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Review

Organometallic solid state chemistry

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Introduction

The last twenty years have witnessed many often unexpected discoveries of new materials with interesting and potentially useful properties. For example the metallic properties of $(SN)_x$ [1], the second harmonic generation and waveguiding properties of $KTiOPO_4$ (KTP) [2], the classic organic metal [TTF][TCNQ] [3], (TTF = tetrathiofulvalene; TCNQ = tetracyano-quinodimethane), and $[TMTSF]_2ClO_4$ (TMTSF = tetramethyltetraselena-fulvalene) the first zero-pressure organic superconductor [4].

During this period, organotransition metal chemistry has been one of the fastest developing areas of chemistry. There has been, however, relatively little study of the solid state properties of organometallic compounds. Here we survey and review the solid state properties of some organometallic materials, including those with interesting conducting, magnetic and optical properties. In this article we define an organometallic compound as one which contains a transition metal bonded to a hydrocarbon ligand.

At this early stage of the development of organometallic solid state chemistry the following areas can be identified; 1. Charge transfer salts, 2. Intercalation compounds, 3. Non-linear optical materials, and 4. Polymers.

1. Organometallic charge-transfer salts

(a) Charge-transfer salts from metallocene donors

1,1′-Dimethylferrocene, [5] decamethylferrocene [5] and [Fe(η-Cp)(η-arene)] (Cp = C_5H_5) [6] form 1:2 charge-transfer salts with TCNQ. Their crystal structures consist of segregated stacks of the TCNQ acceptor and the metallocene donor. The TCNQ units are equally spaced within the stack and Resonance Raman measurements on $[Fe(\eta\text{-MeCp})_2][TCNQ]_2$ indicate that the TCNQ molecules possess a charge of -0.42 ± 0.1 [5].

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These salts show semiconductor behaviour with $\sigma(300\ \text{K})$ in the range 10–0.3 $\Omega^{-1}\ \text{cm}^{-1}$. The conductivity is well described by an equation of the form

$$\sigma = e\mu\eta_0 e^{-\Delta/\kappa T}$$

decomposing it into the product of mobility μ (varying as T^{-4}) and carrier concentration (exponentially activated, Δ ca. 0.1–0.15 eV).

In these conductive salts the transport and spectral properties are determined by the nature of the interactions within the TCNQ stacks. At high temperature the chains are nearly uniform with delocalised electrons. At low temperature these salts are characterised by non-regular charge distribution within the stacks. This is shown not only by the appearance of an energy gap of ca. 0.2 eV but also directly by the presence of new absorption bands in the infrared spectrum characteristic of $[\text{TCNQ}]^{\delta-}$ with $0.3 < \delta < 0.6$.

In contrast to conducting charge-transfer solids, linear chain molecular solids with alternate $\ldots D^+A^-D^+A^-\ldots$ stacks are poor conductors. However, they can have interesting optical and cooperative magnetic properties. For example, bulk meta- and ferromagnetism as well as spin-Peierls transitions have been reported [7–9].

Rapid crystallisation of the 1:1 salt of $[\text{Fe}(\eta\text{-C}_5\text{Me}_5)_2][\text{TCNQ}]$ [10–12] leads to isolation of the kinetic phase which has a 1-D structural motif based on chains of alternating $[\text{Fe}(\eta\text{-C}_5\text{Me}_5)_2]^+$ cation donors (D^+) and $[\text{TCNQ}]^-$ anion acceptors (A^-) i.e. $\ldots D^+A^-D^+A^-\ldots$. Both donor and acceptor are $S = 1/2$ radicals. The effective moment, μ_{eff}, deviates significantly from the temperature-independent Curie behaviour characteristic of normal ferrocenium salts. Studies of the magnetisation reveal metamagnetic behaviour. At magnetic fields $(H) < 1600$ G the magnetisation is characteristic of an antiferromagnet (T_{Neel} ca. 2.55 K), whereas for $H > 1600$ G a sharp rise and approach to magnetisation saturation characteristic of ferromagnetic behaviour is observed.

The susceptibility of $[\text{Fe}(\eta\text{-C}_5\text{Me}_5)_2][\text{TCNE}]$ [13] (TCNE = tetracyanoethylene) obeys the Curie–Weiss expression with $\theta = +30$ K, suggesting dominant ferromagnetic interactions. Below 15 K the magnetisation is no longer proportional to the magnetic field.

