The Anion of Pyrimidine-2-thiol as a Ligand to Molybdenum, Tungsten, and Iron. Preparation of Complexes, their Structure* and Reactivity

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The syntheses and structures of [FeL$_3$]$^-$ and [MoL$_4$] are described (L = pyrimidine-2-thiolate). The structures are similar to those of the known Co and W homologous complexes. The unbound nitrogens can be cleanly protonated and alkylated, but they are weak donors to Lewis acids such as Fe and Cu.

The active site of the enzyme nitrogenase is believed to contain iron and molybdenum in an environment dominated by sulphur, with possibly oxygen or nitrogen atoms.[1] This collection of several iron atoms and a molybdenum is probably linked by sulphide bridges in the form of an iron–molybdenum–sulphur cluster assembly, and has been partly characterised as the iron–molybdenum cofactor (FeMoco).[2] On the other hand, it is conceivable that the structure is held together by linkages through O and N in addition to S, but not in a conventional cluster. We therefore synthesised new mononuclear thiopyrimidine complexes of molybdenum and iron, determined their structure by X-ray crystallography, studied their electron-transfer chemistry, and explored the potential of unco-ordinated nitrogens to build metal ion assemblies.

Thiopyrimidines such as pyrimidine-2-thiol have the potential to bind to a single metal through sulphur, through nitrogen, or through one nitrogen and the sulphur. In any case, such binding will leave a potential donor free, since it is not feasible for all three donors to bind to the same metal atom. This is confirmed by the structures of the known tungsten and cobalt complexes [WL$_4$][3] and [CoL'$_3$][4] (L = pyrimidine-2-thiolate, L' = 4,6-dimethylpyrimidine-2-thiolate). The former compound has dodecahedral *mmmm* co-ordination symmetry but little chemistry has been done with it, its principal interest being the eight-co-ordination. The latter is distorted octahedral, but again little chemistry has been discussed. Both compounds have free nitrogens on the pyrimidines which are potential binding sites for further acids.

There are other modes of binding of pyrimidinethiolates to transition and main-group metals,[5,6] for example, to form clusters, but these need not concern us here.

Results and Discussion

The compounds [MoL$_4$]·CH$_2$Cl$_2$, [WL$_4$], and [NMe$_4$][FeL$_3$] were prepared by the reaction of [MCl$_4$(thf)$_2$] (M = Mo or W, thf = tetrahydrofuran) or [FeCl$_2$(H$_2$O)$_2$] with pyrimidine-2-thiol in thf using triethylamine or sodium hydride as a base (see Experimental section). The molybdenum and iron compounds

HL
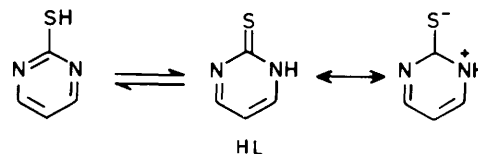
are new, and this synthesis of the tungsten compound is much preferable to that already reported.[3]

Green air-stable crystals of the molybdenum complex were obtained from dichloromethane–diethyl ether, and the structure determined by X-ray analysis. The crystals are monoclinic in the space group $P2_1/c$ with four molecules in the unit cell. A diagram of the molecular structure is shown in Figure 1 and the important bond lengths and angles are detailed in Table 1. The atomic positional parameters are in Table 2. The co-ordination around each molybdenum is slightly distorted from idealised dodecahedral D_{2d} geometry. The pyrimidines bond, as in the tungsten case, along the *mmmm* edges. The ligand bite is relatively short (*ca.* 2.5 Å) and consequently the edges *m* are the only ones which can accommodate adequately the ligand span. The edges *a*, *g*, and *b* have mean lengths 2.988, 3.106, and 3.122 Å, respectively (see Figure 2 and Table 3).

The range of S–N separations (*g* edges) is narrow, and is not unexpected. There are only two edge S–S separations, the *a* edges, and at *ca.* 3.0 Å they appear to indicate some S–S bonding since this is well within the range for which weak S–S interactions have been postulated.[7] The N–N distances (*b* edges) seem to fall into two pairs, *ca.* 3.3 and *ca.* 2.9 Å, and it is not clear why they are not all closer to the mean value. Apparently, the nitrogen atoms can move fairly freely within the co-ordination shell, and an arrangement with two pairs of nitrogens in the tetrahedron just touching (the van der Waals radius of N is *ca.* 1.5 Å) seems to be more stable than the all-equal arrangement.

The orientation of the ligands with respect to the *m* edges is consistent with theoretical predictions. The two ends of an *m* edge in a dodecahedral co-ordination sphere have different π- and σ-bonding capabilities, as indicated by the designations A and B in Figure 2.[8,9] The A sites are those which tend to attract π-donor or non-π-bonding ligands, whereas the B sites attract π-acceptor ligands.[9] In the case in point, the nitrogens (presumably π-acceptors) form a flattened tetrahedron occupying the B sites, whereas the sulphur atoms occupy another tetrahedron consisting of the A sites.[9] The parallel with the tungsten structure[3] is essentially complete. The *m* edges
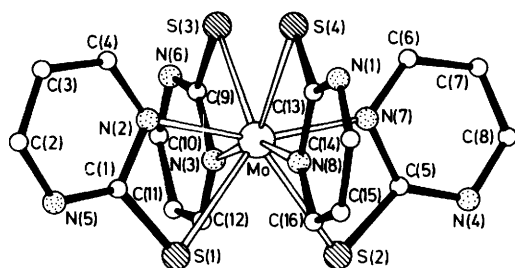
Figure 1. ORTEP representation and numbering scheme for the molecular structure of [MoL₄] (hydrogen atoms omitted)

Figure 2. Characteristic dodecahedral co-ordination, showing A and B sites, and the edges a, m, g, and b

