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SYNTHESIS AND SPECTROSCOPIC STUDIES OF THIOCYANATO-DERIVATIVES OF Cu-Mo-S CLUSTERS

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Abstract

The complexes $[MoS_4(CuNCS)_X]^{-2}$ when x = 2, 3, 4 and $[MoOS_3(CuNCS)_Y]^{-2}$ when y = 2, 3 have been prepared by the reaction of CuSCN with $[P(C_6H_5)_4]_2[MoS_4]$ or $[P(C_6H_5)_4]_2[MoOS_3]$ in dry degassed acetone or DMF solution and recrystallized from dichloromethane, the attempted preparation of $[MoS_4(AgSCN)_X]^{-2}$ and $[MoOS_3(AgSCN)_Y]^{-2}$ failed. The Raman, IR, UV/VIS, ^{13}C-nmr and ^{95}Mo-nmr spectra of the complexes are discussed.

Introduction

The chemistry of Cu-Mo-S compounds has been of interest for over a century [1]-recent studies of Cu-Mo-S clusters have been stimulated by general interest in $[MoS_4]^{-2}$ as a ligand for other metals [2] and by the implication that species derived from copper - thiomolybdate interactions may be responsible for the biological antagonism between copper and molybdenum that leads to copper deficiency in ruminant animals [3].

Results and Discussion

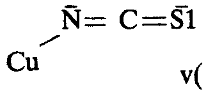
(1) Raman and IR Spectroscopy

The thiocyanate ion has been much studied [4] as an ambidentate ligand (in which either S or N is the donor atom); it can also act as a bidentate bridging ligand (-SCN-). A preliminary indication of the mode of coordination can somtimes be obtained from vibrational spectroscopy since N-coordination increased both v (CN) and v (CS) relative to the values of the uncoordinated ion. The increasing C-N frequency on N-coordination is caused by the removed of repulsive interactions between the lone-pair electrons on the N-atom [5, 6]. The S-coordination increases v (CN) and decrease v (CS) relative to the values of the uncoordinated ion. The bridging mode tends to increase both v (CN) and v (CS).

Because the C-S stretching vibration of low intensity gives rise in the same region (730- 830 cm^{-1}) as the vibrational bands of the (C_6H_5) rings appear, it was difficult for us to assign any features in this frequency range to the C-S stretching vibration. The reported [4] frequencies of the C-N stretching vibrations (Table I) have been applied to the analysis of the Raman and IR spectra of the Cu-Mo-S clusters in this work.

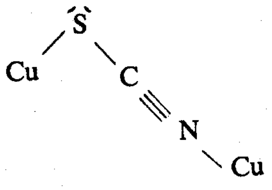
Table 1- Bonding modes of SCN

(1) Isothiocyanate



v(CN) ≈ 2076 cm^{-1}
v(CS) ≈ 780 cm^{-1}

(2) Bridging



v(CN) ≈ 2127 cm^{-1} v(CS) ≈ 794 cm^{-1}

Key words: Copper - thiomolylidate clusters

(3) Free $SC\bar{N}$ ion $(1\bar{N}=C=\bar{S}1)^-$

$v(CN) \approx 2055\ cm^{-1}$ $v(CS) \approx 737\ cm^{-1}$

(a) $[P(C_6H_5)_4]_3[MoS_4Cu_3(SCN)_4]$

IR Spectrum:

2078 (S), 2054 (SH), 801 (m), 262 (W), 240 (W), 225 (W)

Raman Spectrum:

2095 (S), 891 (m), 446 (S), 300 (W).

N.B. W = weak, m = medium, S = strong, SH = shoulder

The infra-red spectrum of the complex exhibits two v(CN) bands at 2054 cm^{-1} and 2078 cm^{-1}. The band at 2054 cm^{-1} which appears in the same region as in the spectrum of NBU_4SCN is characteristic of the free $SC\bar{N}$ ion. Bands at 2095 cm^{-1} (Raman) and 2078 cm^{-1} (IR) are assigned to the symmetric and the asymmetric C-N stretching vibrations of a complex containing $SC\bar{N}$ ion bonded to Cu^+ ion through the N-atom. The IR spectrum of the complex in CH_2Cl_2 at room temperature exhibits also two v(CN) bands at 2060 cm^{-1} and 2092 cm^{-1} due to the free and (N-bonded $SC\bar{N}$ ions. It is probable that at room temperature there is a fast exchange between free and bridging SCN ligand, but at lower temperatures the free $SC\bar{N}$ ion bind rigidly as a bridging ligand. The situation is similar to that observed in $[NPr_4]_2[ReS_4Cu_3Cl_4]$ which shows three terminal and one bridging chlorine ligand in it's crystal structure [7].

