Charge-transfer Salts formed from Redox-active Cubane Cluster Cations $[M_4(\eta\text{-}C_5H_4R)_4(\mu_3\text{-}E)_4]^{n+}$ (M = Cr, Fe or Mo; E = S or Se) and Various Anions[†]

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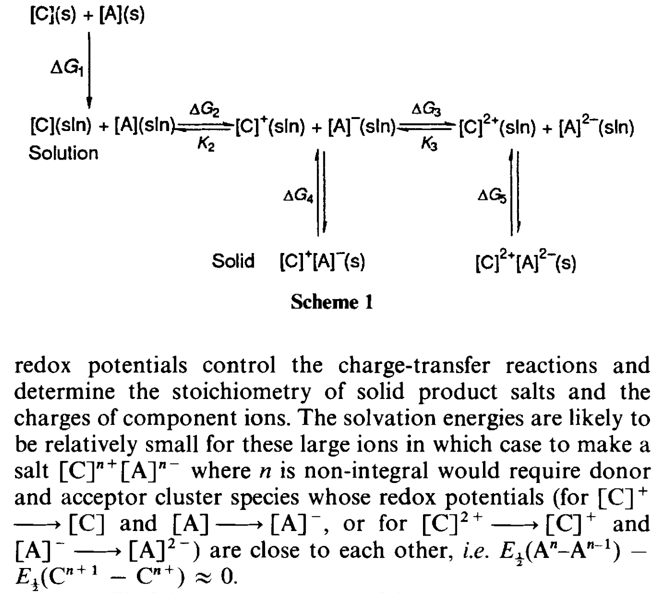
The synthesis and properties of the cluster salts $[C]^+[A]^-$ {C = $Mo_4(\eta\text{-}C_5H_4Pr^i)_4(\mu_3\text{-}S)_4$,* $Mo_4(\eta\text{-}C_5H_4Pr^i)_4(\mu_3\text{-}Se)_4$, $Fe_4(\eta\text{-}C_5H_5)_4(\mu_3\text{-}S)_4$,• $Fe_4(\eta\text{-}C_5H_4Me)_4(\mu_3\text{-}S)_4$,• $Cr_4(\eta\text{-}C_5H_5)_4(\mu_3\text{-}S)_4$, $Cr_4(\eta\text{-}C_5H_4Me)_4(\mu_3\text{-}S)_4$, or $Cr_4(\eta\text{-}C_5H_4Me)_4(\mu_3\text{-}Se)_4$; A = $Fe_4(NO)_4(\mu_3\text{-}S)_4$} and $[Mo_4(\eta\text{-}C_5H_4Pr^i)_4(\mu_3\text{-}S)_4]_2[Os_6(CO)_{18}]$* are described along with the cluster salts of tetracyanoquinodimethane (tcnq) or tetracyanoethylene (tcne) $[Mo_4(\eta\text{-}C_5H_4Pr^i)_4(\mu_3\text{-}S)_4][tcnq]$,• $[Fe_4(\eta\text{-}C_5H_5)_4(\mu_3\text{-}S)_4][tcnq]$, $[Fe_4(\eta\text{-}C_5H_4Me)_4(\mu_3\text{-}S)_4][tcnq]$,* $[Cr_4(\eta\text{-}C_5H_5)_4(\mu_3\text{-}S)_4][(tcnq)_2]$, $[Cr_4(\eta\text{-}C_5H_4Me)_4(\mu_3\text{-}S)_4][tcnq]$, $[Cr_4(\eta\text{-}C_5H_4Me)_4(\mu_3\text{-}S)_4][(tcnq)_2]$, $[Cr_4(\eta\text{-}C_5H_4Me)_4(\mu_3\text{-}Se)_4][tcnq]$, $[Cr_4(\eta\text{-}C_5H_4Me)_4(\mu_3\text{-}Se)_4][(tcnq)_2]$, $[Mo_4(\eta\text{-}C_5H_4Pr^i)_4(\mu_3\text{-}Se)_4][tcnq]$, $[Mo_4(\eta\text{-}C_5H_4Pr^i)_4(\mu_3\text{-}Se)_4][tcnq]_3$, and $[Cr_4(\eta\text{-}C_5H_4Me)_4(\mu_3\text{-}S)_4][tcne]$. The cluster dithiolene salts $[C]^{n+}[Mo\{S_2C_2(CF_3)_2\}_3]^{n-}$ {C = $Mo_4(\eta\text{-}C_5H_4Pr^i)_4(\mu_3\text{-}Se)_4$, $Mo_4(\eta\text{-}C_5H_4Pr^i)_4(\mu_3\text{-}S)_4$, $[Mo_4(\eta\text{-}C_5H_4Pr^i)_4(\mu_3\text{-}S)_4]_2$, $Cr_4(\eta\text{-}C_5H_4Me)_4(\mu_3\text{-}S)_4$, or $Cr_4(\eta\text{-}C_5H_4Me)_4(\mu_3\text{-}Se)_4$} and $[Mo_4(\eta\text{-}C_5H_4Pr^i)_4(\mu_3\text{-}S)_4][Ni\{S_2C_2(CN)_2\}_2]$ are also reported. Crystal structures have been determined for the compounds marked• and also for the neutral selenium cubane $[Mo_4(\eta\text{-}C_5H_4Pr^i)_4(\mu_3\text{-}Se)_4]$. The crystal structures of the cluster salts are not always those predicted from idealized ionic model considerations. Electrical conductivities and magnetic properties are described. The compound $[Mo_4(\eta\text{-}C_5H_4Pr^i)_4(\mu_3\text{-}S)_4][tcnq]$ has an unusual ribbon arrangement of the $tcnq^-$ anions and shows weak antiferromagnetic behaviour with $T_N \approx 12$ K.

More than fifty homonuclear cubane clusters of general class $[ML_4(\mu_3\text{-}X)_4]$ are known.[1–6] Typical examples are the compounds $[Mo_4(\eta\text{-}C_5H_4Pr^i)_4(\mu_3\text{-}S)_4]^{n+}$ (n = 0, 1 or 2)[5] which undergo reversible redox equilibria, and the photoelectron spectrum of the neutral compound, $n = 0$, has a very low first ionization energy (4.99 eV). Further, the crystal structures of the compounds with n = 0–2 show that the structural parameters of the Mo_4S_4 core change only slightly with sequential removal of the electrons.[5] Other clusters, for example $[Fe_4(NO)_4(\mu_3\text{-}S)_4]^n$, $n = 0$, undergo reversible uptake of electrons giving anions where $n = -1$ or -2.[6]

If a reducing cluster and an oxidizing cluster are brought together charge transfer would be expected to occur and a cluster salt of general stoichiometry $[C]^{n+}[A]^{n-}$, where $[C]^{n+}$ indicates a cluster cation and $[A]^{n-}$ a cluster anion, should be formed. Here we describe the preparation and study of the physical properties of such cluster salts. We were interested to discover whether the lattice structures formed by the component ions would be well described by simple electrostatic considerations. Furthermore, given the availability of multiple redox states to both [C] and [A], there is the interesting possibility that n could be non-integral, for example there could be a mixture of cations with n = 1 and 2, and correspondingly anions with n = 1 or 2. A preliminary account of part of this work has been published.[7]

The process of forming a simple ionic salt, $[C]^{n+}[A]^{n-}$, by a charge-transfer reaction in a solution may be decomposed into the series of steps in Scheme 1. Both solvation energies and redox potentials control the charge-transfer reactions and determine the stoichiometry of solid product salts and the charges of component ions. The solvation energies are likely to be relatively small for these large ions in which case to make a salt $[C]^{n+}[A]^{n-}$ where n is non-integral would require donor and acceptor cluster species whose redox potentials (for $[C]^+ \longrightarrow [C]$ and $[A] \longrightarrow [A]^-$, or for $[C]^{2+} \longrightarrow [C]^+$ and $[A]^- \longrightarrow [A]^{2-}$) are close to each other, *i.e.* $E_{\frac{1}{2}}(A^n\text{-}A^{n-1}) - E_{\frac{1}{2}}(C^{n+1} - C^{n+}) \approx 0$.



Scheme 1

The radii of the component ions of these cluster salts are large compared with the radii of simple ions and therefore relatively low lattice energies are to be expected. For this reason we refer to these molecular cluster salts as 'soft salts'. To date we have not found in the literature any examples of salts of this type formed by direct charge-transfer reactions. However, previously described cluster salts are $[Li_4Cl_2(Et_2O)_{10}]^{2+}[(Li_2Cu_3Ph_6)_2]^{2-}$ and $[Li_6Br_4(Et_2O)_{10}]^{2+}[(Ag_3Li_2Ph_6)_2]^{2-}$ (ref. 8) whose crystal structures have been determined. Since our original communication other workers have reported some related soft salts.[9]

[†] *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1991, Issue 1, pp. xviii–xxii.

Non-SI units employed: eV ≈ 1.60×10^{-19} J, G = 10^{-4} T, X (SI) ≈ X (cgs) × $4\pi \times 10^{-6}$.

Table 1 Analytical and spectroscopic data and physical properties

Compound	Analysis (%)[a] C	H	N	ν(NO) or ν(CN) (cm^{-1})	R.t. conductivity (Ω^{-1} cm^{-1})	E_a/eV
1 $[Mo_4(\eta\text{-}C_5H_4Pr^i)_4(\mu_3\text{-}Se)_4]$[b]	34.1 (34.0)	4.0 (3.9)				
2 $[Cr_4(\eta\text{-}C_5H_4Me)_4(\mu_3\text{-}Se)_4]$[c]	34.4 (34.3)	3.6 (3.3)				
3 $[Mo_4(\eta\text{-}C_5H_4Pr^i)_4(\mu_3\text{-}S)_4][Fe_4(NO)_4(\mu_3\text{-}S)_4]$[d]	27.0 (27.2)	3.0 (3.1)	3.9 (4.0)	1755 1696	7.6 × 10^{-9}	0.41
4 $[Mo_4(\eta\text{-}C_5H_4Pr^i)_4(\mu_3\text{-}Se)_4][Fe_4(NO)_4(\mu_3\text{-}S)_4]$	24.2 (24.0)	2.7 (2.7)	3.4 (3.5)	1752 1694		
5 $[Fe_4(\eta\text{-}C_5H_5)_4(\mu_3\text{-}S)_4][Fe_4(NO)_4(\mu_3\text{-}S)_4]$[e]	24.4 (24.2)	2.2 (2.3)	4.8 (4.9)	1755 1695	4.7 × 10^{-9}	0.91
6 $[Fe_4(\eta\text{-}C_5H_4Me)_4(\mu_3\text{-}S)_4][Fe_4(NO)_4(\mu_3\text{-}S)_4]$	25.3 (25.3)	2.2 (2.5)	4.8 (4.9)	1758 1709	1.5 × 10^{-9}	0.36
7 $[Cr_4(\eta\text{-}C_5H_5)_4(\mu_3\text{-}S)_4][Fe_4(NO)_4(\mu_3\text{-}S)_4]$	22.2 (22.5)	2.0 (1.9)	5.0 (5.2)	1761 1704		
8 $[Cr_4(\eta\text{-}C_5H_4Me)_4(\mu_3\text{-}S)_4][Fe_4(NO)_4(\mu_3\text{-}S)_4]$	25.9 (25.6)	2.5 (2.5)	5.0 (5.0)	1758 1712	5.4 × 10^{-9}	0.37
9 $[Cr_4(\eta\text{-}C_5H_4Me)_4(\mu_3\text{-}Se)_4][Fe_4(NO)_4(\mu_3\text{-}S)_4]$	21.5 (22.0)	2.1 (2.1)	4.1 (4.3)	1756 1710		
10 $[Mo_4(\eta\text{-}C_5H_4Pr^i)_4(\mu_3\text{-}S)_4]_2[Os_6(CO)_{18}]$	27.9 (27.9)	2.3 (2.5)				
11 $[Mo_4(\eta\text{-}C_5H_4Pr^i)_4(\mu_3\text{-}S)_4][tcnq]$	46.4 (46.2)	4.2 (4.2)	4.9 (4.9)	2179[f]	4.9 × 10^{-8}	0.73
12 $[Fe_4(\eta\text{-}C_5H_5)_4(\mu_3\text{-}S)_4][tcnq]$	46.6 (47.1)	2.8 (2.9)	6.8 (6.9)		4.4 × 10^{-5}	0.28
13 $[Fe_4(\eta\text{-}C_5H_4Me)_4(\mu_3\text{-}S)_4][tcnq]$	49.8 (49.5)	4.1 (3.7)	6.5 (6.4)			
14 $[Cr_4(\eta\text{-}C_5H_5)_4(\mu_3\text{-}S)_4][(tcnq)_2]$	52.9 (52.6)	3.0 (2.8)	11.1 (11.2)	2199[f]	5.8 × 10^{-5}	0.28
15 $[Cr_4(\eta\text{-}C_5H_4Me)_4(\mu_3\text{-}S)_4][tcnq]$	50.9 (50.5)	3.7 (3.7)	7.1 (6.5)			
16 $[Cr_4(\eta\text{-}C_5H_4Me)_4(\mu_3\text{-}S)_4][(tcnq)_2]$	54.3 (54.3)	3.3 (3.4)	10.5 (10.6)	2199[f]	2.3 × 10^{-6}	0.30
17 $[Cr_4(\eta\text{-}C_5H_4Me)_4(\mu_3\text{-}Se)_4][tcnq]$	41.9 (41.4)	3.3 (3.1)	5.9 (5.4)			
18 $[Cr_4(\eta\text{-}C_5H_4Me)_4(\mu_3\text{-}Se)_4][(tcnq)_2]$	46.3 (46.2)	3.0 (2.9)	8.8 (9.0)	2199[f]		
19 $[Mo_4(\eta\text{-}C_5H_4Pr^i)_4(\mu_3\text{-}Se)_4][tcnq]$	39.0 (39.6)	3.6 (3.6)	3.8 (4.2)			
20 $[Mo_4(\eta\text{-}C_5H_4Pr^i)_4(\mu_3\text{-}Se)_4][tcnq]_3$	46.6 (46.9)	3.6 (3.2)	8.9 (9.6)	2183[f]		
21 $[Mo_4(\eta\text{-}C_5H_4Pr^i)_4(\mu_3\text{-}Se)_4][Mo\{S_2C_2(CF_3)_2\}_3]$[g]	27.9 (27.8)	2.2 (2.3)				
22 $[Mo_4(\eta\text{-}C_5H_4Pr^i)_4(\mu_3\text{-}S)_4][Mo\{S_2C_2(CF_3)_2\}_3]$[h]	30.5 (30.8)	2.5 (2.6)				
23 $[Mo_4(\eta\text{-}C_5H_4Pr^i)_4(\mu_3\text{-}S)_4]_2[Mo\{S_2C_2(CF_3)_2\}_3]$	34.3 (34.4)	3.5 (3.3)				
24 $[Cr_4(\eta\text{-}C_5H_4Me)_4(\mu_3\text{-}S)_4][Mo\{S_2C_2(CF_3)_2\}_3]$	30.7 (30.3)	2.1 (2.0)				
25 $[Cr_4(\eta\text{-}C_5H_4Me)_4(\mu_3\text{-}Se)_4][Mo\{S_2C_2(CF_3)_2\}_3]$	27.0 (26.8)	1.8 (1.7)				
26 $[Mo_4(\eta\text{-}C_5H_4Pr^i)_4(\mu_3\text{-}S)_4][Ni\{S_2C_2(CN)_2\}_2]$	37.6 (37.5)	3.5 (3.4)	4.4 (4.4)			
27 $[Cr_4(\eta\text{-}C_5H_4Me)_4(\mu_3\text{-}S)_4][tcne]$	45.8 (46.1)	3.8 (3.6)	7.2 (7.2)		5.5 × 10^{-6}	0.47

[a] Data given as found (calculated) (w/w). [b] Proton NMR data (in C_6D_6, 300 MHz): δ 1.05 (d, *J* 6.7, 24 H, CH*Me*$_2$), 2.80 (spt, *J* 6.8, 4 H, C*H*Me$_2$), 5.08 (virtual t, *J* 2.1, 8 H, $C_5H_4Pr^i$) and 5.24 (m, *J* 2.1 Hz, 8 H, $C_5H_4Pr^i$). [c] Proton NMR data (in C_6D_6, 300 MHz): δ 1.85 (s, 12 H, CH_3), 5.08 (m, 8 H, C_5H_4Me) and 5.24 (m, 8 H, C_5H_4Me). Cr 23.9 (24.7%). [d] Fe 15.4 (15.9%). [e] Fe 38.6 (39.2%). [f] For neutral tcnq, $[NEt_3H]^+[(tcnq)_2]^-$, and $K^+[tcnq]^-$ ν(CN) is 2221, 2199 and 2179 cm^{-1}, respectively. [g] ν(C=C) of $[Mo\{S_2C_2(CF_3)_2\}_3]$: 1530 cm^{-1}. $\chi_{corr} = -9.7 \times 10^{-4}$ emu mol^{-1}. [h] ν(C=C) of $[Mo\{S_2C_2(CF_3)_2\}_3]$: 1531 cm^{-1}. Proton NMR data (in C_6D_6, 300 MHz): δ 1.23 (d, *J* 6.9, 24 H, CH*Me*$_2$), 2.80 (spt, *J* 6.9 Hz, 4 H, C*H*Me$_2$), 5.80 (m, 8 H, $C_5H_4Pr^i$) and 6.32 (m, 8 H, $C_5H_4Pr^i$).

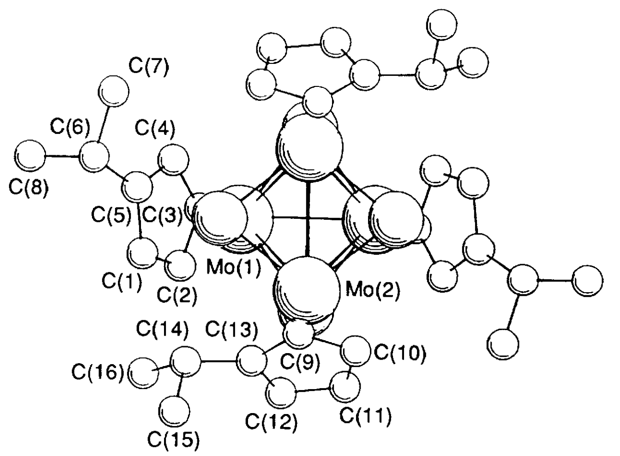


Fig. 1 Molecular structure of $[Mo_4(\eta\text{-}C_5H_4Pr^i)_4(\mu_3\text{-}Se)_4]$. Hydrogen atoms omitted for clarity

Results

Synthesis of New Cubane Clusters of Molybdenum and Chromium.—During this study we prepared some new neutral cubane cluster compounds and this work is described first.

