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Synthesis and Crystal Structure of $[(CH_3)_4N]_4Na_2[As_2Mo_{12}O_{42}]\cdot 6H_2O$

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A novel dodecamolybdodiarsenate(III) salt $[(CH_3)_4N]_4Na_2[As_2Mo_{12}O_{42}]\cdot 6H_2O$ is synthesized and its crystal structure is determined. The trivalent As heteroatoms with an unshared electron pair are bonded to three O atoms with the distances of 1.79 Å to form AsO_3 trigonal pyramids. The polyanion molecule has no symmetry elements, consisting of twelve distorted MoO_6 octahedra.

Heteropolymolybdates of trivalent arsenic were first reported late in the 19th century.[1] A hexamolybdoarsenate(III) salt $(CN_3H_6)_3[As(Mo_2O_7)_3]\cdot H_2O$, was described by Rosenheim et al.,[2] but no further investigation either in crystal or in solution has been developed. Recently we have synthesized a new heteropoly compound with As/Mo ratio of 1/6 and determined its crystal structure. The polyanion molecule is proved to be a dimeric formula ($As_2Mo_{12}O_{42}^{6-}$) of Rosenheim's.

We have got two types of crystals from arsenate(III)-molybdate mixture at different pH areas. A 1.0 g (5 mmol) of diarsenic trioxide and a 1.5 g of NaOH were dissolved in 20 cm^3 of water. The solution was added to a 40 cm^3 aqueous solution containing 14.7 g (60 mmol) of $Na_2MoO_4\cdot 2H_2O$. The mixture was kept cooling in an ice bath and acidified with HCl. The solution became pale yellow at pH ca. 6, and then turned deep yellow at pH ca. 3. At pH <3 the polyanion was reduced and the solution became gradually dark green. This reduction also occurred in higher pH area when the As/Mo ratio in the solution was increased. Yellow columnar crystals of $[(CH_3)_4N]_4Na_2[As_2Mo_{12}O_{42}]\cdot 6H_2O$ were obtained from the pH 3 solution by the addition of $(CH_3)_4NBr$ and slow evaporation below 5 °C, while from the pH 6 solution, colorless octahedron of unknown composition crystallized in the orthorhombic form.

A single crystal with dimensions of 0.30x0.10x0.05 mm was used for X-ray diffraction measurement. The crystal data for $[(CH_3)_4N]_4Na_2[As_2Mo_{12}O_{42}]\cdot 6H_2O$ are triclinic, $P\bar{1}$, FW=2323.78, a=23.666(5), b=13.591(3), c=10.760(3) Å, α=110.88(2), β=95.72(2), γ=84.52(3)°, V=3211(1) $Å^3$, Z=2, Dx=2.51 g cm^{-3}, Dm=2.61 g cm^{-3}, μ(for Mo Kα)=33.44 cm^{-1}. Intensities were collected by use of RIGAKU AFC-5R four-circle diffractometer and RU-1000 X-ray generator (50 kV-1000 mA) with graphite monochromatized Mo Kα radiation.

Table 1. Positional parameters ($\times 10^4$; for As and Mo $\times 10^5$) and equivalent isotropic thermal parameters ($Å^2$) with e.s.d.'s in parentheses

