BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 41 1864—1870 (1968)

Magnetic Moments and d–d Bands of *N*-*n*-Propanol-salicylaldiminato-copper(II)[*1]

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(Received February 29, 1968)

The reaction of cupric acetate with the reaction mixture of γ-aminopropyl alcohol and substituted salicylaldehydes in ethanol gave dimeric copper(II) complexes. The postulated structure of these complexes makes it possible to test the substituent effect transmitted to the coordinating atoms which are not in the superexchange pathway between copper(II) ions in a pair. The magnetic moments observed at room temperature were corrected for the temperature variations to those at 25°C by graphic method based on Bleaney and Bowers' equation. The observed substituent effect on the relation between $\mu_{\text{eff}}^{25^\circ\text{C}}$ and λ_{max} is different from that observed for dimeric cupric halides complexes of substituted pyridine *N*-oxides. In these complexes the substituent effect transmits to the bridging oxygen atom in the superexchange pathway. As compared with the parent complex (H), methyl, chloro and benzo groups weakened the magnetic interaction but nitro group strengthened it. An interpretation of the substituent effect is given based on the idea of the mutual influences on the coordinate bonds.

The correlation of the magnetic interaction between copper(II) ions in a pair in dimeric copper(II) complexes or of some other physicochemical properties of the complexes with their chemical structures has primarily been our interest.[1-3] Several papers of investigation along this line have recently been pub-

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[*1] A part of this study was presented a) by 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 Vol. II, p. 75; b) by Y. Muto, M. Kato, H. B. Jonassen, H. N. Ramaswamy and K. Imai at the 10th International Conference on Coordination Chemistry, Nikko, September, 1967, Proceedings, p. 337; and c) by M. Kato, Y. Muto, H. B. Jonassen, K. Imai and A. Harano at the 17th Conference on Coordination Chemistry of the Chemical Society of Japan, Hiroshima, December, 1967, Proceedings, p. 196. d) The parent compound of this study and some related compounds were reported by S. Yamada, Y. Kuge, and K. Yamanouchi in *Inorg. Chim. Acta*, **1**, 139 (1967). e) A. Nakahara and his coworkers also reported the parent compound and its related compounds at the 17th Conference on Coordination Chemistry of the Chemical Society of Japan, Hiroshima, December, 1967, Proceedings, p. 29.

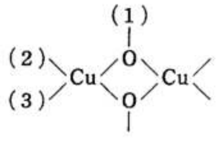
1) Y. Muto and H. B. Jonassen, This Bulletin, **39**, 58 (1966).

2) Y. Muto, M. Kato, H. B. Jonassen and H. N. Ramaswamy, *ibid.*, **40**, 1535 (1967).

3) M. Kato, Y. Muto and H. B. Jonassen, *ibid.*, **40**, 1738 (1967).

lished.[4-9] Unfortunately, however, the observed phenomena are often too complicated to give consistent, clear-cut interpretation throughout the whole studies. In the preceding communication,[3] we reported some empirical rules which were observed for dimeric complexes of cupric halides with pyridine *N*-oxide derivatives. In these complexes, the effect of substituents attached to the pyridine ring essentially propagates to the bridging oxygen atoms in the superexchange interaction pathway.[10,11]

This study reports observations in which the substituent effect transmits to the coordinate bonds not in the pathway of magnetic interaction. Such bonds are shown as (2) or (3) in I.



I

The most suitable compounds for the study of this problem are those with unidentate ligands at (2) or (3) because in such a case the pathway of transmission of the substituent effect is definitely established. However, very few stable dimeric copper(II) complexes with an unidentate ligand containing a variety of substituents have been reported.

For the present purpose, chelation between positions 2 and 3 should not as a first approximation, introduce any important complexity in the interpretation of obtained data. However, the coordinate bonds at (2) or (3) should be electronically insulated from that of (1). The postulated structure of the complexes reported here essentially satisfies the above structural conditions (*cf.* structure II): The mesomeric effect of substituent X is insulated by three methylene groups, between the π-electron system being attached to X and the bridging alcoholic oxygen atoms. The inductive effect of X can also be ignored at the bridging alcoholic oxygen atom owing to its rapid attenuation through the three methylene groups.