The binuclear compound $[Mo_2(\eta\text{-}C_5H_4Pr^i)_2(\mu\text{-}Cl)_4]$[10] was treated with an excess of LiSeH giving slightly air-sensitive, black needle-like crystals of $[Mo_4(\eta\text{-}C_5H_4Pr^i)_4(\mu_3\text{-}Se)_4]$ **1**. Single crystals suitable for X-ray structural analysis were obtained by recrystallization from acetone solution. The compound $[Cr(\eta\text{-}C_5H_4Me)_2]$ was treated with H_2Se giving black needle-like crystals of $[Cr_4(\eta\text{-}C_5H_4Me)_4(\mu_3\text{-}Se)_4]$ **2**, in >90% yield. Analytical data for **1**, **2**, and all the other new compounds described herein are given in Table 1.

An X-ray crystal structure determination of compound **1** has been carried out. The molecular structure (Fig. 1) is closely similar to that of the cluster $[Mo_4(\eta\text{-}C_5H_4Pr^i)_4(\mu_3\text{-}S)_4]$.[5] Table 2 summarizes the crystal data and data collection and processing parameters, selected bond lengths and angles are listed in Table 3, and final fractional atomic coordinates are shown in Table 4.

The cyclic voltammograms of compounds **1** and **2** each show two reversible one-electron oxidation waves corresponding to the formation of the mono- and di-cations. The data in Table 5 show that the selenium clusters are more reducing than the corresponding sulphur analogues. The He I and He II photoelectron specta of **1** and **2** have been recorded and the adiabatic first ionization energies are given in Table 5. The detailed assignment and the metal–metal bonding in these clusters is discussed elsewhere.[11]

Table 6 summarizes the published half-wave reduction potentials of some cubane clusters and other electron donor or acceptor compounds used in the studies described below. These data were determined using different solvents and reference electrodes which preclude precise comparisons. We have compiled a list of estimated redox potentials using ferrocene–ferrocenium as the reference electrode. Since the shift in solution redox potential induced by a change of solvent and/or supporting electrolyte is typically small (normally less than 0.1 V), and cannot be easily rationalized or unified, we only consider the reference electrodes and neglect the effects caused by the solvents. The half-wave reduction potential of ferrocene–ferrocenium was found to be +0.84 V *versus* platinum wire in

Table 2 Crystal data, data collection and processing parameters[a]

	1	**3a**	**3b**
Formula	$C_{32}H_{44}Mo_4Se_4$	$C_{32}H_{44}Fe_4Mo_4N_4O_4S_4$	$C_{32}H_{44}Fe_4Mo_4N_4O_4S_4$
M	1128.9	1412.35	1412.35
Crystal size/mm	0.15 × 0.20 × 0.35	0.18 × 0.23 × 0.60	0.45 × 0.48 × 0.58
Crystal system	Monoclinic	Monoclinic	Orthorhombic
Space group	$I2/a$	$P2_1/n$	$Pbcn$
a/Å	18.043(2)	12.625(6)	31.530(8)
b/Å	8.629(1)	30.348(7)	13.621(3)
c/Å	23.274(3)	12.734(6)	22.033(6)
α/°	90	90	90
β/°	108.57(1)	109.92(4)	90
γ/°	90	90	90
U/Å^3	3435.1	4590.0	9462.0
Z	4	4	8
D_c/g cm^{-3}	2.18	2.05	1.98
μ/cm^{-1}	56.14	26.50	25.7
$F(000)$	2160	2784	5568
2θ limits/°	2–60	2–50	2–55
Total unique data collected	3575	5894	7891
No. of observations [$I > 3\sigma(I)$]	3499	5200	7820
No. of variables	182	506	506
Observations/variables	19.2	10.3	15.5
Weighting coefficients	13.93, −10.96, 10.15	70.9, 95.6, 31.0	1058.8, 1450.7, 417.1
Largest residual peak in final difference map/e Å^{-3}	0.21	0.63	0.16
R(merg)	0.018	0.016	0.030
R[b]	0.027	0.036	0.039
R'[c]	0.030	0.052	0.058

	5·Me_2CO	**6**	**10a**
Formula	$C_{23}H_{26}Fe_8N_4O_5S_8$	$C_{24}H_{28}Fe_8N_4O_4S_8$	$C_{82}H_{88}Mo_8O_{18}Os_6S_8$
M	1141.68	1139.71	3526.46
Crystal size/mm	0.12 × 0.65 × 0.45	0.34 × 0.56 × 0.06	0.40 × 0.55 × 0.46
Crystal system	Triclinic	Monoclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/c$	$C2/c$
a/Å	9.642(1)	19.451(2)	22.377(19)
b/Å	12.546(3)	19.911(6)	20.007(10)
c/Å	17.137(10)	19.413(6)	22.282(8)
α/°	113.74(4)	90	90
β/°	91.67(2)	95.72(2)	95.23(4)
γ/°	100.30(1)	90	90
U/Å^3	1855.0	7481	9934
Z	2	8	4
D_c/g cm^{-3}	2.04	2.02	2.36
μ/cm^{-1}	3.58	3.55	9.26
$F(000)$	1136	4544	6576
2θ limits/°	0–55	2–50	0–55
Total unique data collected	8499	8958	11 355
No. of observations [$I > 3\sigma(I)$]	6813	6585	7257
No. of variables	520	828	576
Observations/variables	13.1	7.9	12.6
Weighting coefficients	223, 300, 88.2	18.2, 12.4	57.7, 72.5, 27.3
Largest residual peak in final difference map/e Å^{-3}	0.24	0.55	0.54
R(merg)	0.013	0.024	0.025
R[b]	0.030	0.059	0.032
R'[c]	0.039	0.069	0.045

	10b	**11**	**13**
Formula	$C_{82}H_{88}Mo_8O_{18}Os_6S_8$	$C_{44}H_{48}Mo_4N_4S_4$	$C_{36}H_{32}Fe_4N_4S_4$
M	3526.46	1144.9	827.8
Crystal size/mm	0.10 × 0.20 × 0.23	0.22 × 0.20 × 0.11	1.03 × 0.83 × 0.13
Crystal system	Monoclinic	Triclinic	Monoclinic
Space group	$P2_1/a$	$P\bar{1}$	$P2/n$
a/Å	30.894(14)	10.689(5)	21.522(9)
b/Å	15.104(3)	10.976(1)	7.498(6)
c/Å	20.962(8)	20.097(4)	21.907(13)
α/°	90	93.626(13)	90
β/°	91.92(4)	95.22(3)	98.52(4)
γ/°	90	105.08(2)	90
U/Å^3	9776.4	2257.8	3496
Z	4	2	4
D_c/g cm^{-3}	2.40	1.68	1.66
μ/cm^{-1}	9.26	12.73	1.93

Table 2 (*continued*)

	10b	**11**	**13**
F(000)	6576	1144	1776
2θ limits/°	2–46	2–50	2–53
Total unique data collected	7782	7257	6729
No. of observations [$I > 3\sigma(I)$]	7323	7135	6233
No. of variables	581	506	436
Observations/variables	12.6	7.9	14.3
Weighting coefficients	9.04, 0.198	3.66, −2.79, 2.68, −0.403	514, 688, 194
Largest residual peak in final difference map/e Å^{-3}	0.70	0.35	0.19
R(merg)	0.033	0.014	0.033
R^b	0.066	0.024	0.043
R'^c	0.082	0.026	0.064

[a] Details in common: Mo-Kα radiation (λ = 0.710 69 Å); scan mode ω–2θ; Chebyshev weighting scheme. [b] $R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$. [c] $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}}$.

Table 3 Average bond distances (Å) and angles (°) for $[Mo_4(\eta\text{-}C_5H_4Pr^i)_4(\mu_3\text{-}E)_4]$ (E = Se, **1**; or S)

	$[Mo_4(\eta\text{-}C_5H_4Pr^i)_4(\mu_3\text{-}Se)_4]$ **1**	$[Mo_4(\eta\text{-}C_5H_4Pr^i)_4(\mu_3\text{-}S)_4]^5$
M–M	2.987	2.904
M–E	2.464	2.344
E • • • E	3.869	3.643
Mo–Mo–Mo	60.0	60.0
Mo–E–Mo	74.67	76.56
E–Mo–E	103.44	101.98
Mo–Cp*	2.348	2.357

* Cp refers to the computed η-$C_5H_4Pr^i$ ring centroid.

Table 4 Fractional atomic coordinates for $[Mo_4(\eta\text{-}C_5H_4Pr^i)_4(\mu_3\text{-}Se)_4]$ **1** with estimated standard deviations (e.s.d.s) in parentheses

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Mo(1)	0.261 29(2)	−0.018 49(3)	0.066 13(1)
Mo(2)	0.336 49(2)	0.227 87(3)	0.012 56(1)
Se(1)	0.137 40(2)	−0.052 47(4)	−0.016 78(2)
Se(2)	0.265 65(2)	0.262 50(4)	0.086 36(1)
C(1)	0.325 4(3)	−0.079 8(6)	0.167 8(2)
C(2)	0.333 4(3)	−0.206 9(6)	0.133 0(2)
C(3)	0.259 2(3)	−0.267 0(5)	0.104 5(2)
C(4)	0.204 6(3)	−0.177 6(5)	0.122 9(2)
C(5)	0.245 3(3)	−0.060 9(5)	0.162 5(2)
C(6)	0.215 7(3)	0.049 1(5)	0.200 4(2)
C(7)	0.131 8(4)	0.097(1)	0.170 5(3)
C(8)	0.227 0(5)	−0.021 9(8)	0.262 6(2)
C(9)	0.394 5(2)	0.473 4(4)	0.028 0(2)
C(10)	0.405 1(3)	0.413 2(6)	−0.024 9(2)
C(11)	0.451 8(2)	0.279 9(6)	−0.008 7(2)
C(12)	0.472 1(2)	0.261 0(5)	0.054 9(2)
C(13)	0.437 2(2)	0.381 5(5)	0.078 4(2)
C(14)	0.451 5(3)	0.423 5(5)	0.143 6(2)
C(15)	0.515 2(3)	0.547 1(6)	0.162 1(2)
C(16)	0.474 0(4)	0.285 1(7)	0.186 7(2)

Table 5 Reduction potentials and first ionization energies for $[M_4(\eta\text{-}C_5H_4R)_4(\mu_3\text{-}E)_4]$ (M = Mo or Cr, R = Pr^i or Me, E = S or Se)

	$E_{\frac{1}{2}}{}^a$/V		
Compound	C^+–C	C^{2+}–C^+	Ionization energy^b/eV
$[Mo_4(\eta\text{-}C_5H_4Pr^i)_4(\mu_3\text{-}Se)_4]$ **1**	−0.91	−0.32	4.88
$[Cr_4(\eta\text{-}C_5H_4Me)_4(\mu_3\text{-}Se)_4]$ **2**	−0.66	−0.06	5.41
$[Mo_4(\eta\text{-}C_5H_4Pr^i)_4(\mu_3\text{-}S)_4]^5$	−0.82	−0.22	4.99
$[Cr_4(\eta\text{-}C_5H_4Me)_4(\mu_3\text{-}S)_4]^{c,11c}$	−0.52	+0.31	5.41

[a] *vs.* ferrocene–ferrocenium. [b] Adiabatic.[5,11a,c] [c] Values measured against Pt–PtO and converted approximately against ferrocene–ferrocenium by taking the latter as being +0.84V *vs.* Pt–PtO.

tetrahydrofuran (thf) and this value has been used when comparing data.

Synthesis of Cluster Salts of the Anions $[Fe_4(NO)_4(\mu_3\text{-}S)_4]^-$ *and* $[Os_6(CO)_{18}]^{2-}$.—The synthesis of the 'soft salts' were carried out by mixing toluene solutions of the neutral donor and acceptor clusters and normally precipitates appeared immediately. Recrystallizations were carried out in acetone. The new soft salts are listed in Table 1, together with characterizing data. All the salts containing the $[Fe_4(NO)_4(\mu_3\text{-}S)_4]$ moiety have the stoichiometry 1:1, *i.e.* $[C]^{n+}[A]^{n-}$, whereas the salt **10** containing the anion $[Os_6(CO)_{18}]^{n-}$ has a cation:anion ratio of 2:1. The question arises as to the magnitude of *n*.

We consider first the salts of the anion $[Fe_4(NO)_4(\mu_3\text{-}S)_4]^{n-}$. The infrared spectrum of the neutral cluster $[Fe_4(NO)_4(\mu_3\text{-}S_4)]$ exhibits one sharp nitrosyl stretching frequency at 1788 cm^{-1} whilst the (4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]-hexacosane)potassium salt of the monoanion $[Fe_4(NO)_4(\mu_3\text{-}S)_4]^-$ shows three bands at 1712s, 1740s and 1755m cm^{-1} assignable to ν(NO).[6]

The infrared spectra of the salts containing the anion $[Fe_4(NO)_4(\mu_3\text{-}S_4)]^{n-}$ (**3**–**9** in Table 1) show two peaks assignable to ν(NO). Typically there is a sharp medium–strong absorption around 1758 cm^{-1} and a broad strong band between 1694 and 1712 cm^{-1}. This suggests that $n = 1$ for the salts of the $[Fe_4(NO)_4(\mu_3\text{-}S_4)]^{n-}$ cluster. The solution NMR spectra of the soft salts **3**–**10** did not show any sharp resonances and this indicates the presence of paramagnetic ions.

The salt $[Mo_4(\eta\text{-}C_5H_4Pr^i)_4(\mu_3\text{-}S)_4][Fe_4(NO)_4(\mu_3\text{-}S)_4]$ **3** was investigated more thoroughly. The magnetic moment of this compound in the solid state at room temperature was found to be 2.48 (Table 7), which corresponds to two unpaired electrons per formula unit assuming the spin-only formula. The neutral $[Mo_4(\eta\text{-}C_5H_4Pr^i)_4(\mu_3\text{-}S)_4]$ and its dication are diamagnetic whilst the monocation is paramagnetic with one unpaired electron.[5] Likewise neutral $[Fe_4(NO)_4(\mu_3\text{-}S)_4]$ is

Table 6 Reduction potentials

(*a*) Donor cluster

Compound	$E_{\frac{1}{2}}$/V C^+–C	 C^{2+}–C^+	Solvent[a]	Reference electrode	Ref.
$[Mo_4(\eta\text{-}C_5H_4Pr^i)_4(\mu\text{-}S)_4]$	−0.33	+0.32	dmf	SCE	8
	−0.82	−0.22	thf	*b*	11*b*
$[Fe_4(\eta\text{-}C_5H_5)_4(\mu\text{-}S)_4]^c$	−0.33	+0.33	MeCN	SCE	1
$[Cr_4(\eta\text{-}C_5H_4Me)_4(\mu\text{-}S)_4]$	+0.32	+1.15	thf	Platinum wire	11*c*
$[Fe_4(\eta\text{-}C_5H_4Me)_4(\mu\text{-}S)_4]^d$	+0.08	+0.67	thf	Platinum wire	12
$[Mo_4(\eta\text{-}C_5H_4Pr^i)_4(\mu\text{-}Se)_4]$	−0.91	−0.32	thf	*b*	11*b*
$[Cr_4(\eta\text{-}C_5H_4Me)_4(\mu\text{-}Se)_4]$	−0.66	−0.06	thf	*b*	11*b*

(*b*) Acceptor molecule

Compound	$E_{\frac{1}{2}}$/V A–A^-	 A^-–A^{2-}	Solvent	Reference electrode	Ref.
$[Fe_4(NO)_4S_4]$	+0.13	−0.65	CH_2Cl_2	SCE	6
$[Os_6(CO)_{18}]$	+0.04[e]		thf	SCE	13*a*
tcnq	+0.17	−0.37	MeCN	SCE	13*b*
tcne	+0.15	−0.57	MeCN	SCE	13*b*
$[Mo\{S_2C_2(CF_3)_2\}_3]$	+0.95	+0.36	MeCN	SCE	14
$[Ni\{S_2C_2(CN)_2\}_2]$	+1.02	+0.23	MeCN	SCE	14

[a] dmf = Dimethylformamide. [b] Ferrocene–ferrocenium. [c] This cluster shows four reversible one-electron waves in the cyclic voltammogram. The other two are at +0.88 (C^{3+}–C^{2+}) and +1.41 V (C^{4+}–C^{3+}). [d] There is a third potential at +1.215 V (C^{3+}–C^{2+}). [e] For $[Os_6(CO)_{18}] + 2e^- \longrightarrow [Os_6(CO)_{18}]^{2-}$.

Table 7 Magnetic data for some cluster salts

Compound	C/emu mol^{-1} k^{-1}	θ	μ_{eff}	χ_0 emu mol^{-1}	χ_{dia} emu mol^{-1}	$\chi_{t.i.p.}$ emu mol^{-1}
3	0.77	−0.67	2.48	-5.44×10^{-4}	-7.83×10^{-4}	$\approx 2.00 \times 10^{-4}$
10	0.932	−0.97	2.73	-1.67×10^{-3}	-1.78×10^{-3}	1.12×10^{-4}
11	0.84	−7.5	2.59	-6.72×10^{-4}	-7.07×10^{-4}	3.54×10^{-5}
16	0.8	−2.26	2.53	-3.30×10^{-4}	-5.95×10^{-4}	2.65×10^{-4}
17	0.58	−1.33	2.15			
21				-9.70×10^{-4}	-9.70×10^{-4}	
27	0.83	−3.8	2.57	-3.19×10^{-4}	-4.40×10^{-4}	1.21×10^{-4}

diamagnetic and the monoanion $[Fe_4(NO)_4(\mu_3\text{-}S)_4]^-$ is paramagnetic.[6] The crystal structure of **3** has been determined and shows that the intramolecular metal–metal distances and other crystal parameters are in good agreement with those found in other salts of the component monocation and monoanion rather than with those of the dication and dianion (see below).

Finally, using the redox data for the component cations and anions (Table 6) we can estimate the magnitude of ΔG for the equilibrium $[C]^+[A]^- \Leftrightarrow [C]^{2+}[A]^{2-}$ given by equation (1).

$$\Delta G = -nFE = -nF[E(A^--A^{2-}) - E(C^{2+}-C^+)]$$
$$= -nF(-0.65 - 0.32) \qquad = 0.97F \geqslant 0 \quad (1)$$

Therefore we estimate the equilibrium constant (K) from the expression (2), giving the value $K = 10^{-16}$. Thus, the redox

$$\log K = n\Delta E/0.059 = -0.97/0.059 = -16 \quad (2)$$

potential data place the equilibrium towards the salt $[C]^+[A]^-$. The redox potentials for the other soft salts **3**–**9** similarly suggest that these compounds are also likely to have the value $n = 1$.

The salt **10** has cation:anion ratio of 2:1, even though reactions between $[Mo_4(\eta\text{-}C_5H_4Pr^i)_4(\mu_3\text{-}S)_4]$ and $[Os_6(CO)_{18}]$ were carried out using varying molar ratios of the neutral cluster precursors. The crystal structure of **10** has been determined and shows the anion to be $[Os_6(CO)_{18}]^{2-}$.

