Nickel(III) Complexes with Cyclic Tetramines and Nitrato- or Sulphato-ligands

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THE number of well established complexes of nickel(III) is relatively small. Nickel(III) complexes of oximes,[1] phosphines,[2] a diphosphine,[3] a di- and a tri-arsine,[4] fluoride,[5] nitrate,[6] and various di-acido-bis(diaminoethane) derivatives[7] (*e.g.*, [Ni en_2Cl_2]Cl) have been reported.

Complexes of nickel(III) with two isomeric cyclic tetramines, *meso*-5,7,7,12,14,14-hexamethyl-1,4,8-11-tetra-aza-cyclotetradecane (tet *a* of reference 8) and a 5,7,7,12,12,14-hexamethyl isomer, probably *racemic*, (tet *c* of reference 8), are prepared by nitric acid oxidation, under mild conditions, of the nickel(II) complexes, the dinitrato-(tetramine)-nickel(III) complexes being obtained as olive green perchlorate salts, with water of crystallization, or as nitrate salts with "nitric acid of crystallization" (*i.e.*, presumably containing the hydrogen dinitrate ion).[9] (Under more vigorous conditions the macrocycles are oxidized.[10]) *trans*-Dinitrato-structures are suggested, since only *trans*-octahedral complexes have been prepared with these amines and other metal ions, *e.g.*, [nickel(II)[11] or cobalt(III)[12]]. The infrared spectral bands assignable to the co-ordinated nitrate ions are normal for monodentate co-ordination to a tervalent ion. The magnetic moments indicate the presence of one unpaired electron, as is usual for nickel(III) compounds,[13] and the susceptibilities obey a normal Curie–Weiss relationship.

If the oxidation of $[\mathrm{Ni(tet}\ a)]^{2+}$ is carried out in the presence of sulphate ions, an olive-green compound of composition

$$[\mathrm{Ni(tet}a)\mathrm{SO_4}]\mathrm{ClO_4},\tfrac{1}{3}\mathrm{H_2SO_4}$$

is obtained. The magnetic susceptibility of this compound is anomalous, the magnetic moment being 1·54 B.M. at room temperature, and decreasing to 0·92 B.M. at 81° K, which suggests the presence of some antiferromagnetic interaction. A polymeric structure with bridging sulphate ions is suggested, super-exchange through the sulphate bridge accounting for the antiferromagnetism.

The compounds are indefinitely stable in the solid state, but are rapidly decomposed in solution. The sulphato-compound is extremely slowly soluble in water.

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