In addition to such structural characteristics, these compounds have the following advantages: 1) They are so stable that they do not decompose in boiling sodium hydroxide solution. 2) The bridging oxygen atoms do not have any vacant orbitals of π character capable of accepting the d-electrons of the metal. This makes the mutual influence of the coordinate bonds quite simple and the experimental results can be interpreted unambiguously.[12-19]

Experimental

Materials. Salicylaldehyde and its 5-chloro, 5-nitro and 5,6-benzo derivatives were obtained commercially. The 5-methyl derivative was prepared by the Reimer-Tiemann reaction of *p*-cresol with chloroform.[20]

The Preparation of the Copper(II) Complexes. The reaction mixture of a slight excess of γ-aminopropyl alcohol and salicylaldehyde or one of the derivatives in ethanol was added to the ethanol solution of cupric acetate monohydrate acidified with few drops of glacial acetic acid. Complete dissolution of cupric acetate monohydrate in ethanol

TABLE 1. ANALYTICAL DATA OF COMPLEXES

Substituent X		Analysis, % Cu	C	H	N
H	Found	26.39	49.88	4.60	5.81
	Calcd	26.14	49.92	4.64	5.91
5-CH_3	Found	24.94	51.86	5.14	5.49
	Calcd	25.11	52.09	5.24	5.81
5-Cl	Found	23.09	43.65	3.66	5.09
	Calcd	22.80	43.67	3.73	5.37
5,6-Benzo	Found	21.84	57.82	4.50	4.81
	Calcd	21.64	58.00	4.55	4.92
5-NO_2	Found	22.23	42.03	3.53	9.80
	Calcd	22.22	42.06	3.61	9.81

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[4] M. Kato, H. B. Jonassen and J. C. Fanning, *Chem. Revs.*, **64**, 99 (1964).

[5] J. Lewis, Y. C. Lin, L. K. Royston and R. C. Thompson, *J. Chem. Soc.*, **1965**, 6464.

[6] W. E. Hatfield and F. L. Bunger, *Inorg. Chem.*, **5**, 1161 (1966).

[7] W. E. Hatfield and J. C. Morrison, *ibid.*, **5**, 1390 (1966).

[8] W. E. Hatfield, C. S. Fountain and R. Whyman, *ibid.*, **5**, 1855 (1966).

[9] L. Dubicki and R. L. Martin, *ibid.*, **5**, 2203 (1966).

[10] H. L. Schäfer, J. C. Morrow and H. M. Smith, *J. Chem. Phys.*, **42**, 504 (1965).

[11] R. S. Sager, R. J. Williams and W. H. Watson, *Inorg. Chem.*, **6**, 951 (1967).

[12] F. Basolo and R. G. Pearson, "Progress in Inorganic Chemistry," Vol. IV, ed. by F. A. Cotton, Interscience Publishers, New York (1962), p. 381.

[13] J. Chatt, L. A. Duncanson and L. M. Venanzi, *J. Chem. Soc.*, **1955**, 4456.

[14] J. Chatt, L. A. Duncanson and L. M. Venanzi, *ibid.*, **1955**, 4461.

[15] J. Chatt, L. A. Duncanson, B. L. Shaw and L. M. Venanzi, *Faraday Soc. Discussions*, No. 26, 131 (1958).

[16] F. Basolo, J. Chatt, H. B. Gray, R. G. Pearson and B. L. Shaw, *J. Chem. Soc.*, **1961**, 2207.

[17] D. M. Adams, J. Chatt, J. Gerratt and A. D. Westland, *ibid.*, **1964**, 734.

[18] J. Chatt, N. P. Johnson and B. L. Shaw, *ibid.*, **1964**, 1662.

[19] G. W. Parshall, *J. Am. Chem. Soc.*, **88**, 704 (1966).

[20] F. Tiemann and C. Schotten, *Ber.*, **11**, 773 (1878).

