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Isolation of a New Tetrahedral Form of Bis(N-isopropyl-5,6-benzosalicylideneiminato)nickel(II)

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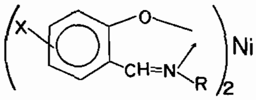
A new pair of isomers is described for a nickel(II) complex. The brown form of bis(N-isopropyl-5,6-benzosalicylideneiminato)nickel(II) was newly isolated by two different methods, in addition to the previously reported green planar form. From electronic absorption spectra and magnetic properties, the brown form was concluded to consist of tetrahedral nickel(II) complexes. The brown tetrahedral form, together with the green planar form previously reported, provides one of a small number of examples for the planar–tetrahedral isomerism in nickel(II) complexes. With the rise of temperature, the green planar form is transformed at 209° C into the brown tetrahedral form.

Introduction

It has been known for several years that nickel(II) complexes of the type $Ni(X–Sal–R)_2$ (I) in non-coordinating solvents exist as an equilibrium mixture, the equilibria being represented by (1).[1,2]



(I)

$$\text{associated} \rightleftarrows \text{planar} \rightleftarrows \text{tetrahedral} \qquad (1)$$

With most complexes of this series, however, one of the possible stereochemical forms was isolated in the solid state, two of them seldom being isolated separately in crystals for a set of R and X. Aside from some pairs of the monomeric planar and the associated forms,[3–5] only one pair of the planar and the tetrahedral form has so far been obtained,[6] although with some nickel(II) halide complexes of diphenylalkylphosphines the isolation of such isomers was reported.[7]

Extensive equilibrium studies have been carried out to show that the difference in stability between the planar and the tetrahedral form of $Ni(X–Sal–R)_2$ is considerably smaller for R = α-branched alkyl than for R = n-alkyl.[1,2] With complexes having α-branched alkyl groups for R, therefore, there seems to be a higher possibility that the pairs of the planar and the tetrahedral species may be obtained in the crystalline state. In a previous communication,[6] we have reported the successful isolation of the two isomers, planar and tetrahedral, of bis(N-isopropyl-3-methoxysalicylideneiminato)nickel(II). The present note deals with isolation of another new pair of such isomers with bis (N-isopropyl-5,6-benzosalicylideneiminato)nickel(II); only the planar form has so far been obtained.

Experimental

Materials

The green form of bis(N-isopropyl-5,6-benzosalicylideneiminato)nickel(II) was obtained by a method similar to that previously reported, except that recrystallization was carried out from chloroform–ethanol, instead of from dichloromethane–n-hexane[8] or from chloroform–cyclohexane.[9]

The brown form of the same compound was prepared by the following two methods. According to the first method, the crude product, which was prepared as previously reported,[8,9] was recrystallized from hot xylene–ethylene glycol to yield brown crystals.

In the second method, the green form of this compound was heated on an oil bath for about 2 hr to give the brown form. The temperature of the oil bath was maintained at about 200°; the temperature of the sample was possibly raised to a temperature somewhat higher than 200°. Heating for too long or at much higher temperature gave rise to partial decomposition or side reactions, yielding impure products. The purity of the product was ascertained by their X-ray powder diffraction patterns.

Some of the typical elemental analyses are as follows. Found: C, 69.61; H, 5.84; N, 5.80%. Calcd. for $Ni(C_{14}H_{14}NO)_2$: C, 69.68; H, 5.78; N, 5.81%.

Bis(N-isopropyl-5,6-benzosalicylideneiminato)zinc (II) was prepared as reported previously.[10]

Measurements

The electronic absorption spectra were measured on a Shimadzu MPS–50L spectrophotometer.

The magnetic measurements were carried out at room temperature by the Gouy method, using CoHg $(SCN)_4$ as a calibrant.

The differential thermal analysis (DTA) curves were obtained with a Shimadzu DTA–20B instrument, using a heating rate of 10°/min in a nitrogen atmosphere.

The X-ray powder diffraction patterns were obtained with a Toshiba ADX–101 diffractometer and a Toshiba AR–9 recorder epuipped with a Geiger–Müller counter, using Cu K_α radiation and a nickel filter.