In the Earth's magnetic field a spontaneous magnetisation up to 8×10^3 emu G mol^{-1} is observed for polycrystalline samples. On aligned single crystals the saturation magnetisation parallel to the stacking axis is 1.6×10^4 emu G mol^{-1} which is 25% greater than iron metal on a mole basis and agrees with the calculated saturation moment for ferromagnetic alignment of the donor ($S = 1/2$; $g_{\parallel} = 4$) and

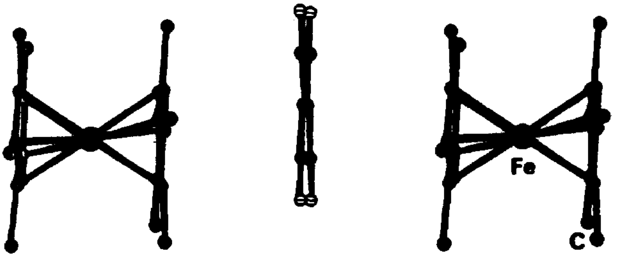

Fig. 1. Alternating donor/acceptor structure of 1-D $[\text{Fe}(\eta\text{-C}_5\text{Me}_5)_2]^+[\text{TCNE}]^-$.

acceptor ($S = 1/2$; $g = 2$). The low temperature ^{57}Fe Mossbauer spectra shows the onset of 3-D magnetic ordering by the observation of Zeeman splitting in zero applied field ($H_{int} = 424$ kG at 4.2 K). More recently, powder neutron diffraction experiments on $[Fe\{\eta\text{-}C_5(CD_3)_5\}_2][TCNE]$ have confirmed the 3-D ferromagnetic ordering at $T < 15$ K [14].

(b) Charge-transfer solids containing M(η-Arene)₂ complexes

The charge-transfer complexes $[M(\eta\text{-}C_6H_3Me_3)_2][TCNQ]_x$ ($M = Fe, Ru$; $x = 2$ or 4) have been prepared using electrocrystallisation techniques by reduction of TCNQ in the presence of the organometallic dication [15]. Selectivity towards the TCNQ phases can be directed by control of the electrode potential during electrocrystallisation. At very negative potentials a poorly conducting 1 : 2 phase is formed as deep purple crystals, whereas a more positive potential favours a black, conducting 1 : 4 phase. The selectivity is determined by the potential-dependent concentrations of TCNQ and $[TCNQ]^-$ at the electrode [16].

The compounds $[M(\eta\text{-Arene})_2][TCNQ]_2$ have relatively low conductivities ($\sigma_{300\,K} < 10^{-7}\ \Omega^{-1}\ cm^{-1}$) and are diamagnetic with temperature-independent susceptibility in the range 2–343 K. In contrast, the 1 : 4 phases ($x = 4$) exhibit much higher conductivities ($\sigma_{300\,K} < 0.1\ \Omega^{-1}\ cm^{-1}$) and the temperature dependence indicates semiconductor behaviour ($E_A = 0.06$ eV), which can be explained in terms of electron localisation along TCNQ arrays as a result of Coulombic repulsion. The 1 : 4 phases exhibit temperature-dependent paramagnetic susceptibility consistent with the random exchange Heisenberg antiferromagnetic exchange (REHAC) model [17]. The linear chain complexes $[M(\eta\text{-}C_6H_3Me_3)_2][C_6(CN)_6]$ ($M = Fe, Ru$) [18] contain mixed stacks of alternating cations and anions with interplanar spacing less than the sum of the van der Waal's radii.

The complexes exhibit strong charge-transfer absorption spectra, the differences between the absorption maxima for the Fe vs. Ru complexes have been related to the differences in the reduction potentials of the Fe and Ru organometallic dications. Linear chain, mixed-metal phases of formula $[Fe(\eta\text{-}C_6H_3Me_3)_2]_x[Ru(\eta\text{-}C_6H_3Me_3)_2]_{1-x}[C_6(CN)_6]$ have been prepared. These materials exhibit optical absorption intensities consistent with Beer's law.

Charge-transfer salts based on bis(η-arene)chromium cations and TCNE exhibit both para- and ferro-magnetic behaviour. For example $[Cr(\eta\text{-}C_6H_6)_2]^+\ [TCNE]^-$ is paramagnetic consisting of 1-D chains of $[Cr(\eta\text{-}C_6H_6)_2]^+$ cations and $[TCNE]_2{}^{2-}$ dimer dianions.

Whereas $[Cr(\eta\text{-}C_6H_3Me_3)_2][TCNE]$ is an 1-D Ising ferromagnet with a nearest neighbour interaction of +2.4 J [14]. $[Cr(\eta\text{-}C_6H_3Me_3]_2][TCNQ]$ forms two phases, the thermodynamic β-phase consists of 1-D chains of alternating $[Cr(\eta\text{-}C_6H_3Me_3)_2]^+$ cations and $[TCNQ]_2{}^{2-}$ dianions. The magnetic susceptibility indicates that the $[TCNQ]_2{}^{2-}$ has an antiferromagnet ground state with a thermally accessible $S = 1$ excited state [14].

Further examples of the magnetic phenomena found in charge transfer solids are shown in Table 1.

(c) Charge transfer salts containing organometallic clusters as donors

Many organometallic clusters are electron rich (i.e. good electron donors) and redox active, for example, the cubane cluster $[Fe_4(\eta\text{-}C_5H_5)_4(\mu_3\text{-}S)_4]$ has four reversible redox states [19].

