Heterobimetallic Aggregates of Copper(I) with Thiotungstates and Thiomolybdates. Synthesis and Characterization of Polymeric $(NEt_4)_3[Cu_4(NCS)_5WS_4]$, $(NEt_4)_2[(CuNCS)_3WS_4]$ and $(NEt_4)_2[(CuNCS)_4MS_4]$, M = Mo, W

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Abstract

Reaction of $(NEt_4)_2MS_4$ (M = Mo, W) with CuCl and KSCN (or NH_4SCN) in acetone or acetonitrile affords a new set of mixed metal–sulfur compounds: infinite anionic chains $Cu_4(NCS)_5MS_4^{3-}$ (1, 2), $(CuNCS)_3WS_4^{2-}$ (3) and two dimensional polymeric dianions $(CuNCS)_4MS_4^{2-}$ (4, 5). Crystals of 1 (M = W) and 3 are triclinic, space group $P\bar{1}$ (1: $a = 10.356$-(2), $b = 15.039(1)$, $c = 17.356(2)$ Å, $\alpha = 78.27(1)°$, $\beta = 88.89(2)°$ and $\gamma = 88.60(1)°$, $Z = 2$, $R = 0.04$ for 3915 independent data; 3: $a = 8.449(2)$, $b = 14.622$-(4), $c = 15.809(8)$ Å, $\alpha = 61.84(3)°$, $\beta = 73.67(3)°$ and $\gamma = 78.23(2)°$, $Z = 2$, $R = 0.029$ for 6585 independent data). Crystals of 4 (M = W) and 5 (M = Mo) are monoclinic, space group $P2_1/m$, $Z = 2$ (4: $a = 12.296(4)$, $b = 14.794(4)$, $c = 10.260(3)$ Å and $\beta = 101.88(3)°$, $R = 0.034$ for 4450 independent data; 5: $a = 12.306(2)$, $b = 14.809(3)$, $c = 10.257(2)$ Å and $\beta = 101.99(3)°$, $R = 0.043$ for 3078 independent data). The crystal structure determinations of 4 and 5 show that four edges of the tetrahedral MS_4^{2-} core are coordinated by copper atoms forming WS_4Cu_4 aggregates linked by eight-membered $-Cu(NCS)_2Cu-$ rings. A two-dimensional network is thus formed in the diagonal $(10\bar{1})$ plane. The space between the anionic two-dimensional networks is filled with the NEt_4^+ cations. Additional NCS groups lead to the $[Cu_4(NCS)_5WS_4]^{3-}$ (1) trianion connected by NCS bridges forming pseudo-dimers. These latter are held together by weak Cu–S(NCS) interactions giving rise to infinite chains along a direction parallel to [100]. In contrast complex 3 develops infinite chains from WS_4Cu_3 aggregates with the same $-Cu-(NCS)_2Cu-$ bridges as in 4 and 5. These chains are running along a direction parallel to [010]. The
structural data of the different types of polymeric compounds containing MS_4^{2-} and CuNCS have been used to interpret vibrational spectroscopic data of the thiocyanate groups.

Introduction

The chemistry of the tetrathiometallates MS_4^{2-} (M = Mo, W) has been extensively developed [1]. This interest has been caused by tetrathiometallate ability to coordinate to transition metals [2] and particularly with copper. The reaction of CuCl [3–7] and CuCN [8] with MS_4^{2-} has led to a large number of polynuclear compounds crystallographically characterized.

We have recently undertaken investigations on complexes formed by reaction of CuSCN with MS_4^{2-} anions. Owing to the bonding versatility of the NCS^- ligand, monomeric $(PPh_4)_2[(CuNCS)_2-MS_4]$ [9] and polymeric anionic structures $[(CuNCS)_4MS_4]^{2-}$ were isolated as NMe_4^+ [10] and PPh_4^+ [9] complexes. As pointed out in our previous works tridimensional or layer arrays are obtained related to the size effect of the associated counterions.

In order to extend our understanding on the influence of the counterion we have prepared homologous complexes with the NEt_4^+ cation. The results of these studies are reported herein.

Experimental

All manipulations were carried out in air. Chemicals were used as purchased. Elemental analysis were performed by the 'Service Central d'Analyses du CNRS'. Infrared spectra (KBr and polyethylene

pellets) were recorded on a Perkin-Elmer 580B spectrophotometer. Electronic spectra were obtained on a Kontron 810 spectrophotometer in DMF solution between 600 and 200 nm.

Preparation of (NEt₄)₃[Cu₄(NCS)₅WS₄] (1)

Cuprous chloride (0.300 g, 3 mmol) and potassium thiocyanate (0.292 g, 3 mmol) were added to a suspension of $(NEt_4)_2WS_4$ (0.572 g, 1 mmol) in 100 cm^3 of acetone or acetonitrile and the mixture was stirred for 30 min at room temperature. After filtration the volume of the resultant solution was reduced to *ca.* 50 cm^3 under reduced pressure. Addition of Et_2O (15 cm^3) prior to standing for 24 h at 0 °C yielded orange crystalline needles (0.120 g). *Anal.* Found: C, 28.08; H, 4.76; S, 22.9; Cu, 20.24; W, 13.06. Calc. for $C_{29}H_{60}N_8S_9Cu_4W$: C, 27.93; H, 4.81; S, 23.11; Cu, 20.38; W, 14.76%.

Preparation of (NEt₄)₃[Cu₄(NCS)₅MoS₄] (2)

The homologous complex of molybdenum was prepared as above starting from $(NEt_4)_2MoS_4$ (0.478 g, 1 mmol). *Anal.* Found: C, 30.28; H, 5.23; N, 9.79; S, 24.69; Cu, 20.76; Mo, 8.48. Calc. for $C_{29}H_{60}N_8S_9Cu_4Mo$: C, 30.05; H, 5.18; N, 9.67; S, 24.87; Cu, 21.93; Mo, 8.29%.

Preparation of (NEt₄)₂[(CuNCS)₃WS₄] (3)

To a suspension of $(NEt_4)_2WS_4$ (0.572 g, 1 mmol) in 100 cm^3 of acetone or acetonitrile were added CuCl (0.200 g, 2 mmol) and KSCN (0.195 g, 2 mmol). After 30 min of stirring at room temperature the mixture was filtered and the resultant filtrate reduced to *ca.* 50 cm^3 by evaporation under reduced pressure. After addition of Et_2O (*ca.* 15 cm^3) to the orange–red filtrate followed by cooling at 0 °C for 48 h the complex formed as orange crystals (0.110 g). *Anal.* Found: C, 24.33; N, 7.51; S, 23.00; Cu, 20.03; W, 17.4. Calc. for $C_{19}H_{40}N_5S_7Cu_3W$: C, 24.34; N, 7.47; S, 23.92; Cu, 20.34; W, 19.64%.

All attempts to prepare the molybdenum homologue failed.

Preparation of (NEt₄)₂[(CuNCS)₄WS₄] (4)

A mixture of $(NEt_4)_2WS_4$ (0.286 g, 0.5 mmol) and CuCl (0.100 g, 1 mmol) was stirred in acetone or acetonitrile (100 cm^3) for *ca.* 30 min and then filtered. NH₄SCN (0.152 g, 2 mmol) was added and after an additional 1 h stirring the solid formed was removed by filtration. A mixture of orange and red crystals was obtained from the filtrate after addition of ether (25 cm^3) followed by cooling 24 h at 0 °C. The orange crystals were separated and analysed satisfactorily as 1 and 3 while for the red plates in minor quantity the complete formula $(NEt_4)_2[(CuNCS)_4WS_4]$ was deduced from the crystallographic results.

