Synthesis, X-Ray Structure and Spin Crossover in the Triple-decker Complex $[(\eta^5\text{-}C_5Me_5)Cr(\mu^2\text{:}\eta^5\text{-}P_5)Cr(\eta^5\text{-}C_5Me_5)]^+[A]^-$ (A = PF_6, SbF_6)

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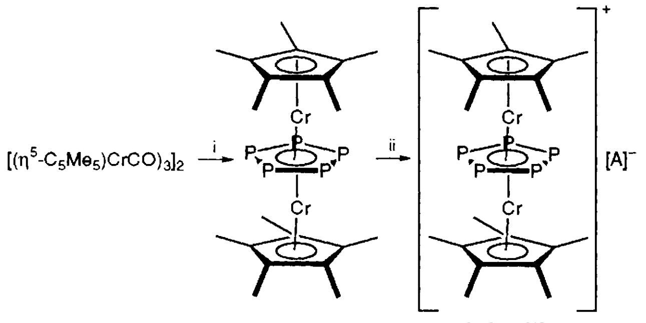
The triple-decker chromium complexes $[(\eta^5\text{-}C_5Me_5)Cr(\mu^2\text{:}\eta^5\text{-}P_5)Cr(\eta^5\text{-}C_5Me_5)]^+[A]^-$ (A = PF_6, SbF_6) can be prepared in high yield by oxidation of $[(\eta^5\text{-}C_5Me_5)Cr(\mu^2\text{:}\eta^5\text{-}P_5)Cr(\eta^5\text{-}C_5Me_5)]$ with either $[Fe(\eta^5\text{-}C_5H_5)_2]^+[A]^-$ (A = PF_6, SbF_6); the single crystal X-ray structure determination for $[(\eta^5\text{-}C_5Me_5)Cr(\mu^2\text{:}\eta^5\text{-}P_5)Cr(\eta^5\text{-}C_5Me_5)]^+[SbF_6]^-$ reveals that the Cr–Cr separation is 3.185(8) Å which is 0.456 Å longer than in the neutral complex; magnetic susceptibility studies show that these 26-electron multidecker cations in these salts undergo spin crossovers at 33 and 23 K respectively.

The synthesis and characterisation of molecular solids which exhibit cooperative magnetic interactions is currently of great scientific interest. Examples of molecular solids which exhibit ferromagnetic ordering include: $[M(\eta^5\text{-}C_5Me_5)_2]^{\cdot+}[TCNE]^{\cdot-}$ (TCNE = tetracyanoethylene; M = Cr, Fe and Mn) with Curie temperatures (T_c) of 3.64, 4.8 and 8.8 K respectively;[1] and Mn(TPP)(TCNE) (TPP = *meso*-tetraphenylporphyrin) with T_c = 18 K.[2]

However, the phenomenon of thermal or pressure induced spin crossover is also of current interest since it has been proposed that such materials could be usefully exploited in displays and information storage devices.[3] For example, Kahn and coworkers have recently described how optical changes brought about by a high-spin low-spin crossover can be used to construct an optical display based on a tri iron complex which has the characteristics of a spin crossover close to ambient temperature with a large thermal hysteresis.[3]

As part of our ongoing interest in the magnetic properties of molecular materials, we have been synthesising new organometallic complexes as potentially interesting magnetic solids. Here we report on the synthesis and magnetic characteristics of some triple decker chromium complexes.

Scherer and coworkers first described the synthesis of the 27-electron triple decker chromium complex $[(\eta^5\text{-}C_5Me_5)Cr(\eta^5\text{-}P_5)Cr(\eta^5\text{-}C_5Me_5)]$ **1** by the reaction of $[Cr(\eta^5\text{-}C_5Me_5)(CO)_3]_2$ with P_4.[4] The $[Cr(\eta^5\text{-}C_5Me_5)(CO)_3]_2$ was initially prepared by the reaction of $Cr(CO)_6$ with C_5Me_5H in refluxing xylene. We found that the overall yield of the triple decker complex **1** could be dramatically improved by specific modification to the reported procedure. In our modified synthesis, $[Cr(\eta^5\text{-}C_5Me_5)(CO)_3]_2$ is prepared in boiling decane, isolated and purified before further reaction. In the second step, involving the reaction with P_4, we employ a careful crystallisation rather than column chromatography as the method of isolation of the final product. These modifications raise the overall yield of **1** to 50–64% based on $Cr(CO)_6$ (literature 8.3%).[3] Typically, we are able to prepare and crystallise up to 4 g of **1** in a single synthesis.