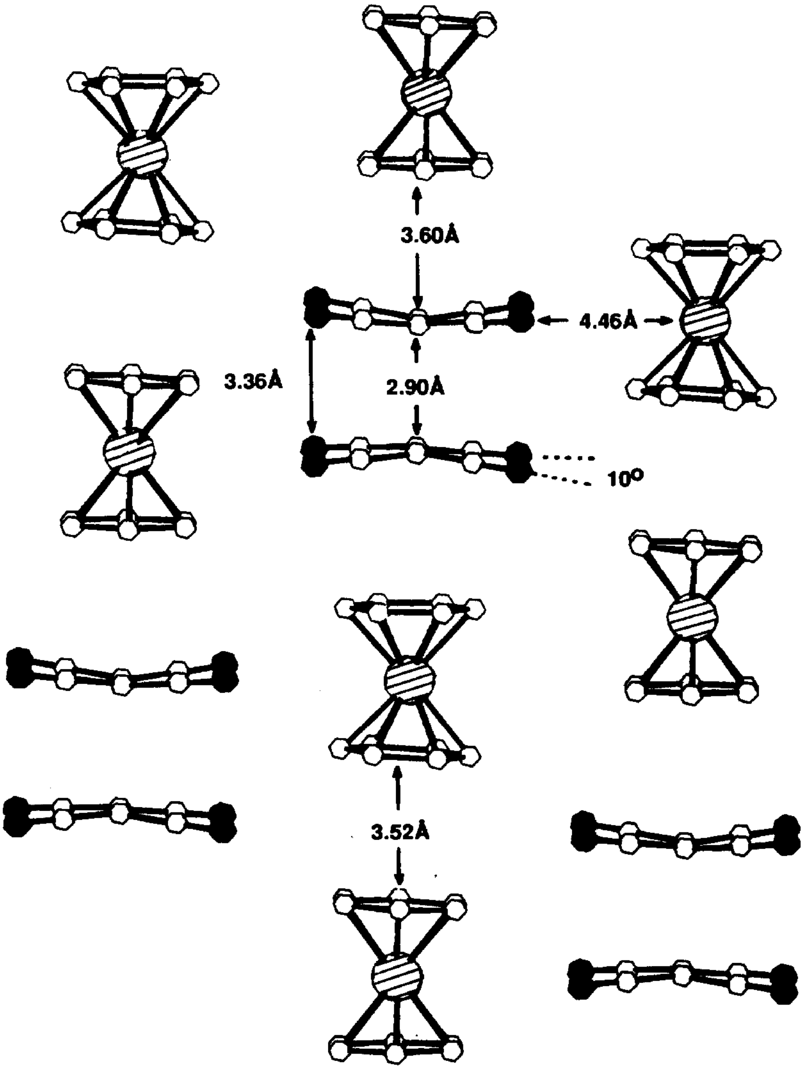

Fig. 2. Molecular structure of $[Cr(\eta\text{-}C_6H_6)_2]^+[TCNE]^-$.

Table 1

Summary of magnetic phenomena found in charge transfer solids

Compound	Magnetic susceptibility [a]	Effect of magnetic field	Magnetic behaviour
$[Fe(C_5H_5)_2][TCNE]$	$< -10^{-3}$	Repulsive	Diamagnetism
$[Fe(C_5Me_5)_2][C_3(CN)_5]$	$> +10^{-2}$ [b]	Attractive	Paramagnetism
$[Ni(C_5Me_5)_2][TCNE]$	$> +10^{-3}$–10^{-5}	Weakly attractive	Antiferromagnetism
$[Fe(C_5Me_5)_2][TCNE]$	$> +10^{2}$	Strongly attractive	Ferromagnetism
$[Cr(C_5Me_5)_2][TCNE]$	> 0 complex	Strongly attractive	Ferrimagnetism
$[Fe(C_5Me_5)_2][TCNQ]$	> 0 complex	Complex	Metamagnetism

[a] emu G mol^{-1} [b] α number of unpaired electrons.