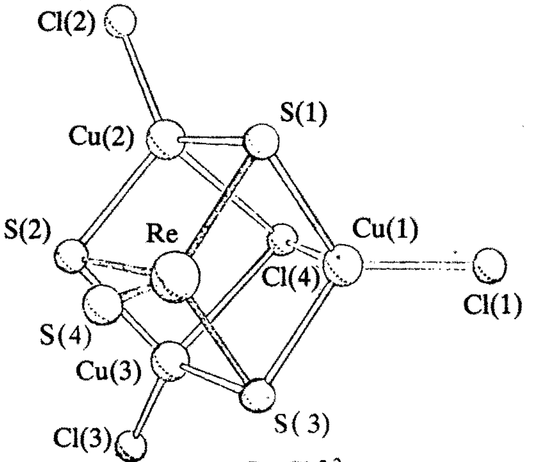


Fig. 1- Crystal Structure of $[ReS_4Cu_3Cl_4]^{-2}$

(b) $[P(C_6H_5)_4]_2[MoOS_3(CuNCS)_3]$

IR Spectrum:

2112 (SH), 2076 (S), 909 (S), 445 (S), 332 (W), 274 (W), 262 (W) 244 (W), 231 (W), 224 (W)

Raman Spectrum:

2110 (SH), 2087 (S), 1585 (m), 1027 (m), 1001 (S), 445 (m), 424 (S), 279 (W), 242 (m).

The IR spectrum of the complex exhibits two v(CN) bands at 2112 cm^{-1} 2076 cm^{-1}. The band at 2112 cm^{-1} which is located 57 cm^{-1} higher than for uncomplexed SCN ligand is due to the presence of the bridging SCN ligand in the complex. The bands at 2087 cm^{-1} (Raman) and 2076 (IR) are associated with the symmetric and asymmetric C-N stretching vibrations of a complex containing N - bonded SCN ions. This assignment was confirmed by crystal structure of the complex [8]**Fig 2.**

The appearance of a strong absorption at 900 cm^{-1} in the IR spectrum indicates the presence of terminal Mo ═ O bound in this complex. On dissolution of the complex in CH_2Cl_2 the higher wave number band (2112 cm^{-1}) in the IR spectrum **disappeared** and a single strong band at 2092 cm^{-1} due to the N - bonded SCN ligand was observed. The disappearance of the extra band at 2112 cm^{-1} in the CH_2Cl_2 solution suggests that the $[MoOS_3(CuNCS)_3]^{-2}$ anions in the solution are not linked by pairs of Cu-NCS-Cu bridges to form centrosymmetric dimers as in the solid.

The variation of the IR spectrum in CH_2Cl_2 with temperature was also investigated. As the temperature decreased from room temperature to - 20°C, no significant change occurred, but at - 30°C the spectrum indicated the presence of bridging SCN ligand. Evidence for this became clearer at lower temperatures. Thus at - 60°C the spectrum shows a band at 2147 cm^{-1} due to the bridging SCN ligand.

Table 2- Variable temperature IR Spectra (RT to -60°C) (2200 - 2000 cm^{-1}) of $[P(C_6H_5)_4]_2[MoOS_3(CuNCS)_3]$ in CH_2Cl_2

Peak threshold (cm^{-1})	**Temperature (°C)**	**o/oT**
2092	RT	27.31
2093	o	27.45
2094	-10	26.71
2095	-20	26.80
2150	-30	50.81
2095	-30	27.59
2150	-40	50.32
2096	-40	27.98
2150	-50	49.72
2096	-50	27.93
2149	-60	48.5
2097	-60	27.46

(c) $[P(C_6H_5)_4]_2[MoOS_3(CuNCS)_2]$

IR Spectrum:

2080(S), 1697(W), 1586(W), 1483(S), 1465(S), 1436(W), 1378(W), 1315(m), 1187(m), 1163(m), 1107(S), 1027(m), 997(m), 906(S), 830(m), 753(S),

