Preparative and Magnetic Studies of Several Binuclear Copper(II) Alkanoate Complexes with Salicylideneamines

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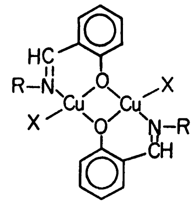
Compounds with the stoichiometry of $Cu(5\text{-}R''\text{-}sal\cdot N\text{-}R)R'COO$ ($5\text{-}R''\text{-}sal\cdot N\text{-}= \cdot\overset{2}{O}\cdot C_6H_3(\overset{5}{R''})\cdot\overset{1}{C}H{=}N\text{-}$; R= methyl, phenyl, *o*-tolyl and *p*-tolyl; R′=ethyl, monochloromethyl and dichloromethyl; R″=H, CH_3 and Cl) have been prepared, and their magnetic and spectral properties have been studied. The magnetic and IR spectral data of the compounds where R=methyl and *o*-tolyl, R′=dichloromethyl, and R″=H indicate that they have phenolic oxygen-bridged dimer units in their crystals. On the other hand, a carboxylate-bridged binuclear structure is postulated for the other complexes on the basis of magnetic and IR spectral data. It has been observed that, in the latter group of complexes, both the $-2J$ (singlet-triplet separation) and ν_{max} (ligand-field transition energy) values decrease in the order of $Cu(Sal\cdot N\text{-}R)C_2H_5COO > Cu(Sal\cdot N\text{-}R)ClCH_2COO > Cu(Sal\cdot N\text{-}R)Cl_2CHCOO$, where $Sal\cdot N\text{-}= \cdot\overset{2}{O}\cdot C_6H_4\cdot\overset{1}{C}H{=}N\text{-}$. The preparation and characterization of the $Cu(Sal\cdot N\text{-}R)HCOO\cdot DMF$ compounds (R=*p*-tolyl and *p*-chlorophenyl; DMF=*N,N*-dimethylformamide) are also reported.

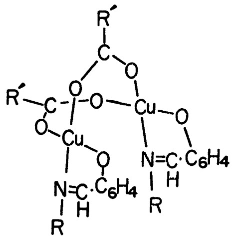
Bis(N-R-salicylideneaminato)copper(II), $Cu(Sal\cdot N\text{-}R)_2$, reacts with copper(II) halide or nitrate to yield binuclear complexes with the structure shown in I, $[Cu(Sal\cdot N\text{-}R)X]_2$, in which the phenolic oxygen atoms act as bridges, where R=alkyl or aryl and X=Cl,[1,2] Br[3] or NO_3.[4,5] These binuclear complexes display antiferromagnetic behavior, in conformity with the Bleaney-Bowers equation (1)[6] formulated for the magnetic susceptibility of an isolated pair of interacting ions of spin 1/2:

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

where $-2J$ is equal to the energy separation between the singlet and triplet states, which gives the degree of strength of the magnetic interaction.



I



II

In the course of our studies of binuclear complexes of the I type, we found that, by the reaction of copper(II) alkanoates, $Cu(R'COO)_2$, with $Cu(Sal\cdot N\text{-}R)_2$, complexes with the $Cu(Sal\cdot N\text{-}R)R'COO$ stoichiometry were isolated when R=phenyl and *p*-tolyl and R′= ethyl.[7] On the basis of the magnetic and IR spectral data of these complexes, it was concluded that they possess the carboxylate-bridged binuclear structure represented in II.[7] It is noteworthy that the antiferromagnetic interaction in these propionate complexes ($-2J$=101 cm^{-1})[7] is much weaker than that in the corresponding chloride complexes ($-2J\approx 350$ cm^{-1}),[7,8] $[Cu(Sal\cdot N\text{-}R)Cl]_2$, where R=phenyl and *p*-tolyl.

As a continuation of those studies, we have newly prepared seven compounds with the $Cu(Sal\cdot N\text{-}R)R'COO$ stoichiometry and two compounds with the $Cu(Sal\cdot N\text{-}R)HCOO\cdot DMF$ stoichiometry, where DMF =*N,N*-dimethylformamide. These new compounds have been characterized on the basis of elemental analyses, the IR and visible spectra, and the temperature dependences of the magnetic susceptibilities. Since no reasonable relationship between the magnitude of the antiferromagnetic interaction in dimeric copper(II) carboxylates and the acidity of the parent carboxylic acids has yet been established,[9–13] the observation of the $-2J$ values in the newly prepared complexes of the II type is of particular interest.

