

## Structure of Potassium Bis(isothiocyanato)octamolybdate(VI) Hexahydrate

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**Abstract.**  $K_6[Mo_8O_{26}(NCS)_2] \cdot 6H_2O$ ,  $M_r = 1642.3$ , monoclinic,  $P2_1/c$ ,  $a = 10.432(4)$ ,  $b = 15.468(8)$ ,  $c = 11.672(6)$  Å,  $\beta = 102.11(5)^\circ$ ,  $V = 1842(2)$  Å<sup>3</sup>,  $Z = 2$ ,  $D_m = 2.87$ ,  $D_x = 2.96$  g cm<sup>-3</sup>,  $\lambda(Mo K\alpha) = 0.7107$  Å,  $\mu = 32.4$  cm<sup>-1</sup>,  $F(000) = 1552$ , room temperature, final  $R = 0.047$  for 4842 independent observed reflections. The structure is built up of  $K^+$  and  $[Mo_8O_{26}(NCS)_2]^{6-}$  ions and water molecules. The centrosymmetric octamolybdate anion consists of two  $SCNMoO_5$  and six  $MoO_6$  edge-sharing octahedra. The Mo–O bond lengths range: terminal O from 1.704 (4) to 1.726 (5) Å, single-bridging O from 1.745 (3) to 2.360 (3) Å, triple-bridging O from 1.878 (4) to 2.289 (3) Å and four-bridging O from 1.925 (3) to 2.433 (3) Å. The Mo–NCS bond length is 2.143 (4) Å.  $K^+$  cations are coordinated by molybdate O, water O and isothiocyanato S. The irregular polyhedra around  $K^+$  form a column along the  $a$  axis.

**Introduction.** The structural study of isopolymolybdates is of growing interest owing to their photochemical properties (Bharadwaj, Ohashi, Sasada, Sasaki & Yamase, 1984), and their importance as models for a better understanding of the reactions between organic molecules and catalytic oxide surfaces (Day, Fredrich, Klemperer & Liu, 1979; McCarron & Harlow, 1983; Williamson, Bouchard & Hill, 1987).  $(C_3H_5NH)_4[(C_3H_5N)_2Mo_8O_{26}]$  was reported as a first example of an isopolymolybdate of the type  $[Mo_8O_{26}(X)_2]^{[2n-4]}$  (where  $n$  is a formal charge of the coordinated  $X$ ) containing a neutral base as the  $N$ -donor ligand (McCarron, Whitney & Chase, 1984). We report now another example of an isopolymolybdate of the same type but containing an anion as the  $N$ -donor ligand. The compound was first described almost a hundred years ago and wrongly formulated as  $KCNS \cdot K_2O \cdot 4MoO_3 \cdot 5H_2O$  (Gmelins *Handbuch der Anorganischen Chemie*, 1935). Its actual formula is  $K_6[Mo_8O_{26}(NCS)_2] \cdot 6H_2O$ .

**Experimental.** Transparent prism-shaped crystals were obtained by cooling saturated warm aqueous solution of KSCN and  $Na_2Mo_4O_{13}$  (freshly prepared). Density