Atom	x	y	z	Beq[a]	Atom	x	y	z	Beq
Mo(1)	44337(5)	27715(9)	57601(13)	1.89(3)	O(29)	2843(4)	3342(7)	4358(9)	1.9(3)
Mo(2)	39300(5)	9042(8)	65199(12)	1.74(3)	O(30)	876(4)	4511(9)	7005(12)	3.4(3)
Mo(3)	26715(5)	14472(9)	85437(12)	1.89(3)	O(31)	3277(4)	638(6)	4649(9)	1.8(3)
Mo(4)	19472(5)	37396(9)	89646(12)	1.85(3)	O(32)	2183(4)	5792(7)	6776(9)	1.8(3)
Mo(5)	26409(5)	59499(9)	87523(12)	1.84(3)	O(33)	1938(4)	2189(7)	8877(9)	2.0(3)
Mo(6)	38143(5)	54243(8)	71320(12)	1.63(3)	O(34)	3145(4)	957(7)	7073(9)	1.8(3)
Mo(7)	31209(5)	19393(8)	41473(11)	1.55(3)	O(35)	2111(4)	751(7)	6598(10)	2.1(3)
Mo(8)	25902(5)	2444(8)	51631(12)	1.86(3)	O(36)	2022(4)	4924(7)	8444(9)	2.0(4)
Mo(9)	13225(6)	11594(10)	71474(14)	2.68(4)	O(37)	2644(4)	2995(6)	7984(9)	1.7(3)
Mo(10)	5917(5)	33627(11)	73216(15)	2.89(4)	O(38)	3557(4)	2511(6)	6395(8)	1.7(3)
Mo(11)	13853(5)	54204(10)	68413(14)	2.38(4)	O(39)	3067(4)	4502(6)	7261(8)	1.5(4)
Mo(12)	25434(5)	47062(8)	52291(11)	1.54(3)	O(40)	2431(4)	1962(6)	5190(9)	1.7(3)
As(13)	33136(5)	34759(10)	79146(13)	1.43(3)	O(41)	1914(4)	3943(7)	5701(9)	2.0(3)
As(14)	17420(6)	26042(11)	52060(14)	1.89(4)	O(42)	1515(4)	2666(7)	6769(9)	2.2(3)
Na(1)	4208(2)	7973(4)	6492(6)	2.5(2)	Ow(1)	3465(5)	7082(8)	4691(11)	3.3(3)
O(1)	4729(4)	3171(8)	7363(10)	2.9(3)	Ow(2)	3416(5)	8421(9)	7848(13)	4.3(4)
O(2)	4979(4)	2681(8)	4797(12)	3.2(3)	Ow(3)	4737(7)	8896(12)	8516(15)	6.3(6)
O(3)	4094(4)	-435(7)	6031(11)	2.9(3)	Ow(4)	2087(6)	8010(11)	6855(16)	5.7(6)
O(4)	4227(4)	1410(8)	8113(10)	3.2(3)	Ow(5)	4097(7)	802(13)	397(20)	8.0(8)
O(5)	2577(5)	316(8)	8849(11)	3.3(4)	Ow(6)	812(12)	9174(24)	9720(33)	16.3(3)
O(6)	3132(4)	2099(8)	9820(10)	2.8(3)	N(1)	4188(5)	4355(9)	2151(11)	2.3(4)
O(7)	2231(4)	4171(8)	10542(9)	2.6(3)	N(2)	3968(5)	8449(9)	1751(12)	2.5(5)
O(8)	2266(4)	7117(7)	9472(10)	2.9(3)	N(3)	571(7)	3162(12)	1934(15)	4.2(4)
O(9)	2985(4)	5632(8)	10052(10)	2.9(3)	N(4)	1464(6)	7173(10)	2527(13)	3.3(6)
O(10)	4183(4)	5256(7)	8516(10)	2.5(3)	C(11)	4443(8)	4957(16)	3499(16)	4.2(8)
O(11)	4191(4)	6288(7)	6772(10)	2.5(3)	C(12)	3559(8)	4327(19)	2157(21)	5.8(10)
O(12)	2856(4)	1317(7)	2567(9)	2.6(3)	C(13)	4459(12)	3268(16)	1691(27)	7.5(10)
O(13)	2819(4)	-989(7)	5201(11)	3.0(3)	C(14)	4319(10)	4824(22)	1167(22)	6.4(6)
O(14)	2149(4)	-57(8)	3743(11)	3.1(3)	C(21)	4261(9)	7614(15)	607(16)	4.6(5)
O(15)	1022(5)	564(10)	5587(12)	4.5(4)	C(22)	3436(7)	8877(13)	1249(18)	3.7(6)
O(16)	1278(5)	314(10)	7986(13)	4.3(4)	C(23)	4368(7)	9288(13)	2487(18)	3.7(6)
O(17)	297(5)	2711(10)	5747(12)	4.0(4)	C(24)	3831(9)	7924(14)	2753(18)	4.2(13)
O(18)	31(4)	3974(10)	8239(13)	4.3(4)	C(31)	171(12)	3373(26)	886(27)	8.5(26)
O(19)	1201(5)	6561(9)	8101(12)	4.1(4)	C(32)	1136(15)	3500(42)	1994(39)	16.2(31)
O(20)	1096(5)	5629(9)	5477(12)	3.6(4)	C(33)	632(25)	2030(31)	1348(58)	20.1(21)
O(21)	2184(4)	4990(8)	3955(10)	2.7(3)	C(34)	345(15)	3466(38)	3225(31)	13.7(8)
O(22)	4424(4)	1270(6)	5568(9)	1.8(2)	C(41)	2097(8)	7204(18)	2679(24)	5.9(12)
O(23)	3830(4)	2100(7)	3942(10)	2.3(2)	C(42)	1330(10)	6183(24)	1385(30)	10.2(19)
O(24)	1209(4)	3951(8)	9137(10)	2.6(2)	C(43)	1253(12)	7104(35)	3706(31)	11.6(23)
O(25)	3232(4)	6466(7)	8127(9)	2.1(2)	C(44)	1224(14)	8003(14)	2024(48)	13.7(7)
O(26)	3160(4)	5416(7)	5495(9)	2.0(3)	Na(21)[b]	1795(8)	9127(19)	8931(19)	4.1(9)
O(27)	735(4)	2168(9)	7933(11)	3.3(3)	Na(22)[b]	1911(10)	10008(21)	10937(24)	5.2(14)
O(28)	4059(4)	4097(7)	5855(9)	1.8(3)	Na(23)[b]	1371(14)	8507(17)	8285(37)	9.1(17)

