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SHORT STRUCTURAL PAPERS

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Structure of a Novel Type of Heteropolyanion: Dicupro(II)-18-molybdodisilicate(12−), $[Cu_2Si_2Mo_{18}O_{66}]^{12-}$

BY H. F. FUKUSHIMA,* A. KOBAYASHI AND Y. SASAKI

Department of Chemistry and Research Centre for Spectrochemistry, Faculty of Science, The University of Tokyo, Hongo, Tokyo 113, *Japan*

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Abstract. $(NH_4)_{12}[Cu_2Si_2Mo_{18}O_{66}].14H_2O$, M_r = 3434·2, triclinic, $P\bar{1}$, $a = 12{\cdot}19$ (2), $b = 15{\cdot}78$ (2), $c = 10{\cdot}81$ (2) Å, $\alpha = 91{\cdot}3$ (6), $\beta = 74{\cdot}6$ (3), $\gamma = 75{\cdot}8$ (2)°, $U = 1989$ Å^3, $Z = 1$, $D_x = 2{\cdot}87$, $D_m = 2{\cdot}91$ Mg m^{-3}, μ(Mo $K\alpha$) = 2·47 mm^{-1}. Block-diagonal least-squares calculations based on 4602 independent intensities reduced the R factor to 0·048. The X-ray structure determination of $(NH_4)_6[CuSiMo_9O_{33}].7H_2O$ has shown that the compound has a dimeric structure and contains the polyanion $[Cu_2Si_2Mo_{18}O_{66}]^{12-}$. Each SiO_4 tetrahedron is surrounded by nine MoO_6 octahedra. The two CuO_6 octahedra, which have a common edge, are attached to both Si atoms. These CuO_6 octahedra are elongated by the static Jahn–Teller effect.

Introduction. Many kinds of heteropolymolybdates and -tungstates containing two different hetero-atoms have recently been prepared and investigated. Anions of the general formula $[H_2X^{m+}Y^{n+}M_{11}O_{40}]^{(12-m-n)-}$ (where M = Mo^{6+} or W^{6+}; X^{m+} = Si^{4+}, Ge^{4+}, P^{5+}, As^{5+}, Co^{2+}, or Co^{3+}; Y^{n+} = transition metals) have the Keggin structure in which one of the Mo or W atoms in the MO_6 octahedra is substituted by Y^{n+} (Baker, Baker, Eriks, Pope, Shibata, Rollins, Fang & Koh, 1966; Weakley & Malik, 1967; Tourné & Tourné, 1969; Tourné, Tourné, Malik & Weakley, 1970; Zonnevijlle, 1976). The $[H_2X_2^{m+}Y^{n+}M_{17}O_{62}]^{(20-2m-n)-}$-type anions ($X^{m+}$ = P^{5+} or As^{5+}; M = Mo^{6+} or W^{6+}; Y^{n+} = transition metals) (Malik & Weakley, 1968) can be regarded as substitution derivatives of the well known $[X_2^{m+}M_{18}O_{62}]^{(16-2m)-}$ anion, in which the geometrical arrangement of the MO_6 octahedra around each XO_4 tetrahedron is common to that found in the Dawson structure.

The $[P_2Co_4(H_2O)_2W_{18}O_{68}]^{10-}$ anion (Weakley, Evans, Showell, Tourné & Tourné, 1973) likewise contains two fragments of the Keggin ion, PW_9O_{34}, but lacks one of the four W_3O_{13} units contained in the Keggin structure. The present paper reports a new type of heteropolyanion containing two different kinds of hetero-atoms (Si and Cu^{II}) with a structure having no resemblance to the Keggin or Dawson structure. The ammonium salt of the present complex was first prepared by Leyrie, Fournier & Massart (1971) together with $[H_2CuSiMo_{11}O_{40}]^{6-}$ salts, and Fournier & Massart (1974) later gave the ammonium salt the monomeric formula $(NH_4)_6[CuSiMo_9O_{34}H_2(H_2O)_3]$. The crystals were prepared by a procedure similar to that described by Leyrie, Fournier & Massart (1971).

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* Present address: Tokyo University of Agriculture and Technology, Koganei, Tokyo 184, Japan.