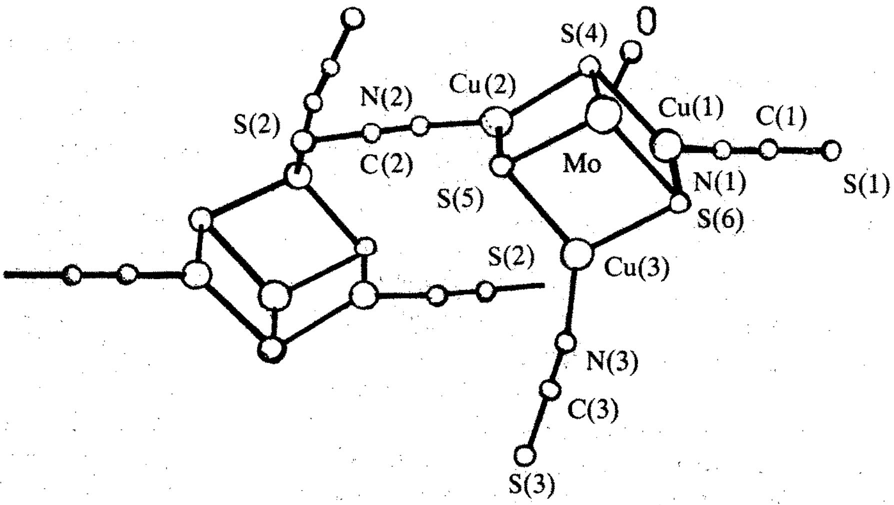


Fig. 2- Crystal Structure of $[MoOS_3 (CUNCS)_3]^{-2}$

722(S), 687(m), 616(m), 526(m), 453(S)
Raman Spectrum:
2086(S), 997(m), 454(S), 423(S), 271(W), 240(W)

Bands at 2086 cm^{-1} (Raman) and 2080 cm^{-1} (IR) are assigned to the symmetric and the asymmetric C-N stretching vibrations of a complex containing SCN ligand bonded to Cu^+ ion through the N-atom. Strong bands at 906 cm^{-1} and 453 cm^{-1} are assigned to the v(Mo = O) and bridged MoS_4 group respectively.

(d) $[P(C_6H_5)_4]_2 [MoS_4(CuNCS)_3 (DMF)_2]$
IR Spectrum:
2077(S), 1665(S), 1464(S), 1378(W), 1106(S), 996(m), 752(S), 722(S), 687(S), 525(m), 469(S)
Raman Spectrum:
2084(S), 464(S), 444(S), 428(m), 173(W), 147(W), 136(W), 119(W).

The vibrational spectra indicates that the SCN ligands are N-bounded in the complex. The C ═ O stretching frequency of the amide (DMF) ligand in the complex (1665 cm^{-1}) is shifted to a lower frequency relative to that for free DMF (1685 cm^{-1}). This indicates a decrease in the stretching force constant, showing that the amide ligand is co-ordinated through an oxygen atom of the carbonyl group. The band at 444 cm^{-1} is associated with the bridged MoS_4 group.

(e) $[P(C_6H_5)_4]_2 [MoS_4(CuNCS)_4]$
IR Spectrum:
2109(S), 2085(SH), 1463(S), 1378(m), 1108(S), 997(m), 723(S), 689(m), 528(S), 456(S), 270(W), 227(W).
Raman Spectrum:
2105(S), 453(S), 428(S).

In the IR spectrum of the polymeric complex two bands are found for the v(CN) stretching mode at 2109 cm^{-1} and 2085 cm^{-1} due to the bridging and N - bonded SCN ligands respectively. Strong band at 450 cm^{-1} is assigned to the bridged MoS_4 group. Bands observed at 270 cm^{-1} and 227 cm^{-1} could be attributed to v(Cu-N) or v(Cu-S).

(f) $[P(C_6H_5)_4]_2 [MoS_4(CuNCS)_2 (DMF)]$
IR Spectrum:
2079(S), 1667(S), 1585(W), 1464(S), 1438(W), 1378(W), 1107(S), 996(m), 753(S), 723(S), 688(S), 527(m), 470(m), 455(S), 341(W).

The IR Spectrum of the complex indicates that the SCN ligands are all N-bound in the complex and the amide ligand is co-ordinated through an oxgen atom of the carbonyl group.