was determined pycnometrically. A crystal of size  $0.36 \times 0.28 \times 0.21$  mm was used; the lattice parameters were determined from 16 reflections in the range  $5 < \theta < 9^\circ$ . Intensity data were collected on a Philips PW 1100 diffractometer (Mo  $K\alpha$ , graphite monochromator), with  $\omega$ – $2\theta$  scan in the range  $2 < \theta < 30^\circ$ ,  $h$ – $13 \rightarrow 12$ ,  $k$ – $0 \rightarrow 19$ ,  $l$ – $0 \rightarrow 14$ . 4842 unique observed reflections with  $I > 5\sigma(I)$  were used in structure determination. Three standard reflections measured every 2 h of exposure time showed no significant change with time. Data were corrected for Lorentz and polarization effects but not for absorption. Atomic scattering factors and anomalous-dispersion corrections for Mo and K atoms were taken from *International Tables for X-ray Crystallography* (1974). A Patterson map indicated positions of Mo atoms; positions of other atoms (except H) were obtained from Fourier-map calculations; least-squares refinement (on  $F$ ) assuming anisotropic thermal parameters for all non-H atoms. Refinement converged with  $R = 0.047$ ,  $wR = 0.056$ ; the function minimized was  $\sum w(|F_o| - |F_c|)^2$  with  $w = 1/[\sigma^2(F_o) + 0.005473|F|^2]$ .  $(\Delta/\sigma)_{max} = 0.24$ . Max. and min. height in final difference Fourier map  $1.39$  and  $-3.43$  e Å<sup>-3</sup>. All calculations performed using the Univac 1110 of the Zagreb University computing Centre, SRCE, with program *SHELX76* (Sheldrick, 1976).

**Discussion.** The structure of the title compound is built up of centrosymmetric  $[Mo_8O_{26}(NCS)_2]^{6-}$  anions, potassium cations and water molecules. Atomic coordinates and thermal parameters are given in Table 1,  $\dagger$  bond lengths and angles in Table 2. The isopolymolybdate anion according to Klemperer & Shum (1976) has the  $\gamma$ - $Mo_8O_{26}$  structure with two additional terminal positions satisfying hexavalency of all Mo atoms. Alternatively, according to Wilson, McKee, Penfold & Wilkins (1984), it belongs to type II with

<sup>†</sup> Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51020 (30 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Table 1. Atomic coordinates ( $\times 10^4$ ,  $\times 10^5$  for Mo) and equivalent isotropic thermal parameters ( $\text{\AA}^2 \times 10^4$ )
$$U_{eq} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	x	y	z	$U_{eq}$
Mo(1)	-6068 (3)	9953 (2)	-5347 (3)	122 (1)
Mo(2)	-8100 (4)	4434 (2)	-33881 (3)	173 (1)
Mo(3)	25471 (3)	6652 (2)	11301 (3)	167 (1)
Mo(4)	21080 (4)	4841 (2)	-17186 (3)	182 (1)
O(1)	-1880 (3)	1709 (2)	-705 (3)	220 (6)
O(2)	-290 (4)	1166 (3)	-4295 (3)	297 (8)
O(3)	-1710 (4)	-302 (3)	-4305 (3)	302 (7)
O(4)	3929 (4)	27 (3)	1359 (4)	378 (10)
O(5)	2939 (4)	1521 (3)	2069 (3)	302 (7)
O(6)	3221 (4)	-342 (3)	-1490 (3)	317 (9)
O(7)	2620 (4)	1165 (3)	-2705 (4)	343 (9)
O(8)	559 (3)	1438 (2)	607 (3)	214 (6)
O(9)	762 (3)	-169 (2)	-2802 (3)	214 (6)
O(10)	2745 (3)	1185 (2)	-319 (3)	249 (7)
O(11)	-1464 (3)	57 (2)	-1862 (3)	178 (6)
O(12)	212 (3)	1224 (2)	-1790 (3)	164 (5)
O(13)	1185 (3)	-41 (2)	-287 (3)	159 (5)
K(1)	2013 (1)	2018 (1)	-4777 (1)	359 (3)
K(2)	5427 (1)	1459 (1)	-339 (1)	337 (2)
K(3)	7953 (1)	1490 (1)	3632 (1)	417 (3)
C	-3288 (5)	1716 (3)	-3220 (4)	269 (9)
N	-2458 (4)	1281 (3)	-3441 (4)	289 (9)
S	-4440 (1)	2346 (1)	-2954 (1)	381 (3)
O(W1)	4267 (6)	1889 (4)	4300 (4)	545 (13)
O(W2)	210 (6)	2018 (3)	3030 (5)	486 (13)
O(W3)	4185 (6)	-391 (5)	6096 (6)	749 (19)