TABLE 2. MAGNETIC DATA OF COMPLEXES

Substituent X	Susceptibility $\chi_g \cdot 10^6$ (cgs, emu.)	Temperature (°K)	$\mu_{\rm eff}$ (B. M.)	$\mu_{\rm eff}^{25^\circ{\rm C}}$ (B. M.)	Difference between the two values of $\mu_{\rm eff}^{25^\circ{\rm C}}$ (B. M.)
H	-0.11	288	0.45_7	0.49_0	0.00_2
	-0.05	303	0.50_5	0.48_8	
5-CH_3	0.00	298	0.55_5	0.55_5	0.00_7
	-0.03	290	0.53_0	0.56_2	
5-Cl	-0.08_6	288	0.49_7	0.52_8	0.00_6
	-0.07	290	0.51_0	0.53_4	
5,6-Benzo	-0.08_4	287	0.54_9	0.58_6	0.01_0
	-0.04	302	0.58_8	0.57_6	
5-NO_2	-0.12_5	303	0.46_3	0.44_7	0.00_7
	-0.16_5	289	0.42_8	0.45_5	

is not required. The mixture was stirred at an elevated temperature for a while. The product precipitated and was filtered off on a glass filter, washed with ethanol and dried. The crude material was recrystallized from pyridine. To obtain a better yield, some ethanol or methanol can be added to the pyridine solution. The preparation was repeated at least twice for each type of compound. The analytical data are listed in Table 1.

Magnetic Susceptibility Determinations. These were obtained by the Gouy method at room temperature. The effective magnetic moment, $\mu_{\rm eff}$, per copper atom was calculated from the expression $\mu_{\rm eff}=2.83\sqrt{\chi_{\rm M}\cdot T}$ B. M., where $\chi_{\rm M}$ is the molar susceptibility corrected using Pascal's constants[21,22] for the diamagnetism of all the atoms in the compounds. The temperature-independent paramagnetism associated with the copper ion was not included in the calculation of $\mu_{\rm eff}$ throughout this work. The magnetic moments were corrected for minor room temperature variations to those at 25°C, $\mu_{\rm eff}^{25^\circ{\rm C}}$, by using Bleaney and Bowers' equation[23] assuming $g=2.2$. The actual correction was made by a graphic method as described in the next section. The susceptibility measurements were made of two different preparations for each compound. The two corrected moment values for each compound coincided within 0.01 B. M. at maximum deviation. The magnetic data were given in Tables 2 and 3.

Graphic Method for Correction of Magnetic Moments for Room Temperature Variations. The Bleaney and Bowers' equation is rearranged as

$$\begin{aligned} J &= \boldsymbol{k}T\ln\{3(g^2/\mu_{\rm eff}{}^2-1)\} \\ &= 2.303\,\boldsymbol{k}T\{0.4771+\log_{10}(g^2/\mu_{\rm eff}{}^2-1)\} \\ &= 2.303\,\boldsymbol{k}TX \qquad (1) \end{aligned}$$

where

$$X=0.4771+\log_{10}(g^2/\mu_{\rm eff}{}^2-1) \qquad (2)$$

J is the energy difference between the singlet and triplet states, $\boldsymbol{k}$, Boltzmann's constant, and g, the Landé splitting factor.

Taking advantage of the constancy of J, from (1) we obtain

$$T_1X_1=T_2X_2 \qquad (3)$$

Assuming $g=2.2$ in Eq. (2), a graph of the plot of X *versus* $\mu_{\rm eff}$ (B. M.) is prepared (Fig. 1). X_1 corresponding the $\mu_{\rm eff}$ observed at T_1 is read from the graph. From Eq. (3) one obtains the value of X_2 for T_2 to which the correction is to be made. The $\mu_{\rm eff}$ corresponding to X_2 is obtained from the graph.