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Table 1. *Fractional coordinates* (×10^4) *and equivalent isotropic temperature factors* (Å^2 ×10^2) *with e.s.d.'s in parentheses*

$B_{\rm eq} = \frac{4}{3}(B_{11}a^2 + B_{22}b^2 + B_{33}c^2 + 2B_{12}ab\cos\gamma + 2B_{23}bc\cos\alpha + 2B_{13}ca\cos\beta)$.

	x	y	z	$B_{\rm eq}$
Mo(1)	4352 (1)	7338 (1)	9372 (1)	169 (4)
Mo(2)	3580 (1)	8966 (1)	7099 (1)	144 (3)
Mo(3)	3425 (1)	6916 (1)	6445 (1)	140 (3)
Mo(4)	1224 (1)	8910 (1)	6207 (1)	135 (3)
Mo(5)	932 (1)	6876 (1)	5878 (1)	158 (3)
Mo(6)	−1163 (1)	8102 (1)	8400 (1)	135 (3)
Mo(7)	1013 (1)	6105 (1)	8675 (1)	135 (3)
Mo(8)	−838 (1)	7451 (1)	11190 (1)	139 (3)
Mo(9)	2255 (1)	6660 (1)	11326 (1)	163 (4)
Cu	929 (2)	10315 (1)	9155 (2)	132 (5)
Si	1408 (4)	8218 (3)	9232 (4)	118 (10)
O(1)	3889 (9)	6383 (7)	10272 (10)	186 (31)
O(2)	5797 (10)	6793 (8)	8724 (12)	267 (36)
O(3)	4334 (11)	7996 (9)	10671 (12)	269 (38)
O(4)	4223 (9)	8280 (7)	8242 (11)	181 (31)
O(5)	4010 (9)	6652 (7)	7758 (11)	194 (32)
O(6)	2340 (8)	7720 (7)	9965 (10)	150 (28)
O(7)	4715 (10)	9396 (8)	6332 (11)	244 (35)
O(8)	2599 (9)	9822 (7)	8200 (10)	160 (29)
O(9)	4192 (9)	7768 (7)	5932 (10)	163 (29)
O(10)	2702 (10)	9170 (8)	5807 (11)	205 (32)
O(11)	2126 (9)	8245 (7)	7726 (10)	139 (28)
O(12)	4207 (10)	6053 (7)	5303 (10)	195 (31)
O(13)	2011 (9)	6531 (7)	7241 (9)	143 (28)
O(14)	2146 (9)	7497 (7)	5420 (10)	156 (29)
O(15)	887 (11)	9124 (8)	4795 (11)	231 (35)
O(16)	436 (9)	9842 (7)	7251 (10)	177 (30)
O(17)	150 (9)	8215 (7)	6947 (10)	154 (29)
O(18)	1529 (11)	5834 (8)	5204 (12)	254 (36)
O(19)	−32 (10)	7268 (8)	4968 (10)	211 (33)
O(20)	−156 (9)	6722 (7)	7527 (10)	157 (30)
O(21)	−1473 (10)	9178 (7)	8999 (11)	182 (31)
O(22)	−2200 (10)	8084 (8)	7613 (12)	249 (36)
O(23)	411 (8)	7658 (6)	9303 (10)	128 (28)
O(24)	−1813 (9)	7650 (7)	9937 (10)	177 (30)
O(25)	1198 (10)	5066 (7)	8060 (11)	192 (32)
O(26)	−290 (9)	6265 (7)	10041 (10)	171 (31)
O(27)	2051 (9)	6004 (7)	9548 (10)	169 (30)
O(28)	−1808 (10)	7130 (7)	12408 (12)	226 (34)
O(29)	−1080 (9)	8584 (7)	11579 (10)	164 (29)
O(30)	2362 (11)	7327 (8)	12521 (11)	234 (35)
O(31)	2340 (11)	5669 (8)	11945 (13)	275 (39)
O(32)	753 (9)	9208 (6)	9850 (10)	140 (28)
O(33)	566 (10)	7056 (8)	11651 (11)	218 (33)
H_2O(1)	6251 (16)	5283 (12)	6416 (19)	592 (66)
H_2O(2)	−2415 (15)	5894 (11)	9824 (20)	567 (67)
H_2O(3)	−1489 (15)	5855 (12)	6535 (18)	554 (66)
H_2O(4)	6130 (21)	7338 (18)	4021 (25)	943 (112)
H_2O(5)	−3579 (15)	8689 (11)	3954 (16)	525 (59)
H_2O(6)	−1426 (15)	8830 (12)	4517 (16)	500 (59)
H_2O(7)	1994 (13)	9184 (9)	2031 (13)	342 (44)
N(1)	−3377 (26)	5878 (21)	3736 (35)	1090 (141)
N(2)	−3254 (20)	7312 (17)	5834 (22)	617 (89)
N(3)	−3974 (15)	8829 (12)	1419 (19)	403 (60)
N(4)	−272 (20)	5747 (13)	3672 (19)	477 (74)
N(5)	3239 (17)	10014 (15)	3418 (19)	478 (69)
N(6)	4334 (20)	7828 (19)	3243 (18)	636 (94)

