Preparation and Properties of Potassium μ-Thio-bis[hexacyanomolybdate(IV)], $K_6[Mo_2(CN)_{12}S]$, the Crystal Structure of its Double Salt with Potassium Tetraoxomolybdate(VI), and a Discussion of Molybdenum–Sulphur Bond Lengths and Bond Orders

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The complexes $K_6[Mo_2(CN)_{12}S]{\cdot}4H_2O$ (1a) and the double salt $K_{6\cdot68}[MoO_4]_{0\cdot34}[Mo_2(CN)_{12}S]{\cdot}5.32H_2O$ (1b) have been prepared by (*a*) reaction of molybdate(VI) with cyanide and hydrogen sulphide in aqueous solution in air and (*b*) aerial oxidation of an aqueous solution of $K_6[Mo_2(CN)_8S_2]{\cdot}4H_2O$ (2) and $K_5[Mo(CN)_7]{\cdot}H_2O$ (3). The overall reaction (*a*) involves intermediate formation of the complexes (2) and (3) *via* abstraction of sulphide by cyanide from thiomolybdate species to give thiocyanate and concomitant two- and four-equivalent reduction of Mo^{VI}. Crystals of the double salt (1b) are orthorhombic, $a = 15.089(10)$, $b = 11.753(9)$, $c = 9.113(8)$ Å, $Z = 2$, space group *Pmmn*, and 1 926 independent above-background reflections have been refined to $R = 0.066$. The $[Mo_2(CN)_{12}S]^{6-}$ ion (1) has imposed C_{2v} symmetry with both molybdenums in seven-co-ordinate pentagonal-bipyramidal environments and bridged *via* an axial sulphur atom [Mo–S 2.173(1) Å; Mo–S–Mo 169.5(2)°]. The metal–carbon bonds are equivalent, ranging from 2.173(8) to 2.190(11) Å. The Mo–S bond length is the same as in the $[MoS_4]^{2-}$ ion. Molybdenum-sulphur bond lengths in (1b) and a series of MoS complexes may be correlated inversely with bond orders. The diamagnetism of complexes (1a) and (1b) and their electronic spectra are consistent with a $S(p\pi)\rightarrow Mo(d\pi)$ bonding interaction and a multiple Mo–S bond. A strong i.r. band at 623 cm^{-1} is assigned ν_{asym}(Mo–S–Mo). The bridging sulphide in (1) is inert to H^+, $[OH]^-$, and $[CN]^-$; there is no monomer–dimer equilibrium in aqueous solution. Abstraction of terminally bound (but not bridging) sulphur by cyanide raises the possibility that this may be the form of sulphur involved in cyanide deactivation of the enzyme xanthine oxidase.

REACTION of potassium tetraoxomolybdate(VI), potassium cyanide, and hydrogen sulphide in aqueous solution gives potassium salts of the complex ions $[Mo_2(CN)_{12}S]^{6-}$ (1),[1] $[Mo_2(CN)_8S_2]^{6-}$ (2),[1a,2] and $[Mo(CN)_7]^{5-}$ (3).[1a,3] We have published a full account of the properties and structures of the sodium and potassium salts of the $[Mo(CN)_7]^{5-}$ ion (which is pentagonal bipyramidal) and a preliminary report [1a] of the structures of the two thio-complexes. In this paper we discuss the preparation and properties of the complex $K_6[Mo_2(CN)_{12}S]{\cdot}4H_2O$ (1a) and the structure of its double salt with potassium molybdate, $K_{6\cdot68}[MoO_4]_{0\cdot34}[Mo_2(CN)_{12}S]{\cdot}5.32H_2O$ (1b).

EXPERIMENTAL

Preparation of Potassium μ-Thio-bis-[hexacyanomolybdate-(IV)] *Tetrahydrate,* $K_6[Mo_2(CN)_{12}S]{\cdot}4H_2O$, *and its Double Salt with Potassium Molybdate,* $K_{6.68}[MoO_4]_{0.34}[Mo_2(CN)_{12}S]{\cdot}5.32H_2O$.—(*a*) *Reaction of molybdate*(VI), *cyanide, and hydrogen sulphide in the presence of air.* Molybdenum trioxide (7.0 g) was dissolved in a solution of potassium hydroxide (5.8 g) and potassium cyanide (25.3 g) in water (100 cm^3). Hydrogen sulphide was bubbled through the solution. An intense blue colour developed which faded within a few minutes to a pale green solution. Hydrogen sulphide was bubbled for another 0.5 h and the solution became brown-green. Air was then drawn through the solution for 2 h; the colour became dark brown and finally dark green. Acetone (100 cm^3) was added to the solution to precipitate a dark green oil. The oil was collected and shaken with successive quantities (25 cm^3) of methanol until a pale green crystalline solid was obtained. This was dissolved in a small amount of water, and methanol was then added until a yellow precipitate formed. The precipitate was filtered off, dried *in vacuo*, and identified as $K_4[Mo(CN)_8]{\cdot}2H_2O$ by its i.r. spectrum and elemental analysis (Found: C, 19.3; H, 0.60; N, 22.6. Calc. for $C_8H_4K_4MoN_8O_2$: C, 19.4; H, 0.80; N, 22.6%).

More methanol was added to the filtrate to produce another precipitate. The suspension was heated to redissolve the precipitate and stored overnight in a refrigerator. Blue-green crystals formed together with a small amount of $K_4[Mo(CN)_8]{\cdot}2H_2O$. The blue-green crystals {which were a double salt containing the $[Mo_2(CN)_{12}S]^{6-}$ and $[MoO_4]^{2-}$ anions, see (*b*) below} were recrystallised several times from methanol-water (1 : 1) until their i.r. spectrum showed no molybdate peak at 830 cm^{-1} (Found: C, 17.0; H, 0.95; K, 27.8; Mo, 22.6; N, 20.0; S, 3.80. Calc. for $C_{12}H_8K_6Mo_2N_{12}O_4S$: C, 17.1; H, 0.90; K, 27.8; Mo, 22.8; N, 20.3; S, 3.80%).

