Binuclear Metal Complexes. VI.[1] Syntheses and Properties of Binuclear Copper(II) Complexes of 2,6-Bis[N-(β-dialkylaminoethyl)iminomethyl]-4-methylphenol[2]

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A new series of binuclear copper(II) complexes, $[\mathrm{Fsal}(=\mathrm{NenNR_2})_2\mathrm{Cu_2X}]^{2+}$ (R=Me and Et, X=Cl, Br, and OH), were synthesized, where $\mathrm{Fsal}(=\mathrm{NenNR_2})_2$ indicates the Schiff base prepared from 2,6-diformyl-4-methylphenol and N,N-dialkylethylenediamine (alkyl=methyl(Me) and ethyl(Et)). Two copper(II) ions are connected with the phenolic oxygen and X. The complexes obtained were characterized by elemental analyses, infrared and visible spectra, molar conductivities in methanol, ESR spectra and magnetic susceptibilities. It was found that the stability of the complexes decreases in the order X=OH$\gg$Br$>$Cl. It was concluded from cryomagnetic measurements that the effect of the bridging group X on spin-coupling decreases in the order OH$\gg$Br$>$Cl.

It is known that 2,6-diformyl-4-methylphenol and its Schiff base derivatives[3-7] form a novel class of binuclear copper(II) complexes, in which two copper(II) ions are bridged with two different groups. We suggested that there is a relationship between the simply coordinating and bridging groups concerning the stability of the binuclear copper(II) complexes.[5] In order to find the relationship it is necessary to synthesize many binuclear copper(II) complexes with a variety of coordinating and bridging groups. We attempted the preparation of some binuclear copper(II) complexes of the Schiff bases 2,6-bis[N-(β-dialkylaminoethyl)iminomethyl]-4-methylphenol made from 2,6-diformyl-4-methylphenol and N,N-dialkylethylenediamine (alkyl=methyl and ethyl).

We synthesized six binuclear copper(II) complexes of the type $[\mathrm{Fsal}(=\mathrm{NenNR_2})_2\mathrm{Cu_2X}]^{2+}$, where $\mathrm{Fsal}(=\mathrm{NenNR_2})_2$ denotes the Schiff bases and X the second bridging group (phenolic oxygen will be called the first bridging group). The structures and properties of the complexes were studied by elemental analyses, IR and visible spectra, molar conductivities in methanol, ESR spectra and magnetic susceptibilities, magnetic exchange interaction also being examined. Since only the second bridging group in the complexes is variable, we can estimate its effect on the spin-coupling between the two copper(II) ions.

Experimental

Syntheses. The synthetic method for 2,6-diformyl-4-methylphenol was described elsewhere.[4]

$[\mathrm{Fsal}(=\mathrm{NenNMe_2})_2\mathrm{Cu_2Cl}]\mathrm{Cl_2}$: 2,6-Diformyl-4-methylphenol (330 mg) and anhydrous copper(II) chloride (538 mg) were dissolved in absolute methanol (30 ml). To the solution was added a solution of N,N-dimethylethylenediamine (352 mg) in absolute methanol (5 ml). The reaction mixture was warmed and concentrated to 15 ml to give green needles. They were recrystallized from anhydrous methanol–benzene.

Found: C, 38.08; H, 5.22; N, 10.59; Cl, 19.64%. Calcd for $\mathrm{C_{17}H_{27}N_4OCl_3Cu_2}$: C, 38.03; H, 5.07; N, 10.44; Cl, 19.81%.

$[\mathrm{Fsal}(=\mathrm{NenNMe_2})_2\mathrm{Cu_2Br}]\mathrm{Br_2}$: To a solution of 2,6-diformyl-4-methylphenol (330 mg) and anhydrous copper(II) bromide (894 mg) in methanol (30 ml) was added a methanolic solution (5 ml) of N,N-dimethylethylenediamine (352 mg). After the reaction mixture was boiled and concentrated to 20 ml, dark green needles were obtained. They were filtered and washed with a small amount of cold absolute methanol.

Found: C, 30.52; H, 4.22; N, 8.36; Br, 35.37%. Calcd for $\mathrm{C_{17}H_{27}N_4OBr_3Cu_2}$: C, 30.47; H, 4.06; N, 8.36; Br, 35.77%.