The Crystal Structures of Compounds **3**, **5**, **6** *and* **10**.—Table 2 summarizes the crystal data and data collection and processing parameters for compounds **3**, **5**, **6** and **10**. Final fractional atomic coordinates are listed in Tables 8–13. The structures of two crystalline forms of the salt **3**, obtained from two separate preparations, were determined. The two forms had different space groups and will be referred to as **3a** (space group $P2_1/n$) and **3b** (space group $Pbcn$). Two crystalline forms of the salt **10** were also obtained using different ratios of starting material and different solvents. Again the two forms belong to different space groups and will be referred to as **10a** ($C2/c$) and **10b** ($P2_1/a$). Here we report in detail only those data which are relevant to the determination of the charge n of the salts and their crystal packing.

Selected average bond lengths of the $[Fe_4(\eta\text{-}C_5H_4R)_4(\mu_3\text{-}S)_4]^{n+}$ (R = H or Me) moiety in the salts **5** and **6** together with the corresponding data for $[Fe_4(\eta\text{-}C_5H_5)_4(\mu_3\text{-}S)_4]Br$, $[Fe_4(\eta\text{-}C_5H_5)_4(\mu_3\text{-}S)_4]^{2+}2PF_6^-$ and $[Fe_4(\eta\text{-}C_5H_5)_4(\mu_3\text{-}S)_4]$ are given in Table 14. The data show that the overall average of the iron–iron distances decreases slightly with increasing n in the series $[Fe_4(\eta\text{-}C_5H_5)_4(\mu_3\text{-}S)_4]^{n+}$ while the sulphur–sulphur distances increase. Thus the average Fe–Fe distances in the $[Fe_4(\eta\text{-}C_5H_4R)_4(\mu_3\text{-}S)_4]^{n+}$ moiety in the salts **5** and **6** are 3.048 and 3.033 Å, which are closer to that observed for $[Fe_4(\eta\text{-}C_5H_5)_4(\mu_3\text{-}S)_4]Br$ (3.053 Å) than that for $[Fe_4(\eta\text{-}C_5H_5)_4(\mu_3\text{-}S)_4]^{2+}2PF_6^-$ (2.974 Å).

Table 15 gives the corresponding selected average bond lengths for the $[Fe_4(NO)_4(\mu_3\text{-}S)_4]^{n-}$ species in the salts **3a**, **3b**, **5**

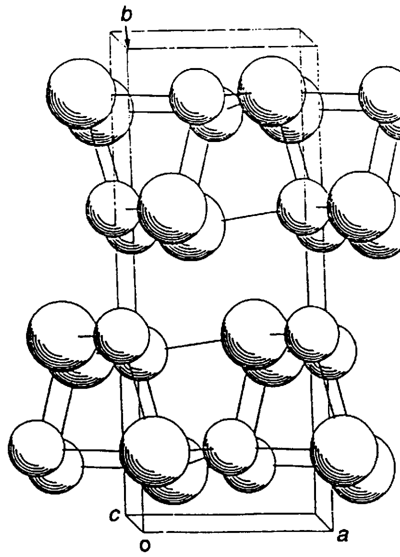


Fig. 2 Molecular packing of $[\mathrm{Mo_4(\eta\text{-}C_5H_4Pr^i)_4(\mu_3\text{-}S)_4}][\mathrm{Fe_4(NO)_4(\mu_3\text{-}S)_4}]$ **3** in its monoclinic form **3a**. The larger spheres represent cations and the smaller, anions

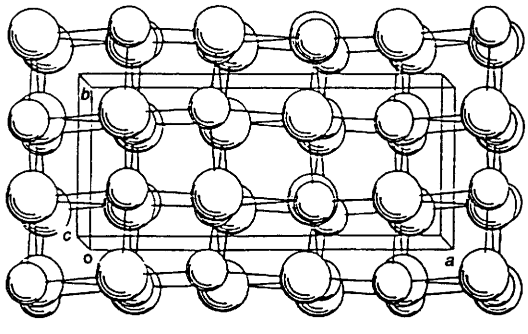


Fig. 3 Molecular packing of compound **3** in its orthorhombic form **3b**

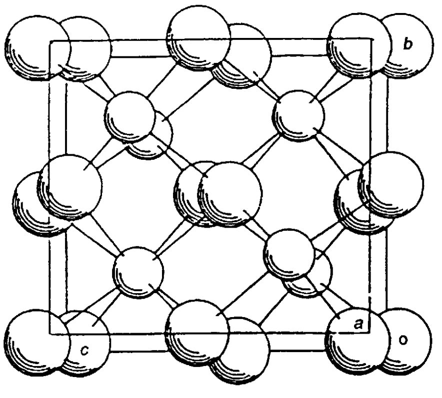


Fig. 4 Molecular packing of $[\mathrm{Mo_4(\eta\text{-}C_5H_4Pr^i)_4(\mu_3\text{-}S)_4}]_2[\mathrm{Os_6(CO)_{18}}]$ **10** in one of its monoclinic forms (**10a**, space group *C*2/*c*)

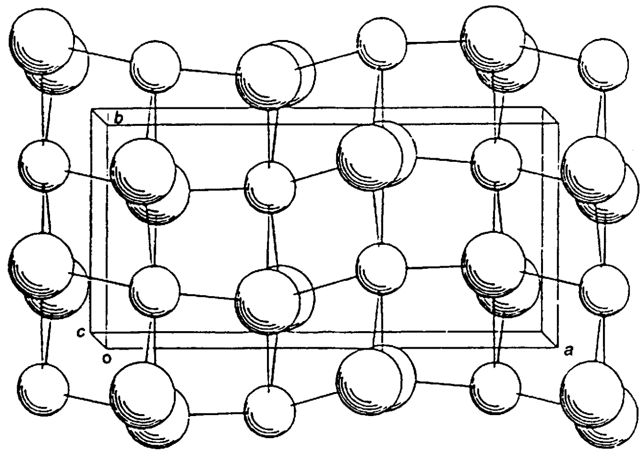


Fig. 5 Molecular packing of compound **10** in one of its monoclinic forms (**10b**, space group *P*2$_1$/*a*)

and **6**. Corresponding distances found for the bicyclohexacosane potassium salt of the monoanion $[\mathrm{Fe_4(NO)_4(\mu_3\text{-}S)_4}]^-$ and neutral cluster $[\mathrm{Fe_4(NO)_4(\mu_3\text{-}S)_4}]$ are also listed for comparison.[6,15] These data show that the average iron–iron distance in monoanionic $[\mathrm{Fe_4(NO)_4(\mu_3\text{-}S)_4}]^-$ (2.693 Å) is longer than that in the neutral cubane $[\mathrm{Fe_4(NO)_4(\mu_3\text{-}S)_4}]$ (2.651 Å). The average iron–iron distances of the salts **3a**, **3b**, **5** and **6** lie in the range 2.688–2.695 Å, in good agreement with those of the monoanion.

Average bond lengths for the $[\mathrm{Mo_4(\eta\text{-}C_5H_4Pr^i)_4(\mu_3\text{-}S)_4}]^{n+}$ cation in the salts **3a**, **3b**, **10a** and **10b** and those for authentic neutral ($n = 0$), monocationic ($n = 1$) and dicationic ($n = 2$) clusters are given in Table 16. It is notable that there is no marked difference in the average Mo–Mo distance when one electron is removed from the neutral cluster, but there is a somewhat larger change when the dication is formed. The observed averaged Mo–Mo distances in the cluster salts are closer to that of the monocation than that of the dication.

The X-ray structures of the salts **10a** and **10b** show that the $\mathrm{Os_6(CO)_{18}}$ moiety is octahedral and has dimensions corresponding to those of the dianion.[13] This is to be expected since the cyclic voltammogram of $\mathrm{Os_6(CO)_{18}}$ shows a reversible two-electron reduction [$E_{\frac{1}{2}} = 0.04$ V *vs.* saturated calomel electrode (SCE)] giving the dianion.[13]

In a first consideration of the packing of the component molecular ions of the salts **3a**, **3b**, **10a** and **10b** the cations and anions were approximated as spheres in the lattices. The resulting packing diagrams of the crystal structures of **3a** and **3b** are shown in Figs. 2 and 3. The structures are not those predicted by the ionic model. For example, compound **3** has an estimated radius ratio $r^+/r^- = 1.3{:}1$ which predicts a CsCl structure but in **3a** the inner co-ordination sphere of the cation is a distorted tetrahedron of anions which pack to give the layered arrangement shown (Fig. 2). In the **3b** form the cation has a distorted trigonal-bipyramidal environment of anions. In contrast, compound **10**, for which the radius ratio is again approximately $r^+/r^- = 1.3{:}1$ (but with two cations and one anion per formula unit), has the expected anti-fluorite arrangement of cations in both alternative monoclinic forms, **10a** and **10b** (Figs. 4 and 5 respectively). A greater contribution to the lattice energy of **10**, arising from the greater charge component, may be responsible in this case for the adoption of a structure predicted by the ionic model. It is possible that we have not found all the different packing arrangements of these salts and that additional forms may be observed.

The electrical conductivities of the salts **3**–**7** have been determined using a two-probe technique. The data are given in Table 1 together with activation energies calculated from the expression $\sigma = \sigma_0 e^{-E_a/kT}$. We conclude that these salts are poor semiconductors.

Static magnetic susceptibility data from room temperature to 4 K for several salts have been determined using the Faraday technique and the data are shown in Table 7. Compound **3** is paramagnetic with an effective magnetic moment, $\mu_{\mathrm{eff}} = 2.48$ corresponding to two unpaired electrons per ion pair, which is consistent with the formulation of this salt as $[\mathrm{Mo_4(\eta\text{-}C_5H_4Pr^i)_4(\mu_3\text{-}S)_4}]^+[\mathrm{Fe_4(NO)_4(\mu_3\text{-}S)_4}]^-$. The temperature dependence of the static susceptibility obeys the Curie–Weiss law. The values of χ_0, C, θ, χ_{dia}, and t.i.p. (temperature-independent paramagnetism) are given in Table 7 ($\chi_0 = \chi_{\mathrm{dia}}$ + t.i.p.). Compound **10** is also paramagnetic (Table 7) with μ_{eff} of

Table 8 Fractional atomic coordinates for $[Mo_4(\eta\text{-}C_5H_4Pr^i)_4(\mu_3\text{-}S)_4][Fe_4(NO)_4(\mu_3\text{-}S)_4]$ **3a** with e.s.d.s in parentheses

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*	Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Mo(1)	0.128 79(6)	0.143 98(3)	0.328 43(6)	C(13)	0.302(1)	0.012 8(4)	0.396(1)
Mo(2)	0.293 48(6)	0.081 70(3)	0.304 21(6)	C(14)	0.224(2)	−0.005 5(5)	0.449(1)
Mo(3)	0.330 53(6)	0.175 84(2)	0.290 27(6)	C(15)	0.204(2)	0.020 4(6)	0.539(1)
Mo(4)	0.157 89(6)	0.130 19(2)	0.114 08(6)	C(16)	0.133(2)	−0.033(1)	0.384(2)
Fe(1)	0.040 1(1)	0.402 28(5)	0.427 7(1)	C(17)	0.478 1(7)	0.214 4(3)	0.256 4(8)
Fe(2)	0.085 1(1)	0.373 91(5)	0.244 4(1)	C(18)	0.516 6(7)	0.200 4(3)	0.368 0(8)
Fe(3)	−0.071 5(1)	0.332 87(5)	0.307 9(1)	C(19)	0.453 7(8)	0.221 5(3)	0.425 3(7)
Fe(4)	0.149 1(1)	0.326 56(5)	0.433 9(1)	C(20)	0.375 1(7)	0.248 4(3)	0.348 8(7)
S(1)	0.096 6(2)	0.079 67(8)	0.220 0(2)	C(21)	0.389 9(7)	0.245 0(3)	0.242 4(7)
S(2)	0.317 5(2)	0.135 42(8)	0.442 0(2)	C(22)	0.328 7(7)	0.273 9(3)	0.141 3(7)
S(3)	0.353 5(2)	0.119 72(7)	0.174 0(2)	C(23)	0.385(1)	0.318 6(4)	0.157(1)
S(4)	0.143 3(2)	0.196 84(7)	0.200 0(2)	C(24)	0.329(1)	0.252 4(4)	0.033 2(8)
S(5)	0.208 8(2)	0.393 94(9)	0.410 0(2)	C(25)	0.165 1(8)	0.137 9(4)	−0.067 4(7)
S(6)	−0.076 6(2)	0.402 5(1)	0.249 0(2)	C(26)	0.085 6(8)	0.167 9(3)	−0.056 6(7)
S(7)	0.065 3(2)	0.302 17(9)	0.259 8(2)	C(27)	−0.002 6(8)	0.143 5(4)	−0.039 5(8)
S(8)	0.004 5(2)	0.338 48(9)	0.492 4(2)	C(28)	0.023 5(8)	0.098 8(4)	−0.043 2(7)
C(1)	0.016 1(8)	0.120 4(4)	0.431 7(8)	C(29)	0.128 7(8)	0.094 5(3)	−0.058 2(7)
C(2)	0.096 1(9)	0.149 7(4)	0.497 0(8)	C(30)	0.189(1)	0.052 9(4)	−0.073 9(9)
C(3)	0.077(1)	0.191 9(4)	0.445(1)	C(31)	0.179(1)	0.048 7(5)	−0.195(1)
C(4)	−0.018 1(9)	0.186 6(3)	0.347 1(9)	C(32)	0.149(2)	0.011 4(5)	−0.031(1)
C(5)	−0.055 9(7)	0.143 9(3)	0.339 1(7)	N(1)	0.034 9(9)	0.441 7(3)	0.514 8(9)
C(6)	−0.165 9(7)	0.128 1(3)	0.252 8(8)	O(1)	0.036(1)	0.467 0(4)	0.585 4(9)
C(7)	−0.263 2(9)	0.147 7(5)	0.279(1)	N(2)	0.117 1(9)	0.384 9(4)	0.132 2(8)
C(8)	−0.176(1)	0.078 4(4)	0.252(1)	O(2)	0.141(1)	0.388 7(4)	0.050 2(8)
C(9)	0.401(1)	0.036 9(3)	0.453(1)	N(3)	−0.193 2(8)	0.305 8(4)	0.266 1(8)
C(10)	0.459(1)	0.041 9(4)	0.379(1)	O(3)	−0.276 3(7)	0.285 0(4)	0.242 7(8)
C(11)	0.399(1)	0.022 7(5)	0.280(1)	N(3)	0.247 1(7)	0.294 7(3)	0.518 9(6)
C(12)	0.300(1)	0.004 0(4)	0.286(1)	O(4)	0.316 9(7)	0.271 9(3)	0.579 8(6)

Table 9 Fractional atomic coordinates for $[Mo_4(\eta\text{-}C_5H_4Pr^i)_4(\mu_3\text{-}S)_4][Fe_4(NO)_4(\mu_3\text{-}S)_4]$ **3b** with e.s.d.s in parentheses

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*	Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Mo(1)	0.645 30(2)	0.277 39(4)	0.433 41(2)	C(13)	0.600 0(2)	0.498 6(5)	0.584 6(3)
Mo(2)	0.636 49(2)	0.352 82(4)	0.554 55(2)	C(14)	0.560 3(3)	0.540 2(6)	0.558 1(4)
Mo(3)	0.685 21(2)	0.175 75(4)	0.531 99(2)	C(15)	0.556 8(4)	0.648 3(8)	0.574 1(6)
Mo(4)	0.593 19(2)	0.174 61(4)	0.520 61(2)	C(16)	0.521 4(3)	0.489(1)	0.580 2(5)
Fe(1)	0.648 10(4)	—0.120 73(8)	0.324 44(5)	C(17)	0.714 2(2)	0.049 4(5)	0.589 7(4)
Fe(2)	0.593 30(4)	—0.267 11(9)	0.346 67(5)	C(18)	0.723 0(3)	0.028 6(6)	0.530 2(4)
Fe(3)	0.639 45(4)	—0.191 23(9)	0.438 47(5)	C(19)	0.749 2(2)	0.101 6(7)	0.507 8(3)
Fe(4)	0.677 63(4)	—0.299 56(8)	0.352 63(5)	C(20)	0.757 6(2)	0.168 7(6)	0.554 2(4)
S(1)	0.583 35(5)	0.332 7(1)	0.481 14(7)	C(21)	0.736 3(2)	0.137 5(5)	0.606 6(3)
S(2)	0.698 82(5)	0.335 0(1)	0.497 61(7)	C(22)	0.737 6(3)	0.181 5(7)	0.669 6(4)
S(3)	0.634 18(5)	0.203 5(1)	0.606 96(7)	C(23)	0.755 0(4)	0.283(1)	0.670 9(6)
S(4)	0.643 83(5)	0.108 7(1)	0.454 21(8)	C(24)	0.761 9(4)	0.114 7(9)	0.712 4(5)
S(5)	0.640 00(8)	—0.257 4(2)	0.271 21(8)	C(25)	0.561 6(2)	0.020 3(5)	0.530 8(4)
S(6)	0.590 08(7)	—0.114 8(2)	0.382 7(1)	C(26)	0.542 7(2)	0.068 4(6)	0.481 3(4)
S(7)	0.628 01(9)	—0.349 4(2)	0.418 1(1)	C(27)	0.520 8(2)	0.149 5(6)	0.502 6(4)
S(8)	0.699 46(7)	—0.156 3(2)	0.390 1(1)	C(28)	0.527 0(2)	0.153 3(6)	0.566 5(4)
C(1)	0.647 7(3)	0.394 7(6)	0.357 0(3)	C(29)	0.551 1(2)	0.070 8(6)	0.584 6(4)
C(2)	0.686 6(3)	0.345(1)	0.356 4(4)	C(30)	0.561 7(3)	0.036 1(8)	0.647 5(5)
C(3)	0.678 9(3)	0.248 0(9)	0.341 6(3)	C(31)	0.539 0(6)	−0.060(1)	0.658 0(7)
C(4)	0.635 2(3)	0.237 6(6)	0.331 7(3)	C(32)	0.546 1(5)	0.111(1)	0.694 0(5)
C(5)	0.615 6(2)	0.327 9(6)	0.339 1(3)	N(1)	0.657 2(3)	−0.026 3(5)	0.279 6(4)
C(6)	0.570 1(3)	0.357 2(9)	0.326 3(4)	N(2)	0.546 9(3)	−0.313 3(7)	0.326 5(4)
C(7)	0.541 4(4)	0.270(1)	0.324 3(6)	N(3)	0.641 4(2)	−0.166 3(6)	0.511 2(3)
C(8)	0.568 5(4)	0.411(1)	0.266 7(6)	N(4)	0.715 1(3)	−0.381 1(6)	0.340 3(4)
C(9)	0.642 3(2)	0.523 1(4)	0.563 0(3)	O(1)	0.662 9(4)	0.037 5(6)	0.244 6(4)
C(10)	0.671 3(2)	0.480 8(5)	0.604 3(3)	O(2)	0.513 7(4)	−0.345(1)	0.312 3(5)
C(11)	0.648 9(2)	0.427 8(5)	0.647 8(3)	O(3)	0.645 9(3)	−0.151 3(7)	0.563 6(3)
C(12)	0.605 5(2)	0.437 1(5)	0.635 4(3)	O(4)	0.743 0(2)	−0.437 5(5)	0.331 3(4)

2.73, approximately corresponding to two unpaired electrons, assuming orbital contributions to be negligible. Since the compound was proved to be $[\{Mo_4(\eta\text{-}C_5H_4Pr^i)_4(\mu_3\text{-}S)_4\}_2]^{2+}$-$[Os_6(CO)_{18}]^{2-}$ the two unpaired electrons must be associated with the cations. The temperature dependence of the static susceptibility of **10** also follows the Curie–Weiss law.