Preparation of (NEt₄)₂[(CuNCS)₄MoS₄] (5)

The various routes of preparation described above for the tungsten compounds led for Mo to $(NEt_4)_2[Cu_4(NCS)_5MoS_4]$ (2). The complex 5 was obtained via an alternative route. A solution of 2 (0.100 g) in 25 cm^3 of acetone was stirred for 15 min at room temperature, then reduced to *ca.* 10 cm^3 by evaporation under reduced pressure. Upon standing 24 h at room temperature crystals of 5 were formed which were filtered off and washed with 20 cm^3 of ether. *Anal.* Found: C, 24.99; H, 4.32; N, 8.59; S, 25.63; Cu, 25.0; Mo, 9.49. Calc. for $C_{20}H_{40}N_6S_8Mo$: C, 24.74; H, 4.12; N, 8.65; S, 26.39; Cu, 26.20; Mo, 9.89%.

Attempts to prepare $(NEt_4)_2[(CuNCS)_4WS_4]$ by this route were not successful.

X-ray Crystallography

The crystals obtained directly from the preparations were suitable for single crystal X-ray works. Following an initial photographic examination to establish approximate cell dimensions and space group, unique data sets were obtained within a predetermined 2θ max limit using Enraf-Nonius CAD4 (for 4 and 5) and Philips PW 1100 (for 1 and 3) four-circle diffractometers fitted with graphite monochromated radiation sources at 293 K. Specific parameters pertaining to the data collection are reported in Table I.

X-ray data collection of 1 and 3

Accurate unit cell dimensions were derived from a least-squares fit to the setting angles of 25 reflections widely dispersed throughout reciprocal space. Intensity data were collected and processed in the usual manner by the $\theta - 2\theta$ scan technique. The intensities of three standard reflections monitored every hour showed no significant variation during data collection. Data reflections were corrected for Lorentz and polarization effects. Absorption corrections employed empirical absorption curves derived from azimuthal scan data [11].

X-ray data collection of 4 and 5

Accurate unit cell dimensions were determined by least-squares refinement of the angular settings of 20 automatically centred reflections in the region $9° < \theta < 12°$ for 4 and $18° < \theta < 26°$ for 5. Intensity data were collected using the $\theta - 2\theta$ flying step scan technique. Examination of the standard reflection intensities measured every hour showed no appreciable trend. The intensities were corrected for polarization and Lorentz effects. Absorption corrections have been carried out for 4 and 5 using the Gaussian integration method [12].

TABLE 1. Crystal Data Details of Structure Analysis for Compounds 1, 3, 4 and 5

Compound	1	3	4	5
Formula	$[NEt_4]_3[Cu_4(NCS)_5WS_4]$	$[NEt_4]_2[(CuNCS)_3WS_4]$	$[NEt_4]_2[(CuNCS)_4WS_4]$	$[NEt_4]_2[(CuNCS)_4MoS_4]$
	$C_{29}H_{60}N_8S_9Cu_4W$	$C_{19}H_{40}N_5S_7Cu_3W$	$C_{20}H_{40}N_6S_8Cu_4W$	$C_{20}H_{40}N_6S_8Cu_4Mo$
M	1247.4	937.5	1059.1	871.9
Crystal system	Triclinic	Triclinic	Monoclinic	Monoclinic
a (Å)	10.356(2)	8.449(2)	12.296(4)	12.306(2)
b (Å)	15.039(1)	14.622(4)	14.794(4)	14.809(3)
c (Å)	15.736(2)	15.809(8)	10.260(3)	10.257(2)
α (°)	78.27(1)	61.84(3)	90.0	90.0
β (°)	88.89(2)	73.67(3)	101.88(3)	101.99(3)
γ (°)	88.60(1)	78.23(2)	90.0	90.0
U (Å^3)	2398.6	1646.5	1826.3	1828.4
Space group	$P\bar{1}$	$P\bar{1}$	$P2_1/m$	$P2_1/m$
Z	2	2	2	2
Radiation (monochromated)	Mo Kα ($\lambda = 0.71069$ Å)	Mo Kα ($\lambda = 0.71069$ Å)	Mo Kα ($\lambda = 0.71069$ Å)	Cu–Kα ($\lambda = 1.5418$ Å)
μ (cm^{-1})	43.7	56.3	56.8	93.3
$F(000)$	1247.8	923.8	1039.8	975.8
2θ max (°)	46 ($\pm h, \pm k, l$)	56 ($\pm h, \pm k, l$)	60 ($\pm h, +k, l$)	136 ($\pm h, +k, l$)
Scan width (°)	$1 + 0.345 \tan\theta$	$1 + 0.345 \tan\theta$	1.20	1.80
Scan rate (deg min^{-1})	1.34–5.46	1.37–5.46	0.90	1.20
Reflections measured	6671	7932	5816	3684
Unique data [$F_o{}^2 > 3(F_o{}^2)$]	3915	6585	4450	3078
No. of parameters	341	316	208	208
Final R	0.040	0.029	0.034	0.043

TABLE II. Fractional Atomic Coordinates for $[N(C_2H_5)_4]_3$-$[Cu_4(NCS)_5WS_4]$ (1)[a]

Atom	x/a	y/b	z/c
W	0.24949(5)	0.07329(4)	0.42348(4)
Cu(1)	0.2499(2)	−0.0702(1)	0.5590(1)
Cu(2)	0.2535(2)	0.1944(1)	0.5222(1)
Cu(3)	0.2613(2)	0.2210(2)	0.2993(2)
Cu(4)	0.2298(2)	−0.0150(1)	0.2951(1)
S(12)	0.3677(3)	0.0625(2)	0.5416(2)
S(14)	0.1332(3)	−0.0507(2)	0.4303(2)
S(23)	0.1169(3)	0.1942(2)	0.4121(2)
S(34)	0.3788(3)	0.0917(2)	0.3060(2)
S(1)	0.5586(4)	−0.3121(2)	0.6025(3)
S(2)	0.2023(7)	0.4251(3)	0.6743(4)
S(3)	0.1428(7)	0.4796(4)	0.1054(5)
S(4)	0.3152(6)	−0.1692(4)	0.0720(3)
S(5)	−0.0410(4)	−0.0869(3)	0.7991(2)
N(1)	0.363(1)	−0.1792(7)	0.5745(7)
N(2)	0.233(1)	0.2794(9)	0.5940(8)
N(3)	0.238(1)	0.319(1)	0.206(1)
N(4)	0.265(1)	−0.0884(8)	0.2128(9)
N(5)	0.140(1)	−0.0787(8)	0.6650(8)
C(1)	0.444(1)	−0.2345(9)	0.5845(8)
C(2)	0.220(1)	0.342(1)	0.626(1)
C(3)	0.202(2)	0.386(1)	0.163(1)
C(4)	0.287(1)	−0.1227(9)	0.155(1)
C(5)	0.067(1)	−0.0823(9)	0.7195(9)
N(10)	0.298(1)	0.6626(8)	0.8510(7)
C(111)[b]	0.358(2)	0.581(1)	0.820(1)
C(112)[c]	0.194(6)	0.588(4)	0.911(4)
C(12)	0.284(2)	0.491(1)	0.871(1)
C(131)[b]	0.155(2)	0.676(1)	0.835(1)
C(132)[c]	0.258(5)	0.651(4)	0.755(4)
C(14)	0.119(2)	0.670(1)	0.737(1)
C(151)[b]	0.373(2)	0.747(1)	0.798(1)
C(152)[c]	0.247(5)	0.747(3)	0.874(3)
C(16)	0.345(2)	0.832(1)	0.832(1)
C(171)[b]	0.318(2)	0.656(1)	0.951(1)
C(172)[c]	0.446(6)	0.632(4)	0.862(4)
C(18)	0.465(2)	0.643(1)	0.969(1)
N(20)	0.277(1)	0.6153(7)	0.3722(7)
C(21)	0.268(2)	0.517(1)	0.419(1)
C(22)	0.151(2)	0.468(1)	0.394(1)
C(23)	0.157(2)	0.673(1)	0.388(1)
C(24)	0.133(2)	0.674(1)	0.484(1)
C(25)	0.402(2)	0.648(1)	0.406(1)
C(26)	0.428(2)	0.751(1)	0.363(1)
C(27)	0.278(2)	0.622(1)	0.274(1)
C(28)	0.402(2)	0.570(2)	0.244(1)
N(30)	0.197(1)	0.1590(8)	0.9030(8)
C(31)	0.220(2)	0.096(1)	0.992(1)
C(32)	0.328(2)	0.123(1)	1.046(1)
C(33)	0.171(2)	0.257(1)	0.912(1)
C(34)	0.053(2)	0.272(1)	0.970(1)
C(35)	0.083(2)	0.119(1)	0.865(1)
C(36)	0.054(2)	0.168(1)	0.771(1)
C(37)	0.318(2)	0.161(1)	0.844(1)
C(38)	0.356(2)	0.069(1)	0.822(1)

[a]e.s.d.s given in parentheses. [b]Site with occupancy factor 0.7. [c]Site with occupancy factor 0.3.

