Structure and Vibrational Spectra of $K_6[Mo_2(\mu_2\text{-S})(CN)_{12}]\cdot 4H_2O$, a Complex with a Linear Mo=S=Mo Bridge

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The structure of potassium μ-thio-bis[hexacyano-molybdate(IV)] tetrahydrate, $K_6[Mo_2(CN)_{12}(\mu_2\text{-}S)]\cdot 4H_2O$, consists of two pentagonal pyramidal $Mo(CN)_6$ moieties sharing an axial S^{2-} ligand with a staggered configuration. The space group is P$\bar{1}$ triclinic with cell dimensions a = 10.201(4), b = 9.025-(3), c = 9.680(3) Å, α = 109.41(3), β = 109.72(3), γ = 104.41(3)°, D_x = 1.92 g cm^{-3} for Z = 1. The structure was solved by conventional methods to R = 0.032 for 4929 reflections. Each molybdenum atom is coordinated to six cyanide anions and to a S^{2-} ligand so as to produce a structure of approximate D_{5d} symmetry for the entire anion. The most interesting feature chemically of the structure is the entire axial unit N≡C–Mo=S=Mo–C≡N which is practically linear with a very short Mo=S bond (2.1716(2) Å). Vibrational and electronic spectra suggest that there is no major stereochemical change for the anion from the solid to solution at room temperature. The distinction between D_{5h} and D_{5d} symmetry groups is not possible from the vibrational analysis. The existence of two identified configurations for the anion in the solid state (C_{2v} or D_{5d}) is in favor of a stereochemical non-rigidity of the anion in solution at ambient temperature.

Introduction

Linear oxo-bridges, M–O–M (M = metal), have been of interest with respect to the problem of correlating their linearity with the π character of the M–O bonds. To our knowledge, discussions of the linear M–S–M bonding scheme are not well-documented [1, 2].

In connection with our current interest concerning the molybdenum and rhenium complexes containing sulfur ligands [3, 4], we have synthesized crystals of $K_6[Mo_2(\mu_2\text{-S})(CN)_{12}]\cdot 4H_2O$ (*1*). Previous structural work undertaken on this sulfido-complex derived from an imperfect double salt [5]:

$K_{6.68}[MoO_4]_{0.34}[Mo_2(\mu_2\text{-S})(CN)_{12}]\cdot 5.32H_2O$ (*2*). We report here the crystal and molecular structure of the anion $[Mo_2(\mu_2\text{-S})(CN)_{12}]^{6-}$ (previously described in another symmetry [5]) and discuss the influence of different environments on this structure.

Experimental

Preparation of Crystals of $K_6[Mo_2(\mu_2\text{-S})(CN)_{12}]\cdot 4H_2O$

The procedure outlined by Drew and Mitchell [5] was used for the synthesis of $K_6[Mo_2(\mu_2\text{-S})_2(CN)_8]\cdot 4H_2O$ (*3*). The blue crystals of *3* were filtered off and the filtrate was left for several days in the open; green crystals of *2* were found to have deposited. These crystals (1.5 g) were added to an ethanol-ethanethiol mixture (10:1, 10 ml) to give a green suspension. Successive additions of KCN (0.65 g, 10 mmol) and water to the stirred mixture gave a dark green solution after intermittent shaking over a 3 h period. The solution was filtered and allowed to stand for 3–5 days under nitrogen at 10 °C. Blue-green crystals were thus formed.

Alternatively, crystals were also prepared starting from the product *1* obtained by Müller and Christophliemk's method [6] and working up in the same manner. The compound has been characterized by full elemental analysis (except for oxygen).

Collection of the X-ray Data and Structure Determination

Cell constants and other pertinent data are presented in Table I. Intensity data were collected on a four circle Philips PW 1100 diffractometer. No intensity decay was observed during the data collection periods. Intensities were collected in the step-scan mode with subsequent computer analysis of the recorded profiles by means of Coppens's program [7]. The structure was solved by using the heavy atom method. Refinements by full-matrix least-squares (all atoms anisotropic) produced the R

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TABLE I. Experimental Details of the X-Ray Diffraction Study of $K_6[Mo_2(\mu_2\text{-S})(CN)_{12}]\cdot 4H_2O$.