Salts formed between Cubane Clusters and Tetracyanoquinodimethane Anions.—We have also prepared salts between various cubane clusters and anionic tetracyanoquinodimethane (tcnq) systems by direct mixing of solutions of donor clusters with tcnq in toluene. The resulting precipitates were then recrystallized. For the most part it was not possible to obtain single crystals suitable for X-ray crystallographic study.

The salts formed by rapid addition of toluene solutions of the chromium clusters $[Cr_4(\eta\text{-}C_5H_4R)_4(\mu_3\text{-}E)_4]$ (R = H or Me; E = S or Se) to toluene solutions of tcnq have the stoichiometry $[Cr_4(\eta\text{-}C_5H_4R)_4(\mu_3\text{-}E)_4][tcnq]_2$. In contrast, when the toluene

Table 10 Fractional atomic coordinates for $[Fe_4(\eta\text{-}C_5H_5)_4(\mu_3\text{-}S)_4][Fe_4(NO)_4(\mu_3\text{-}S)_4]\cdot Me_2CO$ **5**$\cdot Me_2CO$ with e.s.d.s in parentheses

Atom	*X/a*	*Y/b*	*Z/c*
Fe(1)	0.843 74(5)	0.018 68(5)	0.214 36(3)
Fe(2)	0.825 77(4)	0.201 40(4)	0.391 40(3)
Fe(3)	0.578 80(4)	0.047 92(4)	0.335 44(3)
Fe(4)	0.857 84(4)	−0.079 14(4)	0.325 41(3)
S(1)	0.669 87(8)	−0.099 16(7)	0.242 12(5)
S(2)	0.747 60(7)	0.047 87(7)	0.423 52(5)
S(3)	0.697 87(9)	0.144 20(8)	0.268 90(5)
S(4)	0.984 70(8)	0.089 59(7)	0.333 77(5)
C(1)	1.027(1)	0.051(2)	0.151 9(6)
C(2)	0.970(2)	−0.073(1)	0.120 1(8)
C(3)	0.829(2)	−0.095(1)	0.084 1(6)
C(4)	0.798(1)	0.015(2)	0.093 7(7)
C(5)	0.921(2)	0.106(1)	0.135 5(8)
C(101)	1.016(1)	−0.016(2)	0.138 1(6)
C(102)	0.907(2)	−0.120(1)	0.102 4(7)
C(103)	0.785(1)	−0.088(2)	0.076 6(6)
C(104)	0.820(3)	0.035(2)	0.097(1)
C(105)	0.962(3)	0.080(1)	0.134 5(8)
C(6)	0.811(1)	0.380 2(6)	0.415 7(6)
C(7)	0.953(1)	0.366 2(6)	0.412 3(5)
C(8)	0.988 4(9)	0.332 8(6)	0.478 8(5)
C(9)	0.868 1(9)	0.325 4(6)	0.522 6(5)
C(10)	0.758(1)	0.354 7(6)	0.483 9(5)
C(106)	0.841(2)	0.381 5(8)	0.411 1(9)
C(107)	0.977(2)	0.362 2(8)	0.429 6(8)
C(108)	0.969(2)	0.327 2(8)	0.498 6(8)
C(109)	0.829(2)	0.324 1(9)	0.521 8(9)
C(110)	0.751(2)	0.357 8(9)	0.468(1)
C(11)	0.409 6(4)	−0.021 0(4)	0.388 0(3)
C(12)	0.372 7(4)	−0.058 9(4)	0.300 7(3)
C(13)	0.374 6(4)	0.043 9(5)	0.285 2(3)
C(14)	0.413 3(4)	0.143 4(4)	0.363 8(4)
C(15)	0.434 3(4)	0.104 1(4)	0.427 4(3)
C(16)	1.032 6(4)	−0.133 2(4)	0.367 7(3)
C(17)	1.001 7(5)	−0.198 5(4)	0.280 7(3)
C(18)	0.860 4(6)	−0.261 6(4)	0.265 4(4)
C(19)	0.806 9(5)	−0.233 6(4)	0.345 2(5)
C(20)	0.914 9(5)	−0.154 4(4)	0.408 0(3)
Fe(5)	0.472 59(5)	0.504 35(4)	0.322 96(3)
Fe(6)	0.214 95(5)	0.470 21(5)	0.241 80(3)
Fe(7)	0.379 39(5)	0.308 96(4)	0.176 90(3)
Fe(8)	0.449 07(6)	0.522 11(5)	0.171 92(3)
S(5)	0.286 11(9)	0.357 99(8)	0.301 40(6)
S(6)	0.380 3(1)	0.638 86(8)	0.295 42(6)
S(7)	0.592 2(1)	0.428 4(1)	0.212 37(6)
S(8)	0.255 3(1)	0.381 98(9)	0.105 55(6)
N(1)	0.569 9(3)	0.560 8(3)	0.418 0(2)
N(2)	0.050 5(4)	0.489 0(3)	0.257 6(2)
N(3)	0.389 6(4)	0.167 9(3)	0.124 4(2)
N(4)	0.524 4(5)	0.588 3(3)	0.112 8(2)
O(1)	0.640 0(4)	0.602 2(3)	0.483 0(2)
O(2)	−0.064 5(4)	0.502 8(4)	0.271 7(3)
O(3)	0.406 4(5)	0.071 1(3)	0.087 5(2)
O(4)	0.581 2(7)	0.630 0(4)	0.069 9(2)
C(50)	0.161(1)	0.576(1)	−0.033 6(7)
C(51)	0.216(1)	0.698 9(9)	0.036 6(5)
C(52)	0.337(2)	0.770(1)	0.018 8(9)
O(51)	0.175 8(8)	0.731 1(8)	0.104 4(4)

solutions were allowed to interdiffuse slowly over a period of 2 months the stoichiometry of the resulting salts was $[Cr_4(\eta\text{-}C_5H_4R)_4(\mu_3\text{-}E)_4][tcnq]$.

Table 1 lists the new tcnq salts of cubane clusters. Single crystals of $[Mo_4(\eta\text{-}C_5H_4Pr^i)_4(\mu_3\text{-}S)_4][tcnq]$ **11**, suitable for X-ray structural study, were obtained by a metathesis reaction between $[Mo_4(\eta\text{-}C_5H_4Pr^i)_4(\mu_3\text{-}S)_4]BF_4$[5] and $[NEt_3H][(tcnq)_2]$.[16] The tcnq salts in Table 1 may be divided into mono (tcnq) salts, *i.e.* those with only one tcnq component, and poly (tcnq) salts which have two or more tcnq groups. We shall discuss these two groups separately. Compounds **11**–**13**, **15**, **17** and **19**, have the 1:1 stoichiometry $[C]^{n+}[tcnq]^{n-}$. Further characterization requires the determination of the charge on the ions. A comparison of redox potential data (Table 6) shows that the $E_{\frac{1}{2}}(tcnq\text{–}tcnq^-)$ value is much more positive than the values of $E_{\frac{1}{2}}(C^+\text{–}C)$ for all cubane clusters employed in this study, but the $E_{\frac{1}{2}}(tcnq^-\text{–}tcnq^{2-})$ value is more negative than the values of $E_{\frac{1}{2}}(C^{2+}\text{–}C^+)$ for the same clusters. Thus, assuming lattice-energy contributions to be relatively small, these salts are most likely to be $[C]^+[tcnq]^-$ rather than $[C]^{2+}[tcnq]^{2-}$.

The X-ray crystal structures of the salts **11** and **13** have been determined. Crystal data, data collection and processing parameters are given in Table 2 and final fractional atomic coordinates in Tables 17 and 18. Only those data pertinent to the value of *n* and to crystal packing will be discussed. The average Fe–Fe bond lengths in **13** are 3.048 and 3.053 Å for the two crystallographically independent cluster units. As shown in Table 14, the average Fe–Fe bond lengths for $[Fe_4(\eta\text{-}C_5H_5)_4(\mu_3\text{-}S)_4]^{n+}$ are 3.124 Å for $n = 0$, 3.053 Å for $n = 1$, and 2.974 Å for $n = 2$. Therefore, the Fe–Fe bond lengths in **13** are consistent with the formulation $[Fe_4(\eta\text{-}C_5H_4Me)_4(\mu_3\text{-}S)_4]^+[tcnq]^-$. Similarly, the average Mo–Mo bond length in **11** (2.890 Å) is very close to that of the authenticated monocation $[Mo_4(\eta\text{-}C_5H_4Pr^i)_4(\mu_3\text{-}S)_4]^+$ (2.894 Å, Table 16).

The bond lengths of the tcnq component are also a useful guide towards an estimate of the charges on tcnq molecules in such salts and three empirical schemes have been used for estimating the degree of charge transfer based on the tcnq geometry.[17–19] These focus on the lengthening of the formal double bonds *a* and *c* and the shortening of the formal single bonds *b* and *d* (see Table 19) as the structure becomes more benzenoid in character with increasing negative charge. The small difference between the methods lies in the fact that each estimates the degree of charge transfer on the basis of slightly different approaches for comparison of the bond lengths, namely by comparison of the values of $(b - c)$ and $(c - d)$,[17] $(a + c)/(b + d)$[18] or $c/(b + d)$,[19] respectively. It was found that in the case of $[tcnq]^-$ the values of $(b - c)$ and $(c - d)$ are both close to zero and $c/(b + d) = 0.500$.[19] Table 19 lists the mean bond lengths of the tcnq components in the compounds **11** and **13**, together with reported data for neutral tcnq[20] and $Rb^+[tcnq]^-$[21] along with the values of $(b - c)$, $(c - d)$ and $c/(b + d)$. It can be concluded that the degree of electron transfer in compounds **11** and **13** is unity, *i.e.* they are composed of a cluster monocation and a tcnq monoanion.

The room-temperature magnetic moment (Table 7) of compound **11** is 2.59, corresponding to two unpaired electrons per formula unit. This is also consistent with the charge assignment as $[Mo_4(\eta\text{-}C_5H_4Pr^i)_4(\mu_3\text{-}S)_4]^+[tcnq]^-$. The magnetic behaviour is discussed further below.

The 1:1 compound $[Cr_4(\eta\text{-}C_5H_4Me)_4(\mu_3\text{-}S)_4][tcne]$ (tcne = tetracyanoethylene) **27** crystallized from acetonitrile as large shiny black crystals. The mull infrared spectrum shows bands at 2182(m) and 2143(s) cm^{-1} assignable to ν(CN) and these are characteristic of the monoanion $[tcne]^-$.[14] The magnetic moment of **27** is 2.57 corresponding to two unpaired electrons per formula unit. The magnetic data were fitted to the Curie–Weiss law with the parameters given in Table 7. Based on these data, we assign **27** as $[Cr_4(\eta\text{-}C_5H_4Me)_4(\mu_3\text{-}S)_4]^+[tcne]^-$. The room-temperature conductivity is $5.5 \times 10^{-6}\ \Omega^{-1}\ cm^{-1}$, and the activation energy is 0.47 eV over the range from room temperature to 100 °C (Table 1).

The poly(tcnq) salts **14**, **16** and **18** have the stoichiometry $[C][tcnq]_2$. Two extreme representations of the anionic systems are $[C]^{2+}2[tcnq]^-$ and $[C]^+[tcnq]^-[tcnq]^0$ or $[C]^+$

Table 11 Fractional atomic coordinates for $[Fe_4(\eta\text{-}C_5H_4Me)_4(\mu_3\text{-}S)_4][Fe_4(NO)_4(\mu_3\text{-}S)_4]$ **6** with e.s.d.s in parentheses

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Fe(1)	0.993 9(1)	0.814 5(2)	1.080 6(1)
Fe(2)	0.933 1(1)	0.665 1(1)	1.051 3(1)
Fe(3)	0.839 7(1)	0.750 9(1)	1.084 8(1)
Fe(4)	0.983 7(1)	0.736 6(1)	1.189 9(1)
S(1)	1.031 0(2)	0.711 8(3)	1.096 6(3)
S(2)	0.912 3(2)	0.766 6(2)	1.008 1(2)
S(3)	0.891 9(2)	0.674 4(2)	1.151 6(2)
S(4)	0.912 8(2)	0.816 7(2)	1.150 2(2)
C(1)	0.993 4(7)	0.906 7(7)	1.018(1)
C(2)	0.992 0(9)	0.930 9(6)	1.086(1)
C(3)	1.050(1)	0.903 8(8)	1.126 7(8)
C(4)	1.086 8(7)	0.863 3(7)	1.083 7(9)
C(5)	1.051 9(7)	0.865 4(6)	1.016 6(8)
C(6)	1.072(1)	0.829 8(7)	0.955(1)
C(7)	0.976(1)	0.568 8(7)	1.038 1(9)
C(8)	0.905(1)	0.559 4(8)	1.048(1)
C(9)	0.875(1)	0.594 1(7)	0.993(1)
C(10)	0.908(1)	0.623 2(8)	0.949(1)
C(11)	0.979(1)	0.605 2(7)	0.980 4(9)
C(12)	1.039(1)	0.627 9(8)	0.948(1)
C(13)	0.758 5(4)	0.809 3(9)	1.035 3(9)
C(14)	0.752 8(4)	0.744 0(8)	1.012 4(9)
C(15)	0.743 6(4)	0.701 1(9)	1.067 4(8)
C(16)	0.743 8(4)	0.743 8(7)	1.125 7(8)
C(17)	0.752 7(4)	0.810 1(8)	1.105 9(9)
C(18)	0.755 5(5)	0.871(1)	1.154(1)
C(19)	1.079(1)	0.706(1)	1.248 2(6)
C(20)	1.064(1)	0.772(1)	1.260 3(6)
C(21)	1.006 6(9)	0.783(1)	1.285 7(6)
C(22)	0.974 1(8)	0.714 5(9)	1.294 4(5)
C(23)	1.024 4(7)	0.671 3(8)	1.270 0(5)
C(24)	1.020(1)	0.595(1)	1.266 1(6)
Fe(5)	0.554 7(1)	0.326 4(1)	0.539 5(1)
Fe(6)	0.524 41(9)	0.167 32(9)	0.560 16(9)
Fe(7)	0.547 68(9)	0.233 64(9)	0.677 64(9)
Fe(8)	0.666 05(9)	0.253 91(9)	0.571 2(1)
S(5)	0.582 3(2)	0.231 4(2)	0.491 1(2)
S(6)	0.477 4(2)	0.262 6(2)	0.587 5(2)
S(7)	0.620 7(2)	0.170 4(2)	0.628 8(2)
S(8)	0.612 6(2)	0.317 2(2)	0.641 6(2)
C(25)	0.505 9(9)	0.420 9(6)	0.541 9(9)
C(26)	0.578(1)	0.432 3(7)	0.537(1)
C(27)	0.593(1)	0.405 9(7)	0.479(1)
C(28)	0.540 2(8)	0.377 3(6)	0.441 8(9)
C(29)	0.478 5(9)	0.386 0(6)	0.481 6(8)
C(30)	0.413(1)	0.364 2(8)	0.461(1)
C(31)	0.522 2(7)	0.082 6(5)	0.497 1(8)
C(32)	0.524 5(8)	0.060 5(6)	0.565 2(9)
C(33)	0.465 8(7)	0.083 8(6)	0.588 7(8)
C(34)	0.426 3(8)	0.119 5(6)	0.538 8(8)
C(35)	0.463 5(7)	0.118 9(5)	0.478 3(8)
C(36)	0.436 2(9)	0.152 9(7)	0.410(1)
C(37)	0.506 8(8)	0.169 0(9)	0.752 0(5)
C(38)	0.574 6(9)	0.188 4(9)	0.775 3(5)
C(39)	0.575(1)	0.255(1)	0.781 0(5)
C(40)	0.514 3(8)	0.280 9(9)	0.763 9(5)
C(41)	0.466 7(8)	0.226 4(8)	0.744 3(5)
C(42)	0.392(1)	0.235(1)	0.722 2(6)
C(43)	0.746 1(5)	0.220 8(9)	0.514 9(9)
C(44)	0.736 6(5)	0.287(1)	0.503(1)
C(45)	0.750 4(5)	0.318 7(9)	0.565 8(9)
C(46)	0.767 7(5)	0.272 3(8)	0.617 0(8)
C(47)	0.765 1(5)	0.207 7(9)	0.582 2(9)
C(48)	0.781 2(6)	0.145(1)	0.620(1)
Fe(9)	0.718 62(9)	0.482 1(1)	0.911 12(9)
Fe(10)	0.745 46(9)	0.382 38(9)	0.823 7(1)
Fe(11)	0.808 4(1)	0.501 6(1)	0.816 1(1)
Fe(12)	0.673 1(1)	0.490 4(1)	0.775 6(1)
S(9)	0.642 1(2)	0.415 6(2)	0.851 9(2)
S(10)	0.819 2(2)	0.429 9(2)	0.904 6(2)
S(11)	0.759 5(2)	0.440 9(2)	0.728 4(2)
S(12)	0.724 7(2)	0.571 0(2)	0.842 3(2)
N(1)	0.701 1(6)	0.500 4(6)	0.990 0(6)
N(2)	0.755 7(6)	0.299 6(6)	0.817 6(7)
N(3)	0.881 9(6)	0.537 4(6)	0.800 3(6)
N(4)	0.609 9(6)	0.516 6(7)	0.718 9(6)
O(1)	0.689 1(6)	0.514 9(7)	1.046 8(6)
O(2)	0.764 5(7)	0.241 4(5)	0.814 7(8)
O(3)	0.935 1(6)	0.561 0(6)	0.790 6(7)
O(4)	0.565 6(8)	0.534 8(8)	0.677 3(7)
Fe(13)	0.329 5(1)	0.031 1(1)	0.212 2(1)
Fe(14)	0.234 5(1)	0.127 5(1)	0.179 1(1)
Fe(15)	0.195 2(1)	0.007 7(1)	0.223 2(1)
Fe(16)	0.240 0(1)	0.019 4(1)	0.097 4(1)
S(13)	0.321 3(2)	0.097 4(2)	0.119 3(2)
S(14)	0.262 8(2)	0.081 5(2)	0.282 6(2)
S(15)	0.146 6(2)	0.065 9(2)	0.133 9(2)
S(16)	0.269 2(2)	−0.060 0(2)	0.176 0(2)
N(5)	0.409 3(7)	0.019 8(8)	0.247 9(8)
N(6)	0.216 6(6)	0.209 2(7)	0.179 4(7)
N(7)	0.138 8(8)	−0.028 4(7)	0.267 7(7)
N(8)	0.228(1)	−0.005 5(8)	0.016 1(8)
O(5)	0.464 0(8)	0.014 9(9)	0.275 5(9)
O(6)	0.202 5(7)	0.265 9(5)	0.178 0(7)
O(7)	0.094 4(8)	−0.052 8(8)	0.298 6(8)
O(8)	0.217(1)	−0.019 4(8)	−0.041 7(8)

[tcnq·tcnq]$^-$; in the last case the charge is distributed equally over the two tcnq molecules. Bloch and co-workers[22,23] have shown that the nitrile stretching frequency of tcnq in the infrared spectra provides a measure of the charge on the anion and hence the degree of charge transfer for many conducting tcnq salts. A plot of the vibrational frequencies (ν) of eight salts against the degree of charge transfer (*Z*) (determined independently) yields a straight line. Using this calibration, the previously unknown values of *Z* for 11 other tcnq salts were determined from measured ν(CN) values.

