

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

By N. F. CURTIS\* and D. F. COOK

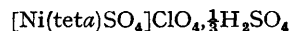
(Chemistry Department, Victoria University of Wellington, Wellington, New Zealand)

THE number of well established complexes of nickel(III) is relatively small. Nickel(III) complexes of oximes,<sup>1</sup> phosphines,<sup>2</sup> a diphosphine,<sup>3</sup> a di- and a tri-arsine,<sup>4</sup> fluoride,<sup>5</sup> nitrate,<sup>6</sup> and various di-acido-bis(diaminoethane) derivatives<sup>7</sup> (e.g.,  $[\text{Ni en}_2\text{Cl}_2]\text{Cl}$ ) 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).<sup>9</sup> (Under more vigorous conditions the macrocycles are oxidized.<sup>10</sup>) *trans*-Dinitrato-

structures are suggested, since only *trans*-octahedral complexes have been prepared with these amines and other metal ions, e.g., [nickel(II)]<sup>11</sup> or cobalt(II)<sup>12</sup>. 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,<sup>13</sup> and the susceptibilities obey a normal Curie-Weiss relationship.

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



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.

(Received, June 19th, 1967; Com. 620.)

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