

## Paramagnetic Cobalt(III) Compounds of the Type $[\text{CoN}_4\text{X}]^0$ (X=Cl,Br,I)

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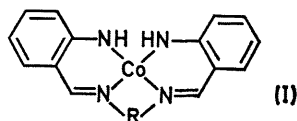
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**Summary** The monohalogeno(quadridentate)cobalt(III) compounds, for which "quadridentate" is a nitrogen-donor tricyclic quadridentate dianion of a Schiff base formed from *o*-aminobenzaldehyde and various diamines, are paramagnetic, with magnetic moments that decrease with temperature and, in one case, approach zero at 5 K.

THE low-spin cobalt(II) compounds (I)<sup>†1,2</sup> react with halogens or various halogenocarbon compounds to form dark-green crystalline cobalt(III) compounds  $[\text{CoN}_4\text{X}]$  (where X = Cl, Br and I) which are paramagnetic.



Preliminary room-temperature magnetic moments are listed in the Table and some temperature-variation data are

*The room-temperature magnetic moments*

Compound	$\bar{\mu}$ (B.M.)
$[\text{Co}(\text{aben})\text{Cl}]$ .. .. .	2.73
$[\text{Co}(\text{aben})\text{py Cl}]\text{H}_2\text{O}$ .. .. .	dia. ( $10^6\chi_M = 180$ cgsu)
$[\text{Co}(\text{abpn})\text{Cl}]$ .. .. .	2.7
$[\text{Co}(\text{abpn})\text{Br}]$ .. .. .	3.15
$[\text{Co}(\text{abpn})\text{I}]$ .. .. .	2.78
$[\text{Co}(\text{abphen})\text{Cl}]$ .. .. .	2.7

represented in the Figure.

† Abbreviations used are as follows: (I) =  $[\text{Co}(\text{aben})]$  for R =  $\cdot\text{CH}_2\cdot\text{CH}_2\cdot$ ; =  $[\text{Co}(\text{abpn})]$  for R =  $\cdot\text{CHMe}\cdot\text{CH}_3\cdot$ ; and =  $[\text{Co}(\text{abphen})]$  for R =  $o\text{-C}_6\text{H}_4\cdot$ .

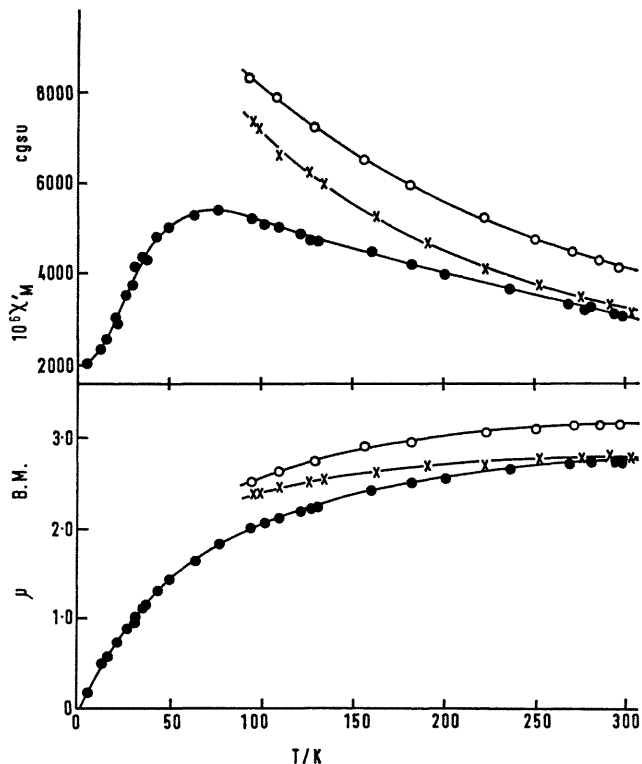
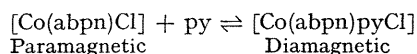


FIGURE. The magnetic data at different temperatures for the compounds  $[\text{Co}(\text{aben})\text{Cl}]$  (●),  $[\text{Co}(\text{abpn})\text{Br}]$  (○), and  $[\text{Co}(\text{abpn})\text{I}]$  (×).

The crystalline *paramagnetic* compound [Co(aben)Cl] dissolves in pyridine, and a new brown *diamagnetic* compound Co(aben)Cl,py,H<sub>2</sub>O crystallises from the solution. This latter, when suspended in CH<sub>2</sub>Cl<sub>2</sub>, reverts to the original paramagnetic compound [Co(aben)Cl] (*X*-ray powder patterns, analyses, and magnetic moments).

