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# Binuclear Metal Complexes. IV.[1] The Preparation and Properties of Binuclear Copper(II) Complexes of Schiff Bases Derived from 2,6-Diformyl-4-methylphenol and Glycine or Alanine[2]

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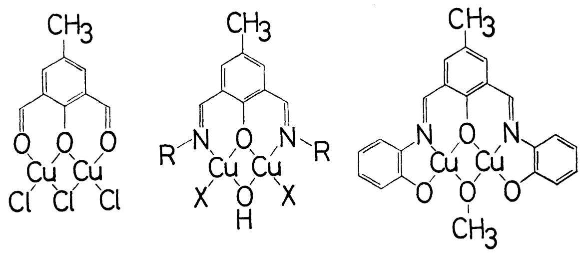
A new series of binuclear copper(II) complexes with different bridging groups, Fsal(=gly)$_2$Cu$_2$X (X=OH, Cl, Br) and Fsal(=ala)$_2$Cu$_2$X (X=Cl), were synthesized, Fsal(=gly)$_2$ and Fsal(=ala)$_2$ being the Schiff bases prepared by condensation of 2,6-diformyl-4-methylphenol with glycine and alanine, respectively. The copper(II) ions are bridged by the phenolic oxygen in the organic moiety and also the X. The properties of the complexes were studied by IR spectra, visible spectra, and magnetic susceptibility measurements at various temperatures. From the cryomagnetic data it was concluded that the effect of the bridging group X upon magnetic exchange interaction decreases in the order: OH$>$Cl$\sim$Br.

It is known that 1,3,5-triketones[3-5] and diethyl cyclopentanone-2,5-diglyoxylate[6,7] form binuclear copper(II) complexes composed of two ligands and two copper(II) ions. Although 2,6-diformyl-4-methylphenol is similar to the ligands in structure, its complex-forming behavior is markedly different. The ligand and copper(II) chloride form a binuclear complex, dichloro-$\mu$-chloro-$\mu$-2,6-diformyl-4-methylphenolatodicopper(II)[8] (Fig. 1, (a)), in which the ratio of copper to the ligand is 2 : 1. Thus the use of 2,6-diformyl-4-methylphenol makes it possible to prepare binuclear copper(II) complexes bridged with two different groups, i.e., the phenolic oxygen (the first bridging group) and a monoatomic or polyatomic anion such as chloride, bromide, hydroxide, or methanolate ion (the second bridging group). Okawa prepared dihalogeno-$\mu$-hydroxo-$\mu$-2, 6-bis-($N$-alkyliminomethyl)-4-methylphenolatodicopper(II)[8] (Fig. 1, (b)), by the reaction of 2,6-diformyl-4-methylphenol, an alkyl amine and copper(II) chloride or copper(II) bromide. A binuclear copper(II) complex of the Schiff base with $o$-aminophenol, in which a methanolate ion acts as the second bridging group, was also prepared[9] (Fig. 1, (c)).

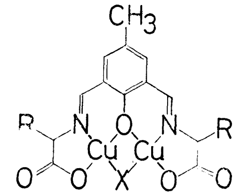


R=alkyl
X=Cl or Br

(a) (b) (c)

Fig. 1.

It is clear that the second bridging group is variable depending upon the nature of the four coordinating atoms other than the bridging atoms. It appears that there is a certain relation between the coordinating and bridging atoms closely associated with the stability of the binuclear copper(II) complex. In order to find the relation, we attempted to synthesize binuclear copper(II) complexes of the Schiff bases derived from 2,6-diformyl-4-methylphenol and $\alpha$-amino acids. We obtained a series of Fsal(=gly)$_2$-Cu$_2$X (X=OH, Cl or Br) and Fsal(=ala)$_2$Cu$_2$X (X=Cl), where Fsal(=gly)$_2$ and Fsal(=ala)$_2$ indicate the Schiff bases with glycine and alanine, respectively, and the X is the second bridging group(Fig. 2).



R=H: Fsal(=gly)$_2$Cu$_2$X (X=OH, Cl or Br)
R=CH$_3$: Fsal(=ala)$_2$Cu$_2$X (X=Cl)

Fig. 2. Structure of complexes.

These complexes are the first series of planar binuclear copper(II) complexes bridged with two different groups.

The magnetic exchange between a pair of copper(II) ions has also been studied. In Fsal(=gly)$_2$Cu$_2$X only the second bridging group, X, varies. Thus the complexes are very suitable for a study of the effects of the bridging groups upon the spin-spin coupling interaction.

