New Organometallic Solids: Synthesis and Solid State Properties of Salts of Redox-active Organometallic Clusters

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The synthesis, structures, and solid state properties of salts of general stoicheiometry $[C]^{n+}[A]^{n-}$, where *C* indicates a cluster cation and *A* represents a cluster anion, are described.

Relatively little attention has been given to the solid state properties of organo-transition metal compounds. Here we describe studies designed to exploit some unique features of organometallic cluster compounds in the synthesis of new solids. There are a substantial number of cubane cluster compounds of general stoicheiometry $[M_4X_4Y_4]$, for example, $[M_4(\eta\text{-}C_5H_4R)_4(\mu^3\text{-}S)_4]$, where M = Fe,[1] Cr,[2] and Mo,[3] and $[Fe_4(NO)_4(\mu^3\text{-}S)_4]$.[4] Many of these clusters can undergo multiple and reversible redox reactions forming stable, isolable cations or anions. For example, the compound $[Fe_4(NO)_4(\mu^3\text{-}S)_4]^n$, $n = 0$,can add up to two electrons giving anions where $n = -1$ or -2,[4] whilst the compounds $[M_4(\eta\text{-}C_5H_4R)_4(\mu^3\text{-}S)_4]^n$, $n = 0$, can form cations where $n = +1$ or $+2$ for M = Cr or Mo, and $n = +1, 2, 3$ or 4 for M = Fe.

We set out to synthesise simple salts of general stoicheiometry $[C]^{n+}[A]^{n-}$, where *C* indicates a cluster cation and *A* represents a cluster anion. We were interested in investigating their bulk properties, to discover whether the structures of such salts were well-described by simple electrostatic considerations and, given the availability of multiple redox states to both *C* and *A*, there is the interesting possiblity that *n* could be non-integral.

We prepared the new cluster $[Mo_4(\eta\text{-}C_5H_4Pr^i)(\mu^3\text{-}Se)_4]$ by treatment of $[Mo(\eta\text{-}C_5H_4Pr^i)Cl_2]_2$ with LiHSe. Further, we found convenient high yield routes to the synthesis of the compounds $[Cr_4(\eta\text{-}C_5H_4R)_4(\mu^3\text{-}Se)_4]$, R = H and Me, by treatment of the corresponding chromocene compounds $[Cr(\eta\text{-}C_5H_4R)_2]$ in toluene with H_2Se. In a typical preparation, equimolar toluene solutions of $[Mo_4(\eta\text{-}C_5H_4Pr^i)_4(\mu^3\text{-}S)_4]$ and $[Fe_4(NO)_4(\mu^3\text{-}S)]_4$ were mixed giving an immediate precipitate. The product was crystallised from acetone.

The new salts (**1**)—(**21**) are detailed in Table 1 together with

Table 1. Conductivity, magnetic and electrochemical data for the soft salts.