[2]^{13}C-nmr. Spectroscopy

Although a variety of physical techniques have been utilized to determine the bonding mode of the coordinated thiocyanate group, infrared spectroscopy has continued to be the most widely used method. Recent studies have also shown ^{14}N-nmr and ^{13}C-nmr spectroscopy to be useful diagnostic tools to establish the bonding mode of thiocyanate group.

In this study the ^{13}C chemical shifts of some metal thiocyanate complexes of known bonding mode [9] have been applied to the analysis of the ^{13}C-nmr spectra of the Cu-Mo-S compounds.

Table 3. ^{13}C Chemical Shift (PPm) Date for the various bonding mode of S C $\bar{N}$.

S-bound	110‧130
N-bound	135-146

bridging mode	132
Ionic Thiocyanate	134

Table 4. ^{13}C Chemical Shift (PPm) Data for the Cu-Mo-S Cluster.

Compound	Chemical Shift (PPm)	Solvent
$[P(C_6H_5)_4]_2[MoOS_3(CuNCS)_2]$	135.7	D_6-DMSO
$[P(C_6H_5)_4]_2[MoS_4(CuNCS)_4]$	137.2	1.5mlDMF +0.5D_7-DMF
$[P(C_6H_5)_4]_3[MoS_4Cu_3(SCN)_4]$	135.8	CD_2Cl_2
$[P(C_6H_5)_4]_3[MoS_4Cu_3(SCN)_4]$	134.5	D_6-DMSO
$[P(C_6H_5)_4]_2[MoS_4(CuNCS)_2]$	136	CD_2Cl_2
$[P(C_6H_5)_4]_2[MoOS_3(CuNCS)_3]$	137.3	CD_2Cl_2
$[P(C_6H_5)_4]_2[MoS(CuNCS)_3(DMF)_2]$	138	$CDCl_2$

The ^{13}C-nmr spectra of the complexes (Table 4) indicate that the SCN ligands are N - bonded complexes.

In conclusion Cu^+ generally acts as a hard cation toward $SC\bar{N}$, contrary to Ag^+ and Au^+ which are known to be softer (10). Consequently, Cu^+ should be considered, like cd^{+2}, as being in a borderline position between hard and soft cations.

[3) UV/visible Absorption Spectroscopy

The spectra of the complexes are listed in Table 5. A simple MO scheme for the $[MS_4]^{-2}$ (M = Mo, W) ions may be devised [2] by assuming nd, (n + 1) S, and (n + 1) P valence orbitals on M and 3S and 3P valence orbitals on S. The longest wavelength absorption at 467 nm can be unambiguously assigned [2] to the one electron transition v_1) t_1 (n, π) $\longrightarrow$ 2e (d). The absorption at 316 nm is due to v_2) $3t_2$ (π, δ) $\longrightarrow$ 2e (d) (Fig. 3)

It is apparent that the UV/VIS spectra of the Cu-Mo-S complexes are dominated by the internal transitions of the $[MoS_4]^{-2}$ and $[MoOS_3]^{-2}$ ions, set out in Table 5. are the band positions resulting from absorption of the complexes together with the $[MoOS_3]^{-2}$ anions in the v_1 and v_2 regions.

However, it should be noted that in all of these spectra, bands often in the form of shoulders are observed which are intermediate between the two regions. In the case of the $[NcCu(MoS_4)]^{-2}$ anion, these additional bands lie closer to the v_1 region [2], whereas for the other complexes (Table 5) they lie closer to v_2 region. These additional bands which are not observed in the spectra of the $[MoS_4]^{-2}$ anion are considered to arise as a result of the lowering of the symmetry in the complexes VS. The $[MoS_4]^{-2}$ and $[MoOS_3]^{-2}$ anions and may be due to removal of the degeneracy of the t_1(n, π) level (Fig 3).

