Some Metal-ion Complexes with Ligands formed by Reaction of Amines with Aliphatic Carbonyl Compounds. Part VI.[1] Formation of *cis*-Di-isothiocyanato[4,6,6-trimethyl-1,9-bis(2-pyridyl)-3,7-diazanon-3-ene]nickel(II)

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Bis[2-(2-aminoethyl)pyridine]di-isothiocyanatonickel(II), (I), reacts slowly with acetone at room temperature to form *cis*-di-isothiocyanato[4,6,6-trimethyl-1,9-bis(2-pyridyl)-3,7-diazanon-3-ene]nickel(II), (II), a complex with a quadridentate ligand formed by linking the primary amino-groups of the starting material to give an amine–imine bridge.

WHEN bis[2-(2-aminoethyl)pyridine]di-isothiocyanato-nickel(II),[2] (I), reacts with acetone at room temperature, the sparingly soluble grey-violet complex dissolves and large blue flakey crystals of a product, (II), crystallize out over a period of weeks. Analysis of (II) indicated a composition incorporating (I) together with two acetone residues condensed with elimination of two molecules of water. The product (II) is sparingly soluble in most solvents, but appreciably soluble in methyl cyanide. It is slowly hydrolysed in water, rapidly in dilute acid, yielding 4-methylpent-3-en-2-one as the only carbonyl product. The i.r. spectrum of (I) showed strong, poorly resolved, and ν(NH) absorption [3 240(sh), 3 200s,br, and 3 115br cm^{-1}]; δ(NH_2) absorption near 1 600 cm^{-1} overlay bands characteristic of the 2-pyridyl group (1 603 and 1 577 cm^{-1} for 2-ethylpyridine).[3a] For (II) the ν(NH) absorption was reduced to a weak sharp band at 3 160 cm^{-1} and the pyridine bands at 1 603 and 1 567 cm^{-1} became much sharper, suggesting that the δ(NH_2) band of (I) is absent. These changes indicate the presence of only secondary amino-groups for (II). In addition, the spectrum of (II) showed a strong band at 1 668 cm^{-1}, typical of co-ordinated

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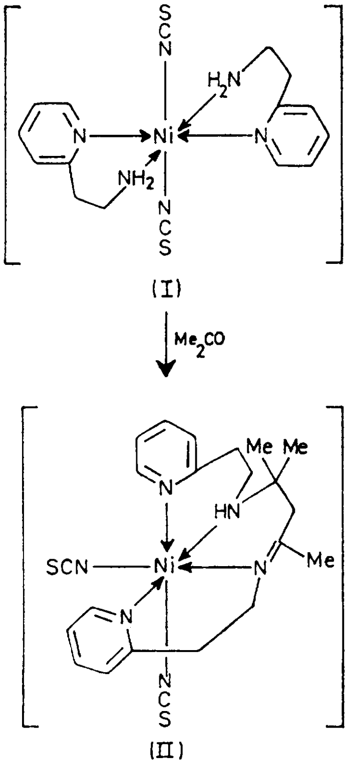
[1] J. W. L. Martin and N. F. Curtis, *J.C.S. Dalton*, preceding paper.

[2] E. Uhlig and M. Maasei, *Z. anorg. Chem.*, 1963, **322**, 25.

[3] (*a*) G. L. Cook and F. M. Church, *J. Phys. Chem.*, 1957, **61**, 458; (*b*) N. F. Curtis, *Co-ordination Chem. Rev.*, 1968, **3**, 3; V. C. Patel and N. F. Curtis, *J. Chem. Soc.* (*A*), 1968, 1265; 1969, 1607 and previous papers in this series.

imino-groups. The changes in the i.r. spectrum when (I) reacts with acetone to form (II) are as expected if (II) contains the quadridentate ligand 4,6,6-trimethyl-1,9-bis(2-pyridyl)-3,7-diazanon-3-ene, formed by linking the amino-groups of the two 2-(2-aminoethyl)pyridine residues to give an amine–imine bridge derived from two acetone residues. Complexes with ligands in which the amino-residues have been converted into this bridging group are formed by reaction of a variety of metal ion–amine complexes with acetone.[3] The complexes typically release 4-methylpent-3-en-2-one when hydrolysed, as does (II).[3b]



