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Complexes of Copper Chlorides with Benzophenoneimine

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We tried to prepare complexes of copper chlorides with benzophenoneimine. The complex $CuCl_2\cdot 2Ph_2C{=}NH$ and the complex $CuCl\cdot Ph_2C{=}NH$ were newly prepared, and some of their properties were investigated by physico-chemical techniques. Besides these, two other complexes were obtained, but they were not completely stoichiometric compounds.

It is well known that aldimines and ketimines which can act as multi-dentate ligands form stable complexes with copper ions.[1] Several investigations have been published on the complexes of amines with copper halides.[2] However, there seems not yet to have been any report on the complex formation of benzophenoneimine with copper halides. The present authors have been interested in the cleavage of the bond between nitrogen and hydrogen[3] and have tried to prepare complexes of copper chlorides with benzophenoneimine in order to clarify the effect of complex formation on the oxidation of benzophenoneimine. In this paper, the authors wish to report on the preparation of such complexes.

Results and Discussion

It was observed that when benzophenoneimine was added to the acetonitrile solution of copper(II) chloride, some precipitates began to appear immediately. They were found to be complexes of copper(II) chloride with benzophenoneimine. From the precipitates, the complex, $CuCl_2\cdot 2Ph_2C{=}NH$ (I) was isolated as a grey-purple powder. It became a green solution in chloroform. The curve of the absorption spectrum (Fig. 1, full line: ν_{max} ~13.7 kK, $\log \varepsilon = 2.3$) was similar to that of copper(II) dipyridine dichloride ($CuCl_2py_2$), though the absorption maximum of $CuCl_2py_2$ due to the d-d transition is at about 13.2 kK (in

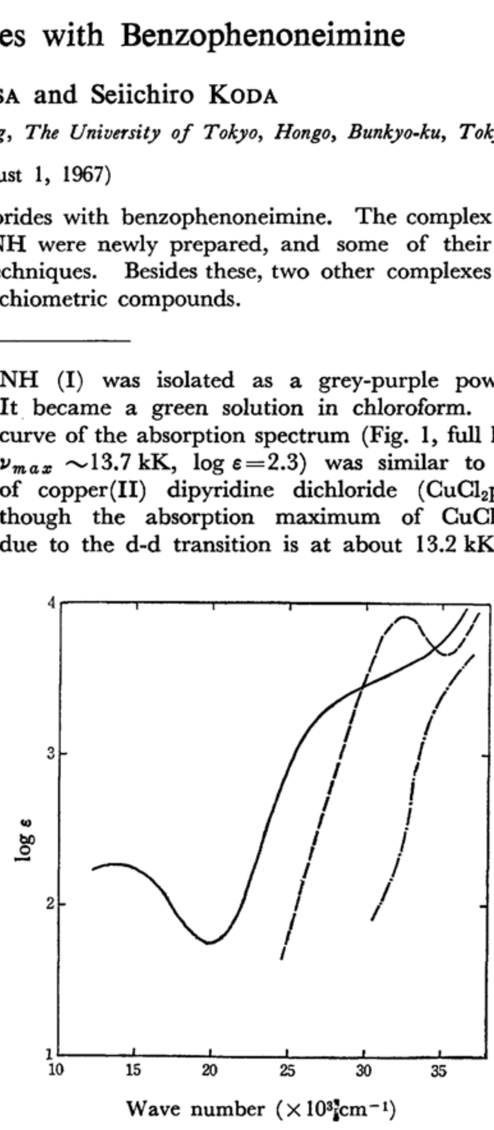

Fig. 1. The absorption spectra in chloroform.
——: $CuCl_2\cdot 2Ph_2C{=}NH$
– – –: $CuCl\cdot Ph_2C{=}NH$
·—·: $Ph_2C{=}NH$

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[1] D. F. Martin, *Preparative Inorg. Reactions,* **1**, 59 (1964).

