# Syntheses and Structural Characterizations of a Series of Mo(W)–Cu–S Compounds of Bidentate Dialkyldithiocarbamate Ligands. Crystal Structure of $[NEt_4]_2[Mo_2Cu_5S_6O_2(Me_2NCS_2)_3]$†

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The complex $[NEt_4]_2[Mo_2Cu_5S_6O_2(Me_2NCS_2)_3]$ has been prepared by the reaction of CuCl, $Na[S_2CNMe_2]$,$NEt_4Br$, and $[NH_4]_2[MoS_2O_2]$ in dimethylformamide solution. It crystallizes in the orthogonal space group *Pnma* with $a = 23.373(3)$, $b = 17.202(3)$, $c = 12.474(4)$ Å, and $Z = 4$. The $Mo_2Cu_5S_6O_2$ framework in the anion consists of two defective cubane-like units $OMoS_3Cu_2$ and $OMoS_3Cu_3$ linked through two weak Cu–S bonds and bridged by two $Me_2NCS_2$ ligands. The synthesis of the series of compounds $[NEt_4]_2[M_2Cu_5S_8(Me_2NCS_2)_3]$, $[PPh_4]_2[M_2Cu_5S_6O_2(Et_2NCS_2)_3]$ (M = Mo or W), and $[NEt_4]_2[MoCu_3S_4(Et_2NCS_2)_3]$ are reported. Their structures are discussed together with their $^1H$, $^{13}C$, and $^{95}Mo$ n.m.r. spectra in solution.

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The thiometalate anions $[Mo^{VI}O_{4-n}S_n]^{2-}$ ($n$ = 1—4) are useful and versatile reagents. One of their important functions is the co-ordination to late transition metals to form linear complexes[1] or cubane-like clusters.[2] Thiomolybdates are reported to react with copper(I) to form Mo–Cu–S clusters of various structure types.[3] These complexes are interesting not only for their crystal and molecular structures, but also for their electronic structures which involve electron delocalization over the entire Mo–S–Cu framework. Furthermore, some of these complexes are biologically relevant, for example, for the antagonism between Cu and Mo which leads to copper deficiency in ruminants.[4]

Two series of M–Cu–S (M = Mo or W) complexes containing cores $MS_4Cu_3$ and $M_2S_6Cu_5$ with $R_2NCS_2$ ligands have been prepared in this laboratory.[5] We report herein the preparation and crystal structure of $[NEt_4]_2[Mo_2Cu_5S_6O_2(Me_2NCS_2)_3]$ (**2**), and the spectroscopic properties of (**2**), $[NEt_4]_2[M_2Cu_5S_8(Me_2NCS_2)_3]$ [M = Mo (**1**) or W (**3**)], $[PPh_4]_2[M_2Cu_5S_6O_2(Et_2NCS_2)_3]$ [M = Mo (**4**) or W (**5**)], and $[NEt_4]_2[MoCu_3S_4(Et_2NCS_2)_3]$ (**6**).

## Results and Discussion

The atomic co-ordinates of compound (**2**) are listed in Table 1. The crystal consists of well separated cations and anions with no unusually close contacts. The cation structure is unexceptional and will not be considered further. The structure of the anion with a mirror plane containing atoms Mo(1), Mo(2), Cu(3), O(1), O(2), S(1), and S(3) is shown in Figure 1. The $Mo_2Cu_5S_6O_2$ framework shown in the Scheme consists of two defective cubane-like units $OMoS_3Cu_2$ and $OMoS_3Cu_3$ whose structures are similar to the core structures in compounds $[MoCu_2S_3O(PPh_3)]$ and $[MoCu_3S_3OCl_3]^{2-}$, respectively.[6] The two units are linked by two weak Cu(2)–S(2) bonds (2.473 Å) and bridged by two $Me_2NCS_2$ ligands at the two sets of copper atoms Cu(1) and Cu(2). The distance between Mo and the terminal oxygen atom [1.68(3) Å] is comparable to that of a double bond Mo=O.[7] Table 2 lists the most important bond distances and angles of compound (**2**).