Table 1. Selected bond lengths (Å) and angles for [MoL₄]·CH₂Cl₂

Mo–S(1)	2.528(3)	Mo–N(2)	2.168(8)
Mo–S(2)	2.535(2)	Mo–N(7)	2.174(8)
Mo–S(3)	2.523(3)	Mo–N(3)	2.185(9)
Mo–S(4)	2.541(3)	Mo–N(8)	2.191(9)

S(1)–C(1)	1.727(11)
S(2)–C(5)	1.730(11)
S(3)–C(9)	1.708(10)
S(4)–C(13)	1.727(11)

N(2)–C(1)	1.349(13)	N(8)–C(13)	1.361(12)
N(2)–C(4)	1.356(13)	N(8)–C(16)	1.335(13)
N(5)–C(1)	1.330(15)	N(1)–C(13)	1.331(14)
N(5)–C(2)	1.306(16)	N(1)–C(14)	1.330(15)
N(4)–C(5)	1.322(14)	C(2)–C(3)	1.378(18)
N(4)–C(8)	1.351(15)	C(3)–C(4)	1.355(17)

N(7)–C(5)	1.348(13)	C(6)–C(7)	1.363(15)
N(7)–C(6)	1.343(13)	C(7)–C(8)	1.353(16)
N(3)–C(9)	1.337(13)	C(10)–C(11)	1.371(17)
N(3)–C(12)	1.352(13)	C(11)–C(12)	1.369(16)
N(6)–C(9)	1.331(14)	C(14)–C(15)	1.372(16)
N(6)–C(10)	1.345(16)	C(15)–C(16)	1.391(14)

S(1)–Mo–S(2)	72.6(1)	S(3)–Mo–N(2)	82.1(2)
S(1)–Mo–S(3)	127.4(1)	S(3)–Mo–N(7)	83.0(2)
S(1)–Mo–S(4)	133.6(1)	S(3)–Mo–N(3)	63.7(2)*
S(1)–Mo–N(2)	63.9(2)*	S(3)–Mo–N(8)	135.3(2)
S(1)–Mo–N(7)	136.2(2)	S(4)–Mo–N(2)	81.3(2)
S(1)–Mo–N(3)	82.4(2)	S(4)–Mo–N(7)	81.3(2)
S(1)–Mo–N(8)	82.2(2)	S(4)–Mo–N(3)	135.2(2)
S(2)–Mo–S(3)	134.3(1)	S(4)–Mo–N(8)	63.9(2)*
S(2)–Mo–S(4)	127.7(1)	N(2)–Mo–N(7)	159.9(3)
S(2)–Mo–N(2)	135.8(2)	N(2)–Mo–N(3)	98.9(3)
S(2)–Mo–N(7)	64.0(2)*	N(2)–Mo–N(8)	84.3(3)
S(2)–Mo–N(3)	82.7(2)	N(7)–Mo–N(3)	86.5(3)
S(2)–Mo–N(8)	82.0(2)	N(7)–Mo–N(8)	97.0(3)
S(3)–Mo–S(4)	72.0(1)	N(3)–Mo–N(8)	160.9(3)

* Ligand 'bite'.

Table 2. Atomic positional parameters for [MoL₄]·CH₂Cl₂

Atom	x	y	z
Mo	0.245 44(7)	0.824 03(10)	0.134 54(5)
S(1)	0.376 8(2)	0.695 6(3)	0.072 1(1)
S(2)	0.442 2(2)	0.802 4(3)	0.204 4(1)
S(3)	0.111 5(2)	1.028 1(3)	0.098 5(1)
S(4)	0.049 0(2)	0.767 6(3)	0.162 6(1)
N(2)	0.162 9(6)	0.735 6(9)	0.045 2(4)
N(5)	0.231 7(8)	0.586 0(11)	−0.029 2(5)
N(4)	0.423 9(7)	0.953 5(9)	0.309 4(4)
N(7)	0.265 8(7)	0.933 2(8)	0.224 5(4)
N(3)	0.324 5(7)	1.010 4(9)	0.099 6(4)
N(6)	0.246 3(8)	1.231 3(10)	0.061 2(4)
N(8)	0.224 6(7)	0.610 5(9)	0.170 6(4)
N(1)	0.062 3(8)	0.492 4(10)	0.200 9(4)
C(1)	0.246 8(9)	0.665 0(11)	0.022 6(5)
C(2)	0.125 8(11)	0.579 6(14)	−0.060 3(6)
C(3)	0.032 6(11)	0.648 1(13)	−0.043 0(6)
C(4)	0.055 0(9)	0.725 6(12)	0.010 6(5)
C(5)	0.375 3(9)	0.907 0(11)	0.253 2(5)
C(6)	0.200 6(9)	1.011 8(11)	0.256 6(5)
C(7)	0.245 3(10)	1.065 4(12)	0.314 4(5)
C(8)	0.356 4(10)	1.034 9(13)	0.339 6(6)
C(9)	0.236 9(8)	1.101 1(11)	0.083 3(5)
C(10)	0.353 0(11)	1.270 1(13)	0.053 2(6)
C(11)	0.447 3(10)	1.182 8(12)	0.067 3(6)
C(12)	0.431 0(9)	1.051 4(12)	0.091 0(5)
C(13)	0.113 3(8)	0.604 7(11)	0.180 4(5)
C(14)	0.128 6(10)	0.378 0(12)	0.212 7(5)
C(15)	0.242 6(9)	0.372 7(10)	0.206 0(5)
C(16)	0.289 3(9)	0.494 7(11)	0.184 4(5)
C(17)	0.828 6(17)	0.061 2(17)	0.127 4(9)
Cl(1)	0.743 0(5)	0.156 9(6)	0.164 2(3)
Cl(2)	0.735 0(6)	−0.087 4(8)	0.087 1(3)