Results and Discussion

The green form of bis(N-isopropyl-5,6-benzosalicylideneiminato)nickel(II), which was previously obtained, was concluded to consist of square-planar complexes, on the basis of its diamagnetism and electronic spectra.[8,9]

In the present work, the brown form with the same composition as that of the green form has newly been isolated in crystals. In contrast to the diamagnetic green form, the brown form is paramagnetic with a magnetic moment of 3.22 B.M. at room temperature. The observed moment, which excludes the diamagnetic square-planar geometry, falls in the range of magnitude expected for the tetrahedral nickel(II) complex; this moment is found to be in good aggreement with the reported moment (3.22 B.M.) of Ni $(5,6\text{-benzo-Sal-t-}C_4H_9)_2$, which was concluded to have a tetrahedral configuration.[8]

As shown in Figure 1, the electronic absorption spectrum of the brown form obviously differs from that of the green planar form and has the main features typical of the tetrahedral nickel(II) complex. Assignment of the d–d bands may be made as previously reported, on the basis of the distorted tetrahedral geometry.[8,9,11] The X-ray powder diffraction data of the brown form are similar to those of the corresponding zinc(II) compound, which were concluded to have a tetrahedral configuration.[12] It is, therefore, concluded that the brown form consists of the tetrahedral nickel(II) complexes. Thus the newly isolated brown form and the previously reported green one provide a new example for the planar–tetrahedral isomerism in nickel(II) complexes with Schiff bases. The spectra of the brown form in non-donor solvents such as chloroform and ethanol are identical with those of the green form in the same solvents. The solution spectra of the green form were previously reported and interpreted as superposition of the diamagnetic planar and the paramagnetic tetrahedral species, which were in equilibrium. The equilibria of this and related complexes in solution were extensively studied previously.[8,9]

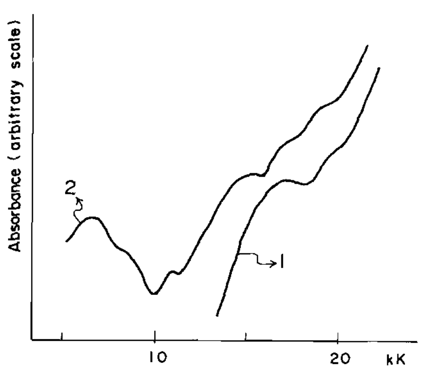


Figure 1. Electronic absorption spectra of $Ni(5,6\text{-benzo-Sal-iso-}C_3H_7)_2$ in the solid state. 1, green form; 2, brown form.

In order to examine thermal behaviour of this complex in connection with the preparation of the tetrahedral form from the green planar form, we have obtained their DTA curves, which are shown in Figure 2. The brown form shows an only one endothermic peak 224°, which corresponds to the melting process. On the repeated runs with the same specimen between 15° und 225°, the same pattern was obtained every time.

On the contrary, the green form shows two endothermic peaks. One of them at 209° probably corresponds to the melting process of the planar form, and the second endothermic peak at 224° coincides with the peak appearing for the brown tetrahedral form of the same complex. The exothermic peak between these two endothermic peaks probably represents the conversion process from the planar to the tetrahedral

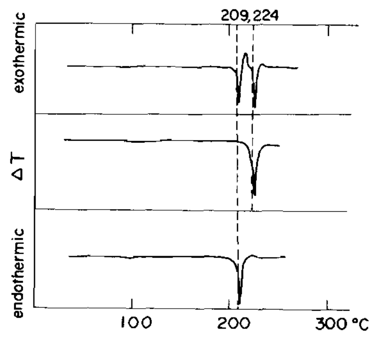


Figure 2. DTA curves of $Ni(5,6\text{-benzo-Sal-iso-}C_3H_7)_2$ and $Ni(5,6\text{-benzo-Sal-n-}C_3H_7)_2$ in the nitrogen atmosphere at the heating rate of 10° per min. 1, $Ni(5,6\text{-benzo-Sal-iso-}C_3H_7)_2$, green form; 2, $Ni(5,6\text{-benzo-Sal-iso-}C_3H_7)_2$, brown form; 3, $Ni(5,6\text{-benzo-Sal-n-}C_3H_7)_2$, green planar complex.

form. In agreement with these data may be the observation that heating the green form at about 224° causes the colour change into brown, eventually yielding the brown tetrahedral form. The X-ray powder pattern and electronic spectrum of the brown substance thus obtained are identical with those of the brown crystals prepared by the other method, that is, the first method in the section of Experimental.

It is interesting to note a difference between the planar forms of Ni(5,6-benzo-Sal-i-C_3H_7)$_2$ and Ni(5,6-benzo-Sal-n-C_3H_7)$_2$. The DTA curve of the latter shows only one endothermic peak at 206°, which corresponds to the melting process; this compound undergoes no configurational change, as temperature is raised up to 300°, as judged by its DTA curve, which shows no peak between 206° and 300°.

Acknowledgments

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