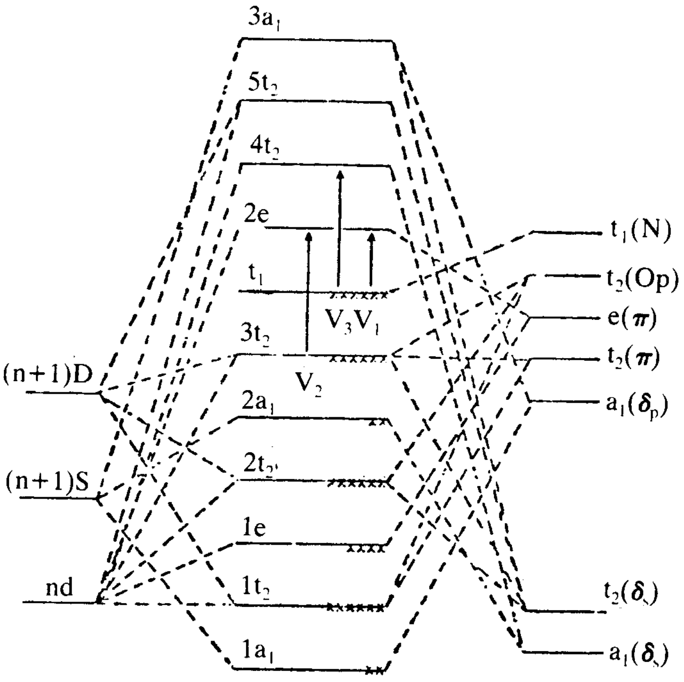


Fig 3- Simplified Molecular orbital for $[MS_4]^{-2}$ (M = Mo, W) Ions with Tetrahedral Symmetry

(b) The v_1 transitions of the complexes listed in Table 5 are all red-shifted with respect to the corresponding transition observed in $[MoS_4]^{-2}$ or $[MoOS_3]^{-2}$. For example the v_1 absorption observed for $[P(C_6H_5)_4]_3[MoS_4Cu_3(SCN)_4]$ at 504. 2nm while it appears at 510. 4nm for $[P(C_6H_5)_4]_2[MoS_4(CuNCS)_4]$. The v_1 appears at 465 nm and 484. 6nm for $[P(C_6H_5)_4]_2[MoOS_3(CuNCS)_2]$ and $[P(C_6H_5)_4]_2[MoOS_3(CuNCS)_3]$ respectively. Therefore, it would appear that the effect of increasing the number of copper atoms bound to $[MoS_4]^{-2}$ from 3 to 4 or in the case of $[MoOS_3]^{-2}$ from 2 to 3 is to produce larger red-shifts of the v_1 transition. a linear relation between the energy of the longest wavelength electronic transition (V_1) and the stretching force constant of the Mo-S bonds in the complexes can be explained through the stabilization of π - bonding levels. (C) The magnitude of the red shift is much smaller for the v_2 transition (d)·All of the compounds having the $[P(C_6H_5)_4]^+$ cation show a structured absorption maximum centred at Ca 270 nm due to $\pi \longrightarrow \pi^*$ transitions occurring in this cation.