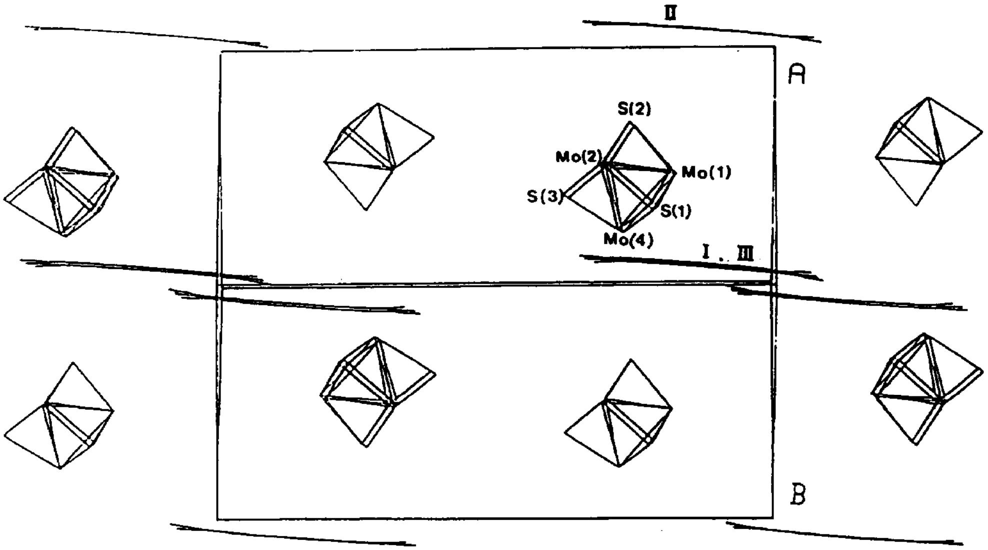

Fig. 3. Molecular packing of $[Mo_4(\eta\text{-}C_5H_4Pr^i)_4(\mu_3\text{-}S)_4]^+[TCNQ]^-$, showing the ribbons of TCNQ. The isopropyl-cyclopentadienyl ligands have been omitted for clarity.

The cluster TCNQ salt $\{[Nb_3(\mu\text{-}Cl)_6(C_6Me_6)_3]\,(TCNQ)_2\}$ was prepared by the reaction of $[Nb_3(\mu\text{-}Cl)_6(C_6Me_6)_3]PF_6$, $Li^+[TCNQ]^-$ and neutral TCNQ in acetonitrile [20]. The crystal structure shows zigzag chains of alternating niobium trimer cations and TCNQ anion dimers. The compound is a semiconductor with $\sigma_{298\ K} = 0.001\ \Omega^{-1}\ cm^{-1}$ and $E_a = 0.35$ eV.

The 1 : 1 charge transfer salt of $[Mo_4(\eta\text{-}C_5H_4Pr^i)_4(\mu_3\text{-}S_4)]^+$ $[TCNQ]^-$ has been synthesised and the crystal structure shows the TCNQ molecules to be arranged in ribbons, separated by cluster cations.

The high magnetic susceptibility shows the salt to be paramagnetic and corresponds to two independent unpaired electrons per formula unit. The material also shows weak antiferromagnetic behaviour with T_{Neel} ca. 12 K, suggesting there is a direct exchange interaction between the electrons on the TCNQ anion and cluster cation.

(d) Charge transfer salts containing cluster cations and cluster anions; "soft salts"

Many organometallic cluster compounds can undergo multiple and reversible redox reactions forming stable cations or anions. For example, the compound $[Fe_4(NO)_4(\mu_3\text{-}S)_3]^n$, can add up to two electrons giving anions where $n = -1$ or

Table 2

Conductivity and magnetic data on some soft salts

Compound	σ_{300} (Ω^{-1}/cm^{-1})	μ_{eff}	Θ
$[Mo_4(\eta\text{-}C_5H_4Pr^i)_4(\mu_3\text{-}S)_4][Fe_4(NO)_4(\mu_3\text{-}S)_4]$	7.6×10^{-9}	2.48	−0.67
$[Fe_4(\eta\text{-}C_5H_5)_4(\mu_3\text{-}S)_4][Fe_4(NO)_4(\mu_3\text{-}S)_4]$	4.7×10^{-9}	–	–
$[Mo_4(\eta\text{-}C_5H_4Pr^i)_4(\mu_3\text{-}S)_4]_2[Os_6(CO)_{18}]$	–	2.73	−0.97
$[Cr_4(\eta\text{-}C_5H_4Me)_4(\mu_3\text{-}S)_4][Fe_4(NO)_4(\mu_3\text{-}S)_4]$	5.4×10^{-9}	–	–

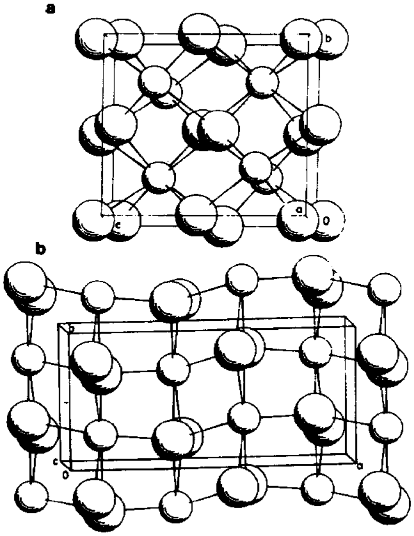

Fig. 4. Molecular packing of the "soft salt" $[Mo_4(\eta\text{-}C_5H_4Pr^i)_4(\mu_3\text{-}S)_4]_2^+ [Os_6(CO)_{18}]^{2-}$ in its two alternative monoclinic forms (a) and (b). The larger spheres represent cations and the smaller anions.

−2, 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, Mo.

Simple cluster salts can be synthesised by using these organometallic cluster anions and cations. If the redox potentials of the component clusters were sufficiently matched then salts $[C]^{n+}$ $[A]^{n-}$, where n is non-integral might exist. Examples of soft salts, prepared by mixing neutral component clusters are given in Table 2, and Fig. 4. All these salts appeared to be simple charge transfer salts. They exhibit paramagnetic susceptibility and electrical conductivity measurements indicate semiconductor behaviour with activation energies ca. 0.5 eV [21].