[2] a) J. F. Weiss, G. Tollin and J. T. Yoke, III, *Inorg. Chem.*, **3**, 1344 (1964). b) J. R. Clifton and J. T. Yoke, III, *ibid.*, **5**, 1630 (1966). c) A. R. Burkin, *J. Chem. Soc.*, **1950**, 122; R. G. Wilkins and A. R. Burkin, *ibid.*, **1950**, 127.

[3] A. Misono, T. Osa and S. Koda, This Bulletin, **40**, 912 (1967).

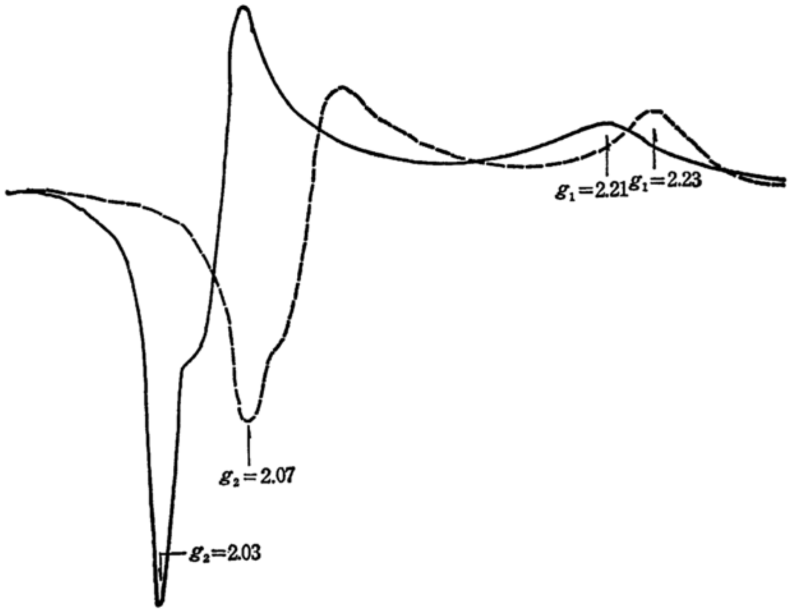

Fig. 2. The e. p. r. signal in the powder state at room temperature.
——: $CuCl_2\cdot 2Ph_2C{=}NH$ – – –: $CuCl_2py_2$

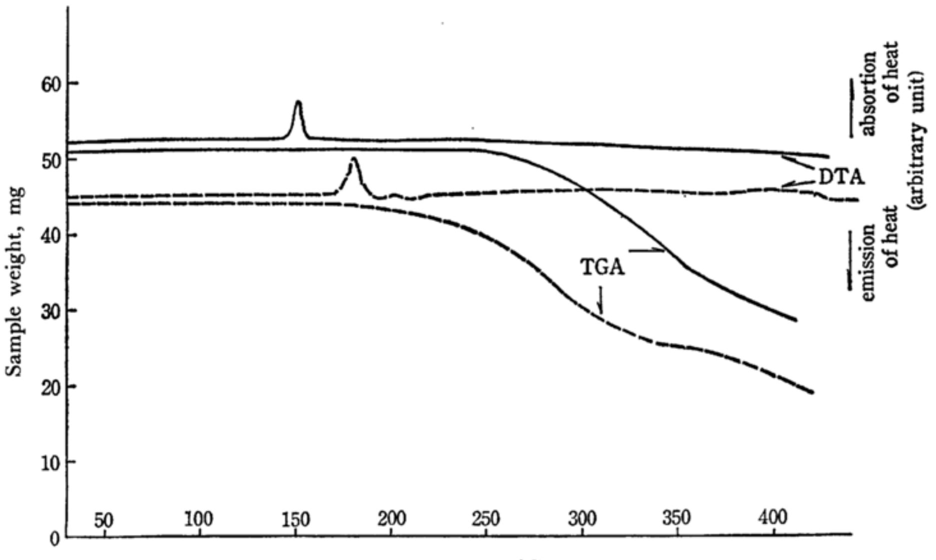

Fig. 3. The differential thermal analyses (DTA) and the thermogravimetric analyses (TGA).
– – –: $CuCl_2\cdot 2Ph_2C{=}NH$ (44 mg) ——: $CuCl\cdot Ph_2C{=}NH$ (51 mg)
The elevating speed of the temperature, 2.5°C/min
In the atmosphere of nitrogen
The reference for DTA, α-alumina