Entry number	Compound[a]	Room temperature conductivity/ ohm^{-1} cm^{-1}	E_a/ eV	Electrochemical data[b] Reductive potential of cation C or anion A E_1[c]	E_2[f]	C (molar)	θ	Magnetic susceptibility data[c] μ_{eff}	χ_o/ emu mol^{-1}	χ_{dia}/ emu mol^{-1} ×10^{-6}	χ_{TIP}[d] ×10^{-6}
1	$[\mathrm{Mo_4(\eta\text{-}C_5H_4Pr^i)_4(\mu^3\text{-}S)_4}][\mathrm{Fe_4(NO)_4(\mu^3\text{-}S)_4}]$[a]	7.6 × 10^{-9}	0.41	C −0.33	+0.32[g,h]	0.77	−0.67	2.48	−5.54 × 10^{-4}	−783	225
2	$[\mathrm{Mo_4(\eta\text{-}C_5H_4Pr^i)_4(\mu^3\text{-}Se)_4}][\mathrm{Fe_4(NO)_4(\mu^3\text{-}S)_4}]$			A +0.13	−0.65[i,j]						
3	$[\mathrm{Fe_4(\eta\text{-}C_5H_5)_4(\mu^3\text{-}S)_4}][\mathrm{Fe_4(NO)_4(\mu^3\text{-}S)_4}]$[a]	4.7 × 10^{-9}	0.91	C −0.33	+0.33[k]						
4	$[\mathrm{Mo_4(\eta\text{-}C_5H_4Pr^i)_4(\mu^3\text{-}S)_4}]_2[\mathrm{Os_6(CO)_{18}}]$[a]				+0.04[l]	0.93	−0.97	2.73	−1.67 × 10^{-3}	−1782	112
5	$[\mathrm{Mo_4(\eta\text{-}C_5H_4Pr^i)_4(\mu^3\text{-}S)_4}][\mathrm{Mo(S_2C_2(CF_3)_2)_3}]$			A +0.95	+0.36[m]						
6	$[\mathrm{Mo_4(\eta\text{-}C_5H_4Pr^i)_4(\mu^3\text{-}Se)_4}][\mathrm{Mo(S_2C_2(CF_3)_2)_3}]$			C −0.91	−0.32[n]				−9.7 × 10^{-4}	−970	
7	$[\mathrm{Fe_4(\eta\text{-}C_5H_5)_4(\mu^3\text{-}S)_4}][\mathrm{Ni(S_2C_2(CN)_2)}]_2$			A +1.02	+0.23						
8	$[\mathrm{Fe_4(\eta\text{-}C_5H_4Me)_4(\mu^3\text{-}S)_4}][\mathrm{Fe_4(NO)_4(\mu^3\text{-}S)_4}]$[a]	1.5 × 10^{-9}	0.36								
9	$[\mathrm{Cr_4(\eta\text{-}C_5H_5)_4(\mu^3\text{-}S)_4}][\mathrm{Fe_4(NO)_4(\mu^3\text{-}S)_4}]$										
10	$[\mathrm{Cr_4(\eta\text{-}C_5H_4Me)_4(\mu^3\text{-}S)_4}][\mathrm{Fe_4(NO)_4(\mu^3\text{-}S)_4}]$	5.4 × 10^{-9}	0.37	C +0.32	+1.15[o]						
11	$[\mathrm{Cr_4(\eta\text{-}C_5H_4Me)_4(\mu^3\text{-}Se)_4}][\mathrm{Fe_4(NO)_4(\mu^3\text{-}S)_4}]$			C −0.66	−0.06[p]						
12	$[\mathrm{Cr_4(\eta\text{-}C_5H_4Me)_4(\mu^3\text{-}S)_4}][\mathrm{Mo(S_2C_2(CF_3)_2)_3}]$										
13	$[\mathrm{Mo_4(\eta\text{-}C_5H_4Pr^i)_4(\mu^3\text{-}S)_4}][\mathrm{TCNQ}]$[a]	4.9 × 10^{-8}	0.73	A +0.17	−0.37[p]	0.84	−8.0	2.59	−672 × 10^{-6}	−707	35
14	$[\mathrm{Fe_4(\eta\text{-}C_5H_5)_4(\mu^3\text{-}S)_4}][\mathrm{TCNQ}]$	4.4 × 10^{-5}	0.28								
15	$[\mathrm{Fe_4(\eta\text{-}C_5H_4Me)_4(\mu^3\text{-}S)_4}][\mathrm{TCNQ}]$[a]			C +0.075	+0.665[q]						
16	$[\mathrm{Cr_4(\eta\text{-}C_5H_5)_4(\mu^3\text{-}S)_4}][\mathrm{TCNQ}]_2$	5.8 × 10^{-5}	0.28								
17	$[\mathrm{Cr_4(\eta\text{-}C_5H_4Me)_4(\mu^3\text{-}S)_4}][\mathrm{TCNQ}]_2$	2.3 × 10^{-6}	0.30			0.80	−2.26	2.53	−330 × 10^{-6}	−595	265
18	$[\mathrm{Cr_4(\eta\text{-}C_5H_4Me)_4(\mu^3\text{-}S)_4}][\mathrm{TCNE}]$	5.5 × 10^{-6}	0.47	A +0.15	−0.57[r]	0.83	−3.8	2.57	−319 × 10^{-6}	−440	121
19	$[\mathrm{Cr_4(\eta\text{-}C_5H_4Me)_4(\mu^3\text{-}Se)_4}][\mathrm{TCNQ}]_2$										
20	$[\mathrm{Cr_4(\eta\text{-}C_5H_4Me)_4(\mu^3\text{-}Se)_4}][\mathrm{TCNQ}]$					0.58	−1.33	2.15			
21	$[\mathrm{Mo_4(\eta\text{-}C_5H_4Pr^i)_4(\mu\text{-}Se)_4}][\mathrm{TCNQ}]_3$										