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## Experimental

*Syntheses.* The synthesis of 2,6-diformyl-4-methylphenol has been described previously.[1]

*Fsal(=gly)$_2$Cu$_2$Cl.* An aqueous solution of glycine (300.3 mg) was added to a solution of 2,6-diformyl-4-methylphenol (330 mg) and copper(II) chloride dihydrate (681 mg) in ethanol (75 m*l*). The clear solution was heated at 70°C for ten minutes and left standing overnight. The separated green needles were collected and washed with ethanol.

Found: C, 35.42; H, 2.67; N, 6.11; Cl, 7.82%; mol wt, 430 (methanol). Calcd for $C_{13}H_{11}N_2O_5ClCu_2$: C, 35.67; H, 2.53; N, 6.40; Cl, 8.10%; mol wt, 437.78.

*Fsal(=gly)$_2$Cu$_2$Br.* An aqueous solution of glycine (300.3 mg) was added to a dark solution of 2,6-diformyl-4-methyl-phenol (330 mg) and anhydrous copper(II) bromide (893.5 mg) in ethanol (100 m*l*). The resulting green solution was heated on a water-bath and then cooled to give green needles, which were collected and washed with ethanol.

Found: C, 32.74; H, 2.41; N, 5.51; Br, 16.71%. Calcd for $C_{13}H_{11}N_2O_5BrCu_2$: C, 32.38; H, 2.30; N, 5.81; Br, 16.57%.

*Fsal(=gly)$_2$Cu$_2$(OH)·H$_2$O:* An aqueous solution of glycine (300.3 mg) was added to an ethanolic solution of 2,6-diformyl-4-methylphenol (330 mg) and copper(II) acetate monohydrate (800 mg) or copper(II) sulfate pentahydrate (1 g). A yellowish green by-product was separated by decantation and the remaining blue product was collected and thoroughly washed with ethanol. Contamination by the yellow by-product was avoided by employing anhydrous copper(II) fluoride as the source of metal ions.

Found: C, 35.88; H, 3.25; N, 6.33%. Calcd for $C_{13}H_{12}N_2O_6Cu_2 \cdot H_2O$: C, 35.70; H, 3.23; N, 6.41%.

The water of crystallization could be removed by heating at 110°C/2 mmHg for 8 hours.

*Fsal(=ala)$_2$Cu$_2$Cl.* This complex was obtained by treating 2,6-diformyl-4-methylphenol (330 mg), *dl*-alanine (360 mg) and copper(II) chloride dihydrate (681 mg) in ethanol. The green solution was concentrated to 30 m*l*, and 20 m*l* of acetone was added. After the reaction mixture was left standing overnight, the separated deep green needles were collected and washed with cold ethanol.

Found: C, 38.88; H, 3.72; N, 5.76; Cl, 7.70%. Calcd for $C_{15}H_{15}N_2O_5ClCu_2$: C, 38.68; H, 3.25; N, 6.01; Cl, 7.61%.

*Measurements.* Magnetic susceptibilities were determined in the range from liquid nitrogen temperature to room temperature by the Gouy method with a magnetic field strength of about 7000 Oersted. The apparatus was similar in design to the one described by Figgis and Nyholm;[10] an electromagnet (Nihon-Komitsu Model 350) and a vacuum semimicro balance with a reading accuracy of ±0.02 mg (Chyo Balance Co.). Temperature control was carried out by an electrically regulated system with an accuracy of ±0.2°K at 150°K. Temperature measurements were carried out by means of a copper-constantan thermocouple. The effective magnetic moment $\mu_{\rm eff}$ was calculated from the expression

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

where $\chi_{\rm A}$ is the atomic susceptibility corrected by use of Pascal's constants[11,12] for diamagnetism and $N\alpha$ is the temperature independent paramagnetism associated with copper(II) ions.

The infrared spectra of the complexes were measured with a Hitachi EPI-S2 spectrophotometer in the region 4000—650 cm$^{-1}$ on a KBr disk. In some cases the hexachlorobutadiene mull method was used for the measurements in the region 4000—2000 cm$^{-1}$. The reflectance spectra and solution spectra of the complexes in water, methanol, and pyridine were measured with a Hitachi EPS-3T spectrophotometer in the near-infrared and visible regions.