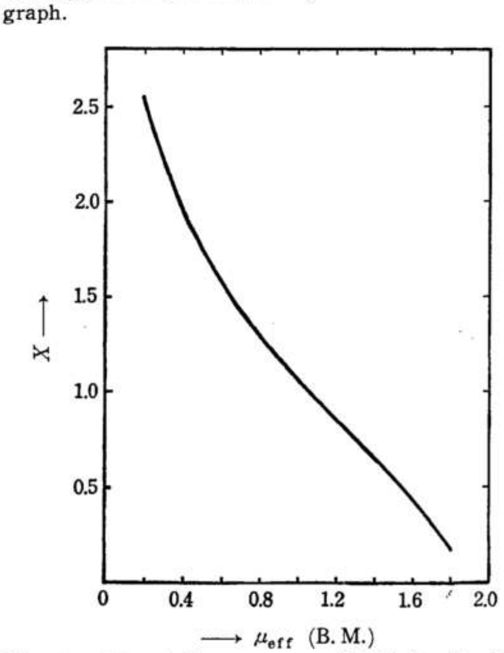

Fig. 1. Plot of X *versus* $\mu_{\rm eff}$ (B. M.) in Eq. (2), where $g=2.2$ is assumed.

Diffuse Reflectance Spectra. The diffuse reflectance spectra of the complexes were measured in 400—1000 mμ region on a Shimadzu QR-50 spectrophotometer with a reflectance attachment. Magne-

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[21] G. Foëx, C. J. Gorter and L. J. Smits, "Constantes Sélectionnées, Diamagnétisme et Paramagnétisme, Relaxation Paramagnétique," Masson & Cie, Paris (1957), p. 222.

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

[23] B. Bleaney and K. D. Bowers, *Proc. Roy. Soc.* (*London*), **A 214**, 451 (1952).

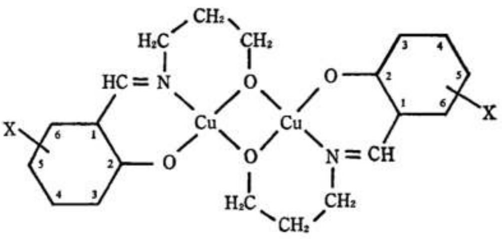
sium carbonate (heavy) was used as the standard of light reflectance and as the base material to dilute the complexes to obtain appropriate intensities in the reflected light. The preparation of the samples for the spectral measurements involves the following steps: A compound was first ground up in a small agate mortar and it was transferred into another agate mortar containing magnesium carbonate which was previously ground up well. The ground complexes and carbonate were mixed up in the mortar. The mortars and other tools for use were kept in a desiccator. The spectrophotometer was checked for wavelength before and after each measurement at 546.1 mμ by use of a mercury lamp. The temperature of the room should be kept as constant as possible during measurement to obtain a good accuracy in wavelength. Using this procedure the greatest variation in the wavelengths at the band maxima was ±1 mμ. The band maxima, λ_{max}, are recorded in Table 3.

TABLE 3. DIFFUSE REFLECTANCE SPECTRAL AND MAGNETIC DATA

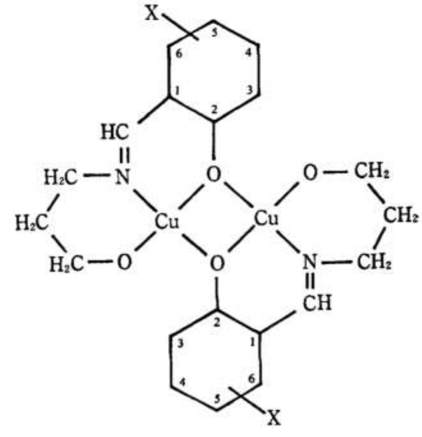
Substituent X	$\mu_{\text{eff}}^{25°\text{C}}$	λ_{max} (mμ)
H (Standard)	0.49	570
5-CH_3	0.56	567
5-Cl	0.53	566
5,6-Benzo	0.58	565
5-NO_2	0.45	566

Results and Discussion

Postulation of Structure. The dimeric nature of the parent compound has been established by molecular weight determinations by Yamada *et al.**1d) and Nakahara *et al.**1e) Two dimeric structures are possible for the complexes under study; one with bridging alcoholic oxygen atoms (II) and the other with bridging phenolic oxygen atoms (III): The data reported here are more in line with structure II and this structure is postulated throughout this study. It was also postulated by Nakahara and coworkers.*1e) Various physicochemical studies of these complexes are presently in progress by our group and Nakahara's group.*1e) The data reported here seem to indicate that structure II is the preferred one. Nakahara and coworkers also prefer this structure. Several experimental facts seem to point in this direction.

