Synthesis and Characterisation of Organometallic Charge-transfer Salts containing the Bis(benzene)molybdenum Radical Cation†

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The salt [Mo(η-C_6H_6)$_2$][PF_6] has been prepared by iodine oxidation of [Mo(η-C_6H_6)$_2$] followed by metathesis with $NaPF_6$. The cyclic voltammogram of [Mo(η-C_6H_6)$_2$][PF_6] in MeCN exhibits a reversible redox couple ($E_{\frac{1}{2}}$) at −730 mV *vs.* a saturated calomel electrode (SCE). The solid-state room-temperature EPR spectrum exhibits an isotropic resonance centred at g = 1.993 which is consistent with an assignment of a $^2A_{1g}$ ground state for the 17-electron [Mo(η-C_6H_6)$_2$]$^+$ radical cation. The salt [Mo(η-C_6H_6)$_2$][$FeBr_4$] has been synthesised from [NEt_4][$FeBr_4$] and [Mo(η-C_6H_6)$_2$][PF_6]. It crystallises in the orthorhombic space group *Pbca*, a = 18.527(17), b = 12.521(5), c = 14.915(6) Å; R and R' = 0.051 and 0.059. The salt [Mo(η-C_6H_6)$_2$][$FeBr_4$] consists of segregated chains of cations and anions. The solid-state room-temperature EPR spectrum exhibits two resonances centred at g = 1.987 and 2.008 assignable to the cation and anion respectively. The solid-state magnetic susceptibility data for [Mo(η-C_6H_6)$_2$][$FeBr_4$] can be fitted to the Curie–Weiss law between 40 and 300 K with C = 3.93 and θ = −5.4 K. Below 15 K the [$FeBr_4$]$^-$ anion sub-lattice orders antiferromagnetically leaving a magnetic susceptibility which is dominated by the [Mo(η-C_6H_6)$_2$]$^+$ cations.

The synthesis and characterisation of low-dimensional molecular solids with desirable electronic and magnetic properties is currently the subject of intensive investigation.[1] In an effort to understand the properties of low-dimensional solids we have sought to prepare new materials that incorporate organometallic compounds. The design of new molecular materials using organometallic reagents is particularly attractive since the diversity of these compounds may afford materials with unusual electronic properties.

Organometallic charge-transfer salts containing the decamethylmetallocenium cations {[M(η-C_5Me_5)]$^+$; M = Fe, Mn or Cr} and planar-organic radical anions tetracyanoethylene (tcne$^-$), tetracyano-*p*-quinodimethane (tcnq$^-$), and $C_4(CN)_6{}^-$ have been shown to possess remarkable magnetic and electronic properties.[2] For example, the tcne salts of both [Fe(η-C_5Me_5)$_2$]$^+$ and [Mn(η-C_5Me_5)$_2$]$^+$ exhibit three-dimensional ferromagnetic ground states with Curie temperatures (T_c) of 4.8 and 8.8 K respectively.[3,4]

Charge-transfer salts based on bis(η-arene)metal cations have not been as extensively investigated, the one-dimensional salt [Cr(η-$C_6H_3Me_3$-1,3,5)$_2$][tcne] has been shown to exhibit ferromagnetic interactions at low temperature.[5] The one-dimensional linear-chain complexes [M(η-C_6Me_6)$_2$][$C_6(CN)_6$] (M = Fe or Ru) containing stacks of alternating [M(η-C_6Me_6)$_2$]$^+$ cations and [$C_6(CN)_6$]$^-$ anions have nominally doubly charged {$D^{2+}A^{2-}$} ground states and {D^+A^-} excited states.[6]

In contrast to these charge-transfer salts which contain organometallic cations and planar organic anions, little synthetic effort has been focused on the preparation of salts containing organometallic cations with inorganic anions. These ions offer advantages over the organic anions, since much larger unpaired spin densities can be achieved using transition-metal based radical anions.

In this paper we report the characterisation of the 17-electron cation [Mo(η-C_6H_6)$_2$]$^+$ and the synthesis of organometallic–inorganic salts [Mo(η-C_6H_6)$_2$][PF_6] and [Mo(η-C_6H_6)$_2$][$FeBr_4$].

Results and Discussion

Synthesis and Characterisation of [Mo(η-C_6H_6)$_2$][PF_6] **1**.—*Synthesis.* Bis(η-benzene)molybdenum was prepared by the Fisher–Hafner reduction of $MoCl_5$ in benzene.[7] Treatment of [Mo(η-C_6H_6)$_2$] with iodine in MeOH gives [Mo(η-C_6H_6)$_2$]I,[8] which can be easily metathesised to the $PF_6{}^-$ salt by addition of $NaPF_6$ in MeOH. Long yellow needle-shaped crystals of [Mo(η-C_6H_6)$_2$][PF_6] **1** were obtained by slow recrystallisation from MeOH. The crystals were found to be very oxygen-sensitive.