Structure Determination

The structures were solved by the heavy-atom method. Three dimensional Patterson maps revealed the positions of the tungsten or molybdenum atoms. Successive least-squares refinements and difference Fourier calculations revealed the positions of the remaining atoms.

For compound **1**, one of the three NEt_4^+ cations is disordered. The high thermal parameters of the α carbon atoms suggested positional disorder. Two positions were observed in the difference Fourier map for the methylenic carbon atoms and these were given occupancy factors of 0.70 and 0.30 respectively and were kept fixed. The refinement was achieved by using isotropic thermal parameters for the NEt_4^+ cations owing to the few reflections selected.

TABLE III. Fractional Atomic Coordinates for $[N(C_2H_5)_4]_2$-$[(CuNCS)_3WS_4]$ (3)[a]

Atom	x/a	y/b	z/c
W	0.19833(3)	0.15237(2)	0.26063(2)
Cu(1)	0.0969(1)	−0.03511(5)	0.36434(6)
Cu(2)	0.3429(1)	0.33004(6)	0.13475(7)
Cu(3)	0.3327(1)	0.07651(7)	0.12719(6)
S(10)	0.1962(2)	0.0529(1)	0.4182(1)
S(13)	0.0633(2)	0.0756(1)	0.2103(1)
S(20)	0.0836(2)	0.3093(1)	0.2338(2)
S(23)	0.4598(2)	0.1615(1)	0.1779(1)
S(1)	0.0774(3)	−0.3862(1)	0.4708(2)
S(2)	0.6498(3)	0.6053(1)	0.0453(1)
S(3)	0.5455(2)	0.1125(1)	−0.1931(1)
N(1)	0.0692(7)	−0.1769(4)	0.4225(4)
C(1)	0.0744(8)	−0.2640(5)	0.4428(5)
N(2)	0.4676(7)	0.4341(4)	0.1236(4)
C(2)	0.5444(8)	0.5047(5)	0.0912(4)
N(3)	0.3867(7)	0.1116(4)	−0.0115(4)
C(3)	0.4514(7)	0.1127(4)	−0.0874(4)
N(11)	−0.0779(6)	0.2664(4)	0.8937(4)
C(11)	−0.0153(9)	0.2887(6)	0.9641(5)
C(12)	−0.143(1)	0.3502(8)	1.0121(7)
C(13)	−0.136(1)	0.3658(6)	0.8118(6)
C(14)	−0.001(1)	0.4420(6)	0.7491(7)
C(15)	0.0682(8)	0.2072(5)	0.8535(5)
C(16)	0.031(1)	0.1715(7)	0.7841(6)
C(17)	−0.2276(8)	0.2021(5)	0.9470(5)
C(18)	−0.192(1)	0.0958(6)	1.0271(6)
N(22)	0.4913(6)	0.2787(4)	0.4568(4)
C(21)	0.6524(8)	0.2263(6)	0.4183(6)
C(22)	0.642(1)	0.2002(7)	0.3377(6)
C(23)	0.435(1)	0.3801(6)	0.3763(6)
C(24)	0.567(2)	0.4587(7)	0.3228(7)
C(25)	0.5281(9)	0.2968(6)	0.5369(5)
C(26)	0.382(1)	0.3498(7)	0.5849(7)
C(27)	0.3494(8)	0.2104(6)	0.4988(6)
C(28)	0.379(1)	0.1029(6)	0.5837(6)

[a]e.s.d.s given in parentheses.

TABLE IV. Fractional Atomic Coordinates for $[N(C_2H_5)_4]_2$-$[(CuNCS)_4WS_4]$ (4)[a]

Atom	x/a	y/b	z/c
W	0.19988(2)	0.25	0.30508(3)
Cu(1)	0.33943(6)	0.38276(5)	0.41185(7)
Cu(2)	0.07030(7)	0.11530(6)	0.18319(8)
S(11)	0.3826(1)	0.25	0.3172(2)
S(12)	0.1527(1)	0.37350(9)	0.4059(1)
S(22)	0.1123(2)	0.25	0.0947(2)
S(1)	0.6313(1)	0.4921(1)	0.7395(1)
S(2)	0.1194(2)	−0.0871(2)	−0.1495(3)
N(1)	0.4452(4)	0.4168(3)	0.5724(4)
C(1)	0.5215(4)	0.4484(3)	0.6411(5)
N(2)	0.1290(4)	0.0259(4)	0.0674(6)
C(2)	0.1255(5)	−0.0209(5)	−0.0206(7)
N(11)	0.3936(6)	0.25	0.8918(6)
C(111)	0.3698(5)	0.3322(4)	0.9717(6)
C(112)	0.3805(7)	0.4236(5)	0.9051(7)
C(121)	0.3203(8)	0.25	0.7520(7)
C(122)	0.1970(8)	0.25	0.753(1)
C(131)	0.5128(7)	0.25	0.871(1)
C(132)	0.601(1)	0.25	0.998(1)
N(22)	0.2008(6)	0.75	0.4729(9)
C(211)[b]	0.308(1)	0.692(1)	0.495(2)
C(221)[b]	0.098(1)	0.6898(9)	0.473(2)
C(231)[b]	0.201(1)	0.816(1)	0.589(2)
C(241)[b]	0.198(2)	0.795(1)	0.336(2)
C(212)	0.3163(9)	0.6274(7)	0.617(1)
C(222)	0.0835(9)	0.6281(8)	0.331(1)

[a]e.s.d.s given in parentheses. [b]Site with occupancy factor 0.5.

TABLE V. Fractional Atomic Coordinateds for $[N(C_2H_5)_4]_2$-$[(CuNCS)_4MoS_4]$ (5)[a]

Atom	x/a	y/b	z/c
Mo	0.20036(5)	0.2500	0.30454(6)
Cu(1)	0.33923(8)	0.38156(7)	0.41197(9)
Cu(2)	0.07086(9)	0.11604(8)	0.1837(1)
S(11)	0.3832(2)	0.2500	0.3178(2)
S(12)	0.1535(1)	0.3742(1)	0.4050(2)
S(22)	0.1121(2)	0.2500	0.0936(2)
S(1)	0.6308(1)	0.4925(1)	0.7400(2)
S(2)	0.1191(2)	−0.0872(2)	−0.1503(3)
N(1)	0.4454(5)	0.4164(4)	0.5724(5)
C(1)	0.5210(5)	0.4485(4)	0.6410(6)
N(2)	0.1287(5)	0.0271(5)	0.0664(7)
C(2)	0.1257(5)	−0.0208(5)	−0.0221(8)
N(11)	0.3936(7)	0.2500	0.8918(7)
C(111)	0.3683(6)	0.3322(5)	0.9714(7)
C(112)	0.3795(8)	0.4239(5)	0.9045(8)
C(121)	0.3220(9)	0.2500	0.7524(9)
C(122)	0.196(1)	0.2500	0.751(1)
C(131)	0.5137(9)	0.2500	0.871(1)
C(132)	0.602(1)	0.2500	1.000(2)
N(22)	0.1993(7)	0.7500	0.470(1)
C(211)[b]	0.305(1)	0.691(1)	0.495(2)
C(221)[b]	0.096(1)	0.689(1)	0.470(2)
C(231)[b]	0.201(1)	0.814(1)	0.590(2)
C(241)[b]	0.197(2)	0.795(1)	0.334(2)
C(212)	0.312(1)	0.6280(8)	0.615(1)
C(222)	0.082(1)	0.6289(9)	0.332(2)

[a]e.s.d.s given in parentheses. [b]Site with occupancy factor 0.5.

