CHEMISTRY LETTERS, pp. 343-346, 1976. Published by the Chemical Society of Japan

SYNTHESIS OF THE COPPER(II) COMPLEX OF BIS(SALICYLIDENEAMINO)MALEONITRILE: [(2,3-DICYANO-*CIS*-2-BUTENE-2,3-DIIMINOMETHYL)DI-*O*-PHENOLATO]COPPER(II)

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The copper(II) complex of the Schiff base derived from a diaminomaleonitrile and two salicylaldehyde molecules was synthesized as deep wine-red crystals. The complex molecule was supported to have a planar structure by the magnetic susceptibility and the infrared and Raman spectra.

2,3-Diamino-*cis*-2-butenedinitrile (diaminomaleonitrile: DAMN), a tetramer of hydrogen cyanide, has been known as an unsaturated electron-rich ligand coordinated to a metal in a number of different ways.[1-3] The DAMN is a unidentate amine in *trans*-dichlorobis(diaminomaleonitrile)palladium(II) prepared in the acidic solution of DAMN and $Na_2[PdCl_4]$, whereas neutral complex of Ni(II), Pd(II), or Pt(II) is obtained from the basic solution of DAMN and the relevant metal(II) salt with a formulation $[M(II)(C_4H_2N_4)_2]$ in which the bidentate ligand $C_4H_2N_4$ has been described as the univalent anion of 2,3-diiminobutanedinitrile (diiminosuccinonitrile) formed by the oxidation of DAMN. The molecular structure of DAMN in its neat crystal was reported to have no symmetry with two amino groups in different configurations, one is an sp^2-like and the other in an sp^3-like, and with a twist angle 6° about the central C=C bond.[4] This biased structure appears not only to be forced by the packing in crystal but also to be deduced from the electron-rich nature of DAMN itself, because DAMN is apt to behave unsymmetrically in several organic reactions[5] as well as in the coordination in *trans*-$[Pd(C_4H_4N_4)_2Cl_2]$. One of those reactions is that with aldehydes, the reaction in which DAMN gives generally 1:1 Schiff base even in the presence of excessive amounts of the aldehyde. Bis-aldimino Schiff base can be prepared only by applying a strong dehydrant such as sulfuric acid or phosphorus pentoxide.[6] In this communication an attempt to synthesize square-planar metal complex of the bis-aldimino Schiff base ligand derived from DAMN and salicylaldehyde will be described as the first example so far has been surveyed in literature.

When DAMN reacted with salicylaldehyde (salH) in ethanol (EtOH), 2-amino-3-salicylideneamino-*cis*-2-butenedinitrile (damnsalH) was obtained irrespectively to the amount of the aldehyde added. Although copper(II) and nickel(II) had been examined as the square-planar metal species, reproducible results have been obtained only for copper(II). The crude products of the desired complex, [(2,3-dicyano-*cis*-2-butene-2,3-diiminomethyl)di-*o*-phenolato]copper(II), were respectively prepared by

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the procedures as follows:
(i) After 10 mmol (1.08 g) of DAMN in 60 ml (1 = 10^3 cm^3) of hot EtOH and 20 mmol (2.44 g) of salH in 30 ml of hot EtOH were mixed slowly, 10 mmol (1.70 g) of $CuCl_2 \cdot 2H_2O$ ($CuCl_2$) in 60 ml of hot EtOH was added drop by drop to the mixture on a steam bath. After a while reddish brown massive needles were crystallized out, and aged overnight. The crystals were filtered out by a fritted glass and washed by decantations three times with 50 ml each of hot EtOH to extract damnsalH formed as a by-product. Yield 23 %. When the more concentrated solutions were used, or when the final mixture was refluxed for 20 min or longer, a brown powdery product, presumably a polymerized solid, was obtained instead of the massive needles.
(ii) By the way similar to (i), 10 mmol each of DAMN, salH, and $CuCl_2$ in 40, 20, and 60 ml of hot EtOH, respectively, were mixed together and treated to give the reddish brown needles (yield 20 % based on the amount of salH). When the more concentrated solutions were used, a powdery product was obtained similarly to (i).
(iii) After 5 mmol (1.06 g) of damnsalH in 100 ml of nearly boiling EtOH and 5 mmol of salH in 10 ml of hot EtOH were slowly mixed, 5 mmol of $CuCl_2$ in 20 ml of hot EtOH was added drop by drop to the mixture. The reddish brown needles, instantly formed with a yield of 24 %, were treated by the way similar to (i).
(iv) Into 5 mmol of damnsalH in 100 ml of nearly boiling EtOH, 5 mmol of $CuCl_2$ in 20 ml of hot EtOH was added drop by drop. After a while the reddish brown needles were obtained with a yield of 16 % based on the net amount of salH. When the finally mixed solution was refluxed for 20 min or longer, the needles once formed dissolved away instantly with the color change of the solution from deep wine-red to dilute orange-red. From the orange-red solution, the brown powdery product was obtained by cooling.