Some of the mean distances and angles of compounds (**1**)—(**3**) and (**6**) are listed in Table 3 for comparison. There is no significant difference in structural parameters among the three

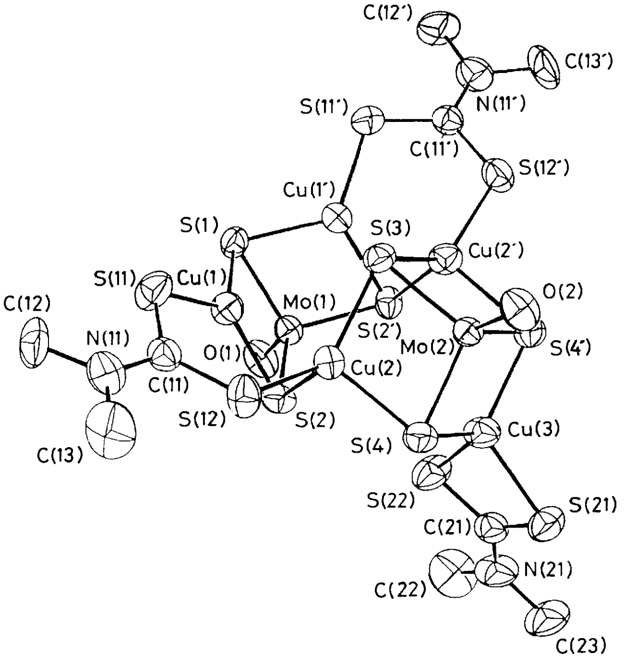

**Figure 1.** A perspective view of the anion $[Mo_2Cu_5S_6O_2(Me_2NCS_2)_3]^{2-}$

isostructural compounds (**1**)—(**3**) except for the distance M=X due to the variation of the terminal atom X (O or S). The $M–S_c$ (c = core) distances are different within a molecule and there is a definite trend of bond lengths M(1)–S(1) [or M(2)–S(3)] > M(1)–S(2) [or M(2)–S(4)], *i.e.* 2.269(14) and 2.233(6) Å for the average values of M–S(1) [S(3)] and M–S(2) [S(4)], respectively (see Table 3 and Scheme). This trend is also present in compound (**6**) where Mo–$\mu_3$-S(1) > Mo–$\mu$-S(2), *i.e.* 2.24(1) *vs.* 2.19(1) Å as shown in the Scheme. Such phenomena are caused mainly by the difference between $\mu$-S and $\mu_3$-S,

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1990, Issue 1, pp. xix—xxii.

**Table 1.** Atomic co-ordinates (× $10^4$) with e.s.d.s. in parentheses for $[NEt_4]_2[Mo_2Cu_5S_6O_2(Me_2NCS_2)_3]$ (**2**)

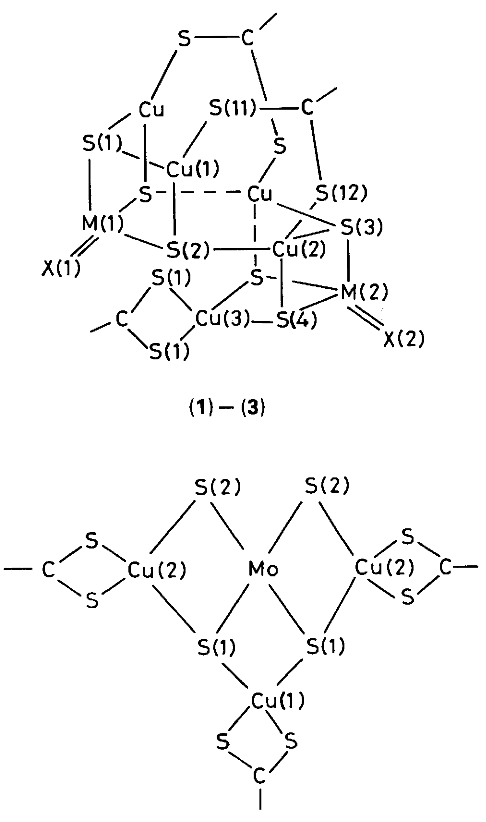
| Atom | *x* | *y* | *z* |
|---|---|---|---|
| Mo(1) | 4 888(1) | 2 500(0) | 3 272(1) |
| Mo(2) | 2 619(1) | 2 500(0) | 3 502(1) |
| Cu(1) | 4 442(1) | 1 477(1) | 1 935(1) |
| Cu(2) | 3 413(1) | 1 402(1) | 2 997(1) |
| Cu(3) | 3 075(1) | 2 500(0) | 5 446(1) |
| S(1) | 4 970(1) | 2 500(0) | 1 456(3) |
| S(2) | 4 397(1) | 1 436(1) | 3 728(2) |
| S(3) | 3 198(1) | 2 500(0) | 2 049(2) |
| S(4) | 2 829(1) | 1 441(1) | 4 477(2) |
| S(11) | 4 242(1) | 558(1) | 791(2) |
| S(12) | 3 338(1) | 153(1) | 2 428(2) |
| S(21) | 3 995(2) | 2 500(0) | 6 310(3) |
| S(22) | 2 867(2) | 2 500(0) | 7 297(3) |
| O(1) | 5 538(3) | 2 500(0) | 3 852(8) |
| O(2) | 1 924(3) | 2 500(0) | 3 158(7) |
| N(11) | 3 794(3) | −819(4) | 1 061(7) |
| N(21) | 3 839(5) | 2 500(0) | 8 421(8) |
| C(11) | 3 798(3) | −86(4) | 1 413(7) |
| C(12) | 4 183(5) | −1 111(5) | 228(8) |
| C(13) | 3 387(4) | −1 402(5) | 1 510(10) |
| C(21) | 3 595(5) | 2 500(0) | 7 460(10) |
| C(22) | 4 472(6) | 2 500(0) | 8 590(10) |
| C(23) | 3 494(7) | 2 500(0) | 9 420(10) |
| N(01) | 1 328(3) | 286(4) | 1 530(6) |
| C(011) | 1 157(4) | 18(6) | 412(8) |
| C(012) | 1 726(4) | −350(6) | 1 930(9) |
| C(013) | 796(5) | 375(7) | 2 240(10) |
| C(014) | 1 615(6) | 1 080(5) | 1 520(10) |
| C(015) | 777(4) | 599(6) | −180(9) |
| C(016) | 1 874(4) | −261(7) | 3 172(8) |
| C(017) | 473(5) | −403(8) | 2 360(10) |
| C(018) | 2 106(5) | 1 139(7) | 0 770(10) |