1

2; A = PF_6
3; A = SbF_6

Scheme 1 i, $[Cr(\eta^5\text{-}C_5Me_5)(CO)_3]_2$ (3.132 g, 17.9 mmol) and white phosphorus (5.5 g, 44 mmol) in 100 cm^3 of xylene were refluxed gently for 3 h. The excess P_4 was removed by sublimation (30 °C at 0.01 mmHg) to a nitrogen cooled probe. **CARE**: P_4 is both highly toxic and pyrophoric (especially when sublimed). Yield 2.2 g, 46%. ii, For **2** and **3** a CH_2Cl_2 solution of **1** (0.079 g, 0.15 mmol) was treated over 5 min with a CH_2Cl_2 solution of either $[Fe(\eta^5\text{-}C_5H_5)_2]^+[PF_6]^-$ (0.049 g, 0.15 mmol) or $[Fe(\eta^5\text{-}C_5H_5)_2]^+[SbF_6]^-$ (0.10 g, 0.26 mmol) giving a green solution. For **2** yield 0.045 g, 45%. For **3** yield 0.10 g, 50%. Satisfactory microanalysis data have been obtained for **2** and **3**.

Compound **1** is a 27-valence electron compound which exhibits both chemically reversible one-electron oxidation and reduction steps (E_{ox} = +0.07 V, E_{red} = −0.97 V, *vs.* SCE).[4] Oxidation of **1** by $[Fe(\eta^5\text{-}C_5H_5)_2]^+[A]^-$ (A = PF_6, SbF_6) in CH_2Cl_2 yields the dark-green crystalline compounds $[(\eta^5\text{-}C_5Me_5)(Cr(\mu^2\text{:}\eta^5\text{-}P_5)Cr(\eta^5\text{-}C_5Me_5)]^+[A]^-$ (A = PF_6; **2**, SbF_6; **3**).

The X-ray crystal structure of **3** has been determined.† A view of the molecular structure of the cation appears in Fig. 1. The molecular structure of the $[(\eta^5\text{-}C_5Me_5)Cr(\mu^2\text{:}\eta^5\text{-}P_5)Cr(\eta^5\text{-}C_5Me_5)]^+$ cation consists of a triple-decker arrangement with the three rings coaxial, we observe no significant structural distortions of the $\eta^5\text{-}C_5Me_5$ or $\mu^2\text{:}\eta^5\text{-}P^5$ ligands from fivefold symmetry. The most striking structural change which occurs

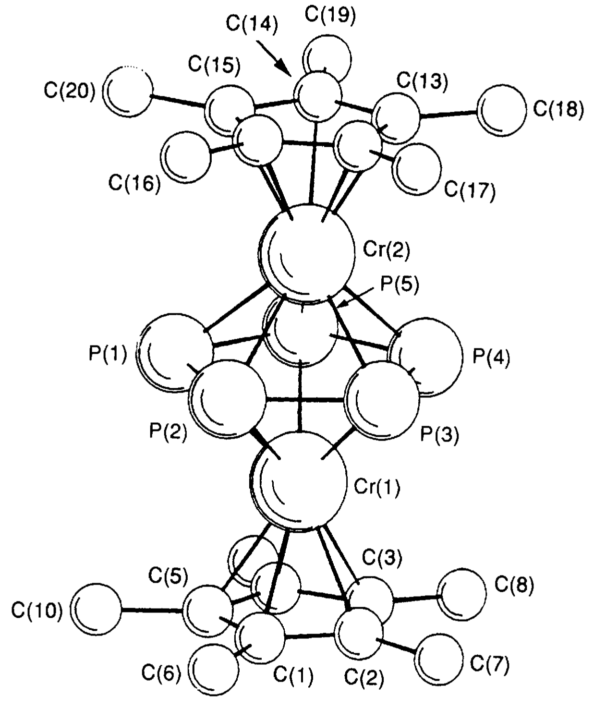


Fig. 1 Molecular structure of **3** showing labelling scheme. All hydrogen atoms and the SbF_6^- counterions have been omitted for clarity. Selected bond lengths (Å) and angles (°): (ESDs are given in parenthesis) Cr(1)–Cr(2) 3.185(1), Cr(1)–P(1) 2.425(4), Cr(1)–P(2) 2.414(4), Cr(1)–P(3) 2.413(4), Cr(1)–P(4) 2.421(4), Cr(1)–P(5) 2.413(4), Cr(2)–P(1) 2.416(4), Cr(2)–P(2) 2.411(4), Cr(2)–P(3) 2.409(4), Cr(2)–P(4) 2.398(4), Cr(2)–P(5) 2.416(4), P(1)–P(2) 2.146(9), P(1)–P(5) 2.134(9), P(2)–P(3) 2.114(9), P(3)–P(4) 2.131(9), P(4)–P(5) 2.137(9); P(1)–P(2)–P(3) 108.3(3), P(2)–P(3)–P(4) 108.2(3), P(3)–P(4)–P(5) 108.0(3), P(1)–P(5)–P(4) 108.0(3), P(2)–P(1)–P(5) 107.5(3).