average 2.50 Å in the tungsten complex compared with 2.51 Å here, and the W–S and W–N bond lengths (2.52 and 2.16 Å, respectively) do not differ appreciably from the analogous lengths determined here (2.53 and 2.18 Å, respectively). The four ligands occupy two planes which contain the molybdenum atom and are mutually perpendicular; the system has pseudo-symmetry $\overline{4}2m$. The dimensions of the pyrimidinethiolates themselves are unexceptional. The average S–C bond length of 1.73 Å compares with 1.68 Å in the pyridine-2-thione,[10] and the estimated single bond length (ca. 1.8 Å). The N–C distances in the pyrimidine rings average 1.34 Å, suggesting an N–C bond
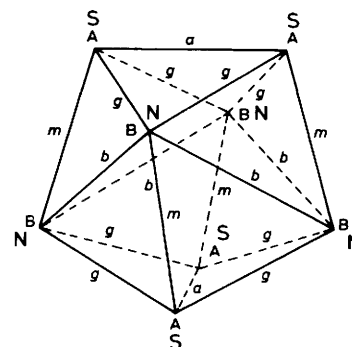
order of ca. 1.5. Consequently the ligand is closer to the pyrimidinethiolate than the thione form.

The average Mo–S and Mo–N distances are 2.532(3) and 2.179(8) Å, respectively, scarcely different from the reported W–S and W–N distances [2.519(3) and 2.162(7) Å, respectively[3]] but, surprisingly, slightly longer. There are not many eight-co-ordinate structures available with which to compare these distances, but Mo–S in [Mo(S₂CPh)₄][11] averages at ca. 2.54 Å, and W–N in the 5-bromoquinolin-8-olato-complex [W(C₉H₅NOBr)₄][12] averages at ca. 2.20 Å. Accordingly, the metal–ligand distances observed here are fairly normal.

These structures suggest that the uncomplexed nitrogens of the pyrimidinethiolates should be available for reaction with acids, and this is indeed the case. Both complexes [ML₄] (M =

Mo or W) react with HBF_4 in ether, yielding intensely coloured precipitates of $[M(HL)_4][BF_4]_4$. The molybdenum complex forms magenta-coloured aqueous solutions which are stable in the presence of HBF_4. The protons can be removed from both complexes by bases such as triethylamine. The products exhibit bands assignable to v(NH) in the region 3 200—3 100 cm⁻¹, and also characteristic bands derived from the anion (Table 4). The NH protons are also visible as a doublet in the ¹H n.m.r. spectra. In addition, in the ¹H n.m.r. spectra of both the parent compounds and these salts, the ring pyrimidine protons are non-equivalent (see Table 5). In the parent (M = Mo), H_A, H_B, and H_C are observed at δ 8.13 (dd), 6.83 (dd), and 9.10 (t) p.p.m. Upon protonation, these signals shift slightly, to 8.35 (dd), 7.33 (t), and 9.30 (dd), the slight downfield shift being expected in view of the positive charge induced in the cation. In these protonated species, the ligand may be better formulated as a pyrimidine-2(1H)-thione rather than as a thiolate, but a structure determination would be necessary to decide this.

Similarly, $[MoL_4]$ reacts with $[Me_3O][BF_4]$ to yield $[Mo(MeL)_4][BF_4]_4$, in which all of the free ring nitrogens are alkylated. The ¹H n.m.r. spectrum shows that all the methyl groups are equivalent, though the protons H_A, H_B, and H_C are still inequivalent (Table 5).

We also attempted to use the uncomplexed pyrimidine nitrogens as donors to further metal ions. For this purpose, we mixed $[MoL_4]$ with $FeCl_2$, $FeCl_3$, or $CuCl_2$ in CH_2Cl_2 or $CHCl_3$. Adducts were precipitated immediately, but the analyses were never reproducible, neither could the materials be

recrystallised to constant composition. These secondary metal–nitrogen interactions are apparently weak, possibly due to the fact that no two nitrogen donors of $[MoL_4]$ are suitably placed to be able to chelate to a further metal ion, but further work is required to establish this conclusively.

Red air-stable crystals of $[NMe_4][FeL_3]$ were obtained by crystallisation of the product from methanol in the presence of $[NMe_4]Cl$. The X-ray crystal structure analysis revealed the structure in Figure 3, important bond angles and distances are presented in Table 6, and atomic positional parameters in Table 7. The co-ordination around each iron is distorted octahedral, the overall shape of the anion resembling a three-bladed propeller, with each nitrogen- and sulphur-donor set being meridional. Each chelating four-membered ring contains one sulphur, one nitrogen, and one carbon, as well as the iron, so that this molecule, too, has a potential donor available, in the shape of the non-complexed nitrogen. Bond lengths suggest that the ligand is in the pyrimidinethiolate form. In principle, isomeric forms of this complex are possible. $[CoL'_3]^4$ $(L' = 4,6$-dimethylpyrimidine-2-thiolate) has a fac arrangement of the donor ligand sets. The reason for this difference is not clear.

The distortion from octahedral symmetry is quite severe, the average angle S–Fe–N being 66°. Consequently, this small bite causes S–Fe–S angles very different from 90° (104 and 98°), and similarly with N–Fe–N $(ca. 96°)$.

The average Fe–S and Fe–N bond lengths are 2.527(2) and

Table 3. Polyhedral edge distances (Å) in $[MoL_4]$

S(1)–S(2) (a)	2.998(3)	S(2)–N(7) (m)	2.513(8)*
S(1)–N(2) (m)	2.504(7)*	S(2)–N(3) (g)	3.129(9)
S(1)–N(3) (g)	3.114(9)	S(2)–N(8) (g)	3.113(9)
S(1)–N(8) (g)	3.112(9)	S(3)–S(4) (a)	2.977(4)
S(3)–N(2) (g)	3.093(9)	S(4)–N(7) (g)	3.085(8)
S(3)–N(7) (g)	3.123(9)	S(4)–N(8) (m)	2.521(9)*
S(3)–N(3) (m)	2.502(8)*	N(2)–N(3) (b)	3.302(12)
S(4)–N(2) (g)	3.080(8)	N(2)–N(8) (b)	2.925(12)
N(7)–N(3) (b)	2.987(12)		
N(7)–N(8) (b)	3.268(12)		

* Ligand 'bite'.