^{95}Mo-nmr Spectroscopy

The data in the table 6 show that all the resonances

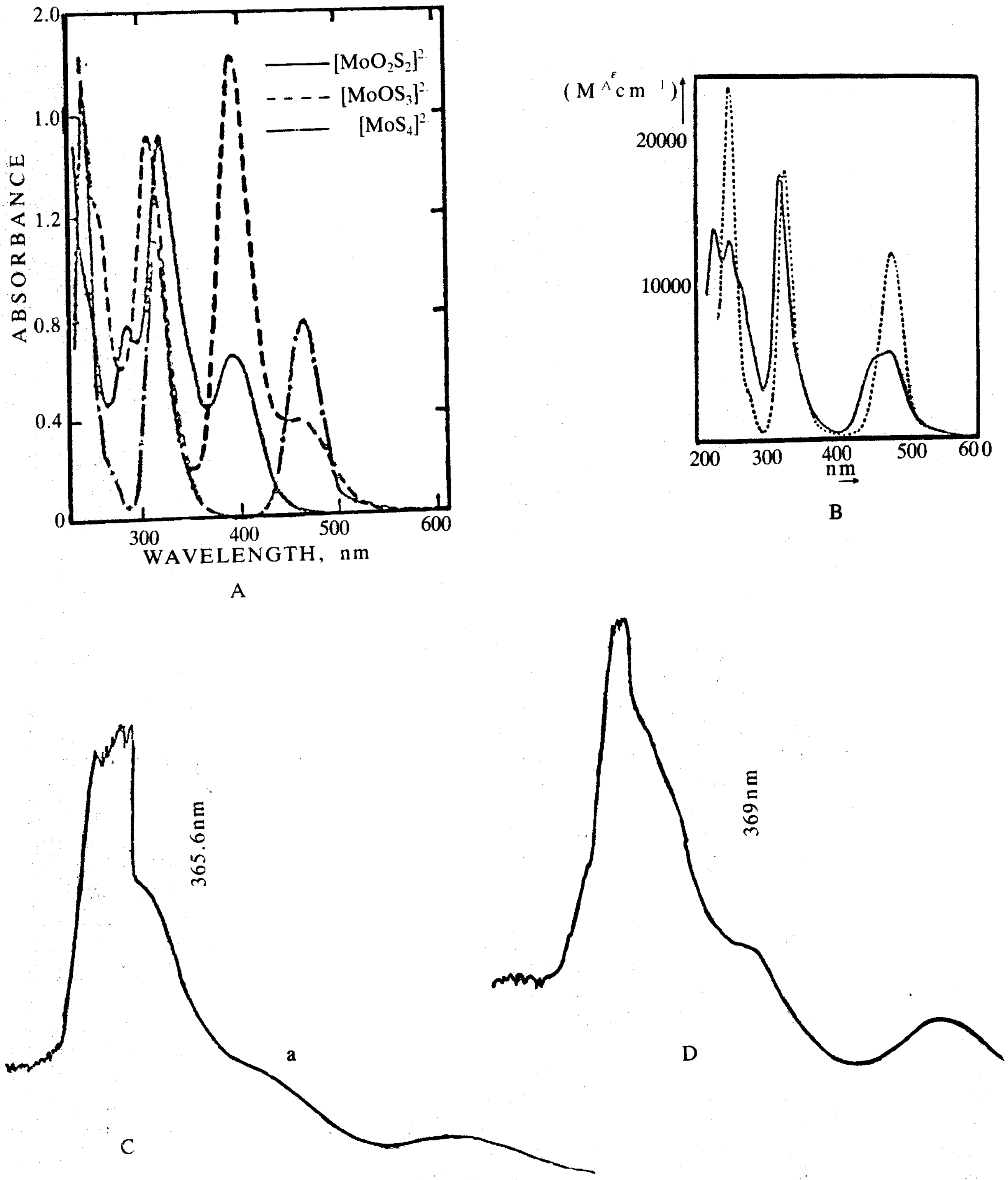


Fig 4- Electronic Spectra of (A) Thiomolybdate in H_2O, (B) $[NCCU(MoS_4)]^{-2}$ in MeCN, (C) $[MoS_4Cu_3(SCN)_4]^{-2}$ in DMF, (D) $[MoS_4(CuNCS)_2(DMF)]^{-2}$ in DMF. a bands arising as a result of a lowering of the Td symmetry of $[MoS_4]^{-2}$.

Table 5. vu/visible Absorption Spectroscopic Data

Compound	Solvent	λmax(nm)(10^{-3} ε:$M^{-1}cm^{-1}$)
$[Et_4N]_2[MoS_4]$	H_2O	467(11.85), 316(16.75), 241(24.7).
$[Et_4N]_2[MoOS_3]$	H_2O	472(14.6), 321(22).
$[P(C_6H_5)_4]_3[MoS_4Cu_3(SCN)_4]$	CH_2Cl_2	494.6(2.97),367.6(6.83),316.9(11.67),286.3(19.28).
$[P(C_6H_5)_4]_3[MoS_4Cu_3(SCN)_4]$	DMF	504.2(2.79),365.6(6.84),292.8(18.3)
$[P(C_6H_5)_4]_3[MoS_4Cu_3(SCN)_4]$	DMSO	511.8(2.72),317.5(7.05),291.5(19.48)
$[P(C_6H_5)_4]_2[MoOS_3(CuNCS)_3]$	DMF	484.6(2.36),401.2(7.53),315(11.04)
$[P(C_6H_5)_4]_2[MoOS_3(CuNCS)_3]$	CH_2Cl_2	479.8(2.36),397.4(8,47),310(11.24)
$[P(C_6H_5)_4]_2[MoOS_3(CuNCS)_2]$	DMF	465(2.58),390(3.83),301(10.152)
$[P(C_6H_5)_4]_2[MoS_4(CuNCS)_3\text{-}(DMF)_2]$	DMF	502.8(3.82), 365.9(8.27)
$[P(C_6H_5)_4]_2[MoS_4(CuNCS)_2\text{-}(DMF)]$	DMF	500.4(4.89), 369(9.49)
$[P(C_6H_5)_4]_2[MoS_4(CuNCS)_4]$	DMF	510.4(3.33),363(8.61),289(25.5)

for $[Mos_4(CuNCS)_X]^{-2}$ and $[MoOS_3(CuNCS)_y]^{-2}$ complexes are shielded with Cu atoms relative to the $[MoS_4]^{-2}$ and $[MoOS_3]^{-2}$ anions respectively [11] and the ^{95}Mo chemical shift decreases by 100 - 200 PPm upon addition of each CuSCN unit to the $[MoS_4]^{-2}$ or $[MoOS_3]^{-2}$ core.

