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# Shielding Effect of *Ortho*-Substituents on Magnetic Moments and d–d Bands in Chloro-*N*-phenylsalicylideneiminatocopper(II)[*1]

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Complexes with the formula, $Cu(\overset{1}{O}\cdot C_6H_4\cdot \overset{2}{C}H{=}N\text{-}Ph\text{-}X)Cl$, where Ph-X is a mono- or di-substituted phenyl group, were prepared. A dimeric structure was postulated for these complexes based on the observed subnormal magnetic moments and the chemical formula. For these complexes, a linear relation was observed to exist between the magnetic moments, $\mu_{\text{eff}}^{25°\text{C}}$, and the d–d band positions, $\tilde{\nu}_{\text{max}}$. The d–d bands of the dimeric complexes with *o*-substituents appeared at shorter wavelengths than those with *m*- or *p*-substituents irrespective of the polar nature of the substituents. A similar *ortho*-effect was also observed for the magnetic moments; complexes with *o*-substituents were observed to have smaller moment values than those with *m*- or *p*-substituents. The *ortho*-effect was also observed in the d–d bands of the monomeric bis-complexes $Cu(\overset{1}{O}\cdot C_6H_4\cdot \overset{2}{C}H{=}N\text{–}Ph\text{–}X)_2$ and their d–d bands when X=*o*-substituents appeared at shorter wavelengths than those with *m*- or *p*-substituents. These *ortho*-effects decreased for the solution spectra of the monomeric complexes.

In a previous paper,1) it was reported that, despite the wide variation in the polar nature of the substituents in dimeric pyridine *N*-oxides copper(II) chloride complexes a linear relation exists between the magnetic moments, $\mu_{\text{eff}}^{25°\text{C}}$, and the d–d band positions, $\tilde{\nu}_{\text{max}}$. No such correlation, however, is found between the polar nature of the substituents in terms of Hammett's $\sigma$ constants and the magnetic moments of the d–d band positions. The breakdown of Hammett's rule in these dimeric systems was correlated to a steric effect of the substituents on the central metal atom overlapped by their polar effect. The substituents in the aromatic ring which rotates around the N–C bond perpendicular to the coordination plane, will, depending on their size or positions, shield the fifth coordinating site of the central metal atom from the influences of other molecules or ions. This type of shielding effect makes the d–d bands shift towards shorter wavelengths and lowers the magnetic moments compared to those of the parent complexes.

In order to test the validity of these observations for other dimeric complexes, we have prepared copper(II) complexes with the formula, Cu(Sal·N–Ph–X)Cl[*2] and studied their magnetic and spectral properties. Spectral measurements were also made for the parent bis-complexes $Cu(Sal\cdot N\text{–}Ph\text{–}X)_2$.

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[*1] A part of this study was presented by a) M. Kato, Y. Muto, H. N. Ramaswamy, H. B. Jonassen and K. Imai at the 16th Conference on Coordination Chemistry of the Chemical Society of Japan, Tokyo, November, 1966, Proceedings, p. 68. b) M. Kato, Y. Muto, K. Imai and H. B. Jonassen at the 20th Annual Meeting of the Chemical Society of Japan, Tokyo, April, 1967, Proceedings II, p. 75. c) Y. Muto, M. Kato H. B. Jonassen, H. N. Ramaswamy and K. Imai at the 10th International Conference on Coordination Chemistry, Nikko, September, 1967, and d) M. Kato, Y. Muto, H. B. Jonassen, K. Imai, K. Katsuki and S. Ikegami at the 18th Conference on Coordination Chemistry of the Chemical Society of Japan, Kyoto, October, 1968, Proceedings, p. 319.

1) Y. Muto, M. Kato, H. B. Jonassen and L. C. Cusachs, This Bulletin, **42**, 417 (1969).

[*2] $Sal\cdot N{=}\cdot\overset{1}{O}\cdot C_6H_4\cdot\overset{2}{C}H{=}N\cdot$ and Ph–X=mono- or di-substituted phenyl group with substituent X.

TABLE 1. ANALYTICAL DATA OF $Cu(\overset{1}{O}\cdot C_6H_4\cdot \overset{2}{C}H=N-Ph-X)Cl$*