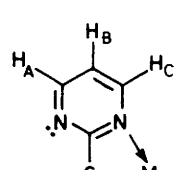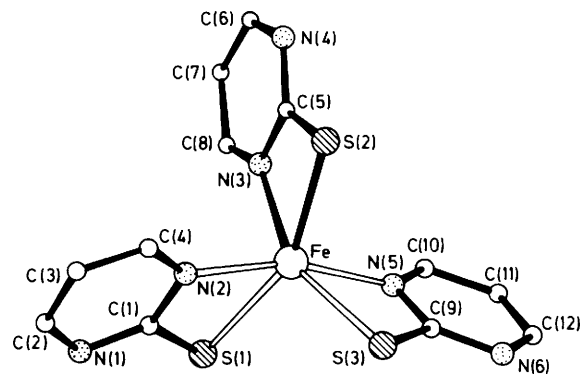**Figure 3.** Structure of the anion and numbering scheme for $[NMe_4][FeL_3]$

Table 4. Selected i.r. stretching frequencies (cm⁻¹) for HL and the new complexes

HL	[MoL₄]	[NMe₄]-[FeL₃]	[WL₄]	[Mo(HL)₄]-[BF₄]₄	[W(HL)₄]-[BF₄]₄	[Mo(MeL)₄]-[BF₄]₄	[Fe(HL)₃]-[BF₄]₂	Assignment
3 170ᵃ				3 120sᵇ	3 110mᵇ		3 150mᵇ	v(N–H)
1 605s	1 535s	1 545s	1 570s	1 610s	1 610s	1 600s	1 620s	} v(C=C) and v(C=N)
1 560s			1 530m	1 575m	1 560m	1 565m	1 595s	} stretching
1 210s	1 170s	1 180s	1 230s	1 195s	1 200s	1 200m	1 200m	Ring vibration
1 185s		1 170s	1 200s				1 185m	v(C=N)
			1 170s					v(NCN), v(NCS) and v(CS)
980s	1 000s	1 010s	1 020s	1 060sᵇ,ᶜ	1 065sᵇ,ᶜ	1 060sᵇ,ᶜ	1 060sᵇ,ᶜ	
790s	800s	810sᵈ	800mᵉ	805mᵇ	790m	800w	820m	}
740s	740s	750s	750sᵉ	765m	745m	750w	790m	} v(C–H) bending
	660w	655m	670s	725m	720m	720w	725m	}
	645w		650m	665m	655m	650w		

ᵃ Doubtful identification, see E. Spinner, *J. Chem. Soc.*, 1960, 1237. ᵇ Broad. ᶜ BF_4^-. ᵈ Multiplet. ᵉ Doublet.

Table 5. Selected n.m.r. data (p.p.m.)*

	HL	[MoL₄]	[WL₄]	[Mo(HL)₄][BF₄]₄	[W(HL)₄][BF₄]₄	[Mo(MeL)₄][BF₄]₄
	H$_B$ 6.83 (dd)	H$_B$ 6.83 (dd)	H$_B$ 6.98 (dd)	H$_B$ 7.33 (t)	H$_B$ 7.42 (t)	N–Me⁺ 4.26 (s)
	H$_A$ 8.13 (dd)	H$_A$ 7.80 (dd)	H$_A$ 8.35 (dd)	H$_A$ 7.89 (dd)	H$_B$ 6.94 (t)
				N–H⁺ 8.43 (d)	N–H⁺ 8.40 (d)	
	H$_A$ + H$_C$ 8.28 (d)	H$_C$ 9.10 (t)	H$_C$ 8.79 (t)	H$_C$ 9.30 (dd)	H$_C$ 8.86 (dd)	H$_A$ + H$_C$ 8.65 (m) (broad)

* Relative to SiMe₄ in CDCl₃, CD₃CN, or CD₂Cl₂ solvents.

Table 6. Selected bond lengths (Å) and angles (°) for the anion in [NMe₄][FeL₃]

Fe–S(1)	2.536(2)	S(1)–Fe–N(2)*	66.3(1)	S(1)–C(1)–N(2)	113.2(4)
Fe–S(2)	2.523(2)	S(2)–Fe–N(3)*	66.2(1)	Fe–N(2)–C(1)	102.0(3)
Fe–S(3)	2.524(2)	S(3)–Fe–N(5)*	66.2(1)	S(1)–C(1)–N(1)	122.1(5)
Fe–N(2)	2.149(5)	S(1)–Fe–S(3)	104.0(1)	N(2)–C(1)–N(1)	124.7(5)
Fe–N(3)	2.180(4)	S(3)–Fe–S(2)	97.7(1)	C(1)–N(1)–C(2)	115.5(6)
Fe–N(5)	2.155(5)	S(2)–Fe–S(1)	154.7(1)	N(1)–C(2)–C(3)	123.8(7)
S(1)–C(1)	1.726(6)	N(2)–Fe–N(3)	95.8(2)	C(2)–C(3)–C(4)	117.0(6)
N(2)–C(1)	1.357(8)	N(3)–Fe–N(5)	95.4(2)	C(3)–C(4)–N(2)	121.2(6)
N(1)–C(1)	1.333(8)	N(5)–Fe–N(2)	163.5(1)	N(1)–C(2)–H(2)	119.4(6)
N(1)–C(2)	1.346(8)	S(1)–Fe–N(5)	100.2(1)	C(3)–C(2)–H(2)	116.7(6)
C(2)–C(3)	1.37(1)	S(2)–Fe–N(2)	95.4(1)	C(2)–C(3)–H(3)	122.4(6)
C(2)–H(2)	1.138(7)	S(3)–Fe–N(2)	106.5(1)	C(4)–C(3)–H(3)	118.4(6)
C(3)–C(4)	1.37(1)	S(2)–Fe–N(5)	100.3(1)	C(3)–C(4)–H(4)	127.0(6)
C(3)–H(3)	1.182(6)	S(1)–Fe–N(3)	97.2(1)	N(2)–C(4)–H(4)	111.2(6)
C(4)–N(2)	1.336(7)	S(3)–Fe–N(3)	153.9(1)		
C(4)–H(4)	0.901(7)	Fe–S(1)–C(1)	78.5(2)		