2. Organometallic intercalation compounds

Many layered solids including metal chalcogenides, oxides and phosphates may act as host lattices and react with a variety of guest atoms or molecules to give intercalation compounds in which the guest is inserted between the host layers. In a true intercalation compound, this insertion should be reversible, and the host lattice should retain its structural integrity [22]. The readily reversible formation of intercalation compounds and the modifications of the physical properties of the host on intercalation have made them natural candidates for electrochemical devices and heterogeneous catalysts [23].

In 1979 Dines reported the intercalation of the metallocenes $CoCp_2$, (Cp = η-C_5H_5), and $CrCp_2$ (guests) into the layered transition-metal dichalcogenides TaS_2, ZrS_2 and NbS_2 (hosts) [24]. This reaction was subsequently extended to other sandwich complexes with low ionisation potentials such as $[M(\eta\text{-arene})_2]$ (M = Mo, Cr), $[Ti(\eta\text{-}C_8H_8)(Cp)]$ $[Cr(\eta\text{-}C_7H_7)(Cp)]$ and a wider range of hosts such as MX_2 (M = Ti, Zr, Hf, or Ta; X = S or Se), FeOCl or MPS_3 (M = Mg, Mn, Fe, Co, Ni, or Zn) to give well characterized intercalation compounds [25–28].

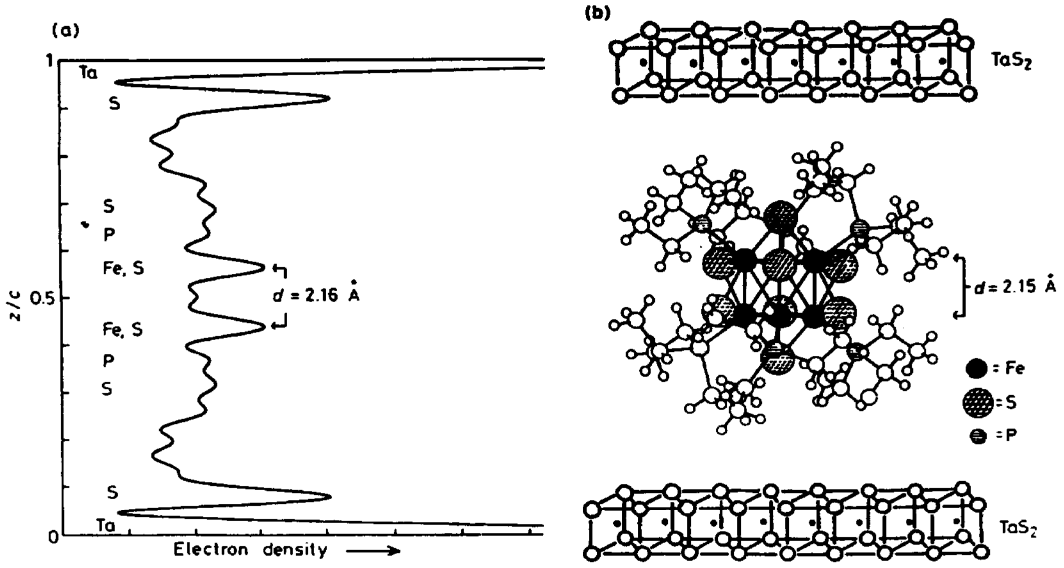

Fig. 5. (a) Projection of the electron density of $[TaS_2\{Fe_6S_8(PEt_3)_3\}_{0.05}]$ along the c-axis. (b) Schematic illustration showing the orientation of the iron cluster between the TaS_2 layers, as deduced from the interlayer electron density.

These intercalation reactions generally proceed by direct reaction of the guest with a suspension of the host in a suitable solvent. It has been found that the solvent system may be critical to the rate of intercalation. Reactions in polar coordinating solvents such as acetonitrile, tetrahydrofuran and dimethoxyethane have proved to be most successful. Techniques such as ion exchange and electrochemical intercalation have also been used.

Jacobson [29] treated a flocculation of TaS_2 layers, formed by exfoliating $Na_{0.33}TaS_2$ in DMF/HO mixtures with $[Fe_6S_8(PEt_3)_5]$ to prepare $[TaS_2\{Fe_6S_8(PEt_3)_3\}_{0.05}]$. In this reaction the layered structure of TaS_2 was in effect, reconstituted whilst incorporating the guest (Fig. 5).

The cubane clusters $[M_4Cp'_4S_4]$ $[Cp' = (\eta\text{-}C_5H_3Pr^i)$ $M = Fe, Mo]$ have been inserted into oxidising hosts such as MoO_3 or FeOCl by direct thermal reaction [32]. A representation of the structure of a “cluster bronze” is shown in Fig. 6.

Crystals of $[MoO_3\{Fe_4(\eta\text{-}C_5H_4Me)_4(\mu_3\text{-}S)_4\}_{0.15}]$ exhibit substantial conductivity of $0.6 \pm 0.5\ \Omega^{-1}\ cm^{-1}$ along the crystal axis, while the conductivity along the shortest axis (interlayer direction) is lower by two orders of magnitude.