## Results and Discussion

The complexes Fsal(=gly)$_2$Cu$_2$Cl and Fsal(=gly)$_2$Cu$_2$Br were obtained quantitatively but the yield of Fsal(=gly)$_2$Cu$_2$(OH)·H$_2$O was low. Only Fsal(=ala)$_2$Cu$_2$Cl was isolated from Fsal(=ala)$_2$ in a very low yield. The syntheses of binuclear copper(II) complexes of the Schiff bases with other α-amino acids such as valine, leucine, isoleucine, and phenylalanine were unsuccessful. A deep green solution was formed when 2,6-diformyl-4-methylphenol, an amino acid and a copper(II) salt were mixed in

Table 1. IR absorption bands of complexes (cm$^{-1}$).

| Fsal(=gly)$_2$Cu$_2$X | | | Fsal(=ala)$_2$-Cu$_2$Cl | Assignment |
|---|---|---|---|---|
| X=OH | X=Cl | X=Br | | |
| 3370 w | | | | O-H |
| 3040 w | 3050 w | 3050 w | 3050 w | C-H |
| 2990 w | | | 2990 w | CH$_3$ |
| 2940 w | 2950 w | 2950 w | 2950 w | |
| 1645 s | 1650 s | 1650 s | 1650 s | C=O |
| 1625 s | 1630 s | 1630 s | 1630 s | C=N |
| 1600 w | 1600 m | 1595 m | 1595 m | skeletal |
| 1555 s | 1555 s | 1555 s | 1560 s | |
| 1455 m | 1455 m | 1455 m | 1455 m | |
| 1418 w | 1415 w | 1415 w | 1410 w | |
| | | | 1390 m | |
| 1357 s | 1375 s | 1377 s | 1360 s | C-O (phenol) |
| 1335 s | 1312 m | 1315 m | 1315 m | |
| 1295 m | 1293 m | 1290 m | 1280 m | |
| 1240 m | 1245 w | 1258 w | 1247 w | |
| | 1235 w | 1233 w | | |
| 1185 w | 1197 w | 1200 w | 1195 w | |
| | | | 1120 w | |
| 1085 s | 1077 s | 1085 s | 1085 s | C-N |
| | | | 1045 w | |
| 1020 w | 1007 w | 1010 w | 1000 w | |
| 990 w | 990 w | 990 w | 990 w | |
| 922 m | 940 m | 935 m | 940 m | |
| 883 w | 890 w | 868 w | 885 w | |
| 837 s | 828 s | 822 s | 825 s | CH out of plane |
| | | | 782 m | |
| 768 s | 762 s | 762 s | 770 m | |
| 758 s | | | 750 m | |

s=strong, m=medium, and w=weak.

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[10] B. N. Figgis and R. S. Nyholm, *J. Chem. Soc.*, **1959**, 331.

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

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

ethanol, but only 2,6-diformyl-4-methylphenol was recovered from the concentrated reaction mixture. The marked differences in isolating the complexes are difficult to explain at present. The molecular weight determination for Fsal(=gly)$_2$Cu$_2$Cl supports the binuclear structure shown in Fig. 2.

The IR spectra of Fsal(=gly)$_2$Cu$_2$X (X=OH, Cl and Br) and Fsal(=ala)$_2$Cu$_2$Cl are very similar to each other (Table 1), suggesting similar structures of the complexes. The spectra in the region 1700—1400 cm$^{-1}$ resemble those of the copper(II) complex of the Schiff base derived from salicylaldehyde and glycine.[13] The complicated bands at 1650—1630 cm$^{-1}$ may be assigned to the C=O and C=N stretching vibrations, while the bands at 1600 and 1455 cm$^{-1}$ have been assigned to the aromatic skeletal vibration.[14,15] Okawa and Kida[9] pointed out that the new band around 1555 cm$^{-1}$ can be attributed to a skeletal vibration of the aromatic ring. The band appears on the low-frequency side of 1550 cm$^{-1}$ in the mononuclear copper(II) complexes of the Schiff bases derived from salicylaldehyde, and on the high-frequency side of 1550 cm$^{-1}$ in the complexes where a phenolic oxygen acts as a bridge.[16] The present complexes are therefore expected to have a binuclear structure bridged with a phenolic oxygen. The very strong band at 1380—1350 cm$^{-1}$ might be assigned to the C–O vibration.[14,15,17] Ueno and Martell[18] assigned the strong band near 1085 cm$^{-1}$ to the C–O stretching vibration. We found that the corresponding band in dichloro-$\mu$-hydroxo-$\mu$-2,6-bis(*N*-alkyliminomethyl)-4-methylphenolatodicopper(II)[7] depends markedly upon the alkyl group (CH$_3$, 1030; C$_2$H$_5$, 1040; *iso*-C$_3$H$_7$, 1065; *tert*-C$_4$H$_9$, 1080 cm$^{-1}$). Consequently this band can be assigned to the C–N stretching vibration. In anhydrous Fsal(=gly)$_2$-Cu$_2$(OH) the O–H vibration was found at 3370 cm$^{-1}$.

