BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 48(10), 2969—2970 (1975)

A Study of Optically Active (Benzoin-α-oxime)dichlorocopper(II)

Tomikatsu Kudo, Sumio Kaizaki, Jinsai Hidaka,* and Yoichi Shimura
Department of Chemistry, Faculty of Science, Osaka University, Toyonaka, Osaka 560

(Received April 24. 1975)

Synopsis. An optically active complex, [(*S*)-benzoin-α-oxime]dichlorocopper(II), was prepared and its absorption and circular dichroism spectra were investigated in organic solvents.

(Benzoin-α-oxime)dichlorocopper(II), [$CuCl_2$(cuprH_2)],[1] was prepared by Jennings *et al.*[2] and studied magnetochemically by Rindorf,[3] who established its monomeric nature from the effective magnetic moment of 1.91 μ_B in contrast to the polymeric subnormal 1 : 1 complex $\{$Cu(cupr)$\}_x$ (0.80 μ_B at 294 K). In the present paper, the dichloro complex with optically active (*S*)-benzoin-α-oxime is reported.

Experimental

Preparation. *$(+)_{589}$-(S)-Benzoin-α-oxime*: Hydrogen phthalate of benzoin was obtained from the reaction of racemic benzoin and phthalic anhydride in trimethylamine, and resolved with $(+)_{589}$-quinidine by a modified method of Kenyon *et al.*;[4] the powdered solid of phthalic anhydride was used instead of its suspension in pyridine. $(+)_{589}$-(*S*)-Benzoin was obtained by the hydrolysis of hydrogen phthalate. $[\alpha]_{589}=+119.2°$ (*c*, 0.0105, in acetone). (lit,[4] $[\alpha]_{589}=+118.4°$). $(+)_{589}$-(*S*)-Benzoin-α-oxime was prepared by the oximation of $(+)_{589}$-(*S*)-benzoin. mp 163—164 °C. $[\alpha]_{589}=+3.0°$ (*c*, 0.0472, in chloroform). Found: C, 74.02; H, 5.71; N, 6.14%. Calcd for $C_{14}H_{13}NO_2$: C, 73.99; H, 5.76; N, 6.16%.

(Benzoin-α-oxime)dichlorocopper(II): This was prepared by a new method as follows. To 30 ml of 2,2′-dimethoxypropane was added 2.7 g (0.0158 mol) of $CuCl_2\cdot2H_2O$ with stirring. The yellow mixture obtained was kept at room temperature, stirring for 30 min. When 3.6 g (0.0159 mol) of cuprH_2 was added to it, the mixture turned immediately to a green solution. A pale-green fine precipitate deposited after standing at room temperature for about 10 min. The product was filtered off, washed with methanol, and then air-dried. Found: C, 45.53; H, 4.72; N, 3.60%. Calcd for [$CuCl_2$(cuprH_2)]·$CH_3OH=C_{15}H_{17}NO_3Cl_2Cu$: C, 45.76; H, 4.35; N, 3.57%. The complex which was recrystallized from methanol, ethanol, acetone, or acetonitrile had one molecule of the solvent. The solvent of crystallization was removed by air-drying for several days. Found: C, 45.98; H, 3.71; N, 3.87%. Calcd for [$CuCl_2$(cuprH_2)]$=C_{14}H_{13}NO_2Cl_2Cu$: C, 46.49; H, 3.62; N, 3.87%.

[$(+)_{589}$-(S)-Benzoin-α-oxime]dichlorocopper(II): To 20 ml of 2,2′-dimethoxypropane was added 2.1 g (0.0123 mol) of $CuCl_2\cdot2H_2O$ with stirring. After 30 min, 2.8 g (0.0123 mol) of (*S*)-cuprH_2 was added to this mixture; the mixture immediately turned into a green solution. In this case, however, the desired complex did not appear because of its high solubility. To the solution was added 20 ml of methanol and the resulted solution was concentrated to half of its original volume in a vacuum rotary evaporator at about 30 °C. After 80 ml of ether was added to it, the solution was kept in a refrigerator for a week. Bright emerald-green needle crystals were obtained. The complex had one molecule of methanol as solvent of crystallization, but lost it easily. Found: C, 45.46; H, 4.29; N, 3.47%. Calcd for [$CuCl_2$$\{$(*S*)-cupr$H_2$$\}$]·$CH_3OH=C_{15}H_{17}NO_3Cl_2Cu$: C, 45.76; H, 4.35; N, 3.56%. Found: C, 46.07; H, 3.71; N, 3.79%. Calcd for [$CuCl_2$$\{$(*S*)-cupr$H_2$$\}$]$=C_{14}H_{13}NO_2Cl_2Cu$: C, 46.49; H, 3.62; N, 3.87%.