| Substituent X | C% | | H% | | N% | | Cu% | |
|---|---|---|---|---|---|---|---|---|
| | Found | Calcd | Found | Calcd | Found | Calcd | Found | Calcd |
| H | 53.15 | 52.89 | 3.64 | 3.41 | 4.76 | 4.74 | 21.38 | 21.52 |
| 2-$CH_3$ | 54.29 | 54.38 | 4.06 | 3.91 | 4.81 | 4.53 | 20.60 | 20.55 |
| 3-$CH_3$ | 54.42 | 54.38 | 4.04 | 3.91 | 4.51 | 4.53 | 20.64 | 20.55 |
| 4-$CH_3$ | 54.46 | 54.38 | 4.00 | 3.91 | 4.50 | 4.53 | 20.60 | 20.55 |
| 2-Cl | 47.67 | 47.36 | 3.17 | 2.75 | 4.32 | 4.25 | 19.24 | 19.27 |
| 3-Cl | 47.51 | 47.36 | 3.03 | 2.75 | 4.16 | 4.25 | 19.27 | 19.27 |
| 4-Cl | 47.66 | 47.36 | 2.99 | 2.75 | 4.18 | 4.25 | 19.33 | 19.27 |
| 2-$NO_2$ | 45.47 | 45.89 | 2.81 | 2.67 | 8.54 | 8.23 | 18.79 | 18.68 |
| 3-$NO_2$ | 46.17 | 45.89 | 3.04 | 2.67 | 8.10 | 8.23 | 18.34 | 18.68 |
| 4-$NO_2$ | 45.77 | 45.89 | 2.98 | 2.67 | 8.02 | 8.23 | 18.73 | 18.68 |
| 2,6-$(CH_3)_2$ | 55.53 | 55.73 | 4.50 | 4.37 | 4.26 | 4.33 | 19.59 | 19.65 |
| 2,4-$(CH_3)_2$ ($\frac{1}{4}C_2H_5OH$) | 56.08 | 55.61 | 4.65 | 4.67 | 4.43 | 4.18 | 18.88 | 18.98 |
| 2,6-$Cl_2$ | 43.88 | 42.88 | 2.30 | 2.21 | 4.05 | 3.85 | 17.45 | 17.45 |
| 2,3-$Cl_2$ ($\frac{1}{4}C_2H_5OH$) | 42.81 | 43.17 | 2.60 | 2.55 | 3.87 | 3.73 | 17.12 | 16.92 |
| 2,5-$Cl_2$ ($\frac{1}{4}C_2H_5OH$) | 43.01 | 43.17 | 2.52 | 2.55 | 3.86 | 3.73 | 16.99 | 16.92 |
| 3,4-$Cl_2$ ($\frac{1}{2}C_2H_5OH$) | 43.58 | 43.43 | 2.49 | 2.86 | 3.92 | 3.62 | 16.63 | 16.41 |

* Ph–X=mono- or di-substituted phenyl group with substituent X.
Indications in the parentheses in the first column are the solvent molecules combined with the complexes for the chemical formula.

The present study also compares the difference in the pathways of polar effect transmittance in pyridine *N*-oxide and *N*-phenylsalicylaldimine complexes, and the magnetic interactions between copper(II) ions in a dimer.

## Experimental

**Materials.** Salicylaldehyde, various aryl amines and anhydrous cupric chloride (Fisher certified reagent) were obtained commercially.

**Preparation of the Copper(II) Complexes.** *a) Parent Bis(N-phenylsalicylideneiminato)copper(II) Complexes.* These were prepared by the general method.[2,3] In most cases, methanol or ethanol was used as solvent but in the preparation of complexes with *o*-chloro or *o*-nitro group, dimethylformamide was employed instead of alcohols to elevate the reaction temperature. The purity of the recrystallized complexes was checked by copper analysis.

*b) Chloro Copper(II) Complexes.* In a typical preparation, a filtered solution of anhydrous cupric chloride in ethanol was added to one of the recrystallized parent complexes in a flask. The mole ratio of cupric chloride to each complex was 1.1 : 1, *i. e.*, ten percent excess of $CuCl_2$ over the stoichiometric quantity was used. The alcoholic mixture in the flask equipped with a condenser was stirred on a hot plate for two hours. The precipitated product was filtered off from solvent on a glass filter, washed several times with ethanol and once with ether, and dried at 70—80°C. The analytical data are listed in Table 1.

**Magnetic Susceptibility Determinations.** These data were obtained by the Gouy method at room temperature. The effective magnetic moment, $\mu_{eff}$, per copper atom was calculated from the expression $\mu_{eff}=2.83\sqrt{\chi_M\cdot T}$ B.M., where $\chi_M$ is the molar susceptibility corrected using Pascal's constants,[4,5] for the diamagnetism of all the atoms in the compounds. The temperature-independent paramagnetism associated with the copper ions was not included in the calculation of $\mu_{eff}$ throughout this work. The magnetic moments observed at room temperature were corrected for minor room temperature variations to those at 25°C, $\mu_{eff}^{25°C}$, by using Bleaney and Bowers' equation assuming $g=2.2$.[6,7] These results are given in Table 2.

**Spectral Measurements.** These were made in 340—2000 m$\mu$ region on the automatic recording Hitachi EPS-3T spectrophotometer. The diffuse reflectance spectra of the parent bis-complexes and the copper(II) chloride complexes were measured with a reflectance attachment. Magnesium oxide or lithium fluoride of optical grade was used as the standard of light reflectance. Instead of diluting the compounds with the reference material, appropriate absorbancy ranges were selected by controlling the sensitivity knobs on the spectrophotometer. The band maxima of these complexes are recorded in Tables 3 and 5. Spectral measurements were also made for some of the paren bis-complexes in chloroform. The data of these solution

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[3] P. Pfeiffer and H. Krebs, *J. prakt. Chem. N.F.*, **155**, 77 (1940).

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[5] P. W. Selwood, "Magnetochemistry," Interscience Publishers, New York (1956), pp 78 and 91.

