The Crystal Structure of Potassium μ-Oxo-bis[oxo tetra(Isothiocyanato)molybdate(V)] Tetrahydrate

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The use of thiocyanate for the analysis of small amounts of molybdenum was reported a long time ago [1]. The method is based on the observation that an acidic solution of Mo(VI) containing NCS^- ions, turns red on the addition of a reducing agent. The deep red species were shown by Wardlaw *et al.* to be Mo(V) complexes. He reported the preparation of three Mo(V) thiocyanato complexes with different Mo:NCS ratios, $[MoO(NCS)_5]^{2-}$ (*1*), $[Mo_2O_3(NCS)_8]^{4-}$ (*2*), and $[Mo_2O_4(NCS)_6]^{4-}$ (*3*) [2]. These complexes were the subject of many spectroscopic, magnetic and theoretical studies [3]. It is generally assumed that the three species exist in solution in equilibrium and their relative concentrations are determined by the concentrations of the acid and NCS^- [3]. There are no structural reports on *1* but spectroscopic results suggested that this monomeric oxo-molybdenum(V) is the isothiocyanato analogue of the well known oxo-halo-Mo(V) complexes of the type $[MoOX_5]^{2-}$ [3]. Recently, the structure of the di-μ-oxo ion *3* as found in the pyridinium salt was reported [4, 5].

We now report the results of an X-ray crystallographic study of the mono-μ-oxo ions, *2*, as found in the compound $K_4[Mo_2O_3(NCS)_8]\cdot 4H_2O$.

Experimental

Crystals of the potassium salt of $[Mo_2O_3(NCS)_8]^{4-}$ were obtained from the trinuclear Mo(IV) cluster $[Mo_3O_2(O_2CCH_3)_6(H_2O)_3]^{2+}$ [6] by the following method. The red Mo(IV) cation was absorbed on a DOWEX 50W cation exchange column (K^+ form) and removed from the column by elution with 0.5 *M* KNCS. The red eluate was placed in an open beaker for air oxidation and evaporation. After several days the color of the solution turned deep purple and dark crystals were deposited. These crystals have a green luster and produce a deep purple solution when dissolved in organic solvents.

TABLE I. Positional Parameters and Estimated Standard Deviations for $K_4[Mo_2O_3(NCS)_8]\cdot 4H_2O$.[a]

Atom	X	Y	Z
Mo	0.53988(4)	0.41840(3)	0.55374(7)
K(1)	0.8521(1)	0.5357(1)	0.4914(2)
K(2)	0.8093(1)	0.2769(1)	0.3956(3)
S(1)	0.7803(1)	0.4273(1)	0.2464(3)
S(2)	0.4672(1)	0.3969(1)	0.0108(2)
S(3)	0.2753(1)	0.3809(1)	0.7531(3)
S(4)	0.6669(1)	0.2072(1)	0.6093(3)
O(1)	0.5	0.5	0.5
O(2)	0.5821(3)	0.4362(3)	0.7198(6)
N(1)	0.6443(3)	0.4332(3)	0.4259(7)
N(2)	0.4918(4)	0.3876(3)	0.3239(8)
N(3)	0.4277(4)	0.3918(3)	0.6357(7)
N(4)	0.5732(4)	0.3190(3)	0.5625(8)
C(1)	0.7005(4)	0.4306(3)	0.3514(8)
C(2)	0.4818(4)	0.3915(4)	0.1937(9)
C(3)	0.3634(5)	0.3872(4)	0.6832(8)
C(4)	0.6108(5)	0.2729(4)	0.5818(9)
OW	0.4122(4)	0.2554(3)	0.3595(8)

[a] Estimated standard deviations in the least significant digits are shown in parentheses.

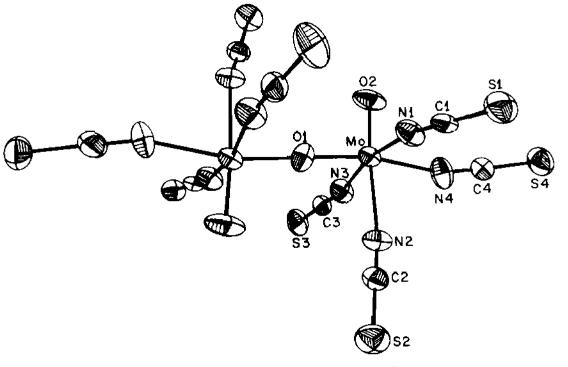

Fig. 1. The structure of $[Mo_2O_3(NCS)_8]^{4-}$.

The crystals were found to belong to the orthorhombic space group *Pbca* with *a* = 16.802(2) Å, *b* = 20.311(3) Å, *c* = 8.783(1) Å and *Z* = 4. A total of 1931 reflections were collected in the range of 3° $< 2\theta <$ 45°, of which 1480 were found to have $I > 2.5\sigma(I)$ and were therefore used in data processing and refining of the structural parameters. The structure was refined by least-squares methods to a conventional *R* factor of 3.2%. Details on data collection and processing have been described elsewhere [7].

The formula of the compound was shown to be $K_4[Mo_2O_3(NCS)_8]\cdot 4H_2O$. The dinuclear anion, *2*, has the structure shown in Fig. 1. The positional parameters are listed in Table I.

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TABLE II. Important Bond Lengths (Å) and Bond Angles (Degrees) for $K_4[Mo_2O_3(NCS)_8]\cdot 4H_2O$.

Mo–O(1)	1.8490(6)
Mo–O(2)	1.661(5)
Mo–N(1)	2.104(6)
Mo–N(2)	2.262(6)
Mo–N(3)	2.089(6)
Mo–N(4)	2.097(6)
O(1)–Mo–O(2)	100.6(2)
O(1)–Mo–N(1)	92.2(2)
O(1)–Mo–N(2)	83.7(2)
O(I)–Mo–N(3)	89.6(2)
O(1)–Mo–N(4)	165.8(2)
O(2)–Mo–N(1)	94.7(2)
O(2)–Mo–N(2)	174.7(3)
O(2)–Mo–N(3)	98.0(3)
O(2)–Mo–N(4)	93.6(3)
N(1)–Mo–N(2)	82.0(2)
N(1)–Mo–N(3)	166.7(3)
N(1)–Mo–N(4)	86.3(3)
N(2)–Mo–N(3)	85.1(2)
N(2)–Mo–N(4)	82.0(3)
N(3)–Mo–N(4)	88.8(3)
Mo–N(1)–C(1)	168.9(6)
Mo–N(2)–C(2)	156.0(6)
Mo–N(3)–C(3)	169.6(6)
Mo–N(4)–C(4)	160.4(7)

The bridging oxygen, O(1), lies on a crystallographic inversion center. The Mo–O–Mo unit is therefore linear and the terminal oxygen atoms, O(2) and O(2)′, are in a *trans* position as previously found in some other Mo_2O_3 structures [8]. Selected bond distances and bond angles in the $[Mo_2O_3(NCS)_8]^{4-}$ ion are given in Table II. The Mo–O$_b$ and Mo–O$_t$ distances, 1.8490(6) Å and 1.661(5) Å respectively, are similar to those found in other μ-oxo-oxomolybdenum(V) dimers [8]. The difference of *ca.* 0.16 Å between M–N(2) and the other M–N(NCS) distances clearly demonstrates the srong *trans* effect of the terminal molybdenyl oxygen atom.

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