* Ligand 'bite'.

Table 7. Atomic positional parameters* for [NMe₄][FeL₃]

Atom	x	y	z	Atom	x	y	z
Fe	0.219 6(1)	−0.077 41(9)	0.248 19(5)	H(8)	−0.0720	0.1216	0.4065
S(1)	0.049 3(2)	−0.213 4(2)	0.343 8(1)	C(9)	0.085 8(8)	−0.186 1(6)	0.077 7(4)
S(2)	0.432 7(2)	0.113 6(2)	0.221 0(1)	C(10)	−0.144 3(9)	−0.031 6(7)	0.125 5(4)
S(3)	0.285 3(2)	−0.255 0(2)	0.109 0(1)	H(10)	−0.1882	0.0360	0.1760
N(1)	0.313 7(7)	−0.246 3(5)	0.462 2(3)	C(11)	−0.230(1)	−0.068 2(7)	0.042 2(5)
N(2)	0.392 2(6)	−0.122 8(5)	0.352 6(3)	H(11)	−0.3674	−0.0292	0.0167
N(3)	0.147 7(6)	0.126 8(5)	0.321 3(4)	C(12)	−0.151(1)	−0.163 8(8)	−0.018 7(5)
N(4)	0.289 9(7)	0.344 3(5)	0.317 0(3)	H(12)	−0.1677	−0.2074	−0.0796
N(5)	0.013 6(6)	−0.090 4(5)	0.142 5(3)	C(13)	0.524 9(9)	0.408 7(7)	0.116 6(4)
N(6)	0.009 5(8)	−0.226 9(5)	−0.005 0(3)	H(13a)	0.4482	0.4649	0.1048
N(7)	0.680 6(6)	0.489 6(5)	0.173 2(3)	H(13b)	0.5925	0.3607	0.0684
C(1)	0.270 7(8)	−0.194 5(6)	0.392 5(4)	H(13c)	0.4457	0.3640	0.1630
C(2)	0.491 8(9)	−0.223 1(7)	0.493 2(4)	C(14)	0.786(1)	0.574 5(8)	0.121 0(4)
H(2)	0.5419	−0.2720	0.5487	H(14a)	0.8191	0.5253	0.0776
C(3)	0.623 4(9)	−0.151 8(6)	0.457 2(4)	H(14b)	0.7005	0.6246	0.1093
H(3)	0.7643	−0.1065	0.4956	H(14c)	0.8838	0.6151	0.1587
C(4)	0.5677(8)	−0.102 3(6)	0.385 3(4)	C(15)	0.601 9(1)	0.580 3(7)	0.252 8(5)
H(4)	0.6326	−0.0437	0.3599	H(15a)	0.5364	0.636 4	0.2274
C(5)	0.278 9(8)	0.205 9(6)	0.292 1(4)	H(15b)	0.7226	0.640 4	0.2984
C(6)	0.163 7(9)	0.403 2(7)	0.374 0(4)	H(15c)	0.5325	0.522 4	0.2857
H(6)	0.1563	0.5203	0.3969	C(16)	0.812(1)	0.393 4(8)	0.201 5(5)
C(7)	0.028 2(9)	0.330 7(7)	0.407 6(4)	H(16a)	0.8956	0.4606	0.2463
H(7)	−0.0728	0.3672	0.4494	H(16b)	0.7453	0.3400	0.2233
C(8)	0.0241(8)	0.188 5(6)	0.378 8(4)	H(16c)	0.8664	0.3671	0.1554

* Those atoms with positional parameters not qualified by an e.s.d. are placed in calculated positions (they are all hydrogen atoms).

2.161(5) Å, which compare well with other reported distances. For example,[13] Fe–S in a range of iron(III) dithiocarbamates is ca. 2.42 Å; Fe–N is a little less consistent, typical average values being 2.24 Å in [Fe(py)₄(NCS)₂] (py = pyridine),[14] 2.17 Å in [Fe(bipy)₂(NCS)₂] (bipy = 2,2′-bipyridyl),[15] and 1.97 Å in

[Fe(phen)₃]³⁺ (phen = 1,10-phenanthroline).[16] Direct comparisons, due to differences in oxidation state, ring size, etc., are difficult.

The tetramethylammonium ions are as usually found and unremarkable.