[6] B. Bleaney and K. D. Bowers, *Proc. Roy. Soc.* (*London*), **A214**, 451 (1952).

[7] M. Kato, Y. Muto, H. B. Jonassen, K. Imai and A. Harano, This Bulletin, **41**, 1864 (1968).

TABLE 2. MAGNETIC DATA OF $Cu(\overset{1}{O}\cdot C_6H_4\cdot\overset{2}{C}H{=}N\text{–}Ph\text{–}X)Cl^*$

| Substituent X | Susceptibility $\chi_g\cdot 10^6$ (cgs, emu) | Temperature (°K) | $\mu_{eff}$ (B.M.) | $\mu_{eff}^{25°C}$ (B.M.) |
|---|---|---|---|---|
| H | 2.23 | 295 | 1.38 | 1.39 |
| $2\text{-}CH_3$ | 1.57 | 303 | 1.26 | 1.24 |
| $3\text{-}CH_3$ | 2.74 | 302 | 1.56 | 1.56 |
| $4\text{-}CH_3$ | 1.96 | 287 | 1.33 | 1.35 |
| 2-Cl | 1.17 | 295 | 1.14 | 1.15 |
| 3-Cl | 1.55 | 299 | 1.28 | 1.27 |
| 4-Cl | 1.67 | 302.5 | 1.32 | 1.31 |
| $2\text{-}NO_2$ | 0.92 | 296 | 1.06 | 1.06 |
| $3\text{-}NO_2$ | 2.47 | 296 | 1.54 | 1.54 |
| $4\text{-}NO_2$ | $0.71_5$ | 300 | 0.98 | 0.97 |
| $2,6\text{-}(CH_3)_2$ | 1.70 | 290 | 1.30 | 1.32 |
| $2,4\text{-}(CH_3)_2$ ($\frac{1}{4}C_2H_5OH$) | 1.51 | 290 | 1.26 | 1.28 |
| $2,6\text{-}Cl_2$ | 1.15 | 285 | 1.17 | 1.21 |
| $2,3\text{-}Cl_2$ ($\frac{1}{4}C_2H_5OH$) | 1.26 | 286 | 1.24 | 1.27 |
| $2,5\text{-}Cl_2$ ($\frac{1}{4}C_2H_5OH$) | 1.02 | 286 | 1.15 | 1.18 |
| $3,4\text{-}Cl_2$ ($\frac{1}{2}C_2H_5OH$) | 1.29 | 286 | 1.27 | 1.30 |

* See the footnote of Table 1.

TABLE 3. DATA OF REFLECTANCE SPECTRA OF $Cu(\overset{1}{O}\cdot C_6H_4\cdot\overset{2}{C}H{=}N\text{–}Ph\text{–}X)_2^{**}$

| Substituent X | Band maxima, $\lambda_{max}$, mμ |
|---|---|
| H | 385 vs,sh 465 vs,sh 530 s,sh 694 s* 1690 vw |
| $2\text{-}CH_3$ | 375 vs,br 465 vs,sh 673 s* 1710 vw |
| $3\text{-}CH_3$ | 377 vs,br 485 vs,br,sh 733 s* 1715 vw |
| $4\text{-}CH_3$ | 362 vs 390 vs,br,sh 470 vs,sh 560 s,sh 710 s* 1710 vw |
| 2-Cl | 375 vs,br 460 vs,sh 545 s,sh 693 s* 1690 vw |
| 3-Cl | 370 vs,br,sh 500 vs,br,sh 736 s* 1685 vw |
| 4-Cl | 380 vs,br 495 vs,sh 730 s* 1690 vw |
| $3\text{-}NO_2$ | (∼ 405) vs,br,dp 495 vs,br,sh 737 s* 1680 vw |
| $4\text{-}NO_2$ | (405 505) vs,br,dp 750 s* 1690 w |
| $2,6\text{-}(CH_3)_2$ | 390 vs,sh 465 s,sh 669 s* 1705 w |
| $2,4\text{-}(CH_3)_2$ | 390 vs,sh 460 vs,sh 668 s* 1710 w |
| $2,6\text{-}Cl_2$ | 385 vs,br,sh 470 vs,sh 690 s* 1690 w |
| $2,3\text{-}Cl_2$ | (400 430) vs,dp 495 vs,sh 590 s,sh 748 s* 1685 w |
| $2,5\text{-}Cl_2$ | 400 vs,br,sh 480 vs,sh 600 vs,sh 794 s* 1690 vw |
| $3,4\text{-}Cl_2$ | (385 445) vs,br,sh 530 vs,sh 776 s* 1690 vw |

** See the footnote of Table 1. vs=very strong s=strong w=weak vw=very weak sh=shoulder br=broad dp=double peak, two bands in contiguity.

*=the d–d band which was employed in the discussion of substituent effect in text.