Experimental

Syntheses. *Cu(Sal·N-R)R′COO Complexes*: A typical synthetic method is as follows. A solution of an anhydrous copper(II) alkanoate (12 mmol) in ethanol (50 ml) was added, through a quantitative filter paper, to one of the parent $Cu(Sal\cdot N\text{-}R)_2$ complexes (10 mmol). The solution was stirred at *ca.* 70° C for 1/2 h and then concentrated to one-third of its volume. After the solution had been allowed to stand overnight at *ca.* 5 °C in a freezer, the separated crystals were collected and washed twice with a small quantity of ethanol and once with ether. They were all green in color.

Cu(Sal·N-R)HCOO·DMF Complexes: To a solution of the parent $Cu(Sal\cdot N\text{-}R)_2$ complex (10 mmol) in DMF (30 ml), we added copper(II) formate tetrahydrate (10 mmol). The mixture was stirred on a hot plate for 1/2 h. The green crystals thus precipitated were collected and recrystallized from DMF.

The data of the elemental analyses of the new compounds are summarized in Table 1.

Physical Measurements. The magnetic susceptibilities were determined by the Gouy method in the range from the temperature of liquid nitrogen to room temperature. The effective magnetic moments per copper ion at room temperature were calculated from this expression:

$$\mu_{eff} = 2.83\sqrt{(\chi_A - N\alpha)\cdot T} \tag{2}$$

where χ_A is the molar magnetic susceptibility corrected for the diamagnetism of the constituted atoms using Pascal's constant[14] and where $N\alpha$ is the temperature-independent paramagnetism per gram-ion of copper(II). The $N\alpha$ was assumed to be 60×10^{-6} emu.[15] The results are given in Table 2. The ESR (X-band) spectra of polycrystalline samples were measured with a JEOL ESR-apparatus, model JES-ME-1X, at room temperature. The IR spectral measurements were made with a Hitachi EPI-G2 IR spectro-

Table 1. Analytical data of new compounds

Complex[a]	C% Found	C% Calcd	H% Found	H% Calcd	N% Found	N% Calcd	Cu% Found	Cu% Calcd
1. Cu(Sal·N-*p*-tol)HCOO·DMF	54.90	55.17	5.11	5.14	7.20	7.15	16.28	16.21
2. Cu(Sal·N-*p*-Clph)HCOO·DMF	49.47	49.52	4.29	4.16	6.78	6.79	15.43	15.41
3. Cu(Sal·N-CH_3)Cl_2CHCOO	36.69	36.89	2.80	2.79	4.26	4.30	19.59	19.51
4. Cu(Sal·N-*o*-tol)Cl_2CHCOO	47.92	47.84	3.32	3.26	3.47	3.49	15.80	15.82
5. Cu(5-CH_3sal·N-ph)C_2H_5COO	58.79	58.86	5.20	4.94	3.87	4.04	18.07	18.32
6. Cu(5-Clsal·N-ph)C_2H_5COO	52.44	52.32	4.08	3.84	3.82	3.81	17.30	17.30
7. Cu(Sal·N-*p*-tol)$ClCH_2COO$	52.23	52.32	3.86	3.84	3.86	3.81	17.60	17.30
8. Cu(Sal·N-ph)Cl_2CHCOO	46.43	46.47	2.90	2.86	3.54	3.61	16.46	16.39
9. Cu(Sal·N-*p*-tol)Cl_2CHCOO	47.82	47.84	3.22	3.26	3.50	3.49	15.92	15.82

a) Sal·N−= $\cdot\overset{2}{\text{O}}\cdot C_6H_4\cdot\overset{1}{\text{C}}\text{H=N}-$, sal·N−= $\cdot\overset{2}{\text{O}}\cdot C_6H_3\cdot\overset{1}{\text{C}}\text{H=N}-$, tol=tolyl, ph=phenyl, and DMF=*N*,*N*-dimethylformamide.