The ligand field bands of the complexes are given in Table 2. The reflectance spectrum of Fsal(=gly)$_2$-Cu$_2$(OH)·H$_2$O showed the ligand field band at 650 m$\mu$, which is higher in energy than those of other complexes. The complexes except for Fsal(=gly)$_2$Cu$_2$-(OH)·H$_2$O are likely to keep their binuclear structures in polar solvents such as water, methanol, and pyridine, since they can be recrystallized from these solvents and their visible spectra in them are similar. On the other hand, Fsal(=gly)$_2$Cu$_2$(OH)·H$_2$O is hardly soluble in most solvents though it is soluble in pyridine. However, it is clear that the complex decomposes in pyridine since the green prisms isolated from the concentrated solution were found to be bis(glycinato)copper(II) by IR spectrum. The thermal decomposition temperatures for Fsal(=gly)$_2$Cu$_2$Cl, Fsal(=gly)$_2$Cu$_2$Br and Fsal(=gly)$_2$Cu$_2$(OH)·H$_2$O are 220—225°, 223—225°, and 217—220°C, respectively. Though the difference in the decomposition temperature of the complexes is small, the results indicate that in the series of complexes Fsal(=gly)$_2$Cu$_2$X (X=OH, Cl, and Br) the relative stability increases with X=Cl$\sim$Br>OH, in spite of the lower bridging ability of the halide atoms.[19] This is in contrast to that found for the series of binuclear copper(II) complexes of the Schiff bases derived from 2,6-diformyl-4-methylphenol and N,N-dialkylethylenediamines.[20] The remarkable stability of the present complexes may be explained by the fact that the organic moieties are suitable for forming binuclear complexes and consequently strongly combine two copper(II) ions.

The $\chi_A$ and $\mu_{eff}$ values at various temperatures are given in Table 3. It was found that Fsal(=gly)$_2$-Cu$_2$(OH)·H$_2$O is antiferromagnetic. The experimental data could be explained in terms of the Bleaney-Bowers equation[21]

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

where $-2J$ is the energy separation between the singlet and triplet states, $k$ the Boltzmann constant, $N$ the Avogadro number, $\beta$ the Bohr magneton and g the Lande $g$-factor (Fig. 3). The $-2J$, $g$ and $N\alpha$ values were obtained by the best fit of susceptibility data to the Bleaney-Bowers equation. The results are given in Table 3.

Fsal(=gly)$_2$Cu$_2$Cl, Fsal(=gly)$_2$Cu$_2$Br and Fsal(=ala)$_2$Cu$_2$Cl obey the Curie-Weiss law (Fig. 4). Approximate values of the Weiss constant $\theta$ were obtained by extrapolating the curves $1/(\chi_A - N\alpha)$ *vs.* T assuming $60\times10^{-6}$ cgs. emu for $N\alpha$.[22] Since all

Table 2. Ligand field bands of complexes (m$\mu$)

| | Solutions | | | Powder |
|---|---|---|---|---|
| | H$_2$O | CH$_3$OH | Py | |
| Fsal(=gly)$_2$Cu$_2$Cl | 680 | 680 | 680 | 695 |
| Fsal(=gly)$_2$Cu$_2$Br | 675 | 675 | 675 | 695 |
| Fsal(=gly)$_2$Cu$_2$(OH)·H$_2$O | | | (663)[a] | 650 |
| Fsal(=ala)$_2$Cu$_2$Cl | 670 | 670 | 668 | 690 |

a) Decomposed in pyridine.