$[\mathrm{Fsal}(=\mathrm{NenNMe_2})_2\mathrm{Cu_2OH}](\mathrm{ClO_4})_2$: 2,6-Diformyl-4-methylphenol (330 mg), N,N-dimethylethylenediamine (352 mg) and copper(II) perchlorate hexahydrate (1482 mg) were mixed in methanol (30 ml). The reaction mixture was concentrated to 15 ml and diluted with water (15 ml) to give greenish blue prisms. They were recrystallized from water to give blue prisms.

Found: C, 31.74; H, 4.58; N, 8.69; Cu, 19.51%. Calcd for $\mathrm{C_{17}H_{28}N_4O_{10}Cl_2Cu_2}$: C, 31.59; H, 4.37; N, 8.67; Cu, 19.66%.

$[\mathrm{Fsal}(=\mathrm{NenNEt_2})_2\mathrm{Cu_2Cl}]\mathrm{Cl_2}$: This compound was prepared by a method similar to that for $[\mathrm{Fsal}(=\mathrm{NenNMe_2})_2\mathrm{Cu_2Cl}]\mathrm{Cl_2}$. Recrystallization was carried out from anhydrous methanol–ethanol.

Found: C, 42.51; H, 6.01; N, 9.13; Cl, 18.12%. Calcd for $\mathrm{C_{21}H_{35}N_4OCl_3Cu_2}$: C, 42.54; H, 5.95; N, 9.45; Cl, 17.94%.

$[\mathrm{Fsal}(=\mathrm{NenNEt_2})_2\mathrm{Cu_2Br}]\mathrm{Br_2}$: This complex was synthesized by treating 2,6-diformyl-4-methylphenol (330 mg), anhydrous copper(II) bromide (894 mg) and N,N-diethylethylenediamine (464 mg) in ethanol. Violet prisms separated were collected and washed with a small amount of ethanol.

Found: C, 32.92; H, 4.83; N, 7.19; Br, 31.62%. Calcd for $\mathrm{C_{21}H_{35}N_4OBr_3Cu_2\cdot 2H_2O}$: C, 33.09; H, 5.1[illegible]; N, [illegible].35; Br, 31.44%.

An anhydrous complex was obtained when the dihydrate was recrystallized from absolute methanol three times and then heated at 110 °C under reduced pressure.

$[\mathrm{Fsal}(=\mathrm{NenNEt_2})_2\mathrm{Cu_2OH}](\mathrm{ClO_4})_2$: The synthetic method for this complex is nearly the same as that for $[\mathrm{Fsal}(=\mathrm{NenNMe_2})_2\mathrm{Cu_2OH}](\mathrm{ClO_4})_2$. The violet needles separated were collected and recrystallized three times from water.

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[2] This work was presented at the 21th Symposium of Coordination Chemistry, Nagoya, November 18, 1971.

[3] H. Okawa, This Bulletin, **43**, 3019 (1970).

[4] H. Okawa and S. Kida, *ibid.*, **44**, 1172 (1971).

[5] H. Okawa, S. Kida, Y. Muto, and T. Tokii, *ibid.*, **45**, 2480 (1972).

[6] R. Robson, *Inorg. Nucl. Chem. Lett.*, **6**, 125 (1970).

[7] B. F. Hoskins, R. Robson, and H. Schaap, *ibid.*, **8**, 21 (1972).

Found: C, 35.95; H, 5.23; N, 7.81%. Calcd for $C_{21}H_{36}N_4O_{10}Cl_2Cu_2$: C, 35.90; H, 5.17; N, 7.98%.

