280(3)$ °, $V = 3253.2(4)$ \AA^3 , formula $(\text{NH}_4)_4[(\text{NH}_3\text{CH}_2\text{CO})_2\text{Mo}_8\text{O}_{28}] \cdot 2 \text{H}_2\text{O}$, $M_r = 1441.86$, $Z = 4$, calc. Density = 2.943 g/cm³, $\mu = 3.101$ mm⁻¹. A total of 3932 reflections were read of which 3730 unique reflections were used for structural determination. The structure was refined against 227 parameters. $R_1 = 0.0300$ for $3201 I > 2\sigma(I)$ and $wR_2 = 0.0740$ for all 3730 data. Goodness of fit was 1.070. The positional and displacement parameters (without H atoms) are given in Table 1. The selected bond lengths and angles are shown in Table 2 and Table 3.

Further details of the crystal structure investigation are available from the Fachinformationszentrum Karlsruhe,

D-76344 Eggeneistein-Leopoldshafen (Germany), on quoting the depository number CSD-411534, the name of the author(s), and citation of the paper.

2.3 Elemental Analysis

$\text{C}_4\text{H}_{30}\text{N}_6\text{O}_{32}\text{Mo}_8$, calc. C, 3.3; H, 2.1; N, 5.8; O, 35.5; Mo, 53.3%; found C, 3.3, H, 2.0; N, 5.8; O35.3; Mo, 53.3%.

3 Results and Discussion

The crystal structure is composed of isolated octamolybdate anions and ammonium cations. The anion (Fig. 1) is in general similar to the anions $[\text{H}_2\text{Mo}_8\text{O}_{28}]^{6-}$ [7] and $[(\text{HCO})_2(\text{Mo}_8\text{O}_{28})]^{6-}$ [6]. Since the anion is centrosymmetric, each asymmetric unit contains half a molecule. This classical octamolybdate anion consists of eight MoO_6 octahedra sharing edges and vertexes with each other, but with four different types of octahedra. The Mo1 octahedron shares edges with Mo2 and Mo4 octahedra, and shares a vertex with a Mo3' octahedron. There are two μ_3 -O, one μ_2 -O, two terminal oxygen atoms and one carboxyl oxygen atom surrounding Mo1. The Mo2 octahedron shares edges with Mo1, Mo3 and Mo4 octahedra. There are one μ_4 -O, one μ_3 -O, two μ_2 -O and two terminal oxygen atoms surrounding Mo2. The Mo3 octahedron shares edges with Mo2, Mo4 and Mo4' octahedra, and shares a vertex with the Mo1' octahedron. There are one μ_4 -O, one μ_3 -O, two μ_2 -O and two terminal oxygen atoms surrounding Mo3. The Mo4 octahedron shares edges with Mo1, Mo2, Mo3, Mo3' and Mo4' octahedra. There are two μ_4 -O, two μ_3 -O, one μ_2 -O and one terminal oxygen atoms surrounding Mo4. Two glycine molecules coordinate to the two Mo1 atoms at the OH position in $[\text{H}_2\text{Mo}_8\text{O}_{28}]^{6-}$ [7]

Table 3 Selected bond angles (in degree)