Table 2. *Selected bond lengths* (Å) *and angles* (°) *in* $[Cu_2Si_2Mo_{18}O_{66}]^{12-}$ (*estimated standard deviations in parentheses*)

Mo(1)–Mo(2)	3·722 (19)	Mo(5)–Mo(6)	3·367 (20)
Mo(1)–Mo(3)	3·729 (10)	Mo(5)–Mo(7)	3·301 (13)
Mo(2)–Mo(3)	3·357 (9)	Mo(6)–Mo(7)	3·663 (9)
Mo(2)–Mo(4)	3·283 (7)	Mo(6)–Mo(8)	3·299 (11)
Mo(3)–Mo(4)	3·664 (9)	Mo(7)–Mo(8)	3·335 (21)
Mo(3)–Mo(5)	3·271 (6)	Mo(7)–Mo(9)	3·757 (11)
Mo(3)–Mo(7)	3·784 (14)	Mo(8)–Mo(9)	3·713 (7)
Mo(4)–Mo(5)	3·336 (6)	Mo(9)–Mo(1)	3·274 (12)
Mo(4)–Mo(6)	3·742 (14)		
Si–O(6)	1·614 (13)	Cu–O(8)	1·971 (12)
Si–O(11)	1·638 (12)	Cu–O(16)	2·442 (15)
Si–O(23)	1·657 (12)	Cu–O(32)	1·954 (13)
Si–O(32)	1·607 (12)	Cu–O(21)$^{\rm i}$	2·440 (16)
		Cu–O(29)$^{\rm i}$	1·955 (14)
		Cu–O(32)$^{\rm i}$	1·991 (12)
O(6)–Si–O(11)	108·1 (6)	O(8)–Cu–O(16)	87·4 (4)
O(6)–Si–O(23)	108·6 (6)	O(8)–Cu–O(32)	93·7 (4)
O(6)–Si–O(32)	112·7 (6)	O(8)–Cu–O(21)$^{\rm i}$	91·3 (4)
O(11)–Si–O(23)	109·8 (6)	O(8)–Cu–O(29)$^{\rm i}$	86·7 (4)
O(11)–Si–O(32)	108·5 (5)	O(16)–Cu–O(32)	88·7 (4)
O(23)–Si–O(32)	109·1 (5)	O(16)–Cu–O(29)$^{\rm i}$	89·6 (4)
		O(16)–Cu–O(32)$^{\rm i}$	93·3 (4)
		O(32)–Cu–O(21)$^{\rm i}$	93·4 (4)
		O(32)–Cu–O(32)$^{\rm i}$	85·1 (4)
		O(21)$^{\rm i}$–Cu–O(29)$^{\rm i}$	88·3 (5)
		O(21)$^{\rm i}$–Cu–O(32)$^{\rm i}$	88·1 (4)
		O(29)$^{\rm i}$–Cu–O(32)$^{\rm i}$	94·5 (4)

Intensity data were collected on a Rigaku automated four-circle diffractometer with graphite-monochromated Mo $K\alpha$ radiation for independent reflections with $2\theta < 55°$. The structure was solved by the direct method, and refined using 4602 reflections $[|F_o| > 3\sigma(|F|)]$. The intensities were corrected for Lorentz and polarization effects but not for absorption. All the non-hydrogen atoms were located and treated anisotropically. The final R value was 0·048. The atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1962). Atomic coordinates are listed in Table 1, selected bond lengths and angles in Table 2.*

Discussion. The molecular structure is shown in Figs. 1 and 2. The anion $[Cu_2Si_2Mo_{18}O_{66}]^{12-}$ has a center of symmetry and a pseudo mirror plane passing through Mo(5), Si, Mo(5)$^{\rm I}$, Si$^{\rm I}$, which means that all the atoms in the $CuSiMo_9O_{33}$ fragment are crystallographically independent.