TABLE 4. DATA OF ABSORPTION SPECTRA IN $CHCl_3$ SOLUTION OF $Cu(\overset{1}{O}\cdot C_6H_4\cdot\overset{2}{C}H{=}N\text{–}Ph\text{–}X)_2^*$

| Substituent X | Absorption maxima and extinction coefficients $\lambda_{max}$, mμ (log $\varepsilon_{max}$) | | |
|---|---|---|---|
| $2\text{-}CH_3$ | 394(4.08) | 460 br,sh | 647(2.16)* |
| $3\text{-}CH_3$ | 399(4.09) | 470 br,sh | 674(2.40)* |
| $4\text{-}CH_3$ | 396(4.23) | 475 br,sh | 677(2.42)* |
| 2-Cl | 397(3.89) | 470 sh | 659(2.09)* |
| 3-Cl | 402(3.94) | 470 br,sh | 668(2.32)* |
| 4-Cl | 401(4.21) | 480 br,sh | 669(2.32)* |

* See the footnotes of Tables 1 and 3.

TABLE 5. DATA OF DIFFUSE REFLECTANCE SPECTRA OF $Cu(\overset{1}{O}\cdot C_6H_4\cdot\overset{2}{C}H{=}N\text{–}Ph\text{–}X)Cl^*$

| Substituent X | Band maxima, $\lambda_{max}$, mμ |
|---|---|
| H | (380 425 515) vs,br,sh 890 s* 1690 vw |
| $2\text{-}CH_3$ | (366 440 520) vs,br,sh 830 s* 1700 vw |
| $3\text{-}CH_3$ | (365 445 525) vs,br,sh (680 s,sh 920 s*)dp 1695 vw |
| $4\text{-}CH_3$ | 370 vs 440 vs,br,sh 535 vs,br,sh 870 s* 1700 vw |
| 2-Cl | 360 vs 415 vs,sh 530 s,br,sh (664 825*) s,dp 1690 vw |
| 3-Cl | 370 vs,sh 420 vs,br,sh 525 s,sh 830 s* 1685 vw |
| 4-Cl | (370 vs 445 vs 530 s) br,sh 880 s* 1690 vw |
| $2\text{-}NO_2$ | 410 vs,br (780 880 br*) s,dp 1690 vw |
| $3\text{-}NO_2$ | (380 vs 465 vs 540 s) br,sh (686 915*) s,dp 1675 vw |
| $4\text{-}NO_2$ | 385 vs,br,sh 440 vs,br,sh 900 vs,br* 1670 vw |
| $2,6\text{-}(CH_3)_2$ | 440 vs,br,sh 871 s* 1690 vw |
| $2,4\text{-}(CH_3)_2$ ($\frac{1}{4}C_2H_5OH$) | 440 vs 530 vs,sh 855 s* 1710 vw |
| $2,6\text{-}Cl_2$ | (380 525) vs,br,sh (673 857*) s,dp 1680 vw |
| $2,3\text{-}Cl_2$ ($\frac{1}{4}C_2H_5OH$) | 385 vs, sh 535 s, sh (675 875*) s, dp 1685 vw |
| $2,5\text{-}Cl_2$ ($\frac{1}{4}C_2H_5OH$) | 390 vs,sh 540 s,sh (680 885*) s,dp 1680 vw |
| $3,4\text{-}Cl_2$ ($\frac{1}{2}C_2H_5OH$) | (380 435 530) vs,br,sh 868 s* 1690 vw |

* See the footnotes of Tables 1 and 3.

spectra are given in Table 4. The bands listed in these tables may be resolved into more than one component.

## Results and Discussion

**Parent Monomeric Complexes.** The parent monomeric complexes give rise to several bands in 340—2000 mμ region in the diffuse reflectance spectra (*cf.* Tables 3 and 4). Many of these bands are not well characterized. The bands at wavelengths shorter than about 500 mμ can probably be attributed to charge-transfer or intra-ligand transition.[8,9] The bands recorded at wavelengths longer than about 1200 mμ, are difficult to assign[10] and do not seem to be important in this discussion. The bands appearing around 700 mμ are the most distinct (marked with an asterisk in Tables 3 and 4), and most of these are considered to be the well-known d–d bands of the planar type of copper(II) complexes.[7–12]

Those of the complexes with a substituent in the *ortho*-position appeared at shorter wavelengths than those with a substituent at the *meta*- or *para*-position, *i. e.*,

$$\lambda_{\max}(o\text{-}) < \lambda_{\max}(m\text{-}) \sim \lambda_{\max}(p\text{-})$$

The difference in $\lambda_{\max}$ between *meta*- and *para*-complexes is small compared to that between the *ortho*- and *meta*- or *para*-complexes. This is illustrated by the spectral curves of the complexes with methyl group in Fig. 1. On the other hand, essentially no difference in $\lambda_{\max}$ of d–d bands was observed among complexes with different substituents at the same ring positions. Figure 2 shows this for the absorption bands of complexes with *m*-Cl, *m*-$CH_3$ and *m*-$NO_2$, all at about 740—745 mμ.