pyridine).4) This complex was slightly soluble in benzene and acetonitrile. The e. p. r. signal of this complex showed a typical resolution of the d^9 Cu(II) resonance according to the anisotropy in the g values ($g_1=2.21$, $g_2=2.03$), as shown in Fig. 2. The g values can be estimated approximately from the e. p. r. spectra of the complex in the

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4) E. Ochiai, *Tetrahedron,* **20**, 1831 (1964); V. S. Sergeeva and S. V. Plyushcheva, *Zh. Neorgan. Khim.,* **7**, 2357 (1962).

powder state.[5] For a comparative study, the e. p. r. spectrum of $CuCl_2py_2$ in the powder state was observed under similar conditions (Fig. 2, dashed line). The observed g values ($g_1=2.23$, $g_2=2.07$) approximated the g values obtained in the vitreous state ($g_{\parallel}=2.241$, $g_{\perp}=2.079$).[6] The g values of the complex I were smaller than those of the triethylamine complex of copper(II) chloride, $CuCl_2\cdot 2Et_3N$ ($g_1=2.27$, $g_2=2.06$).[2a] Generally speaking, the g values decrease with an increase in the "covalency" between ligands and the central metal ion.[7] Therefore, smaller g values of the complex I in comparison with the complex $CuCl_2\cdot 2Et_3N$ may indicate a greater "covalency", which can be expected from the existence of a C=N double bond and the phenyl groups adjacent to it in the ligand, benzophenoneimine. The complex I was stable at room temperature in the solid state, as can be seen from the invariable results of the two elementary analyses, one of which was performed soon after the preparation, and the other, after 12 days. However, it was gradually decomposed at higher temperatures to yield a dark complicated mass, while the e. p. r. signal due to the divalent copper disappeared. This complex or its mixture with its decomposition products melted at about 180°C (Fig. 3, dashed line), at which time, the e. p. r. signal decreased rapidly (Fig. 4). The decomposition products seemed to be composed of various components, from which $CuCl\cdot Ph_2C=NH$ (*cf.* the next section) was isolated. The decomposition of the complex I may be a thermal-induced oxidation-reduction, similar to that of the triethylamine complex of copper(II) chloride, $CuCl_2\cdot 2Et_3N$.[2a] However, it is interesting to note that this complex, I, was considerably more stable than $CuCl_2\cdot 2Et_3N$, which has been reported to decompose completely at 20°C.[2a]

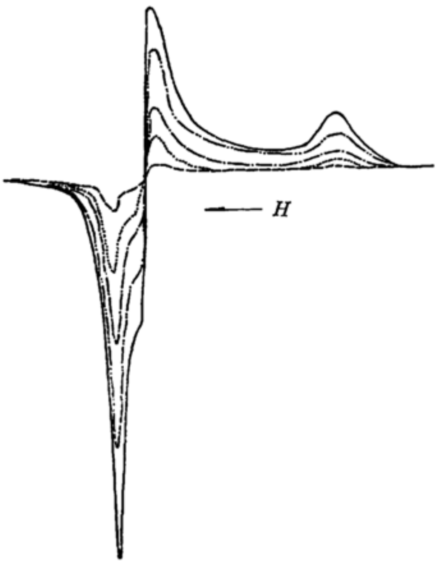

Fig. 4. The decrease of the e. p. r. signal according to the thermal decomposition.
——: Before heating and/or after 30 min (100°C)+10 min (130°C)
—··—: After additional 15 min (150°C)+20 min (160°C)+5 min (165°C)+5 min (170°C)
—·—·: After additional 5 min (177°C)
·········: After additional 5 min (180°C)
— — —: After additional 20 min (180°C)

