

A Dimeric Nickel(II) Complex of 7-Azaindole

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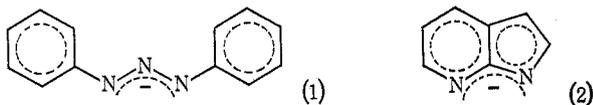
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Abstract

The synthesis and properties of the red dimeric nickel(II) complex $[\text{Ni}_2(\text{C}_7\text{H}_5\text{N}_2)_4]$, where $\text{C}_7\text{H}_5\text{N}_2^-$ is the anion of 7-azaindole (1*H*-pyrrolo[2,3-*b*]pyridine), are reported. The diamagnetism and electronic spectrum are consistent with a square-planar environment about each nickel atom. A dimeric molecular structure with four anionic 7-azaindole ligands bridging a pair of bonded nickel atoms is proposed.

Despite an increase in the number of nickel(II) cluster complexes reported recently, the number of known dimeric clusters of nickel(II) is still remarkably small when compared with those of divalent copper.

One of the first examples of binuclear nickel(II) coordination compounds was the red, diamagnetic complex $\text{Ni}_2(\text{dpt})_4$,¹⁻⁴ where dpt is the anion derived from 1,3-diphenyltriazene (1). In the $\text{Ni}_2(\text{dpt})_4$ molecule, two nickel atoms are bridged by the terminal nitrogen atoms of four ligand groups, each in a *syn-syn* configuration,⁵ so that the environment about each metal atom of the dimer is almost square-planar. The metal-to-metal separation (0.2395 nm) is extremely short (by comparison Ni-Ni is 0.250 nm in metallic nickel).



The anion of 7-azaindole (2) (1*H*-pyrrolo[2,3-*b*]pyridine; denoted by L) is an entity with a similar bridging potential to dpt and it might be expected to act as a versatile binucleating ligand for a number of the transition metals. The azaindoles (alternatively pyrrolopyridines or diazaindenes) are also of pharmacological as well as of chemical interest and their properties have been surveyed comprehensively in recent reviews.^{6,7} Fusion of the electron-withdrawing (or π -deficient) pyridine ring

¹ Dwyer, F. P., and Mellor, D. P., *J. Amer. Chem. Soc.*, 1941, **63**, 81.

² Harris, C. M., Hoskins, B. F., and Martin, R. L., *J. Chem. Soc.*, 1959, 3728.

³ Corbett, Madeline, and Hoskins, B. F., *Chem. Commun.*, 1968, 1602.

⁴ Corbett, Madeline, Hoskins, B. F., McLeod, N. J., and O'Day, B. P., Rep. 9th Int. Congr. Crystallogr., Kyoto (Japan), 1972, S76.

⁵ Martin, R. L., and Waterman, H., *J. Chem. Soc.*, 1959, 1359.

⁶ Willette, R., *Advan. Heterocycl. Chem.*, 1968, **9**, 27.

⁷ Adler, T. K., and Albert, A., *J. Med. Chem.*, 1963, **6**, 480.

with the electron-releasing (or π -excessive) pyrrole ring results in a molecule with the characteristics of both. Biologically the presence of 7-azaindole in animals results in paralysis and respiratory depression.

The indolic N-H bond is extremely weakly acidic and no reports of metal complexes have appeared. We describe here the synthesis and characterization of the dimeric nickel complex Ni_2L_4 . Because of the difficulty associated with removal of the N-H proton in 7-azaindole, it is necessary to employ strongly basic conditions to prepare the complex. Solutions of nickel acetate tetrahydrate (1.24 g in 100 ml methanol) and 7-azaindole (1.18 g in 10 ml methanol) were mixed and the resulting solution was evaporated to dryness. The green solid so obtained was dissolved in toluene, and the solution was heated at 100°C for 2 h. Gradually, small red crystals separated. These were filtered, washed with toluene and dried under vacuum (Found: C, 57.2; H, 3.6; N, 18.9; Ni, 20.0. Calc. for $\text{C}_{14}\text{H}_{10}\text{N}_4\text{Ni}$: C, 57.4; H, 3.4; N, 19.1; Ni, 20.0%).