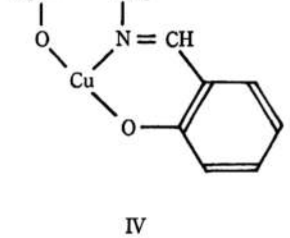


II



III

The first is related to the various synthetic efforts to make the complexes with the two ligands given in structure IV and V. The stability of the dimeric complexes should essentially be determined by the nature of the bridging groups and the electronic atmosphere of its neighbors in the chelate ring. If the phenolic oxygen atoms bridge between the two copper ions the stability of the two complexes represented in IV and V should be about the same since the electronic atmosphere in the chelating rings are the same (structure VI). On the other hand if the alcohol oxygens are the bridging atoms, the stabilities of the two complexes should be quite different. As structures VII and VIII show the sizes of the chelate rings involving the bridging oxygen are different in the two cases.



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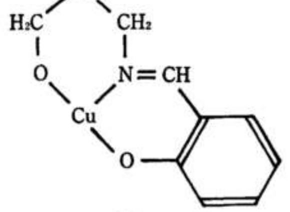
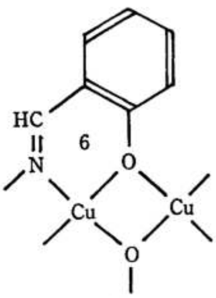
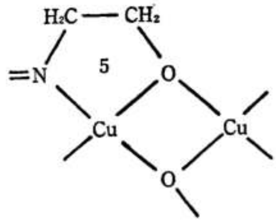


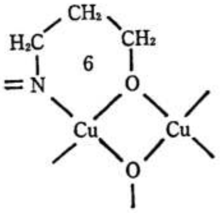
V



VI



VII



VIII

Nakahara and coworkers[24] have reported that they were able to prepare the monomeric complex of IV with a water molecule occupying the fourth coordination position. This complex could not be prepared for the ligand from V. On the other hand, the dimeric complex can be prepared with ligand V but not with ligand from IV. Such differences would be expected if the structural difference were large enough such as shown in VII and VIII. Nakahara and coworkers[*1e,24-26] are presently investigating the correlation between the stability of complexes with fused rings and the number of members in the fused ring.

The second experimental fact is related to magnetic studies. Comparative studies of magnetic studies of dimeric copper(II) complexes indicate that the magnetic moments of complexes with bridging phenolic oxygen atoms are usually greater than those of complexes with bridging alcoholic oxygen atoms.[*1a,b,27-29] The observed moments of about 0.5 B. M. for copper(II) ion for the complexes are much smaller than those complexes containing phenolic oxygen bridges.

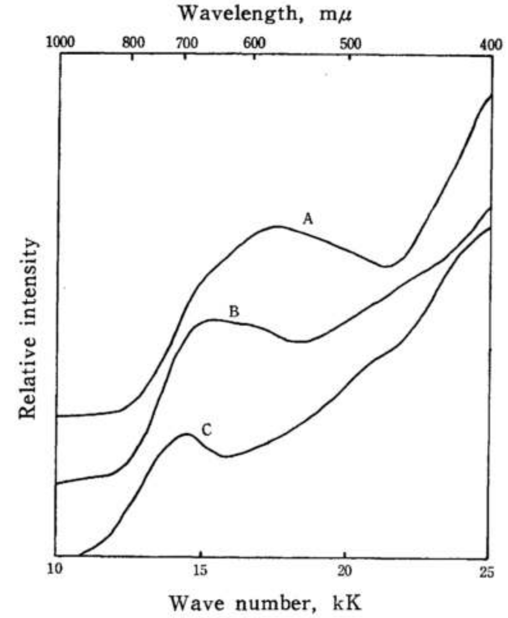


Fig. 2. Diffuse reflectance spectra of *N*-*n*-propanolsalicylaldiminato-copper(II) (A), bis (*N*-methylsalicyl-aldiminato)-copper(II) (B), and bis(*N*-phenylsalicylaldiminato)-copper(II) (C).

