A New Pair of Isomers of a Schiff Base Nickel(II) Complex

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It is well known that the bis(*N*-alkyl- or bis(*N*-aryl-salicylideneiminato)nickel(II) complex (abbreviated as Ni(X-SAL·R)$_2$, Fig. 1) in non-donor solvents exists as an equilibrium mixture consisting of the planar, tetrahedral and polymeric species. The equilibrium depends upon the nature of X and R, as well as upon concentration and temperature.[1,2] From the solutions, however, only one component is usually obtained as crystals. Two forms of crystals consisting of complexes with different configurations have so far been isolated for only a few sets of X and R.[3,4] For the complexes with R=*iso*-C_3H_7, where there is remarkable steric hindrance, either the planar or the tetrahedral form was isolated as crystals, depending upon the nature of X. No pair of isomers has ever been isolated for any substituent X. The present communication deals with successful isolation of two isomers of Ni(3-CH_3O-SAL·*iso*-C_3H_7)$_2$.

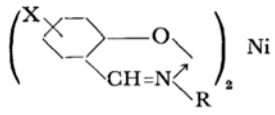

Fig. 1. Ni(X-SAL·R)$_2$

Isopropyl amine (0.04 mol) was added to a suspension of bis(3-methoxysalicylaldehydato)-nickel(II) dihydrate (0.02 mol) in methanol (100 m*l*), and the resulting solution was heated on a water-bath at about 40°C for one hour. A brown crystalline precipitate separated out from the brown solution. Recrystallization of the precipitate from methanol yielded brown crystals (Form I) of the desirable complex, Ni(3-CH_3O-SAL·*iso*-C_3H_7)$_2$. Spontaneous evaporation of a green solution of the precipitate in ethyl ether-methanol or ethyl ether - chloroform (20:1) yielded green crystals (Form II) of the same complex. Elemental analysis of both Form I and Form II agree with the formula Ni(3-CH_3O-SAL·*iso*-C_3H_7)$_2$. Both forms, when dissolved in the same solvents, show the same electronic spectra which are also dependent upon the concentration, solvents and temperature.

Since Form II is diamagnetic, it is considered to consist of uninuclear, planar complexes. The conclusion is supported by the electronic spectrum in the solid state, which is typical of the planar nickel(II) complex of this series. Form I is paramagnetic with a magnetic moment of 3.32 B. M. at room temperature, showing that this form does not consist of the planar species. The electronic spectrum of Form I in the solid state is typical of the tetrahedral nickel(II) complex, and is indeed quite similar to that of Ni(H-SAL·*iso*-C_3H_7)$_2$,[5] which was previously concluded to consist of the tetrahedral nickel(II) species.[6] So far as we know, this is the first isomeric pair of tetrahedral and planar nickel(II) complexes with the Schiff base to be isolated as crystals.

It is also interesting to note that on raising the temperature, Form II is transformed at 157—158°C into Form I, eventually showing the same behaviour as Form I, which melts at 187—188°C after sintering at 169—170°C.

The details of the work will be published elsewhere.

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