# Spin Crossover in Chromium(II) Complexes and the Crystal and Molecular Structure of the High Spin Form of Bis[1,2-bis(diethylphosphino)ethane]di-iodochromium(II)

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From the variation of magnetic properties with temperature *trans*-bis[1,2-bis(diethylphosphino)ethane]-di-iodochromium(II) undergoes a sharp $S = 2$ to $S = 1$ spin-state transition between 165 and 175 K.

Weak field ligands produce high-spin chromium(II) ($3d^4$) complexes ($S = 2$) with four unpaired electrons ($^5E_g$ ground term) and strong field ligands low-spin complexes ($S = 1$)† with two unpaired electrons ($^3T_{1g}$ ground term). Examples of the two classes of complex are $[Cr(en)_3]X_2$ (en = ethylenediamine) and $[Cr(2,2'\text{-bipyridyl})_3]X_2$, for which the essentially temperature-independent effective magnetic moments are respectively 4.8 and 2.9 $\mu_B$.[1] Earlier attempts to produce spin-crossover behaviour in six co-ordinate chromium(II) complexes in which two iodides replaced one bipyridyl (bipy) molecule to give $[CrI_2(bipy)_2]$,[2] or the ligands contained one heterocyclic and one amino nitrogen atom as in 2-aminomethylpyridine, (2-picolylamine, pic),[3] were unsuccessful: $[CrI_2(bipy)_2]$ is low spin and although $[CrI_2(pic)_2]$ is high spin, $[Cr(pic)_3]^{2+}$ salts could not be isolated. Some planar chromium(II) complexes show a slowly changing, continuous decrease in effective magnetic moment as the temperature is lowered, but it remains unclear whether this is due to spin-state transition or antiferromagnetic behaviour.[4] We have now found that although complexes of chromium(II) halides (Table 1) with the chelating tertiary diphosphines 1,2-bis(dimethylphosphino)ethane (dmpe) and 1,2-bis-(diethylphosphino)ethane (depe) are generally low-spin, the iodo-complex $[CrI_2(depe)_2]$, from magnetic susceptibility investigations shows a sharp spin crossover between 165 and 175 K (Figure 1). From the experimental data, and by assuming temperature-independent magnetic moments of 4.85 and 2.90 $\mu_B$ for the $S = 2$ and $S = 1$ spin states, the transition temperature, when both are present in equal concentrations, is *ca.* 171 K.

The complexes were prepared by the addition of the phosphine to a solution of the hydrated chromium(II) halide in methanol. Satisfactory microanalyses have been obtained. A sample of $[CrI_2(depe)_2]$ prepared from anhydrous chromium(II) iodide showed the same unusual magnetic behaviour as the sample from the hydrated iodide. The magnetic behaviour is typical of a discontinuous spin transition taking place within a narrow temperature range but, from our limited measurements, it does not show hysteresis. The value of 3.3 $\mu_B$ for the bromo-complex $[CrBr_2(depe)_2]$ at 295 K is higher than

**Table 1.** Effective magnetic moments at 295 and 90 K.

| Complex | $\mu_{eff}^{295}/\mu_B$ | $\mu_{eff}^{90}/\mu_B$ |
|---|---|---|
| $[CrCl_2(dmpe)_2]$[a] | 2.8[b] | — |
| $[CrBr_2(dmpe)_2]$ | 2.92 | 2.82 |
| Red | | |
| $[CrI_2(dmpe)_2]$ | 3.04 | 2.93 |
| Reddish purple | | |
| $[CrCl_2(depe)_2]$[c] | 2.83 | 2.83 |
| Yellow | | |
| $[CrBr_2(depe)_2]$[d] | 3.30 | 3.02 |
| Orange | | |
| $[CrI_2(depe)_2]$ | 4.84[e] | 2.85[d] |
| Purple brown | 4.87[f] | 2.82[e] |

[a] Ref. 5. [b] At 25 °C in toluene. [c] (Cr–Cl) at 335 cm$^{-1}$. [d] (Cr–Br) at 295 cm$^{-1}$. [e] From hydrated $CrI_2$ in methanol. [f] From anhydrous $CrI_2$ in methanol.

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† Strictly an intermediate spin state because further spin pairing can, in principle, occur in distorted $d^4$ complexes.

the values for the other low-spin complexes, suggesting that a small amount of high-spin form may be present at this temperature.