(*b*) *Reaction of* $K_5[Mo(CN)_7]{\cdot}H_2O$ *and* $K_6[Mo_2(CN)_8S_2]{\cdot}4H_2O$ *in the presence of air.* The salts $K_5[Mo(CN)_7]{\cdot}H_2O$ [1a,3] (1.0 g) and $K_6[Mo_2(CN)_8S_2]{\cdot}4H_2O$ [1a,2] (0.75 g) were dissolved in degassed water (50 cm^3) to give an emerald green solution. When air was bubbled through the solution it became first brown-green, then brown, and finally green. Methanol was added to the solution to precipitate a yellow powder which was filtered off and dried *in vacuo*. It was identified as $K_4[Mo(CN)_8]{\cdot}2H_2O$ by its i.r. spectrum and C, H, and N analysis (Found: C, 19.5; H, 0.70; N, 22.7%). The remaining solution was evaporated to dryness to give well formed green crystals and more $K_4[Mo(CN)_8]{\cdot}2H_2O$. An i.r. spectrum of the green crystals showed that they were a mixture of $K_6[Mo_2(CN)_{12}S]{\cdot}4H_2O$ and $K_2[MoO_4]$. There was insufficient material to purify by fractional crystallisation; a few crystals picked by hand gave a poor C, H, and N analysis for $K_6[Mo_2(CN)_{12}S]{\cdot}4H_2O$ (Found: C, 15.1; H, 1.00; N, 17.6. Calc. for $C_{12}H_8K_6Mo_2N_{12}O_4S$: C, 17.1; H, 0.90; N, 20.3%). After completing the *X*-ray structural analysis of these crystals we realised that they were an imperfect double salt of $K_6[Mo_2(CN)_{12}S]{\cdot}4H_2O$ and $K_2[MoO_4]$ with the formula $K_{6.68}[MoO_4]_{0.34}[Mo_2(CN)_{12}S]{\cdot}5.32H_2O$. The complex $K_6[Mo_2(CN)_{12}S]{\cdot}4H_2O$ formed fine whiskerlike crystals which were unsuitable for X-ray analysis. However, the double salt with molybdate consisted of well-formed rectangular parallelopipeds and the X-ray structural determination was therefore carried out.

Physical Measurements.—Infrared spectra (Nujol mulls and KBr discs) were recorded on a Perkin-Elmer 577 spectrophotometer. Ultraviolet and visible spectra were obtained for powdered solids by diffuse reflectance on a Unicam SP 700C spectrophotometer against MgO reference, and for solutions with a Unicam SP 1800 spectrophotometer. Magnetic susceptibilities were measured at room temperature by the Faraday method.

Crystal Data.—$C_{12}H_{10.56}K_{6.68}Mo_{2.34}N_{12}O_{6.68}S$, $M = 946.6$, Orthorhombic, $a = 15.089(10)$, $b = 11.753(9)$, $c = 9.113(8)$ Å, $F(000) = 1\,089.8$, $U = 1\,616.1$ Å^3, $D_m = 1.89$, $Z = 2$, $D_c = 1.94$ g cm^{-3}, $\lambda = 0.710\,7$ Å, μ(Mo-K_α) = 18.38 cm^{-1}, space group $Pmmn$ from systematic absences $hk0$, $h + k = 2n + 1$.

Structure Determination.—A small regularly shaped crystal (*ca.* 0.6 × 0.4 × 0.4 mm) was picked out from the reaction vessel and was positioned on a G.E.XRD 5 diffractometer with the c axis parallel to the machine axis. The unit-cell dimensions were measured *via* least-squares refinement of high-angle reflections. The instrument was equipped with a manual goniostat, scintillation counter, and pulse-height discriminator. Zirconium-filtered Mo-K_α radiation was used with a 4° take-off angle. A counting time of 10 s was used for each measurement. 2 864 Independent reflections were measured with $2\theta < 60°$ of which 1 926 with $I > 3\sigma(I)$ were used in subsequent refinement. Individual background measurements were taken for those reflections seriously affected by the streaking of other orders. Otherwise, backgrounds were taken from plots of background as a function of 2θ. No crystal decay was observed. No absorption or extinction corrections were applied.

A Patterson map revealed the position of the molybdenum atoms and subsequent Fourier maps revealed the positions of the remaining atoms. We had considerable difficulty in working out the correct structure represented by these peaks. A discrete anion of formula $[Mo_2(CN)_{12}S]^{6-}$ was discernible together with $5K^+$ and $3H_2O$. A discrete $[MoO_4]^{2-}$ anion was observed with an occupancy factor $\ll 1$. One more atom, KO(4), was located in a general position which, when regarded as *solely* K^+, refined with an occupancy factor of 0.7. However, symmetry-related positions of this peak were only 2.64 Å apart, too close for $K^+ \cdots K^+$ contacts {*cf.*[1,3] the shortest contact in $K_5[Mo(CN)_7]\cdot H_2O$, 3.8 Å}. We decided that there was disorder at this site between K^+ and H_2O and that the amount of K^+ was $\leqslant 0.5$. The occupancy factor of K^+ is, of course, related to that of molybdate. The latter was set at x; concomitantly occupancy factors in the KO(4) site were $\frac{1}{4} + \frac{1}{2}x$ for K^+ and $\frac{3}{4} - \frac{1}{2}x$ for H_2O. Using the SHELX system of programs,[4] it is possible to refine x in full-matrix least squares together with the positional and thermal parameters of the atoms. The final value of x was 0.34(1). The molybdate anion is somewhat disordered; the peak shape for O(3) suggests that it is positioned slightly off the two-fold axis. Presumably, the disorder arises because the KO(4) site can be occupied by either K^+ or H_2O. The disorder extends *via* the molybdate to O(2) and K(1), both of which have rather large thermal parameters.