Table 8. Electrochemical data [*] for pyrimidine-2-thiol complexes of Mo, W, and Fe, and their protonated derivatives

	[MoL$_4$]	[WL$_4$]	[NMe$_4$][FeL$_3$]	[Mo(HL)$_4$][BF$_4$]$_4$	[W(HL)$_4$][BF$_4$]$_4$
	$E^{ox}_{\frac{1}{2}}$ +0.05	$E^{ox}_{\frac{1}{2}}$ −0.15	E^{ox}_{p} +0.65	$E^{ox}_{\frac{1}{2}}$ +0.12	$E^{ox}_{\frac{1}{2}}$ +0.15
	E^{red}_{p} −1.53	E^{red}_{p} −2.31	$E^{ox}_{\frac{1}{2}}$ −0.31	E^{red}_{p} −1.06	E^{red}_{p} −1.09
				−1.32	−1.97
			E^{red}_{p} −2.60	−1.49	−2.15

[*] All values are quoted *vs.* ferrocene–ferrocenium couple (in thf +0.535 *vs.* s.c.e., in CH$_2$Cl$_2$ +0.36 *vs.* s.c.e., in CH$_3$CN +0.38 *vs.* s.c.e.).

The i.r. spectrum of [FeL$_3$]$^-$ (Table 5) is as expected, with all the bands observed in the spectra of [ML$_4$] (M = Mo or W). The complex is a 1:1 electrolyte in methanol (Λ_M = 96.5 ohm^{-1} cm^2 mol^{-1}) but we could observe no ^{1}H n.m.r. spectrum, consistent with the presence of a paramagnetic species.

Reaction of [FeL$_3$]$^-$ in dichloromethane with HBF$_4$·Et$_2$O (3 mol equiv.) produces an immediate yellow precipitate, and the collected analytical and spectral data [*e.g.* ν(NH) at *ca.* 3 150 cm^{-1}; Λ_M = 200 ohm^{-1} cm^2 mol^{-1} in acetonitrile] are consistent with the formulation [Fe(HL)$_3$][BF$_4$]$_2$. We also attempted the reaction of several different molybdenum compounds, such as [MoCl$_4$A$_2$] (A = thf, MeCN, or PEt$_3$), [Mo(N$_2$)$_2$(Ph$_2$PCH$_2$-CH$_2$PPh$_2$)$_2$] and [Mo(CO)$_6$] with [FeL$_3$]$^-$ in different proportions and under various reaction conditions. Although adducts of some kind undoubtedly form in these systems, we were unable to isolate and characterise any stable products. The most promising system consists of the approximately 1:1 adduct (based on metal analysis) of [FeL$_3$]$^-$ with [MoS$_4$]$^{2-}$, which analysed for [B][FeL$_2$·MoS$_4$·X$_2$] (B = NEt$_4$ or PPh$_4$, X = Cl or Br). However, these insoluble, air-sensitive products could not be structurally characterised since no suitable crystals could be obtained. We conclude that, as with [ML$_4$], the free pyrimidine nitrogens in [FeL$_3$]$^-$ are not suitably disposed in space to permit strong, chelate binding of further metal atoms.

Electrochemical Studies.—Both the oxidation and reduction of [ML$_4$] have been studied by cyclic voltammetry. In dichloromethane, [MoL$_4$] undergoes a reversible, diffusion-controlled one-electron oxidation, at +0.40 V *vs.* s.c.e. (saturated calomel electrode), to yield [MoL$_4$]$^+$. Similarly, [WL$_4$] can be reversibly oxidised, but at +0.20 V *vs.* s.c.e. It is not unexpected that the tungsten complex should here be the easier to oxidise, though this is not invariably the case. In closed-shell complexes of zero oxidation state comparable molybdenum and tungsten compounds may oxidise at the same potential,[17] and of the M^{II} diazenido-complexes those of tungsten(II) are marginally more difficult to oxidise.[18]

The reductions of [ML$_4$] are considerably less reversible, which is not unexpected since any product [ML$_4$]$^-$ would be a 19-electron species. The reduction of [WL$_4$] (E_p = −1.95 V) is less reversible than that of [MoL$_4$] (E_p = −1.17 V). The chemistry of Mo^{III} indicates that it is an oxidation state more easily accessible than W^{III}, and this may, in part, explain the observations.

The cyclic voltammetry of [FeL$_3$]$^-$ (also summarised in Table 8) shows a diffusion-controlled one-electron oxidation process at +0.07 V, and a further irreversible process at E_p = +0.27 V. At least on the cyclic voltammetry time scale [FeL$_3$] is a stable species, though we have not attempted to prepare it.

The subsequent oxidation, formally to [FeL$_3$]$^+$, would involve the reactive Fe^{IV} state, so it is likely that this oxidation is finally ligand based. Independent tests showed that no L$^-$ is generated. [FeL$_3$]$^-$ also shows an irreversible multi-electron reduction wave, but this was not investigated further.

The protonated species [M(HL)$_4$]$^{4+}$ show complicated

oxidation and reduction chemistry. Proton loss makes the systems complex. The cyclic voltammetry has not been studied in detail, but peak potential data for the primary irreversible redox steps are given in Table 8.

Conclusions

This work confirms earlier data, particularly with W and Co, showing that pyrimidinethiolato-complexes are easily formed and are stable despite the fact that only two of the three potential donor sites are involved in bonding. The remaining nitrogen has weak donor power, towards both the proton and Lewis acids. However, the stereochemistry of the adducts prepared is such that the nitrogens not complexed to the principal co-ordination centre cannot act co-operatively, for example, in chelation, so that adducts with further acids are rather labile. However, it is clear that pyrimidinethiols can form the basis of multi-metal assemblies and suitable choice of metals should allow study of the mutual influence of different metal ions.

Experimental

All operations were carried out under dry dinitrogen using standard Schlenk techniques, and all solvents were distilled from drying agents prior to use. The compounds [MoCl$_4$-(thf)$_2$],[19] [WCl$_4$(MeCN)$_2$],[20] and [FeCl$_2$(H$_2$O)$_n$][21] were synthesised by published methods. All other materials were obtained commercially and used as received. The following instrumentation was used: u.v., Pye Unicam SP 1800; i.r., Pye Unicam SP 2000 and SP3; conductivity, Portland Electronics Ltd. bridge with Mullard cell, type 7591(B); n.m.r., JEOL FX90Q; atomic absorption, Instrumentation Laboratory 151.