The nitrile stretching frequencies for the mono(tcnq) salt $[Mo_4(\eta\text{-}C_5H_4Pr^i)_4(\mu_3\text{-}S)_4]$[tcnq] **11**, the poly(tcnq) salts **14**, **16** and **18**, and neutral tcnq, $[NEt_3H]^+$[(tcnq)$_2$]$^-$, and K^+-[tcnq]$^-$ are compared in Table 1.

The infrared spectra of the cluster salts **14**, **16** and **18** do not show absorptions assignable to neutral [tcnq]^0 or [tcnq]$^-$, but have a frequency at 2199 cm^{-1}, the same as for $[NEt_3H]^+$-[(tcnq)$_2$]$^-$ and $[PMePh_3]^+$[(tcnq)$_2$]$^-$, which have been assigned as having the anion [tcnq·tcnq]$^-$.[23] Thus, by analogy, these three cluster salts may be written as [C]$^+$[tcnq·tcnq]$^-$. This formulation implies the presence of a significant interaction between the two tcnq molecules. For example, tcnq molecules may arrange as isolated dimers, as in $[Nb_3(\eta\text{-}C_6Me_6)_3(\mu\text{-}Cl)_6]$[(tcnq)$_2$][24] and in $[V_5(\eta\text{-}C_5Me_5)_5S_6]$[(tcnq)$_2$].[25]

The charges on the tcnq ions in solution may also be obtained from ultraviolet–visible electronic spectra. Thus, Murakami and Yoshimura[26] derived expression (3) where I_{395} and I_{842}

$$\{[\text{tcnq}]^0/[\text{tcnq}]^-\} = 0.759\,[(I_{395}/I_{842}) - 0.422] \quad (3)$$

are the absorption intensities at 395 and 842 nm respectively, and we have used it to analyse the solution spectra of the present complex cluster salts. The electronic spectral data for the cluster tcnq salts in acetonitrile solution are given in Table 20. These indicate that in acetonitrile there are essentially 1:1 neutral [tcnq]^0 and monoanionic [tcnq]$^-$ species. Since the infrared spectra in the solid state (Nujol mulls) do not show any nitrile frequency due to either neutral [tcnq]^0 or anionic [tcnq]$^-$ species, we propose that in the solid state these salts exist as [C]$^+$[tcnq·tcnq]$^-$, and the two tcnq species might arrange as dimers. In solutions, on the other hand, the two tcnq molecules must separate and the charge will be

Table 12 Fractional atomic coordinates for $[Mo_4(\eta\text{-}C_5H_4Pr^i)_4(\mu_3\text{-}S)_4]_2[Os_6(CO)_{18}]$ **10a** with e.s.d.s in parentheses

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*	Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Os(1)	0.439 49(2)	0.165 95(2)	0.718 71(2)	C(3)	0.156 3(6)	0.389 9(7)	0.559 8(6)
Os(2)	0.442 22(2)	0.309 43(2)	0.718 63(2)	C(4)	0.203 6(5)	0.371 8(6)	0.603 2(5)
Os(3)	0.536 46(2)	0.234 27(2)	0.670 36(2)	C(5)	0.199 7(4)	0.413 1(5)	0.655 0(4)
C(101)	0.361 9(6)	0.173 6(7)	0.739 9(6)	C(6)	0.238 5(5)	0.404 3(6)	0.713 1(4)
C(102)	0.417 1(6)	0.152 8(7)	0.637 6(6)	C(7)	0.229 1(8)	0.459 2(8)	0.758 2(7)
O(102)	0.399 9(5)	0.145 7(6)	0.586 8(5)	C(8)	0.228 0(7)	0.335 6(6)	0.739 8(6)
C(103)	0.439 9(6)	0.074 0(6)	0.733 5(7)	C(9)	0.161 4(5)	0.607 9(5)	0.403 8(4)
O(103)	0.434 0(6)	0.017 3(5)	0.739 4(7)	C(10)	0.212 1(5)	0.649 7(6)	0.401 7(5)
O(101)	0.311 3(4)	0.177 9(6)	0.750 3(5)	C(11)	0.210 2(5)	0.698 8(5)	0.447 0(6)
C(104)	0.376 2(6)	0.294 5(6)	0.663 5(7)	C(12)	0.159 8(5)	0.685 1(5)	0.479 5(5)
C(105)	0.402 3(6)	0.368 5(7)	0.765 7(7)	C(13)	0.129 3(4)	0.628 8(5)	0.452 2(5)
O(105)	0.377 8(5)	0.408 4(6)	0.793 3(6)	C(14)	0.072 2(5)	0.596 8(7)	0.470 7(7)
C(106)	0.472 8(6)	0.380 2(8)	0.676 7(7)	C(15)	0.022 2(8)	0.650(1)	0.466(1)
O(106)	0.487 1(5)	0.424 0(6)	0.647 1(6)	C(16)	0.054 8(7)	0.533 4(8)	0.433 9(8)
O(104)	0.336 4(4)	0.289 2(5)	0.626 9(5)	C(17)	0.358 7(6)	0.475 8(7)	0.408 5(6)
C(107)	0.497 3(6)	0.270 1(8)	0.599 6(6)	C(18)	0.405 1(7)	0.507 0(8)	0.444 3(8)
O(107)	0.475 7(6)	0.288 1(7)	0.553 6(5)	C(19)	0.420 2(6)	0.467 5(9)	0.495 9(8)
C(108)	0.547 9(6)	0.148 1(7)	0.641 0(5)	C(20)	0.385 5(6)	0.409 3(7)	0.489 9(6)
O(108)	0.555 2(4)	0.094 7(5)	0.622 5(4)	C(21)	0.347 9(5)	0.413 6(6)	0.436 3(5)
C(109)	0.612 3(6)	0.263 8(7)	0.650 9(6)	C(22)	0.305 9(6)	0.358 7(6)	0.409 8(6)
O(109)	0.657 8(5)	0.277 7(7)	0.635 1(6)	C(23)	0.282 2(9)	0.311 6(8)	0.455 8(9)
Mo(1)	0.220 99(4)	0.482 25(4)	0.573 04(4)	C(24)	0.337 8(9)	0.319 3(9)	0.362 7(8)
Mo(2)	0.224 92(4)	0.595 07(4)	0.494 49(4)	C(25)	0.371 0(7)	0.583 7(7)	0.692 3(6)
Mo(3)	0.321 81(4)	0.500 97(5)	0.501 14(4)	C(26)	0.317 5(6)	0.619 4(8)	0.703 4(6)
Mo(4)	0.307 97(4)	0.587 16(5)	0.602 90(4)	C(27)	0.314 1(6)	0.677 8(8)	0.669 7(6)
S(1)	0.203 3(1)	0.594 6(1)	0.595 7(1)	C(28)	0.364 3(6)	0.680 5(7)	0.638 0(6)
S(2)	0.221 1(1)	0.482 2(1)	0.468 0(1)	C(29)	0.400 5(5)	0.624 7(7)	0.650 6(6)
S(3)	0.327 9(1)	0.617 8(1)	0.505 2(1)	C(30)	0.460 6(6)	0.606(1)	0.625 8(8)
S(4)	0.323 6(1)	0.471 5(1)	0.602 9(1)	C(31)	0.477 6(9)	0.656(1)	0.580(1)
C(1)	0.150 6(5)	0.456 5(6)	0.642 8(6)	C(32)	0.510(1)	0.594(1)	0.675(1)
C(2)	0.125 6(5)	0.442 6(7)	0.583 1(7)				

concentrated on one tcnq, leaving the other as a neutral molecule, *i.e.* the species in solution are $[C]^+[(tcnq)^-(tcnq)^0]$. In fact, the infrared and electronic spectroscopic behaviour of these cluster salts of $[C]^+[(tcnq)_2]^-$ closely parallels that of $[NEt_3H]^+[(tcnq)_2]^-$.

Microanalysis (Table 1) shows that compound **20** has the stoichiometry $[Mo_4(\eta\text{-}C_5H_4Pr^i)_4(\mu_3\text{-}Se)_4][tcnq]_3$. The compound $[Mo_4(\eta\text{-}C_5H_4Pr^i)_4(\mu_3\text{-}Se)_4]$ is the most reducing of all the clusters used in this work and has a second reduction potential $E_{\frac{1}{2}}(C^{2+}\text{–}C^+)$ which is more negative than $E_{\frac{1}{2}}(\text{tcnq–tcnq}^-)$. Therefore, the formation of a dication would be acceptable. The infrared spectrum of solid **20** shows only one nitrile frequency of 2183 cm^{-1} characteristic of the $[tcnq]^-$ monoanion. The ultraviolet–visible spectrum in acetonitrile solution, however, shows $I_{395} = 0.594$ and $I_{842} = 0.328$, corresponding to a $[tcnq]^0/[tcnq]^-$ ratio of *ca.* 1:1. Thus the IR and ultraviolet–visible spectra are inconclusive and it is not possible based on these data alone to draw a conclusion concerning assignment of the component charges.

The crystal structures of compounds **11** and **13** have been determined (see above). Interestingly, the tcnq moieties in **11** are arranged in 'ribbons' [Fig. 6(*a*) and (*b*)] separated by cluster cations, with a separation of *ca.* 9.4 Å. The closest contacts between molecules are given in Table 21 and the atomic labelling is shown in Fig. 7. The Mo(1), Mo(2), Mo(3) plane is almost parallel (interplanar angle 3.12°) to the tcnq plane and is capped by S(2). The distance between S(2) and the tcnq plane is 3.528 Å, and S(2) $\cdots$ C(107^c) (see Fig. 7 and Table 21) is 3.56 Å, which is slightly shorter than the sum of the van der Waals radii (3.6 Å). This indicates a significant contact between the cluster and the tcnq ribbon. Moreover, this ribbon-type arrangement is very unusual for tcnq ions, which are normally arranged in a face-to-face manner.

The electrical conductivities of four tcnq salts were measured on either a single crystal (for **11**) or pressed pellets (for **12**, **14** and **16**). The data are shown in Table 1 and Fig. 8. The conductivities are in the range expected for semiconductors and are slightly higher than those of the soft salts.

Static magnetic susceptibilities of three tcnq salts (**11**, **16** and **17**) are given in Table 7. The salts **16** and **17** are simple paramagnetic compounds which obey the Curie–Weiss law. Compound **11** shows paramagnetic behaviour at high temperatures with a moment of 2.59 and a Weiss constant of −7.5 K. However, at low temperature, this material also shows weak antiferromagnetic behaviour with $T_N \approx 12$ K. As discussed above, **11** has a charge assignment as $[Mo_4(\eta\text{-}C_5H_4Pr^i)_4(\mu_3\text{-}S)_4]^+[tcnq]^-$; in view of the short contact between the cluster and the tcnq ribbon it seems reasonable to propose that this antiferromagnetic ordering is due to the co-operative interaction between the moments on the cluster cations and the moments on the tcnq anions.

Salts formed from Cubane Clusters and Anionic Metal Dithiolenes.—The metal bis-[27] and tris-dithiolene compounds $[Mo\{S_2C_2(CF_3)_2\}_3]$[27,28] and $[Ni\{S_2C_2(CN)_2\}_2]^{n-}$ are strong electron acceptors and have reduction potentials for the process $[A]^- \longrightarrow [A]^{2-}$ close to those of some cubane cluster donors for the process $[C]^{2+} \longrightarrow [C]^+$. Therefore we synthesised salts of the cubane clusters containing $[Mo\{S_2C_2(CF_3)_2\}_3]^{n-}$ or $[Ni\{S_2C_2(CN)_2\}_2]^{n-}$ as counter ions to find whether mixed-valence materials might result. Salts of $[Mo\{S_2C_2(CF_3)_2\}_3]^{n-}$ with the cubane clusters were prepared by direct mixing of toluene solutions of donor and acceptor species giving precipitates which were crystallized from acetone or acetonitrile. The resulting five new salts **21**–**25** are shown in Table 1.

The reaction between $[Mo_4(\eta\text{-}C_5H_4Pr^i)_4(\mu_3\text{-}S)_4]$ and $[Mo\{S_2C_2(CF_3)_2\}_3]$ yielded two products with the stoichiometries of 1:1 and 2:1, *i.e.* $[Mo_4(\eta\text{-}C_5H_4Pr^i)_4(\mu_3\text{-}S)_4][Mo\{S_2C_2(CF_3)_2\}_3]$ **22** and $[Mo_4(\eta\text{-}C_5H_4Pr^i)_4(\mu_3\text{-}S)_4]_2[Mo\{S_2C_2(CF_3)_2\}_3]$ **23**. The latter compound was precipitated from the original reaction mixture after isolation of the 1:1 phase by

Table 13 Fractional atomic coordinates for $[Mo_4(\eta\text{-}C_5H_4Pr^i)_4(\mu_3\text{-}S)_4]_2[Os_6(CO)_{18}]$ **10b** with e.s.d.s in parentheses

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*	Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Os(1)	0.122 94(5)	0.077 8(1)	0.790 35(7)	C(12)	0.286 8(9)	0.262(3)	1.102(2)
Os(2)	0.118 62(5)	0.256 5(1)	0.837 93(7)	C(13)	0.301(1)	0.224(3)	1.158(2)
Os(3)	0.195 25(4)	0.196 1(1)	0.777 55(7)	C(14)	0.311(1)	0.266(3)	1.221(2)
Os(4)	0.066 83(5)	0.199 7(1)	0.726 72(7)	C(15)	0.341(2)	0.206(4)	1.264(3)
Os(5)	0.145 02(5)	0.146 0(1)	0.667 50(7)	C(16)	0.272(2)	0.298(4)	1.249(3)
Os(6)	0.136 44(5)	0.323 2(1)	0.715 47(7)	C(17)	0.391(1)	0.036(2)	0.889(2)
O(101)	0.102 9(7)	−0.092(2)	0.721(1)	C(18)	0.437(2)	0.057(3)	0.889(2)
O(102)	0.045 9(6)	0.047(2)	0.871 4(9)	C(19)	0.457(1)	0.017(2)	0.939(2)
O(103)	0.186 2(7)	−0.012(2)	0.880(1)	C(20)	0.428(1)	−0.040(3)	0.969(2)
O(104)	0.182 4(7)	0.407(2)	0.879(1)	C(21)	0.383(1)	−0.017(3)	0.936(2)
O(105)	0.042 1(7)	0.361(2)	0.882(1)	C(22)	0.339(2)	−0.066(3)	0.954(2)
O(106)	0.123 9(7)	0.157(2)	0.964(1)	C(23)	0.305(2)	−0.018(4)	0.918(3)
O(107)	0.248 6(7)	0.041(2)	0.742(1)	C(24)	0.339(2)	−0.160(4)	0.932(3)
O(108)	0.228 9(7)	0.189(1)	0.912(1)	C(25)	0.394(1)	0.449(3)	0.984(2)
O(109)	0.268 4(7)	0.318(1)	0.742(1)	C(26)	0.438(1)	0.440(3)	0.985(2)
O(110)	−0.011 0(7)	0.224(2)	0.810(1)	C(27)	0.449(2)	0.395(3)	0.939(2)
O(111)	0.030 0(7)	0.316(2)	0.620(1)	C(28)	0.417(2)	0.369(3)	0.897(2)
O(112)	0.027 3(7)	0.036(2)	0.674(1)	C(29)	0.377(1)	0.414(2)	0.931(2)
O(113)	0.215 3(6)	0.239(2)	0.598(1)	C(30)	0.332(2)	0.417(3)	0.899(2)
O(114)	0.182 4(7)	−0.035(2)	0.641(1)	C(31)	0.295(2)	0.424(4)	0.948(2)
O(115)	0.085 2(7)	0.129(1)	0.552(1)	C(32)	0.327(2)	0.491(4)	0.851(3)
O(116)	0.122 5(7)	0.359(1)	0.575 3(9)	Mo(5)	0.326 1(1)	0.083 3(2)	0.520 7(1)
O(117)	0.068 6(7)	0.454(1)	0.754(1)	Mo(6)	0.391 7(1)	0.106 0(2)	0.620 5(1)
O(118)	0.202 6(7)	0.461(1)	0.732(1)	Mo(7)	0.411 6(1)	0.136 6(2)	0.487 5(1)
C(101)	0.112 0(7)	−0.028(2)	0.749(1)	Mo(8)	0.357 26(9)	0.258 2(2)	0.555 1(1)
C(102)	0.076 8(6)	0.058(2)	0.841 7(9)	S(5)	0.320 1(3)	0.159 1(7)	0.617 3(4)
C(103)	0.162 9(7)	0.023(2)	0.844(1)	S(6)	0.390 9(3)	0.004 3(7)	0.536 7(4)
C(104)	0.159 9(7)	0.349(1)	0.865(2)	S(7)	0.430 2(3)	0.224 5(7)	0.576 5(4)
C(105)	0.070 6(7)	0.319(2)	0.863(1)	S(8)	0.345 1(3)	0.198 3(7)	0.452 4(4)
C(106)	0.124 1(7)	0.196(2)	0.916(1)	C(33)	0.707(1)	0.007(2)	0.558(2)
C(107)	0.229 0(7)	0.102(2)	0.757(1)	C(34)	0.706(1)	0.058(3)	0.502(2)
C(108)	0.215(1)	0.195(1)	0.860(1)	C(35)	0.728(1)	0.018(3)	0.457(2)
C(109)	0.239 2(6)	0.274(1)	0.755(2)	C(36)	0.749(1)	−0.057(3)	0.481(2)
C(110)	0.019 6(7)	0.217(2)	0.780(1)	C(37)	0.737(1)	−0.073(3)	0.545(2)
C(111)	0.042 9(8)	0.272(2)	0.662(1)	C(38)	0.753(1)	−0.129(3)	0.600(2)
C(112)	0.044 2(6)	0.100(2)	0.694(1)	C(39)	0.788(1)	−0.084(3)	0.640(2)
C(113)	0.189 4(7)	0.202(2)	0.627(1)	C(40)	0.773(2)	−0.214(4)	0.570(3)
C(114)	0.166 6(6)	0.033(2)	0.652(2)	C(41)	0.556(1)	−0.029(3)	0.317(2)
C(115)	0.108(1)	0.132(1)	0.597(1)	C(42)	0.560(2)	−0.109(4)	0.294(2)
C(116)	0.128(1)	0.341(1)	0.629(1)	C(43)	0.598(2)	−0.136(4)	0.272(3)
C(117)	0.093 8(8)	0.401(1)	0.740(1)	C(44)	0.624(2)	−0.058(3)	0.277(2)
C(118)	0.178 0(6)	0.404(1)	0.726(2)	C(45)	0.599(1)	0.009(3)	0.300(2)
Mo(1)	0.439 91(9)	0.195 6(2)	1.103 8(1)	C(46)	0.614(2)	0.113(4)	0.318(3)
Mo(2)	0.348 70(9)	0.193 8(2)	1.070 7(1)	C(47)	0.665(2)	0.117(5)	0.306(3)
Mo(3)	0.408 3(1)	0.110 0(2)	0.986 9(1)	C(48)	0.593(2)	0.158(3)	0.263(2)
Mo(4)	0.407 0(1)	0.300 4(2)	0.996 8(1)	C(49)	0.481(1)	0.103(3)	0.454(2)
S(1)	0.391 3(3)	0.314 0(6)	1.104 9(4)	C(50)	0.453(1)	0.044(3)	0.421(2)
S(2)	0.394 5(3)	0.072 2(7)	1.092 7(4)	C(51)	0.427(2)	0.104(4)	0.384(3)
S(3)	0.351 6(3)	0.206 9(7)	0.959 6(4)	C(52)	0.439(1)	0.187(4)	0.393(2)
S(4)	0.467 4(3)	0.206 2(7)	1.001 5(4)	C(53)	0.474(1)	0.191(3)	0.436(2)
C(1)	0.463(1)	0.246(3)	1.203(2)	C(54)	0.504(1)	0.268(3)	0.459(2)
C(2)	0.460(1)	0.156(3)	1.212(2)	C(55)	0.484(1)	0.359(3)	0.450(2)
C(3)	0.487(1)	0.112(3)	1.170(2)	C(56)	0.544(1)	0.254(4)	0.423(2)
C(4)	0.512(1)	0.177(2)	1.139(2)	C(57)	0.333(1)	0.374(3)	0.620(2)
C(5)	0.499(1)	0.260(3)	1.162(2)	C(58)	0.302(1)	0.364(3)	0.567(2)
C(6)	0.517(1)	0.354(3)	1.140(2)	C(59)	0.323(1)	0.386(3)	0.511(2)
C(7)	0.552(2)	0.346(3)	1.090(2)	C(60)	0.366(1)	0.409(2)	0.530(2)
C(8)	0.538(2)	0.393(4)	1.201(3)	C(61)	0.374(1)	0.400(2)	0.596(2)
C(9)	0.301(1)	0.129(3)	1.144(2)	C(62)	0.414(1)	0.430(3)	0.635(2)
C(10)	0.285(1)	0.117(4)	1.079(2)	C(63)	0.416(2)	0.535(4)	0.633(3)
C(11)	0.274(1)	0.199(3)	1.054(2)	C(64)	0.416(2)	0.393(4)	0.699(2)