The final molecular stoicheiometry was therefore $K_{6.68}[MoO_4]_{0.34}[Mo_2(CN)_{12}S]\cdot 5.32H_2O$. Disorder between K^+ and H_2O has previously been observed[5] in $K_5[Co_2(CN)_{10}(O_2)]\cdot H_2O$ where one site is occupied by $0.5K^+$ and $0.5H_2O$. Since x did not refine to 0.5 (indeed when fixed at 0.5, R was 0.070) it is unlikely that the crystal structure could be described by a less symmetric space group.

In the full-matrix refinement the weighting scheme chosen to give average values of $w\Delta^2$ independent of the values of F_o and $(\sin\theta)/\lambda$ was $w^{\frac{1}{2}} = 1$ for $F_o < 100$ and $w^{\frac{1}{2}} = 100/F_o$ for $F_0 > 100$. In the final cycle the shifts in parameters were less than 0.1σ. The final difference-Fourier map showed no large peaks; the reflections given zero weight showed no serious discrepancies. We were not able to locate the hydrogen atoms on the water molecules. The final R value was 0.066.

Scattering factors and anomalous-dispersion corrections were taken from ref. 6. Calculations were made on the C.D.C. 7600 at the University of London Computer Centre using the programs of ref. 4. Positional parameters are given in Table 1 and molecular dimensions in Table 2. The thermal parameters and observed and calculated

TABLE 1

Final positional parameters for $K_{6.68}[MoO_4]_{0.34}[Mo_2(CN)_{12}S]\cdot 5.32H_2O$ (1b), with estimated standard deviations in parentheses

Atom	x	y	z
Mo(1)	1 066(1)	2 500 [a]	1 393(1)
S	2 500 [a]	2 500 [a]	1 611(4)
C(1)	−0 369(7)	2 500 [a]	1 035(11)
N(1)	−1 119(7)	2 500 [a]	0 798(13)
C(2)	0 767(7)	2 500 [a]	3 731(13)
N(2)	0 620(9)	2 500 [a]	4 948(11)
C(3)	0 999(6)	0 729(7)	2 069(8)
N(3)	1 009(6)	−0 202(7)	2 427(8)
C(4)	1 158(5)	1 428(6)	−0 559(8)
N(4)	1 235(6)	0 908(7)	−1 616(8)
O(1)	2 500 [a]	7 500 [a]	2 290(35)
O(2)	2 500 [a]	0 585(10)	4 968(12)
Mo(2) [b]	7 500 [a]	2 500 [a]	4 232(4)
O(3) [b]	7 500 [a]	3 717(26)	3 170(31)
O(4) [b]	8 418(16)	2 500 [a]	4 980(27)
K(1)	7 500 [a]	0 833(3)	0 173(6)
K(2)	0 464(2)	7 500 [a]	2 469(3)
K(3)	7 500 [a]	7 500 [a]	3 355(5)
KO(4) [b]	−0 699(3)	0 323(4)	4 234(4)

[a] Parameter fixed. [b] These atoms have occupancy factors dependent upon the refined parameter x [=0.34(1)] as follows: Mo(2) x, O(3) x, O(4) x; and KO(4) was $\frac{1}{4} + \frac{1}{2}x$ for K and $\frac{3}{4} - \frac{1}{2}x$ for O.

TABLE 2

Bond lengths (Å) and angles (°)

Mo(1)–S	2.173(1)	C(1)–N(1)	1.15(1)
Mo(1)–C(1)	2.190(11)	C(2)–N(2)	1.13(1)
Mo(1)–C(2)	2.178(12)	C(3)–N(3)	1.14(1)
Mo(1)–C(3)	2.173(8)	C(4)–N(4)	1.15(1)
Mo(1)–C(4)	2.184(7)	Mo(1)–S–Mo(1^{I})	169.5(2)
S–Mo(1)–C(1)	176.7(3)	Mo(1)–C(1)–N(1)	177.8(9)
S–Mo(1)–C(2)	96.7(3)	Mo(1)–C(2)–N(2)	179.3(9)
S–Mo(1)–C(3)	91.2(2)	Mo(1)–C(3)–N(3)	176.6(8)
S–Mo(1)–C(4)	90.6(2)	Mo(1)–C(4)–N(4)	176.4(7)
C(1)–Mo(1)–C(2)	86.6(4)		
C(1)–Mo(1)–C(3)	89.8(2)		
C(1)–Mo(1)–C(4)	86.6(4)	Mo(2)–O(3)	1.72(3)
C(2)–Mo(1)–C(3)	73.3(2)	Mo(2)–O(4)	1.54(2)
C(2)–Mo(1)–C(4)	144.1(2)	O(3)–Mo(2)–O(4)	104.3(6)
C(3)–Mo(1)–C(4)	71.4(3)	O(3)–Mo(2)–O(3^{II})	112.1(14)
C(3)–Mo(1)–C(3^{II})	146.6(3)	O(4)–Mo(2)–O(4^{I})	127.5(13)
C(3)–Mo(1)–C(4^{II})	141.8(3)		
C(4)–Mo(1)–C(4^{II})	70.4(3)		

structure factors are in Supplementary Publication No. SUP 22497 (15 pp.).*

RESULTS AND DISCUSSION

Structures.—(*a*) *Geometry of the complex ion.* The $[Mo_2(CN)_{12}S]^{6-}$ anion (1) (Figure 1) has C_{2v} symmetry imposed by the space group. Each molybdenum is seven-co-ordinate, bound to six cyanide ligands and a shared axial sulphur atom in pentagonal-bipyramidal (p.b.) geometry. The structure is another example of the preference for the pentagonal bipyramid in seven-co-ordination with unidentate ligands.[3,7] All $[M(CN)_7]^{n-}$ species of which the structures have been determined by *X*-ray crystallography have p.b. geometry (although other geometries may have been postulated, probably erroneously, on spectroscopic grounds).[3] The structure of the dimer is not unprecedented as there are other examples [7] of pentagonal bipyramids sharing an axial atom {*e.g.* $[\{NbF_2(bipy)(O_2)\}_2O]$ (bipy = 2,2′-bipyridyl)}.[8]