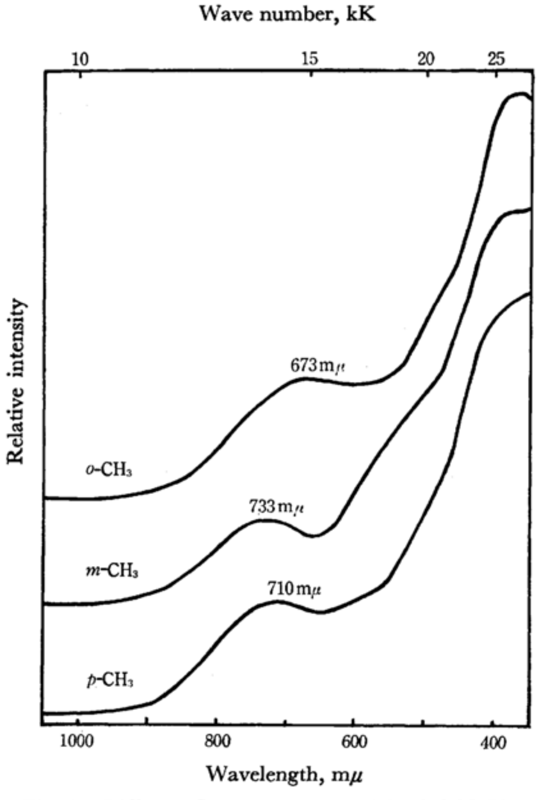

Fig. 1. Diffuse reflectance spectra of Cu(Sal·N-Ph-$CH_3$)$_2$.

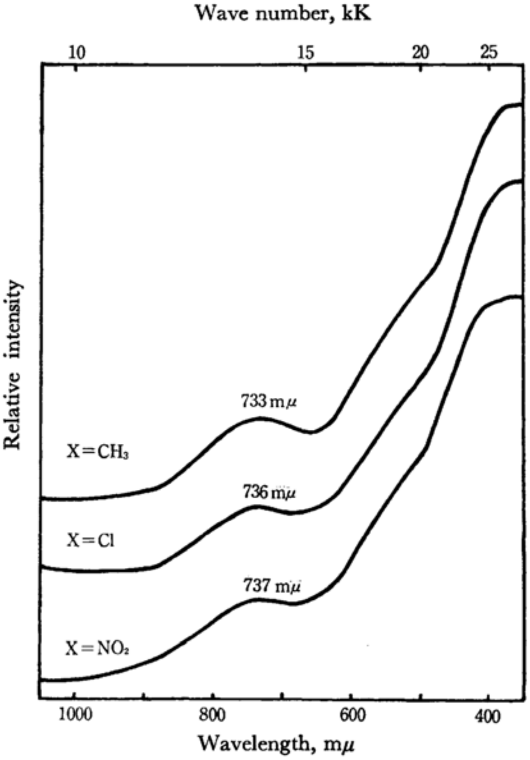

Fig. 2. Diffuse reflectance spectra of Cu(Sal·N-Ph-X)$_2$ with X=*m*-$CH_3$, *m*-Cl, and *m*-$NO_2$.

An X-ray analysis of the parent compound, bis(*N*-phenyl-salicylideneiminato)copper(II)[13] has shown that the plane of the *N*-phenyl group is nearly perpendicular to the $\left(\begin{smallmatrix}O\\N\end{smallmatrix}\!>\!Cu\!<\!\begin{smallmatrix}N\\O\end{smallmatrix}\right)$ plane. Under such conditions, substituents attached in the *ortho*-position of the phenyl group should have a great tendency to shield the fifth coordination site of the copper(II) ions. Such shielding effect is said to stabilize the complexes and to produce the observed "blue shift" of the d–d band.[1,14–17]

The "blue shift" effect of *ortho*-substituents on the d–d bands in chloroform solution was apparently retained even though it decreased compared to

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[11] J. Ferguson, *J. Chem. Phys.*, **35**, 1612 (1961).

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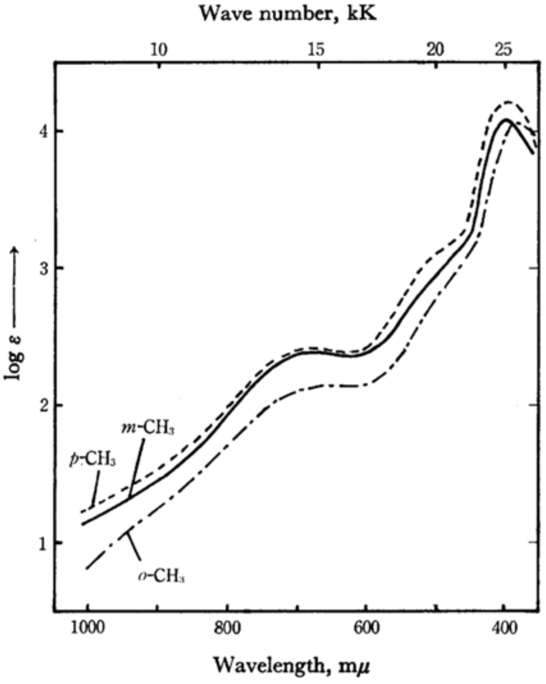

Fig. 3. Spectra of Cu(Sal·N-Ph-CH$_3$)$_2$ in CHCl$_3$.

that in the solid state (*cf.* Fig. 3).