Although we have no unequivocal structural data, we currently believe that the paramagnetic compounds [Co-(quadridentate)X] are five-co-ordinate with a square-pyramidal geometry—[Co(abpn)Cl] is essentially a non-electrolyte in nitromethane—and that the diamagnetic pyridine compound has the six-co-ordinate structure [Co(aben)pyCl],H<sub>2</sub>O. These postulates will be checked by full *X*-ray structural analyses.

In parallel with the unusual paramagnetism of these compounds, they have unusual electronic absorption spectra, with a high-intensity band at *ca.* 13 kK ( $\epsilon$  3000—7000). The same bands occur in the spectra of the solids and the deep green solutions in various non-donor solvents. With donor solvents such as pyridine and water, however, the solutions are brown and contain large amounts of the six-co-ordinate species [Co(quadridentate)(solvent)X] analogous to the diamagnetic solid compound [Co(aben)pyCl],H<sub>2</sub>O. But, both the intensity of a residual peak at 13 kK in the electronic absorption spectrum of [Co(abpn)Cl] in pyridine, and the magnetic moment in pyridine, agree in indicating an equilibrium:



in which only 75—80% of the compound is in the diamagnetic form.

This equilibrium is nicely confirmed by the <sup>1</sup>H n.m.r. spectrum of [Co(abpn)Cl] in perdeuteriopyridine. The residual proton resonances of the pyridine are sharp and not significantly shifted; whereas the resonances of the quadridentate ligand protons are broad unresolved peaks, with large paramagnetic contact shifts.

In ligand-field terms, we see the paramagnetism of these compounds arising from the low symmetry and field aniso-

tropy rather than from unusual ligand-field strengths. The strong in-plane ligand field of the Schiff-base dianion, and the weak axial field of the halogen remove the degeneracy of the parent octahedral *t<sub>2g</sub>* and *e<sub>g</sub>* orbitals, and may leave the *d<sub>xy</sub>* and *d<sub>z</sub><sup>2</sup>* orbitals with similar energies. In this case, a *d<sub>xy</sub><sup>2</sup> d<sub>yz</sub><sup>2</sup> d<sub>yz</sub><sup>1</sup> d<sub>z</sub><sup>1</sup>* configuration may be a thermally-accessible, or even ground, state of the molecules. The behaviour of the magnetic moments of [Co(aben)Cl] and [Co(abpn)X] (X = Br, I) with temperature (Figure) strongly suggests a thermal equilibrium between the spin-singlet and spin-triplet states, *d<sub>xy</sub><sup>2</sup> d<sub>yz</sub><sup>2</sup> (d<sub>yz</sub> or d<sub>z</sub><sup>2</sup>)<sup>2</sup>* and *d<sub>xy</sub><sup>2</sup> d<sub>yz</sub><sup>2</sup> d<sub>yz</sub><sup>1</sup> d<sub>z</sub><sup>1</sup>*, respectively; with the singlet state lower in energy. At 5 K the paramagnetic moment of [Co(aben)Cl] has nearly vanished. The unlikely possibility that such temperature dependence of the moment may result from spin-triplet states alone must await detailed calculations.

Another alternative to the 'spin-equilibrium' model with a monomeric species is a dimeric species in which the two paramagnetic halves interact antiferromagnetically. We do not favour this latter since it would involve essentially octahedral, paramagnetic cobalt(III) entities—*cf.* the diamagnetic compound [Co(aben)pyCl],H<sub>2</sub>O—although we are uncertain how to assess the possibility of the nitrogen bridging which would seem to be required.

We may rationalize why paramagnetism has not previously been observed for the variety of known, related cobalt(III) compounds of macrocyclic, quadridentate nitrogen ligands by considering the in-plane ligand field. In the porphyrins, for example, the 'hole' in the macrocycle is too large to allow an in-plane field as strong as in the present compounds—the M-N bond distances would be *ca.* 2.01 Å for an undistorted ligand.

The only other known examples of related paramagnetic cobalt(III) compounds (excluding the fluoro-species) are the bisdithiolene species,<sup>3</sup> for which a four co-planar geometry is proven,<sup>4</sup> and the compounds [Co(PEt<sub>3</sub>)<sub>2</sub>X<sub>3</sub>] (X = Cl, Br)<sup>5</sup> which have room-temperature magnetic moments similar to those of our compounds, and probably a trigonal-bipyramid five-co-ordinate structure.

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