Doublet–Quartet Equilibria in Five-co-ordinate Cobalt(II) Complexes

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BIVALENT iron, cobalt, and nickel compounds of co-ordination number five may be either high-spin or low-spin, the choice of spin multiplicity depending on the nature of the ligand donor atoms.[1–3] Recently we reported[2] the first case of the co-existence in equilibrium of high- and low-spin forms in a five-co-ordinate nickel(II) complex, Ni(pnp)Cl_2 [pnp = 2,6-di-(β-diphenylphosphinoethyl)-pyridine]. There is now much interest in the possibility of spin isomerism in five-co-ordinate cobalt(II) and in the ligand-field conditions which might produce it.[3] We here report the first examples.

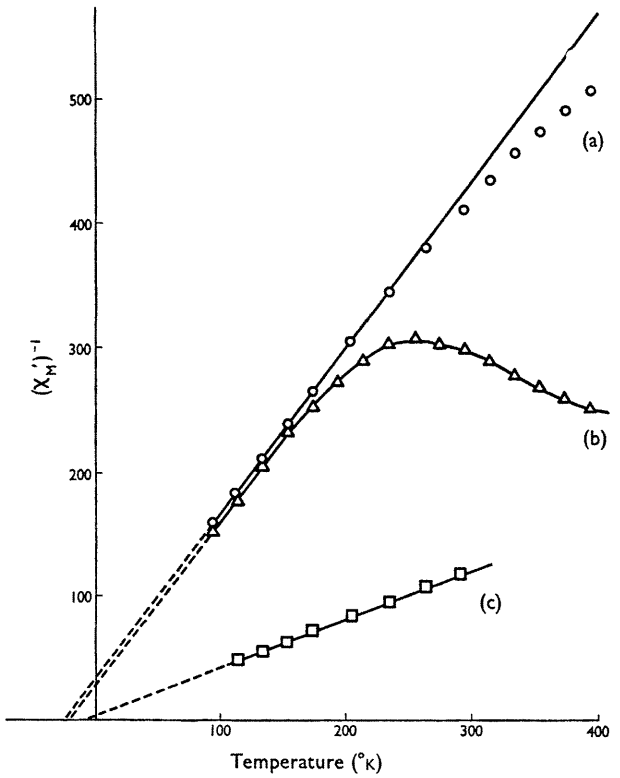

FIGURE. *Plots of* $1/\chi'_M$ *against* T: (a) Co(pnp)Cl_2; (b) Co(pnp)Br_2 (c) Co(pnp)I_2. (χ'_M = *molar susceptibility corrected for diamagnetism of ligands*).

The compounds which exhibit the phenomenon are Co(pnp)Br_2 and Co(pnp)I_2. These, and the corresponding chloro-complex, are isomorphous with each other and with the corresponding nickel(II) compounds, known to have five-co-ordinate structures.[2] The magnetic behaviour, which is reversible and independent of field strength, in the temperature range 90—400° K, is summarised in the Figure. (An account of other properties is deferred; they are, however, fully consistent with the structure indicated by the *X*-ray measurements). The chloride is high-spin (μ_{eff} at 293° K = 4·47 B.M.) and obeys the Curie–Weiss law over the temperature range investigated (Weiss constant = 6°). The iodide (μ_{eff} at 293° K = 2·39 B.M.) shows Curie–Weiss behaviour below 250° K (Weiss constant = 24°) but with a deviation above this temperature too large to be accounted for in terms of temperature-independent paramagnetism. In the case of the bromide (μ_{eff} at 293° K = 2·81 B.M.) the Curie–Weiss plot is linear only below 150° K (Weiss constant = 21°). The moment increases continuously with temperature from a value of 2·24 B.M. at 93° K to 3·54 B.M. at 393° K. We interpret the behaviour of the bromide and iodide in terms of a doublet ground state with a thermally accessible quartet excited state. The linear sections of the $1/\chi'_M$ against *T* plots indicate that both compounds exist almost completely in the low-spin form at low temperatures. Simple calculations assuming a high-spin moment of 4·5 B.M. for both compounds indicate that at 373° K about 50% of the bromide, and about 6% of the iodide, exist in the high-spin form. The room-temperature electronic spectrum of the bromide shows features attributable to both high- and low-spin species. A point of major interest is that the "magnetic cross-over" in five-co-ordinate cobalt(II) and nickel(II) should occur with such closely similar ligand fields.

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[3] L. Sacconi and I. Bertini, *J. Amer. Chem. Soc.*, 1968, **90**, 5443; and earlier papers.