Table 2. Magnetic data of new compounds

Complex	μ_{eff} B. M. (°C)	$-2J$ (cm^{-1})	g[a]
1. Cu(Sal·N-*p*-tol)-HCOO·DMF	1.00 (18)	498	2.20
2. Cu(Sal·N-*p*-Clph)-HCOO·DMF	0.99 (24)	514	2.20
3. Cu(Sal·N-CH_3)-Cl_2CHCOO	0.84 (15)	572	2.18
4. Cu(Sal·N-*o*-tol)-Cl_2CHCOO	1.39 (12)	335	2.20
5. Cu(5-CH_3sal·N-ph)C_2H_5COO	1.72 (25)	96	2.14(2.18)
6. Cu(5-Clsal·N-ph)-C_2H_5COO	1.72 (22)	96	2.14(2.18)
7. Cu(Sal·N-*p*-tol)-$ClCH_2COO$	1.74 (14)	88	2.14(2.14)
8. Cu(Sal·N-ph)-Cl_2CHCOO	1.78 (17)	61	2.13(2.13)
9. Cu(Sal·N-*p*-tol)-Cl_2CHCOO	1.77 (16)	61	2.13(2.13)

a) The data in parentheses were determined by ESR measurements on the polycrystalline samples.

photometer in the 400—4000 cm^{-1} region on Nujol mulls. The reflectance spectra were measured with a Hitachi EPS-3T recording spectrophotometer.

Results and Discussion

Synthesis. It was observed that the dichloroacetate complexes, 8 and 9, listed in Table 1 were most readily obtainable, even though dichloroacetic acid has the lowest pK_a value among the parent carboxylic acids employed in the preparation in this study.[10,16,17] It was also found that, in the reaction of copper(II) formate with Cu$(Sal\cdot N\text{-}ph\text{-}Y)_2$, where ph-Y=a monosubstituted phenyl group with the Y substituent, no formate complexes were isolated when Y=*o*-CH_3, *o*-Cl, *m*-CH_3, and *m*-Cl. This finding is in accord with the previous observation that, in a preparation of DMF adduct complexes of the [Cu(Sal·N-ph-Y)X·DMF]$_n$ type, where X=Cl[2] or NO_3,[5] the complexes with Y at the *p*-position of the phenyl ring were easily obtained, while a synthesis of complexes with Y at the *o*- or *m*-position was unsuccessful; *i.e.*, the Y substituent attached at the *o*- or *m*-position hinders the coordination of the DMF molecule to the central metal ion much more than the one at the *p*-position, since the former is present at a position closer to the metal ion than the latter.

Magnetic Susceptibility. The magnetic susceptibilities of the complexes were determined over the temperature range of 80—300 K; the data are shown in Figs. 1—3 as plots of the molar magnetic susceptibility (χ_A) *vs.* the temperature (T). The magnetic data for the complexes, except for Compound 4, are well represented by Eq. 1 (*cf.* Figs. 1 and 3). The $-2J$ and g values listed in Table 2 were evaluated from the best fit of the cryomagnetic data to Eq. 1, assuming $N\alpha = 60\times10^{-6}$ emu.[15] The g values for some of the complexes were in good agreement with the average g values determined from ESR measurements of the polycrystalline samples (*cf.* Table 2). The close agreement between the observed and calculated temperature dependences of the magnetic susceptibility is powerful evidence for a binuclear structure of these complexes. For Compound 4, the observed magnetic data could not satisfactorily fit Eq. 1 when the following values were used: J was estimated from the $-2J\approx1.6\,kT_C$ relation, where k is the Boltzmann constant, and T_C, the temperature of the maximum susceptibility; g ranged

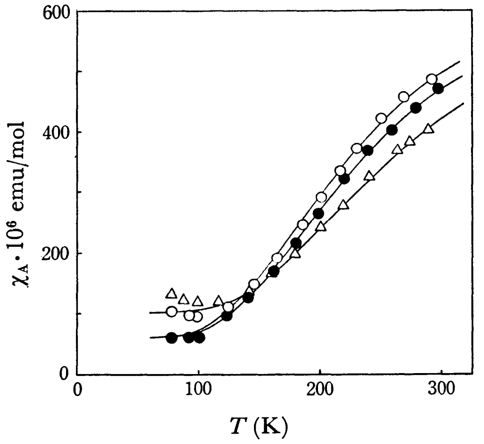


Fig. 1. Temperature dependence of magnetic susceptibilities of (○) Cu(Sal·N-*p*-tol)HCOO·DMF, (●) Cu(Sal·N-*p*-Clph)HCOO·DMF, and (△) Cu(Sal·N-CH_3)Cl_2CHCOO.