Measurements. Infrared spectra were measured with a Hitachi EPI-S2 spectrophotometer in the region 4000—650 cm^{-1} on a KBr disk. Electronic spectra on solids and in solutions (methanol, water and pyridine) were determined with a Hitachi EPS-3T recording spectrophotometer. ESR spectra (X-band) were measured on powder and in solutions with a JES-ME-3 spectrometer at various temperatures. Magnetic susceptibilities were determined by the Gouy method in the range from liquid nitrogen to room temperature. The apparatus for the measurements was described elsewhere.[5] Effective magnetic moments μ_{eff} were calculated by the equation

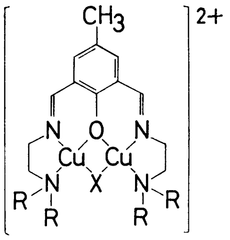
$$\mu_{eff} = 2.83\sqrt{(\chi_A - N\alpha)T},$$

where χ_A is the atomic susceptibility corrected by use of Pascal's constants[8,9] for diamagnetism and $N\alpha$ the temperature independent paramagnetism of copper(II) ion. Molar conductivities of the complexes were determined in an absolute methanol solution (*ca.* 10^{-3} mol) at 25 °C.

Results and Discussion

Some IR absorption bands of the complexes are given in Table 1. Very sharp peaks at 3510 cm^{-1} in $[Fsal(=NenNMe_2)_2Cu_2OH](ClO_4)_2$ and $[Fsal(=NenNEt_2)_2Cu_2OH](ClO_4)_2$ are assigned to the O–H stretching vibration. Two peaks in the region 1650—1635 cm^{-1} may be assigned to the C=N stretching vibrations. The skeletal vibration[10] observed at 1555—1560 cm^{-1} supports the binuclear structure bridged with a phenolic oxygen.[11] Two strong bands near 1320 and 1080 cm^{-1} are tentatively assigned to the C–O and =C–N stretching vibrations, respectively.[10] Two OH-bridged complexes show a broad, strong band due to perchlorate ion[12] in the region 1120—1060 cm^{-1}.

Molar conductivities of the complexes in absolute methanol are given in Table 1. All complexes were found to be 1 : 2 electrolytes. The mass spectrum of $[Fsal(=NenNEt_2)_2Cu_2Cl]Cl_2$ exhibits two peaks at m/e= 521 and 523, attributable to the $[Fsal(=NenNEt_2)_2Cu_2Cl]^+$ ion. Thus two peaks at m/e=458 and 460 and two peaks at m/e=359 and 360 may be assigned to the $Fsal(=NenNEt_2)_2CuCl^+$ and $Fsal(=NenNEt_2)_2^+$ ions respectively. We concluded that the complexes possess the binuclear structure shown in Fig. 1.



R=CH_3 and C_2H_5 X=Cl, Br, and OH

Fig. 1. Structure of $[Fsal(=NenNR_2)_2Cu_2X]^{2+}$.

The d-d bands of the complexes are given in Table 2. As was expected from spectrochemical series, the reflection spectra of the OH-bridged complexes have a d-d band at higher energy than those of the corresponding halogen-bridged complexes. However, the energy difference in d-d band (2.1—5.5 kK) between the OH-bridged and the halogen-bridged complexes is markedly larger than that in the case of the glycine-Schiff base complexes (0.9—1.0 kK).[5] This indicates

Table 1. IR absorption bands and molar conductivity

$[Fsal(=NenNR_2)_2Cu_2X]^{2+}$		IR (cm^{-1})							Molar conductivity
R	X	O–H	C=N		skeletal	C–O	=C–N	ClO_4^-	(Ω^{-1} cm^2 mol^{-1})
CH_3	Cl		1650	1634	1556	1322	1080		181
CH_3	Br		1650	1635	1558	1318	1080		173
CH_3	OH	3510	1650	1635	1556	1332		1120—1060	220
C_2H_5	Cl		1650	1634	1555	1328	1082		179
C_2H_5	Br		1653	1640	1560	1325	1080		199
C_2H_5	OH	3510	1650	1640	1567	1323		1120—1070	216

Table 2. Ligand field bands (mμ).

$[Fsal(=NenNR_2)_2Cu_2X]^{2+}$		Powder		Solution (ε)		
R	X			MeOH	H_2O	py
CH_3	Cl	700	500_{sh}	680(109)		
CH_3	Br	730	500_{sh}	690(125)		
CH_3	OH	610		630(99)	630(90)	650(110)
C_2H_5	Cl	770	510_{sh}	690(120)		
C_2H_5	Br	790	500_{sh}	680(127)		
C_2H_5	OH	550		625(115)	610(111)	665(138)

sh: shoulder

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

[10] H. Okawa, and S. Kida, This Bulletin, **45**, 1759 (1972).