(A) Crystal parameters at 23 °C

Crystal class: triclinic	Space group: P $\bar{1}$

a, b, c, Å: 10.201(4), 9.025(3), 9.680(3)

α, β, γ, deg.: 109.41(3), 109.72(3), 104.41(3)

V, Å^3: 722.9	mol. wt.: 842.8
Z: 1	
ρ(calcd): 1.94 g cm^{-3}	ρ(obsd)[a]: 1.92 g cm^{-3}

Cryst. size, mm: 0.24 × 0.18 × 0.06

(B) Experimental conditions for data processing

Diffractometer: Philips PW 1100
Radiation: Mo Kα (λ = 0.71069 Å),
  graphite monochromated
abs: μ = 16.5 cm^{-1}
Transmission factors: 0.85–0.96
Scan width, deg.: 1.30
Scan speed, deg./s: 0.025
Stds: three reflectns (42$\bar{2}$), ($\bar{2}\bar{2}$4)
  and ($\bar{4}$24) measured every hour
2θ limits, deg.: $4 \leqslant 2\theta \leqslant 70$
No. of reflectns collected: 6099,
  yielding 4929 symmetry independent
  data with Fo^2 > 3σ(Fo^2)
Corrn: Lorentz, polarisation, absorption,
  anomalous dispersion for Mo[b]
Final no. of parameters varied: 169
Error in observation of unit wt.: 1.31
R: 0.032   Rw: 0.041

[a]By flotation in benzene–carbon tetrachloride mixture.
[b]Reference [8].

factors[≠]: R = 0.032 and R_w = 0.041. Values of the atomic scattering factors for all other atoms were obtained from the usual source [8].

The final difference map showed no peaks of structural significance.

The anisotropic thermal parameters for all atoms, provided as U_{ij}, and the observed and calculated structure factors, are all available as supplementary

[≠]All calculations have been performed by using the CII IRIS 80 computer of the Atelier d'Informatique. In addition to various local programs, modified versions of the following were employed: Ibers' AGNOST absorption program which includes the Coppens-Leiserowitz-Rabinovitch logic for Gaussian integration; Zalkin's FORDAP Fourier summation program; Johnson's ORTEP thermal ellipsoid plotting program; Busing and Levy's ORFFE error function program; Ibers' NUCLS full-matrix program which in its non-group form closely resembles the Busing and Levy's ORFLS program.

The function minimized was $\Sigma w(|F_o| - |F_c|)^2$ where $w = 4F_o^2/\sigma^2(F_o^2)$, the unweighted and weighted residuals are defined as follows:
$R = (\Sigma \|F_o| - |F_c\|)/\Sigma|F_o|$ and $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$.

material. The final positional parameters are listed in Table II.

TABLE II. Final Positional Parameters[a] in $K_6[Mo_2(\mu_2\text{-S})(CN)_{12}]\cdot 4H_2O$.

Atom	x	y	z
Mo	0.23014(2)	0.15262(2)	0.05764(2)
K(1)	0.6724(1)	0.3397(1)	0.4518(1)
K(2)	0.5905(1)	0.7632(1)	0.2701(1)
K(3)	0.8532(1)	0.4178(1)	0.1211(1)
S	0	0	0
C(1)	0.3295(3)	−0.0038(3)	0.1476(3)
N(1)	0.3795(3)	−0.0877(4)	0.1958(3)
C(2)	0.1966(3)	0.3891(3)	0.1341(3)
N(2)	0.1736(3)	0.5111(3)	0.1722(3)
C(3)	0.3146(3)	0.2634(3)	0.3225(3)
N(3)	0.3644(3)	0.3188(3)	0.4631(3)
C(4)	0.4560(3)	0.3114(3)	0.1012(3)
N(4)	0.5706(3)	0.3951(3)	0.1184(3)
C(5)	0.1434(3)	0.1921(3)	−0.1583(3)
N(5)	0.1001(4)	0.2138(4)	−0.2722(3)
C(6)	0.2249(3)	−0.0483(3)	−0.1456(3)
N(6)	0.2164(3)	−0.1608(3)	−0.2525(3)
O(1)	0.7458(3)	0.0885(3)	0.5484(3)
O(2)	0.0882(3)	0.4080(4)	0.5341(4)