The i.r. spectrum of (I) also showed a very strong singlet ν(C≡N) band at 2 103 cm^{-1}, with ν(CS) probably at 777 cm^{-1}, features indicative of a *trans*-di-isothiocyanato-structure. Bis[2-(2-aminoethyl)pyridine]-copper(II) iodide has a relatively strain-free structure with the amines in approximately square-planar co-ordination,[4] so the *trans*-structure for (I) is as expected. In contrast, the i.r. spectrum of (II) showed doublet ν(C≡N) absorption (2 092vs,sp and 2 073vs,sp cm^{-1}, the latter band somewhat more intense) with ν(CS) probably at 788 cm^{-1}. This suggests a structure for (II) with *cis*-isothiocyanato-groups {*cf.* *cis*-[Ni(tren)(NCS)$_2$] [tren = tris(2-aminoethyl)amine] 2 076 and 2 089 cm^{-1}}.[5] This structure must be adopted to minimize strain within the quadridentate ligand, since di-anionotetra-amine complexes usually adopt a *trans*-structure to minimize interanion repulsion. The N–Cu–N angle subtended by the 2-(2-aminoethyl)pyridine chelate in two complexes studied previously was greater than 90°,[4,6] as was the angle subtended by the amine–imine bridging group in a number of complexes.[7] Accumulated strain when three such chelate rings are linked is less for 'folded' co-ordination. The *abcd*-configuration represented in formula (II) is probably preferred since it permits the imino-group to remain planar.

Attempts to isolate crystalline products from the reaction of the copper(II) analogue of (I), or the bis-[2-(2-aminoethyl)pyridine]-nickel(II) or -copper(II) diperchlorates were unsuccessful, as were attempts to replace the acetone by ethyl methyl ketone. Attempts to reduce the imino-group of (II) with sodium tetrahydroborate were also unsuccessful.

EXPERIMENTAL

cis-*Di-isothiocyanato*[4,6,6-*trimethyl*-1,9-*bis*(2-*pyridyl*)-3,7-*diazanon*-3-*ene*]*nickel*(II), (II).—Bis[2-(2-aminoethyl)pyridine]di-isothiocyanatonickel(II) [2] was treated with acetone at room temperature. When the starting material had all dissolved (weeks to months, depending on the quantities employed) the blue *product* was filtered off and recrystallized from hot methyl cyanide–propan-2-ol (Found: C, 52·9; H, 5·8; N, 16·9; Ni, 12·2. Calc. for $C_{22}H_{28}N_6NiS_2$: C, 52·9; H, 5·7; N, 16·8; Ni, 11·8%). The magnetic susceptibility of (II) was normal for triplet ground state, pseudo-octahedral, nickel(II) (gram susceptibility χ_g = 8·13 × 10^{-3} c.g.s.u. at 300 K, effective magnetic moment $\mu_{eff.}$ = 3·26 B.M.* calculated from the Curie law with correction for diamagnetism.) The reflectance spectrum showed bands at 10 000 and 16 900 cm^{-1}, assigned to the transitions $^3T_{2g} \leftarrow {}^3A_{1g}$ and $^3T_{1g} \leftarrow {}^3A_{2g}$ in O_h. The spectrum of (I) showed bands at 10 200 and 17 400 cm^{-1}, similarly assigned. With three pairs of dissimilar nitrogen-donor atoms present (pyridine, amine, and isothiocyanate), the absence of observable splitting of the $^3T_{2g} \leftarrow {}^3A_{1g}$ band in the reflectance spectrum is not considered to preclude the *trans*-configuration for (I).

[4/810 *Received*, 22*nd April*, 1974]

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* 1 B.M. = 0·927 × 10^{-23} A m^2.

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