Besides the complex I, another complex, II, was produced. It did not seem to be a simple species, but was perhaps mainly a 1 : 1 complex. This complex was produced as a yellow precipitate and as a by-product when the complex I was recrystallized from a hot chloroform solution. Besides, a similar yellow precipitate was formed when copper(II) chloride was stirred into a chloroform solution of the complex I. This complex, II, was insoluble in chloroform or in other ordinary solvents. It seemed probable that this complex was a binuclear (or sometimes polynuclear) complex bridged by chloride ions. The relation between the complex I and the complex II may correspond to that between the copper(II) chloride complexes of acetonitrile ($CuCl_2\cdot 2CH_3CN$ and $Cu_2Cl_4(CH_3CN)_2$, $Cu_3Cl_6(CH_3CN)_2$).[8]

The complex I was also produced in chloroform by mixing copper(II) chloride with benzophenoneimine.

A pale yellow complex, $CuCl\cdot Ph_2C=NH$ (III), and a red complex, $CuCl\cdot nPh_2C=NH$ (IV) (n is about two), were obtained by mixing benzophenoneimine with copper(I) chloride in benzene. The molecular weight of the complex III in benzene, obtainable from the vapor pressure osmometry at about 30°C, corresponded to 1.35 times the formula weight. Considering the facts[9] that the copper(I) halide complexes with phosphine derivatives were tetrameric in crystalline state and were in equilibrium with tetrameric and monomeric forms in solutions, this value seems not to be unreasonable. This complex was mostly transparent in the visible region (Fig. 1, dashed line). The complex III was quite stable against oxygen in the solid state, but the benzene solution of this complex absorbed oxygen rather easily and turned gradually greenish-brown. This complex melted at about 135°C. Correspondingly, the absorption of heat was observed to begin at about

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[5] *Jikken Kagaku Koza, zoku* 13 *(Lectures on Experimental Chemistry,* the second series, Volume 13), p. 195, ed. by Chemical Society of Japan, Maruzen Co., Ltd., Tokyo (1967).

[6] H. R. Gersmann and J. D. Swalen. *J. Chem. Phys.*, **36**, 3221 (1962).

[7] D. Kivelson and R. Neiman, *ibid.*, **35**, 149 (1961).

[8] R. D. Willett and R. E. Rundle, *ibid.*, **40**, 838 (1964).

[9] F. G. Mann, D. Purdie and A. F. Wells, *J. Chem. Soc.*, **1936**, 1503.

140°C (Fig. 3, full line). The discrepancy in the temperatures may be caused by the faster elevating speed of the temperature in the differential thermal analysis.

The complex IV was unstable, judging from the fact that the n value often easily changed. For example,[2b] the complex $CuCl\cdot(C_2H_5)_2NH$ is known to be more stable than the complex, $CuCl\cdot 2(C_2H_5)_2NH$.

The coordinated benzophenoneimine showed, at different positions, absorption peaks corresponding to those at 3252 (N-H stretching), 1363, 1197, and 892 cm^{-1} in the free benzophenoneimine. The other peaks in the region from 4000 to 500 cm^{-1} shifted slightly in the coordinated benzophenoneimine (Fig. 5).