For compounds 4 and 5, the nitrogen atoms of the NEt_4^+ cations lie on an imposed mirror plane. For the first NEt_4^+ cation the mirror plane contains N(11), C(121), C(122), C(131) and C(132), while for the other cation only N(22) has imposed *Cs* symmetry. Difference Fourier maps showed the possible positions for the α carbon atoms. The superposition of two unsymmetrical geometries for the α carbon atoms (with fixed occupancy factors of 0.50 and 0.50 respectively) together with the non-disordered positions of the β carbon atoms is consistent with the evidence of the imposed *Cs* symmetry for N(22).

Anisotropic temperature factors were introduced for all atoms of the anions and the cations except for compound 1 as mentioned before. Hydrogen atoms were not included in the refinements. Neutral atom scattering factors with anomalous dispersion corrections were taken from ref. 13. Refinements of atomic parameters were by full-matrix least-squares refinement using SHELX 76 with a unit weighting scheme. Final agreement indices are given in Table I.

All calculations were performed on a GOULD Concept 32/87 computer. Positional parameters for 1, 3, 4 and 5 are given in Tables II–V respectively. Selected bond lengths and angles for 1, 3 and 4 and 5 are given in Tables VI–VIII respectively. The structures of 1, 3 and 4 are shown in Figs. 1–3 respectively together with the atomic numbering scheme.

Results and Discussion

Crystal Structure

Compound 1

The structure of 1 consists of one crystallographic independent $[Cu_4(NCS)_5WS_4]^{3-}$ trianion and three NEt_4^+ cations. The structure determination confirms the expected 4:1 Cu:W stoichiometry, the asymmetric unit including five different thiocyanato groups. The tungsten atom is at the centre of an essentially tetrahedral unit in which the W–S bond lengths are quite similar. Four copper atoms are bound to the central WS_4 core with W...Cu distances ranging from 2.624(2) to 2.708(2) Å. The Cu...W...Cu angles concerning the two mutually *trans* copper atoms (166.35(6) and 175.04(8)°) lead to an approximate D_{2d} symmetry for the WS_4-Cu_4 aggregate as in the parent polymeric complexes

TABLE VI. Selected Interatomic Distances (Å) and Angles (°) for $[N(C_2H_5)_4]_3[Cu_4(NCS)_5WS_4]$ (1)[a]

W–S(12)	2.222(4)	W–S(23)	2.231(3)
W–S(14)	2.228(4)	W–S(34)	2.237(4)
W...Cu(1)	2.708(2)	W...Cu(3)	2.647(2)
W...Cu(2)	2.624(2)	W...Cu(4)	2.648(2)
Cu(1)–S(12)	2.331(4)	Cu(1)–S(14)	2.342(4)
Cu(1)–N(1)	1.97(1)	Cu(1)–N(5)	1.98(1)
Cu(2)–S(12)	2.253(4)	Cu(2)–S(23)ʹ	2.257(4)
Cu(2)–N(2)	1.88(1)	Cu(3)–N(3)	1.87(1)
Cu(2)–S(1)[ii]	3.062(4)	Cu(3)–S(1)[ii]	2.974(5)
Cu(3)–S(23)	2.277(4)	Cu(3)–S(34)	2.254(4)
Cu(4)–S(14)	2.301(4)	Cu(4)–S(34)	2.287(4)
Cu(4)–S(5)[i]	2.722(4)	Cu(4)–N(4)	1.89(1)
N(1)–C(1)	1.16(2)	C(1)–S(1)	1.63(1)
N(2)–C(2)	1.16(2)	C(2)–S(2)	1.60(2)
N(3)–C(3)	1.15(2)	C(3)–S(3)	1.63(2)
N(4)–C(4)	1.14(2)	C(4)–S(4)	1.63(2)
N(5)–C(5)	1.13(2)	C(5)–S(5)	1.65(1)
S(12)–W–S(14)	111.0(1)	S(14)–W–S(23)	109.3(1)
S(12)–W–S(23)	108.9(1)	S(14)–W–S(34)	109.2(1)
S(12)–W–S(34)	109.6(1)	S(23)–W–S(34)	108.8(1)
Cu(1)...W...Cu(2)	94.12(6)	Cu(3)...W...Cu(4)	85.28(7)
Cu(1)...W...Cu(3)	175.04(8)	Cu(2)...W...Cu(3)	81.71(6)
Cu(2)...W...Cu(4)	166.35(6)	Cu(1)...W...Cu(4)	99.07(6)
S(12)–Cu(1)–S(14)	103.4(1)	N(1)–Cu(1)–N(5)	107.9(5)
N(1)–Cu(1)–S(12)	111.9(3)	N(5)–Cu(1)–S(12)	107.9(4)
N(1)–Cu(1)–S(14)	111.6(4)	N(5)–Cu(1)–S(14)	114.1(4)
N(2)–Cu(2)–S(12)	130.4(4)	N(2)–Cu(2)–S(23)	121.1(4)
N(2)–Cu(2)–S(1)[ii]	93.6(4)	S(12)–Cu(2)–S(23)	106.9(2)
S(12)–Cu(2)–S(1)[ii]	98.2(1)	S(23)–Cu(2)–S(1)[ii]	90.4(1)
S(23)–Cu(3)–S(34)	106.5(1)	S(23)–Cu(3)–S(1)[ii]	92.3(1)
N(3)–Cu(3)–S(34)	129.6(5)	N(3)–Cu(3)–S(23)	121.1(5)
N(3)–Cu(3)–S(1)[ii]	96.6(5)	S(34)–Cu(3)–S(1)[ii]	97.0(1)
S(14)–Cu(4)–S(34)	105.0(2)	N(4)–Cu(4)–S(5)[i]	95.0(4)
N(4)–Cu(4)–S(14)	130.1(4)	N(4)–Cu(4)–S(34)	117.0(4)
S(14)–Cu(4)–S(5)[i]	101.6(1)	S(34)–Cu(4)–S(5)[i]	102.2(1)
W–S(12)–Cu(1)	72.9(1)	W–S(12)–Cu(2)	71.8(1)
W–S(14)–Cu(1)	72.6(1)	W–S(14)–Cu(4)	71.5(1)
W–S(23)–Cu(2)	71.5(1)	W–S(23)–Cu(3)	71.9(1)
W–S(34)–Cu(3)	72.2(1)	W–S(34)–Cu(4)	71.6(1)
Cu(1)–S(12)–Cu(2)	116.8(2)	Cu(2)–S(23)–Cu(3)	99.0(2)
Cu(1)–S(14)–Cu(4)	122.7(2)	Cu(3)–S(34)–Cu(4)	104.3(2)
Cu(1)–N(1)–C(1)	170(1)	Cu(1)–N(5)–C(5)	172(1)
Cu(2)–N(2)–C(2)	169(1)	Cu(3)–N(3)–C(3)	163(2)
Cu(4)–N(4)–C(4)	171(1)	N(3)–C(3)–S(3)	177(2)
N(1)–C(1)–S(1)	178(1)	N(4)–C(4)–S(4)	178(1)
N(2)–C(2)–S(2)	178(1)	N(5)–C(5)–S(5)	180(2)
C(1)–S(1)–Cu(2)[ii]	92.6(5)	C(1)–S(1)–Cu(3)[ii]	99.5(5)
Cu(2)–S(1)[ii]–Cu(3)	69.7(1)	C(5)–S(5)–Cu(4)[i]	97.4(5)

[a]e.s.d.s given in parentheses. i: $-x, -y, 1-z$; ii: $1-x, -y, 1-z$.