Diffuse Reflectance Spectra. The five complexes investigated show essentially the same absorption characteristics and are very similar to that of the parent complex given in Fig. 2. The monomeric complexes of some of these ligands have been studied by X-ray analysis and were found to be planar: [bis(*N*-phenylsalicylaldiminato)-copper(II)[30] and bis(*N*-methylsalicylaldiminato)-copper(II)[31]]. For comparison, in Fig. 2, are given the reflectance spectra of these complexes. Their solution spectra have also been reported.[*1d,32,33] A comparative study of the spectra of the dimeric and monomeric complexes indicates that both types can be described as square coplanar.[34,35] Even though in the dimeric

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24) A. Nakahara, H. Yamamoto and H. Matsumoto, *Sci. Rep., College of Gene. Edu., Osaka Univ.*, **12**, 11 (1963).

25) A. Nakahara, H. Yamamoto and H. Matsumoto, This Bulletin, **37**, 1137 (1964).

26) A. Nakahara and his coworkers, Paper presented at 20th Annual Meeting of the Chemical Society of Japan, Tokyo, April, 1967, Proceedings Vol. II, p. 9.

27) M. Kato, Y. Muto, H. N. Ramaswamy, H. B. Jonassen, K. Imai and K. Ito, Paper presented at the 19th Annual Meeting of the Chemical Society of Japan, Tokyo, April, 1966, Proceedings Vol. II, p. 135.

28) J. A. Bertrand and R. I. Kaplan, *Inorg. Chem.*, **4**, 1657 (1965).

29) E. Uhlig and K. Staiger, *Z. anorg. u. allgem. Chem.*, **346**, 21 (1966).

30) L. Wei, R. M. Stogsdill and E. C. Lingafelter, *Acta Cryst.*, **17**, 1058 (1964).

31) E. C. Lingafelter, G. L. Simmons, B. Morosin, C. Scheringer and C. Freiburg, *ibid.*, **14**, 1222 (1961).

32) Y. Muto, This Bulletin, **33**, 604 (1960).

33) S. Yamada and H. Nishikawa, *ibid.*, **36**, 755 (1963).

34) The present authors, unpublished data.

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

complexes the ratio of the number of oxygen atoms to the number of nitrogen atoms is greater than in the monomeric complexes, the d-d bands of the dimers occur at shorter wavelengths than the monomers. This seems to indicate that the ligand fields of the alcoholic oxygen atoms are stronger than those of the imino nitrogen atoms.[36]

Sacconi and Ciampolini[37] determined the λ_{max} of a series of planar monomeric bis-salicylaldimine-copper(II) complexes with variation in substituent X. They found a maximum difference of 90 mμ in λ_{max} with variation in X.

Careful measurements of the dimeric complexes of the series reported have shown a maximum difference of only 5 mμ. Since the number of substituent X in dimeric complexes is one per one copper atom compared to two in the monomeric complexes, it would be expected that the monomeric complexes should show a larger substituent effect. However, this effect is very much larger (20 times) in the monomeric species. A study is under way to clarify this anomaly which cannot be explained at the present time.

Relation of Spectra and Magnetism. A linear relationship[3] between λ_{max} and $\mu_{\text{eff}}^{25°\text{C}}$ has recently been shown to exist for the dimeric complexes of copper(II) halides with substituted pyridine *N*-oxides. The parent complex (X=H) has a greater μ_{eff} and its λ_{max} is at longer wavelength than the X=CH_3, Cl, *etc*. In the complexes reported in this study, however, the parent complex (X=H) has a smaller μ_{eff} and a larger λ_{max} than those complexes in which X=Cl, CH_3, benzo. The nitro substituted complex again behaves normally just as found for the nitro-substituted pyridine *N*-oxide complex; As was observed in the previous study[3] a smaller value in $\mu_{\text{eff}}^{25°\text{C}}$ leads to a shorter wavelength for λ_{max}.