a) $Beq=(8/3)\pi^2\Sigma_{ij}U_{ij}a_i^*a_j^*a_i.a_j$.
b) The occupancies of Na(21), Na(22), and Na(23) are 1/3.

No intensity decreasing of standard reflections was observed during the measurement. Absorption correction was not applied.

Of total 14760 independent reflections in the range of 4 °<2θ<55 °, 8806 data with $Fo>5.0$ and $Fo\geqq3\sigma(Fo)$ were used for structure determination and refinement. The positions of Mo and As atoms were solved from three-dimensional Patterson maps. The O atoms, cations, and waters of crystallization were located by successive Fourier syntheses. All the non-hydrogen atoms were found and the positional and the thermal parameters were refined by block-diagonal

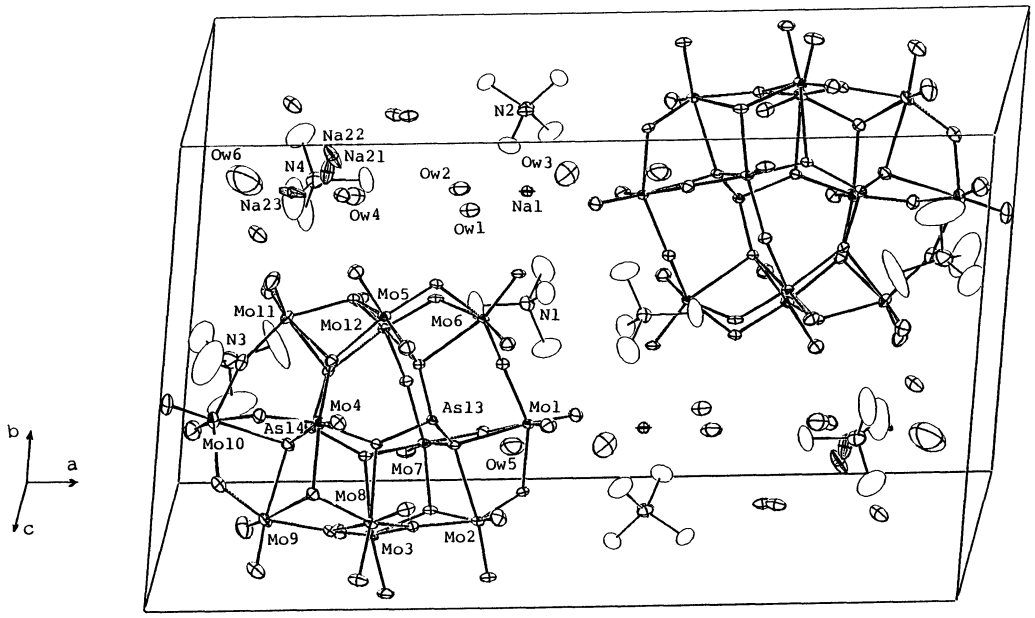

Fig. 1. The crystal structure of $[(CH_3)_4N]_4Na_2[As_2Mo_{12}O_{42}]\cdot 6H_2O$ projected along the c^*-axis with ORTEP plotting.

