The Molecular Structure and Magnetic Properties of Bistrimethylaminechromium Trichloride

By G. W. A. FOWLES and P. T. GREENE
(*Chemistry Department, The University, Reading*)

and J. S. WOOD*
(*Chemistry Department, The University, Southampton*)

DEFINITIVE information on the effect of the varying *d*-electron configuration on the stereochemistry of pentaco-ordinate complexes of the transition metals is scarce, in spite of the current interest in the preparation and characterisation of such molecules. This is principally because the symmetries of the idealised polyhedra cannot be attained, either for purely stoicheiometric reasons, or frequently because the ground-state geometry is determined by the constraints of chelating ligands.[1] However, for the series of compounds of formulation $MX_3,2NMe_3$ ($M = Ti,^{2a}\ V,^{2b}\ Cr,^{2c}$ and $X = Cl$ or Br) the idealised symmetry, D_{3h}, of the trigonal bipyramid, can be achieved and the effect of the *d*-electron configuration evaluated.

Detailed magnetic, structural, and spectroscopic studies have been carried out on these molecules and have provided important information on their ground-state geometries.

In an earlier publication,[3] we reported preliminary *X*-ray results on the titanium complex, $TiBr_3,2NMe_3$, which showed a very small, but significant, deviation away from D_{3h} symmetry. Structural analysis of the chromium analogue, $CrCl_3,2NMe_3$, whose isolation was recently reported by two of us,[2c] shows this to be isomorphous and virtually isostructural with the titanium and vanadium complexes. Here, in contrast to the titanium complex, the deviation from D_{3h} symmetry is much greater, although it is of the same type and the molecule possesses C_{2v} symmetry to within the estimated standard deviations (the crystallographically required symmetry is *Cs*). Refinement of approximately 500 visually estimated Weissenberg data ($R = 8\%$) gives the following molecular parameters for the co-ordination polyhedron (standard deviations in parentheses): Cr–Cl, 2·216 (7) Å; Cr–Cl(m), **2·244** (8) Å; Cr–N(1), **2·198** (17) Å; Cr–N(2), **2·168** (**20**) Å; Cl–

Cr–Cl(m), 124·2 (0·2)°; Cl–Cr–Cl′, 111·6 (0·2)°; Cl(m)–Cr–N(1), 89·5 (0·6)°; and Cl(m)–Cr–N(2), 91·7 (0·6)°. A view of the molecule is given in Figure 1. There are no short intermolecular contacts and the observed molecular symmetry can be considered to be representative of the "true" ground-state geometry of the molecule. For a molecule with three *d*-electrons possessing D_{3h} symmetry, the ground-state configuration (assuming a spin-free complex) would be $(e'')^2$ (e'). Since the doubly degenerate e'-orbital in an MO scheme is antibonding, this molecular symmetry would be unstable (when this orbital is singly occupied) relative to one, *e.g.*, C_{2v}, in which this orbital degeneracy is removed. Although spin-orbit coupling can remove the degeneracy, the magnitude of this effect is obviously insufficient to stabilise the D_{3h} configuration.

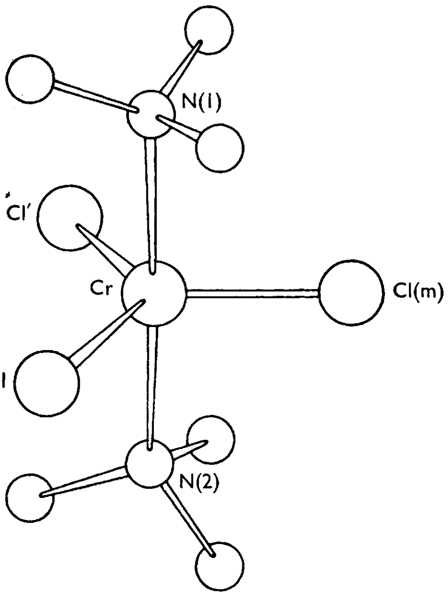

FIGURE 1. *Configuration of* $CrCl_3,2NMe_3$.

Magnetic measurements for the chromium complex carried out over a temperature range also indicate considerable distortion from D_{3h} symmetry, and that the ground state of the molecule is an orbital singlet. The compound conforms with the Curie–Weiss law, over the temperature range 298—89° K with $\theta = 7°$. The magnetic moment is thus virtually independent of temperature and is 3·88 B.M. at 298° K—corresponding to the spin-only value for three unpaired electrons with no orbital contribution. For the $^4E'$ ground state in D_{3h} symmetry, one anticipates much different behaviour, and for a powdered sample this has been calculated[4] to have the variation shown in Figure 2. The room-temperature value (300° K) for Cr^{3+} is indicated.

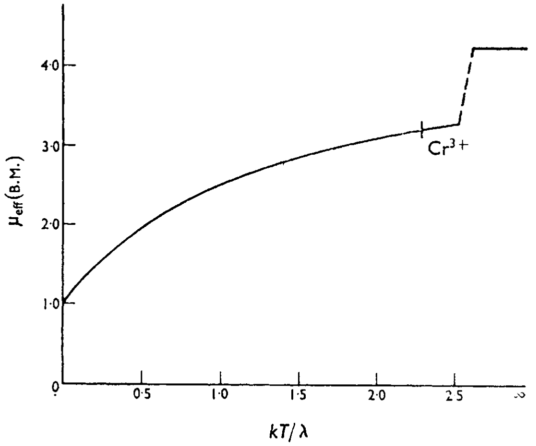

FIGURE 2. *Theoretical variation of magnetic moment as a function of* kT/λ *for the* ^{4}E′ *crystal-field term in* D_{3h} *symmetry.*

Similar results have also been observed for the titanium complex, $TiCl_3,2NMe_3$. The magnetic moment for this complex falls from 1·64 at 298° K to 1·49 B.M. at 85° K and it has been shown that these results cannot be explained on the basis of D_{3h} symmetry.[4] On the other hand, detailed ligand field calculations for the d^2-configuration,[4] indicate that both the magnetic properties and the recently reported[5] electronic (ligand-field) spectra of the vanadium complexes, are compatible with a regular trigonal bipyramidal geometry for these molecules, as might be anticipated for the $^3A_2'$ ground state.

(*Received, July* 17*th*, 1967; *Com.* 736.)

---

[1] See, for example, M. Ciampolini and G. P. Speroni, *Inorg. Chem.*, 1966, **5**, 45.

[2] (a) M. Antler and A. W. Laubengayer, *J. Amer. Chem. Soc.*, 1955, **77**, 5250; (b) G. W. A. Fowles and C. M. Pleass, *J. Chem. Soc.*, 1957, 2078; (c) G. W. A. Fowles and P. T. Greene, *Chem. Comm.*, 1966, 784.

[3] B. J. Russ and J. S. Wood, *Chem. Comm.*, 1966, 745.

[4] J. S. Wood, unpublished work.

[5] M. W. Duckworth, G. W. A. Fowles, and P. T. Greene, *J. Chem. Soc.* (*A*), 1967, 1592.