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A NEW BINUCLEATING LIGAND, 3-FORMYLSALICYLIC ACID, AND ITS COPPER(II) AND NICKEL(II) COMPLEXES[1)]

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A new binucleating ligand, 3-formylsalicylic acid, was prepared and its copper(II) and nickel(II) complexes were characterized. On the basis of the analytical, IR, electronic, and magnetic data, it was demonstrated that these complexes have a binuclear structure bridged by the phenolic oxygens. No monomeric complex could be obtained.

It has been known[2)] that 2,6-diformyl-4-methylphenol and its Schiff bases form binuclear metal complexes with copper(II) and nickel(II) ions. 3-Formylsalicylic acid itself and its Schiff bases with amines are expected to act as new binucleating ligands, since 3-formylsalicylic acid is similar in structure to 2,6-diformyl-4-methylphenol. In this paper the characterization of binuclear copper(II) and nickel(II) complexes of 3-formylsalicylic acid are reported.

3-Formylsalicylic acid (abbreviated to H_2fsac) was prepared after the method of Duff and Mill.[3)] In an aqueous solution of sodium carbonate(0.21 g), H_2fsac (0.33 g) was dissolved. To this solution was added an aqueous solution of copper(II) acetate monohydrate (0.4 g) or nickel(II) acetate tetrahydrate (0.5 g), and the mixture was heated on a water-bath for ten minutes. The complex obtained was throughly washed with hot water. The copper complex forms green needles. Found: C, 41.75; H, 2.06; Cu, 27.25%. Calcd for Cu(fsac) (fsac=$C_8H_4O_4$) : C, 42.21; H, 1.77; Cu, 27.91%. The nickel complex forms yellowish green needles. Found: C, 37.07; H, 3.43; Ni, 22.82%. Calcd for Ni(fsac)·$2H_2O$: C, 37.12; H, 3.12; Ni, 22.68%.

The IR spectra of the complexes show a coordinated formyl group near 1620 cm^{-1} and the band due to $-COO^-$ group near 1550 cm^{-1}, indicating that the formyl, carboxyl, and phenolic hydroxyl groups all form coordination bond with a metal ion. The powder spectrum of Cu(fsac) shows a band around 14.1 kK. The powder spectrum of Ni(fsac).$2H_2O$ possesses three bands at 11.0, 15.6 and 24.2 kK. This clearly indicates that the configuration around the nickel(II) ion is nearly octahedral. The magnetic moment of Cu(fsac) at room temperature is 0.82 B.M., that is lower than the spin-only value. The magnetic moment of Ni(fsac)·$2H_2O$ is 2.93 B.M., that is lower than those of most nickel(II) complexes. All of these data mentioned above suggest a binuclear structure for both complexes.

Magnetic susceptibilities were measured over a temperature range 78-300°K by the Faraday method. The magnetism of Cu(fsac) is well interpreted on the basis of the Bleaney-Bowers equation,[4)]

$$\chi_A = \frac{Ng^2\beta^2}{3kT}\left[\, 1 + \frac{1}{3}\exp(-2J/kT)\,\right]^{-1} + N\alpha \,,$$

where each symbol has the general meaning. This fact clearly indicates the binuclear

structure of the copper complex. The magnetic parameters, -2J, g, and Nα, are estimated to be 620 cm^{-1}, 2.20, and 80×10^{-6} c.g.s./mol respectively. On the other hand, Ni(fsac)·$2H_2O$ obeys the Curie-Weiss law, in which the temperature-independent paramagnetism, Nα, for the nickel(II) ion is evaluated at 193×10^{-6} c.g.s./mol.[5] However, the Weiss constant is large (50°K) and comparable to the values of the binuclear nickel(II) complexes derived from 2,6-diformyl-4-methylphenol. From the above basis, it may be concluded that the complexes have the structure shown in Fig. 2.

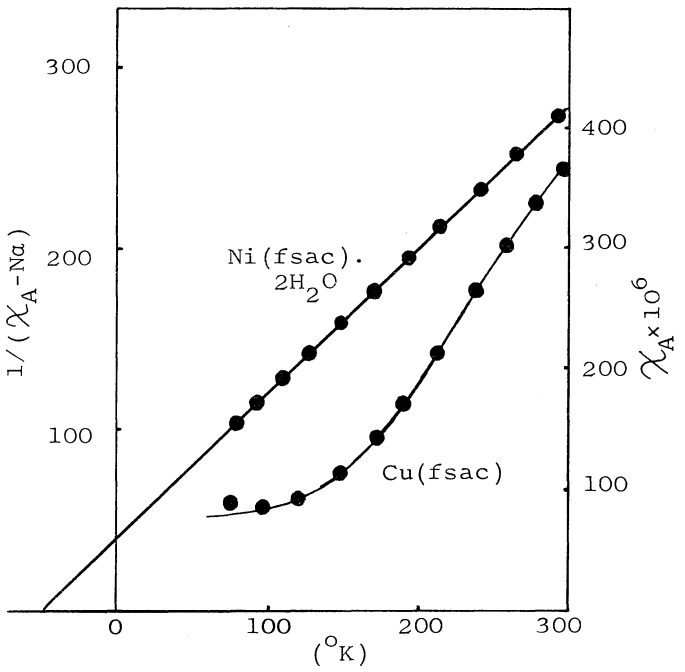

Fig. 1. Temperature variations of molar susceptibilities for Cu(fsac) and inverse susceptibilities for Ni(fsac)·$2H_2O$.

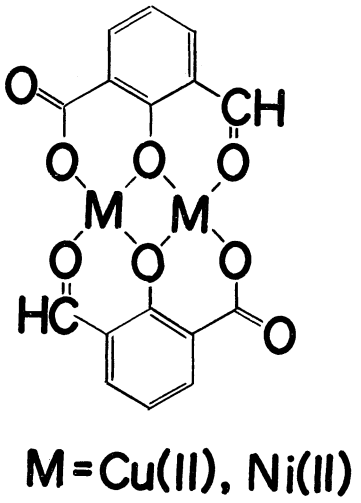

Fig. 2. Binuclear structure of complexes.
Four water molecules coordinate to apical positions in the case of M=Ni(II).

It is to be noted that H_2fsac forms binuclear complexes, $M_2(fsac)_2$ (M:H_2fsac= 1:1), but no mononuclear complexes, $M(Hfsac)_2$, on the other hand 2,6-diformyl-4-methylphenol (Hfsal) forms both binuclear and mononuclear complexes such as $Cu_2(fsal)$-Cl_3(M:Hfsal=2:1) and $Cu(fsal)_2$.

REFERENCES AND NOTES

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