eight condensed octahedra and 16 terminal positions (Fig. 1). Of these 16 terminal positions 14 are occupied by O atoms with Mo=O bond lengths varying from 1.704 (4) to 1.726 (5) Å, and two isothiocyanato N atoms with Mo-N bond length of 2.143 (4) Å. Each 'peripheral' Mo atom in the octamolybdate is bonded to two terminal O atoms while two 'central' Mo atoms [Mo(1) and Mo(1')] are bonded to only one terminal O atom. Of the remaining 12 oxygen atoms, six [O(8), O(9), O(10) and their centrosymmetric pairs] are single bridging two Mo atoms, four [O(11), O(12) and their centrosymmetric pairs] are triple bridging three Mo atoms, two [O(13) and the centrosymmetric O(13')] are four bridging four Mo atoms. Consequently the Mo-O distances are significantly different: in the single bridges Mo-O-Mo they vary from 1.745 (3) to 2.360 (3) Å, in the triple-bridging Mo<sub>3</sub>O core from 1.878 (4) to 2.289 (3) Å, while the Mo-O distances within the four-bridging Mo<sub>4</sub>O core are between 1.925 (3) and 2.433 (3) Å. The most significant lengthening of the Mo-O bonds is due to the *trans* influence of the terminal O atoms.

The Mo-N bond length of 2.143 (4) Å agrees well with the values found for such bonds in some other isothiocyanato Mo complexes (e.g. Głowiak, Sabat, Sabat & Rudolf, 1975; Kamenar & Penavić, 1979; Schlemper, Hussain & Murmann, 1982) but is longer than the Mo-N bond in  $(C_5H_5NH)_4[(C_5H_5N)_2Mo_8O_{26}]$ , where the Mo to pyridine N bond length amounts to 2.279 (5) Å. In the present structure the relative strength of the Mo-N bond, *s*, derived from  $s = (d/1.882)^{-6.0}$  where *d* is the bond length, is 0.46. This value is close to 0.51 found for *s* of the Mo-O bond in the structure of  $(NH_4)_6[(HCOO)_2Mo_8O_{26}] \cdot 2H_2O$

Table 2. Bond lengths (Å) and angles (°)

