A Five-co-ordinated Complex Compound of Chromium(II)

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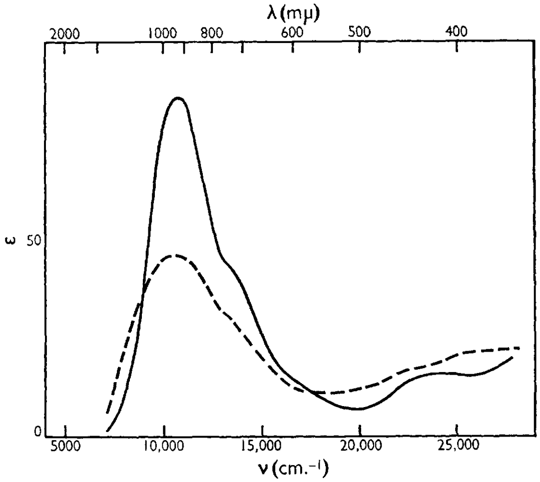
LITTLE is known on the stereochemistry of the co-ordination compounds of chromium(II). Particularly, no unambiguous evidence has been given for five-co-ordinated chromous complexes.

In this laboratory, the quadridentate ligand tris-(2-dimethylaminoethyl)amine = Me_6tren, $N[CH_2CH_2N(CH_3)_2]_3$, has been recently found to form five-co-ordinated complexes with bivalent transition-metal ions from manganese to zinc, having the general formula $[M(Me_6tren)X]X$ ($X = Cl, Br, I, NO_3, ClO_4$).[1] A three-dimensional *X*-ray investigation on the complex $[Co(Me_6tren)Br]Br$, still in progress, has shown the metal atom to have a trigonal bipyramidal configuration with symmetry C_3.[2] The three dimethylamino-groups lie at the corners of the basal equilateral triangle and the co-ordinated bromine is on the three-fold axis.

We report here the preparation of the first high-spin five-co-ordinated chromous compound. Under oxygen-free nitrogen, anhydrous chromous bromide reacts in hot butanol with a 10% excess of Me_6tren, precipitating the pale sky-blue product $[Cr(Me_6tren)Br]Br$. The crystals, tetrahedral in shape, do not appreciably oxidize when exposed for a few hours in dry air. Under pure nitrogen, they are stable at least for a few weeks. The effective magnetic moment of this compound at room temperature is 4·85 B.M., a value typical of chromous compounds with four unpaired electrons.[3] *X*-Ray powder photographs show the complex $[Cr(Me_6tren)Br]Br$ to be strictly isomorphous with the cobalt analogue. Therefore, the chromium(II) complex must be attributed the same trigonal bipyramidal structure. In accordance with this five-co-ordinated structure, the compound behaves as a uni–univalent electrolyte in butanol.

The electronic absorption spectrum of $[Cr(Me_6tren)Br]Br$ in butanol or dichloromethane solutions closely resembles the solid reflectance spectrum (Figure). The asymmetrical band in the 10,000—15,000 cm.$^{-1}$ region clearly contains under its envelope at least two fairly intense transitions. These are tentatively assigned to the spin-allowed transitions between the ^5A-ground state and the two excited ^5E-states arising from the splitting of the $^5D(3d^4)$-term of gaseous chromium(II) under the influence of a crystal field of C_3 symmetry. The weaker bands found at higher energies can be most probably attributed to spin-forbidden transitions from the quintet ground state to triplet states of chromium(II). Nevertheless, it cannot be excluded that these weak bands are due to traces of chromic species, in spite of the care employed to prevent oxidation.



FIGURE

Spectra of the compound $[Cr(Me_6tren)Br]Br$: ——— *in* CH_2Cl_2 *solution*; – – – – – *by diffuse reflectance (arbitrary absorbance scale)*

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[3] B. N. Figgis, *Nature*, 1958, **182**, 1568; *Trans. Faraday Soc.*, 1960, **56**, 1553; A. Earnshaw, L. F. Larkworthy, and K. S. Patel, *Z. anorg. Chem.*, 1964, **334**, 163.