Electrochemistry. The cyclic voltammogram of **1** in acetonitrile shows a reversible redox wave at −730 mV *vs.* a saturated calomel electrode (SCE) (ferrocene–ferrocenium couple at +0.355 mV *vs.* SCE[9]). The peak-to-peak separation (ΔE_p = 60 mV) and the ratio $i_{pc}/v^{\frac{1}{2}}$ was independent of scan rate (v) over a wide range of scan rates as expected for a reversible diffusion-controlled electron-transfer system.[10]

EPR Spectroscopy. Compound **1** exhibits a room-temperature EPR spectrum (X-band) in both dilute solution and in the solid state. The room-temperature EPR spectrum of **1** in CH_2Cl_2 solution exhibits a single narrow isotropic resonance centred at g = 1.991 and a peak-to-peak separation (ΔH_{pp} = 15 G). Neither hyperfine couplings to the ^{97,95}Mo ($I = \frac{5}{2}$) isotopes nor to the ring protons of the η-C_6H_6 ligands were resolvable. The room-temperature EPR spectrum of a solid sample exhibits a slightly broader isotropic resonance centred at g = 1.993 (ΔH_{pp} = 34 G).

The highest occupied molecular orbital (HOMO) in [Mo(η-C_6H_6)$_2$] has been assigned A_{1g} symmetry by previous gas-phase photoelectron spectroscopy experiments.[11] Ionisation from this singly degenerate MO would yield a radical cation with $^2A_{1g}$ symmetry. The EPR spectra of ^{2}A-state radicals are typically narrow isotropic resonances, the absence of any

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1992, Issue 1, pp. xx–xxv.

Non-SI unit employed: G = 10^{-4} T.

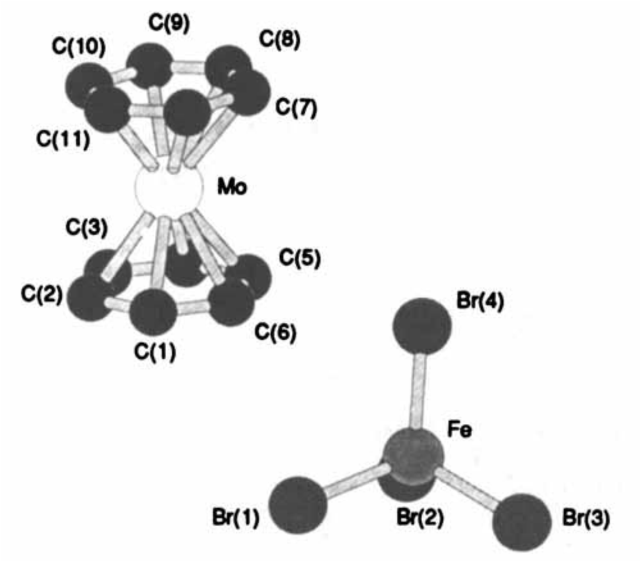

Fig. 1 Molecular structure of $[Mo(\eta\text{-}C_6H_6)_2][FeBr_4]$

Table 1 Bond lengths (Å) and angles (°) for $[Mo(\eta\text{-}C_6H_6)_2][FeBr_4]$ **2** with estimated standard deviations (e.s.d.s) in parentheses