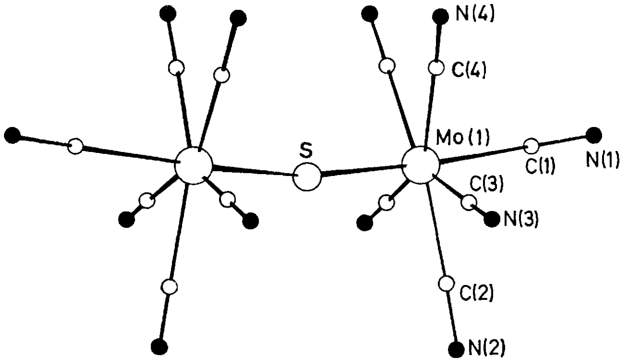

FIGURE 1 Structure of the $[Mo_2(CN)_{12}S]^{6-}$ ion. Important dimensions: Mo–S 2.173(1) Å; Mo–S–Mo 169.5(2)°

The complex is, to our knowledge, the only example of a binuclear molybdenum complex based on a Mo_2S unit, *i.e.* a *single* bridging sulphur, in contrast to the much commoner Mo_2S_2 unit (two bridging sulphurs).

(*b*) *Bond lengths and angles.* Data are given in Table 2. We discuss first Mo–C and C–N bonds. The Mo–C_{ax} (ax = axial) bond is slightly longer [2.190(11) Å] than the average of the Mo–C_{eq} (eq = equatorial) bonds (2.178 Å). This difference is the opposite of that often found in p.b. geometry [7] where M–L_{ax} distances are shorter than M–L_{eq}, and suggests a *trans*-weakening effect of the axial sulphur on the axial Mo–C bond (*cf.* the *trans* effect of oxide in oxomolybdenum complexes).[9] However, this can only be a small effect as in $Na_5[Mo(CN)_7]\cdot 10H_2O$ where Mo–C_{ax} is only 0.01 Å less than Mo–C_{eq}. It is interesting that the average Mo–C_{eq} bond length in the $[Mo_2(CN)_{12}S]^{6-}$ ion (1) (2.178 Å) is slightly longer than in the $[Mo(CN)_7]^{5-}$ ion (3) (2.141 Å), although we might have expected the latter to be longer on the grounds that the radius of Mo^{II} should be greater than that of Mo^{IV}.[1] Presumably, back donation Mo→CN^- contributes less to the Mo–C bond strength in the molybdenum(IV) complex (1) than in the molybdenum(II) complex (3). In agreement with this suggestion, the average C_{eq}–N bond length in (1) (1.14 Å) is less than in (3) (1.16 Å).[1] The C_{ax}–Mo–C_{eq} and S–Mo–C_{eq} angles are close to 90° with the exception of S–Mo(1)–C(2) [96.7(3)°]. Calculations of a least-squares plane through the MoC_5 plane [Mo 0.07, C(2) −0.09, C(3) 0.05, C(4) −0.04, C(3^{II}) 0.05, C(4^{II}) −0.04 Å] show that the C(2) atom is most displaced from the girdle plane in a direction away from the sulphur bridge.

The Mo–S_b bond length [2.173(1) Å] (b = bridging) is the same as the Mo–S_t (t = terminal) bond in tetrathiomolybdates (2.17 Å) [10] and shorter than Mo–S_b bonds (*ca.* 2.3 Å) in complexes containing the Mo_2S_2 unit (see *General Discussion*, below).[11,12] Thus the Mo–S_b bond in the Mo_2S unit apparently has some multiple-bond character (see also discussion of i.r. spectra and bonding, below). The Mo–S–Mo angle [169.5(2)°] is bent but the reason for this is not obvious. The bending could be due to the O(3) $\cdots$ N(1^{III}) contact of 3.33 Å but this implies that the $Mo(CN)_6S$ unit behaves as a rigid body pivoting about the sulphur atom, whereas the behaviour of the $[Mo(CN)_7]^{5-}$ ion in $K_5[Mo(CN)_7]\cdot H_2O$ shows that lattice-imposed distortions can be easily accommodated by bending of one equatorial cyanide out of the equatorial plane. It is also inappropriate to describe the structure as a bridging sulphur atom spanning a metal–metal bond to form a M_2S triangle since the Mo–Mo distance (4.33 Å) is far too great for Mo–Mo bonding (*ca.* 2.7 Å in the Mo_2S_2 unit).[12]

(*c*) *Lattice packing.* Intermolecular distances less than 3.5 Å are listed in Table 3. The packing around the potassium cations is unremarkable. That the $[MoO_4]^{2-}$ sites are only partly occupied is determined by the inability of the structure to allow complete occupation of the KO(4) sites by potassium ions, because only then would charge neutrality allow the $[MoO_4]^{2-}$ sites to be fully occupied. Since two of the KO(4) sites (x, y, z; $\bar{x}, \bar{y}, 1 - z$) are only 2.64 Å apart they cannot both accommodate K^+ ions. This value is, however,

TABLE 3

Intermolecular distances $\leqslant 3.5$ Å *

$K(1) \cdots N(1^{III})$	2.92	$K(2) \cdots N(3^{IV})$	2.82
$K(1) \cdots N(4^{VII})$	3.09	$K(2) \cdots O(1)$	3.08
$K(1) \cdots C(4^{VII})$	3.36	$K(2) \cdots O(4^{V})$	2.87
$K(1) \cdots N(3^{VII})$	3.35	$K(2) \cdots C(4^{IX})$	3.26
$K(1) \cdots O(1^{VI})$	2.98	$K(2) \cdots N(1^{IX})$	3.14
$K(3) \cdots N(2^{V})$	3.23	$K(2) \cdots N(2^{VIII})$	2.87
$K(3) \cdots O(2^{V})$	2.72	$KO(4) \cdots O(4^{XIII})$	2.96
$K(3) \cdots N(4^{VI})$	3.11	$KO(4) \cdots N(3)$	3.12
$K(3) \cdots C(4^{VI})$	3.49	$KO(4) \cdots N(2)$	3.31
$O(3) \cdots N(1^{III})$	3.33	$KO(4) \cdots O(2^{X})$	3.01
$O(4) \cdots N(2^{III})$	3.32	$KO(4) \cdots KO(4^{X})$	2.64
$O(2) \cdots N(3)$	3.36	$KO(4) \cdots N(2^{X})$	3.40
$C(3) \cdots O(2)$	3.48	$KO(4) \cdots N(3^{X})$	3.08
$O(4) \cdots O(1^{V})$	2.85	$KO(4) \cdots N(4^{XI})$	2.91
$Mo(2) \cdots O(1^{V})$	3.17	$KO(4) \cdots C(2)$	3.41
$O(2) \cdots O(3^{XII})$	2.77	$KO(4) \cdots C(3)$	3.27