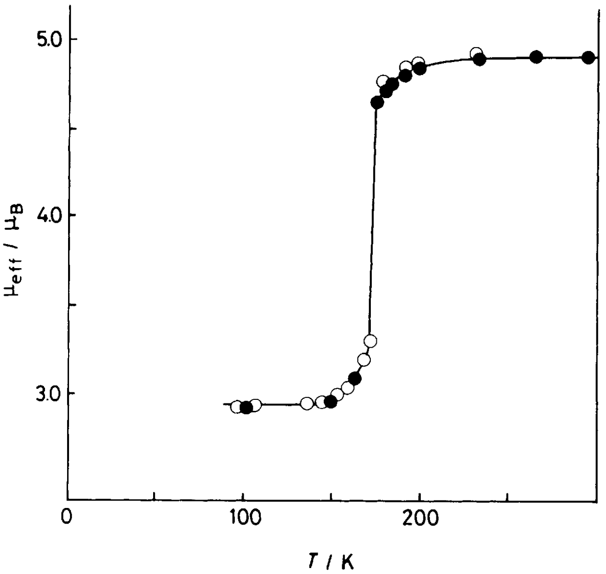

**Figure 1.** Variation with absolute temperature of effective magnetic moment, cooling (●), heating (○), of [CrI$_2$(depe)$_2$].

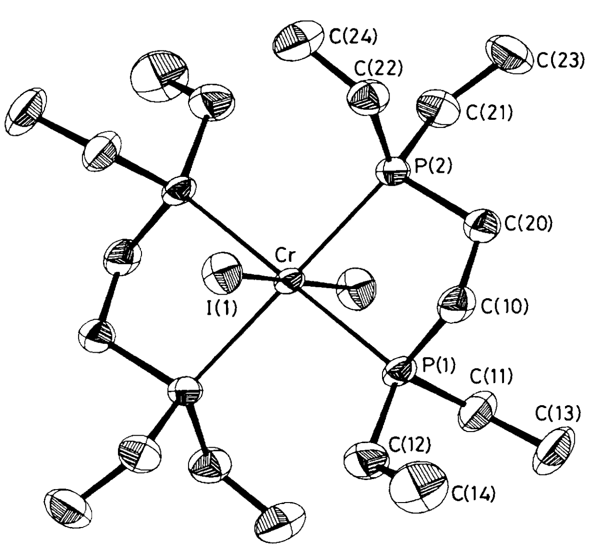

**Figure 2.** The molecular structure of [CrI$_2$(depe)$_2$]. Selected bond lengths and angles are Cr–I 3.068(0), Cr–P(1) 2.503(1), Cr–P(2) 2.533(1) Å, I(1)–Cr–P(1) 85.50(3), I(1)–Cr–P(2) 88.40(3), P(1)–Cr–P(2) 80.33(4)°.

The molecular structure‡ of [CrI$_2$(depe)$_2$] has been determined at room temperature. It has a *trans*-configuration (Figure 2) with Cr–I bond distances of 3.068(0) Å and Cr–P distances of 2.503(1) and 2.533(1) Å. The Cr–P distances are *ca.* 0.15 Å longer than those reported (2.365—2.371 Å) for the low-spin analogue [CrCl$_2$(dmpe)$_2$][5] as might be expected, and the Cr–I distances are comparable with values (*ca.* 3.1 Å) found for the long (distortion axis) bonds in CsCrI$_3$[6] and CrI$_2$.[7] There are many examples of spin state transitions in complexes with the d$^5$, d$^6$ and d$^7$ configurations,[8] but few[9] with the d$^4$ configuration.

Since [CrI$_2$(dmpe)$_2$] is low-spin it is clear that minor differences in the phosphine ligand markedly affect the magnetic behaviour. The more heavily substituted chelating diphosphine, 1,2-bis(di-isopropylphosphino)ethane (dippe), forms[10] halide-bridged dimers [CrX$_2$(dippe)$_2$], where X = Cl or Br, quite different in structure from *trans*-octahedral [CrI$_2$(depe)$_2$] or [CrCl$_2$(dmpe)$_2$]. The dimers have magnetic moments in acetonitrile consistent with high-spin chromium(II). The complex [CrBr$_2$(dippe)(MeCN)] also is high-spin.[10] Clearly there is a rich chemistry of chromium(II)–phosphine ligands to be explored.

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‡ *Crystal data*: C$_{20}$H$_{48}$CrI$_2$P$_4$, triclinic, space group $P\bar{1}$, $Z = 1$; $a = 8.960(3)$, $b = 10.275(3)$, $c = 8.393(5)$ Å, $\alpha = 98.56(37)$, $\beta = 104.28(39)$, $\gamma = 96.04(28)$°, $U = 732.3$ (1.2) Å$^3$, $D_c = 1.629$ g cm$^{-3}$, $F(000) = 358$, $\mu$(Mo-$K_\alpha$) = 26.9 cm$^{-1}$, $R = 0.035$, $R_w = 0.046$, for 2405 reflections [$I > 3\sigma(I)$] measured on an Enraf-Nonius CAD-4 diffractometer. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.