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Table 3. Molar magnetic susceptiblities (cgs. emu) and effective magnetic moments (B. M.) over a temperature range

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| Fsal(=gly)$_2$Cu$_2$(OH)·H$_2$O | | | | $-2J=447$ cm$^{-1}$; $g=2.16$; $N\alpha=70\times10^{-6}$ | | | | |
| T (°K) | 76.2 | 92.7 | 118.4 | 140.6 | 160.5 | 179.2 | 199.1 | |
| $\chi_A\times10^6$ | 79 | 92 | 140 | 201 | 265 | 323 | 384 | |
| $\mu_{eff}$ | 0.07 | 0.13 | 0.26 | 0.40 | 0.50 | 0.60 | 0.71 | |
| T (°K) | 229.1 | 249.2 | 283.0 | | | | | |
| $\chi_A\times10^6$ | 461 | 499 | 553 | | | | | |
| $\mu_{eff}$ | 0.85 | 0.93 | 1.05 | | | | | |
| Fsal(=gly)$_2$Cu$_2$Cl | | $\theta\simeq-22$°K | | | | | | |
| T (°K) | 76.2 | 95.2 | 125.2 | 142.6 | 159.6 | 197.9 | 218.4 | |
| $\chi_A\times10^6$ | 3837 | 3368 | 2726 | 2491 | 2273 | 1910 | 1716 | |
| $\mu_{eff}$ | 1.52 | 1.59 | 1.64 | 1.67 | 1.68 | 1.71 | 1.70 | |
| T (°K) | 250.6 | 283.3 | 289.8 | | | | | |
| $\chi_A\times10^6$ | 1508 | 1346 | 1343 | | | | | |
| $\mu_{eff}$ | 1.71 | 1.71 | 1.71 | | | | | |
| Fsal(=gly)$_2$Cu$_2$Br | | $\theta\simeq-7$°K | | | | | | |
| T (°K) | 76.2 | 97.3 | 139.8 | 180.5 | 219.1 | 259.9 | 288.3 | |
| $\chi_A\times10^6$ | 4775 | 3918 | 2813 | 2265 | 1807 | 1559 | 1396 | |
| $\mu_{eff}$ | 1.70 | 1.73 | 1.75 | 1.78 | 1.75 | 1.76 | 1.76 | |
| Fsal(=ala)$_2$Cu$_2$Cl | | $\theta\simeq-48$°K | | | | | | |
| T (°K) | 76.3 | 94.4 | 123.4 | 158.9 | 195.5 | 222.4 | 256.0 | 285.3 |
| $\chi_A\times10^6$ | 3515 | 3123 | 2566 | 2149 | 1844 | 1665 | 1498 | 1362 |
| $\mu_{eff}$ | 1.45 | 1.52 | 1.57 | 1.63 | 1.67 | 1.69 | 1.72 | 1.72 |

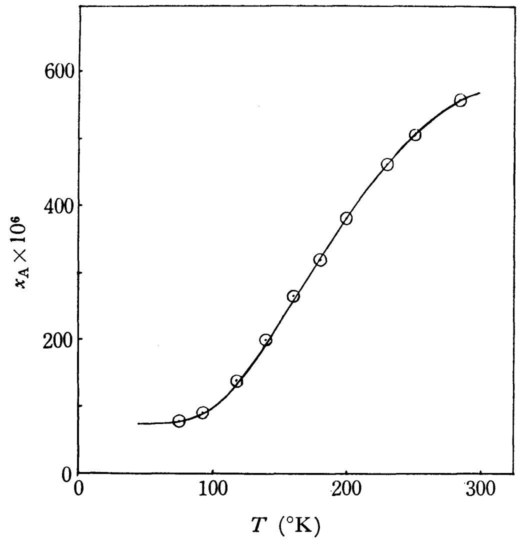

Fig. 3. Variation of molar magnetic susceptibilities with temperature for Fsal(=gly)$_2$Cu$_2$(OH)·H$_2$O. The curve was calculated from the Bleaney-Bowers equation using the sets of parameters listed in Table 3.