Mo–C(1)	2.22(3)	Fe–Br(3)	2.33(1)
Mo–C(2)	2.30(2)	Fe–Br(4)	2.210(5)
Mo–C(3)	2.34(3)	C(1)–C(2)	1.41(4)
Mo–C(4)	2.30(3)	C(1)–C(6)	1.33(5)
Mo–C(5)	2.25(3)	C(2)–C(3)	1.55(5)
Mo–C(6)	2.24(3)	C(3)–C(4)	1.46(5)
Mo–C(7)	2.34(3)	C(4)–C(5)	1.44(6)
Mo–C(8)	2.28(3)	C(5)–C(6)	1.32(6)
Mo–C(9)	2.20(3)	C(7)–C(8)	1.58(5)
Mo–C(10)	2.20(4)	C(7)–C(12)	1.46(6)
Mo–C(11)	2.26(4)	C(8)–C(9)	1.37(5)
Mo–C(12)	2.27(4)	C(9)–C(10)	1.25(6)
Fe–Br(1)	2.336(5)	C(10)–C(11)	1.29(8)
Fe–Br(2)	2.30(1)	C(11)–C(12)	1.32(7)
Br(2)–Fe–Br(1)	109.8(3)	C(5)–C(4)–C(3)	121.1(29)
Br(3)–Fe–Br(1)	109.2(3)	C(6)–C(5)–C(4)	120.9(27)
Br(3)–Fe–Br(2)	109.8(3)	C(5)–C(6)–C(1)	123.3(30)
Br(4)–Fe–Br(1)	107.9(2)	C(12)–C(7)–C(8)	107.2(29)
Br(4)–Fe–Br(2)	109.6(5)	C(9)–C(8)–C(7)	118.1(33)
Br(4)–Fe–Br(3)	110.5(6)	C(10)–C(9)–C(8)	125.0(34)
C(6)–C(1)–C(2)	123.4(23)	C(11)–C(10)–C(9)	122.3(46)
C(3)–C(2)–C(1)	117.4(26)	C(12)–C(11)–C(10)	122.0(40)
C(4)–C(3)–C(2)	113.7(26)	C(11)–C(12)–C(7)	125.3(39)

orbital contribution to the *g* tensor, and slow electronic relaxation, results in signals observable at room temperature and *g* values close to the free electron value. Thus the EPR data for **1** are consistent with this assignment. The absence of any resolvable hyperfine coupling to the ^{97,95}Mo isotopes can be attributed to the fact that the unpaired electron occupies an almost pure molybdenum d_{z^2} orbital with negligible molybdenum s orbital character.[10]

Synthesis and Characterisation of $[Mo(\eta\text{-}C_6H_6)_2][FeBr_4]$, **2**.—*Synthesis*. Addition of one equivalent of $[NEt_4][FeBr_4]$ to a solution of **1** in CH_2Cl_2 yields on cooling to −40 °C for 2–3 d small black cubic crystals of the 1:1 salt $[Mo(\eta\text{-}C_6H_6)_2]$-$[FeBr_4]$ **2**. Compound **2** has been characterised by elemental microanalysis, infrared spectroscopy, variable-temperature EPR spectroscopy, magnetic susceptibility measurements and a single-crystal X-ray structure determination.

X-Ray structure determination. Compound **2** crystallises in the centrosymmetric orthorhombic crystal system with space group *Pbca*. The molecular structure together with atomic labelling scheme is shown in Fig. 1, selected bond lengths and angles are given in Table 1, and the positional parameters are given in Table 2. The results of the X-ray analysis confirm the molecular composition proposed on the basis of the elemental analysis.

Table 2 Fractional atomic coordinates for $[Mo(\eta\text{-}C_6H_6)_2][FeBr_4]$ **2** with e.s.d.s in parentheses

Atom	*X/a*	*Y/b*	*Z/c*
Mo	0.370(1)	0.2478(2)	−0.0030(1)
Fe	0.3754(3)	−0.2968(3)	−0.2078(2)
Br(1)	0.3741(2)	−0.2822(3)	−0.0517(2)
Br(2)	0.2767(8)	−0.3935(7)	−0.2552(3)
Br(3)	0.4811(9)	−0.382(1)	−0.2522(2)
Br(4)	0.3704(9)	−0.1265(3)	−0.2669(3)
C(1)	0.304(1)	0.115(2)	0.052(2)
C(2)	0.355(1)	0.139(2)	0.120(2)
C(3)	0.436(2)	0.137(3)	0.094(3)
C(4)	0.449(2)	0.107(3)	0.001(3)
C(5)	0.390(2)	0.083(2)	−0.059(2)
C(6)	0.323(2)	0.086(2)	−0.030(2)
C(7)	0.438(2)	0.363(3)	−0.093(3)
C(8)	0.355(2)	0.362(3)	−0.120(2)
C(9)	0.305(2)	0.381(3)	−0.055(3)
C(10)	0.319(2)	0.403(3)	0.025(3)
C(11)	0.385(4)	0.413(3)	0.053(3)
C(12)	0.441(2)	0.395(3)	0.001(4)

Table 3 Selected intermolecular distances (Å) for $[Mo(\eta\text{-}C_6H_6)_2]$-$[FeBr_4]$ **2** with e.s.d.s in parentheses