Thus, the molyddenium chemical shift of $[MoS_4(CuNCS)_X]^{-2}$ or a $[MoOS_3(CuNCS)_y]^{-2}$ cluster provides a direct measure of the number of CuSCN units in the cluster.

In summary, this work clearly demonstrates that ^{95}Mo - nmr chemical shifts can be used to identify various $[MoS_4(CuNCS)_X]^{-2}$ or $[MoOS_3(CuNCS)_Y]^{-2}$ ions in solution and hence is a simple direct probe for determining the CuSCN: MoS_4 or CuSCN: $MoOS_3$ ratio for unknown complexes in solution. This research also provides good evidence that the Cu-Mo-S clusters do not associate in solution because each complex gives only one ^{95}Mo resonance.

Experimental Section

Reactions were carried out under an atmosphere of purified dinitrogen, using Schlenk tubes, with solvent and solution transfers being accomplished through Gallenkamp Suba-seal stoppers by syringes or siphen - tube. Solvents were distilled from CaH_2 under a dinitrogen atmosphere; sodium - dried diethyl ether was used. DMF was distilled before use.

Microanalyses were carried out by Mr. M. Hart and his staff at the University of Manchester, in the Microanalytical Chemistry Department. Infrared spectra were recorded, for Nujol mulls of the samples between CsI plates, in the range 4000 - 200 cm^{-1} on a 1710 FTIR instrument. Raman spectra were obtained on a Cary 82 instrument. UV/VIS Spectra were recorded on a Perkin - Elmer 402 Spectrometre ^{95}Mo - nmr and ^{13}C- nmr Spectra were obtained on a Varian XL - 300 instrument, with the help of Mr. D. Moorcroft at the University of Manchester, England. $[NH_4]_2[MoS_4]$ and $[NH_4]_2[MoOS_3]$ are formed by the reaction of the Na_2MoO_4, $2H_2o$ with H_2S in basic aqueous solution [12].

Organic cations such as $[P(C_6H_5)_4]^+$ are important because they can be used for the synthesis of clusters in organic solvents. This was readily achieved by a simple cation exchange reaction [2]. Solid thioanions were stored under an inert atmosphere.

(a) Preparation of $[P(C_6H_5)_4]_3[MoS_4Cu_3(SCN)_4]$

$[P(C_6H_5)_4]_2[MoS_4]$ (0.6325 g., 0.7 m mol) was partially dissolved in analar acetone (250 ml). Solid CuSCN (0.2558 g., 2.1 m mol) was added and the mixture stirred for 18 h. A small amount of black precipitate was removed by filtration. All the solvent of the filtrate was removed by Buchi - rotary evaporator. The dark red residue was redissolved in dichloromethane (30 ml) and filtered to remove any insoluble material. The filtrate was vacuum evaporated to dryness leaving a residue which was washed with dry diethyl ether (2 × 2 ml) and vacuum dried for 12 h. (yield, 85%). Analysis showed—
54.5 ^{C}(54.8); 3.6 ^{H}(3.6), 3.9 ^{N}(3.36), 5.4 ^{P}(5.58), 15.1 ^{S}(15.38) 11.3 ^{Cu}(11.44), 4.7 ^{Mo}(5.76)
N. B. Calculated in parentheses.

(b) Preparation of $[P(C_6H_5)_4]_2[MoOS_3(CuNCS)_3]$

This orange red complex was prepared in the same method described in (a) by the reaction of $[P(C_6H_5)_4]_2[MoOS_3]$ (0.4642 g., 0.52 m mol) with the CuSCN (0.1911 g. 1.57 m mol) in analar acetone (250 ml).