$\text{Ni}(\text{C}_7\text{H}_5\text{N}_2)_2$ is diamagnetic; this suggests that each nickel atom has a low-spin d^8 configuration arising from a square-planar environment. The compound has a very limited solubility in solvents such as acetone and chloroform. However, a molecular weight determination in acetone by vapour pressure osmometry is consistent with a dimeric formulation for the complex in solution (found 543, calc. 584). The electronic spectrum in acetone shows two major bands at 20100 (ϵ c. 80) and 28700 cm^{-1} (ϵ c. 1500). These absorptions are also evident in the diffuse reflectance spectrum, where two other bands are also observed, viz., 13800 cm^{-1} (shoulder) and 34500 cm^{-1} (characteristic of the ligand). The two bands at 20100 and 28700 cm^{-1} are characteristic of low-spin nickel(II) square-planar complexes.⁸

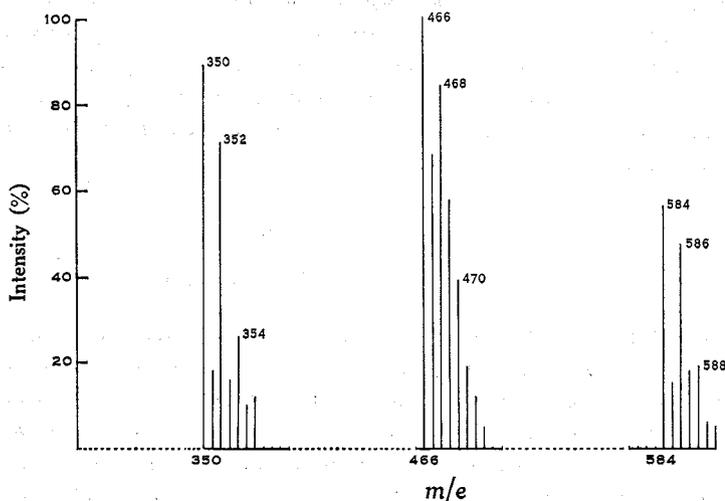


Fig. 1. Mass spectrum of NiL_2 (above m/e 300).

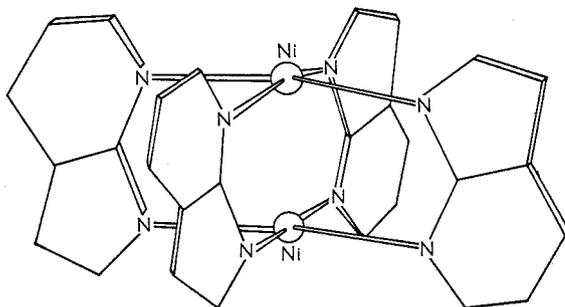
The mass spectrum supports the dimeric formulation for this complex. Certain features of the mass spectrum are depicted in Fig. 1. The dimeric molecular ion peak corresponding to $[\text{Ni}_2\text{L}_4]^+$ occurs at m/e 584; the isotope pattern is that expected for the dimeric species Ni_2 . The ion appears to fragment first by the loss of $[\text{LH}]$ to give a peak at m/e 466, followed by the loss of $[\text{L}-\text{H}]$ to give $[\text{Ni}_2\text{L}_2]^+$ at m/e 350.

⁸ Lever, A. B. P., 'Inorganic Electronic Spectroscopy' p. 343 (Elsevier: Amsterdam 1968).

The major peak assignments are as follows: m/e 584 (61%), $[\text{Ni}_2\text{L}_4]^+$; 466 (100), $[\text{Ni}_2\text{L}_2(\text{L}-\text{H})]^+$; 350 (89), $[\text{Ni}_2\text{L}_2]^+$; 292 (14), $[\text{NiL}_2]^+$; 265 (12), $[\text{NiL}(\text{L}-\text{HCN})]^+$; 175 (41), $[\text{NiL}]^+$; 148 (14), $[\text{Ni}(\text{L}-\text{HCN})]^+$; 118 (82), $[\text{LH}^+]$; 91 (82), $[\text{LH}-\text{HCN}]^+$. m^* 372 (584 \rightarrow 466), 70 (118 \rightarrow 91).

The close similarity between the *syn-syn* conformation of the OCO and NNN groupings in the anions of acetic acid and 1,3-diphenyltriazene and the NCN of 7-azaindole makes it probable that, in the 7-azaindole complex, each pair of nickel atoms is bridged by four binucleating ligands to give the dimeric structure illustrated in Fig. 2.

Fig. 2. Postulated structure for NiL_2 .



The corresponding $\text{Cu}_2(\text{OAc})_4$ and $\text{Cu}_2(\text{dpt})_4$ compounds⁹ are known, and this led to the expectation that a similar dimer of the 7-azaindole anion might also be obtained. We have prepared the copper(II) complex $\text{CuL}_2(\text{Me}_2\text{SO})_2$ which exhibits very similar magnetic and e.s.r. properties to $\text{Cu}_2(\text{OAc})_4$, indicating that the complex should probably be formulated as a dimer. This and other metal complexes in which the anion of 7-azaindole functions as a binucleating bridge between pairs of metal atoms have been characterized and will be reported elsewhere.

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⁹ Harris, C. M., and Martin, R. L., *Proc. Chem. Soc.*, 1958, 259.