[11] E. Sinn and C. M. Harris, *Coord. Chem. Rev.*, **4**, 391 (1969).

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that the OH- and the halogen-bridged complexes possess a molecular structure differing from each other in solid states, depending on the counter ions. Since no appreciable coordination is expected for perchlorate ion, the coordination around the copper(II) ion in the OH-bridged complexes may be practically planar. In this case a larger steric requirement of the ethyl group compared with the methyl group will exclude the fifth coordination in the apical position. The coordination bonds in tetragonal plane in [Fsal(=NenNEt$_2$)$_2$-Cu$_2$OH](ClO$_4$)$_2$ are therefore much strengthened and its solid spectrum has a band at higher energy than [Fsal(=NenNMe$_2$)$_2$Cu$_2$OH](ClO$_4$)$_2$. On the other hand the halogeno ion in [Fsal(=NenNR$_2$)$_2$Cu$_2$X]X$_2$ (X=Cl and Br) will coordinate to the copper(II) ion to form a five-coordination. Such a tetragonal-pyramidal structure was found for similar binuclear copper(II) complexes.[13] In the five-coordinate complexes the ethyl group will make a larger internal strain compared with the methyl group. In fact, [Fsal(=NenNEt$_2$)$_2$Cu$_2$X]X$_2$ has a d-d band at lower energy than the corresponding [Fsal(=NenNMe$_2$)$_2$Cu$_2$X]X$_2$ (X=Cl and Br).

All the above complexes appear to take a five- or six-coordinate structure in methanol with the solvent molecule in an apical position. However, the six-coordination seems impossible judging from the steric hindrance between the R and methanol molecules. The OH-bridged complexes have a d-d band at a lower energy in methanol than in a solid state. This suggests that the coordination around copper(II) is tetragonal-pyramidal in methanol. The halogeno-bridged complexes possess a d-d band at higher energy in methanol than in a solid state. This implies that a halogeno atom in the fifth coordination position was replaced by a solvent molecule in methanol.

Both the OH-bridged complexes may keep the same structure in water, in methanol and in pyridine. The halogeno-bridged complexes are only stable in absolute methanol and easily decomposed in water and in pyridine. The Br-bridged complexes seem to be more stable than the corresponding Cl-bridged complexes, since [Fsal(=NenNR$_2$)$_2$Cu$_2$Cl]Cl$_2$ was partly decomposed after long exposure to air. Thus the relative stability of the complexes increases in the order X=OH$\gg$Br>Cl. This is the reverse of that found for the series of binuclear copper(II) complexes derived from 2,6-diformyl-4-methylphenol and glycine.[5]

The powder ESR spectra of the [Fsal(=NenNMe$_2$)$_2$-Cu$_2$X]$^{2+}$ complexes (X=Cl, Br, and OH) are given in Fig. 2. Each spectrum is very similar to the corresponding spectrum of the [Fsal(=NenNEt$_2$)$_2$Cu$_2$X]$^{2+}$ complexes. The Cl-bridged complex showed a broad band (*ca.* 6000 gauss width) centered around 3500 gauss. Similar broad spectra was observed for dichloro-μ-chloro-μ-(2,6-diformyl-4-methylphenolato)dicopper(II)[3] and for the binuclear copper(II) complexes of the Schiff bases derived from 2,6-diformyl-4-methylphenol and α-amino acids.[5] The spectrum of the Br-bridged complex was also broad. The signal observed at 1700 gauss may be assigned to the $\Delta M_s=2$ transition. A signal at 3200 gauss may be due to the presence of a trace of impurity of mononuclear species. The spectrum of the OH-bridged complex showed two signals at 6000 and 1600 gauss, tentatively assigned to the $\Delta M_s=1$ and the $\Delta M_s=2$ transitions respectively. The ESR spectra of the complexes in methanol and of the OH-bridged complexes in water and in pyridine showed no signal except for a weak band at 3200 gauss due to paramagnetic impurity.