* Roman numeral superscripts refer to the following equivalent positions relative to the reference set of x, y, z in Table 1: I $\frac{1}{2} - x, y, z$; II $x, \frac{1}{2} - y, z$; III $1 + x, y, z$; IV $x, 1 + y, z$; V $1 - x, 1 - y, 1 - z$; VI $1 - x, 1 - y, -z$; VII $1 - x, -y, -z$; VIII $-x, 1 - y, 1 - z$; IX $-x, 1 - y, -z$; X $-x, -y, 1 - z$; XI $-x, -y, -z$; XII $1 - x, -\frac{1}{2} + y, 1 - z$; XIII $-1 + x, y, z$.

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* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1978, Index issue.

acceptable for a K $\cdots$ O or for a hydrogen-bonded O $\cdots$ O distance. We were able to refine the occupancy of the site by K^+ to 0.42 (see Experimental section) but it is perhaps surprising that it did not refine to 0.50 which would mean that each unit cell contained $K^+ \cdots OH_2$ pairs related by false centres of symmetry. This result also rules out the slight possibility of alternative non-centrosymmetric space groups.

The dimensions of the molybdate anion are somewhat inaccurate {expected values: Mo–O 1.76(1) Å, O–Mo–O 108—113°, as in $K_2[MoO_4]$ }[13] and this may be due to some disorder in the oxygen position caused by the K^+/H_2O variation in the KO(4) site.

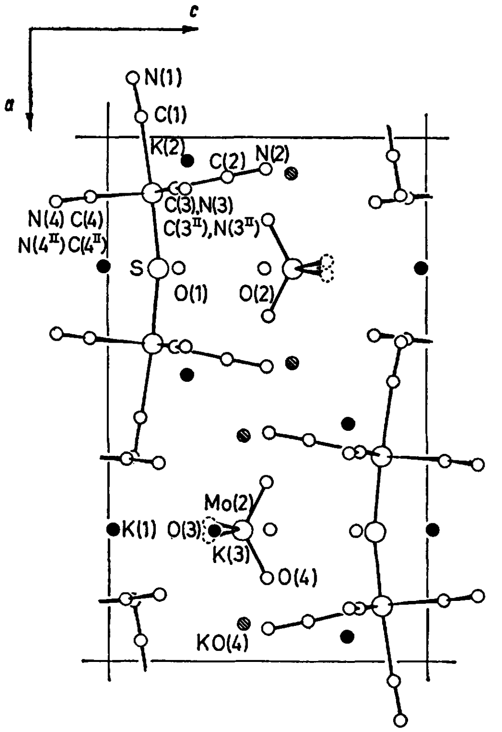

FIGURE 2 The unit cell of $K_{6.68}[MoO_4]_{0.34}[Mo_2(CN)_{12}S]\cdot 5.32H_2O$ in the *b* projection, showing the complex anion, $[MoO_4]^{2-}$ ions, K^+ ions (as full circles), disordered KO(4) sites (closed circles), and disordered O(3) sites (hatched circles). C(3), N(3), C(4), N(4) are superimposed on C(3II), N(3II), C(4II), N(4II) in this projection

The two short O $\cdots$ O distances in Table 3 (2.85, 2.77 Å) suggest hydrogen-bond formation between the molybdate oxygens and the water molecules.

Packing of the unit cell in the *b* projection is shown in Figure 2. The $[Mo_2(CN)_{12}S]^{6-}$ ions pack in columns lying parallel to the *a* axis. Also parallel to *a* are continuous chains of KO(4) and $[MoO_4]^{2-}$ ions which occupy channels between the complex ions.

Magnetic Properties.—The magnetic susceptibility, after correcting for diamagnetic contributions, corresponded to an apparent magnetic moment 0.2 B.M. at 293 K.* Thus the $[Mo_2(CN)_{12}S]^{6-}$ ion is diamagnetic in contrast to the isoelectronic (d^2) $[V(CN)_7]^{4-}$ ion which is paramagnetic (two unpaired electrons). The diamagnetism is discussed further under ' bonding ' below.

Spectra.—Infrared. Peak positions are listed in Table 4. In the salt (1b) the $[Mo_2(CN)_{12}S]^{6-}$ ion has crystallographically imposed C_{2v} symmetry and we expect 10 i.r.-active ν(CN) fundamental modes ($4a_1 + 4b_1 + 2b_2$). The i.r. spectrum has one strong broad band in the ν(CN) region; evidently the expected bands are too close to be resolved. For $K_6[Mo_2(CN)_{12}S]\cdot 4H_2O$ there are three closely spaced bands in the ν(CN) region which suggests D_{5h} symmetry (three i.r.-active fundamental modes, $2a_2'' + e'$), *i.e.* a linear Mo–S–Mo unit. The strong band at 623 cm^{-1}, previously assigned to δ(Mo–C–N),[1b] we now assign to ν_{asym}(Mo–S–Mo). On the assumption that the force constant of the Mo–S bond in the $[Mo_2(CN)_{12}S]^{6-}$ ion is the same as in the $[MoS_4]^{2-}$ ion (2.84×10^{-2} N m^{-2}) (since the Mo–S bond lengths are the same) [10] and ignoring any interaction constant across the sulphur atom, we calculate a value of *ca.* 600 cm^{-1} for ν(Mo–S–Mo) using equation (1) [9] ($L = 5.889 \times 10^{-7} \times \nu^2$ where ν is the vibration frequency in cm^{-1}, *u* is a reciprocal atomic mass, ϕ is the angle Mo–S–Mo, *k* is the force constant of the Mo–S bond, and k_i the interaction constant).