**Table 2.** Selected bond distances (Å) and angles (°) for complex (**2**)

| | | | |
|---|---|---|---|
| Mo(1)–Cu(1) | 2.639(1) | Cu(1)–S(1) | 2.231(2) |
| Mo(2)–Cu(2) | 2.721(1) | Cu(1)–S(2) | 2.240(2) |
| Mo(2)–Cu(3) | 2.648(1) | Cu(2)–S(3) | 2.284(1) |
| Mo(1)–S(2) | 2.232(2) | Cu(2)–S(4) | 2.299(2) |
| Mo(2)–S(4) | 2.243(1) | Cu(3)–S(4) | 2.260(2) |
| Mo(1)–S(1) | 2.274(3) | Cu(2)–S(2) | 2.473(2) |
| Mo(2)–S(3) | 2.261(2) | Cu(1)–S(11) | 2.181(5) |
| Mo(1)–O(1) | 1.683(3) | Cu(2)–S(12) | 2.271(2) |
| Mo(2)–O(2) | 1.681(3) | Cu(3)–S(21) | 2.404(2) |
| Cu(1)–Cu(2) | 2.747(2) | Cu(3)–S(22) | 2.359(2) |
| | | | |
| S(1)–Mo(1)–S(2) | 107.29(6) | S(4)–Cu(2)–S(12) | 103.4(2) |
| S(1)–Mo(1)–O(1) | 110.6(1) | S(4)–Cu(3)–S(4′) | 107.33(9) |
| S(2)–Mo(1)–O(1) | 110.80(6) | S(4)–Cu(3)–S(21) | 117.88(5) |
| S(2)–Mo(1)–S(2′) | 109.88(9) | S(4)–Cu(3)–S(22) | 118.10(5) |
| S(3)–Mo(2)–S(4) | 107.71(5) | S(21)–Cu(3)–S(22) | 75.26(7) |
| S(3)–Mo(2)–O(2) | 111.9(2) | Mo(1)–S(1)–Cu(1) | 71.74(7) |
| S(4)–Mo(2)–O(2) | 110.43(6) | Mo(1)–S(2)–Cu(1) | 72.35(6) |
| S(4)–Mo(2)–S(4′) | 108.52(8) | Mo(2)–S(3)–Cu(2) | 73.56(6) |
| S(1)–Cu(1)–S(2) | 108.50(9) | Mo(2)–S(4)–Cu(2) | 73.62(5) |
| S(1)–Cu(1)–S(11) | 121.0(2) | Mo(2)–S(4)–Cu(3) | 72.03(5) |
| S(2)–Cu(1)–S(11) | 128.4(2) | Mo(1)–S(2)–Cu(2) | 113.87(7) |
| S(2)–Cu(2)–S(3) | 112.04(7) | Cu(1)–S(1)–Cu(1′) | 104.1(2) |
| S(2)–Cu(2)–S(4) | 104.82(6) | Cu(1)–S(2)–Cu(2) | 71.12(5) |
| S(2)–Cu(2)–S(12) | 102.2(1) | Cu(2)–S(3)–Cu(2) | 111.5(1) |
| S(3)–Cu(2)–S(4) | 105.1(1) | Cu(2)–S(4)–Cu(3) | 107.56(7) |
| S(3)–Cu(2)–S(12) | 127.1(2) | | |

