Intramolecular Ring Stacking in a Distorted Tetrahedral Nickel Complex with 3,4-Dihydro-1-phenyl-1H-[1,4]-oxazino[4,3-a]benzimidazole, NiL_2Cl_2

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Received June 23, 1983

We have investigated the complexes formed between nickel(II) and 3,4-dihydro-1-phenyl-1H-[1,4]-oxazino[4,3-a]benzimidazole (L) in order to extend the range of first coordination spheres in complexes of this metal with a view to providing model compounds for comparison in EXAFS studies of nickel-containing biological molecules [1]. For example, nickel is known to occur in the enzymes urease [2] and hydrogenase [3].

With NiX_2 (X = Cl, Br, I, or SCN) and L, a series of complexes of stoichiometry NiL_2X_2 were formed. Physical measurements indicated that NiL_2X_2 (X = Cl, Br, or I) are tetrahedral, but that $NiL_2(SCN)_2$ is square planar. Although NiL_2Cl_2 was thought to be tetrahedral there was some doubt as to the regularity of its coordination. Its room temperature magnetic moment of 3.68 is closer to the values (3.8–4.0) found for nickel(II) in environments having regular or near regular tetrahedral symmetry than those (3.2–3.3) observed for paramagnetic complexes of nickel bromide with tertiary phosphines [4], where marked distortion occurs at the metal atom. In contrast to this, the diffuse reflectance spectrum of NiL_2Cl_2 shows a marked splitting of the ν_3 band (Table I) which is indicative of distortion from regular tetrahedral symmetry [4]. In view of this, and of the paucity of structural information on tetrahedral nickel(II) complexes with two monodentate nitrogen donors and two chloride atoms, we have carried out a single-crystal X-ray study on the title complex.

TABLE I.

ν_{max} (cm^{-1})	Assignment in T_d symmetry
18,180	$^3T_1(F) \rightarrow {}^3T_2 = \nu_1$
16,650 sh	
15,850 sh	
10,310	$^3T_1(F) \rightarrow {}^3A_2 = \nu_2$
7,580	$^3T_1(F) \rightarrow {}^3T_1(P) = \nu_3$
6,100	

Crystals suitable for X-ray study were obtained by the following procedure. The ligand (0.01 mol) was dissolved in 100 cm^3 of cold acetone. To this, $NiCl_2 \cdot 6H_2O$ (0.005 mol) in 15 cm^3 of ethanol was added dropwise. The resulting deep blue solution was filtered and the filtrate left standing for about one week in a stoppered flask. The blue crystals that formed were filtered off, washed with a small quantity of acetone and air dried. Microanalytical results were: *Found* C, 61.2; H, 5.0; N, 9.2. *Calc.* for $Ni(C_{16}H_{14}ON_2)_2Cl_2$: C, 61.0; H, 4.5; N, 8.9%.

The blue crystals are monoclinic, with unit-cell dimensions a = 10.828(2), b = 15.169(2), C = 18.398(3) Å, β = 102.57(1)° (at 19 °C), space group Cc, and Z = 4. X-ray diffraction data were collected on a Nicolet R3m/Eclipse S140 diffractometer system using an ω scan technique with graphite-monochromated Cu-Kα radiation. A total of 1835 independent reflections were measured (to θ = 55°), of which 45 were judged to be 'unobserved'. The structure was solved by Patterson and Fourier methods, and least-squares refinement has now reached R = 0.035. The program system SHELXTL [5] was used throughout the calculations.

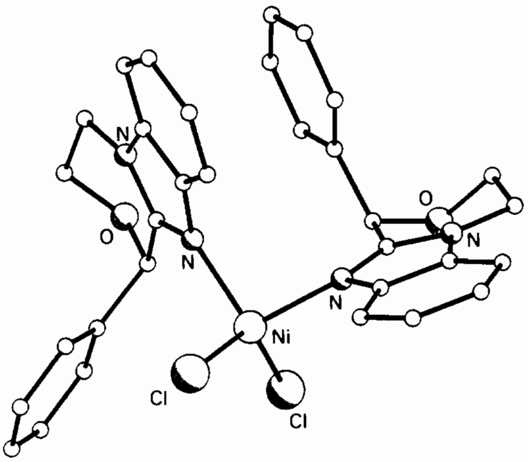

Fig. 1. Molecular structure of the title complex.

Figure 1 shows the molecular structure in which the nickel atom has a distorted tetrahedral coordination. The two Ni–Cl bonds are 2.213(2) and 2.240(2) Å, and these lengths may be compared to mean Ni–Cl distances of 2.245 Å in $(Et_4N)_2NiCl_4$ [6] and 2.269 Å in $(Ph_3AsMe)_2NiCl_4$ [7], where the coordination is almost regular tetrahedral. The Ni–N bond lengths are 1.992(4) and 2.002(5) Å, and are unexceptional.

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0020-1693/83/$3.00

The extent of the distortion of the tetrahedral coordination can be gauged from the Cl–Ni–Cl angle of 124.6(1)° and the N–Ni–N angle of 98.5(2)°. Thus despite the bulkiness of the benzimidazole ligands the N–Ni–N is the smallest in the coordination sphere. The angle between the planes Cl–Ni–Cl and N–Ni–N is 98.5°.

While the conformation at the six-membered oxazine ring in both ligands is essentially the same, with the phenyl ring being axial, there are some minor differences in the puckering of the two rings. As expected the benzimidazole part of each ligand is planar. The chirality at the asymmetric carbon atom in the two L ligands is the same within each molecule, although the space group requires that there are equal numbers of molecules of opposite chirality.

An interesting feature of the molecular geometry is the intramolecular ring stacking between a phenyl ring of one ligand and the imidazole ring of the benzimidazole moiety in the other ligand, with a ring separation of *ca.* 3.4 Å. The interaction between these rings may have some influence on the N–Ni–N angle.

Acknowledgement

We thank the SERC for the diffractometer system.

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