In solid complexes the vacant coordination sites of the copper(II) ion are subjected to the influences of adjacent atoms, ions, or molecules. However, in solutions of weak-coordinating solvents such as chloroform, these influences should decrease as the distances between the complexes increases. Since the solvent molecules display a kind of shielding effect, it is then quite probable that the shielding effect due to the steric condition of the *ortho*-substituents is much decreased. Since the copper(II) ion has one unpaired electron, a continuous variation in the influence of the ligand field or in the stereochemistry, seems to be possible.[18] The *ortho*-substituent effect for the di-substituted complexes, was retained in some cases (those with methyl group) but in other cases it became obscure (those with the chloro group) (*cf.* Table 3). This may be due to an additional steric effect which interferes with the existence of stable planar complex due to the preparatory method used for the solid complexes.[1,8,18,19]

**Dimeric Chloro Copper(II) Complexes.** No X-ray analysis for dimeric chloro copper(II) complexes similar to those we prepared has been reported. On the basis of the chemical formula of these complexes which contain only three coordinating atoms, and of the observed low magnetic moments, we have assumed a dimeric structure of the type given in Fig. 4. Of the three types of coordinating atoms in the dimeric complexes, the phenolic oxygen atom is most probably the bridging atom because (1) the imino-nitrogen atom can not span the copper(II) ions because of steric hindrance of the *N*-phenyl group, and (2) a low magnetic moment of 1—1.5 B.M. recorded for these dimeric complexes has never been observed in copper(II) complexes with chlorine-bridges.[20]

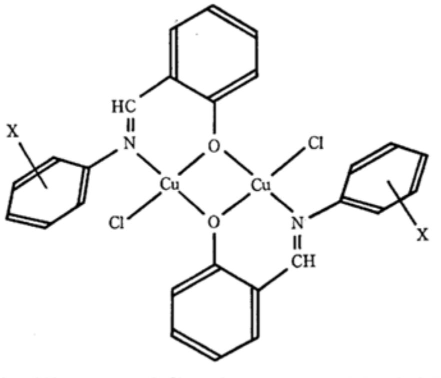

Fig. 4. The assumed dimeric structure of Cu(Sal·N-Ph-X)Cl.

*a) Diffuse Reflectance Spectra.* The diffuse reflectance spectra of the chloro copper(II) complexes revealed several bands in the 340—2000 mμ region similar to the parent monomeric complexes (*cf.* Table 5). The main d–d band which corresponds to that of the parent complexes can easily be distinguished from the other bands. The d–d band maximum occurs at a much longer wavelengths (800—900 mμ) than that of the monomeric complexes suggesting a distorted planar or pseudo-tetrahedral structure for these complexes.[8–10,19,21–23] Sacconi found that the salicylideneiminato-copper(II) of pseudo-tetrahedral type are maroon,[8] and these dimeric copper(II) chloride complexes are all maroon or brown. Chloro(*N*-alkylsalicylideneiminato)copper(II) complexes which we studied previously*[1–b,24] are closely related to chloro(*N*-phenylsalicylideneiminato)copper(II); they also are brown. They showed three bands in the 340—1500 mμ range with essentially the same spectral features as those of bis(*N*-alkylsalicylideneiminato)-

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copper(II) with pseudo-tetrahedral structure.[8,21] The magnetic moments and the main d–d band positions of these chloro copper(II) complexes with *N*-alkyl groups fall in the range of 1—1.4 B.M. and of 800—900 m$\mu$ respectively, the same ranges as those observed for the dimeric complexes with *N*-phenyl groups of the present study.

Each copper(II) ion in these dimeric complexes is effectively surrounded by three coordinating atoms, one of which is the chloride ion which has a position in the early part of the spectrochemical series.[25] The ligand field strength is therefore much weaker than that of the monomeric complexes. The diffuse reflectance spectra of the dimeric complexes with mono-substituted *N*-phenyl group, showed a "blue shift" effect of *ortho*-substituents just as the parent monomeric complexes (*cf.* Fig. 5 and Table 5). This suggests that a structural feature important in bis(*N*-phenylsalicylideneiminato)copper(II), namely the upward rotation of the *N*-phenyl group perpendicular to the coordination plane, is substantially retained in these dimeric complexes. The same type of *ortho*-substituent effects was observed in the d–d bands and in the magnetic interaction between copper(II) ions in a pair[1] for the dimeric copper(II) chloride complexes with pyridine *N*-oxides. The structure of the parent copper(II) chloride complex with pyridine *N*-oxide shows that the pyridine ring is rotated about the O–N bond such that its plane is essentially perpendicular to the coordination sphere of a distorted square-planar geometry.[26,27]