$$L = [u_{Mo} + u_S(1 - \cos\phi)](k - k_i) \qquad (1)$$

TABLE 4

Infrared spectra of $K_6[Mo_2(CN)_{12}S]\cdot 4H_2O$ (1a) and $K_{6.68}[MoO_4]_{0.34}[Mo_2(CN)_{12}S]\cdot 5.32H_2O$ (1b) *

(1a)	(1b)	Assignment
(3 580)	3 600s	$\nu(H_2O)$
3 500s	3 400s,br	
2 139s		
2 129s	2 118s,br	ν(C–N)
2 118s		
1 630s	1 615s	δ(HOH)
	(850)	$\nu([MoO_4]^{2-})$
	835s	
623s	620s	ν_{asym}(MoSMo)
530br		$\rho(H_2O)$
484w	482w	
444m	444m	ν(Mo–C)
382m		
(360)		
350s	355s,br	δ(Mo–C–N) $+\delta([MoO_4]^{2-})$
(340)		

* KBr discs. Peak positions (cm^{-1}), relative intensities (s = strong, m = medium, w = weak, br = broad; shoulders in parentheses), and assignments (ν = vibrational, δ = bending, ρ = rocking mode) are given.

Electronic. Peak positions, absorption coefficients, and assignments are given in Table 5 which also includes data and assignments for the (d^2) $[V(CN)_7]^{4-}$ ion. For the paramagnetic d^2 configuration in a pentagonal–bipyramidal (D_{5h}) environment three spin-allowed ' *d–d* ' transitions are expected and are observed for the $[V(CN)_7]^{4-}$ and related ions {*e.g.* $[Mo(CN)_7]^{n-}$, *n* = 4 and 5}.[3] The low-intensity peak at 15 900 cm^{-1} of the $[Mo_2(CN)_{12}S]^{6-}$ ion is clearly due to a ' *d–d* ' transition, but the absorption peak at 27 100 cm^{-1} is much too intense for a ' *d–d* ' transition and so is assigned to a charge-transfer transition, presumably $Mo^{4+} \longleftrightarrow S^{2-}$

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* Throughout this paper: 1 B.M. ≈ 9.27×10^{-24} A m^2.

TABLE 5

Ultraviolet–visible spectra [a]

$[Mo_2(CN)_{12}S]^{6-}$ (aq)	$\tilde{\nu}/10^3$ cm^{-1}	15.9	27.1	(33.4)	(38.3)	41.8	(43.1)
ε/dm^3 mol^{-1} cm^{-1}		116	75 000	(5 200)	(5 900)	9 100	(8 900)
$[V(CN)_7]^{4-}$ (mull) [b]	$\tilde{\nu}/10^3$ cm^{-1}	20.6	22.8	28.6			

[a] Peak positions ($\tilde{\nu}$) and absorption coefficients (ε), with shoulders in parentheses. [b] Ref. 14.

since transitions involving $[CN]^-$ are generally at higher wavenumbers (*cf.* Table 5). This intense charge-transfer peak will obscure '*d–d*' peaks expected at *ca.* 25 000—29 000 cm^{-1} and so they are not observed. The electronic spectrum is discussed further below.

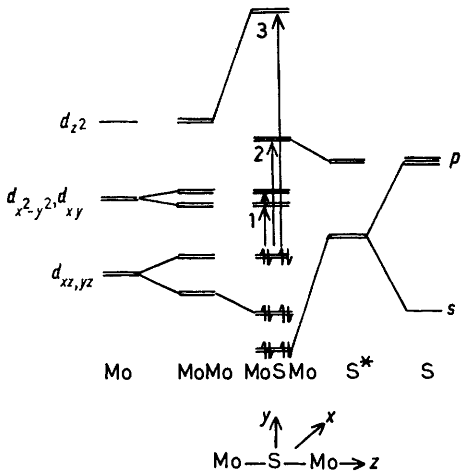
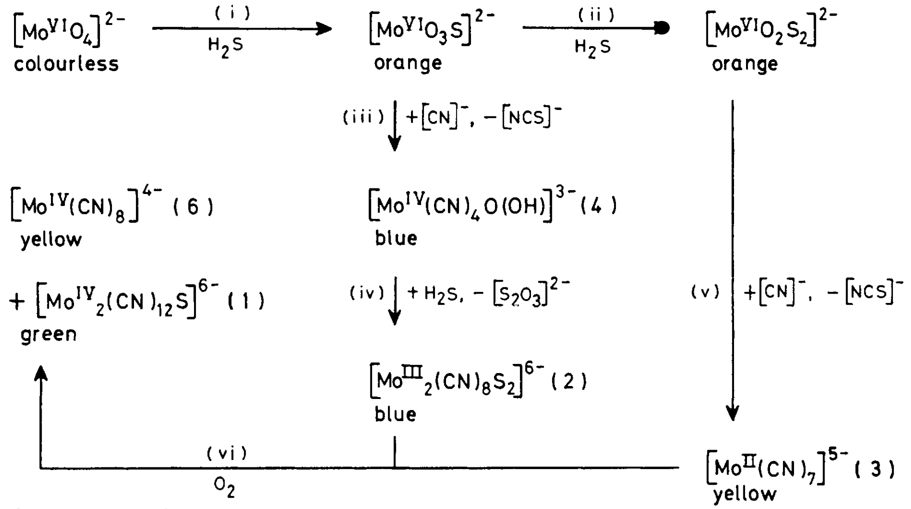