[a]Estimated standard deviations in the least significant figure(s) are given in parentheses.

Physical Measurements

Infrared spectra were recorded on a Perkin-Elmer 580 B spectrometer (KBr discs and KRS 5 cells for the aqueous solution). Raman spectra were obtained on a Coderg double monochromator with Ar$^+$ and Kr$^+$ laser excitations. The solid state spectra were obtained using a rotating ring of pressed powder. Peak positions are accurate within ±2 cm^{-1}.

Results and Discussion

Crystal Structure

The coordination geometry of the title compound is shown in Fig. 1; bond distances and angles are presented in Table III. There are no unusual intermolecular contacts.

The crystal structure consists of $[(NC)_6MoS\text{-}Mo(CN)_6]^{6-}$ anions lying on an inversion center (the sulfur atom site), and of K$^+$ cations situated in general positions, the water molecules also being in general positions. The most salient features of the complex are a central linear Mo–S–Mo linkage, a staggered configuration (required by symmetry) of the two $Mo(CN)_6$ moieties, and a rather short Mo–S bond distance of 2.1716(2) Å. The latter is not significantly different from the similar distance (2.173(1) Å) in the imperfect double salt *2* which has a different Mo–S–Mo angle (169.5(2)°) and an eclipsed
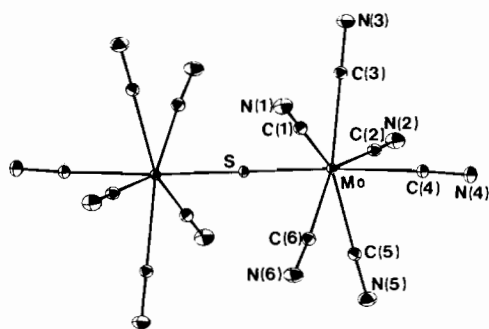
Fig. 1. Perspective representation of $[(NC)_6MoSMo(CN)_6]^{6-}$. The vibrational ellipsoids are drawn at the 50% probability level. The labeling scheme is also shown. Half of the anion is generated through an inversion center located at the sulfur atom.

TABLE III. Selected Bond Lengths and Angles in the $[(NC)_6MoSMo(CN)_6]^{6-}$ Ion.

A. Bond lengths (Å)

Mo–C(1)	2.170(4)	C(1)–N(1)	1.148(5)
Mo–C(2)	2.169(3)	C(2)–N(2)	1.149(5)
Mo–C(3)	2.166(3)	C(3)–N(3)	1.146(5)
Mo–C(5)	2.164(4)	C(5)–N(5)	1.144(5)
Mo–C(6)	2.161(3)	C(6)–N(6)	1.143(5)
Mo–C(eq)	av = 2.166(4)	C–N(eq)	av = 1.146(3)
Mo–C(4)	2.200(3)	C(4)–N(4)	1.145(4)
Mo–S	2.1716(2)		

B. Bond angles (deg)

S–Mo–C(1)	94.62(9)	C(4)–Mo–C(1)	88.9(1)
S–Mo–C(2)	91.98(9)	C(4)–Mo–C(2)	86.4(1)
S–Mo–C(3)	94.83(9)	C(4)–Mo–C(3)	88.3(1)
S–Mo–C(5)	90.68(9)	C(4)–Mo–C(5)	85.2(1)
S–Mo–C(6)	91.98(9)	C(4)–Mo–C(6)	87.1(1)
S–Mo–C(eq)	av = 92.8(1.8)	C(4)–Mo–C(eq)	av = 87.2(1.1)
S–Mo–C(4)	175.8(1)		
	C(1)–Mo–C(3)	71.0(1)	
	C(3)–Mo–C(2)	72.9(1)	
	C(2)–Mo–C(5)	72.8(1)	
	C(5)–Mo–C(6)	71.7(1)	
	C(6)–Mo–C(1)	71.1(1)	

configuration (required by symmetry) of the two $Mo(CN)_6$ fragments [5].