The solid curves represent the Bleany-Bowers equation.

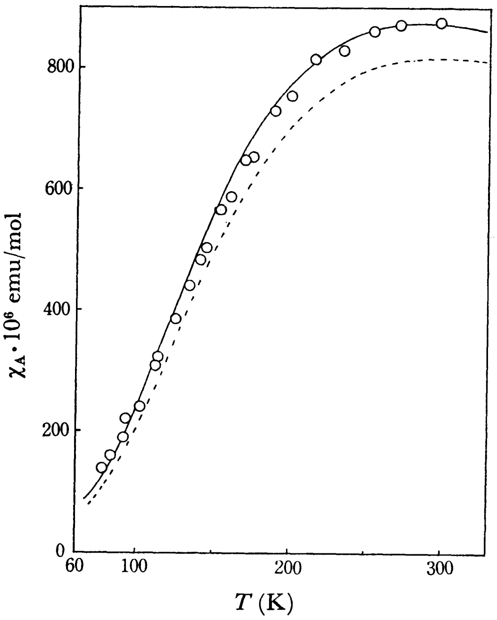


Fig. 2. Temperature dependence of magnetic susceptibilities of (○) Cu(Sal·N-*o*-tol)Cl_2CHCOO.
The broken curve was calculated from the Bleaney-Bowers equation (1) with $-2J$=335 cm^{-1}, g=2.20, and $N\alpha$=60×10^{-6} emu. The solid curve was calculated from the modified equation (3) with $-2J$=335 cm^{-1}, g=2.20, $N\alpha$=60×10^{-6} emu and θ=+20 K.

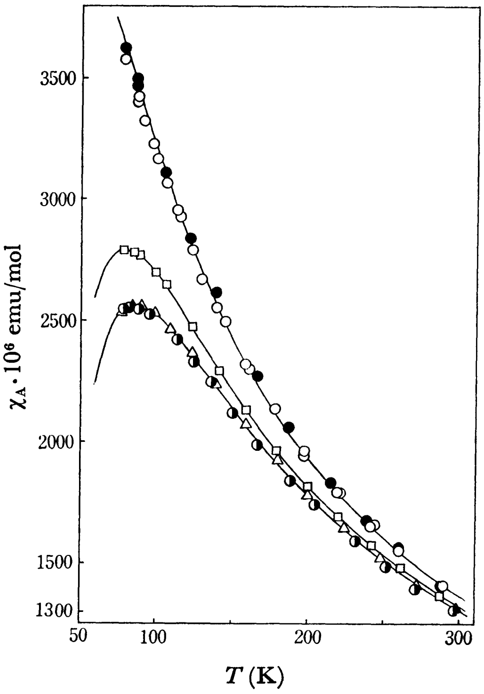


Fig. 3. Temperature dependence of magnetic susceptibilities of (△) Cu(5-CH_3sal·N-ph)C_2H_5COO, (◑) Cu(5-Clsal·N-ph)C_2H_5COO, (□) Cu(Sal·N-*p*-tol)-$ClCH_2COO$, (●) Cu(Sal·N-ph)Cl_2CHCOO, and (○) Cu(Sal·N-*p*-tol)Cl_2CHCOO.
The solid curves represent the Bleaney-Bowers equation.

from 2.10 to 2.20, and $N\alpha$ was 60×10^{-6} emu (*cf.* Fig. 2). However, a better fit was obtained for the data to the theoretical curve drawn based on a modification of the Bleaney-Bowers equation (3):[18]

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

where the Weiss constant, θ, allows for intermolecular interaction between dimers (*cf.* Fig. 2). From a best-fitting procedure of the experimental data to Eq. 3, the $-2J$ and g values listed in Table 2 and the value of θ=+20 K were evaluated. The positive value for θ suggests the presence of ferromagnetic spin interaction between the dimers.

The complexes described here can be classified into two groups based on the magnetic data. Group (A): in Compounds 1—4, the effective magnetic moments at room temperature are definitely smaller than the spin-only value, 1.73 B.M., for one unpaired electron, and the $-2J$ values are larger than 300 cm^{-1}. Group (B): in Compounds 5—9, the moments are close to the spin-only value, and the $-2J$ values are smaller than 100 cm^{-1}.