Primed atoms are the mirror image of the unprimed atoms as shown in Figure 7.

because Cu(2)–S(2) in compounds (**1**)—(**3**) is a very weak bond for its distance (2.473 Å) is much longer than a normal Cu–$S_c$ bond (Table 3) and atom S(2) functions as μ-S. As for the short Mo(2)–S(4) distance compared to that of Mo(2)–S(3), it is believed that atom S(4) in compounds (**1**)—(**3**) is in an environment more like that of S(1) in compound (**6**), which is linked to the Cu atom chelated to a terminal $R_2NCS_2$ ligand, while atom S(3) is attached to two Cu atoms bridging $R_2NCS_2$ ligands. The bonds Mo–$S_c$ of (**6**) are slightly shorter than similar ones in (**1**)—(**3**). The molybdenum atom in any of these compounds is in a tetrahedral centre as can be seen from the average angle S–M–Y close to 109° in Table 3 with low estimated standard deviations (e.s.d.s).



(**1**) – (**3**)

(**6**)

**Scheme.** Schematic view of compounds (**1**)—(**3**) and (**6**)

The n.m.r. spectra of the complexes reported herein have been recorded and the results are summarized in Table 4. Proton n.m.r. spectra of compounds (**1**)—(**6**) show very sharp peaks: a singlet for the anions with $Me_2NCS_2$ ligands and a triplet and a quartet for those with $Et_2NCS_2$ ligands. The chemical shifts of the ligands in the complexes concerned are almost the same as those of the sodium salts of the corresponding free ligands. Carbon-13 n.m.r. chemical shifts of the compounds with $Me_2NCS_2$ ligands are at 208.2(2) and 46.2(3) p.p.m. and those with $Et_2NCS_2$ at 206.9(2), 50.5(6), and 12.3(1) p.p.m. Both of these types of resonance spectra are also similar to those of the sodium salts of the corresponding free ligands. The $^{13}C$ n.m.r. chemical shifts of compound (**6**) are slightly different from those of the others and are at 208.2, 48.1, and 12.5 p.p.m. for the $Et_2NCS_2$ ligand. Another important feature for these compounds is that the resonance lines of the primary carbon in compounds (**1**)—(**3**) and of the secondary carbon in (**4**) and (**5**) are broadened or split as shown in Figure 2 with typical spectra for complexes (**2**) and (**5**), while those of the tertiary carbon in all the compounds are relatively sharp. This feature indicates that only one type of $R_2NCS_2$ with two inequivalent R groups is present in dimethylformamide (dmf) or dimethyl sulphoxide (dmso) solutions of these compounds.

**Table 3.** Comparison of bond lengths (Å) and angles (°)*

| | Compound | | | |
|---|---|---|---|---|
| | **(1)** | **(2)** | **(3)** | **(6)** |
| M(1)–S(2) | 2.229 | 2.232(2) | 2.230 | 2.19(1) |
| M(2)–S(4) | 2.235 | 2.243(1) | 2.226 | |
| M(1)–S(1) | 2.289 | 2.274(3) | 2.269 | 2.24(1) |
| M(2)–S(3) | 2.273 | 2.261(3) | 2.248 | |
| M(1)–X(1) | 1.942 | 1.683(3) | 2.116 | |
| M(2)–X(2) | 2.123 | 1.681(3) | 2.127 | |
| Cu(2)–S(2) | 2.495 | 2.473(2) | 2.51 | |
| Cu(1)–$S_c$ | 2.24(1) | 2.24(1) | 2.25(1) | 2.25(1) |
| Cu(2)–$S_c$ | 2.30(1) | 2.29(1) | 2.30(1) | 2.25(1) |
| Cu(3)–$S_c$ | 2.27 | 2.260(2) | 2.29 | |
| Cu(1)–$S_l$ | 2.189 | 2.181(5) | 2.180 | 2.40(5) |
| Cu(2)–$S_l$ | 2.265 | 2.271(2) | 2.280 | 2.40(2) |
| Cu(3)–$S_l$ | 2.40(3) | 2.38(3) | 2.38(3) | |
| S–M(1)–Y | 109.5(1.4) | 109.5(1.5) | 109.5(1.5) | 109.5(1.4) |
| S–M(2)–Y | 109.9(2.3) | 109.8(1.5) | 109.7(1.9) | |