Cyclic voltammetry was undertaken in dry dioxygen-free solvents under dinitrogen using a two-compartment three-electrode cell at 20 ± 2 °C, a High-Tek Instruments Ltd. potentiostat, type DT2101, a Chemical Electronics (Birtley) Ltd. waveform generator, type 01, and a Philips recorder, type PM8041.

Analyses were by Mr. C. Macdonald and Mr. F. B. Normanton, both of A.F.R.C. Unit of Nitrogen Fixation.

Tetrakis(pyrimidine-2-thiolato)molybdenum–Dichloromethane (1/1).—Pyrimidine-2-thiol (HL) (1.25 g, 11.1 mmol) and [MoCl$_4$(thf)$_2$] (1.0 g, 2.8 mmol) were suspended in thf (50 cm^3) and triethylamine (1.12 g, 11.1 mmol) added. The colour of the solution immediately turned dark red, and it was stirred overnight. The thf was removed at 10^{-3} mmHg yielding a brown solid which was extracted in a Soxhlet apparatus with chloroform (100 cm^3). The resulting red solution was reduced to *ca.* 35 cm^3 and stored at −16 °C overnight. This afforded green-brown *crystals* which were washed with methanol (15 cm^3) and diethyl ether (20 cm^3) and dried *in vacuo* at room temperature. Yield 1.7 g, 80%. Green crystals suitable for *X*-ray structural analysis were obtained by recrystallisation from dichloromethane. Such crystals contained dichloromethane,

detectable by ^{1}H n.m.r. spectroscopy (Found: C, 33.6; H, 3.50; N, 17.9. $C_{17}H_{14}Cl_2MoN_8S_4$ requires C, 32.6; H, 2.25; N, 17.9%); m.p. 261—263 °C; $\lambda_{max.}$ (CHCl$_3$) = 514 nm (ϵ 18 250 dm^3 mol^{-1} cm^{-1}).

Tetrakis(pyrimidine-2-thiolato)tungsten–Dichloromethane (1/1).—This was prepared similarly, from [WCl$_4$(MeCN)$_2$]. Recrystallisation from CH$_2$Cl$_2$ yielded golden brown crystals. Yield *ca.* 70% (Found: C, 28.6; H, 2.0; N, 15.3. $C_{17}H_{14}Cl_2$-N$_8$S$_4$W requires C, 28.6; H, 2.0; N, 15.7%); m.p. 250—253 °C (decomp.); $\lambda_{max.}$ (CHCl$_3$) = 573 nm (ϵ 22 460 dm^3 mol^{-1} cm^{-1}).

Tetramethylammonium Tris(pyrimidine-2-thiolato)ferrate- (II).—Sodium pyrimidine-2-thiolate (1.0 g, 9.0 mmol) was generated in thf from pyrimidine-2-thiol and sodium hydride. A solution of [FeCl$_2$(H$_2$O)$_2$] (0.48 g, 3.0 mmol) in thf was added to it. On stirring for 2 h at room temperature the mixture turned red, and produced a red precipitate. This was filtered off, and extracted with cold methanol into a methanolic solution of [NMe$_4$]Cl. Storing at -15 °C for 15 h produced bright red crystals. Yield 0.97 g (70%), m.p. 223—225 °C (Found: C, 41.4; H, 4.6; N, 20.9. $C_{16}H_{21}FeN_7S_3$ requires C, 41.4; H, 4.5; N, 21.1%).

Tetrakis(pyrimidinium-2-thiolato)molybdenum Tetrakis(tetra-fluoroborate).—The neutral molybdenum complex (0.15 g, 0.28 mmol) was dissolved in chloroform and ethereal fluoroboric acid added dropwise to the rapidly stirred solution. A red *suspension* formed immediately, and was filtered off after 1 h and dried *in vacuo.* Yield 0.22 g (90%), m.p. 204—206 °C (Found: C, 21.6; H, 2.2; N, 11.9. $C_{16}H_{16}B_4F_{16}MoN_8S_4$ requires C, 21.1; H, 1.7; N, 12.3%).

Tetrakis(pyrimidinium-2-thiolato)tungsten Tetrakis(tetra-fluoroborate)–Acetonitrile (1/1).—The neutral tungsten complex (0.25 g, 0.40 mmol) was dissolved in chloroform and ethereal fluoroboric acid added dropwise to the rapidly stirred solution. A purple-blue solid formed immediately, and was filtered off after 1 h and dried *in vacuo.* Yield 0.28 g, 90%. Recrystallisation from acetonitrile yielded the solvate, m.p. 229—231 °C (decomp.) (Found: C, 21.4; H, 2.0; N, 12.2. $C_{18}H_{19}B_4F_{16}N_9S_4W$ requires C, 21.1; H, 1.9; N, 12.3%).

Tetrakis(3-methylpyrimidinium-2-thiolato)molybdenum Tet-rakis(tetrafluoroborate).—The neutral molybdenum complex (0.20 g, 0.36 mmol) was dissolved in chloroform (50 cm^3) and an excess of [Me$_3$O][BF$_4$] added. The mixture was stirred for 1 h at room temperature and the red *precipitate* filtered off. It was dissolved in methanol (50 cm^3), stirred for 0.5 h, concentrated to half-volume, and stored at -20 °C for 15 h. The resulting red solid was filtered off and dried *in vacuo.* Yield 0.28 g (87%), m.p. 235 °C (decomp.) (Found: C, 25.5; H, 3.0; N, 12.1. $C_{20}H_{24}B_4F_{16}MoN_8S_4$ requires C, 25.3; H, 2.5; N, 11.8%).