Table 14 Comparison of selected average bond lengths (Å) for the $[Fe_4(\eta\text{-}C_5H_4R)_4(\mu_3\text{-}S)_4]^{n+}$ moiety in compounds **5** and **6** with those reported previously for *n* = 0, 1 and 2[1,15]

	$[Fe_4(\eta\text{-}C_5H_5)_4(\mu_3\text{-}S)_4]$	$[Fe_4(\eta\text{-}C_5H_5)_4(\mu_3\text{-}S)_4]^+Br^-$	**5**	**6**	$[Fe_4(\eta\text{-}C_5H_5)_4(\mu_3\text{-}S)_4]^{2+}2PF_6^-$
Fe–Fe	3.124	3.053	3.048	3.033	2.974
S···S	3.040	3.110	3.105	3.097	3.143
Fe–S	2.223	2.214	2.211	2.200	2.191

Table 15 Comparison of selected average bond lengths (Å) for the $[Fe_4(NO)_4(\mu_3\text{-}S)_4]^{n-}$ moiety in compounds **3a**, **3b**, **5** and **6** with those reported previously for $n = 0$ or 1 [6,15]

	$[Fe_4(NO)_4(\mu_3\text{-}S)_4]$	$[Fe_4(NO)_4(\mu_3\text{-}S)_4]^-$	**3a**	**3b**	**5**	**6**
Fe–Fe	2.651	2.693	2.695	2.691	2.688	2.689
S···S	3.503	3.510			3.508	3.508
Fe–S	2.217	2.231	2.230	2.227	2.229	2.229

Table 16 Comparison of selected average bond lengths (Å) for the $[Mo_4(\eta\text{-}C_5H_4Pr^i)_4(\mu_3\text{-}S)_4]^{n+}$ moiety in compounds **3a**, **3b**, **10a** and **10b** with those reported previously for $n = 0$, 1 and 2 [5]

	$[Mo_4(\eta\text{-}C_5H_4Pr^i)_4(\mu_3\text{-}S)_4]$	$[Mo_4(\eta\text{-}C_5H_4Pr^i)_4(\mu_3\text{-}S)_4]^+BF_4^-$	**3a**	**3b**	**10a**	**10b**	$[Mo_4(\eta\text{-}C_5H_4Pr^i)_4(\mu_3\text{-}S)_4]^{2+}2I_3^-$
Mo–Mo	2.904	2.894	2.897	2.888	2.889	2.893	2.858
S···S	3.643	3.647			3.645	3.641	3.668
Mo–S	2.344	2.343	2.342	2.341	2.341	2.341	2.343

Table 17 Fractional atomic coordinates for $[Mo_4(\eta\text{-}C_5H_4Pr^i)_4(\mu_3\text{-}S)_4][tcnq]$ **11** with e.s.d.s in parentheses

Atom	*X/a*	*Y/b*	*Z/c*
Mo(1)	0.586 14(3)	0.108 55(2)	0.188 03(1)
Mo(2)	0.722 63(2)	0.216 17(2)	0.317 57(1)
Mo(3)	0.507 94(2)	−0.008 55(2)	0.307 84(1)
Mo(4)	0.459 40(2)	0.232 14(2)	0.283 94(1)
S(1)	0.644 09(7)	0.320 64(7)	0.231 66(4)
S(2)	0.707 49(7)	0.016 73(7)	0.262 91(4)
S(3)	0.549 51(6)	0.173 31(6)	0.383 57(3)
S(4)	0.375 17(7)	0.038 43(7)	0.219 35(4)
C(1)	0.716 2(4)	0.075 9(4)	0.103 9(2)
C(2)	0.606 9(5)	−0.027 6(4)	0.099 6(2)
C(3)	0.495 8(5)	0.012 7(4)	0.081 8(2)
C(4)	0.538 2(4)	0.144 9(4)	0.076 8(2)
C(5)	0.676 1(4)	0.183 3(3)	0.089 5(2)
C(6)	0.758 2(5)	0.314 7(4)	0.080 2(2)
C(7)	0.891 3(6)	0.349 6(6)	0.119 1(3)
C(8)	0.770 5(8)	0.326 7(6)	0.005 9(2)
C(9)	0.848 3(3)	0.379 2(3)	0.395 4(2)
C(10)	0.898 0(3)	0.398 3(3)	0.333 7(2)
C(11)	0.946 2(3)	0.295 2(3)	0.315 4(2)
C(12)	0.928 8(3)	0.213 0(3)	0.367 4(2)
C(13)	0.868 1(3)	0.263 6(3)	0.417 7(1)
C(14)	0.843 0(3)	0.216 8(3)	0.485 1(2)
C(15)	0.949 3(4)	0.294 2(4)	0.538 2(2)
C(16)	0.831 3(5)	0.077 1(4)	0.485 7(2)
C(17)	0.479 8(3)	−0.228 5(3)	0.302 3(2)
C(18)	0.542 9(3)	−0.175 3(3)	0.366 4(2)
C(19)	0.456 8(3)	−0.124 4(3)	0.400 3(2)
C(20)	0.340 6(3)	−0.143 2(3)	0.356 9(2)
C(21)	0.353 1(3)	−0.211 2(3)	0.296 5(1)
C(22)	0.244 0(3)	−0.266 4(3)	0.241 0(2)
C(23)	0.289 7(5)	−0.299 2(4)	0.174 7(2)
C(24)	0.149 9(4)	−0.382 0(3)	0.264 1(2)
C(25)	0.258 1(3)	0.255 5(3)	0.309 6(2)
C(26)	0.272 2(4)	0.283 6(4)	0.242 4(2)
C(27)	0.374 8(4)	0.389 8(4)	0.242 0(2)
C(28)	0.425 6(3)	0.430 9(3)	0.308 6(2)
C(29)	0.352 1(3)	0.350 6(3)	0.351 2(1)
C(30)	0.362 3(4)	0.372 9(4)	0.426 4(2)
C(31)	0.292 0(5)	0.257 5(5)	0.459 2(2)
C(32)	0.307 4(6)	0.485 7(5)	0.442 9(3)
C(101)	0.071 1(4)	0.153 7(3)	−0.160 3(2)
C(102)	0.096 9(4)	0.166 3(4)	−0.092 4(2)
C(103)	0.202 3(4)	0.263 7(3)	−0.059 0(2)
C(104)	0.279 2(4)	0.347 6(3)	−0.099 6(2)
C(105)	0.252 7(4)	0.334 9(3)	−0.167 5(2)
C(106)	0.148 2(3)	0.237 2(3)	−0.201 7(2)
C(107)	0.122 6(3)	0.222 0(3)	−0.272 2(2)
C(108)	0.022 6(3)	0.120 4(3)	−0.305 9(2)
C(109)	0.199 3(3)	0.303 7(3)	−0.313 7(2)
C(110)	0.231 3(4)	0.274 4(4)	0.011 6(2)
C(111)	0.333 3(4)	0.371 0(4)	0.046 5(2)
C(112)	0.160 8(6)	0.188 1(5)	0.052 3(3)
N(1)	−0.058 9(3)	0.038 3(3)	−0.333 4(2)
N(2)	0.260 6(3)	0.369 9(3)	−0.347 7(2)
N(3)	0.417 0(4)	0.448 1(4)	0.076 1(2)
N(4)	0.104 8(7)	0.118 8(6)	0.086 0(3)

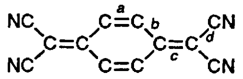
filtration. Compound **26** was prepared by a metathesis reaction between $[Mo_4(\eta\text{-}C_5H_4Pr^i)_4(\mu_3\text{-}S)_4][BF_4]_2$ and $Na_2[Ni\{S_2C_2(CN)_2\}_2]$ in an alcohol–water mixture.

It has previously been noted that the C=C stretching frequency of tris(dithiolene) complexes increases as the charge on the $M(S_2C_2R_2)_3$ unit increases. For example, in the $[Mo\{S_2C_2(CF_3)_2\}_3]^{n-}$ system, ν(C=C) increases from 1455 ($n = 0$) *via* 1508 ($n = 1$) to 1538 cm^{-1} ($n = 2$).[29] The infrared spectrum of compound **21** shows a band at 1530 cm^{-1} which may be assigned to the C=C stretching frequency, indicating a dianion. The ^1H NMR spectrum shows sharp resonances assignable to a $\eta\text{-}C_5H_4Pr^i$ moiety indicating the compound **21** to be diamagnetic. This was confirmed by determination of the magnetic susceptibility of a solid sample which gave the value $\chi_{corr} = -9.7 \times 10^{-4}$ emu mol^{-1}. The anion $[Mo\{S_2C_2(CF_3)_2\}_3]^{2-}$ is known to be diamagnetic,[29] therefore compound **21** must have a charge assignment of $[Mo_4(\eta\text{-}C_5H_4Pr^i)_4(\mu_3\text{-}Se)_4]^{2+}[Mo\{S_2C_2(CF_3)_2\}_3]^{2-}$. The cation $[Mo_4(\eta\text{-}C_5H_4Pr^i)_4(\mu_3\text{-}Se)_4]^{2+}$ would be expected to be diamagnetic, by analogy with the diamagnetic dication $[Mo_4(\eta\text{-}C_5H_4Pr^i)_4(\mu_3\text{-}S)_4]^{2+}$.[5] The infrared spectrum of **22** also shows a band assignable as ν(C=C) at 1531 cm^{-1}, suggesting the presence of dianionic $[Mo\{S_2C_2(CF_3)_2\}_3]^{2-}$; however, the solution ^1H NMR spectrum of this compound in $(CD_3)_2CO$ reveals the $C_5H_4Pr^i$ ring protons at *ca.* δ 30, suggesting that the compound is paramagnetic. Thus, the solution ^1H NMR and solid-state infrared data are not consistent. The EPR spectrum of $[Mo_4(\eta\text{-}C_5H_4Pr^i)_4(\mu_3\text{-}S)_4]^+BF_4^-$ showed no features at room temperature but below 100 K there appeared a broad resonance with $\Delta H_{pp} = 240$ G, $g = 2.235$. That of $NEt_4^+[Mo\{S_2C_2(CF_3)_2\}_3]^-$ at room temperature showed a sharp resonance ($\Delta H_{pp} = 20$ G, $g = 1.998$). The spectrum of a solid sample of compound **22** at room temperature showed a resonance at $\Delta H_{pp} = 23$ G, $g = 2.010$ with weak satellites attributable to hyperfine coupling with the ^{95}Mo and ^{97}Mo nuclei ($I = \frac{5}{2}$). This resonance may be assigned to the presence of the monoanion in **22**. The spectrum at *ca.* 50 K showed an additional broad band at higher *g* value which may be due to the cation $[Mo_4(\eta\text{-}C_5H_4Pr^i)_4(\mu_3\text{-}S)_4]^+$. Finally, the magnetic susceptibility of **22** determined in solution by the Evans method showed the compound to be paramagnetic, $\mu_{eff} = 2.9$, a value consistent with the salt $[Mo_4(\eta\text{-}C_5H_4Pr^i)_4(\mu_3\text{-}S)_4]^+[Mo\{S_2C_2(CF_3)_2\}_3]^-$ in which both the cation and anion have one unpaired electron. We conclude on the basis of the magnetic

Table 18 Fractional atomic coordinates for $[Fe_4(\eta\text{-}C_5H_4Me)_4(\mu_3\text{-}S)_4][tcnq]$ **13** with e.s.d.s in parentheses

Atom	*X/a*	*Y/b*	*Z/c*	Atom	*X/a*	*Y/b*	*Z/c*
Fe(1)	0.805 86(3)	0.074 19(8)	0.311 95(3)	C(17)	0.333 7(2)	0.056 7(7)	0.130 0(2)
Fe(2)	0.712 52(3)	0.301 33(8)	0.311 43(3)	C(18)	0.288 9(3)	0.029(1)	0.071 7(3)
S(1)	0.807 63(5)	0.358 8(1)	0.290 18(5)	C(19)	0.372 3(3)	0.378 8(7)	0.391 8(2)
S(2)	0.704 49(5)	0.017 1(1)	0.289 46(5)	C(20)	0.410 0(2)	0.399 3(7)	0.345 8(3)
C(1)	0.894 9(3)	0.101 1(7)	0.369 6(3)	C(21)	0.394 7(3)	0.562 6(7)	0.316 7(3)
C(2)	0.847 7(3)	0.081 3(7)	0.407 5(2)	C(22)	0.346 7(3)	0.643 5(6)	0.344 8(2)
C(3)	0.818 2(3)	−0.083 1(7)	0.392 5(2)	C(23)	0.331 9(3)	0.528 6(7)	0.393 2(2)
C(4)	0.847 0(2)	−0.164 1(6)	0.345 5(2)	C(24)	0.286 3(4)	0.561(1)	0.436 5(3)
C(5)	0.895 6(2)	−0.049 6(7)	0.331 6(3)	C(101)	0.970 6(2)	1.581 8(6)	0.045 2(2)
C(6)	0.939 9(3)	−0.083(1)	0.286 4(4)	C(102)	0.951 8(2)	1.416 2(6)	0.023 9(2)
C(7)	0.641 6(3)	0.269 6(8)	0.368 7(3)	C(103)	0.979 5(2)	1.328 1(6)	−0.022 2(2)
C(8)	0.700 0(3)	0.292 3(8)	0.405 9(2)	C(104)	0.958 7(2)	1.158 9(6)	−0.045 0(2)
C(9)	0.723 7(3)	0.455 3(8)	0.392 5(2)	C(105)	0.908 8(2)	1.068 9(7)	−0.021 3(2)
C(10)	0.680 7(3)	0.536 9(7)	0.346 2(3)	C(106)	0.982 2(3)	1.073 1(7)	−0.094 1(2)
C(11)	0.628 3(2)	0.418 5(7)	0.331 3(2)	N(105)	0.868 8(2)	0.998 4(7)	−0.001 9(3)
C(12)	0.569 7(3)	0.447(1)	0.286 7(3)	N(106)	1.000 7(3)	1.007 0(8)	−0.134 9(3)
Fe(3)	0.312 67(3)	0.174 53(7)	0.213 22(3)	C(107)	0.530 7(2)	1.078 0(6)	−0.04 48(2)
Fe(4)	0.313 01(3)	0.402 80(7)	0.304 89(3)	C(108)	0.548 1(2)	0.912 3(6)	−0.023 0(2)
S(3)	0.290 27(5)	0.458 9(1)	0.205 18(5)	C(109)	0.518 6(2)	0.827 7(6)	0.023 2(2)
S(4)	0.290 81(5)	0.117 7(1)	0.306 78(5)	C(110)	0.539 0(2)	0.655 8(7)	0.045 8(2)
C(13)	0.372 8(2)	0.207 6(7)	0.144 4(2)	C(111)	0.590 3(3)	0.567 9(7)	0.026 4(3)
C(14)	0.409 6(2)	0.182 7(8)	0.201 7(3)	C(112)	0.511 7(3)	0.572 3(7)	0.093 5(3)
C(15)	0.394 3(2)	0.014 6(8)	0.224 5(3)	N(111)	0.632 5(3)	0.497 2(8)	0.010 4(3)
C(16)	0.346 5(3)	−0.062 5(7)	0.180 7(3)	N(112)	0.490 0(3)	0.504 0(8)	0.132 1(3)

Table 19 Comparison of selected structural data (Å) for the tcnq component in compounds **11** and **13** with those reported previously for $tcnq^0$ and $tcnq^-$ [20,21]



Compound	*a*	*b*	*c*	*d*	(*b* − *c*)	(*c* − *d*)	*c*/(*b* + *d*)	Charge transfer
$tcnq^0$	1.346	1.448	1.374	1.441	0.074	−0.067	0.476	0
$tcnq^-$	1.373	1.423	1.420	1.416	0.003	0.004	0.500	1
11	1.359	1.421	1.421	1.410	0.009	0.002	0.498	1
13	1.366	1.416	1.420	1.417	−0.004	0.003	0.501	1

Table 20 Comparison of selected ultraviolet–visible spectroscopic data for compounds **14**, **16** and **18** with those of $[NEt_3H][(tcnq)_2]$

Compound	I_{395}/I_{842}	$tcnq/C^+$	$tcnq^0/tcnq^-$
14	1.71	1.97	0.97
16	1.72	1.98	0.98
18	1.74	2.00	1.00
$[NEt_3H][(tcnq)_2]$	1.74	2.00	1.00

susceptibility data that the diamagnetic **21** is a 2+/2− salt whilst **22** is a 1+/1− salt. The presence of a dication in **21** and only a monocation in **22** is consistent with the observation that the first ionization energy of $[Mo_4(\eta\text{-}C_5H_4Pr^i)_4(\mu_3\text{-}Se)_4]$ is lower than that of $[Mo_4(\eta\text{-}C_5H_4Pr^i)_4(\mu_3\text{-}S)_4]$.