Mo···Fe	6.471(4), 5.73(2), 5.48(2), 6.44(2), 6.33(2)
Mo···Br(1)	5.931(5), 4.87(2), 4.56(2)
Mo···Br(2)	6.10(1), 4.95(1), 6.02(1), 4.91(1)
Mo···Br(3)	6.30(2), 5.01(1), 6.27(2), 4.88(1)
Mo···Br(4)	6.47(2), 6.14(2), 5.905(4), 6.13(2), 5.86(2)
Fe···Br(1)	5.223(5)
Fe(1)···Br(2)	5.822(9)
Fe(1)···Br(3)	5.87(1)
Fe(1)···Br(4)	6.22(1), 6.645(5), 6.26(1)
Br(1)···Br(2)	6.376(8), 5.262(7), 6.618(7)
Br(1)···Br(3)	6.74(1), 5.298(9), 6.40(1)
Br(1)···Br(4)	4.397(5), 6.94(1)
Br(2)···Br(2)	6.337(5)
Br(2)···Br(3)	5.480(7)
Br(2)···Br(4)	4.00(2)
Br(3)···Br(3)	6.301(4)
Br(3)···Br(4)	4.12(2)

The calculated geometrical parameters of the $[FeBr_4]^-$ anion in **2** are similar to those obtained from X-ray structure determinations of other salts containing the tetrahedral $[FeBr_4]^-$ anion.[12,13] The calculated Fe–Br(av.) distance and Br–Fe–Br(av.) angle are 2.32(1) Å and 109.4(3)° respectively. The molecular structure of the 17-electron $[Mo(\eta\text{-}C_6H_6)_2]^+$ cation has not been previously determined. The η-arene ligands are parallel and adopt a staggered (D_{6d}) conformation in the solid state. The Mo–C distances range from 2.20(4) to 2.34(3) Å with a mean value of 2.26(3) Å. The Mo–C_6H_6(centroid) is 1.78(1) Å. The internal mean C–C bond length and C–C–C angle of the η-C_6H_6 ligands are 1.40(6) Å and 119.9(3)° respectively.

We were particularly interested in the three-dimensional arrangements of the cations and anions within the lattice. Figs. 2 and 3 show views of the cation and anion packing. The structure consists of segregated chains of $[Mo(\eta\text{-}C_6H_6)_2]^+$ cations and $[FeBr_4]^-$ anions. Along the $[FeBr_4]^-$ chains, alternate bromine atoms point between molybdenum atoms on the adjacent $[Mo(\eta\text{-}C_6H_6)_2]^+$ stack. Table 3 gives some of the closest intermolecular distances. The inter-ion Br(2)···Br(4) distance of 4.00(2) Å is close to the sum of the van der Waals radii.