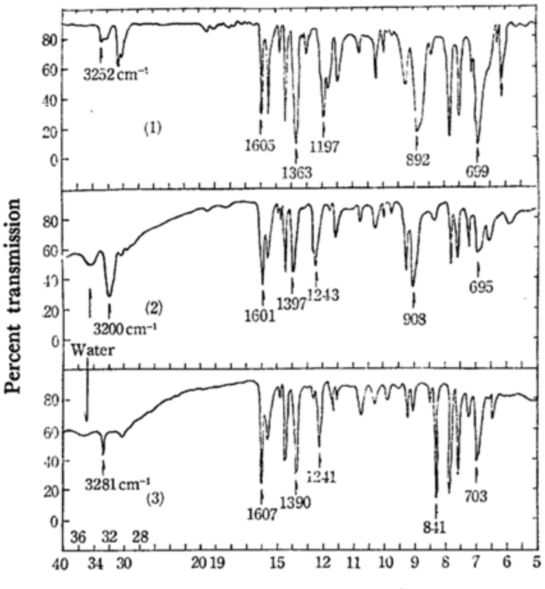

Fig. 5. The infrared spectra.
(1) Free $Ph_2C{=}NH$ (capillary)
(2) $CuCl\cdot Ph_2C{=}NH$ (KBr)
(3) $CuCl_2\cdot 2Ph_2C{=}NH$ (KBr)

Experimental

Reagents. *Copper(II) Chloride.* Anhydrous copper(II) chloride was prepared through the dehydration by thionyl chloride from commercial copper(II) chloride dihydrate.[10]

Copper(I) Chloride. Commercial copper(I) chloride was treated by dilute sulfurous acid.[11]

Benzophenoneimine. Benzophenoneimine was prepared from phenyl magnesium bromide and benzonitrile[12] and was then distilled and stored under dried nitrogen (bp 146.5—148°C/7.5 mmHg). It contained a small amount of benzophenone as an impurity, judging from its infrared spectrum.

Benzene and n-Hexane. Commercial solvents were dried with sodium, distilled, and stored under dried nitrogen.

Acetonitrile. Commercial acetonitrile was dried with phosphorus pentoxide, distilled, and stored under dried nitrogen.

Chloroform. Commercial chloroform was passed through an alumina column, distilled, and stored under dried nitrogen.

Copper(II) Dipyridine Dichloride ($CuCl_2py_2$). This complex was precipitated by adding pyridine to a methanol solution of copper(II) chloride.

Found: C, 40.66; H, 3.36; N, 9.52%. Calcd. for $CuCl_2\cdot 2C_5H_5N$: C, 41.03; H, 3.45; N, 9.57%.

Procedure. All parts of the preparation of the complexes were carried out under dried nitrogen.

The e. p. r. spectra were observed with a Japan Electron Optics Laboratory Co., Ltd., e. p. r. spectrometer, Model JS-3BS-X. The value of field strength was calculated from the observed signal of the manganese marker. The estimation of the g values were based on accurate measurements of the changes in field strength from the point of approximate calibration.

The infrared spectra were measured with two Japan Spectroscopic Co., Ltd., infrared spectrometers, Model DS-402G and Model DS-301. The spectra of the complexes were measured in the KBr disk (sample 1 mg/KBr 150 mg).

The absorption spectra were observed with a Hitachi Co., Ltd., Hitachi spectrometer, Model ESP-2.

The thermal analyses were carried out with a Rigaku-Denki Co., Ltd., differential thermal and thermogravimetric analyzer.

The melting points were observed with a Yanagimoto Seisakusho Co., Ltd., micro-melting-point apparatus.

Copper(II) Chloride Complexes. a) To 150 m*l* of acetonitrile there were added 0.618 g (4.59 mmol) of copper(II) chloride and 1.701 g (9.40 mmol) of benzophenoneimine. The mixture was then stirred for 1 hr at room temperature, and the precipitates thus formed were separated (1.990 g). These precipitates were recrystallized from a chloroform solution. A grey-purple powder was thus obtained.

Found: C, 61.59; H, 4.30; N, 5.69%. Calcd for $CuCl_2\cdot 2Ph_2C{=}NH$: C, 62.85; H, 4.47; N, 5.64%.

After it had been stored for 12 days under nitrogen at room temperature, the powder was again analyzed.

Found: C, 61.54; H, 4.30; N, 5.67%.