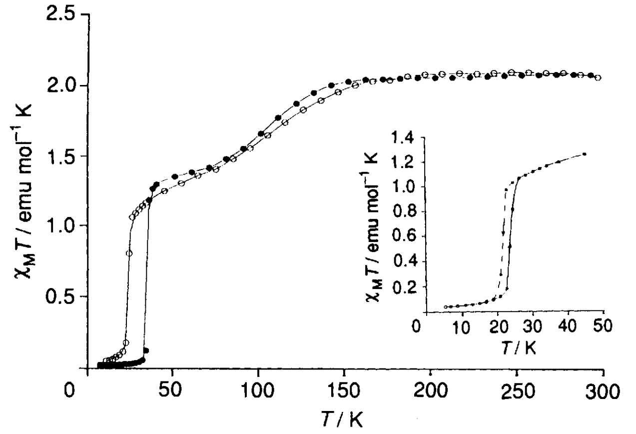


Fig. 2 Temperature variation of $\chi_M T$ for **2** (●) and **3** (○). Inset: Expansion of $\chi_M T$ *vs.* T plot for **2** showing the thermal hysteresis.

on oxidation of **1** is a very significant lengthening of the Cr–Cr separation to 3.185(8) Å, this compares to the Cr–Cr distance in **1** of 2.729(5) Å,[3] all other distances are very similar between **1** and **3**. We presume that this large perturbation to the Cr–Cr separation is a result of removal of an electron from a Cr–Cr bonding orbital. The very slightly shorter P–P distances in the cation may be due to increased P–P bonding as the Cr–Cr bonding is reduced.

We have measured the solid state susceptibility of compounds **1–3** in the temperature range 5–295 K using a SQUID magnetometer. For **1** the molar magnetic susceptibility (χ_M) can be fitted to the Curie expression ($\chi_M = C/T$) with C = 0.38, giving an effective moment (μ_{eff}) of 1.73 μ_B. This is entirely consistent with the EPR data reported by Scherer who proposed an $^2A_1$ ground state for the neutral 27-electron compound.

The magnetic behaviour of the 26-electron compounds **2** and **3** is more complicated. Fig. 2 shows a plot of $\chi_M T$ against T for these two salts $[\mu_{eff} = (8\chi_m T)^{\frac{1}{2}}]$. At high temperature (150–300 K) the molar susceptibility for both **2** and **3** can be fitted to the Curie law with $\mu_{eff} = 4.1$ μ_B. This value is entirely consistent with the value predicted for two non-interacting d^4 Cr^{II} centres and is in agreement with the long Cr–Cr separation observed in the crystal structure of **3**. Between 150–35 K $\chi_M T$ decreases for both **2** and **3** indicative of intramolecular antiferromagnetic spin-spin interactions. At 33 K for **2** and 23 K for **3** $\chi_M T$ exhibits a sharp discontinuity. Below the transition both **2** and **3** are essentially diamagnetic except for a small residual TIP. This sharp spin transition shows some thermal hysteresis, the inset to Fig. 2 shows how $\chi_M T$ varies for **2** as the sample is warmed through the transition temperature, then cooled again and subsequently warmed. The inset to Fig. 2 also shows that the sample can be cycled around this hysteresis loop for at least 2 cycles without any measurable change in the response. The magnitude of the thermal hysteresis for each salt is of the order of 2 K.

The data also indicates that the salts undergo spin transition at a temperature which is a function of the anion. The sharpness of the transition is characteristic of cooperative behaviour and suggests that there may be a substantial structural change at the transition temperature. This is further evidenced by the facts that the crossover temperature depends on the identity of the anion, and the observation of thermal hysteresis. We believe that the observed spin transition is a result of spin-pairing of the odd electron on each Cr centre. This is presumably brought about by a structural distortion which results in a shortening of the Cr–Cr separation.

Further investigations on the electronic structure of these and related systems are in progress using a range of physical techniques including photoelectron spectroscopy.

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† *Crystal data*: Dark-green crystal, $C_{20}H_{30}Cr_2F_6P_5Sb$, M = 765.059, orthorhombic, a = 21.519(7), b = 29.693(11), c = 36.031(9) Å, U = 23 022 Å^3, space group *Fddd*, Z = 32, μ(Mo-Kα) = 19.8019 cm^{-1}, D_c = 1.72 g cm^{-3}, $F(000)$ = 12 096 at room temp. Of the 4526 reflections measured, Mo-Kα, $3 \leqslant 2\theta \geqslant 48°$, 2811 were unique with $I > 3\sigma(I)$. Data were corrected for Lorentz, polarisation effects and absorption (Diffabs). The structure was solved by direct-methods, to yield final R = 0.069, R_w = 0.082 for 310 least-squares parameters. Atomic coordinates, bond lengths, angles and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

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