Structural data on different Mo(V) binuclear complexes containing terminal sulfido ligands (similar Mo(IV) binuclear complexes are not available for comparison) give $Mo=S_t$ distances in the range 2.085-(3)–2.135(2) Å [9–13]. Furthermore, the $Mo-S_b$ (b = bridging ligand) bonds in the di-μ-sulfido bridged binuclear Mo(V) [9–13] or Mo(IV) [14] complexes give distances ranging from 2.297(2) to 2.344(2) Å. Thus a double bond character can be assumed for Mo–S in the present compound. This inference is

supported by a MO scheme [5, 15, 16] effected on the $[(NO)_6MoSMo(CN)_6]^{6-}$ anion of the imperfect double salt [5] *2*, which also has the $C_{5v}Mo(CN)_6$ fragments. Therefore it is best to represent the bonding in the central linkage as Mo=S=Mo, in which the molybdenum d orbitals of π symmetry overlap with sulfur p_π orbitals.

The configuration of the ligands about the molybdenum atom is pentagonal-bipyramidal (pb) as in the related d^2 species $[V(CN)_7]^{4-}$ [17]. The carbon 'atoms of the pentagonal girdle are coplanar, none of them being displaced more than 0.0065(35) Å out of the least-squares plane, while the molybdenum central atom is displaced by 0.1062 Å out of the equatorial least-squares plane.

The $Mo-C_{ax}$ (ax = axial) bond (2.200(3) Å), *trans* to the sulfido ligand, is significantly longer than that found in the equatorial plane ($Mo-C_{eq}$ range from 2.161(3) to 2.170(4) Å). In most ML$_7$ complexes the metal–ligand axial bonds are shorter than the equatorial bonds [18]. Presumably, a reduced contribution to the $Mo-C_{ax}$ bond strength can be attributed to the π bonding character of the Mo=S=Mo linkage. The C≡N bonds have values consistent with other structural results. Noteworthy is the entire axial unit N≡C–Mo=S=Mo–C≡N, which is practically (but not rigorously) linear.

Infrared and Raman Spectra

The potassium salt *1* gives excellent Raman spectra. The Raman spectra (Fig. 2) for both solid and aqueous solution are very similar, as is the case for the infrared spectra in the 2000–2200 cm^{-1} region; this and the close similarity of the solid state and aqueous solution electronic spectra of *1*, suggest that there is no major stereochemical change for the anion from the solid to solution at room temperature.
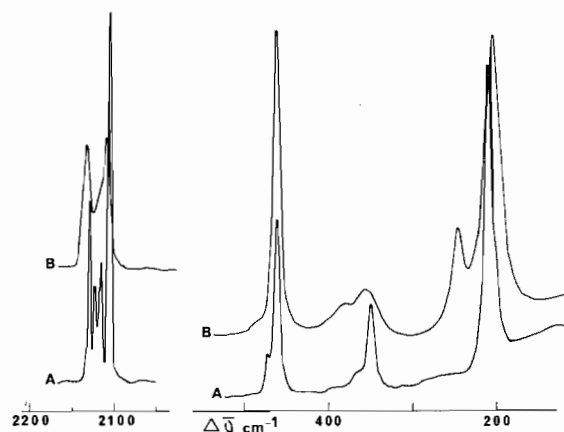

Fig. 2. Raman spectra of $K_6[Mo_2(\mu_2\text{-}S)(CN)_{12}] \cdot 4H_2O$. A) Powder; λ_o = 530.8 nm; 100 mW; spectral slit width: 3 cm^{-1}. B) Aqueous solution; 3.10^{-3} mol l^{-1}; λ_o = 457.9 nm; 150 mW; spectral slit width: 5 cm^{-1}.