[a] Indicates that a satisfactory *X*-ray crystal structure determination has been made. TCNE = tetracyanoethylene; TCNQ = tetracyanoquinodimethane. [b] Data in volts, reference to the standard calomel electrode in MeCN unless otherwise stated. [c] Parameters relate to $\chi = \chi_o + C/(T\text{-}\theta)$ fit. [d] T.I.P. (Temperature Independent Paramagnetism) (emu/mol), corrected for dimagnetism. [e] Half-wave potentials for C^+/C, or for A/A^-. [f] Half-wave potentials for C^{2+}/C^+, or for A^-/A^{2-}. [g] In dimethylformamide. [h] Ref. 3. [i] In CH_2Cl_2. [j] Ref. 4. [k] Ref. 1. [l] For $\mathrm{Os_6(CO)_{18}} + 2e^- \rightleftarrows \mathrm{Os_6(CO)_{18}}^{2}$, in tetrahydrofuran (THF).[10] [m] Ref. 11. [n] Reference to ferrocene/ ferrocenium in THF. [o] Reference to Pt wire in THF. [r] Ref. 12.

some physical properties. Satisfactory microanalyses were obtained in all cases. The radii of the component ions of these salts are large compared with the radii of simple ions and correspondingly relatively low lattice energies are to be expected. For this reason we refer to these molecular cluster salts as 'soft salts'.

The crystal structures of six of the salts were determined (see Table 1). Here we are not so much concerned with the molecular structures of the component cations and anions but rather with the packing of the cations and anions, which are approximated as spheres. Examples of these crystal structures are represented in Figures 1 and 2. Most structures are not necessarily those predicted by the ionic model. For example, the 1 : 1 compound (**1**) occurs in both monoclinic (**1**$_\mathrm{m}$) and orthorhombic (**1**$_\mathrm{o}$) forms. Compound (**1**) has an approximate radius ratio $r^+/r^- = 1.3$ which would suggest a CsCl structure, but in (**1**$_\mathrm{m}$) the inner co-ordination sphere of the cation is a distorted tetrahedron of anions which pack in the layered arrangement shown. In the (**1**$_\mathrm{o}$) form the cation has a distorted trigonal bipyramidal environment of anions.

In contrast, the 2 : 1 compound (**4**), for which the radius ratio is again approximately $r^+/r^- = 1.3$, has the expected anti-fluorite arrangement of cations in both alternative monoclinic forms [(**4a**), *C*2/*c*; (**4b**), *P*2$_1$/*a*]. Possibly the greater contribution to the lattice energy of (**4**) arising from the greater charge component is responsible for the adoption of a structure predicted by the ionic model. It is also possible that we have not found all the different packing arrangements of these salts and that additional forms could be observed.

The determination of the magnitude of the charge on the cations and anions is not straightforward. Magnetic susceptibility data (Table 1) shows (**1**) to be paramagnetic, corresponding to this salt having a mono-cation and mono-anion. In contrast, (**6**) is diamagnetic, indicating a di-cation and di-anion in this salt. The observation that both C^+A^- and $C^{2+}A^{2-}$ salts are formed suggests that when the redox properties are suitably matched a material $C^{n+}A^{n-}$, possibly metallic, where $1 < n < 2$, might exist. Close examination of the crystal structure of (**13**)† (Figure 3) shows the TCNQ molecules to be arranged in ribbons, separated by cluster cations. This ribbon arrangement is very unusual for TCNQ