* X = terminal S or O, Y = O or S (terminal or core), c = core, and l = ligand; atomic numbering refers to the Scheme.

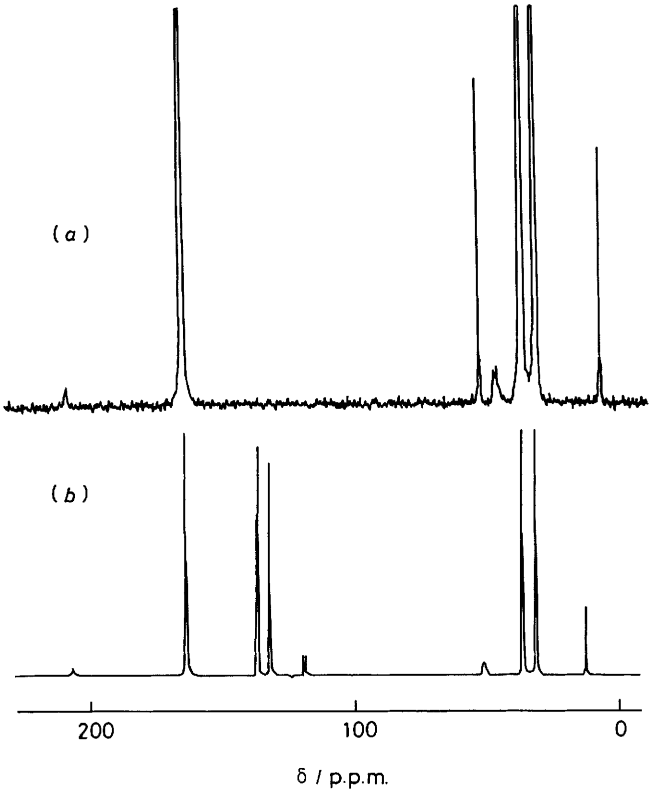


**Figure 2.** Carbon-13 n.m.r. spectra of (*a*) $[NEt_4]_2[Mo_2Cu_5S_6O_2(Me_2NCS_2)_3]$ **(2)** and (*b*) $[PPh_4]_2[W_2Cu_5S_6O_2(Et_2NCS_2)_3]$·dmf **(5)** in dmf solutions

Molybdenum-95 n.m.r. spectra show a single broad line in dmf for all the compounds, although the environments of the two molybdenum atoms in each molecule are not identical from crystallographic evidence (see Figure 1). The $^{95}Mo$ chemical shift of compound **(6)** is 1 296 p.p.m. which agrees quite well with that of $[MoCu_3S_4X_3]^{2-}$ (X = Cl, Br, or I), 1 258 ± 24 p.p.m.[3a] When the terminal oxygen atom is replaced by a sulphur atom as when going from **(2)** to **(1)**, the increase of chemical shift by 165 p.p.m. is much smaller compared with an increase of 500—700 p.p.m. for the change from a $MoS_3O$ core to a $MoS_4$ core,[8] such as when going from $[MoS_3O]^{2-}$ (1 654 p.p.m.) to $[MoS_4]^{2-}$ (2 259 p.p.m.).[9]