Angle	β°	Angle	β°	Angle	β°
O2-Mo1-O1	106.01(13)	O14-Mo2-O3	83.69(10)	O8-Mo4-O5 ^{a)}	74.22(10)
O2-Mo1-O11	101.99(12)	O11-Mo2-O3	73.86(10)	O6-Mo4-O8	178.81(12)
O1-Mo1-O11	100.03(12)	O8-Mo2-O3	73.81(10)	O7-Mo4-O8	77.25(11)
O2-Mo1-O4	91.35(12)	O10-Mo3-O9	105.01(14)	O3-Mo4-O8	75.60(10)
O1-Mo1-O4	94.30(13)	O10-Mo3-O5 ^{a)}	98.82(12)	O8-Mo4-O8 ^{a)}	75.82(12)
O11-Mo1-O4	156.79(11)	O9-Mo3-O5	102.95(12)	O5-Mo4-O8	79.89(9)
O2-Mo1-O5	158.06(12)	O10-Mo3-O14	97.59(13)	Mo4-O3-Mo1	108.62(12)
O1-Mo1-O5	92.54(12)	O9-Mo3-O14	104.49(12)	Mo4-O3-Mo2	112.58(12)
O11-Mo1-O5	85.79(11)	O5-Mo3-O14 ^{a)}	142.96(11)	Mo1-O3-Mo2	92.15(10)
O4-Mo1-O5	75.36(10)	O10-Mo3-O8	102.12(12)	C1-O4-Mo1	135.8(3)
O2-Mo1-O3	92.10(11)	O9-Mo3-O8	152.86(12)	Mo3-O5-Mo4 ^{a)}	106.65(12)
O1-Mo1-O3	161.88(12)	O5-Mo3-O8 ^{a)}	71.64(10)	Mo3-O5-Mo1 ^{a)}	148.91(14)
O11-Mo1-O3	76.08(10)	O14-Mo3-O8	72.55(10)	Mo4-O5-Mo1	103.88(11)
O4-Mo1-O3	84.63(11)	O10-Mo3-O7	172.50(12)	Mo4-O7-Mo3	115.89(13)
O5-Mo1-O3	69.65(10)	O9-Mo3-O7	82.39(12)	Mo4-O8-Mo2 ^{a)}	151.53(14)
O13-Mo2-O12	104.41(13)	O5-Mo3-O7 ^{a)}	80.35(10)	Mo4-O8-Mo3 ^{a)}	101.97(11)
O13-Mo2-O14	101.05(12)	O14-Mo3-O7	79.14(10)	Mo2-O8-Mo3	94.00(10)
O12-Mo2-O14	96.01(11)	O8-Mo3-O7	70.51(9)	Mo4-O8-Mo4 ^{a)}	104.18(12)
O13-Mo2-O11	96.05(12)	O6-Mo4-O7	103.41(13)	Mo2-O8-Mo4	97.21(9)
O12-Mo2-O11	99.80(12)	O6-Mo4-O3	105.21(12)	Mo3-O8-Mo4	96.30(10)
O14-Mo2-O11	153.00(12)	O7-Mo4-O3	99.52(12)	Mo1-O11-Mo2	114.11(13)
O13-Mo2-O8	90.25(12)	O6-Mo4-O8 ^{a)}	103.07(12)	Mo3-O14-Mo2	115.26(13)
O12-Mo2-O8	163.55(12)	O7-Mo4-O8 ^{a)}	98.50(11)	O15-C1-O4	127.5(4)
O14-Mo2-O8	73.50(10)	O3-Mo4-O8 ^{a)}	141.67(11)	O15-C1-C2	118.4(3)
O11-Mo2-O8	85.77(10)	O6-Mo4-O5	99.42(12)	O4-C1-C2	114.1(3)
O13-Mo2-O3	161.49(11)	O7-Mo4-O5	157.10(12)	N1-C2-C1	112.4(3)
O12-Mo2-O3	92.75(12)	O3-Mo4-O5	76.08(11)		

^{a)} symmetric code 7565: +x, 1 - y, -0.5 + z.

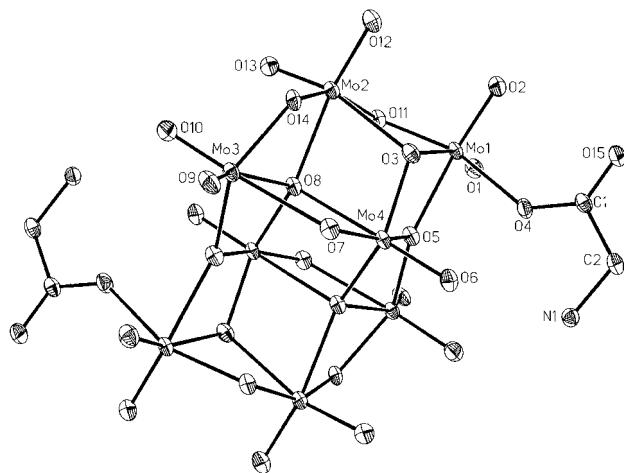


Fig. 1 The structure of the octamolybdate(4-) anion with 50% probability displacement ellipsoids. Hydrogen atoms are omitted for clarity. Atomic labelling according to Table 1.

and at the position of the formic acid ligand in $[(\text{HCO})_2(\text{Mo}_8\text{O}_{28})]^{6-}$ [6]. In $[\text{H}_2\text{Mo}_8\text{O}_{28}]^{6-}$, the distance between Mo and the protonated O is 1.97 Å, longer than the distances between Mo and other unshared O atoms (1.70–1.73 Å) [7]. In $[(\text{NH}_3\text{CH}_2\text{CO})_2(\text{Mo}_8\text{O}_{28})]^{4-}$, the distances between Mo and unshared O atoms (except O4) are also 1.70–1.73 Å, but the distance between Mo1 and O4 (the carboxyl oxygen atom) is 2.107 Å, much longer than the others. According to the bond valence approach of Brown [8], the bond order between Mo1 and O4 is only 0.5. So