In Fig. 1, Mo(2), Mo(3), Mo(4) and Mo(6), Mo(7), Mo(8) form two Mo_3O_{13} groups having the pseudo-trigonal symmetry which is commonly found in many other heteropolyanions. These two units are linked

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* Lists of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36057 (28 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

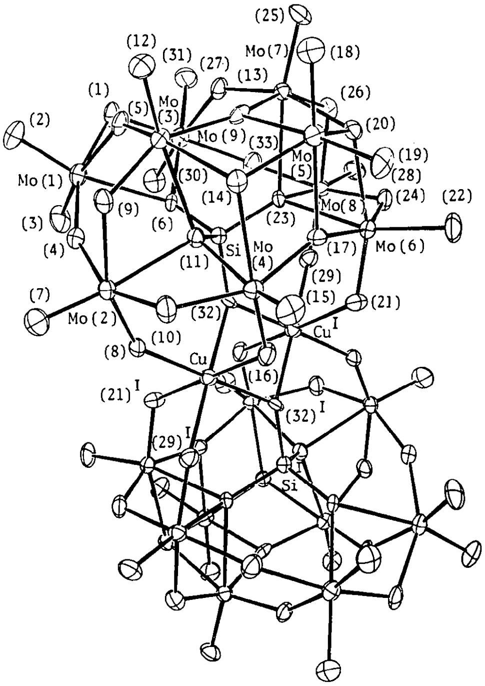

Fig. 1. Drawing of the anion $[Cu_2Si_2Mo_{18}O_{66}]^{12-}$ with the atom numbering. Superscript I indicates the inversely related atom.

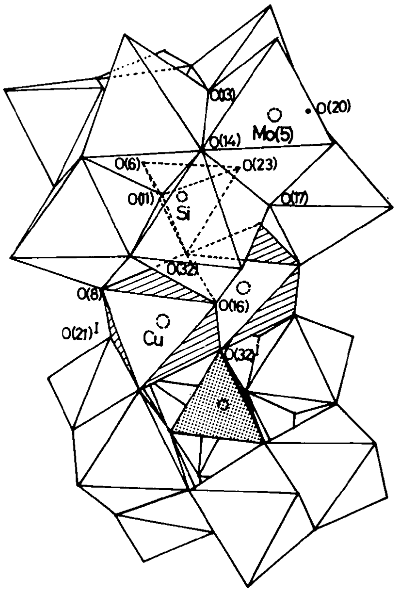

Fig. 2. Polyhedral model of the $[Cu_2Si_2Mo_{18}O_{66}]^{12-}$ anion.

through the two shared O atoms O(13) and O(17). The central O atoms, O(11) and O(23), of each of these trigonal groups occupy two corners of the SiO_4 tetrahedron.

One of the remaining O atoms of the SiO_4 tetrahedron, O(6), is shared by Mo(1) and Mo(9). These two metal atoms form two MoO_6 octahedra sharing an edge, O(1)–O(6), and Mo(1) is linked to Mo(2) and Mo(3) through O(4) and O(5) respectively, while Mo(9) is bridged to Mo(7) and Mo(8) by O(27) and O(33).

The fourth O atom, O(32), attached to the Si is shared by two Cu atoms, and the two CuO_6 octahedra have a common edge, $O(32)$–$O(32)^I$. The two Cu atoms are crystallographically equivalent. It will be seen that Cu shares O(8), O(16), $O(21)^I$, and $O(29)^I$ with Mo(2), Mo(4), $Mo(6)^I$, and $Mo(8)^I$ respectively.

Among the six independent Cu–O bond lengths, the two longest [2·44 (2) Å] are those between the Cu and the two *trans* O atoms not attached to the Si atoms. All the other four Cu–O distances (to the remaining Mo atoms and to the Si atoms) are 1·97 (1) Å. Such an elongation of the CuO_6 octahedron may be attributed to the static Jahn–Teller effect.

A notable feature of this anion is the presence of the MoO_6 octahedron containing the Mo(5) atom. This Mo(5) is linked to the two Mo_3O_{13} units sharing the bridging O(13) and O(17), and to each Mo_3O_{13} unit by O(14) and O(20) respectively. Thus the octahedron around Mo(5) covers what would otherwise be a hole (as compared with the Keggin structure) between the two Mo_3O_{13} units.

On the other side of the Si atom diagonally opposite Mo(5) there are, however, no MoO_6 octahedra. The elongation of the CuO_6 octahedra seems to explain the restricted development of the heteropolyanion restrained in this direction.

Calculations were carried out on the HITAC 8800/8700 computer at the Computer Centre of the University of Tokyo.

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