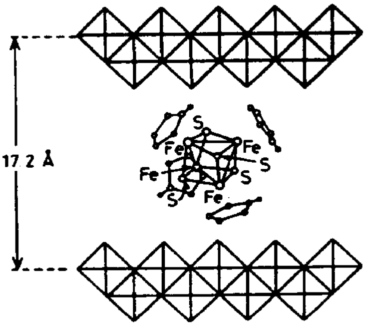

Fig. 6. Representation of the cluster bronze $[MoO_3\{Fe_4(\eta\text{-}C_5H_4Me)_4(\mu_3\text{-}S)_4\}_{0.15}]$.

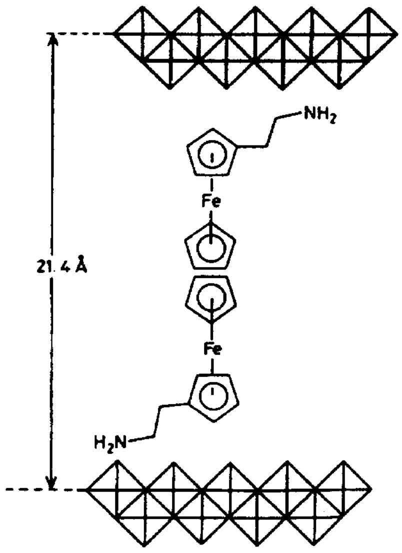

Fig. 7. Representation of the intercalate $[MoO_3\{Fe(\eta\text{-}C_5H_4CH_2CH_2NH_2)(\eta\text{-}C_5H_5)\}_{0.05}]$.

Ferrocene will intercalate into FeOCl; [30] however, it will not intercalate into 1T-TaS_2 or MoO_3. This may be attributed to the greater oxidising ability of FeOCl. The intercalation of organoamines into layered compounds such as 2H-TaS_2 and MoO_3 is well known [31]. We found that the amino-ferrocenes readily intercalate into MoO_3. The monoamino-ferrocenes form bi-layers, as indicated by the stoicheiometry and the large inter-layer separations (Fig. 7) [32].

It has been demonstrated that ultrasound can greatly enhance the rate of many intercalation reactions, for example, the chemical synthesis of $[ZrS_2\{CoCp_2\}_{0.33}]$ requires 50 h at 20 °C thermally whereas sonochemically it only requires 2 h at 20 °C [33]. Rate enhancements of up to 200-fold have been observed. The ultrasonic irradiation does not increase intercalation rates through improvement of mass transport, and when host solid suspensions are irradiated in an inert solvent and subsequently treated with the guest without any further sonication, the rate of intercalation is significantly enhanced.

Since intercalation materials may often be polycrystalline or contain amorphous domains, structural characterisation is often difficult. Primary evidence for the intercalation of guest molecules into layered solids is the observation of low angle powder X-ray diffraction peaks corresponding to an increase of the inter-lamellar spacing. It is generally found that the stoichiometry of guest intercalate corresponds approximately to close packing of the guest molecules between the layers of the host. Although elemental composition and spectroscopic techniques provide strong evidence for interaction of solids there is also the possibility that the guest molecules bind to the surface of the host. This is a difficult matter to estimate, and one approach is to intercalate the guest molecules into single crystals of the host and cleave them under carefully controlled conditions to give clean surfaces. Additional evidence for intercalation can be gained by oxidative de-intercalation reactions or by ion exchange reactions which recover the initial guest molecule in the oxidised state.

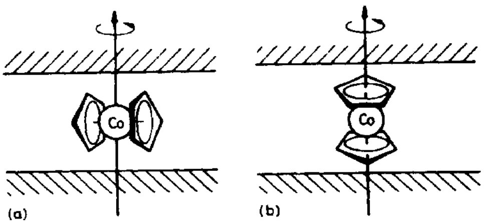

Fig. 8. Proposed models for TaS_2-metallocene intercalation compounds, with the principal axis (a) parallel to and (b) perpendicular to the interlamellar plane.

In principle, intercalated metallocene cations could lie with their principal axis either parallel or perpendicular to the host layers. Broad line ^1H NMR studies by Silbernagel [34] and 1-D F.T. X-ray data [29] have suggested that cobaltocene in 1T-TaS_2 has the parallel orientation. However, variable temperature solid state ^2H NMR has shown that, at room temperature, both the perpendicar and parallel orientations of $[Co(\eta\text{-}C_5D_5)_2]$ in TaS_2 exist in the solid state (Fig. 8) [35].

Magnetic susceptibility [36] and EXAFS measurements [37] have been performed on various lamellar intercalates of the type $[Mn_{1-x}PS_3\{Co(Cp)_2\}_{2x}(H_2O)_y]$ obtained from $MnPS_3$ by cation ion-exchange. Intercalation is found to reduce the interlayer antiferromagnetic coupling. In addition, intercalates with $x = 0.1\text{–}0.2$ exhibit an intense spontaneous magnetisation on cooling which is ascribed to the onset of weak ferromagnetism. EXAFS measurements on these materials have been interpreted in terms of local distortions around the manganese ions created upon intercalation.