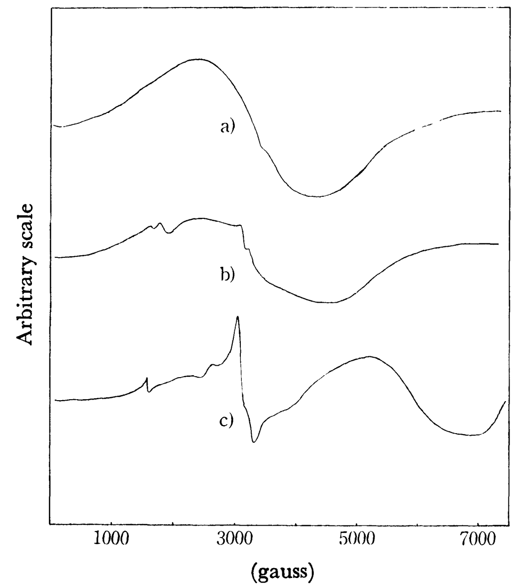

Fig. 2. ESR spectra of [Fsal(=NenNMe$_2$)$_2$Cu$_2$X]Y$_2$.
a) X=Cl, Y=Cl; b) X=Br, Y=Br;
c) X=OH, Y=ClO$_4$.

The ESR spectrum of [Fsal(=NenNEt$_2$)$_2$Cu$_2$OH](ClO$_4$)$_2$ was measured at various temperatures. The results are given in Fig. 3. Intensities of the signals at 5500 and 1600 gauss decrease with the lowering of temperature; the signal at 5500 gauss practically disappeared at 133 K. It is clear that an antiferro-

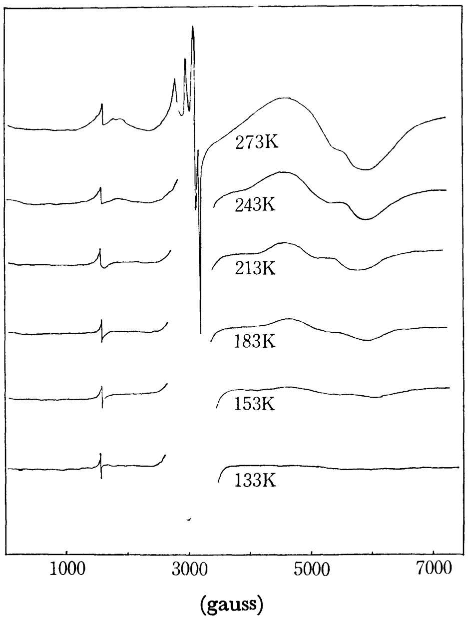

Fig. 3. ESR spectra of [Fsal(=NenNEt$_2$)$_2$Cu$_2$OH](ClO$_4$)$_2$ at various temperatures.

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magnetic exchange interaction occurs between the two copper(II) ions.

All the complexes showed demagnetisation by spin-pairing in line with the results of the ESR data. Magnetic susceptibilities were measured over a temperature range 70—300 K. Experimental data can be explained on the basis of the Bleaney-Bowers equation[14]

$$\chi_A = \frac{Ng^2\beta^2}{3kT}\left[1+\frac{1}{3}\exp(-2J/kT)\right]^{-1} + N\alpha,$$

where the symbols have their usual meanings. The $-2J$, g, and $N\alpha$ values were determined by the best fit of the χ_A value to the Bleaney-Bowers equation (Fig. 4). The values are given in Table 3. The $-2J$ value, which is the energy separation between the singlet and triplet states, indicates the degree of the spin-exchange interaction between the copper(II) ions.