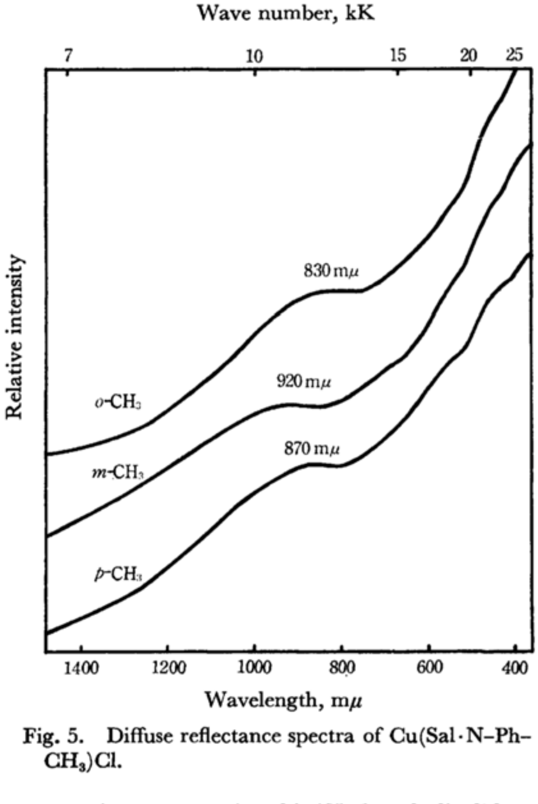

Fig. 5. Diffuse reflectance spectra of Cu(Sal·N–Ph–CH$_3$)Cl.

In the dimeric chloro copper(II) complexes with *N*-phenylsalicylaldimines, as for copper(II) chloride complexes with pyridine *N*-oxides, no correlation was observed to exist between Hammett's $\sigma$ constants of substituents and the d–d band positions.

*b) Magnetic Moments.* For the complexes with a disubstituted *N*-phenyl group, the *ortho*-substituent effect of "lowering at magnetic moment" was observed in these dimeric complexes (*cf.* Table 2), with a few exceptions

$$\mu_{\text{eff}}^{25^\circ\text{C}}(o\text{-}) < \mu_{\text{eff}}^{25^\circ\text{C}}(m\text{-}) \sim \mu_{\text{eff}}^{25^\circ\text{C}}(p\text{-})$$

However, no correlation exists between the polar nature of the substituents in terms of Hammett's constants and the moments. These observations are the same as those in copper(II) chloride complexes with pyridine *N*-oxides.[1]

*c) Linear Relation between d–d Band Positions and Magnetic Moments.* Even though no correlation exists between Hammett's $\sigma$ constants of substituents and the d–d band positions, $\tilde{\nu}_{\max}$, or the magnetic moments corrected to those at 25°C, $\mu_{\text{eff}}^{25^\circ\text{C}}$, a linear relation between $\tilde{\nu}_{\max}$ and $\mu_{\text{eff}}^{25^\circ\text{C}}$ (*cf.* Fig. 6) is found, the same relation observed for the copper(II) chloride complexes with pyridine *N*-oxides.[1,28] In the postulated structure of [Cu(Sal·N–Ph–X)Cl]$_2$ (Fig. 4) the magnetic interac-

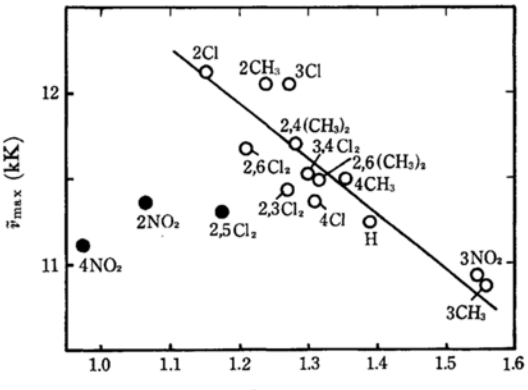

Fig. 6. The plot of the wave number ($\tilde{\nu}_{\max}$ in kK) of d–d bands of Cu(Sal·N–Ph–X)Cl against the corrected magnetic moments ($\mu_{\text{eff}}^{25^\circ\text{C}}$ in B.M.).

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tion between copper(II) ions in a dimeric molecule will most probably occur by a superexchange mechanism through the bridging phenolic oxygen atoms.[29–32] Since the orbital overlap scheme of relevant orbitals for the superexchange interaction should essentially be the same for these two systems, a $\sigma$ type and a $\pi$ type pathway for the superexchange interaction are possible. The $\sigma$ type seems to be more important for the same reason as that given for copper(II) chloride complexes with pyridine *N*-oxides.[1]

In the dimeric complexes with pyridine *N*-oxides, the polar effect of substituents transmits directly to the oxygen atoms which are in the superexchange pathway. On the other hand in [Cu(Sla·N–Ph–X)Cl]$_2$, the substituent effect should transmit to the coordinating nitrogen atoms not in the superexchange pathway. Despite such difference in the transmittance of substituent-polar effect, the steric effect of the substituents appears to be more important in the determination of physicochemical properties of these complexes than the electronic effect of the substituents.

The anomalous properties of *o*-NO$_2$ and *p*-NO$_2$ complexes may be due to a different structure (*cf.* Table 2 and Fig. 6). These compounds have magnetic moments smaller than those expected from the linear relation between $\tilde{\nu}_{\max}$ and $\mu_{\rm eff}^{25^\circ{\rm C}}$; furthermore, whereas the other complexes are brown, these two complexes are greenish-orange in color and their d–d bands are broad. The *o*-NO$_2$ and *p*-NO$_2$ compounds are thus seemingly quite similar to the orange one of the two modifications of Cu(Sal·N–CH$_3$)Cl[*1–b,24]; the orange compound has a moment of 0.9 B.M. and the brown one a moment of 1.47 B.M. at room temperature. The spectral curves of these two modifications are given with those of *p*-NO$_2$ and *m*-NO$_2$ compounds in Fig. 7. The compound with *m*-NO$_2$ group is brown and its spectral feature is essentially the same as that of all other complexes.