Single crystal vibrational and EPR studies on $[CdPS_3\{Co(Cp)_2\}_{0.34}]$ [38] and a detailed study on single crystals of $[SnS_2\{Co(Cp)_{0.29}]$ [39] indicate that complete oxidation of the cobaltocene does not occur and that a complex electronic equilibra is established within the host.

The layered transition-metal disulphides such as TaS_2 have a superconducting state at very low temperature (0.8 K), the T_c was raised to ca. 3.2 K on intercalation of simple metallocenes [40].

3. Organometallic nonlinear optical materials (NLO)

When electromagnetic radiation interacts with a bulk medium the induced polarisation can be expressed by the infinite power series:

$$P = \chi^{(1)} \cdot E + \chi^{(2)} \cdot EE + \chi^{(3)} \cdot EEE + \ldots$$

where P is the polarisation, E is the external field, and the coefficients $\chi^{(n)}$, are the n^{th} order electronic susceptibilities. The first or linear term in the power series is responsible for the refractive properties of a material, while the second or first non-linear term can give rise to second harmonic generation (SHG) or frequency doubling of the incident radiation. However, for most materials this is a very weak interaction and has only been investigated since the availability of lasers. For efficient second harmonic generation the material must crystallise in a non-centrosymmetric space group, and molecules should have a large hyperpolarizability, i.e. it

Table 3

Some organometallic compounds exhibiting second harmonic generation

No	Compound	SHG signal	Reference [a] (signal = 1)
A	Cr-(*S*)-(+)-(2-methylbutyl)benzene(CO)$_3$	1.7	ADP
B	Cr(nopolbenzyl ether)(CO)$_3$	1.3	ADP
C	Cr(styrene)(CO)$_3$	1.8	ADP
D	ReCl(bipyridine)(CO)$_3$	1.6–3	urea
E	ReCF$_3$SO$_3$(bipyridine)(CO)$_3$	1.7–2	urea
F	Pt(bipyridine)Cl$_4$	1.2	urea
G	*Z*-[1-Ferrocenyl-2-(4-nitrophenyl)]ethylene	64.0	urea

[a] $\chi^{(2)}$ value of urea is 2.3 times that of ADP.

should possess a large dipole moment either in the ground state or in a low-lying excited state. Normally the molecules have a donor and acceptor group connected by a delocalised π-system [41].

Materials which combine non-linear optical behaviour with practical or commercial properties include inorganic crystals [42] such as KH_2PO_4 (KDP), $LiNbO_3$, $KTiOPO_4$ (KTP), and β-BaB_2O_4, while organic compounds such as urea and 2-methyl-4-nitroaniline have been extensively investigated [43].

There have been few studies on NLO organometallics. Frazier et al. [44] have measured the SHG efficiencies of over 60 transition metal-organic compounds such as group VI metal carbonyl arene, pyridyl or chiral phosphine complexes (Table 3). Three of them doubled the laser frequency as well as or better than inorganic ADP (ammonium dihydrogen phosphate) (Table 3, A–C).

Further metal-pyridine and -bipyridine complexes which also generate second-harmonic radiation are shown in Table 3 D–F [45].

Eaton and co-workers have prepared a number of organometallic nonlinear optical materials by the method of host-guest inclusion complexation [46]. They used the chiral β-cyclodextrin, thiourea, tris(*o*-thymotide) and deoxycholic acid as the hosts and a variety of organic and organometallic compounds as the guests. Some of their results are shown in Table 4.

The compound *Z*-[1-ferrocenyl-2-(4-nitrophenyl)]ethylene was designed and synthesised to contain many of the features thought to be important for second harmonic generation. A large dipole moment was induced by having the electron withdrawing nitro group linked by a conjugated backbone to an electron donating

Table 4

Examples of organometallic inclusion compounds exhibiting SHG [a]

Guest	host/guest	SHG signal
Cr(η-benzene)(CO)$_3$	3/1	2.3
Cr(η-fluorobenzene)(CO)$_3$	3/1	2.0
Re(η-cyclopentadienyl)(CO)$_3$	[b]	0.5
Fe(η-1,3-butadiene)(CO)$_3$	[b]	0.5
Cr(η-cyclopentadienyl)(CO)$_2$(NO)	3/1	0.1

[a] The host is thiourea, SHG relative to urea. [b] Not determined.