Tetraethylammonium trichlorocuprate(II): An aqueous solution containing $CuCl_2\cdot2H_2O$ and [$N(C_2H_5)_4$]Cl (1 : 1) was concentrated by evaporation to dryness. The brick red crystals obtained were recrystallized from acetone. Found: C, 31.07; H, 6.51; N, 4.41%. Calcd for [$N(C_2H_5)_4$]$CuCl_3=C_8H_{20}NCl_3Cu$: C, 32.01; H, 6.71; N, 4.67%.

Measurement. Visible and ultraviolet absorption spectra were measured with a Shimadzu spectrophotometer QR-50 or UV-200. Diffuse reflectance spectra were obtained by a Hitachi spectrophotometer EPU-2. CD spectra were recorded on a JASCO MOE-1 spectropolarimeter, and optical rotation were checked by a JASCO ORD/UV-5 spectropolarimeter.

Results and Discussion

The absorption and CD data of [$CuCl_2$$\{$(S)-cupr$H_2$$\}$] in various organic solvents are shown in Figs. 1 and 2. The spectral behavior in the visible region depends remarkably upon the kind of solvents, which can be classified into three groups, [A], [B], and [C].

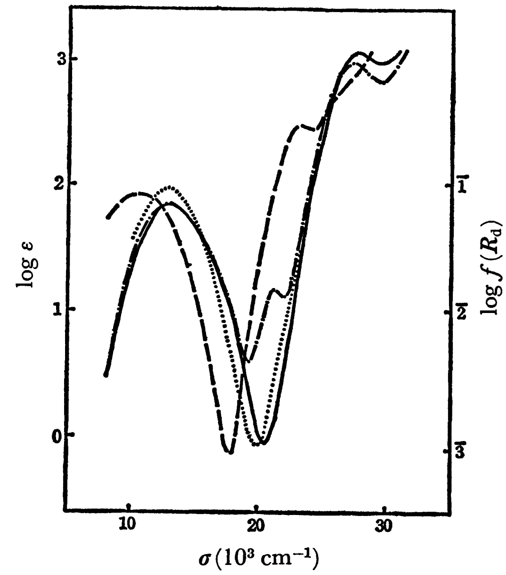

Fig. 1. Absorption curves of [$CuCl_2$(cuprH_2)] in organic solvents (10^{-2} M): - - - Dimethylformamide ([A] group), —— Chloroform ([B] group), —·— Acetone ([C] group), and ······ Diffuse reflectance spectra (the right ordinate).

---

* Present address: Department of Chemistry, The University of Tsukuba, Ibaraki, 300—31.

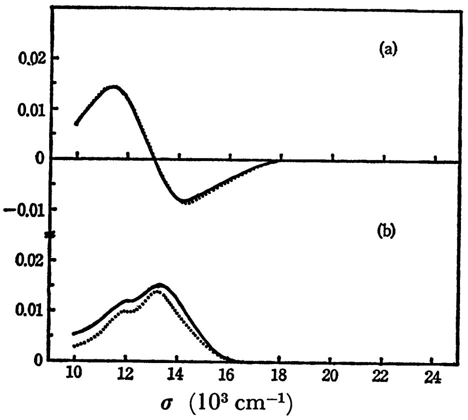

Fig. 2. CD curves of $[CuCl_2\{(S)\text{-}cuprH_2\}]$ in organic solvents; (a) Chloroform ([B] group), (b) Acetone ([C] group), (—— 10^{-2} M, ······10^{-3} M solution).

The d-d absorption band in [A] group solvents differs markedly from those in [B] or [C] solvents (Fig. 1), and no CD band appears in the visible region. It seems that the [A] group solvents, dimethyl sulfoxide, dimethylformamide, and pyridine, coordinate strongly to copper(II) ion; accordingly, the coordinated (*S*)-$cuprH_2$ may be substituted by the solvent employed.

In the [B] group solvents, chloroform, dichloromethane, methanol, and ethanol, the complex shows a broad but relatively strong ligand field absorption band at about 13000 cm^{-1}, which obeyed Beer's law in the range 10^{-2}—10^{-4} M. The absorption spectra in [B] group solvents resemble closely the powder diffuse reflectance spectrum of the complex (Fig. 1). In the d-d absorption band region, two CD components, (+) and (−) from the lower frequency side, were observed and the net CD sign was positive.