Mo(1)-O(1)	1.706 (3)	Mo(3)-O(4)	1.721 (4)
Mo(1)-O(8)	1.745 (3)	Mo(3)-O(5)	1.713 (4)
Mo(1)-O(11)	2.174 (3)	Mo(3)-O(8)	2.360 (3)
Mo(1)-O(12)	1.878 (4)	Mo(3)-O(10)	1.923 (4)
Mo(1)-O(13)	2.433 (3)	Mo(3)-O(13)	2.228 (3)
Mo(1)-O(13')	1.925 (3)	Mo(3)-O(11')	1.913 (3)
Mo(2)-O(2)	1.704 (4)	Mo(4)-O(6)	1.709 (4)
Mo(2)-O(3)	1.713 (4)	Mo(4)-O(7)	1.726 (5)
Mo(2)-O(9)	1.893 (3)	Mo(4)-O(9)	1.961 (3)
Mo(2)-O(11)	2.123 (4)	Mo(4)-O(10)	1.957 (3)
Mo(2)-O(12)	2.289 (3)	Mo(4)-O(12)	2.271 (3)
Mo(2)-N	2.143 (4)	Mo(4)-O(13)	2.248 (4)
C-N	1.167 (7)		
C-S	1.627 (5)		
O(1)-Mo(1)-O(8)	103.6 (2)	O(4)-Mo(3)-O(5)	105.3 (2)
O(1)-Mo(1)-O(11)	98.9 (1)	O(4)-Mo(3)-O(8)	173.0 (2)
O(1)-Mo(1)-O(12)	104.9 (1)	O(4)-Mo(3)-O(10)	97.8 (2)
O(1)-Mo(1)-O(13)	179.1 (1)	O(4)-Mo(3)-O(11')	98.6 (2)
O(1)-Mo(1)-O(13')	103.7 (1)	O(4)-Mo(3)-O(13)	102.5 (2)
O(8)-Mo(1)-O(11)	157.4 (1)	O(5)-Mo(3)-O(8)	81.5 (2)
O(8)-Mo(1)-O(12)	99.4 (1)	O(5)-Mo(3)-O(10)	100.6 (2)
O(8)-Mo(1)-O(13)	76.9 (1)	O(5)-Mo(3)-O(13)	152.1 (2)
O(8)-Mo(1)-O(13')	99.3 (1)	O(5)-Mo(3)-O(11')	104.5 (2)
O(11)-Mo(1)-O(12)	75.9 (1)	O(8)-Mo(3)-O(10)	79.1 (1)
O(11)-Mo(1)-O(13)	80.5 (1)	O(8)-Mo(3)-O(13)	70.6 (1)
O(11)-Mo(1)-O(13')	73.6 (1)	O(8)-Mo(3)-O(11')	80.9 (1)
O(12)-Mo(1)-O(13)	75.7 (1)	O(10)-Mo(3)-O(13)	73.8 (1)
O(12)-Mo(1)-O(13')	140.8 (1)	O(10)-Mo(3)-O(11')	145.0 (1)
O(13)-Mo(1)-O(13')	75.5 (2)	O(11')-Mo(3)-O(13)	72.6 (1)
O(2)-Mo(2)-O(3)	104.9 (2)	O(6)-Mo(4)-O(7)	105.4 (2)
O(2)-Mo(2)-O(9)	100.8 (2)	O(6)-Mo(4)-O(9)	95.0 (2)
O(2)-Mo(2)-O(11)	155.0 (2)	O(6)-Mo(4)-O(10)	100.6 (2)
O(2)-Mo(2)-O(12)	90.3 (2)	O(6)-Mo(4)-O(12)	160.1 (2)
O(2)-Mo(2)-N	86.8 (2)	O(6)-Mo(4)-O(13)	89.8 (2)
O(3)-Mo(2)-O(9)	102.0 (2)	O(7)-Mo(4)-O(9)	99.5 (2)
O(3)-Mo(2)-O(11)	96.0 (2)	O(7)-Mo(4)-O(10)	96.9 (2)
O(3)-Mo(2)-O(12)	164.7 (2)	O(7)-Mo(4)-O(12)	93.3 (2)
O(3)-Mo(2)-N	93.3 (2)	O(7)-Mo(4)-O(13)	163.2 (2)
O(9)-Mo(2)-O(11)	87.8 (1)	O(9)-Mo(4)-O(10)	153.6 (1)
O(9)-Mo(2)-O(12)	75.5 (1)	O(9)-Mo(4)-O(12)	74.7 (1)
O(9)-Mo(2)-N	160.3 (2)	O(9)-Mo(4)-O(13)	86.1 (1)
O(11)-Mo(2)-O(12)	69.0 (1)	O(10)-Mo(4)-O(12)	83.8 (1)
O(11)-Mo(2)-N	78.3 (1)	O(10)-Mo(4)-O(13)	72.7 (1)
O(12)-Mo(2)-N	86.5 (1)	O(12)-Mo(4)-O(13)	72.8 (1)
Mo(1)-O(8)-Mo(3)	115.6 (2)	Mo(2)-O(12)-Mo(4)	91.0 (1)
Mo(2)-O(9)-Mo(4)	115.1 (2)	Mo(1)-O(13)-Mo(3)	96.9 (1)
Mo(3)-O(10)-Mo(4)	115.0 (2)	Mo(1)-O(11)-Mo(2)	96.4 (1)
Mo(1)-O(11)-Mo(2)	104.7 (1)	Mo(3)-O(13)-Mo(4)	93.9 (1)
Mo(1)-O(12)-Mo(2)	109.0 (1)	N-C-S	177.8 (5)
Mo(1)-O(12)-Mo(4)	114.3 (2)	Mo(2)-N-C	165.9 (4)

Primed atoms are related to unprimed atoms by a centre of symmetry at (0,0,0).