Table 2. Bond distances and angles within the AsO_3 moieties

As(13)	- O(37)	1.79(1)	Å
	- O(38)	1.80(1)	
	- O(39)	1.80(1)	
As(14)	- O(40)	1.77(1)	
	- O(41)	1.78(1)	
	- O(42)	1.79(1)	
O(37)-As(13)-O(38)		101.2(4)	°
O(37)-As(13)-O(39)		99.3(4)	
O(38)-As(13)-O(39)		97.7(4)	
O(40)-As(14)-O(41)		100.8(4)	
O(40)-As(14)-O(42)		102.2(5)	
O(41)-As(14)-O(42)		97.3(4)	

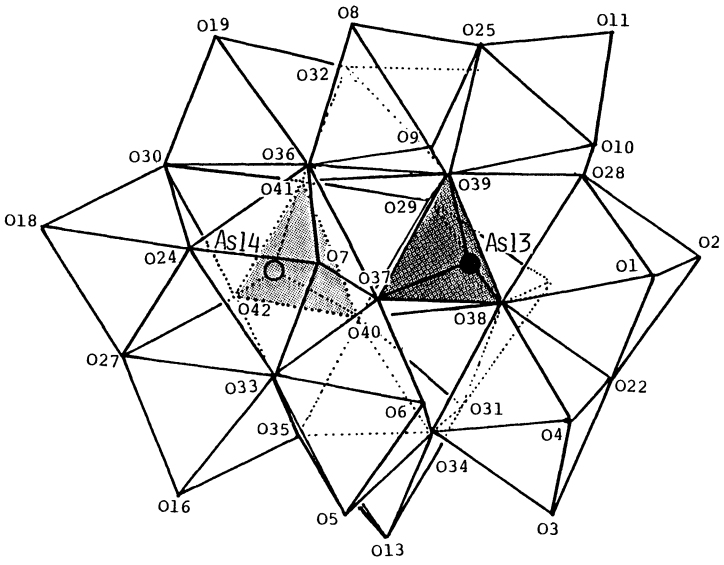

Fig. 2. The $As_2Mo_{12}O_{42}^{6-}$ polyanion with polyhedral representation.

least-squares. The anisotropic thermal factors were applied for all the atoms and the final R value ($R=\Sigma||Fo|-|Fc||/\Sigma|Fo|$) was 0.053.

The crystal structure of $[(CH_3)_4N]_4Na_2[As_2Mo_{12}O_{42}]\cdot 6H_2O$ is shown in Fig. 1. All the positional and the equivalent thermal parameters are given in Table 1. One Na atom is disordered into three positions (Na(21), Na(22), Na(23)), of which the occupancies are estimated to be 1/3 during the refinement. The dodecamolybdodiarsenate(III) anion (Fig. 2) has an entirely novel structure which can be

described as a fuse of two six-membered rings of MoO_6 octahedra (Mo(1)-Mo(6) and Mo(7)-Mo(12)) that are found in the $CH_3AsMo_6O_{27}H_{12}^{2-}$[5] by sharing O atoms. The two trivalent As atoms are located in the center of each ring and coordinated by only three O atoms in the form of AsO_3 trigonal pyramids toward opposite directions of each other. These AsO_3 moieties are regarded as discrete arsenite anions (AsO_3^{3-}). There are four groups of O atoms with respect to the number of bonded Mo and As atoms. The Mo-O(terminal : bonded to one Mo atom) bond distances of 1.68-1.72 Å corresponds to Mo-O double bond.[6] The Mo-O distances in the other three groups of 1.76-2.27 Å(bonded to two Mo atoms), 1.89-2.41 Å(bonded to three Mo atoms or to one As atom and two Mo atoms), and 2.27-2.49 Å(bonded to one As and three Mo atoms) are widely varied, and the MoO_6 octahedra are distorted to make up the polyanion. The whole molecule has no symmetry elements. The sums of calculated Mo-O bond valences [7] around each Mo atom (av. 5.85) are close to the oxidation number of Mo (6). The As-O bond lengths and bond angles are given in Table 2. O(37), O(40), and O(41) are shared by two Mo atoms while O(38), O(39), and O(42) are shared by three. Unlike the Mo-O bond, there is no apparent deviation of As-O bond distance. The AsO_3 moieties seem to be little influenced by the surroundings.

References

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