SHORT COMMUNICATIONS

Red and Green Forms of Bis(*N*-isopropyl-3-methoxysalicylideneiminato) copper(II)

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The structural versatility of bis(*N*-alkylsalicylideneiminato)copper(II) complexes*1 now seems to be fairly well known,[1] and their geometries may be expected to become even more complicated, when the *N*-substituent R denotes an α-branched alkyl. For example, because of the steric effect caused by considerably bulky isopropyl groups, 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] Only one of them, however, is usually obtained as crystals, and two forms of crystals consisting of complexes with different configurations have never been isolated for a set of X and R. The present communication deals with successful isolation of two forms of Cu(3-CH_3O-SAL·*iso*-C_3H_7)$_2$.

The compound Cu(3-CH_3O-SAL·*iso*-C_3H_7)$_2$ was obtained in two forms, one being olive-green (Form I) and the other red-brown (Form II). The crude product was prepared by the reaction between bis(3-methoxysalicylaldehydato)copper(II) (0.02 mol) and isopropylamine (0.045 mol) in 90% methanol (75 m*l*) at about 40°C for a few hours. Evaporation at about 30°C of a concentrated solution of the crude product in methanol, ethyl ether, chloroform or dioxane yielded pure red-brown crystals (Form II) of the required complex. Olive-green crystals (Form I) of the same complex were obtained by spontaneous evaporation of a concentrated methanolic solution of the crude product at 5—10°C.

Elementary analyses of both the red-brown and the olive-green forms agree with the formula Cu(3-CH_3O-SAL·*iso*-C_3H_7)$_2$. Found: C, 58.84; H, 6.08; N, 6.14% (for the red-brown form). C, 59.00; H, 6.46; N, 6.14% (for the olive-green form). Calcd for $C_{22}H_{28}N_2O_4Cu$: C, 58.98; H, 6.30; N, 6.25%. Both forms, when dissolved in chloroform, benzene or ethanol, show the same electronic absorption spectra.

The solid spectrum of Form II is almost the same as that of its solution in non-donor solvents, having absorption bands at about 9.0, 14.5 and 21.5 kK. This is also similar to that of Cu(H-SAL·*iso*-C_3H_7)$_2$, which was previously concluded to have a distorted tetrahedral configuration.[2-4]

On the contrary, the *d–d* absorption band of Form I in the solid state, which appears at about 13.5 kK with a shoulder at about 11.0 kK, is shifted toward a much lower frequency, as compared with the spectra of the planar copper(II) complexes such as Cu(H-SAL·*n*-C_4H_9)$_2$[5] and Cu(3-CH_3O-SAL·*n*-C_3H_7)$_2$. The solid spectrum of Form I is remarkably similar to the spectrum of the binuclear Cu_2(H-SAL·CH_3)$_4$ containing copper(II) ions with a bipyramidal five-coordination,[6] suggesting this geometry for Form I.

Form II melts at 121—122°C, while with the rise of temperature Form I is transformed into Form II (red-brown) at 101°C, whose X-ray powder diagram and solid spectrum agree with those of the red-brown crystals (Form II) obtained by evaporation at about 30°C of the solution.

In the case of the corresponding nickel(II) complex Ni(3-CH_3O-SAL·*iso*-C_3H_7)$_2$, there are brown tetrahedral (Form I) and green planar (Form II) forms, and with the rise of temperature the planar form is transformed into a tetrahedral one at 157—158°C.[7] Comparison seems to indicate that the bis(*N*-substituted salicylideneiminato)nickel(II) complexes have a greater tendency to assume a planar structure than the corresponding copper(II) complexes, in agreement with a previous result.[2]

*1 The complexes of this series are abbreviated as Cu(X-SAL·R)$_2$, where R and X denote an alkyl group on the nitrogen atom and a substituent on the benzene ring, respectively.

1) D. Hall, S. V. Sheat and T. N. Waters, *Chem. Commun.*, **1966**, 436.

2) L. Sacconi, "Essays in Coordination Chemistry," ed. by W. Schneider, G. Anderegg and R. Gut, Birkhäuser Verlag, Basel (1964), p. 148.

3) S. Yamada and H. Nishikawa, This Bulletin, **36**, 755 (1963).

4) P. L. Orioli and L. Sacconi, *J. Amer. Chem. Soc.*, **88**, 277 (1966).

5) D. Hall, R. H. Sumner and T. N. Waters, *J. Chem. Soc., A*, **1969**, 420.

6) L. Sacconi, M. Ciampolini and G. P. Speroni, *J. Amer. Chem. Soc.*, **87**, 3102 (1965).

7) A. Takeuchi and S. Yamada, This Bulletin, **42**, 3046 (1969).