The mechanism which determines the relation between $\mu_{\text{eff}}^{25°\text{C}}$ and λ_{max} seems to be different for the dimeric copper(I) complexes of substituted pyridine *N*-oxides and the dimeric copper(II) complexes under investigation here. This must be due to the fact that the pathway for transmission of the substituent effect is different for the two types of complexes.

On first thought it might be argued that this observed difference might be due to differences in the structures of the two types of complexes. This, in turn, would then lead to differences in the superexchange pathway since in the pyridine *N*-oxide complexes this pathway is through bridging oxygen atoms slightly out of the plane, whereas in the salicylaldiminato-complexes, the superexchange occurs through bridging oxygen atoms in the plane. However, as Goodenough points out[38] as long as the Cu-O-Cu angle remains about 90° the superexchange pathway is not effected by the structural differences between the pyridine *N*-oxide and the salicylaldiminato dimeric complexes.

The substituent effect in the pyridine *N*-oxide dimers is directly transmitted to bridging oxygen atom in the superexchange pathway and changes in the copper-bridging oxygen distance will directly effect the μ_{eff} and the λ_{max}.

In the substituted salicylaldiminato-complexes, on the other hand, it is proposed that the alcohol oxygen bridges and is in the superexchange pathway. Under these conditions the substitution on the benzene ring effects primarily the phenolic oxygen or imino nitrogen *not* in the superexchange pathway. The effect on the alcoholic oxygen should only be secondary and opposite in divertion as shown below.

If a methyl group is substituted into the benzene ring of the parent compound the inductive character of this group would increase the σ electron donor capacities of the phenolic oxygen and the imino nitrogen atoms. This would enhance the ligand field around the copper(II) ion and shift the d-d band toward shorter wavelengths. However, simultaneously by the increase in σ electron density in the copper(II) orbitals would decrease its electron affinity. This in turn leads to a weakening of the σ bond of the bridging alcoholic oxygen atoms trans to the phenolic oxygen or the imino nitrogen bond. Such a decrease in the covalent bond character in the superexchange pathway will in turn result in a decrease in the superexchange itself. This should produce an increase in the magnetic moment which indeed was observed as shown in Table 3.

The chloro and benzo groups in this series seem to act in the same manner. The nitro group, on the other hand, being a strong electron withdrawing enhances markedly the π backbonding capacities of the aromatic π-electron system from the copper(II) ion. As a result, compared to the parent compound

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36) H. Ojima and K. Sone, *Z. anorg. u. allgem. Chem.*, **309**, 110 (1961).

37) L. Sacconi and M. Ciampolini, *J. Chem. Soc.*, **1964**, 276.

38) J. B. Goodenough, "Magnetism and the Chemical Bond," Interscience Publishers, New York, London (1963), pp. 180—183.

(X=H), the splitting of the d–d levels of the nitro compound will be increased.[39] Such was indeed observed by Sacconi[37] who reported the greatest "blue shift" in λ_{max} for the monomeric nitro substituted salicylaldimine-copper(II) complexes.

The mechanism of the "blue shift" seems to be the same for these monomeric and dimeric complexes. Backbonding from the copper(II) d-orbitals into the aromatic π-electron system increases the electron affinity of the copper(II) ion. This will increase the covalency of the bond from the copper(II) ion to the alcoholic oxygen atom. This, in turn, will increase its superexchange capacity and will lower the value of μ_{eff}.

The data reported in this study indeed indicate that in these complexes the alcoholic oxygen atoms are the bridging atom rather than the phenolic oxygen attached to the benzene ring.

Fruitful discussions with Dr. L. C. Cusachs are gratefully acknowledged.

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[39] D. W. Herlocker, R. S. Drago and V. I. Meek, *Inorg. Chem.*, **5**, 2009 (1966).