The reason for the deviation from linearity for the 2,5-Cl$_2$ compound is not clear at present. However, it is one of the disubstituted compounds and its d–d band is composed of two bands in contiguity (double peak).

The extent of magnetic interaction found in [Cu(Sal·N–Ph–X)Cl]$_2$ ranges from 1 to 1.5 B.M. This is weaker than that observed for the copper(II) chloride complexes with pyridine *N*-oxides (0.2—1 B.M.). On the basis of the p*K* values of ligand molecules[33–36] the Cu–O coordinate bonds in the bridging framework is considered to be stronger in salicylideneiminato-complexes than in pyridine *N*-oxide complexes.

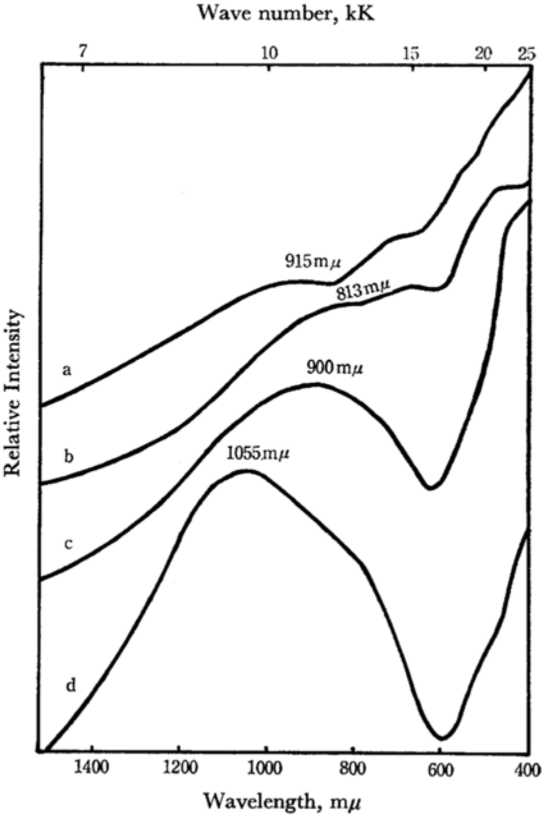

Fig. 7. Diffuse reflectance spectra of (A) Cu(Sal·N–Ph–X)Cl and (B) Cu(Sal·N–CH$_3$)Cl.
(A): curve a, X=*m*-NO$_2$ and curve c, X=*p*-NO$_2$.
(B): curve b, brown modification and curve d, orange modification (*cf.* text).

In the preceding paper, we suggested that the most important factor in the determination of the electron exchange is the bond angle rather than the bond strengths in a pathway, because an effective electron exchange requires a successive overlapping of the relevant orbitals of atoms in a superexchange pathway.[37]

A comparison of the total coordinate bonds in the two complexes shows in [Cu(PyO)Cl$_2$]$_2$[*3] one

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[*3] PyO=pyridine *N*-oxide or its derivatives.

Cu–O (PyO–O) and two Cu–Cl bonds *versus* one Cu–O (phenolic-O), one Cu–N (imino-N) and one Cu–Cl bond for [Cu(Sal·N–Ph–X)Cl]$_2$. This would indicate greater total covalent bond strength in the latter, however, their d–d bands are practically at the same energy (760—900 m$\mu$) for [Cu(PyO)Cl$_2$]$_2$ and (830—900 m$\mu$) for [Cu(Sal·N–Ph–X)Cl]$_2$. This seeming contradiction can be resolved if it is postulated that the stereochemistry of the [Cu(Sal·N–Ph–X)Cl]$_2$ complexes has a greater tetrahedral distortion than [Cu(PyO)Cl$_2$]$_2$.[8,21,22)

This assumption is consistent with the lower range of magnetic moments (0.2—1 B.M.) in the pyridine *N*-oxide and with the higher range (1—1.5 B.M.) in *N*-phenylsalicylideneiminato-complexes. On the basis of the assumed pathways the orbital overlap effective for the superexchange interaction should be weaker in the system with a greater pseudo-tetrahedral framework than in that with greater planar framework.

A linear relationship between d–d band position and magnetic moments in dimeric [Cu(Sal·N–Ph–X)Cl]$_2$ has been established similar to that found previously for dimeric [Cu(PyO)Cl$_2$]$_2$. It holds even though in the two complexes there is a difference in the position of the coordinate bonds through which the substituent polar effect is transmitted in the superexchange pathway.

A shielding effect of the substituents on d–d band position and magnetic moments has also been observed which is greatest for *ortho* substitution (*ortho*-effect) even though a change in polarity of the substituents has no effect on either d–d band position or magnetic moments.