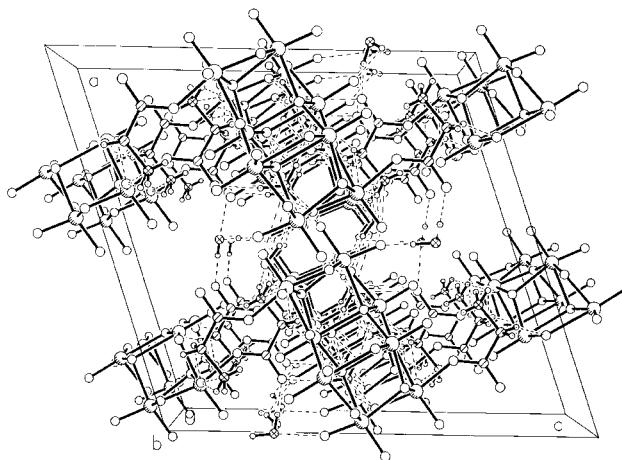


Fig. 2 The crystal structure viewed down the b axis. Hydrogen bonding network is indicated by broken lines.

the anion can be regarded as $[(\text{NH}_3\text{CH}_2\text{COO})(\text{Mo}_8\text{O}_{26})]^4-$, and fit the common description $[\text{Mo}_8\text{O}_{26}\text{X}_2]^{2n-4}$ very well. The replacement of formic acid by glycine decreases the charge of the octamolybdate anion by protonating the amino group to form zwitterionic glycine ligands.

The compound forms a 3D hydrogen bond network in the crystal (see Fig. 2). All the hydrogen atoms except those of methylene take part in hydrogen bonding (Table 4). There are three hydrogen atoms of the amino group, and they are located at the certain direction by intromolecular and intermolecular hydrogen bonds. So the whole structure is steadier than those

Table 4 Hydrogen bonds in the crystal

Hydrogen bond	d/Å	β°	Hydrogen bond	d/Å	β°
N1–H3...O16 ^{a)}	2.832(4)	166.3(2)	N3–H10...O16 ^{f)}	2.854(4)	144.9(2)
N1–H4...O13 ^{b)}	2.890(4)	144.9(2)	N3–H11...O15 ^{f)}	3.040(4)	157.3(2)
N1–H5...O6	2.909(4)	137.7(3)	N4–H12...O13	2.846(4)	165.3(2)
N2–H6...O15 ^{c)}	2.878(4)	160.4(2)	N4–H13...O15 ^{d)}	2.930(4)	174.8(2)
N2–H7...O12	2.846(4)	173.2(2)	O16–H14...O3	2.697(4)	172.7(2)
N2–H8...O11 ^{d)}	2.874(4)	144.3(2)	O16–H15...O14 ^{f)}	2.785(4)	155.3(2)
N2–H9...O9 ^{e)}	3.087(5)	170.1(2)			

^{a)} symmetric code 6555: 0.5 – x, 0.5 + y, 0.5 – z; ^{b)} symmetric code 8566: 0.5 + x, 1.5 – y, 0.5 + z; ^{c)} symmetric code 5555: –x, +y, 0.5 – z; ^{d)} symmetric code 3575: –x, 2 – y, –z; ^{e)} symmetric code 2455: –0.5 + x, 0.5 + y, z; ^{f)} symmetric code 3565: –x, 1 – y, –z.

containing OH and formic acid ligands. In Fig. 2, it can be clearly seen how the intromolecular hydrogen bonds act and how the ammonium cations and water molecules connect the octamolybdate anions into a 3 D network *via* intermolecular hydrogen bonds.

An interesting feature of the title compound is that the crystal is photosensitive, its color changes from colorless to red-brown on exposure in air. During X-ray study, the color change was also observed. Similar phenomenon was also observed in cases of the anions $[\text{H}_2\text{Mo}_8\text{O}_{28}]^{6-}$ [7] and $[(\text{HCO})_2(\text{Mo}_8\text{O}_{28})]^{6-}$ [6]. Yamase et al. proved that when crystals of $[\text{H}_2\text{Mo}_8\text{O}_{28}]^{6-}$ were irradiated with ultraviolet rays, some of the Mo^{VI} ions were reduced to Mo^V [5]. Since the structures of these three compounds are similar, it should be the same reason why the color of the title compound changes. Further optical investigation is in process in our laboratory.

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