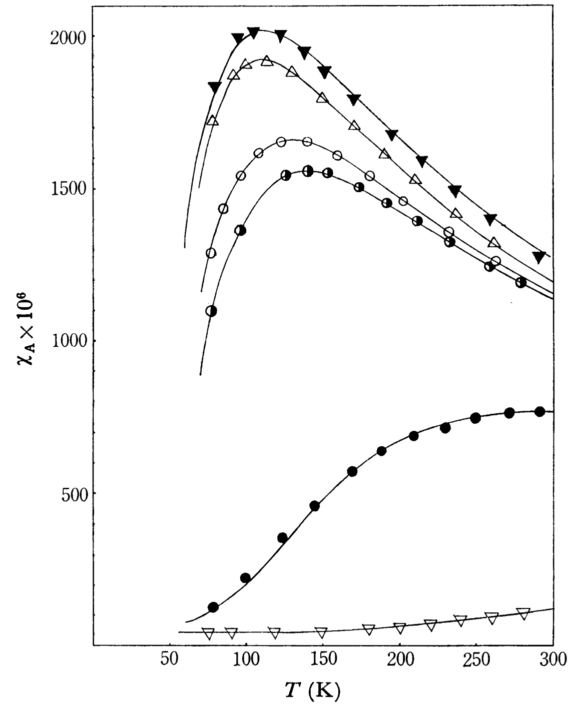

Fig. 4. Variation of molar susceptibilities with temperature of complexes; (○) R=Me X=Cl, (◑) R=Me X=Br, (●) R=Me X=OH, (△) R=Et X=Cl, (▼) R=Et X=Br, and (▽) R=Et X=OH.

TABLE 3. VALUES OF $-2J$(cm^{-1}), g, $N\alpha$ (c.g.s., e.m.u.) AND μ_{eff} (B.M.)

R	X	$-2J$	g	$N\alpha \times 10^6$	μ_{eff}(K)
CH_3	Cl	143	2.10	45	1.61(299.3)
CH_3	Br	155	2.10	60	1.61(301.1)
CH_3	OH	330	2.11	60	1.29(291.8)
C_2H_5	Cl	123	2.10	40	1.66(302.6)
C_2H_5	Br	125	2.16	60	1.68(291.6)
C_2H_5	OH	865	2.15	46	0.49(303.4)

The spin-exchange interaction may be caused by a super exchange mechanism rather than direct overlapping of 3d-orbitals, since the distance between two metal ions is about 2.9 Å for the complex of a structure similar to the present complexes.[7] The halogen-bridged complexes were found to have nearly the same molecular structure, their powder X-ray diffraction spectra being practically the same. If we suppose as a first approximation that the degree of the spin-exchange through the first bridging group is the same throughout the series of complexes, then the $-2J$ value reflects the effect of the second bridging group on spin-pairing between the copper(II) ions. The results given in Table 3 indicate that the bromide bridge is more effective in spin-coupling than the chloride bridge in both series of complexes. This is in line with the results obtained for the copper(II) halides[15] and the cobalt(II) complexes.[16] On the other hand, the two OH-bridged complexes have much larger $-2J$ values than the others. It is well-known[15] that oxygen-bridges are generally more effective than halogeno-bridges in spin-coupling. It may be said that the effect of the second bridging group on the antiferromagnetic exchange interaction increases in the order X=OH≫Br>Cl.

It is interesting to consider the correlation between the d-d band and the $-2J$ value of the complexes. It is clear that [Fsal(=NenNEt$_2$)$_2$Cu$_2$OH](ClO$_4$)$_2$ has a d-d band at higher energy and a larger $-2J$ value than [Fsal(=NenNMe$_2$)$_2$Cu$_2$OH](ClO$_4$)$_2$. In the halogeno-bridged complexes, [Fsal(=NenNMe$_2$)$_2$Cu$_2$X]X$_2$ (X=Cl and Br) always shows a d-d band at higher energy and a larger $-2J$ value than the corresponding [Fsal(=NenNEt$_2$)$_2$Cu$_2$X]X$_2$. This implies that the more planar the configuration around the copper(II) ion the larger the magnetic exchange between the copper(II) ions. This trend in the d-d band and $-2J$ value has been found by Muto *et al.*[17] and Kato *et al.*[18] for the binuclear copper(II) complexes of pyridine-*N*-oxides and *N*-aryl-salicylaldimines. The binuclear copper(II) complex prepared from pyridine-*N*-oxide and copper(II) bromide has a magnetic moment 0.29 B.M., which is smaller than 0.63 B.M. for the complex made from copper(II) chloride. It was recently demonstrated by X-ray analysis[19] that these magnetic moments are explained in terms of the planarities of the complexes.

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