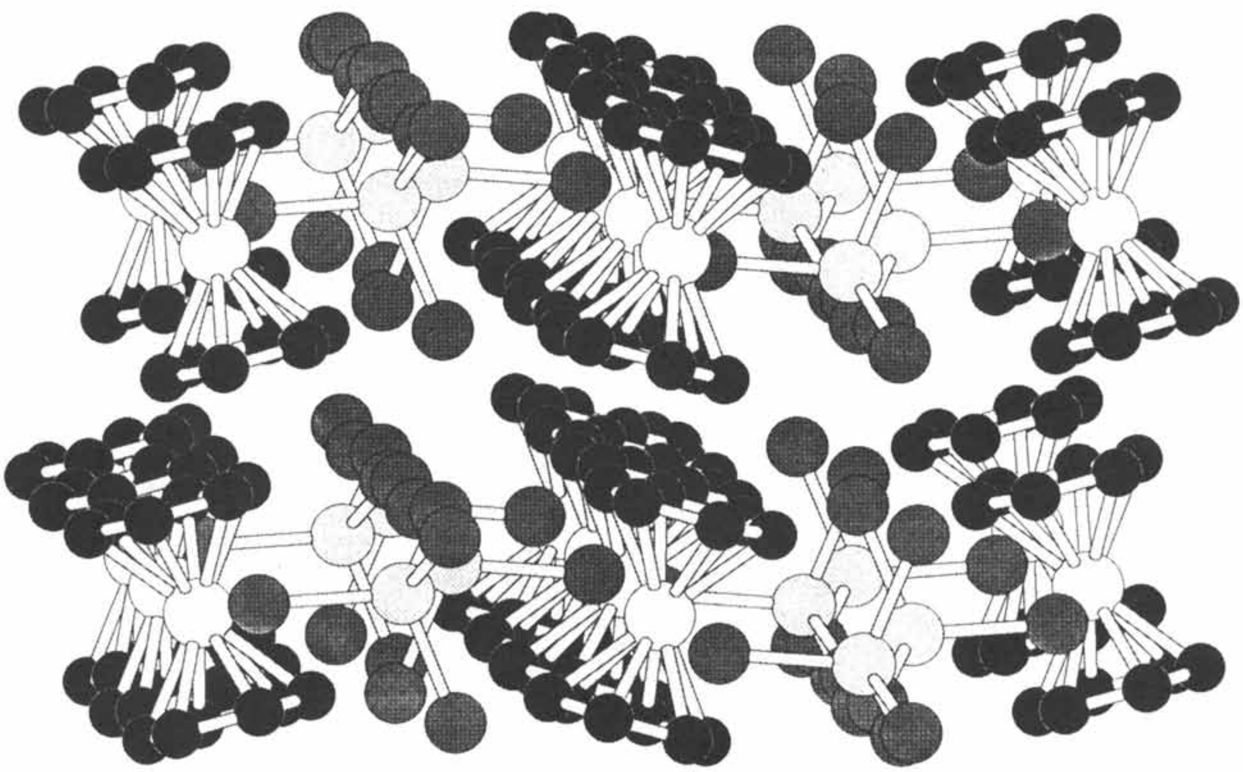

Fig. 2 Packing diagram for $[Mo(\eta-C_6H_6)_2][FeBr_4]$

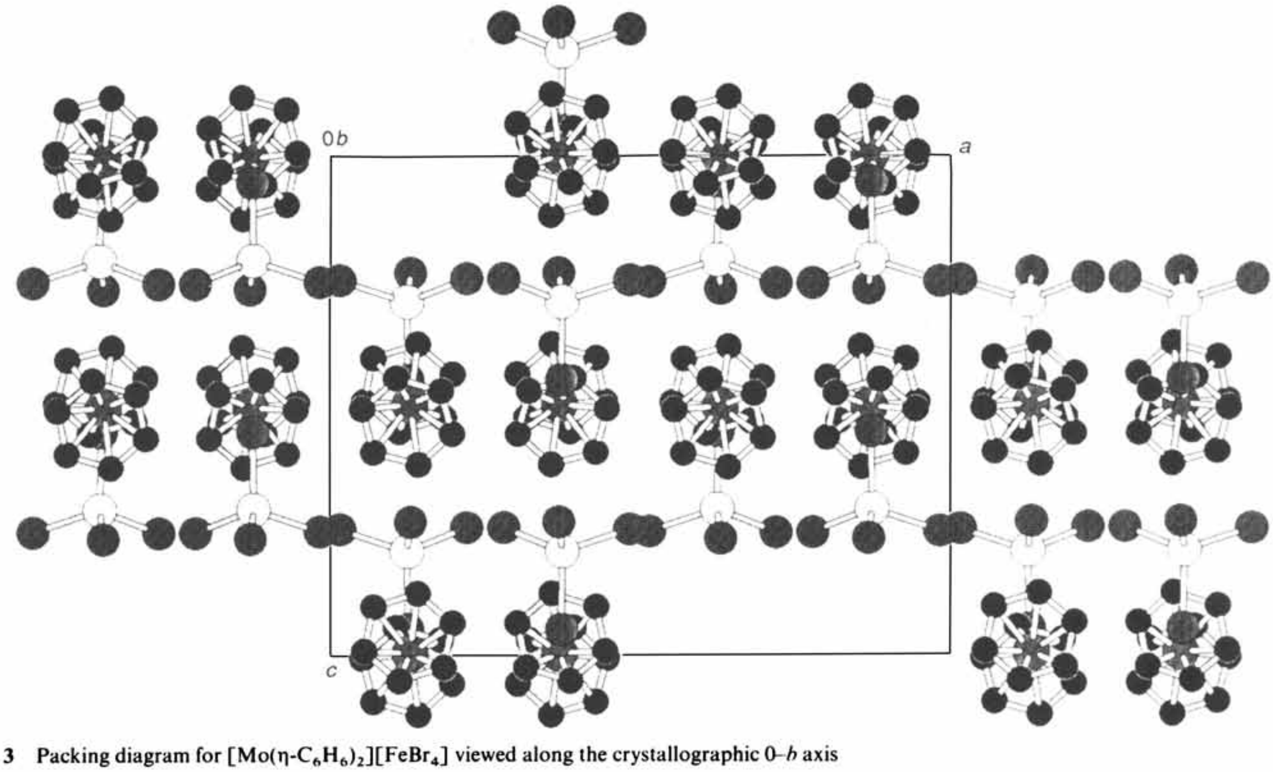

Fig. 3 Packing diagram for $[Mo(\eta-C_6H_6)_2][FeBr_4]$ viewed along the crystallographic 0–*b* axis