$(NMe_4)_2[(CuNCS)_4WS_4]$ [10] and $(PPh_4)_2[(Cu-NCS)_4WS_4]$ [9]. One copper atom Cu(1) displays a distorted tetrahedral coordination geometry forming a CuS_2N_2 unit (two sulphur atoms S_b bridging W and Cu and two N-bonded (NCS groups) with Cu—N-(NCS) bond lengths (1.97(1) and 1.98(1) Å) slightly longer than the similar distances previously observed [9]. The other copper atoms are three coordinated and pseudo-trigonal planar with the coordination sites satisfied by two bridging sulphur atoms and one S-bonded NCS group. The sum of the angles about these copper atoms is between 350° and 360° as a consequence of weak interactions between Cu and S(NCS) atoms. The Cu(4) environment shows a short copper—sulphur distance Cu(4)...S(5)i = 2.722(4) Å, between Cu(4) and a sulphur atom S(5) of a

TABLE VII. Selected Interatomic Distances (Å) and Angles (°) for $[N(C_2H_5)_4]_2[(CuNCS)_3WS_4]$ (3)[a]

|			
W—S(10)	2.211(2)	W—S(13)	2.251(2)
W—S(20)	2.189(2)	W—S(23)	2.222(1)
W...Cu(1)	2.6200(8)	W...Cu(2)	2.6922(7)
W...Cu(3)	2.706(1)	Cu(1)—N(1)	1.865(6)
Cu(1)—S(10)	2.228(3)	Cu(1)—S(13)	2.261(2)
Cu(2)—N(2)	1.937(7)	Cu(3)—N(3)	1.936(6)
Cu(2)—S(20)	2.288(2)	Cu(3)—S(13)	2.285(2)
Cu(2)—S(23)	2.305(2)	Cu(3)—S(23)	2.305(2)
Cu(2)—S(2)[i]	2.527(2)	Cu(3)—S(3)[ii]	2.551(2)
N(1)—C(1)	1.150(9)	C(1)—S(1)	1.623(7)
N(2)—C(2)	1.156(9)	C(2)—S(2)	1.627(7)
N(3)—C(3)	1.163(9)	C(3)—S(3)	1.638(7)
S(10)—W—S(20)	111.63(8)	S(13)—W—S(23)	108.64(7)
S(10)—W—S(13)	108.21(7)	S(20)—W—S(13)	110.53(8)
S(10—W—S(23)	108.25(6)	S(20)—W—S(23)	109.50(7)
Cu(1)...W...Cu(2)	169.74(3)	Cu(1)...W...Cu(3)	81.30(3)
Cu(2)...W...Cu(3)	89.03(3)		
N(1)—Cu(1)—S(10)	129.0(2)	N(2)—Cu(2)—S(20)	117.8(2)
N(1)—Cu(1)—S(13)	123.3(2)	N(2)—Cu(2)—S(23)	119.6(2)
S(10)—Cu(1)—S(13)	107.28(7)	S(20)—Cu(2)—S(23)	103.29(6)
N(3)—Cu(3)—S(13)	120.8(2)	N(3)—Cu(3)—S(23)	117.4(2)
S(13)—Cu(3)—S(23)	104.7(8)		
N(2)—Cu(2)—S(2)[i]	98.7(2)	N(3)—Cu(4)—S(3)[ii]	99.0(2)
S(20)—Cu(2)—S(2)[i]	114.74(9)	S(13)—Cu(3)—S(3)[ii]	106.58(6)
S(23)—Cu(2)—S(2)[i]	102.05(8)	S(23)—Cu(3)—S(3)[ii]	107.04(8)
W—S(10)—Cu(1)	72.34(8)	W—S(20)—Cu(2)	73.88(6)
W—S(13)—Cu(1)	70.99(6)	W—S(23)—Cu(2)	72.94(4)
W—S(13)—Cu(3)	73.22(7)	W—S(23)—Cu(3)	73.38(5)
Cu(1)—S(13)—Cu(3)	99.5(6)	Cu(2)—S(23)—Cu(3)	110.34(8)
C(2)—S(2)—Cu(2)[i]	99.4(3)	C(3)—S(3)—Cu(3)[ii]	97.7(2)
Cu(1)—N(1)—C(1)	166.9(6)	N(1)—C(1)—S(1)	178.6(9)
Cu(2)—N(2)—C(2)	162.1(6)	N(2)—C(2)—S(2)	179.1(7)
Cu(3)—N(3)—C(3)	162.4(5)	N(3)—C(3)—S(3)	178.8(7)

[a]e.s.d.s given in parentheses. i: $1 - x, 1 - y, -z$; ii: $1 - x, -y, -z$.

NCS group belonging to the nearest neighbouring trianion generated by the symmetry centre in 0, 0, $\frac{1}{2}$. The two symmetrically related $[(Cu_4(NCS)_5-WS_4]$ units form a pseudo-dimer based on a twelve-membered ring as shown below.
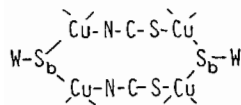
Furthermore it is of interest to note that the diminution of the sum of the angles about Cu(2) and Cu(3), respectively 358.4° and 357.4°, is paralleled by the formation of additional weak Cu—S(NCS) interactions, respectively Cu(2)...S(1)ii = 3.062(4) and Cu(3)...S(1)ii = 2.974(5) Å. Therefore the coordination geometry around Cu(2) and Cu(3) can be described as squashed tetrahedrons. The sulphur atom S(1) (NCS) acts as a bridge between three independent copper atoms Cu(1), Cu(2)ii

and Cu(3)ii of two symmetrically related pseudo-dimers in a way already observed [14].
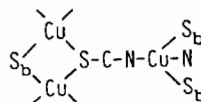
Dimeric units linked in this way form chains extending along directions parallel to *a*. The Cu—S—C angles are close to 100° and the Cu—N—C angles lie within the range 160–180°.

Compound 3

The crystal structure of 3 consists of one crystallographic independent dianion $[(CuNCS)_3WS_4]^{2-}$ and two NEt_4^+ cations. The $[(CuNCS)_3WS_4]^{2-}$ unit is a slightly distorted WS_4^{2-} tetrahedron coordinated by three CuNCS groups leaving an open S—W—S angle. The copper atom Cu(1) has a pseudo-trigonal planar coordination geometry with an angle

TABLE VIII. Selected Interatomic Distances (Å) and Angles (°) for $[N(C_2H_5)_4]_2[(CuNCS)_4MS_4]$ (M = W, Mo)[a]

