

A High-Spin Nickel(III) Complex

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THE number of known nickel(III) compounds is small;¹ most of them are complexes in which the nickel(III) state is stabilised by organic ligands or fluorine. In all cases the nickel(III) ion is in the low-spin (one unpaired electron) configuration. For the organic complexes μ_{eff} is near 2.0 B.M., and μ_{eff} for K_3NiF_6 is 2.15 B.M.²

We have now isolated a tetranitratonickel(III) complex which we believe to be the first example of the nickel(III) oxidation state in high-spin configuration. The product of reaction of anhydrous nickel(II) chloride, or nickel(II) nitrate dihydrate with excess of dinitrogen pentoxide is a flocculent, pale green powder of composition $\text{Ni}(\text{NO}_3)_3 \cdot \text{N}_2\text{O}_5$. The NO_2^+ ion is well characterised in the infrared spectrum, and comparison of the spectrum with

those^{3,4} for $[\text{Fe}(\text{NO}_3)_4]^-$, $[\text{Al}(\text{NO}_3)_4]^-$, $\text{Pd}(\text{NO}_3)_4$, and $\text{Sn}(\text{NO}_3)_4$ leave no doubt that the solid complex contains the anion $[\text{Ni}^{\text{III}}(\text{NO}_3)_4]^-$. In freshly prepared aqueous solutions the $\text{Ni}:\text{NO}_3$ ratio is 1:5, and the iodine liberated from potassium iodide corresponds to conversion of all the nickel content from Ni^{3+} to Ni^{2+} . Under vacuum, N_2O_5 is evolved, and below room temperature the composition approaches that of the simple nitrate $\text{Ni}(\text{NO}_3)_3$.

The magnetic susceptibility of the complex $(\text{NO}_2^+)[\text{Ni}^{\text{III}}(\text{NO}_3)_4]^-$ is 4.54 ± 0.02 B.M. at 21° . This is to be compared with the spin-only value of 3.83 B.M. for 3 unpaired electrons, but is of the same order as μ_{eff} for four-co-ordinate high-spin cobalt(II) complexes (4.2—4.8 B.M.¹).

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¹ B. N. Figgis and J. Lewis, *Progr. Inorg. Chem.*, 1964, **6**, 37.

² W. Klemm, W. Brandt, and R. Hoppe, *Z. anorg. Chem.*, 1961, **308**, 179.

³ C. C. Addison, P. M. Boorman, and N. Logan, *J. Chem. Soc.*, 1965, 4978.

⁴ C. C. Addison and W. B. Simpson, *J. Chem. Soc.*, 1965, 598.