EPR Spectroscopy. Variable-temperature EPR spectra of a non-orientated single crystal of **2** were recorded in the temperature range 4.4–300 K. At room temperature the spectra exhibit two absorptions centred at $g = 2.008$ ($\Delta H_{pp} = 450$ G) and at $g = 1.987$ ($\Delta H_{pp} = 35$ G) which can be assigned to the $[FeBr_4]^-$ and $[Mo(\eta-C_6H_6)_2]^+$ radical ions respectively. The $[FeBr_4]^-$ anion exhibits a characteristically broad absorption due to rapid electronic relaxation *via* an efficient spin–spin mechanism. The g value of the resonance assignable to the $[Mo(\eta-C_6H_6)_2]^+$ cation is close to the value found for this cation in compound **1**.

The temperature dependence of the integrated intensity of the EPR signal assigned to the $[Mo(\eta-C_6H_6)_2]^+$ cation was measured in the range 4.4–300 K. The integrated signal intensity obeys the Curie law ($I \propto 1/T$) suggesting no short range intermolecular spin–spin exchange interactions involving the $[Mo(\eta-C_6H_6)_2]^+$ cations. It was not possible to get reliable measurement of the integrated intensity of the signal assignable

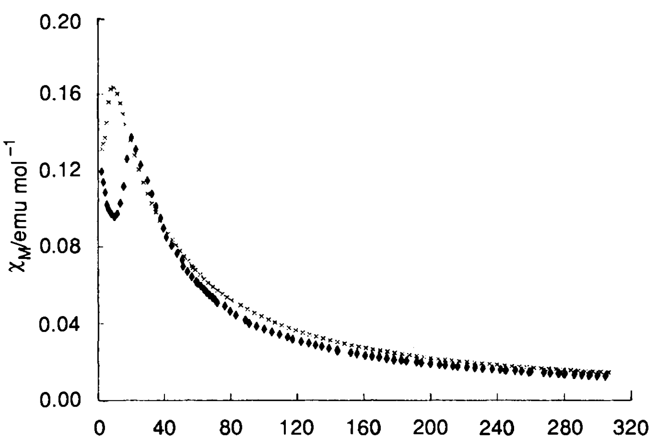

Fig. 4 Temperature variation of the molar magnetic susceptibility (χ_M) for **2** (◆) and for $[NEt_4]^+[FeBr_4]^-$ (+)

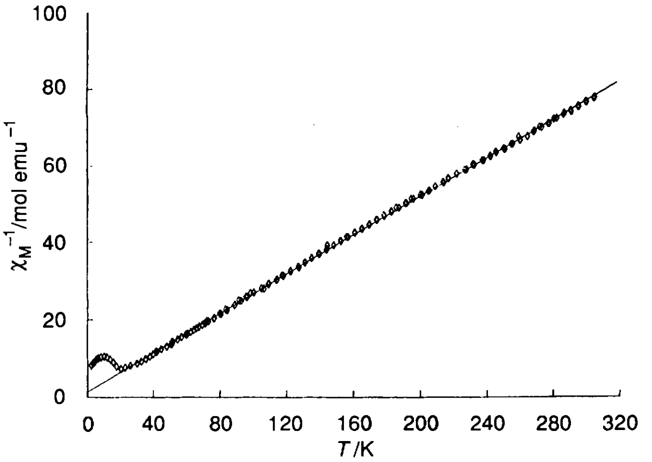

Fig. 5 Plot of inverse molar susceptibility (χ_M^{-1}) *vs.* temperature for **2**

to the $[FeBr_4]^-$ due to the large linewidth, and no appreciable narrowing was observed at low temperature.

Magnetic susceptibility. The molar magnetic susceptibility of **2** has been measured in the temperature range 2–300 K using the Faraday technique. At high temperature (40–300 K) the compound obeys the Curie–Weiss law [$\chi_M = C/(T - \theta)$] with $C = 3.93$ and $\theta = -5.4$ K (Fig. 5), yielding an effective moment ($\mu_{eff} = 5.61$) which is consistent with the existence of two non-interacting $S = \frac{5}{2}$ ($[FeBr_4]^-$) and $S = \frac{1}{2}$ {$[Mo(\eta\text{-}C_6H_6)_2]^+$} spins in this temperature regime. The negative Weiss constant is indicative of short range intermolecular antiferromagnetic interactions. The effective moment is lower than the value of 6.18 calculated on the basis of the spin-only formula for two non-interacting spins: $\chi_{total} = \chi_{cation} + \chi_{anion}$; $\mu_{eff}^2 = g_{cation}^2[S(S+1)] + g_{anion}^2[S(S+1)]$.