FIGURE 3 Orbital-energy diagram of the $[Mo_2(CN)_{12}S]^{6-}$ ion. Molybdenum *d* orbitals are combined with S *s* and *p* orbitals giving six bonding m.o.s to accommodate the electrons of the MoSMo unit, thus accounting qualitatively for the short MoS bond and the diamagnetism of the complex ion, and three peaks in the visible spectrum (transitions shown by vertical arrows: 1 and 3, '*d–d*' at 15 900 and 33 400 cm^{-1}; 2, charge transfer at 27 100 cm^{-1})

Electronic Structure.—An orbital-energy diagram, based on a treatment of the $[V(CN)_7]^{4-}$ ion,[14] which accounts for the diamagnetism, electronic spectrum, and short Mo–S bond length in the $[Mo_2(CN)_{12}S]^{6-}$ ion is shown in Figure 3. For a monomeric d^2 ion in D_{5h} symmetry the ordering of energy levels would lead to paramagnetism {two unpaired electrons as found for the $[V(CN)_7]^{4-}$ ion}. However, the dimeric $[Mo_2(CN)_{12}S]^{6-}$ ion is diamagnetic. The diamagnetism can be accounted for by an interaction of the Mo (d_{xz}, d_{yz}) degenerate pairs *via* bridging S as shown in Figure 3; there are six electron pairs in six bonding molecular orbitals. Each Mo–S bond then consists of one σ bond [Mo (d_{z^2}) + S (p_z)] and two half π bonds [Mo (d_{xz}, d_{yz}) + S (p_x, p_y)] giving a multiple bond in agreement with the short bond length. The electronic spectrum (two *d–d* transitions and one charge-transfer transition) can also be qualitatively accounted for (see Figure 3).

Preparative Chemistry and Related Reactions.—The sequence of reactions which yields the $[Mo_2(CN)_{12}S]^{6-}$ ion (1) is shown in the Scheme. Apparently this species is not formed directly in the reaction of molybdate with hydrogen sulphide and cyanide, but indirectly in the aerial oxidation of the species $[Mo_2(CN)_8S_2]^{6-}$ (2) and $[Mo(CN)_7]^{5-}$ (3), which are the products of the reaction in the absence of oxygen. Formation of (1) from (2) requires additional cyanide. In reaction (vi) cyanide is liberated in the oxidation of (2) to molybdate and the $[Mo(CN)_8]^{4-}$ ion (both of which are products of the reactions). Thus the overall reaction is (2). Reducing equivalents for the initial reduction of Mo^{VI} are provided

$$2[Mo(CN)_7]^{5-} + [Mo_2(CN)_8S_2]^{6-} + 2O_2 \longrightarrow [Mo(CN)_8]^{4-} + [Mo_2(CN)_{12}S]^{6-} + [MoO_4]^{2-} + 2[CN]^- + S^{2-} \qquad (2)$$



SCHEME Reaction of molybdate with hydrogen sulphide and cyanide in aqueous solution: all reactions except (vi) are carried out in the absence of oxygen. In air the products are species (1) and (5) which are also formed, together with $[MoO_4]^{2-}$, by aerial oxidation of a mixture of (2) and (3) [reaction (vi)]. All species have been isolated and fully characterised and shown to be present in the reaction mixture by isolation from, or spectrophotometric (u.v.–visible) identification in, the solution formally by reaction (3). Since neither molybdate nor sulphide ions reacted separately with cyanide the reactive species must be thiomolybdate ions [equations (4) and (5)]. The blue colour observed during the

$$S^{2-} + [CN]^- \longrightarrow [SCN]^- + 2e^- \qquad (3)$$

$$[MoO_3S]^{2-} + [CN]^- \longrightarrow [Mo^{IV}] + [SCN]^- \qquad (4)$$

$$[MoO_2S_2]^{2-} + 2[CN]^- \longrightarrow [Mo^{II}] + 2[SCN]^- \qquad (5)$$

reaction was due to the oxomolybdenum(IV) species $[Mo(CN)_4O(OH)]^{3-}$ (4), which was found in separate experiments to react as shown in the Scheme.

The presence of thiocyanate and/or thiosulphate and trace amounts of sulphite among the reaction products was shown by evaporating the filtrates from the preparations and recording the i.r. spectra of the residues, and by qualitative tests. In the reduction of (4) to (2) [reaction (iv)] thiosulphate was formed but not thiocyanate. Evidently, in reaction (iv) hydrogen sulphide is the reducing agent and the sulphur formed reacts with potassium hydroxide added in the work-up procedure to give thiosulphate and sulphite.

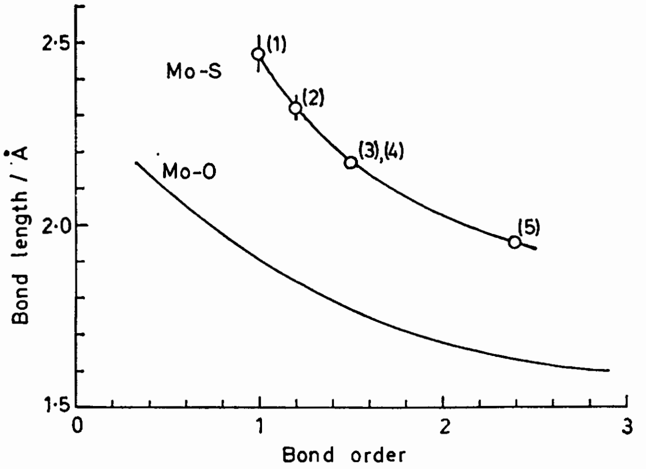


FIGURE 4 A plot of bond length against bond order for Mo–S and Mo–O bonds. The plot for Mo–O bonds is taken from ref. 9*b*. Data points for Mo–S bonds (mean distances and standard deviations where applicable) correspond to the following complexes or types of complex and bonds: (1) Mo–SR (23 complexes, mostly alkylthio and dithiocarbamato);[12] (2) $Mo_2(S_b)_2$ (10 complexes);[12] (3) $[Mo_2(CN)_{12}S]^{6-}$ (this work); (4) $[MoS_4]^{2-}$;[10] (5) $[Mo_2S_4(S_2CNBu_2)_2]$(Mo–S_t).[16] Subscripts t and b represent terminal and bridging

General Discussion.—We now discuss three matters of general interest related to our work concerning the structures and chemical properties of thiomolybdenum compounds.