Ten fundamental CN stretching vibrations are expected for the $[(NC)_6Mo=S=Mo(CN)_6]^{6-}$ anion. In D_{5h} symmetry (eclipsed configuration), they can be classified in four Raman active $(2A'_1 + E'_2 + E''_1)$ and three infrared-active $(2A''_2 + E'_1)$ modes. In D_{5d} symmetry (staggered configuration), they are also classified in four Raman active $(2A_{1g} + E_{1g} + E_{2g})$ and three infrared-active $(2A_{2u} + E_{1u})$ modes, so that no distinction is to be expected from the vibrational analyses. All are observed in the solid state, but they are not entirely resolved in the solution spectra. The highest Raman mode, which is polarized, may be assigned to the axial CN stretch (A'_1 in D_{5h} or A_{1g} in D_{5d}) in agreement with the structural data.

The low-frequency Raman spectrum is dominated by two strong polarized vibrations at 459 and 203 cm^{-1}: one of these should be the Mo=S symmetric stretch. Taking into account the assignment of the Mo=S antisymmetric stretch to the 626 cm^{-1} infrared band [5], simple model calculations are in favor of the assignment of the 203 cm^{-1} Raman band to the symmetric stretch.

Previous studies [19] on the Raman and infrared spectra of $[Mo(CN)_7]^{x-}$ (x = 4; 5) are in agreement with this assignment: data on solids and solutions do not contain strong Raman shifts or bands in this region. The Raman and infrared spectra are listed in the Table IV with the assignment of some modes.

Our results compared with the previous structural work [5] suggest that the energies of the staggered configuration (D_{5d}) and eclipsed model (C_{2v} or D_{5h} for the idealized configuration) are not very different, since the two forms have been obtained in very similar conditions. It appears likely therefore that the C_{2v} geometry found in 2 is due to the effect of the MoO_4^{2-} anion. These observations correlate well with the EHMO calculations of Mealli et al. [16] on $[(H_3P)_3Ni=S=Ni(PH_3)_3]^{2+}$ and with the stereochemical non-rigidity of $[(\eta^5-C_5H_5)Cr(CO)_2]_2S$ in solution at ambient temperature [2], to suggest linear M=S=M (or Cr≡S≡Cr) bridges with low barriers of rotation. Hence, these new types of chemical bond in the 'metallo-sulfo-allenes' differ markedly from the allenes $R_2C=C=CR_2$.

Acknowledgements

Supplement Material Available

Listings of anisotropic thermal parameters for all atoms provided as U_{ij} and structure factor amplitudes (31 pages).

TABLE IV. Infrared and Raman Spectra of $K_6[Mo_2(\mu_2\text{-}S)(CN)_{12}]\cdot4H_2O$.

Infrared[a] (powder)	Infrared (solution)	Raman (powder)	Raman (solution)	Assignment
		210s	203p;s	$\nu_s(Mo=S)$
			243p;m	
(345)m		345m		
355s	356s	(353)m	351p;m	$\delta(Mo-CN)$
(365)m				$\nu(Mo-CN)$
		379w	(374)m	
386m	(380)m	389w		
447m	443m	459s	459p;s	
489w	478m	(469)m		
530br				
626s	641s			$\nu_{as}(Mo=S=Mo)$
1633m				
(1645)m				
		2103s	2109p;m	$\nu_s(CN_{eq})$
2119s	2110s	2113w		
2130s	2122s,br	2121w	(2118)dp	
2139s		2127m	2132p;m	$\nu_s(CN_{ax})$
(3242)m				
3504s				
(3562)s				

[a]KBr discs. Wave numbers (cm^{-1}), relative intensities (s = strong, m = medium, w = weak, br = broad, shoulders in parentheses, p = polarised, dp = depolarised).

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