The one-dimensional charge-transfer salt [bettf][$FeBr_4$] {bettf = bis(ethylenedithio)tetrathiafulvalene [tetrathiafulvalene = 2-(1′,3′-dithiol-2′-ylidene)-1,3-dithiole]} which also contains non-interacting $[bettf]^+$ ($S = \frac{1}{2}$) cations and $[FeBr_4]^-$ ($S = \frac{5}{2}$) anions ions obeys the Curie–Weiss law with $\mu_{eff} = 5.9(1)$ which is significantly lower than the calculated paramagnetic value.[13]

Below 40 K substantial deviation from the Curie–Weiss law is observed and a maximum in the molar susceptibility is observed at 25 K (Fig. 4). The susceptibility falls to $2\chi_{max}/3$ at 15 K. On further cooling below 15 K the data can be again fitted to the Curie–Weiss expression with $\mu_{eff} = 1.7$.

The temperature dependence of the molar magnetic susceptibility of **2** is consistent with two non-interacting $[Mo(\eta\text{-}C_6H_6)_2]^+$ ($S = \frac{1}{2}$) and $[FeBr_4]^-$ ($S = \frac{5}{2}$) spin systems in the temperature regime 40–300 K. Below 15 K the $[FeBr_4]^-$ anion sub-lattice appears to order antiferromagnetically leaving the paramagnetic $[Mo(\eta\text{-}C_6H_6)_2]^+$ radical cations to dominate the observed magnetic susceptibility at low temperature. This compares to the molar susceptibility of [NEt_4][$FeBr_4$] which obeys the Curie–Weiss law between 30 and 300 K. However, at 15 K a maximum in the susceptibility is observed due to antiferromagnetic ordering of the $[FeBr_4]^-$ anions.

Conclusion

The $[Mo(\eta\text{-}C_6H_6)_2]^+$ cation has been shown by EPR spectroscopy to possess a $^2A_{1g}$ ground state which has been proposed by previous photoelectron spectroscopy experiments and extended Hückel calculations. The salt [$Mo(\eta\text{-}C_6H_6)_2$][$FeBr_4$] has been characterised by magnetic susceptibility measurements, EPR spectroscopy and a crystal structure determination. The solid-state magnetic susceptibility data can be interpreted using a model in which there are no significant magnetic exchange interactions between the cations and anions. However, the anion sub-lattice appears to order antiferromagnetically at 15 K leaving a magnetic susceptibility which solely originates from the $[Mo(\eta\text{-}C_6H_6)_2]^+$ cations.

Experimental

General.—The reactions were carried out in an inert atmosphere of nitrogen by the use of a vacuum line or an inert atmosphere dry-box. Solvents were pre-dried over molecular sieves (type 4 Å) and refluxed with rigorous drying agents under a continuous stream of nitrogen. Dichloromethane was dried by refluxing over P_2O_5, and acetonitrile by refluxing over CaH_2. Solvents were distilled prior to use and were stored over molecular sieves in flame-dried ampoules under nitrogen.

Equipment.—Infrared spectra were recorded on a Mattison Instruments Polaris Fourier transform spectrometer as Nujol mulls between KBr plates. The EPR spectra were obtained using an X-band Varian spectrometer and an Oxford Instruments cryostat. The samples were prepared under an atmosphere of nitrogen and recorded in 4 mm high-purity Spectosil quartz tubes fitted with a Young's Teflon stopcock. Solution spectra were recorded in either CH_2Cl_2 or tetrahydrofuran.

The magnetic susceptibility data were collected over the range 1.8–325 K by using a high-sensitivity computer-interfaced Faraday balance which is described in detail elsewhere.[14] The susceptibilities have been corrected for the intrinsic diamagnetism of the sample container and the diamagnetism of the electronic cores of the constituent atoms ($\chi_{diam} = -319 \times 10^{-6}$ emu mol^{-1} for **2**; $\chi_{SI} = \chi_{cgs} \times 4\pi/10^6$). Crystallographic calculations were performed on a MicroVax 3000 computer in the Chemical Crystallography Laboratory using the Oxford CRYSTALS system[15] and plotted using the CHEMX package.[16]

Elemental microanalyses were performed by the Analytical Services of the Inorganic Chemistry Laboratory.