In the [C] group solvents, acetone, acetonitrile, acetophenone, ethyl acetate, and tetrahydrofuran, a sharp absorption band appeared at about 21000 cm^{-1} in addition to the d-d band at about 13000 cm^{-1}. The intensity of the former band depends markedly upon the concentration of the solution (Fig. 3). Two positive CD bands were obtained in the d-d absorption band region, but the CD intensity also depends upon the concentration of the solution (Fig. 2). No CD band appeared in the 21000 cm^{-1} band region. The 21000 cm^{-1} absorption band was intensified by the addition of $[N(C_2H_5)_4]Cl$ to the solution. An intense d-p_π charge transfer band was observed at 21000 cm^{-1} for $[N(C_2H_5)_4]CuCl_3$ dissolved in acetone: the absorption bands appear at 8600 cm^{-1} (log ε_{max}=0.89), 11000 (1.93), and 21000 (3.18). Manahan and Iwamoto⁵⁾ reported a stability constant study of the Cu^{2+}–Cl^- system in organic solvents and showed that the main species is $CuCl_3^-$. Indeed, the intensity of the 21000 cm^{-1} band of $[N(C_2H_5)_4]CuCl_3$ decreases with addition of $[N(C_2H_5)_4]Cl$ and a new band appears at 24300 cm^{-1}. The band at about 24000 cm^{-1} has been attributed to a charge transfer transition of the $CuCl_4^{2-}$ species.⁶,⁷⁾ In conclusion, the 21000 cm^{-1} band is ascribed to the charge transfer band of a small amount of the $CuCl_3^-$ species which is the dissociation product of $[CuCl_2(cuprH_2)]$ in the [C] group solvents.

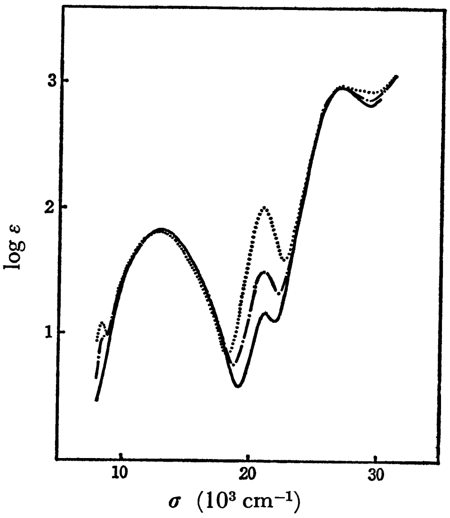

Fig. 3. Absorption curves of $[CuCl_2(cuprH_2)]$ in Acetone; —— 10^{-2} M, —·— 10^{-3} M, ······ 10^{-4} M.

The CD intensities of $[CuCl_2\{(S)\text{-}cuprH_2\}]$ in Fig. 2 are comparable to those of the (*S*)-α-amino acidato copper(II) complexes and the net CD sign is positive both in the [B] and [C] group solvents. It has been well established that the copper(II) complexes of ordinary (*S*)-α-amino acids,⁸,⁹⁾ their amides,¹⁰⁾ and simple peptides¹¹⁾ have a net negative CD sign in the d-d absorption band region, and this negative Cotton effect has been explained from a true vicinal contribution⁹⁾ of the (*S*) asymmetric carbon atom, from a conformational contribution¹²⁾ of the δ chiral chelate ring, or from a regional contribution¹¹⁾ of the large substituent on the (*S*) asymmetric carbon atom. A molecular model examination of the interaction between the two phenyl groups in the present ligand (*S*)-benzoin-α-oxime shows that the ligand prefers axial disposition of the phenyl group attached to the asymmetric carbon atom, producing a λ chiral chelate ring. Thus, it is concluded that the net positive CD of the present copper(II) complex is due to the regional contribution of the axial phenyl group and/or the conformational contribution of the λ chelate ring.

References

1) Benzoin-α-oxime, $C_6H_5C(NOH)CH(OH)C_6H_5$, has been called cupron, which is abbreviated as $cuprH_2$.

2) J. S. Jennings, E. Sharratt, and C. K. Wardlaw, *J. Chem. Soc.*, **1935**, 818.

3) G. Rindorf, *Acta Chem. Scand.*, **25**, 774 (1971).

4) J. Kenyon and R. L. Patel, *J. Chem. Soc.*, **1965**, 453.

5) S. E. Manahan and R. T. Iwamoto, *Inorg. Chem.*, **4**, 1409 (1970).

6) R. D. Willett and O. L. Liles, Jr., *ibid.*, **6**, 1666 (1967).

7) W. Ludwig and M. Texton, *Helv. Chim. Acta*, **54**, 1144 (1971).

8) T. Yasui, This Bulletin, **38**, 1746; T. Yasui, J. Hidaka, and Y. Shimura, *J. Amer. Chem. Soc.*, **87**, 2762 (1965).

9) C. J. Hawkins and C. L. Wong, *Aust. J. Chem.*, **23**, 2237 (1970).

10) T. Komorita, J. Hidaka, and Y. Shimura, This Bulletin, **42**, 168 (1969).

11) J. M. Tsangaris and R. B. Martin, *J. Amer. Chem. Soc.*, **92**, 4255 (1970).

12) K. M. Wellman, W. Mungall, T. G. Mecca, and C. R. Hare, *ibid.*, **89**, 3647 (1967).