**Table 4.** Proton $^{13}C$, and $^{95}Mo$ n.m.r. chemical shifts (p.p.m.) and linewidth[a] (Hz) of the M–Cu–S anions and the free ligand anions

| Anion | $^1H^b$ | $^{13}C^c$ | $^{95}Mo^d$ |
|---|---|---|---|
| $Na[S_2CNMe_2]$ | 3.51 | 208.3, 45.9 | — |
| **(1)** | 3.52(5) | 208.0, 46.5(90) | 995(800) |
| **(2)** | 3.51(5) | 208.1, 45.9(90) | 830(600) |
| **(3)** | *e* | 208.3, 46.1(90) | — |
| $Na[S_2CNEt_2]$ | 4.0, 1.2 | 206.7, 49.4, 12.4 | — |
| **(4)** | 3.97, 1.25 | 207.0, 50.3(80), 12.3 | 830(600) |
| **(5)** | 3.96, 1.23 | 206.8, 50.8(90), 12.3 | — |
| **(6)** | *e* | 208.2, 48.1, 12.5 | 1 296(800) |
| e.s.d. | 0.04(2) | 0.1(10) | 4(100) |

[a] Linewidth (full width at half maximum) in parentheses. [b] In $(CD_3)_2SO$ solution at 295 K with nominal radiation frequency of 80 MHz. [c] In dmf solution at 298 K with frequency of 100 MHz. [d] In dmf solution at 298 K with frequency of 26 MHz. [e] Not measured.

## Experimental

Reactions were carried out under an atmosphere of purified dinitrogen, using Schlenk techniques. The salts $Na[S_2CNR_2]$ (R = Me or Et) were synthesized by reaction of $NHR_2$ and NaOH in $CS_2$ solution, and $[NH_4]_2[MS_2X_2]$ (M = Mo or W, X = O or S) were synthesized according to literature methods.[10] Copper(I) chloride was purchased from Beijing Hongxin Chemical Plant. Solvents were dried, distilled, and degassed before use. Elemental analyses were carried out by Mr. Enshui Lin and his associates in the Analytical Chemistry Section of this Institute.

*Preparations*.—$[NEt_4]_2[Mo_2Cu_5S_6O_2(Me_2NCS_2)_3]$ **(2)**. A dmf (30 $cm^3$) solution of CuCl (0.30 g, 3 mmol), $Na[S_2CNMe_2]$ (0.55 g, 3 mmol), and $NEt_4Br$ (0.21 g, 1 mmol) was stirred for 20 min at room temperature. Solid $[NH_4]_2[MoS_2O_2]$ (0.23 g, 1 mmol) was added and the brown solution gradually turned dark on mixing. After stirring for 24 h the reaction mixture was filtered and tetrahydrofuran (thf) (30 $cm^3$) added to the filtrate. A black crystalline solid separated after several days at 5 °C and was collected, washed with EtOH and $Et_2O$, and dried *in vacuo* to afford 0.20 g (37%) of product. The i.r. spectrum (KBr) showed characteristic absorptions of Mo=O at 900 $cm^{-1}$ and of Mo–$S_b$ (b = bridging) at 450, 438, and 415 $cm^{-1}$.

$[PPh_4]_2[Mo_2Cu_5S_6O_2(Et_2NCS_2)_3]$·dmf **(4)**. A dmf solution (100 $cm^3$) of CuCl (1.49 g, 15 mmol), $PPh_4Br$ (2.10 g, 5 mmol), and $Na[S_2CNEt_2]\cdot 3H_2O$ (3.38 g, 15 mmol) was stirred for 30 min at room temperature and solid $[NH_4]_2[MoS_2O_2]$ (1.14 g, 5 mmol) was added. After stirring for 22 h the solution was added to thf (100 $cm^3$) and the precipitate thus formed was removed by filtration. Diethyl ether was then added to the filtrate to bring the total volume to 240 $cm^3$. On standing for 24 h at 5 °C, the black square-plate crystals formed were collected, washed with EtOH and $Et_2O$, and dried *in vacuo* to afford 2.0 g (40%) of product. The i.r. (KBr) spectrum shows characteristic absorptions of Mo=O at 905 $cm^{-1}$ and of Mo–$S_b$ at 450, 435, and 415 $cm^{-1}$ (Found: C, 39.8; H, 3.95; Cu, 16.0; Mo, 9.9; N, 3.3; P, 3.2; S, 19.9. $C_{66}H_{77}Cu_5Mo_2N_4O_3P_2S_{12}$ requires C, 41.0; H, 4.0; Cu, 16.4; Mo, 9.9; N, 2.9; P, 3.2; S, 19.9%).