Electronic Spectra. The electronic spectra of all the complexes investigated were recorded by the diffuse reflectance technique. The frequencies of the ligand-field band maxima are collected in Table 3. Some of the spectral curves of the Group (A) and (B) complexes are shown in Fig. 4 and Fig. 5 respectively. It is apparent from Table 3 and Figs. 4 and 5 that there is a marked difference in the spectra between Group (A) and (B) complexes. This is indicative of a structural difference between them. The spectra of the Group (A) complexes are similar to one another and closely resemble those of DMF adducts of the I type complexes, [Cu(Sal·N–R)X·DMF]$_2$, to which a five-coordinated square pyramidal configuration with axially coordinated DMF molecules was assigned.[2,5] For comparison, the reflectance spectral curve of [Cu(Sal·N-*p*-tol)NO_3·DMF]$_2$, where *p*-tol=*p*-tolyl,[5] is given in Fig. 4. Group (B) complexes have a ligand-field band in an energy region ((15—16)×10^3 cm^{-1}) much higher than that of Group (A) complexes. As can be seen in Fig. 5, the spectral features of Group (B) complexes are very similar to one another, indicating that they are isostructural.

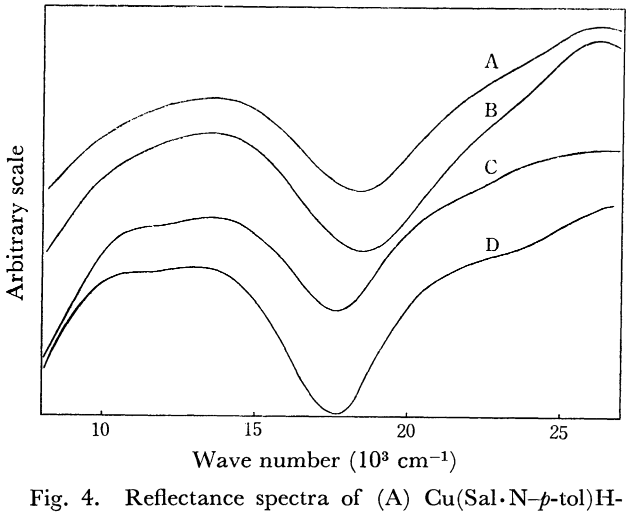


Fig. 4. Reflectance spectra of (A) Cu(Sal·N-*p*-tol)H-COO·DMF, (B) Cu(Sal·N-*p*-Clph)HCOO·DMF, (C) Cu(Sal·N-*o*-tol)Cl_2CHCOO, and (D) Cu(Sal·N-*p*-tol)NO_3·DMF.[5]

TABLE 3. REFLECTANCE AND IR SPECTRAL DATA OF NEW COMPOUNDS AND THE RELATED COMPOUNDS

Complex	Ligand field band maximum ν_{max}, kK[d]	IR absorption, cm^{-1}			
		band maximum[e] near 1540 cm^{-1}	$\nu_{as}CO_2$	ν_sCO_2	Δ_{as-s}
1. Cu(Sal·N-*p*-tol)HCOO·DMF	13.9, 10.9sh	1552(+19)			
2. Cu(Sal·N-*p*-Clph)HCOO·DMF	13.3, 10.5sh	1549(+15)			
3. Cu(Sal·N-CH_3)Cl_2CHCOO	13.5, 11.5sh	1553(+19)	1641	1371	270
4. Cu(Sal·N-*o*-tol)Cl_2CHCOO	14.6, 11.1sh	1555(+15)	1658 1650	1377	277
5. Cu(5-CH_3sal·N-ph)C_2H_5COO	15.8	1537(+ 6)	1590	1426	164
6. Cu(5-Clsal·N-ph)C_2H_5COO	15.8	1529(+ 2)	1590	1429	161
Cu(Sal·N-ph)C_2H_5COO[a]	15.8	1538(+ 7)	1588	1428	160
Cu(Sal·N-*p*-tol)C_2H_5COO[a]	15.8	1538(+ 5)	1589	1433	156
Cu$(C_2H_5COO)_2$[b]			1589	1420	169
7. Cu(Sal·N-*p*-tol)$ClCH_2COO$	15.5	1537(+ 4)	1630	1414 1400	223
8. Cu(Sal·N-ph)Cl_2CHCOO	15.6	1536(+ 5)	1657 1650	1410 1401	248
9. Cu(Sal·N-*p*-tol)Cl_2CHCOO	15.3	1540(+ 7)	1653 1647	1406 1401	246
Cu$(Cl_2CHCOO)_2$(α-picoline)$_2$ (purple)[c]			1657 1643	1376	274

a) Ref. 7. b) Ref. 22. c) Ref. 24. d) sh=shoulder. e) The numerical values in parentheses indicate the increased wave numbers from the bands in the parent Cu(Sal·N-R)$_2$ complexes.

