

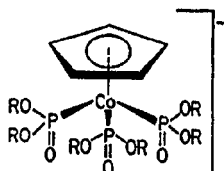
High Spin–Low Spin Equilibrium in a Six-co-ordinate Cobalt(III) Complex

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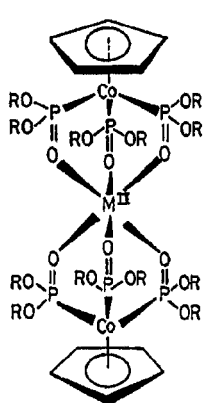
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Summary A new six-co-ordinate cobalt(III) complex is described which exhibits a high spin–low spin equilibrium.

SPIN crossovers are possible in octahedral transition metal complexes with the d^4 , d^5 , d^6 , or d^7 electron configuration. Among d^6 complexes those of Fe^{II} with phenanthroline, bipyridine, and tris-(1-pyrazolyl)borate as ligands have become known as crossover systems in the last few years.¹ In the isoelectronic Co^{III} d^6 -series all complexes known until now are diamagnetic, the only exception being the high-spin $[\text{CoF}_6]^{3-}$ complex ion.² Since the $[\text{Co}(\text{H}_2\text{O})_6]^{3+}$ ion is low spin³ the condition for a spin equilibrium $\pi \approx \Delta$ can only be met with ligands having a high nephelauxetic ratio β and a ligand field strength between that of F^- and H_2O .



(1) $\text{R} = \text{Et}$

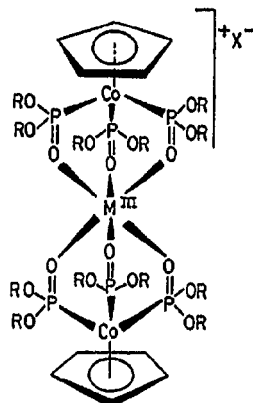


$\text{R} = \text{Et}$

(2) $\text{M} = \text{Co}^{II}$

(3) $\text{M} = \text{Ni}^{II}$

(4) $\text{M} = \text{Cu}^{II}$



$\text{R} = \text{Et}$

(5) $\text{M} = \text{Ln}^{III}$, $\text{X} = \text{BF}_4$

(6) $\text{M} = \text{Co}^{III}$, $\text{X} = \text{PF}_6$

(7) $\text{M} = \text{Co}^{III}$, $\text{X} = \text{ClO}_4$

We have recently prepared a diamagnetic anionic half-sandwich complex (1) which reacts with divalent and trivalent metal ions to give trinuclear sandwich complexes, e.g. (2)–(5).^{4–6} The electronic spectra of (2)–(4) clearly demonstrate that the ligand (1) is a hard oxygen donor with a ligand field strength comparable to that of H_2O . During these studies we have tried to synthesize electrochemically complexes of this type with metals M in such oxidation states that their hexa-aqua-ions are not stable in solution or not well characterised. We have found that (2) can be oxidised (Pt electrode, + 1.0 V in CH_2Cl_2) to give the corresponding cobalt(III) complex, which can easily be isolated as the hexafluorophosphate or perchlorate salt (6) or (7) depending on the supporting electrolyte.⁷ These cobalt(III) compounds are dark green at room temperature in the solid state, as well as in solution, and gradually become light yellow upon cooling. The green colour is due to a charge transfer band of the tripod ligand (1) at λ 328 nm and a broad absorption band at λ 640 nm. At low temperature the 640 nm band disappears and a band at 710 nm becomes visible. Since this latter absorption is of lower intensity, the appearance of (6) and (7) at low temperature is dominated by the yellow colour of the tripod ligand (1).

The magnetic moment of the green cobalt(III) compounds (6) and (7) at 300 K in CH_2Cl_2 solution is μ_{eff} 2.6 B.M. The corresponding solid-state value for (6) is μ_{eff} 2.2 B.M. Upon heating the solid-state magnetic moment of (6) increases steadily, e.g. $\mu_{\text{eff}} = 4.1 \pm 0.05$ B.M. at 393 K. Unfortunately decomposition of the compound makes measurements above ca. 410 K impracticable. Below room temperature the magnetic moment decreases and at 4.2 K $\mu_{\text{eff}} = \text{ca. } 0.4$ B.M. This value is probably accurate only to ± 0.2 B.M. The residual paramagnetism observed at 4.2 K therefore cannot be interpreted in terms of a fraction of molecules staying in the high-spin state or the temperature-independent paramagnetism of the low-spin state. The observed range of μ_{eff} , ca. 0.4–4.1 B.M. rules out, however, the possibility of a quintet–triplet or a singlet–triplet transition.⁸

To my knowledge this is the first report which provides conclusive evidence for a quintet–singlet spin equilibrium in an octahedral Co^{III} complex.

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