A yellow-brown powder was also obtained as a by-product in the course of recrystallization. This was washed with sufficient amounts of acetonitrile and chloroform.

Found: C, 47.51; H, 3.43; N, 4.52%. Calcd for $CuCl_2\cdot Ph_2C{=}NH$: C, 49.46; H, 3.52; N, 4.44%.

b) In 90 m*l* of chloroform, 4.031 g (30.0 mmol) of copper(II) chloride and 3.567 g (19.7 mmol) of benzophenoneimine were stirred for 45 min at room temperature. The resulting mixture was then filtered. To the green filtrate 90 m*l* of acetonitrile were added, and the resulting precipitate was separated. A grey-purple powder was thus obtained; 0.820 g.

Found: C, 61.23; H, 4.43; N, 5.81; Cl, 15.11%. Calcd for $CuCl_2\cdot 2Ph_2C{=}NH$: C, 62.85; H, 4.47; N, 5.64; Cl, 14.27%.

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[10] A. R. Pray, *Inorg. Syn.*, **5**, 153 (1957).
[11] R. N. Keller and H. D. Wycoff, *ibid.*, **2**, 1 (1946).
[12] P. L. Pickard and T. L. Tolbert, *Org. Syn.*, **44**, 51 (1964).

Thermal Decomposition of the Copper(II) Chloride Complex, I, $CuCl_2 \cdot 2Ph_2C{=}NH$. The complex I was introduced into an e. p. r. sample tube under reduced pressure. This tube was heated in a thermostat at a certain temperature for a desired period. Then the e. p. r. spectrum was observed at room temperature. This procedure was repeated until the signal due to divalent copper disappeared (100°C, 30 min; 130°C, 10 min; 150°C, 15 min; 160°C, 20 min; 165°C, 5 min; 170°C, 5 min; 175°C, 5 min; 177°C, 5 min; 180°C, 5 min; 180°C, 20 min).

The complex I, in a sealed tube under dried nitrogen, was heated at 175°C for 30 min. A dark mass (viscous around 175°C) remained. This was washed with *n*-hexane, and then with hot benzene. From the benzene washing, a yellow powder was obtained after evaporating the benzene. This powder was again dissolved in benzene. By adding *n*-hexane to this benzene solution, a yellow powder was precipitated. The infrared spectrum of this powder was almost identical with that of the complex III.

Found: C, 55.84; H, 4.00; N, 5.53; Cl, 13.69%. Calcd for $CuCl \cdot Ph_2C{=}NH$: C, 55.71; H, 3.91; N, 5.00; Cl, 12.65%.

Copper(I) Chloride Complexes. In 25 m*l* of benzene, 1.064 g (10.7 mmol) of copper(I) chloride and 5.874 g (32.4 mmol) of benzophenoneimine were mixed and then stirred for 140 min at room temperature; this resulted in a red solution. To this solution were added 50 m*l* of *n*-hexane. A red viscous liquid was then separated. This liquid was dried under reduced pressure (about 20 mmHg) for 90 min. To the residue there were then added 25 m*l* of benzene. Some insoluble pale yellow needles were obtained after filtration; 2.160 g.

Found: C, 56.02; H, 4.23; N, 4.98; Cl, 12.58%. Calcd for $CuCl \cdot Ph_2C{=}NH$: C, 55.71; H, 3.96; N, 5.00; Cl, 12.65%.

From the benzene solution, there remained a red viscous mass after the benzene had been stripped off. This mass gradually crystallized to yield a red, needle-like powder. The powder was then washed with a small amount of *n*-hexane, and analyzed.

Found: C, 68.77; H, 4.93; N, 6.03%. Calcd for $CuCl \cdot 2Ph_2C{=}NH$: C, 67.66; H, 4.81; N, 6.07; Cl, 7.68%.
In another case, however, the powder was washed with a larger amount of *n*-hexane and then analyzed.

Found: C, 61.42; H, 4.36; N, 5.81; Cl, 10.23%.