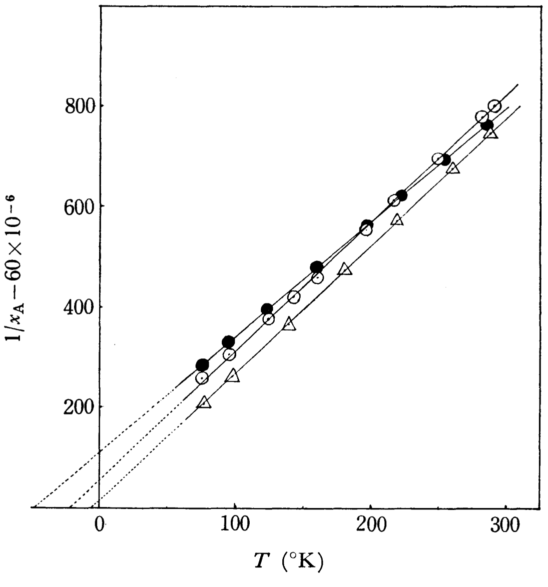

Fig. 4. Variation of reciprocal molar magnetic susceptibilities with temperature.
○: Fsal(=gly)$_2$Cu$_2$Cl, △: Fsal(=gly)$_2$Cu$_2$Br,
●: Fsal(=ala)$_2$Cu$_2$Cl.

these complexes possess negative Weiss constants, it is evident that there is antiferromagnetic exchange interaction between the copper(II) ions in the complexes. In most oxygen-bridged copper(II) complexes,[23–26] the Cu-O bond lengths and the Cu-O-Cu bond angles are in the ranges 1.8—2.0 Å and 100—115°, respectively. If the Cu-O bond length and the Cu-O-Cu bond angle in the present complexes are assumed to be 1.9 Å and 110° respectively, then the copper-copper interatomic distance is about 3.4 Å. Since this interatomic distance is much greater than

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the 2.56 Å of metallic copper, a direct exchange interaction between copper(II) ions is not likely to occur. Thus the superexchange through the bridging groups is most important in the magnetic interaction in the complexes.

The powder X-ray diffraction spectra of Fsal($=$gly)$_2$Cu$_2$Cl and Fsal($=$gly)$_2$Cu$_2$Br are quite similar to each other, but differ from that of Fsal($=$gly)$_2$-Cu$_2$(OH)$\cdot$H$_2$O. This implies that the crystal structures of Fsal($=$gly)$_2$Cu$_2$Cl and Fsal($=$gly)$_2$Cu$_2$Br are very similar to each other but differ from the structure of Fsal($=$gly)$_2$Cu$_2$(OH)$\cdot$H$_2$O. Nevertheless, in the present discussion we regard the molecular structures of all these complexes as practically the same, since the 5-6-6-5 condensed ring system makes a rigid skeleton for each of the complexes. This is supported by the consideration on the series of tetranuclear copper(II) complexes[27-31] of the type $Cu_4OX_6L_4$ (X is chloride or bromide atom and L is a unidentate ligand), in which the bond angles and bond lengths in one bridge are fixed and another bridging group is replaceable.

We assume that the spin-spin coupling through the phenolic oxygen is the same in all complexes. Consequently, the difference in magnetic behavior of the complexes reflects the effect of the second bridging groups upon the spin exchange interaction. From the data given in Table 3 the effect is found to be in the order: OH>Cl∼Br. As it is known that most binuclear copper(II) complexes with phenolic oxygen bridges show demagnetisation,[16] it is remarkable that Fsal($=$gly)$_2$Cu$_2$Cl, Fsal($=$gly)$_2$Cu$_2$Br, and Fsal($=$ala)$_2$Cu$_2$Cl have relatively large magnetic moments close to the spin-only value of 1.73 B.M. This might be due to the out-of-plane distortion of the Cu-O-Cu plane of the complexes.

From the Weiss constants of the complexes it can be assumed that the chloride bridge is more effective than the bromide bridge in spin coupling. It is usually found that the spin exchange interaction in binuclear complexes bridged with bromide ions is greater than that in the corresponding complexes bridged with chloride ions. For example, anhydrous copper(II) bromide has a lower magnetic moment (1.31 B.M.) than anhydrous copper(II) chloride (1.75 B.M.).[32] In the binuclear copper(II) complexes[14] of the Schiff bases derived from 2,6-diformyl-4-methylphenol and *N,N*-dialkylethylenediamines, the complexes bridged with a bromide ion exhibit a greater antiferromagnetic interaction than the complexes bridged with a chloride ion. Lever *et al.*[33] prepared some tetrahedral binuclear cobalt(II) complexes of a phthalazine derivative containing one halide bridge. From cryomagnetic measurements they found that the bromide-bridged complex shows a larger $-2J$ value than the corresponding chloride-bridged complex. However, the difference of effect between chloride and bromide bridging groups is usually small, and insofar as our complexes are concerned, it is reasonable to say that the chloride and bromide bridges exert a comparable effect on the spin exchange interaction.

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