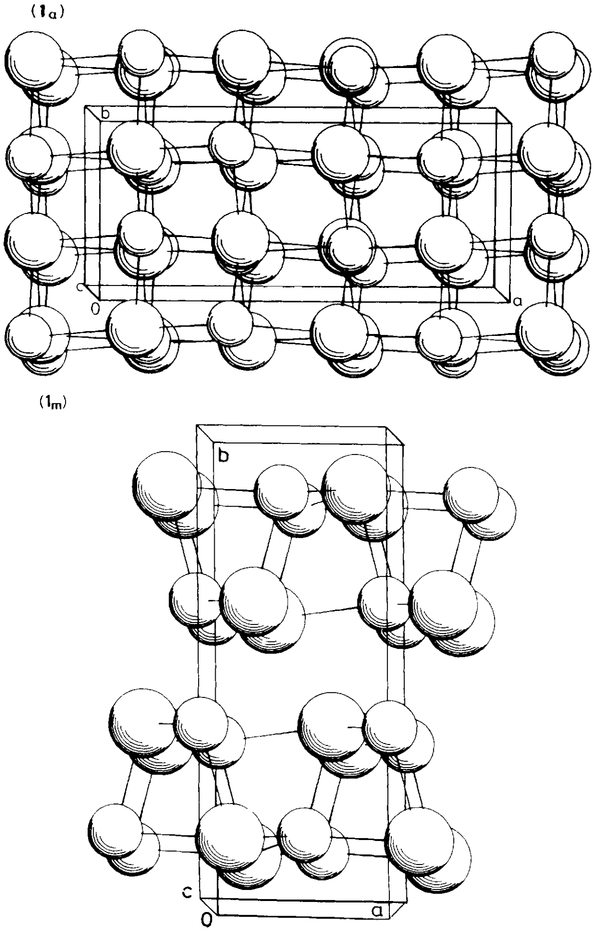

Figure 1. Molecular packing of $[\mathrm{Mo_4(\eta\text{-}C_5H_4Pr^i)_4(\mu^3\text{-}S)_4}]^+[\mathrm{Fe_4(NO)_4(\mu^3\text{-}S)_4}]^-$ (**1**) in its monoclinic (**1**$_\mathrm{m}$) and orthorhombic (**1**$_\mathrm{o}$) forms. The larger spheres represent cations and the smaller, anions.

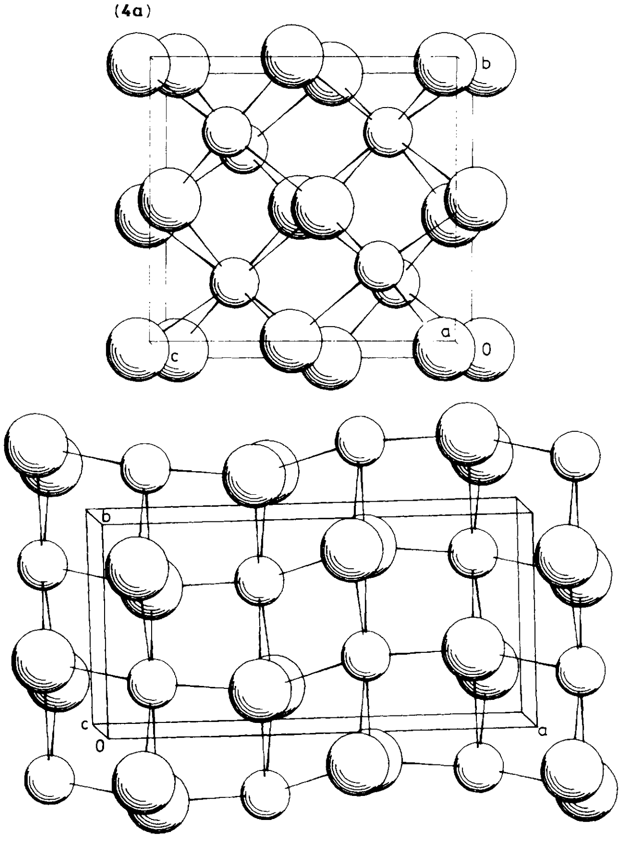

Figure 2. Molecular packing of $[\mathrm{Mo_4(\eta\text{-}C_5H_5Pr^i)_4(\mu^3\text{-}S)_4}]^+{}_2[\mathrm{Os_6(CO)_{18}}]^{2-}$ in its two alternative monoclinic forms (**4a**) and (**4b**). The larger spheres represent cations and the smaller, anions.

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† *Crystal data* for (**13**): $\mathrm{C_{44}H_{48}Mo_4N_4S_4}$, $M = 1144.9$, triclinic, space group $P1$, $a = 10.689(5)$, $b = 10.976(1)$, $c = 20.097(4)$ Å, $\alpha = 93.626(13)$, $\beta = 95.22(3)$, $\gamma = 105.08(2)°$, $U = 2258$ Å^3, $D_c = 1.68$ mg m^{-3}, $Z = 2$, $\mu(\text{Mo-}K_\alpha)$ 12.73 cm^{-1}, $F(000)$ 1144, (Mo-K_α) 0.70930 Å, $R = 0.024$, $R_w = 0.026$ for 7135 observed reflections $[I > 3\sigma(I)]$. Structure solution and refinement used the Oxford CRYSTALS system on the VAX 11/750 computer of the Chemical Crystallography Laboratory, Oxford.[9] Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Centre. See Notice to Authors, Issue No. 1.