Table 6 ^{95}Mo-nmr Data for Cu-Mo-S Complexes

Compound	δ (Mo)ppm*	Solvent
$[P(C_6H_5)_4]_2\,[MoS_4(CuNCS)_3(DMF)_2]$	1230(766)	1.5mlDMF+0.5ml d^7-DMF
$[P(C_6H_5)_4]_2\,[MoS_4Cu_3(SCN)_4]$	1080(650)	CD_2Cl_2
$[P(C_6H_5)_4]_2\,[MoS_4(CuNCS)_2(DMF)]$	1340(1000)	CD_2Cl_2
$[P(C_6H_5)_4]_2\,[MoS_4(CuNCS)_4]$	990.4(1100)	1.5DMF+0.5mld^7-DMF
$[P(C_6H_5)_4]_2\,[MoOS_3(CuNCS)_2]$	720(71.22)	CD_2Cl_2
$[P(C_6H_5)_4]_2\,[MoOS_3(CuNCS)_3]$	499.45(60)	d^6-DMSO

*N.B = Line width in HZ in parentheses;
Relative to external 2 M Na_2MoO_4 in D_2O effective PH = 11

(yield, 80%). Analysis showed% 49.4 ^{C}(48.92), 3.2 ^{H}(3.19), 3.6 ^{N}(3.35), 14.3 (15.34), 4.9 (4.95) ^{Cu}14.3 (15.22), 6.9^{Mo} (7.6)

(c) Preparation of $[P(C_6H_5)_4]_2\,[MoOS_3(CuNCS)_2]$

This orange red complex was prepared with the same method described in (a) by the reaction of $[P(C_6H_5)_4]_2$ $[MoOS_3]$ (0.7431 g., 0.83 m mol) with the CuSCN (0.204 g, 1.67 m mol) in analar acetone (250 ml). (yield, 83%). Analysis showed% 53.5 ^{C}(53.14), 3.7 ^{H}(3.54), 2.7 ^{N}(2.48), 13.95 ^{S}(14.17), 5.3(5.49) 11 ^{Cu}(11.25), 7.4 ^{Mo}(8.5).

(d) Preparation of $[P(C_6H_5)_4]_2\,[MoS_4(CuNCS)_3(DMF)_2]$

$[P(C_6H_5)_4]_2\,[MoS_4]$ (0.4234 g., 0.46 m mol) was dissolved in DMF (50 ml) under an atmosphere of dinitrogen. Solid CuSCN (0.1712 g., 1.4 m mol) was added and the mixture was stirred for 6 h. The solution was filtered and dry diethyl ether (50 ml) was added to the filtrate and refrigerated overnight leaving a dark red oily residue. The supernatant was decanted and the oily product was heated for 30 min. at 80°C/10^{-1} Torr to remove unbonded DMF, leaving a dark red solid which was washed with dry diethyl ether (2 × 5 ml) and vacuum dry for 12 h.
47.65 ^{C}(48.37), 3.5 ^{H}(3.8), 4.25 (4.95), 16.2 ^{S}(15.85), 4.7 ^{P}(4.38) ^{Cu}13.25 (13.57), 6.7 ^{Mo}(6.79)

(e) Preparation of $[P(C_6H_5)_4]_2\,[MoS_4(CuNCS)_4]$

This complex was prepared by dissolving $[P(C_6H_5)_4]_2$ $[MoS_4(CuNCS)_3(DMF)_2]$ in the minimum volume of CH_2Cl_2. After standing the solution in the refrigerator for two days a precipitate was obtained which was separated by filtration. The precipitate which is insoluble in all usual organic solvent except DMF and DMSO was first washed with CH_2Cl_2 (2 × 2 ml) then with dry Et_2O (2 × 5ml) and finally vacuum dried (yield, 42%). Analysis showed
44.1 ^{C}(44.94), 2.9 ^{H}(2.88), 3.7 ^{N}(4.03), 16.4 ^{S}(18.43), 4.3 ^{P}(4.46) 17.9 ^{Cu}(18.29), 7 (6.91)^{Mo}

(f) Preparation of $[P(C_6H_5)_4]_2\,[MoS_4(CuNCS)_2(DMF)]$

The supernatant obtained from procedure (e) was evaporated to dryness leaves a residue that was washed with dry Et_2O (2 × 5 ml) and vacuum dried for 12 hours. (yield, 48%) Analysis showed
50.5 ^{C}(52.2), 3.6 ^{H}(3.8), 3.4 ^{N}(3.44), 14.4 ^{S}(15.75), 5.15 ^{P}(5.08) 10.6 ^{Cu}(10.42), 7 ^{Mo}(7.87).

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