All the reddish brown needles obtained by the above procedures showed the infrared spectra and the powder x-ray diffraction patterns similar to each other. However, their analytical results showed considerable deviations from sample to sample with poor agreements with regard to the C and N contents. The recrystallizations were examined from the acetone and the benzene solutions. After 0.1 g of the needles was dissolved into 50 ml of acetone or benzene by heating, the resulting wine-red solution was filtered. The filtrate, followed by the addition of 20 ml of cold EtOH, was left overnight at room temperature. The massive needles were recrystallized out with 80-90 % recoveries. The analytical results were still not satisfactory. When the mixture of 0.5 g of the needles and 30 ml of benzene were heated on a steam bath, the dissolution of the needles was followed by the precipitation of deep-colored cube-shaped crystals. After the mixture was heated for 20 more min, it was cooled down to room temperature. Only the cube-shaped crystals with a metallic luster were obtained by filtering off the liquid phase. The crystals were washed with cold EtOH and diethyl ether successively, and kept in a silica-gel desiccator. The infrared spectrum was similar to those of the massive needles, but the x-ray diffraction pattern was quite different as shown in Fig. 1. Anal. Found: C, 57.25; H, 2.59; N, 14.84; Cu, 16.83 %. Calcd for $C_{18}H_{10}N_4O_2Cu$: C, 57.22; H, 2.67; N, 14.83; Cu, 16.82 %. From the filtrate the massive needles were obtained again by leaving overnight. The analytical results were still as unsatisfactory as those for the previous needles. Found: C, 53.77; H, 3.03; N, 14.32 %. Therefore it has been concluded that the cube-shaped crystals are so far

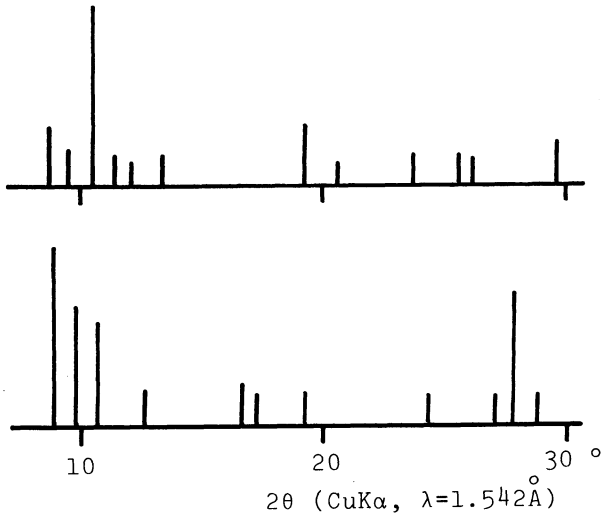

Fig. 1. The powder x-Ray Diffraction Patterns of the Massive Needles(above) and the Cube-shaped Crystals(bottom).

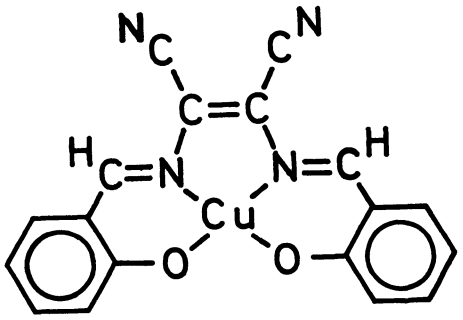

Fig. 2

in the purest form of the desired complex.

The effective magnetic moment was calculated from the magnetic susceptibility measured by the Gouy method at 288 K after the correction for the diamagnetic contributions. The value 1.92 B.M. supports the 2+ oxidation state of the copper which does not suffer any redox reaction after all. In the infrared and Raman spectra, the latter being observed for the acetone and benzene solutions (Ar^+ laser at 514.5 nm), any bands due to amino group were not observed in comparison with those spectra of DAMN and damnsalH. The distinctive infrared and Raman bands (in cm^{-1}), the latter being shown in parentheses, are: 2225w (2222vw); 1612s(1615m); 1578s; (1562s); 1515s(1518m); 1464m(1464m); 1445s(1445w); 1415w; 1390m; (1375s); 1335m; 1318m(1318m); 1257vw(1256m); 1188s(1188m); 1149m (1154m); 958w; 918vw(923w); 758m; 597vw(598s); 568vw(571m); (550m); (308s). The experimental accuracy in wave number reading was ± 3 cm^{-1}. Although some Raman bands appeared not to be observed owing to the low solubilities in the solvents at room temperature, these features can be interpreted in terms of the C_{2v} symmetry of the complex molecule as shown in Fig. 2. The tentative assignments are: 1612(1615) to the C=C stretch A_1 mode of DAMN skeleton, 1578 to the iminomethyl C=N stretch A_1 mode, and (1562) to the C=N stretch A_2 mode.

The remarkable difference in appearance and in x-ray diffraction pattern between the massive needles and the cube-shaped crystals may be due to the polymorphism of the crystal structures. The brown powdery products formed by refluxing the reaction mixture or by using the more concentrated solutions are supposed to be polymerized species. Their analytical results varied from sample to sample with considerably high copper contents 23-29 %. In the infrared spectra, several bands due to amino or imino groups were observed along with those due to salicylidene group. They are sparingly soluble in common organic solvents.

The DAMN used in this work was kindly supplied from Kyowa Gasu Kagaku Kogyo Co., Ltd. A part of this work was supported by Grants-in-Aid from the Ministry of Education.

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(Received February 19, 1976)