	W	Mo		W	Mo
M–S(11)	2.224(2)	2.226(2)	M–S(12)	2.234(1)	2.241(2)
M–S(22)	2.205(2)	2.210(2)			
M...Cu(1)	2.6885(7)	2.674(1)	M...Cu(2)	2.6932(8)	2.682(1)
Cu(1)–S(11)	2.301(1)	2.289(1)	Cu(2)–S(22)	2.292(1)	2.289(2)
Cu(1)–S(12)	2.288(2)	2.275(2)	Cu(2)–S(12)[iii]	2.307(2)	2.291(2)
Cu(1)–S(1)[i]	2.489(2)	2.507(2)	Cu(2)–S(2)[ii]	2.324(2)	2.331(2)
Cu(1)–N(1)	1.943(4)	1.946(5)	Cu(2)–N(2)	2.008(6)	2.011(7)
N(1)–C(1)	1.150(6)	1.147(8)	N(2)–C(2)	1.132(9)	1.15(1)
C(1)–S(1)	1.643(5)	1.647(6)	C(2)–S(2)	1.634(7)	1.631(8)
S(11)–M–S(12)	109.25(4)	109.00(5)	S(12)–M–S(12)[iii]	109.73(7)	110.24(9)
S(11)–M–S(22)	109.80(7)	110.16(9)	S(12)–M–S(22)	109.40(5)	109.22(5)
Cu(1)...M...Cu(1)[iii]	93.86(3)	93.56(4)	Cu(2)...M...Cu(2)[iii]	95.45(4)	95.43(5)
Cu(1)...M...Cu(2)	175.35(5)	175.71(6)	Cu(1)...M...Cu(2)[iii]	85.16(2)	85.35(3)
S(11)–Cu(1)–S(12)	104.76(6)	105.67(8)	S(22)–Cu(2)–S(12)[iii]	103.94(6)	104.77(8)
N(1)–Cu(1)–S(11)	114.0(2)	114.0(2)	N(2)–Cu(2)–S(22)	101.6(2)	101.0(2)
N(1)–Cu(1)–S(12)	122.1(2)	122.2(2)	N(2)–Cu(2)–S(12)[iii]	119.7(2)	119.7(2)
N(1)–Cu(1)–S(1)[i]	100.3(1)	99.7(2)	N(2)–Cu(2)–S(2)[ii]	105.4(2)	105.2(2)
S(11)–Cu(1)–S(1)[i]	107.21(6)	107.01(7)	S(22)–Cu(2)–S(2)[ii]	113.5(1)	113.5(1)
S(12)–Cu(1)–S(1)[i]	107.52(5)	107.05(7)	S(12)–Cu(2)–S(2)[ii]	112.52(8)	112.5(1)
M–S(11)–Cu(1)	72.88(5)	72.60(6)	M–S(22)–Cu(2)	73.54(5)	73.15(6)
M–S(12)–Cu(1)	72.94(5)	72.59(6)	M–S(12)–Cu(2)[iii]	72.74(4)	72.53(5)
Cu(1)–S(11)–Cu(1)[iii]	117.21(9)	116.7(1)	Cu(1)–S(12)–Cu(2)[iii]	104.83(6)	105.30(8)
Cu(2)–S(22)–Cu(2)[iii]	120.7(1)	120.1(1)			
C(1)–S(1)–Cu(1)[i]	96.7(2)	96.8(2)	C(2)–S(2)–Cu(2)[ii]	96.1(2)	96.3(3)
C(1)–N(1)–Cu(1)	160.7(5)	161.0(6)	C(2)–N(2)–Cu(2)	156.3(5)	157.1(5)
N(1)–C(1)–S(1)	179.2(7)	178.8(6)	N(2)–C(2)–S(2)	179(1)	178.5(6)

[a]e.s.d.s given in parentheses. i: $1 - x, 1 - y, 1 - z$; ii: $-x, -y, -z$; iii: $x, \frac{1}{2} - y, z$.

sum of 359.58° giving a S_2CuN arrangement involving two bridging sulphur atoms and one nitrogen atom of the NCS group as in $(PPh_4)_2[(CuNCS)_2WS_4]$ [9]. The other atoms have a distorted tetrahedral geometry forming CuS_3N units. The tetrahedral apices are occupied by two bridging sulphur atoms, one nitrogen and one sulphur atom of two symmetrically related (symmetry centre in $\frac{1}{2}$, $\frac{1}{2}$, 0) NCS groups, generating a system of eight-membered $-Cu(NCS)_2Cu-$ rings of the same type reported in $(PPh_4)_2[(CuNCS)_4WS_4]$ [9]. The two independent thiocyanate groups N(2)C(2)S(2) and N(3)C(3)S(3) are involved in bridging two copper atoms of different $[(CuNCS)_3WS_4]^{2-}$ units. The resulting anionic polymeric zig-zag chains, shown in Fig. 2, run along a direction parallel to b, with $[(CuNCS)_3WS_4]$ units linked through inversion centres. The three copper atoms together with the unidentate thiocyanato species lie approximately in one plane. The Cu–S–C angles are close to 100° and the Cu–N–C angle lies between 160° and 170°.

Compounds 4 and 5

The structures of the isostructural compounds 4 and 5 consist of one crystallographically independent $[(CuNCS)_4MS_4]^{2-}$ (M = Mo, W) dianion and two

NEt_4^+ cations with the broad general features observed for $(PPh_4)_2[(CuNCS)_4WS_4]$ [9]. The tungsten or molybdenum atom has an essentially tetrahedral coordination geometry (angles close to 109°) with W or Mo and two sulphur atoms lying in a crystallographic mirror plane. The structure closely resembles that of the recently studied $(PPh_4)_2[(Cu-NCS)_4WS_4]$ [9] with a MS_4Cu_4 aggregate showing nearly a D_{2d} symmetry. The copper atoms are bound to the MS_4 core, each being attached to one edge of the MS_4 tetrahedron. The two independent copper atoms are pseudo-tetrahedrally four-coordinated by a pair of bridging sulphur atoms, one N and one S of two symmetry related NCS groups forming CuS_3N units. The corresponding NCS ligands are involved in inter-aggregate bridges between copper atoms of the nearest MS_4Cu_4 unit forming a system of eight-membered $-Cu(NCS)_2Cu-$ rings of the type observed in $(NEt_4)_2[(CuNCS)_3WS_4]$ and $(PPh_4)_2[(CuNCS)_4-WS_4]$ [9].

In these complexes as in the corresponding PPh_4^+ complex, the linked $[(CuNCS)_4MS_4]$ fragments form infinite zig-zag chains extending along the screw axes. Furthermore these infinite chains are held together by similar $-Cu(NCS)_2Cu-$ linkages as above generated by inversion centres forming a
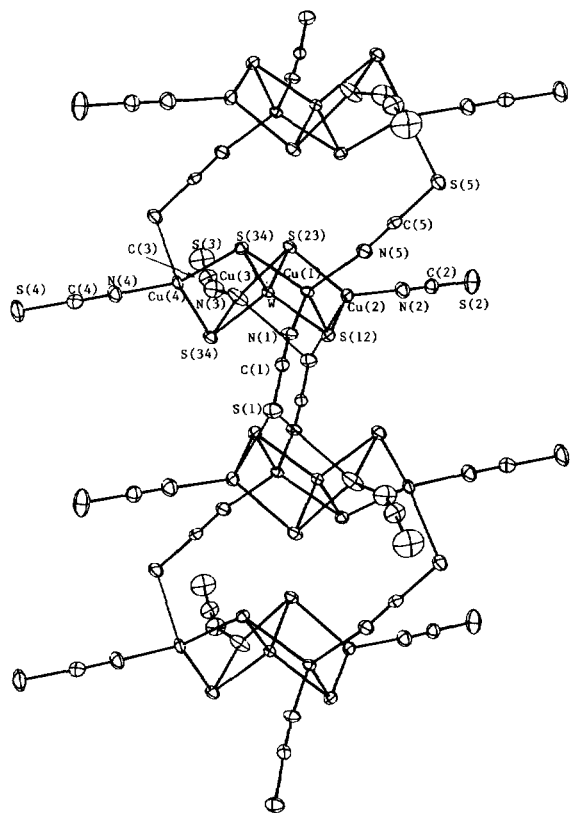
Fig. 1. Perspective view (50% ellipsoids) of the anionic chains present in (NEt₄)₃[Cu₄(NCS)₅WS₄]. The chain runs in a direction parallel to [100]. Atom labelling is indicated about the crystallographically independent unit. Two dimeric units (linked via an N(5)–C(5)–S(5) group) connected by an N(1)–C(1)–S(1) group are shown.

bidimensional polymeric structure. Thus this latter can be described as infinite sheets comprising the diagonal (10Ī) plane as mean plane, the W or Mo atoms being alternatingly above and below these

mean planes by almost 0.9 Å. The spaces between the anionic bidimensional sheets are filled with the NEt₄⁺ cations with no usually short van der Waals contacts. In contrast with the corresponding PPh₄⁺ complex a different arrangement of the NCS groups is observed, all the copper atoms having a pseudo-tetrahedral coordination geometry. As can be seen in Fig. 3 the six-membered motif comprising six linked [(CuNCS)₄WS₄] observed in (PPh₄)₂-[(CuNCS)₄WS₄] is lost. A more compact four-membered motif comprising solely four linked [(CuNCS)₄MS₄] is formed by the approach of the two three-coordinated copper atoms in closer proximity in order to achieve a pseudo-tetrahedral coordination. An anionic polymeric chain involving (μ_2-Br₂) linkages between MoS₄Cu₄ aggregates occurred in (PPh₄)₂[(CuBr)₄MoS₄] [15]. The deviation from linearity of the Cu–N–C angles is more pronounced than in the corresponding PPh₄⁺ complex while the Cu–S–C angles lie around 96°.