Syntheses.—[$Mo(\eta\text{-}C_6H_6)_2$][PF_6] **1**. The complex [$Mo(\eta\text{-}C_6H_6)_2$] (1 g, 3.96 mmol) was suspended in benzene and mixed with a benzene solution of iodine (0.5 g, 3.94 mmol). An orange-yellow precipitate formed. The liquor was filtered off and the remaining precipitate dissolved in hot methanol (60 cm^3), and filtered through Celite.

To the filtrate was added $NaPF_6$ (1.5 g, 8.93 mmol) in degassed methanol and after stirring for a few minutes a pale yellow precipitate appeared. The mixture was cooled to −15 °C to ensure that all the product had precipitated. The mixture was filtered and the solid washed twice with cold ethanol and dried *in vacuo* to give [$Mo(\eta\text{-}C_6H_6)_2$][PF_6] (1.96 g; 80% yield) [Found (Calc.) for $C_{12}H_{12}F_6MoP$: C, 36.6 (36.30); H, 3.1

(3.05)%]. IR: 841 cm^{-1} (PF_6^-). EPR (r.t.): solid $g = 1.993$ ($\Delta H_{pp} = 34$ G), solution (CH_2Cl_2) $g = 1.991$ ($\Delta H_{pp} = 15$ G).

$[Mo(\eta\text{-}C_6H_6)_2][FeBr_4]$ **2**. The salt $[Mo(\eta\text{-}C_6H_6)_2][PF_6]$ (250 mg, 0.62 mmol) was dissolved in CH_2Cl_2 and added to a solution of $[NEt_4][FeBr_4]$ (318 mg, 0.62 mmol) in CH_2Cl_2. A dark red solution was formed. On cooling, this solution yielded three types of crystals: large black needles shown to be $[NEt_4][FeBr_4]$, yellow needles shown to be $[Mo(\eta\text{-}C_6H_6)_2]$-$[PF_6]$, and small black rectangular crystals of $[Mo(\eta\text{-}C_6H_6)_2]$-$[FeBr_4]$. The black rectangular crystals were separated by hand; yield 100 mg, 25% [Found (Calc.) for $C_{12}H_{12}Br_4FeMo$: C, 23.0 (22.95); H, 2.3 (1.90)%]. EPR (r.t.): $g = 2.008$ ($\Delta H_{pp} =$ 450 G) and 1.987 (35).

Crystal Structure Determination.—Crystals of complex **2** were sealed under nitrogen in Lindemann glass capillaries.

Crystal data. $C_{12}H_{12}Br_4FeMo$, $M = 627.63$, orthorhombic, space group *Pbca*, $a = 18.527(17)$, $b = 12.521(5)$, $c = 14.915(6)$ Å, $U = 3460.42$ Å^3 (by least-squares refinement on diffractometer angles of 25 automatically centred reflections, $\lambda = 0.710\,69$ Å), $Z = 8$, $D_c = 2.41$ g cm^{-3}. Black rectangular air-sensitive tablets. Crystal dimensions 0.47 × 0.52 × 0.13 mm, μ(Mo-Kα) = 106.83 cm^{-1}, $F(000) = 2336$.

Data collection and processing. CAD4 diffractometer, ω–2θ mode with scan width = $0.9 + 0.5\tan\theta$, scan speed 1.0–6.6° min^{-1}, graphite-monochromated Mo-Kα radiation; 1768 unique reflections measured ($1.00 \leqslant \theta \leqslant 22$, h,k,l) (merging $R = 0.043$ after absorption correction), giving 634 with $I \geqslant 3\sigma(I)$. Linear and approximately isotropic crystal decay of *ca.* 1%, corrected during processing. Correction for Lorentz and polarisation effects.[17]

Structure analysis and refinement. Direct methods (Mo and Fe atoms) followed by normal heavy-atom procedures. Full-matrix least-squares refinement with molybdenum, iron and bromine atoms with anisotropic thermal parameters and isotropic thermal parameters for the carbon atoms due to the relatively low ratio of observations to least-squares parameters. Hydrogens placed in calculated positions (C–H 1.0 Å). Corrections for anomalous dispersion isotropic extinction[18] were made in the final cycles of refinement; a four-term Chebysev weighting scheme[19] was applied with coefficients 13.0, −12.3, 11.4, −3.33. Final R and R' values of 0.051 and 0.059. Final residual electron density <1.5 e Å^{-3}. Atomic scattering factors and anomalous dispersion coefficients were taken from ref. 20.

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

Acknowledgements

We would like to thank the SERC and the Nuffield Foundation for support, and S. McLean, CR&D, E.I. duPont, USA for the magnetic susceptibility measurements.

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Received 27th August 1991; Paper 1/04455I