Isomerism and Configurational Change by Adduct Formation in Bis(*N*-cyclohexyl-3-methoxysalicylideneiminato)copper(II)

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In a previous communication,[1] we reported on the isolation of two forms having different configurations for bis(*N*-isopropyl-3-methoxysalicylideneiminato)copper(II) (abbreviated as Cu(3-CH_3O-isopropyl)$_2$). The steric effect arising from the isopropyl group is remarkable in that the complexes of the type Cu(X-SAL·*iso*-C_3H_7)$_2$ take either a tetrahedral or a planar configuration, depending upon the nature of X.[2,3] Since the cyclohexyl group is somewhat similar to the isopropyl group with respect to the steric effect in the complexes of this series,[2] we found it desirable to extend our study to the corresponding cyclohexyl complexes. This resulted in the successful isolation of green (Form I) and red forms (Form II) of Cu(3-CH_3O-SAL·Ch)$_2$, where the notation Ch denotes a cyclohexyl group. Moreover, it has been found that the green form absorbs chloroform and bromoform to yield red-brown adducts.

Form I was obtained as olive-green crystals by recrystallizing from methanol-chloroform or benzene the crude product, which had been prepared by a reaction of bis(3-methoxysalicylaldehydato)-copper(II) with cyclohexyl amine in methanol.

With the rise of temperature, Form I was converted into a red-brown substance (Form II) at about 180°C, the change being reversible. Elementary analysis of Form II agrees with that of Form I, both forms being represented by Cu(3-CH_3O-SAL·Ch)$_2$.

Electronic absorption spectra for many copper(II) complexes of this series have so far been reported, and it now seems to be possible to determine the configuration of a copper(II) complex on the basis of its spectra in many cases.[1-4] Examination of the solid spectra reveals that Forms I and II consist of planar and tetrahedral complexes, respectively. They show identical spectra in solution, and spectra typical of the distorted tetrahedral complex in non-donor solvents.

Red-brown crystals (Form III) were obtained by evaporating a solution of Form I in chloroform, or by exposing Form I to the vapour of chloroform in a desiccator for a few days. Elementary analysis shows that Form III is represented by Cu(3-CH_3O-SAL·Ch)$_2$·2$CHCl_3$. The crystals of Form III may be kept in a tightly closed sample-tube without decomposition for at least a few weeks. When allowed to stand in the atmosphere, Form III is transformed into Form I, losing two molecules of chloroform, as confirmed by the weight-loss measurement.

The remarkable colour change on the adduct formation apparently indicates that some configurational change takes place in this process, and that Form III does not contain the planar copper(II) complex of the starting compound. Combination of the chloroform molecule with the copper(II) ion to form complexes with coordination number five or six seems to be unlikely, in view of the finding that the electronic absorption spectrum of Form III as well as that of Form I in chloroform are similar to those of their ethanol solutions, and also to the solid spectrum of Form II; all of them are typical of the distorted tetrahedral complexes. It may thus be presumed that Form III in the solid state consists of the distorted tetrahedral complex, and that the chloroform molecule is not involved in the bonding with the copper(II) ion. It may be remembered that the chloroform molecule was previously reported to function in a similar way in its adduct with *N,N'*-ethylenebis(salicylideneiminato)-copper(II).[5]

When bromoform was employed instead of chloroform, an adduct represented by Cu(3-CH_3O-SAL·Ch)$_2$·2$CHBr_3$ was obtained as red-brown crystals. Its properties are similar to the chloroform adduct, and it is considered to consist of the copper(II) complexes with a similar configuration.

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