Electronic Spectra

The electronic spectra for [(CuNCS)₄MS₄]²⁻ dianions are given in Table IX. The influence of the nature and of the number of the additional CuX species (X = Cl [5], CN [8], NCS [9], PhS [16]) of this series can now be better examined.

The electronic spectra of WS₄²⁻ (or MoS₄²⁻) in DMF solution display maxima at 400 (or 376) and 280 (or 322) nm respectively. It can be seen from Table IX that the addition of CuNCS units to MS₄²⁻ shifts the spectra to lower energies. The position of the maximum absorption peak follows the trends previously observed for the [(CuCl)ₙ-MS₄] [5] series, *i.e.* this transition is shifted to lower energy in the order n = 1, 2, 3. It can be noted that the electronic spectra of the [(CuNCS)₄MS₄]²⁻ anionic polymers are similar in profile, wavelength and intensity. Hence, whatever may be the nature of the polymer extension there is convincing spec-

TABLE IX. Electronic Absorption Spectra in DMF Solution

Compound	λ (nm) (ε (l mol⁻¹ cm⁻¹))[a]
(PPh₄)₂[(CuNCS)₂WS₄][b]	416(6880) 310(sh) 292(18800)
(NEt₄)₂[(CuNCS)₃WS₄] (3)	422(5650) 308(sh) 290(sh)
(PPh₄)₂[(CuNCS)₄WS₄][b]	430(4400) 320(sh)
(NEt₄)₂[(CuNCS)₄WS₄] (4)	430(4690) 320(sh)
(NMe₄)₂[CuNCS)₄WS₄][c]	430(4480) 320(sh)
(NEt₄)₃[Cu₄(NCS)₅WS₄] (1)	424(5320) 320(sh) 290(sh)
(PPh₄)₂[(CuNCS)₂MoS₄][b]	494(4040) 348(sh) 316(15000)
(PPh₄)₂[(CuNCS)₄MoS₄][b]	510(3050) 360(sh)
(NEt₄)₂[(CuNCS)₄MoS₄] (5)	510(3000) 360(sh)
(NMe₄)₂[(CuNCS)₄MoS₄][c]	510(3300) 360(sh)
(NEt₄)₃[Cu₄(NCS)₅MoS₄] (2)	504(3400) 360(sh)

[a]Abbreviation: sh, shoulder. [b]Ref. 9. [c]Ref. 10.

TABLE X. Infrared Vibrational Absorptions (cm⁻¹)ᵃ

Compound	ν(CN)	ν(CS)	δ(NCS)	ν(MS)
(PPh₄)NCS	2050(s)	746(m)	486(m), 471(m)	
(PPh₄)₂[(CuNCS)₂WS₄]ᵇ	2100(sh), 2088(s)	830(m)	743(sh)	455(s)
(NEt₄)₂[(CuNCS)₃WS₄] (3)	2112(m), 2100(s)	826(m)		471(m), 461(m), 444(m), 433(m)
(PPh₄)₂[(CuNCS)₄WS₄]ᵇ	2109(s), 2090(s)	826(vw), 796(w)	462(w)	443(s)
(NEt₄)₂[(CuNCS)₄WS₄] (4)	2109(s)	759(m), 723(vw)	467(sh)	455(m), 435(s)
(NMe₄)₂[(CuNCS)₄WS₄]ᶜ	2122(s), 2087(s)	794(w), 776(w), 764(w), 747(w)	470(w)	440(s)
(NEt₄)₃[Cu₄(NCS)₅WS₄] (1)	2105(s)	811(m), 724(vw)	467(w), 419(sh)	442(s)
(PPh₄)₂[(Cu(NCS)₂MoS₄]ᵇ	2100(sh), 2087(s)	831(m)		467(s)
(PPh₄)₂[(CuNCS)₄MoS₄]ᵇ	2108(s), 2090(s)	830(vw), 799(w)		454(s)
(NEt₄)₂[(CuNCS)₄MoS₄] (5)	2109(s)	759(m), 723(vw)		458(m), 447(s)
(NMe₄)₂[(CuNCS)₄MoS₄]ᶜ	2122(s), 2087(s)	796(w), 776(w), 767(w), 747(w)	469(w)	450(s)
(NEt₄)₃[Cu₄(NCS)₅MoS₄] (2)	2105(s)	811(m), 724(vw)	419(sh)	456(s)

ᵃAbbreviation: s, strong; m, medium; w, weak; vw, very weak; sh, shoulder. ᵇRef. 9. ᶜRef. 10.
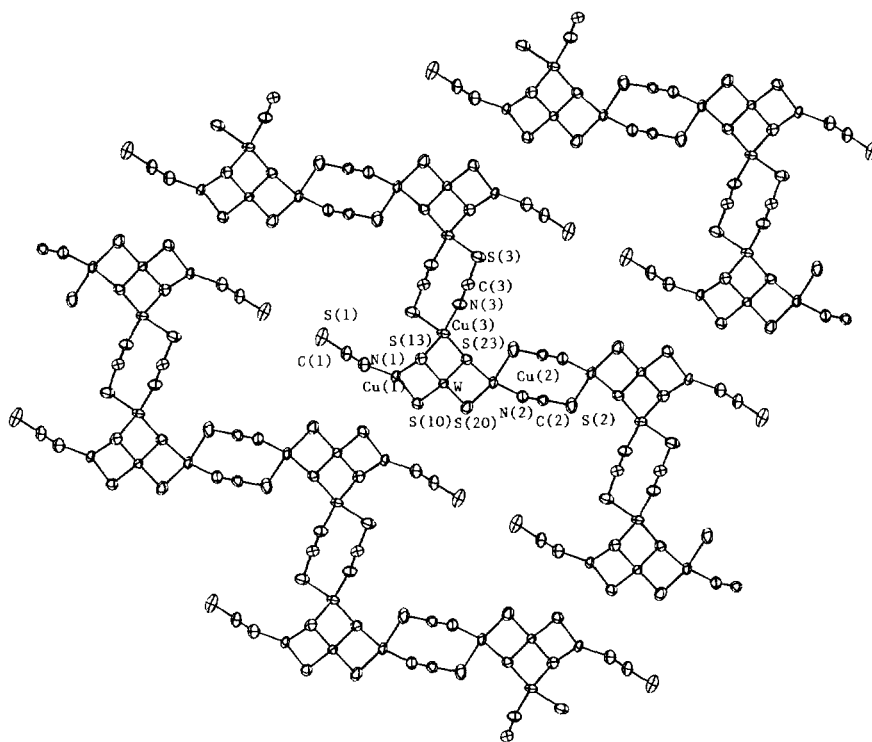

Fig. 2. Perspective view (50% ellipsoids) of zig-zag anionic chains in (NEt₄)₂[(CuNCS)₃WS₄]. Atom labelling is indicated about the crystallographically independent unit. The view is normal to the W–Cu(2)/W–Cu(3) plane.

troscopic evidence that the three different polymeric arrangements cleave in DMF solution to give the same absorbing species.