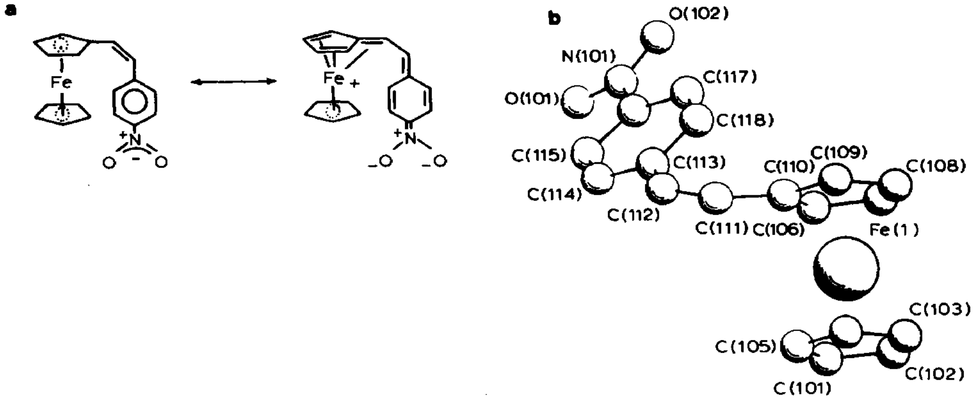

Fig. 9. (a) Two canocial representations of [Fe{η-$C_5H_4(CH)_2C_6H_4NO_2$}(η-C_5H_5)]; (b) Molecular structure, hydrogens are ommited for clarity.

ferrocene group. In fact this material was found to be 64 times better at second harmonic generation than urea (Table 3, G) [47]. The structure is shown in Fig. 9.

4. Organometallic polymeric materials

Several ferrocene copolymers (**A** and **B**) and polyferrocenylene (**C**) (Fig. 10) have been prepared and all exhibit a low conductivity ($> 10^{-12}$ Ω^{-1} cm^{-1}). However, upon partial oxidation, for example with DDQ (dichlorodicyanoquinone) or benzoquinone, and Fe^{II}–Fe^{III} mixed valence compounds are produced and the conductivity increases by as much as 5 orders of magnitude [48]. The maximum value of conductivity observed thus far among ferrocene polymers is 6×10^{-3} Ω^{-1} cm^{-1} for **D** [49].

Bis(η-chlorobenzene)molybdenum reacts with a range of organomagnesium halides to form monomers such as bis(η-allylbenzene)molybdenum, bis(η-styrene)molybdenum. These monomers polymerise under free radical conditions to give soluble, air sensitive polymers. The spectroscopic data suggest the cyclic ladder structures shown in Fig. 11, resulting from propagation involving an intramolecular cyclisation step followed by an intermolecular addition step. Molecular weight studies indicate a number average degree of polymerisation of $\bar{X}_n = 33$ [50].

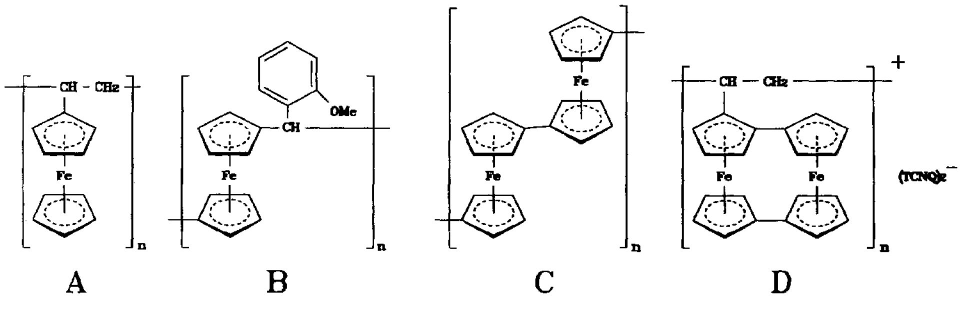

Fig. 10. Examples of some ferrocene based organometallic polymers.

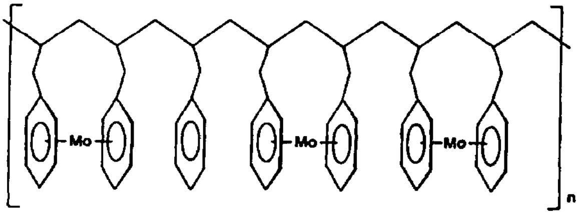

Fig. 11. Ladder polymer of bis(η-allylbenzene)molybdenum.

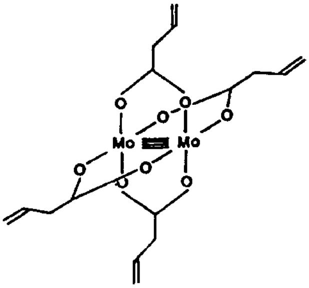

Fig. 12. Structure of tetrakis(μ-vinylacetato)dimolybdenum.

The quadruply bonded molybdenum dimers such as tetrakis(μ-vinylacetato)dimolybdenum (Fig. 12) have been successfully homopolymerised in the presence of AIBN (azoisobutrionitrile), and copolymerised with styrene and vinylacetate.

Conclusion

The study of the solid state properties of materials based on organometallic compounds is at a very early stage of development. Nonetheless, it is clear from observations such as the ferromagnetic behaviour of the decamethylferrocene charge transfer complexes, from the non-linear optical properties of the ferrocene derivatives, and from the electrical properties of the cluster bronzes that materials based on organometallic compounds can give rise to bulk properties of not only academic interest, but also there is clearly the potential for materials with useful applications.

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