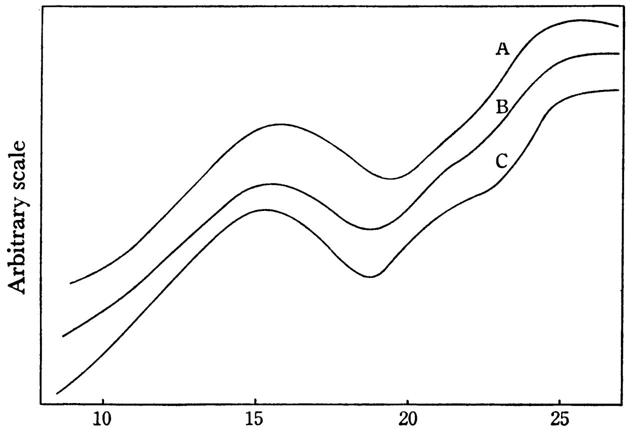


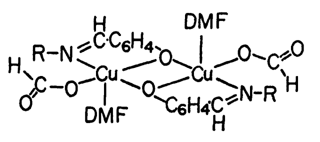
Fig. 5. Reflectance spectra of (A) Cu(Sal·N-*p*-tol)-C_2H_5COO,[7] (B) Cu(Sal·N-*p*-tol)$ClCH_2COO$, and (C) Cu(Sal·N-*p*-tol)Cl_2CHCOO.

IR Spectra. For the present complexes and the previously reported propionate complexes, Cu(Sal·N-R)C_2H_5COO, where R=phenyl and *p*-tolyl,[7] the absorption near 1540 cm^{-1}, and those due to antisymmetric($\nu_{as}CO_2$) and symmetric(ν_sCO_2) carboxylate stretching vibrations were measured to obtain information concerning the coordination mode of the phenolic oxygen atoms and carboxylate groups in the complexes. The assignment of the observed bands was made by comparing the bands of these complexes with those of the parent Cu(Sal·N-R)$_2$ complexes and the corresponding binuclear chloro and nitrato complexes of the I type. The results are listed in Table 3, together with the data reported for the related alkanoate compounds.

Although there have been tentative assignments for the absorption near 1540 cm^{-1} in Cu(Sal·N-R)$_2$ (*e.g.*, to νC=N,[19] νC-O(phenolic)[1,20] or to the skeltal vibration of the aromatic ring[21]), no definite conclusion has yet been reached as to the origin of the band. However, a shift of the band to higher energies by 10—20 cm^{-1} near 1540 cm^{-1} is now at least taken as an unambiguous criterion of the formation of a phenolic oxygen-bridging between metal ions in polymeric salicylideneamine complexes.[1–3,7,8,20,21] As is shown in Table 3, the band shift was observed for all the complexes of Group (A), indicating the presence of phenolic oxygen-bridges between the copper(II) ions in these complexes. On the other hand, no significant band shift was observed for any of the complexes of Group (B), indicating that, in these complexes, no phenolic oxygen-bridge exists.