Tris(pyrimidinium-2-thiolato)iron Bis(tetrafluoroborate).— The iron anionic complex (0.20 g, 0.43 mmol) was dissolved in dichloromethane (25 cm^3) and three equivalents of ethereal fluoroboric acid added dropwise with vigorous stirring, producing a yellow precipitate. The mixture was stirred for 1 h and filtered, and the *solid* washed with dichloromethane (20 cm^3) and diethyl ether (20 cm^3), and dried *in vacuo.* Yield 0.22 g (89%), m.p. 188—190 °C (decomp.) (Found: C, 25.7; H, 3.4; N, 12.7. $C_{12}H_{12}B_2F_8FeN_6S_3$ requires C, 25.0; H, 2.1; N, 14.5%).

Reactions of [MoL$_4$] with other Lewis Acids.—Saturated solutions of FeCl$_2$, FeCl$_3$, and CuCl$_2$ in thf, chloroform, and acetone, respectively, were allowed to react with solutions of

[MoL$_4$] in chloroform at room temperature for 1—20 h. The resultant purple-red or bright red solids were investigated by C, H, N microanalysis, electrochemistry, and atomic absorption spectroscopy. The Lewis acid content was never consistent and always less than 4 mol equiv.

Reactions of [NMe$_4$][FeL$_3$] *with other Lewis Acids.*— Reaction of [NMe$_4$][FeL$_3$] with [MoCl$_4$A$_2$] (A = thf,[19] MeCN,[22] PPh$_3$,[23] or dppe[23]), [Mo(CO)$_6$], or [Mo(N$_2$)$_2$-(dppe)$_2$][24] gives mixtures of variable Fe:Mo proportions. [NH$_4$]$_2$[MoS$_4$] gives an insoluble brown-black product. The reaction time was 5—48 h at room temperature, the conditions involved refluxing thf and tungsten-filament irradiation for [Mo(CO)$_6$] and [Mo(N$_2$)$_2$(dppe)$_2$]. Otherwise the solvent was chloroform.

Structure Determinations.—*Crystal data for* [MoL$_4$]·CH$_2$Cl$_2$ at 23 °C. $C_{17}H_{14}Cl_2MoN_8S_4$, $M = 624$, $a = 11.737(2)$, $b = 4.446(2)$, $c = 21.508(4)$ Å, $\alpha = 90.00$, $\beta = 100.09(1)$, $\gamma = 90.00°$, $U = 2$ 355.4 Å^3, space group $P2_1/c$ (monoclinic), $Z = 4$, $D_c = 1.76$ g cm^{-3}, $F(000) = 1$ 264.

Measurement of intensity data. Nicolet $R3m$ instrument, Mo-K_α radiation ($\lambda = 0.710$ 73 Å), graphite monochromator. Reflections measured: $\pm h$, $+k$, $+l$; scan mode, coupled θ (crystal)—2θ(counter); scan range, $0 < 2\theta \leqslant 45°$; scan rate variable, within range 6—30° min^{-1}; scan length, 1.2°. Background measurement: stationary counter-stationary crystal at beginning and end of each 2θ scan, each for half of time taken for 2θ scan. Standards: three measured every 197 data reflections, no significant deviations. Reflections collected: 3 893, including standards, 1 818 independent with $I \geqslant 3\sigma(I)$.

Data reduction and structure solution. Absorption coefficient, 7.83 cm^{-1}. Data corrected for background, Lorentz and polarisation effects in the usual fashion; no absorption correction ($T_{max.}/T_{min.} = 1.11$). Structure solution used the SHELXTL program package.[25] Mo was located from a three-dimensional Patterson synthesis. Subsequent difference Fourier maps yielded all non-hydrogen atoms. Hydrogen atoms were introduced as fixed contributions in idealised positions in the final cycles of refinement. Atomic scattering factors for neutral atoms were from ref. 26. Real and imaginary components of anomalous dispersion were used for all atoms.[27] $R[= \Sigma(|F_o| - |F_c|)/\Sigma|F_o|] = 0.053$, R' $[= \{\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2\}^{\frac{1}{2}}] = 0.051$; goodness of fit, $[\Sigma w(|F_o| - |F_c|)^2/(N_o - N_v)]^{\frac{1}{2}}$, where N_o is the number of observations and N_v the number of variables, was 1.55.

Crystal data for [NMe$_4$][FeL$_3$] *at* -45 °C. $C_{16}H_{21}FeN_7S_3$, $M = 463$, $a = 7.165(4)$, $b = 9.993(4)$, $c = 15.483(7)$ Å, $\alpha = 103.19(4)$, $\beta = 91.40(4)$, $\gamma = 91.83(4)°$, $U = 1$ 078 Å^3, space group $P\bar{1}$ (triclinic), $Z = 2$, $D_c = 1.43$ g cm^{-3}, $F(000) = 504$.

Measurement of intensity data. Syntex $P3$ instrument, Mo-K_α radiation ($\lambda = 0.710$ 73 Å), graphite monochromator. Reflections measured: $\pm h$, $\pm k$, $\pm l$; scan mode, $\omega/2\theta$; scan range, $2 < 2\theta < 42°$; scan rate variable, within range 2.0—29.3° min^{-1}; scan length, 1.0°. Background measurement: ratio of total background time to scan time, 0.4. Standards: one measured every 100 data reflections, no significant deviations. Reflections collected: 2 321, without standards, 1 875 independent with $I \geqslant 2\sigma(I)$.

Data reduction and structure solution. Absorption coefficient, 10.1 cm^{-1}. Data corrected for background, Lorentz and polarisation effects in the usual fashion; no absorption correction. Structure solution used direct methods and the SHELXTL program package.[25] All hydrogen atoms found, but not refined. Atomic scattering factors for neutral atoms were from ref. 26. Real and imaginary components of anomalous dispersion were used for all atoms.[27] $R = 0.044$, $R' = 0.046$ (both defined as above).

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