The ^1H NMR spectra of compounds **23**–**25** in $(CD_3)_2CO$ indicate them to be paramagnetic since the chemical shifts of the $C_5\mathit{H}_4Pr^i$ ring protons were observed at *ca.* δ 30. It was not possible to identify clearly a band assignable to the ν(C=C) mode in the infrared spectra of these salts. Further studies to characterise these compounds are in progress.

In conclusion, this work has initiated the study of 'soft salts' formed by redox-active cluster cations and anions and related systems. The results raise questions concerning the forces controlling the packing of the component ions. Evidence for co-operative effects between the ions arises from the observation of antiferromagnetic behaviour for **11**. It appears that all the new salts **3**–**27** are best described as having integral values for *n*. However, the observation that **21** has a dication whilst **22** has a monocation clearly suggests the possibility of there being a cation of intermediate reducing ability which could give a non-integral value for *n*. Towards this end we have recently prepared a mixture of the mixed sulphur–selenium cubane molecules $[Mo_4(\eta\text{-}C_5H_4Pr^i)_4(\mu_3\text{-}S)_x(\mu_3\text{-}Se)_{4-x}]$, where $x = 0$–4, but we are unable to separate the component compounds.

Experimental

All manipulations were carried out under an inert atmosphere of dinitrogen using standard vacuum-line and Schlenk-vessel techniques. All solvents were predried over molecular sieves and then distilled from potassium [toluene, benzene, light petroleum (b.p. 100–120 °C), cyclohexane, 2,5,8-trioxanonane (diglyme)], sodium-potassium alloy [pentane, light petroleum (b.p. 40–60 °C), diethyl ether, tetrahydrofuran], calcium hydride (acetonitrile) or phosphorus pentaoxide (dichloromethane) under an inert atmosphere of dinitrogen. Where necessary solvents were stored under dinitrogen over activated 4 Å molecular sieves. Deuteriated solvents for NMR spectroscopy were stored in ampoules over activated molecular sieves or a potassium film and transferred by vacuum distillation. Elemental analyses were carried out by the Analytical Service of the Inorganic Chemistry Laboratory, Oxford. Infrared spectra were recorded as Nujol or perfluorodecalin mulls between KBr or CsI plates on a Philips Analytical SP2000 double-beam grating spectrophotometer, or on a Perkin-Elmer 1510 FT interferometer. Electronic spectra were measured in solution with a Perkin-Elmer 552 ultraviolet–visible spectrophotometer. All NMR spectra were recorded at 300 MHz using a Brüker WH300 spectrometer. Chemical shifts are calibrated against

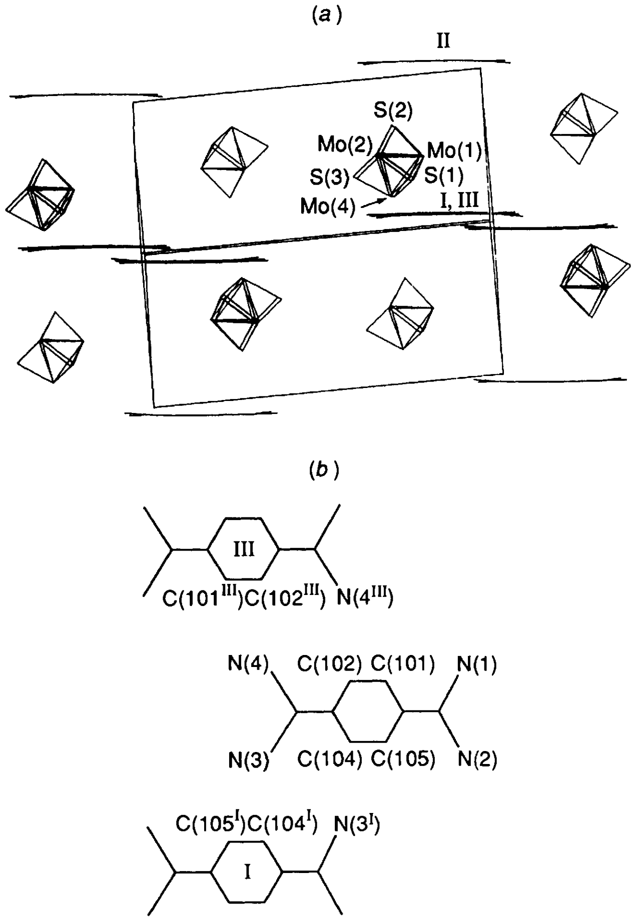


Fig. 6 (*a*) Molecular packing of [$Mo_4(\eta\text{-}C_5H_4Pr^i)_4(\mu_3\text{-}S)_4$][tcnq] **11**. The $\eta\text{-}C_5H_4Pr^i$ ligands have been omitted for clarity. Superscripts I, II and III denote entries generated by the symmetry operators (1 − *x*, 1 − *y* and 1 − *z*), (1 − *x*, −*y*, −*z*) and (−*x*, −*y*, −*z*) respectively. (*b*) Packing of adjacent tcnq molecules in one ribbon of **11**

Table 21 Closest intermolecular molecular contacts (Å) for compound **11**

(*i*) tcnq ··· tcnq			
C(102) ··· N(4^a)	3.324	H(102) ··· N(4^a)	2.549
C(104) ··· N(3^b)	3.405	H(103) ··· N(3^b)	2.504
(*ii*) Cluster ··· tcnq			
C(9) ··· N(2^b)	3.415	H(12) ··· N(2^b)	2.848
C(10) ··· N(2^b)	3.415	H(13) ··· N(2^b)	2.859
C(12) ··· N(1^c)	3.455	H(15) ··· N(1^c)	2.509
C(17) ··· N(2^c)	3.592		
C(18) ··· N(2^c)	3.591	H(24) ··· N(2^c)	2.771
C(20) ··· N(1^a)	3.498	H(26) ··· N(1^a)	2.573
C(25) ··· N(1^a)	3.460	H(34) ··· N(1^a)	2.493
C(26) ··· N(4)	3.595	H(35) ··· N(4)	2.604
C(27) ··· N(3)	3.483	H(36) ··· N(3)	2.549
C(28) ··· N(2^b)	3.483	H(37) ··· N(2^b)	2.535
S(1) ··· H(104^b)	3.166	S(2) ··· C(107^c)	3.560

Superscripts indicate entries generated by the following symmetry operators: *a* −*x*, −*y*, −*z*; *b* 1 − *x*, 1 − *y*, −*z*; *c* 1 − *x*, −*y*, −*z*.

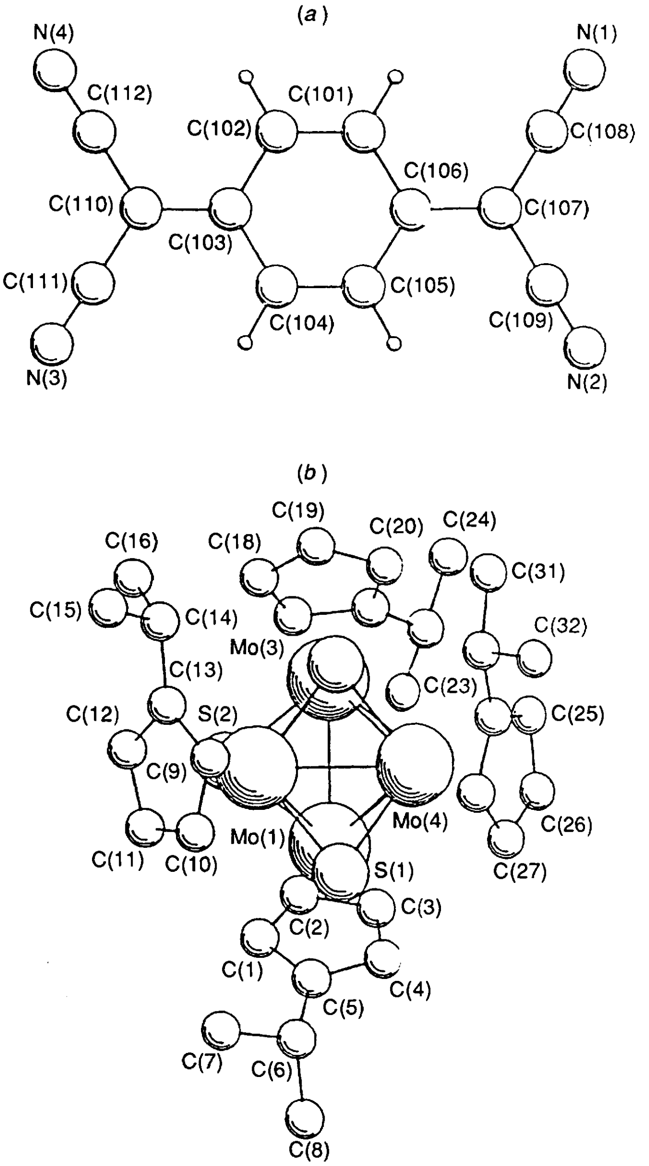


Fig. 7 Atomic labelling scheme for compound **11**: (*a*) tcnq; (*b*) molybdenum cluster

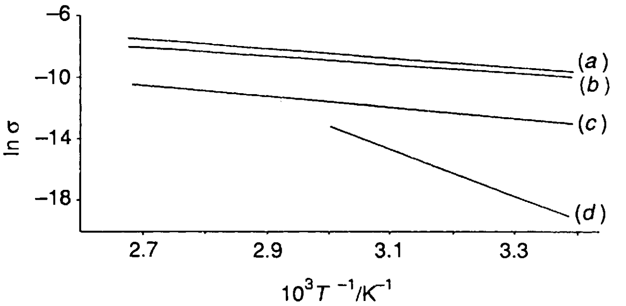


Fig. 8 Temperature dependence of the conductivities of some tcnq salts: (*a*) **14**, (*b*) **12**, (*c*) **16** and (*d*) **11**

internal solvent peaks and are quoted as δ (ppm), with data given as: position (multiplicity, integral, assignment). Abbreviations used in multiplicities are s = singlet, d = doublet and m = multiplet.

Chromatography columns, typically 40 cm × 3 cm^2, were wet-packed with light petroleum (b.p. 40–60 °C) using alumina deactivated by the addition of 8% (w/w) distilled water as the stationary phase. A solution of the mixture to be separated was added to alumina (5–10 g) and the solvent was removed under reduced pressure. The resulting solids were then introduced to the prepared column which had been purged with dinitrogen. Separation was effected by elution with progressively more polar solvents, which were saturated with nitrogen prior to use. The crystal growth by diffusion methods employed cells described elsewhere.[30] The cyclic voltammetry experiments were carried out using an Oxford Electrodes potentiostat with built-in waveform generator. The voltammograms were recorded on a Gould series 6000 A3 chart recorder. The electrochemical cell was of the three-chamber type which contained approximately millimolar solutions of sample in dry, oxygen-free thf with tetrabutylammonium hexafluorophosphate as supporting electrolyte. The $E_{\frac{1}{2}}$ values were determined using the ferrocene–ferrocenium couple as an internal reference.

Electrical conductivities were measured on single crystals or compressed pellets using two-probe techniques as appropriate. The room temperature (r.t.) static susceptibilities of polycrystalline samples were measured using a model MSBMKI magnetic susceptibility balance, made by Johnson Matthey Chemical Limited Equipment Division. The Guoy method was used either in Oxford or in Belfast by Dr. S. Nelson who we thank. The Evans NMR method[31] was also used to measure the susceptibility of a compound in a solution. Most measurements of static susceptibility were performed using the Faraday technique on a Cahn electrobalance at magnetic fields of 0.3–0.9 T between 4 and 300 K. Samples were measured in at least two magnetic fields and a Honda–Owen analysis was performed at r.t. in order to correct for ferromagnetic impurities. These were found to be generally less than 10 ppm as iron.

Preparations.—LiSeH. Butyllithium (30 cm^3 of a 2.7 mol dm^{-3} solution in hexane, 81 mmol) was diluted to 100 cm^3 with light petroleum (b.p. 100–120 °C) and H_2Se (6.3 g, 78 mmol) was distilled onto the solution. The resulting white precipitate was separated by filtration, washed with light petroleum (b.p. 40–60 °C) and dried *in vacuo*. Yield 4.1 g (60%).

$[Mo_4(\eta\text{-}C_5H_4Pr^i)_4(\mu_3\text{-}Se)_4]$ **1**. A slurry of $[Mo_2(\eta\text{-}C_5H_4Pr^i)_2(\mu\text{-}Cl)_4]$, (3.8 g, 6.93 mmol), prepared as previously described,[10] in toluene (150 cm^3) was treated with a large excess of LiSeH (5 g) and the mixture stirred for 3 d at r.t. The resulting dark red solution was separated from the residual solids, pumped to dryness *in vacuo*, and then extracted with light petroleum (b.p. 40–60 °C) until the extracts were colourless. The petroleum extracts were combined, concentrated, and cooled to −80 °C for 24 h giving black needle crystals (2.1 g) which were collected by filtration; the mother-liquor was concentrated and again cooled to −80 °C, yielding another 250 mg of product. The combined yield was 30%. Crystals suitable for X-ray single-crystal analysis were obtained by crystallization from acetone.

$[Cr_4(\eta\text{-}C_5H_4Me)_4(\mu_3\text{-}Se)_4]$ **2**. The compound $[Cr(\eta\text{-}C_5H_4Me)_2]$[32] (2 g, 9.5 mmol) in thf ($\approx$50 cm^3) was treated with H_2Se (0.5 cm^3, *ca.* 12 mmol) by trap-to-trap distillation. The mixture was stirred at r.t. for 16 h, then pumped to dryness and extracted with light petroleum (b.p. 40–60 °C) (3 × 100 cm^3). The extracts were concentrated and left at −25 °C for 24 h. Black needle crystals separated and were dried *in vacuo*. Further concentration of the mother-liquor and cooling to −25 °C for 12 h gave a further crop of product. The combined yield was 1.8 g (90%).

$[Os_6(CO)_{18}]$. The salt $[NEt_4]_2[Os_6(CO)_{18}]$ was prepared by the method reported by Hayward and Shapley[33a] except that a potassium film was used instead of a sodium dispersion. Thus, $[Os_3(CO)_{12}]$[33b] (567 mg, 0.62 mmol), suspended in diglyme (90 cm^3), was added to a glass Schlenk vessel containing a potassium mirror (formed from 29.6 mg of potassium). The mixture was refluxed for 12 h, yielding an orange-brown solution. This was cooled and then added to aqueous NEt_4Br (200 cm^3, 3.3 g, 10 mmol). The resulting mixture was kept at 0 °C for 2 d. The orange-brown solid was separated by filtration, washed with water and dried *in vacuo*. Yield 566 mg (86%).

To a solution of $[NEt_4]_2[Os_6(CO)_{18}]$ (500 mg, 0.23 mmol) in dichloromethane (500 cm^3) was added a 10% aqueous solution of iron(III) chloride (60 cm^3, *ca.* 40 mmol) dropwise with vigorous stirring. The mixture was stirred for 2 h after addition was complete. The brown dichloromethane layer was separated from the aqueous layer in air, dried over anhydrous magnesium sulphate, and concentrated to *ca.* 10 cm^3. Preparative-scale thin-layer chromatography [silica gel, hexane–toluene (9:1)] gave two small yellow bands and one main brown band. The brown band was collected and extracted with dichloromethane. The solvent was removed *in vacuo*, leaving a dark solid. Yield 72 mg (19%).

$[Cr_4(\eta\text{-}C_5H_4Me)_4(\mu_3\text{-}S)_4]$.[11c] Hydrogen sulphide gas was passed through a solution of $[Cr(\eta\text{-}C_5H_4Me)_2]$ (1.75 g, 8.33 mmol) in thf (120 cm^3) for 5 min at r.t. The solvent was then removed under reduced pressure. The solid was extracted with hot light petroleum (b.p. 40–60 °C). The extracts were concentrated and left at −80 °C for 24 h. Black crystals separated and were dried *in vacuo*. Yield 670 mg (49%).

$[Cr_4(\eta\text{-}C_5H_5)_4(\mu_3\text{-}S)_4]$. Hydrogen sulphide gas was passed through a solution of $[Cr(\eta\text{-}C_5H_5)_2]$ in thf at r.t. for 5 min. The solvent was removed under reduced pressure and the residue extracted with light petroleum (b.p. 40–60 °C). The extracts were concentrated and left at −80 °C for 24 h. A black microcrystalline material separated and was dried *in vacuo*. [Found (required): C, 41.4 (40.3); H, 3.5 (3.4)%]. ^1H NMR data (in $CDCl_3$, 300 MHz): δ 4.93 (s, $\eta\text{-}C_5H_5$).

$[Mo_4(\eta\text{-}C_5H_4Pr^i)_4(\mu_3\text{-}S)_4][Fe_4(NO)_4(\mu_3\text{-}S)_4]$ **3**. The compound $[Mo_4(\eta\text{-}C_5H_4Pr^i)_4(\mu_3\text{-}S)_4]$ (100 mg, 0.11 mmol) in toluene (50 cm^3) was treated with $[Fe_4(NO)_4(\mu_3\text{-}S)_4]$[3] (50 mg, 0.11 mmol) in toluene (50 cm^3). A precipitate appeared immediately. The mixture was left overnight. The resulting solid was separated by filtration, then washed twice with toluene and dried *in vacuo*. The crude product was recrystallized from concentrated acetone solution by cooling to −80 °C for 2 d. The long black needle crystals were separated and dried *in vacuo*. Yield 113 mg (75%).

