Copper and Nickel Chelates of Pyridine-2-carboxamide*

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The metal chelates of pyridine-2-carboxamide, picolinic acid amide, have scarcely been studied at all; only a copper chelate containing two moles of the ligand was known.[1] Recently another chelate of copper with 1 mol. of the same ligand was reported.[2] The present communication deals with the syntheses of copper and nickel chelates of this ligand and with studies of their properties. In the following the ligand, pyridine-2-carboxamide, $C_5H_4NCONH_2$, will be abbreviated as "piaH."

The chelates prepared were: (1), $Cu(pia)_2 \cdot 5H_2O$; (2), $Cu(piaH)_2Cl_2 \cdot 2H_2O$; (3), $Ni(pia)_2 \cdot 2H_2O$ and (4), $Ni(piaH)_2Cl_2 \cdot 2H_2O$.

1) $Cu(pia)_2 \cdot 5H_2O$. This chelate was prepared after the method of Emmert and Brandl[1] by adding 1 g. of the ligand to a solution containing 2 g. of tetramminecopper(II) sulfate. Reddish-violet crystals were produced; they were soluble in cold water and chloroform only with difficulty. Emmert and Brandl reported the anhydrous compound, but the chelate prepared by the present authors had the formula, $C_{12}H_{10}O_2N_4Cu \cdot 5H_2O$.

Found: Cu, 16.06; N, 13.76; H_2O 23.13%, Calcd. for $C_{12}H_{10}O_2N_4Cu \cdot 5H_2O$: Cu, 16.05; N, 14.15; H_2O, 22.76%.

2) $Cu(piaH)_2Cl_2 \cdot 2H_2O$. If 0.7 g. of copper(II) chloride was used instead of tetramminecopper(II) sulfate in the above preparation and if the mixed solution was concentrated on a water-bath, fine blue crystals of this chelate were crystallized.

Found: Cu, 15.34; N, 13.81; H_2O, 8.97%. Calcd. for $C_{12}H_{12}O_2N_4CuCl_2 \cdot 2H_2O$: Cu, 15.32; N, 13.51; H_2O, 8.69%.

3) $Ni(pia)_2 \cdot 2H_2O$. To an aqueous solution containing 2 g. of the ligand, 0.75 g. of sodium hydroxide dissolved in a small amount of water and then 2 g. of nickel chloride dissolved in 20 ml. of water were added. Fine orange-red crystals were precipitated; they were soluble in chloroform and ethanol only with difficulty and were insoluble in water.

Found: Ni, 17.44; N, 16.88; H_2O, 10.43%. Calcd. for $C_{12}H_{10}O_2N_4Ni \cdot 2H_2O$: Ni, 17.32; N, 16.63; H_2O, 10.63%.

4) $Ni(piaH)_2Cl_2 \cdot 2H_2O$. Prepared in a way similar to that used for 2). Blue crystals.

Found: Ni, 14.20; N, 14.01; H_2O 9.10%. Calcd. for $C_{12}H_{12}O_2N_4NiCl_2 \cdot 2H_2O$: Ni, 14.32; N, 13.67; H_2O, 8.79%.

In the solution of pH 8.2 of $Ni(piaH)_2^{2+}$ the bands are at 602 and 995 mμ, and while in a more alkaline solution they shift to a shorter wavelength, with the precipitation of insoluble $Ni(pia)_2$. In an acid solution of pH 0.9, the bands are at 645 and >1050 mμ, rather close to those of the nickel aquo ion.[3] These facts suggest that, in a strongly acid solution, the nickel chelate (4) dissociates into the nickel aquo ion and the ligand, while in an alkaline solution the chelate (3) is formed. The copper chelates show a similar change in absorption spectra.

The infrared absorption bands of these chelates are listed in Table I, together with the tentative assignments.

TABLE I

Chelate	C=O Str. vibr.	C-N Str. vibr.	M-N Str. vibr.	Magnetic moment
piaH	1659	1390	—(cm⁻¹)	—
$Cu(pia)_2 \cdot 5H_2O$	1624	1395	567	1.87 (B.M.)
$Cu(piaH)_2Cl_2 \cdot 2H_2O$	1667	1440	510	1.90
$Ni(pia)_2 \cdot 2H_2O$	1640	1400	592	diamagnetic
$Ni(piaH)_2Cl_2 \cdot 2H_2O$	1660	1433	518	3.25

The ligand molecule in these chelates seems to be coordinated to the metal by nitrogen atoms, acting as a bidentate ligand.[4] Of these four chelates chelate (3) is diamagnetic, while the other three are paramagnetic; the magnetic moments are as shown in Table I. It is well known that nickel often forms, with the same ligand, paramagnetic and diamagnetic chelates of different colors. The present chelates add another example of this class of compounds.

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[1] B. Emmert and F. Brandl, *Ber.*, **60**, 2211 (1927).

[2] K. Nagano, H. Kinoshita and A. Hirakawa, *Chem. Pharm. Bull.*, **12**, 1198 (1964).

[3] H. Ito, *J. Chem. Soc. Japan, Pure Chem. Sect.* (*Nippon Kagaku Zasshi*), **77**, 1385 (1956).

[4] The crystal structures of these nickel chelates are now under investigation by Professer Y. Saito of the Universiy of Tokyo.