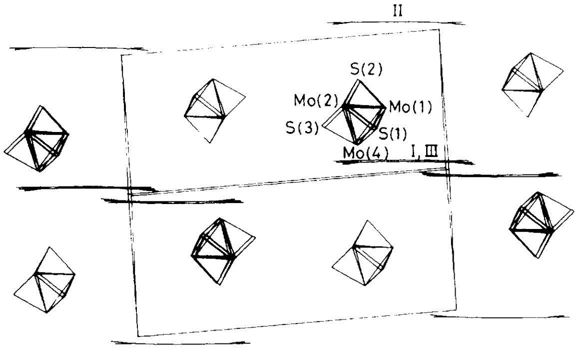

Figure 3. Molecular packing of (**13**). The isopropyl-cyclopentadienyl ligands have been omitted for clarity.

Table 2. Closest contacts between molecules in (**13**) (in Å).

(a) TCNQ ··· TCNQ			
C(102)–N(4^{III})	3.324	H(102)–N(4^{III})	2.549
C(104)–N(3^{I})	3.405	H(103)–N(3^{I})	2.504
(b) Cluster ··· TCNQ			
C(9)–N(2^{I})	3.415	H(12)–N(2^{I})	2.848
C(10)–N(2^{I})	3.415	H(13)–N(2^{I})	2.859
C(12)–N(1^{II})	3.455	H(15)–N(1^{II})	2.509
C(17)–N(2^{II})	3.592		
C(18)–N(2^{II})	3.591	H(24)–N(2^{II})	2.771
C(20)–N(1^{III})	3.498	H(26)–N(1^{III})	2.573
C(25)–N(1^{III})	3.460	H(34)–N(1^{III})	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^{I})	3.483	H(37)–N(2^{I})	2.535
S(1)–H(104^{I})	3.166		
S(2)–C(107^{II})	3.560		

Superscripts denote entries generated by symmetry operators: I $1-x$, $1-y$, $-z$; II $1-x$, $-y$, $-z$; III $-x$, $-y$, $-z$.

ions which normally form segregated stacks. The separation of these ribbons is approximately 9.4 Å, the constituent TCNQ molecules not being exactly coplanar. The closest contacts between the TCNQ molecules and between the cluster ions are given in Table 2. The Mo(1), Mo(2), Mo(3) plane is almost parallel (interplanar angle 3.12°) to the TCNQ plane generated by the symmetry operator $1-x$, $-y$, $-z$. This Mo$_3$ plane is capped by S(2) which itself is located 3.528 Å out of the TCNQ plane. In addition, the isopropylcyclopentadienyl ligand on Mo(4) is approximately coplanar with the TCNQ in the same asymmetric unit [planes defined by C(25)—C(29) and C(101)—C(106), inclusive, give an interplanar angle of 2.32°]. This ligand fits into the gap created by the TCNQ defined in the asymmetric unit and its closest neighbours (I and II, Figure 3), and completes the ribbon. The dimensions of the cluster and TCNQ molecules, when compared with the literature values,[3,5] support the assignment of charge as $[\mathrm{Mo_4}(\eta\text{-}\mathrm{C_5H_4Pr^i})_4\text{-}\mathrm{S_4}]^+\mathrm{TCNQ}^-$. This charge assignment is also supported by the high temperature magnetic susceptibility data, which show the crystal to be paramagnetic with a moment of 2.59 BM and a Weiss constant of −8 K. The material also shows weak antiferromagnetic behaviour with $T_\mathrm{N} \sim 12$ K, suggesting a direct exchange interaction between the moments on the TCNQ anion and the cluster cation. From Table 2 we see that there is actually sufficient contact between the cluster and the TCNQ layer to allow this kind of interaction. For example S(2)–C(107^{II}) is 3.56 Å, a similar distance to those found in antiferromagnetic organic charge-transfer salts.[6]

The effective magnetic moment found in the six samples measured (see Table 1) all lie in the region of 2.5 BM, the value expected for two isolated spins. Deviations from this value (+ 0.23 to −0.35) may be due to spin-orbit coupling, but further measurements are need to confirm this. The temperature independent paramagnetism arises from the Van Vleck term in the susceptibility and is comparable to those found in other cluster compounds.[7]

There is a striking variation of the stoicheiometries of the TCNQ salts $C^{n+}[\mathrm{TCNQ}]_x^{n-}$, and values of $x = 1$, 2, or 3 are found. We assume $n = 1$ in all these compounds. The electronic spectrum in solution shows (**17**) to contain one neutral TCNQ and one anion $[\mathrm{TCNQ}]^-$.[8] All the salts listed in Table 1 are semi-conductors with small values for room temperature conductivity, in the range 10^{-5}—10^{-9} ohm^{-1} cm^{-1}.

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