Dinitro- and Dinitrito-bis-(*NN'*-diethylethylenediamine)nickel(II): a Pair of Linkage Isomers

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Summary Pink, crystalline dinitrobis-(*NN'*-diethylethylenediamine)nickel(II) has been prepared and can be kept for several days before it reverts into the blue dinitrito-isomer, the form stable at room temperatures.

PAIRS of linkage isomers are rare and the reported nitro–nitrito examples have been confined to complexes of cobalt(III), rhodium(III), iridium(III), and platinum(IV),[1] where the metastable nitrito-form is the first product of a reaction and isomerises gradually and apparently irreversibly to the nitro-form. Goodgame and Hitchman[2,3] prepared stable six-co-ordinate complexes, $NiL_2(NO_2)_2$, of several bidentate aliphatic amines, L, and found some to be pink nitro-compounds and others blue nitrito-compounds, depending on the nature of L. In some instances (*e.g.* L = *NN'*-diethylethylenediamine) they showed that both forms could coexist in equilibrium in solution, but no pairs of solid linkage isomers were characterised.

By cooling chloroform solutions of the known[2] blue dinitritobis–(*NN'*-diethylethylenediamine)nickel(II) (I) in a dry-ice–acetone mixture, we have observed the deposition of pink crystals. Evaporation of the cold solution to dryness *in vacuo* gave a quantitative yield of a homogeneous, paramagnetic, pink crystalline solid (II) of the same composition, (elemental analysis correct for $C_{12}H_{32}N_6O_4Ni$). That it is the nitro-isomer of (I) is confirmed by the i.r. spectrum. Whereas (I) has a very strong band near 1215 cm.$^{-1}$, assigned by Goodgame and Hitchman[2] to the –ONO asymmetric stretch, in (II) this band is replaced by a strong band at 1310 cm.$^{-1}$ characteristic[3] of co-ordinated $-NO_2$. The spectra of the two compounds also differ in the N–H stretching region: (I) has strong broad bands at 3190 and 3280 cm.$^{-1}$; and (II) has strong sharp bands at 3230, 3275, and 3290 cm.$^{-1}$.

Kept in a specimen tube, (II) remained unchanged for four days and then reverted within two days into (I) without change in weight. This reversion of solid (II) into (I), which could be followed by the i.r. spectrum, was complete in 3 days in a Nujol mull, in 8 hr. in the presence of chloroform vapour, and in less than 5 min. at 100°. There is at present no evidence to show whether (II) is metastable at all temperatures or whether there is a transition temperature at which (I) and (II) can coexist.

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[1] F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," Wiley, New York, 2nd edn., 1967, p. 293.
[2] D. M. L. Goodgame and M. A. Hitchman, *Inorg. Chem.*, 1964, **3**, 1389.
[3] D. M. L. Goodgame and M. A. Hitchman, *Inorg. Chem.*, 1966, **5**, 1303.