(*a*) Mo–S *bond lengths and bond orders.* With the structure described in the present paper we now have Mo–S bond lengths in complexes with molybdenum bound to terminal sulphide (S_t) and one or two bridging sulphides (S_b). For analogous oxomolybdenum complexes previous workers [9a,b] have obtained smooth (but different) correlations between Mo–O bond length and bond order [9] and we can now enquire whether such a correlation exists in Mo–S complexes. In Figure 4 we plot bond lengths against bond orders for Mo–S and Mo–O bonds (using data from ref. 9*b* for the latter). We assume a bond order of one for the Mo–SR bond in complexes with thiolate and dithiocarbamate ligands [12] and a bond order of 2.4 for the Mo–S bond in the complex $[Mo_2S_4(S_2CNBu_2)]$ [15] by analogy with the Mo–O_t bond in the $Mo_2O_2S_2$ unit.[16] Then the Mo–S_b bond in the $[Mo_2(CN)_{12}S]^{6-}$ ion lies on a smooth curve of the *same form* as the curve for Mo–O bonds if the bond order is 1.5. The Mo–S_b bond lengths in complexes containing two bridging sulphurs [16] are said to correspond to a bond order of 1.2 compared to 1.0 for analogous oxygen complexes.[9b,16] For the species $[MoS_4]^{2-}$,[10] the Mo–S_b bond fits on the curve of Figure 4 if we assume a bond order of 1.5 as for the corresponding Mo–O bonds.[9b] We conclude that a similar bond-length–bond-order correlation exists for Mo–S as for Mo–O bonds at least up to a bond order of 2. The Mo–S and Mo–O curves are not parallel; the separation decreases as the bond order increases. At a bond order of 1 the separation is *ca.* 0.57 Å, and 2.5 the separation is *ca.* 0.30 Å. This result implies increasing electron donation from sulphur, as from oxygen, with increase of bond order (according to Figure 4), presumably through S $(p_\pi)\rightarrow$Mo (d_π) bonding (*cf.* the differences of radii: S^{2-}–O^{2-}, 0.44; S–O, 0.28 Å). Following the procedure of Schröder,[9b] we obtain the relation (6) between bond length [*d*(Mo–S)] and bond order [*b*(Mo–S)] for Mo–S bonds. This

$$d(\text{Mo–S}) = 2.45 - 1.425 \log [b(\text{Mo–S})] \qquad (6)$$

relation predicts a length of 1.77 Å for a Mo–S bond of order three, *i.e.* $Mo(S_t)_1$ [*cf.* 1.60 Å for $Mo(O_t)_1$]. To our knowledge there are no well characterised molybdenum complexes which contain just one sulphide as a terminal ligand, whereas the corresponding oxygen complexes are well known (*e.g.* $MoCl_3O$ in contrast to $MoCl_3S$ where the sulphide may be a bridging ligand).* Finally, in view of the limited data on Mo–S bonds, our correlations must be regarded as tentative.

(*b*) *Chemical properties of* MoS *compounds.* Previously we have drawn attention to the inertness towards hydrolysis of bridging sulphide in molybdenum complexes.[17] The thio-bridged cyanide complexes (1) and (2) are similarly inert; they are not decomposed by strong acids and alkalis and there is no evidence (no changes in u.v.–visible spectra and no e.s.r. signals) for a pH-dependent dimer–monomer equilibrium of the kind found for oxo-complexes. The different structures of the oxo- and thio-molybdenum(IV) cyano-complexes illustrate strikingly the difference between sulphide and oxide as ligands. The oxo-complex (4) is monomeric with terminal oxide, the thio-complex (1) is dimeric with bridging sulphide.

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* The i.r. spectrum of $MoCl_3S$ suggests the presence of bridging rather than terminal sulphur but its structure is unknown (D. A. Rice, *Co-ordination Chem. Rev.*, 1978, **25**, 199).

(*c*) *Reactions with cyanide*. The reaction of thiomolybdates with cyanide (see Scheme) is of interest in that a similar reaction occurs when cyanide deactivates the molybdoenzyme xanthine oxidase (formation of thiocyanate and two-electron reduction of molybdenum).[18] We find[19] that the only form of sulphur bound to molybdenum which reacts with cyanide is terminal sulphide as in the thiomolybdates and also the complex $[Mo_2S_2(\mu\text{-}S)_2(S_2CNEt_2)_2]$ {which with cyanide gives the $[Mo_2(CN)_8(\mu\text{-}S)_2]^{6-}$ species (2), the bridging sulphides remaining intact}. Bound sulphur which does *not* react with cyanide includes bridging sulphide, persulphide {as in the complex $[MoO(S_2)(S_2CNEt_2)_2]$}, and thiolate. Thus the form of sulphur bound to molybdenum which has the same properties as the sulphide of xanthine oxidase is terminal sulphide bound to molybdenum, *i.e.* Mo=S. Our work, therefore, raises the possibility that this is the labile form of sulphur in xanthine oxidase.

Conclusions.—We have shown that one of the products of the reaction of molybdate, cyanide, and hydrogen sulphide is a species $[Mo_2(CN)_{12}S]^{6-}$ (1) with a bridging sulphide. The shortness of the Mo–S bond and the diamagnetism and electronic spectrum of the species provide evidence for multiple bonding, *i.e.* a Mo–S π interaction. For a series of Mo–S complexes there is a bond-length–bond-order correlation as found for Mo–O complexes. The sulphide bridge in (1) is inert to hydrolysis, like other thio-bridged molybdenum complexes, and there is *no* evidence for a monomer–dimer equilibrium.

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