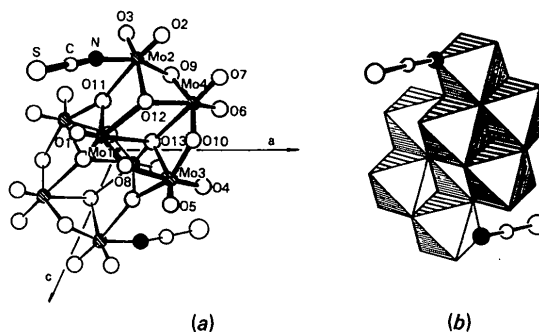


Fig. 1. (a) The structure of the  $[Mo_8O_{26}(NCS)_2]^{6-}$  anion with atom-labelling scheme, and (b) an alternative representation.

(Adams, Klemperer & Liu, 1979) due to the fact that both O from HCOO and N from NCS carry the same formal negative charge. By contrast, the interaction between Mo and N from the neutral pyridine is

significantly weaker and  $s$  therefore smaller, with a value of 0.32 (McCarron, Whitney & Chase, 1984). In the former cases such behaviour reflects the presence, in the latter the absence of an electrostatic component to the bonding.

The O—Mo—O bond angles vary from 69.0 (1) to 105.4 (2)°, indicating the distortion of the MoO<sub>6</sub> octahedra. The N—C—S anion is not linear; the angle at C amounts to 177.8 (5)°.

Potassium ion K(1) is irregularly surrounded by eight O atoms, six from octamolybdate anions and two from water molecules, at distances varying from 2.711 (5) to 3.132 (4) Å. Potassium ion K(2) is at the same time surrounded by four octamolybdate O atoms [from 2.736 (5) to 2.954 (4) Å], one water O atom [2.821 (6) Å] and two isothiocyanato S atoms at 3.320 (2) and 3.376 (2) Å, while K(3) is similarly surrounded by four octamolybdate O atoms [from 2.730 (4) to 3.102 (4) Å], two water O [2.720 (7) and 2.874 (7) Å] and one S at 3.311 (2) Å. The polyhedra around the K ions form a column extended along the crystallographic  $a$  axis.

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## A New Tetraamidodimolybdenum Complex with a Quadruple $M—M$ Bond

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**Abstract.** Tetrakis- $\mu$ -(*N-tert*-butylacetamido-*O,N*)-dimolybdenum(II)( $Mo—Mo$ ), [Mo<sub>2</sub>(C<sub>6</sub>H<sub>12</sub>NO)<sub>4</sub>],  $M_r = 648.56$ , orthorhombic,  $Pbca$ ,  $a = 12.475$  (2),  $b = 15.073$  (4),  $c = 15.876$  (2) Å,  $V = 2985.2$  Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 1.44$  g cm<sup>-3</sup>, Mo  $K\alpha$ ,  $\lambda = 0.71073$  Å,  $\mu = 8.5$  cm<sup>-1</sup>,  $F(000) = 1344$ ,  $T = 296$  (2) K,  $R = 0.045$  for 1546 observed reflections. The molecule is a quadruple-bonded dimer of crystallographic  $\bar{1}$  ( $C_2$ ) site symmetry. Each *N-tert*-butylacetamide ligand bridges the dimolybdenum core with its N atom bound to one metal and its O atom bound to the other metal. The four bridging ligands are arranged such that the two N atoms and the two O atoms bound to each Mo atom are in a *cis* conformation. The Mo—Mo distance of 2.063 (1) Å is among the shortest reported Mo—Mo quadruple-bond distances.

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