Infrared Spectra

There have been several vibrational spectrosocpic studies on complexes involving the MS₄Cuₙ core (*n* = 1 to 4) which provide significant data to assign the IR frequencies of complexes containing this moiety. For these compounds bands attributed to M–S (M = Mo, W) stretching vibrations [17] have been found in the region 422–516 cm⁻¹. The IR spectra of thiocyanate and related complexes have been also extensively studied because of the valuable tool of this technique in distinguishing the bonding mode of coordinated thiocyanate [18, 19].
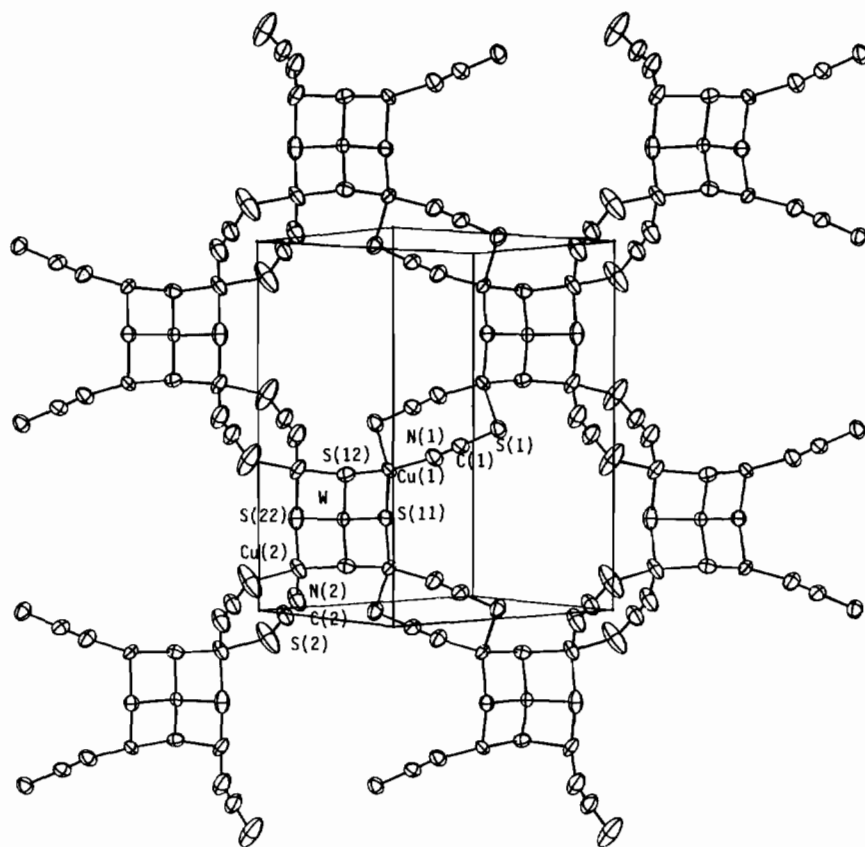
Fig. 3. Perspective view (50% ellipsoids) of the polymeric $(NEt_4)_2[(CuNCS)_4WS_4]$ complex showing one of the polymeric sheets. Atom labelling is indicated about the crystallographic independent unit. Atoms W, S(11) and S(22) lie on the mirror plane.

The NCS deformation mode can be used to characterize the bond type, being a single band at 450–490 cm^{-1} for M–NCS and a band at 440–400 cm^{-1} for M–SNC. Consequently the assignments of the bands attributed to $\delta(NCS)$ and $\nu(MS)$ falling in the same region preclude any reasonable assignment. The IR spectra for the studied complexes are compared in Table X. This Table also includes spectral data for $(NMe_4)_2[(CuNCS)_4MS_4]$ and $(PPh_4)_2[(CuNCS)_4-MS_4]$. As pointed out in the literature [18, 19] the $\nu(CN)$ stretching frequency is generally observed in the range 2100–2050 cm^{-1} for N-bonded thiocyanate, 2130–2085 cm^{-1} for S-bonded and 2165–2065 cm^{-1} for bridged NCS groups. In the present compounds the bands attributable to the CN stretching mode are observed between 2100 and 2110 cm^{-1}. This broad bond pattern is consistent with the presence of bridging and N-bonded thiocyanate.

The C–S frequency of NCS containing compounds lies in the 690–850 cm^{-1} region. The position of the C–S band is a good reliable feature for N- or S-bonding. It is currently admitted that absorptions near 700 cm^{-1} are related to S-bonding and near or above 800 cm^{-1} to N-bonding.

Intense bands of the NEt_4^+ cation in the strategic region 765–800 cm^{-1} prevent any complete observation of the M–NCS–M configuration. Nevertheless compounds 1 and 2 display a band at 811 cm^{-1} and compound 3 shows a band at 826 cm^{-1}. These $\nu(CS)$ bands could be assigned without ambiguity to the unidentate N-bonded thiocyanate species. Furthermore compounds 4 and 5 present bands at 759 cm^{-1}, these observations together with the informations given before on the stretching $\nu(CN)$ bands reveal the presence of bridging thiocyanate groups as reported in the crystal structure. In the infrared region weak absorption bands are observed, tentatively assigned to the Cu–NCS stretching.

Supplementary Material

Anisotropic thermal parameters, non-selected bond distances and angles and structure factors are available from the first author on request.

References

1 A Müller, E. Diemann, R. Jostes and H. Bögge, *Angew. Chem., Int. Ed. Engl., 20*, 934 (1981).
2 D. Coucouvanis, *Acc. Chem. Res., 14*, 201 (1981).
3 J. M. Manoli, C. Potvin and F. Secheresse, *J. Chem. Soc., Chem. Commun.*, 1159 (1982).
4 C. Potvin, J. M. Manoli, M. Salis and F. Secheresse, *Inorg. Chim. Acta, 83*, L19 (1984).
5 F. Secheresse, M. Salis, C. Potvin and J. M. Manoli, *Inorg. Chim. Acta, 114*, L19 (1986).
6 W. Clegg, C. D. Garner and J. R. Nicholson, *Acta Crystallogr., Sect. C, 39*, 552 (1983).
7 W. Clegg. C. D. Scattergood and C. D. Garner, *Acta Crystallogr., Sect. C, 43*, 786 (1987).
8 S. F. Gheller, T. W. Hambley, J. R. Rodgers, R. T. C. Brownlee, M. J. O'Connor, M. R. Snow and A. G. Wedd, *Inorg. Chem., 23*, 2519 (1982).
9 C. Potvin, J. M. Manoli, F. Secheresse and S. Marzak, *Inorg. Chem., 26*, 4370 (1987).
10 J. M. Manoli, C. Potvin, F. Secheresse and S. Marzak, *J. Chem. Soc., Chem. Commun.*, 1557 (1986).
11 A. C. T. North, D. C. Phillips and F. J. Mathews, *Acta Crystallogr., Sect. A, 24*, 351 (1968).
12 D. Cahen and J. A. Ibers, *J. Appl. Crystallogr., 5*, 298 (1972).
13 D. T. Cromer and J. T. Waber, 'International Tables for X-ray Crystallography', Vol. 1V, Kynoch, Birmingham, U.K., 1974, Tables 2.2A and 2.3.1.
14 C. L. Raston, B. Walter and A. H. White, *Aust. J. Chem., 32*, 2757 (1979).
15 J. R. Nicholson, A. C. Flood, C. D. Garner and W. Clegg, *J. Chem. Soc., Chem. Commun.*, 1179 (1983).
16 S. R. Acott, C. D. Garner, J. R. Nicholson and W. Clegg, *J. Chem. Soc., Dalton Trans.*, 713 (1983).
17 R. J. H. Clark, T. J. Dines and M. L. Wolf, *J. Chem. Soc., Faraday Trans., 2, 78*, 679 (1982).
18 R. J. H. Clark and C. S. Williams, *Spectrochim. Acta, 22*, 1081 (1966).
19 R. A. Bailey, S. L. Kozak, T. W. Nicholson and W. N. Milles, *Coord. Chem. Rev., 6*, 407 (1971).