$[Mo_4(\eta\text{-}C_5H_4Pr^i)_4(\mu_3\text{-}Se)_4][Fe_4(NO)_4(\mu_3\text{-}S)_4]$ **4**. The compound $[Mo_4(\eta\text{-}C_5H_4Pr^i)_4(\mu_3\text{-}Se)_4]$ (56 mg, 0.05 mmol) in toluene (25 cm^3) was added to $[Fe_4(NO)_4(\mu_3\text{-}S)_4]$ (28 mg, 0.06 mmol) in toluene (25 cm^3). The mixture was left at r.t. for 2 d. The resulting solid was separated by filtration, washed with toluene, dried *in vacuo* and crystallized from acetone. Yield 48 mg (60%).

$[Fe_4(\eta\text{-}C_5H_4R)_4(\mu_3\text{-}S)_4][Fe_4(NO)_4(\mu_3\text{-}S)_4]$ (R = H, **5**; *or* Me, **6**). The compound $[Fe_4(\eta\text{-}C_5H_5)_4(\mu_3\text{-}S)_4]$[3] (56 mg, 0.092 mmol) in toluene (30 cm^3) was added to a solution of $[Fe_4(NO)_4(\mu_3\text{-}S)_4]$[34] (43.5 mg, 0.092 mmol) in toluene (30 cm^3). The mixture was left for 2 h. The resulting precipitate was separated by filtration, washed with toluene, dried *in vacuo* and then dissolved in hot acetone. The saturated solution was allowed to cool slowly to −80 °C. Black needle crystals separated which were dried *in vacuo*. The product was $[Fe_4(\eta\text{-}C_5H_5)_4(\mu_3\text{-}S)_4][Fe_4(NO)_4(\mu_3\text{-}S)_4]\cdot Me_2CO$. Yield 84 mg (80%). Compound **6** was prepared in a similar manner.

$[Cr_4(\eta\text{-}C_5H_4R)_4(\mu_3\text{-}S)_4][Fe_4(NO)_4(\mu_3\text{-}S)_4]$ (R = H, **7**; *or* Me, **8**). The compound $[Cr_4(\eta\text{-}C_5H_5)_4(\mu_3\text{-}S)_4]$ (62.6 mg, 0.105 mmol) in toluene was added to a solution of $[Fe_4(NO)_4(\mu_3\text{-}S)_4]$ (50 mg, 0.106 mmol) in toluene. A precipitate appeared gradually and the mixture was allowed to stand overnight and then filtered. The resulting solid was washed with toluene and dried *in vacuo*. Yield 70 mg (62%). Compound **8** was prepared in a similar manner.

$[Cr_4(\eta\text{-}C_5H_4Me)_4(\mu_3\text{-}Se)_4][Fe_4(NO)_4(\mu_3\text{-}S)_4]$ **9**. The compound $[Fe_4(NO)_4(\mu_3\text{-}S)_4]$ (240 mg, 0.5 mmol) in toluene (100 cm^3) was added to a solution of $[Cr_4(\eta\text{-}C_5H_4Me)_4(\mu_3\text{-}Se)_4]$ (420 mg, 0.5 mmol) in toluene (100 cm^3). The mixture was allowed to stand overnight at r.t. The precipitate was filtered off, washed with toluene, and then dried *in vacuo*. The crude product was recrystallized from acetone, yielding black microcrystals (490 mg). The mother-liquor was concentrated and left at −80 °C and additional product (70 mg) was obtained. Total yield 560 mg (85%). Single crystals suitable for X-ray diffraction analysis were obtained by recrystallization from dichloromethane.

$[Mo_4(\eta\text{-}C_5H_4Pr^i)_4(\mu_3\text{-}S)_4]_2[Os_6(CO)_{18}]$ **10**. *Method A, using an excess of* $[Mo_4(\eta\text{-}C_5H_4Pr^i)_4(\mu_3\text{-}S)_4]$. To a solution of $[Mo_4(\eta\text{-}C_5H_4Pr^i)_4(\mu_3\text{-}S)_4]$ (94 mg, 0.1 mmol) in toluene (40

cm^3) was added $[Os_6(CO)_{18}]$ (32 mg, 0.02 mmol) in toluene (30 cm^3). The solution became cloudy immediately and the mixture was left overnight at r.t. The resulting precipitate was separated, *washed with* toluene, and then dried *in vacuo*. The product was then extracted with acetone (3 × 30 cm^3), the extract concentrated under reduced pressure and allowed to cool slowly to −80 °C. Long black crystals were isolated and dried *in vacuo*. Yield 50 mg {70% based on $[Os_6(CO)_{18}]$}.

Method B, using an excess of $[Os_6(CO)_{18}]$. To a solution of the compound $[Os_6(CO)_{18}]$ (40 mg, 0.024 mmol) in thf (40 cm^3) was added dropwise a solution of $[Mo_4(\eta\text{-}C_5H_4Pr^i)_4(\mu_3\text{-}S)_4]$ (20.7 mg, 0.02 mmol) in thf (30 cm^3). The resulting mixture was left overnight at r.t. The solvent was removed under reduced pressure and the residue was washed thoroughly with toluene (40 cm^3 × 3) and then extracted with acetone. The extracts were concentrated and allowed to cool slowly to −80 °C. Black crystals were isolated by filtration and dried *in vacuo*. Analysis of the product indicated that it was also $[Mo_4(\eta\text{-}C_5H_4Pr^i)_4(\mu_3\text{-}S)_4]_2[Os_6(CO)_{18}]$.

$[Mo_4(\eta\text{-}C_5H_4Pr^i)_4(\mu_3\text{-}S)_4][tcnq]$ **11**. *Method A, from direct reaction of* $[Mo_4(\eta\text{-}C_5H_4Pr^i)_4(\mu_3\text{-}S)_4]$ *with* tcnq. A solution of tcnq (40.8 mg, 0.2 mmol) in toluene (50 cm^3) was added to $[Mo_4(\eta\text{-}C_5H_4Pr^i)_4(\mu_3\text{-}S)_4]$ (94 mg, 0.1 mmol) in toluene (50 cm^3). The mixture was left for 12 h at r.t. without stirring. The resulting microcrystalline precipitate was isolated, washed with toluene, and dried *in vacuo*. Attempts to grow single crystals suitable for X-ray analysis by recrystallization were unsuccessful. Yield 75 mg (65%).

Method B, from metathesis of $[NEt_3H][(tcnq)_2]$ *with* $[Mo_4(\eta\text{-}C_5H_4Pr^i)_4(\mu_3\text{-}S)_4]BF_4$. A solution of $[NEt_3H][(tcnq)_2]$ [16] (20 mg, 0.04 mmol) in acetonitrile (40 cm^3) was added to a solution of $[Mo_4(\eta\text{-}C_5H_4Pr^i)_4(\mu_3\text{-}S)_4]BF_4$ [5b] (40 mg, 0.04 mmol) in acetonitrile (20 cm^3). The solution was concentrated and allowed to cool to −25 °C over 2 weeks. Black crystals were filtered off and dried *in vacuo*. Some were suitable for an X-ray crystal structure analysis.

$[Fe_4(\eta\text{-}C_5H_4R)_4(\mu_3\text{-}S)_4][tcnq]$ (R = H, **12**; *or* Me, **13**). The compound tcnq (33 mg, 0.16 mmol) in toluene (25 cm^3) was added to a solution of $[Fe_4(\eta\text{-}C_5H_5)_4(\mu_3\text{-}S)_4]$ (85 mg, 0.14 mmol) in toluene (25 cm^3). The mixture was left for 16 h. The black microcrystalline precipitate was filtered off, washed with toluene and dried *in vacuo*. Yield 85 mg (75%). Attempts to grow suitable crystals for X-ray analysis by recrystallization from various solvents were unsuccessful. Compound **13** was prepared in a similar manner.

$[Cr_4(\eta\text{-}C_5H_5)_4(\mu_3\text{-}S)_4][(tcnq)_2]$ **14**. A solution of tcnq (40.8 mg, 0.2 mmol) in toluene (25 cm^3) was added to one of $[Cr_4(\eta\text{-}C_5H_5)_4(\mu_3\text{-}S)_4]$ (59.6 mg, 0.1 mmol) in toluene (25 cm^3). After 24 h the resulting precipitate was filtered off, washed with toluene, dried *in vacuo* and recrystallized from acetone. Yield 50%.

$[Cr_4(\eta\text{-}C_5H_4Me)_4(\mu_3\text{-}S)_4][tcnq]$ **15**. Separate solutions of $[Cr_4(\eta\text{-}C_5H_4Me)_4(\mu_3\text{-}S)_4]$ (65.2 mg, 0.1 mmol) and tcnq (40.8 mg, 0.2 mmol) each in toluene (25 cm^3) were allowed to diffuse through glass frits into a central compartment also containing toluene. After 2 months at r.t. black microcrystals appeared and were collected, washed with toluene and dried *in vacuo*. Yield 65 mg (75%).

$[Cr_4(\eta\text{-}C_5H_4Me)_4(\mu_3\text{-}S)_4][(tcnq)_2]$ **16**. The compound $[Cr_4(\eta\text{-}C_5H_4Me)_4(\mu_3\text{-}S)_4]$ (65.2 mg, 0.1 mmol) in toluene (30 cm^3) was added to a solution of tcnq (40.8 mg, 0.2 mmol) in toluene (25 cm^3). A precipitate appeared rapidly and was separated by filtration, washed with toluene and dried *in vacuo*. Recrystallization from acetone gave black microcrystals. Yield 78 mg (73%).

$[Cr_4(\eta\text{-}C_5H_4Me)_4(\mu_3\text{-}Se)_4][tcnq]$ **17**. Separate solutions of $[Cr_4(\eta\text{-}C_5H_4Me)_4(\mu_3\text{-}Se)_4]$ (84 mg, 0.1 mmol) and tcnq (40.8 mg, 0.2 mmol) each in toluene (25 cm^3) were allowed to diffuse through glass frits into a central compartment also containing toluene. After 40 d at r.t. many small black, needle-like crystals were formed. These were collected, washed with toluene and dried *in vacuo*. Yield 84 mg (80%).

$[Cr_4(\eta\text{-}C_5H_4Me)_4(\mu_3\text{-}Se)_4][(tcnq)_2]$ **18**. A solution of tcnq (105 mg, 0.51 mmol) in toluene (25 cm^3) was added to $[Cr_4(\eta\text{-}C_5H_4Me)_4(\mu_3\text{-}Se)_4]$ (84 mg, 0.1 mmol) in toluene (25 cm^3). A precipitate appeared immediately. The mixture was left overnight and then the solid was isolated by filtration, washed thoroughly with toluene, and dried *in vacuo*. Fine black crystals were obtained upon recrystallization from acetone. Yield 80 mg (64%).

$[Mo_4(\eta\text{-}C_5H_4Pr^i)_4(\mu_3\text{-}Se)_4][tcnq]$ **19**. Solutions of $[Mo_4(\eta\text{-}C_5H_4Pr^i)_4(\mu_3\text{-}Se)_4]$ (48 mg, 0.043 mmol) in toluene (20 cm^3) and tcnq (60 mg, 0.29 mmol) in toluene (20 cm^3) were allowed to diffuse through separate glass frits into pure toluene (20 cm^3) contained in a central chamber. After 1 month black featherlike crystals were harvested from the central chamber, washed with toluene five times, and dried *in vacuo*. Yield 20 mg (35%).

$[Mo_4(\eta\text{-}C_5H_4Pr^i)_4(\mu_3\text{-}Se)_4][tcnq]_3$ **20**. A solution of tcnq (90 mg, 0.44 mmol) in toluene (30 cm^3) was added to $[Mo_4(\eta\text{-}C_5H_4Pr^i)_4(\mu_3\text{-}Se)_4]$ (95 mg, 0.084 mmol) in toluene (30 cm^3). Microcrystals appeared almost immediately. The mixture was left to stand overnight, and then the dark crystals were isolated by filtration, washed with toluene, and dried *in vacuo*. Yield 58 mg (40%).

$[Mo_4(\eta\text{-}C_5H_4Pr^i)_4(\mu_3\text{-}Se)_4][Mo\{S_2C_2(CF_3)_2\}_3]$ **21**. The compound $[Mo_4(\eta\text{-}C_5H_4Pr^i)_4(\mu_3\text{-}Se)_4]$ (214 mg, 0.19 mmol) in toluene (20 cm^3) was added to $[Mo\{S_2C_2(CF_3)_2\}_3]$ [27,28] (147 mg, 0.19 mmol) in toluene (20 cm^3). A precipitate appeared immediately. The reaction mixture was left overnight at r.t. and then filtered. The solid was washed with toluene and dried *in vacuo*. Recrystallization from acetone (−20 °C, 6 d) yielded some large black crystals (120 mg). Upon cooling to −80 °C the mother-liquor deposited further black needle crystals (130 mg), giving a combined yield of 70%. Analysis showed that both sets of crystals had identical stoichiometry.

$[Mo_4(\eta\text{-}C_5H_4Pr^i)_4(\mu_3\text{-}S)_4][Mo\{S_2C_2(CF_3)_2\}_3]$ **22**. The compound $[Mo_4(\eta\text{-}C_5H_4Pr^i)_4(\mu_3\text{-}S)_4]$ (110 mg, 0.12 mmol) in toluene (160 cm^3) was added to a solution of $[Mo\{S_2C_2(CF_3)_2\}_3]$ (200 mg, 0.26 mmol) in toluene (30 cm^3). A precipitate appeared immediately. The mixture was left to stand overnight at r.t., and the solids were filtered off, washed with toluene and dried *in vacuo*. Crystallization from a mixture of thf–toluene gave a black powder. Yield 60 mg (30%).

$[Mo_4(\eta\text{-}C_5H_4Pr^i)_4(\mu_3\text{-}S)_4]_2[Mo\{S_2C_2(CF_3)_2\}_3]$ **23**. The compound $[Mo_4(\eta\text{-}C_5H_4Pr^i)_4(\mu_3\text{-}S)_4]$ (107 mg, 0.11 mmol) in toluene (50 cm^3) was treated with an excess of $[Mo\{S_2C_2(CF_3)_2\}_3]$ (250 mg, 0.32 mmol) in toluene. The resulting mixture was left to stand for 3 d and the solids were isolated by filtration (and were proved later to be the 1:1 salt, $[Mo_4(\eta\text{-}C_5H_4Pr^i)_4(\mu_3\text{-}S)_4][Mo\{S_2C_2(CF_3)_2\}_3]$). The filtrate was left to stand for a further 5 d, and some shiny microcrystals appeared. They were isolated by filtration, washed thoroughly with toluene and dried *in vacuo*. Yield 25 mg (12%).

$[Cr_4(\eta\text{-}C_5H_4Me)_4(\mu_3\text{-}S)_4][Mo\{S_2C_2(CF_3)_2\}_3]$ **24**. The compound $[Cr_4(\eta\text{-}C_5H_4Me)_4(\mu_3\text{-}S)_4]$ (58 mg, 0.09 mmol) in toluene was added to a solution of $[Mo\{S_2C_2(CF_3)_2\}_3]$ (80 mg, 0.1 mmol) in toluene. A microcrystalline precipitate appeared in a few minutes. The mixture was left at r.t., and after 12 h was filtered. The precipitate was washed with toluene and then dissolved in hot acetonitrile. The extract was cooled to −25 °C for 5 d giving black shiny, plate-like crystals. Yield 70 mg (55%).

$[Cr_4(\eta\text{-}C_5H_4Me)_4(\mu_3\text{-}Se)_4][Mo\{S_2C_2(CF_3)_2\}_3]$ **25**. The compound $[Mo\{S_2C_2(CF_3)_2\}_3]$ (70 mg, 0.09 mmol) in toluene was treated with $[Cr_4(\eta\text{-}C_5H_4Me)_4(\mu_3\text{-}Se)_4]$ (70 mg, 0.08 mmol) in toluene. Shiny microcrystals appeared gradually, which were isolated by filtration after 24 h, then washed with toluene and dried *in vacuo*. Recrystallization from acetonitrile afforded black crystals. Yield 80 mg (62%).

$[Mo_4(\eta\text{-}C_5H_4Pr^i)_4(\mu_3\text{-}S)_4][Ni\{S_2C_2(CN)_2\}_2]$ **26**. A refluxing solution of $Na_2S_2C_2(CN)_2$ [28] (372 mg, 2 mmol) in ethanol (8 cm^3) was added to a solution of $NiCl_2\cdot 6H_2O$ (238 mg, 1 mmol) in EtOH–water (1:1 v/v) (8 cm^3). Part (0.8 cm^3) of this mixture was added to a solution of $[Mo_4(\eta\text{-}C_5H_4Pr^i)_4(\mu_3\text{-}S)_4][BF_4]_2$ [13]

(43 mg, 0.04 mmol) in methanol (20 cm^3). Purple microcrystals appeared immediately, which were filtered off, washed with water, ethanol, and finally diethyl ether and then dried *in vacuo*. Yield 40 mg (78%).

$[Cr_4(\eta\text{-}C_5H_4Me)_4(\mu_3\text{-}S)_4][tcne]$ **27**. A solution of tcne (64 mg, 0.5 mmol) in toluene (25 cm^3) was added to a solution of $[Cr_4(\eta\text{-}C_5H_4Me)_4(\mu_3\text{-}S)_4]$ (80 mg, 0.12 mmol) in toluene (25 cm^3). A precipitate appeared after a few minutes. This was filtered off after 24 h, washed twice with toluene and dried *in vacuo*. Crystallization from acetonitrile gave black crystals. Yield 78 mg (82%).

General Procedure for the X-Ray Crystal Structure Determinations.—Crystal data and data collection and processing parameters are given in Table 2. The general procedure was as follows. A crystal was sealed in a Lindemann glass capilliary and transferred to the goniometer head of an Enraf–Nonius CAD4-F diffractometer. Unit-cell parameters were calculated from the setting angles of 25 carefully centred reflections. Three reflections were chosen as intensity standards and were measured every 3600 s of X-ray exposure time, and three orientation controls were measured every 250 reflections.

The data were corrected for Lorentz and polarization effects and an empirical absorption correction[35] based on an azimuthal scan was applied. Equivalent reflections were merged and systematically absent reflections rejected. The possibility that compounds **3a** and **3b** are of higher symmetry was examined and rejected. The structures were solved using direct methods. Subsequent Fourier difference syntheses revealed the positions of other non-hydrogen atoms. Non-hydrogen atoms were refined with anisotropic thermal parameters by least-squares procedures and hydrogen atoms were placed in estimated positions (C–H 0.96 Å). A Chebyshev weighting scheme[36] was applied and the data were corrected for the effects of anomalous dispersion and isotropic extinction (*via* an overall isotropic extinction parameter[37]) in the final stages of refinement. All crystallographic calculations were performed using the CRYSTALS suite[38] on a VAX 11/750 computer. Scattering factors were taken from the usual sources.[39]

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

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