$[PPh_4]_2[W_2Cu_5S_6O_2(Et_2NCS_2)_3]$·dmf **(5)**. A solution of CuCl (1.49 g, 15 mmol), $Na[S_2CNEt_2]\cdot 3H_2O$ (3.38 g, 15 mmol), and $PPh_4Br$ (2.10 g, 5 mmol) in dmf (100 $cm^3$) was stirred for 30 min at room temperature. After addition of solid $[NH_4]_2$-

**Table 5.** Crystallographic data for $[NEt_4]_2[Mo_2Cu_5S_6O_2(Me_2NCS_2)_3]$

| | | | |
|---|---|---|---|
| Formula | $C_{25}H_{58}Cu_5Mo_2N_5O_2S_{12}$ | $M$ | 1 355.1 |
| Crystal system | Orthogonal | Space group | *Pnma* |
| $a$/Å | 23.373(3) | $T$/°C | 22 |
| $b$/Å | 17.202(3) | $\lambda$/Å | 0.710 73 |
| $c$/Å | 12.474(4) | $D_c$/g cm$^{-3}$ | 1.795 |
| $U$/Å$^3$ | 5 015.4(30) | $F$(000) | 2 720 |
| $Z$ | 4 | $\mu$/cm$^{-1}$ | 30.71 |
| Reflections measured | 5 470 | Absorption correction | 0.7607—1.1320 |
| $R$ | 0.041 | Unique data [$I > 3\sigma(I)$] | 2 823 |
| $R'$ | 0.049 | | |

$R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w(F_o)^2]^{\frac{1}{2}}, w = 4(F_o)^2/\sigma^2(F_o)^2$.

$[WS_2O_2]$ (1.59 g, 5 mmol) and stirring for 24 h, the solution was added to thf (100 cm$^3$) and the precipitate thus formed was removed by filtration. Solvent $Et_2O$ (40 cm$^3$) was then added to the cooled filtrate and after standing for 1 week at 5 °C the purple-red square-plate crystals were collected, washed with EtOH and $Et_2O$, and dried *in vacuo* to afford 3.1 g (59%) of product. The i.r. spectrum (KBr) shows characteristic absorptions of W=O at 920 cm$^{-1}$ and of W–$S_b$ at 448 and 423 cm$^{-1}$ (Found: C, 37.7; H, 3.8; Cu, 14.3; N, 2.6; P, 3.0; S, 18.1. $C_{66}H_{77}Cu_5N_4O_3P_2S_{12}W_2$ requires C, 37.6; H, 3.7; Cu, 15.1; N, 2.7; P, 2.9; S, 18.3%).

The preparations of $[NEt_4]_2[Mo_2Cu_5S_8(Me_2NCS_2)_3]$ (**1**),[5b] $[NEt_4]_2[W_2Cu_5S_8(Me_2NCS_2)_3]$ (**3**),[5c] and $[NEt_4]_2[MoCu_3S_4(Et_2NCS_2)_3]$ (**6**)[5d] have been described previously.

*Spectroscopic Measurements.*—I.r. spectra were recorded on a Digilab-20 E/D or a Perkin-Elmer 577 spectrophotometer, proton n.m.r. spectra on a Varian FT-80A spectrometer with $(CD_3)_2SO$ as solvent and $SiMe_4$ as internal standard, downfield shifts being regarded as positive. Carbon-13 and $^{95}$Mo n.m.r. data were measured in dmf solution on a Bruker MSL-400 spectrometer, relative to the CHO (162.7 p.p.m.) of dmf and 2 mol dm$^{-3}$ $Na_2MoO_4$ in $D_2O$, respectively.

*Crystal Structure Determination.*—The crystallographic data for compound (**2**) are summarized in Table 5. Diffraction data were collected at room temperature on an Enraf–Nonius CAD4 diffractometer using graphite-monochromatized Mo-$K_\alpha$ radiation. The single crystal was protected from air by a coating of epoxy resin. An empirical absorption correction ($\psi$ scan) was applied. After data reduction (including correction for Lorentz and polarization effects), the remaining unique reflections with $I > 3\sigma(I)$ were used for subsequent structure solution and refinement. Calculations were performed on a VAX 11/785 computer with the SDP program package.[11] All metal atoms were located from an $E$ map. A Fourier map phased by the metal atoms contained most of the remaining non-hydrogen atoms. Full-matrix least-squares refinement with anisotropic thermal parameters for all non-hydrogen atoms led to convergence.

Additional material available from the Cambridge Crystallographic Data Centre comprises thermal parameters and remaining bond distances and angles.

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