For the carboxylate coordination, a comparison of the carboxylate stretching frequencies in the present complexes with those in the related copper(II) alkanoates is informative. All the propionate complexes described here exhibit $\nu_{as}CO_2$ and ν_sCO_2 bands in an energy region very similar to that reported for anhydrous copper(II) propionate,[22] Cu$(C_2H_5COO)_2$, which has a copper(II) acetate monohydrate type of binuclear structure[23] (*cf.* Table 3). The close similarity in absorption energy leads to the conclusion that the propionate complexes have carboxylate bridges of a syn-syn arrangement[16] between copper(II) ions, as is shown in II. In the case of the dichloroacetate complexes, the frequencies of $\nu_{as}CO_2$ and ν_sCO_2 and the separation between them, Δ_{as-s}, in the complexes belonging to Group (A), 3 and 4, markedly differ from those in the complexes belonging to Group (B), 8 and 9. The $\nu_{as}CO_2$, ν_sCO_2, and Δ_{as-s} in the Group (A) complexes are nearly the same as those reported for the purple isomer of bis(α-picoline)copper(II) dichloroacetate, Cu$(Cl_2CHCOO)_2$(α-pic)$_2$, for which the carboxylate coordination was identified as intermediate between a strictly unidentate type and a strictly bidentate-chelate type.[24] It seems, therefore, reasonable to conclude that, in the dichloroacetate complexes of Group (A), no carboxylate bridges of the syn-syn type exist. No unambiguous assignment for carboxylate coordination in the dichloroacetate complexes, 8 and 9 (Group (B)), and in the monochloroacetate complex, 7, could be drawn from their IR data. However, the magnetic and reflectance spectral features of these chloroacetate complexes (7, 8 and 9) are very similar to those of the propionate complexes. The appearance of IR bands at *ca.* 1540 cm^{-1} indicates that the magnetic interaction in the chloroacetate complexes probably takes place through carboxylate bridging rather than through phenolic oxygen bridging. These facts suggest that the carboxylate coordination mode in these chloroacetate complexes is of a syn-syn bridging type, as is seen in the propionate complexes.

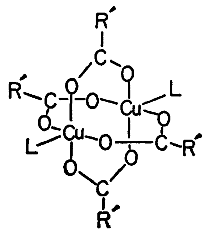
Structure and Magnetic Interaction. The magnetic and IR spectral data for Group (A) complexes clearly indicate that the complexes have phenolic oxygen-bridged dimer units of the I type in crystals. The reflectance spectra showed them to have a penta-coordinated square pyramidal configuration. Accordingly, the most probable structure for the formate complexes, 1 and 2, seems to be III, in which the DMF molecule occupies the fifth coordination site of the copper ion. The penta-coordination in the dichloroacetate complexes, 3 and 4, seems to be possible when the carboxylate group acts as a bidentate chelate or a bridging group (triatomic -O–C–O- or monoatomic -O(CO)-) between the dimer units. The presence of inter-dimer magnetic interaction observed for the Cu(Sal·N-*o*-tol)Cl_2CHCOO complex, 4, is indicative of the carboxylate bridges between the dimer units in this complex.



III

The $-2J$ values determined for Group (A) complexes are considerably larger than those reported for the I type complexes with a pseudo-tetrahedral configuration,[2,25] but they are comparable with those reported for the I type complexes with a square pyramidal configuration.[2] This can be seen in Table 4.

The carboxylate-bridged binuclear structure shown in II may be assigned to Group (B) complexes on the basis of their magnetic and spectral data. An analogous dimeric structure bridged by two carboxylate groups in the syn-syn manner exists in crystals of the *p*-toluidine adduct of copper(II) propionate, $[Cu_2(C_2H_5COO)_4(p\text{-toluidine})_2]_n$, the structure of which has recently been determined by X-ray analysis.[26] The structure is basically composed of carboxylate-bridged dimers which are linked into one-dimensional polymeric chains by relatively long monoatomic Cu–O(CO)–Cu carboxylate bridges. Yawney *et al.*[26] have interpreted the magnetic data conforming to Eq. 1 with $-2J=105$ cm^{-1} in terms of a superexchange interaction between copper ions through bridging two carboxylate groups of Cu–O–C–O–Cu linkages rather than in terms of a direct metal–metal interaction, since the Cu–Cu separation (3.197 Å) is too large to allow any significant interaction between them. The $-2J$ values (96—101 cm^{-1}) of the present propionate complexes, 5 and 6, and Cu(Sal·N-R)C_2H_5COO complexes, where R=phenyl and *p*-tolyl, are practically identical with that reported for $[Cu_2(C_2H_5COO)_4(p\text{-toluidine})_2]_n$. This also supports the assignment of the II structure for the present propionate complexes.



IV

The magnetic properties of Group (B) complexes significantly differ from those of the corresponding dimeric carboxylates, $Cu_2(R'COO)_4$, or their adduct complexes with the structure shown in IV, $Cu_2(R'COO)_4L_2$, where L is an additional unidentate ligand: (1) The magnitude of antiferromagnetic interaction observed in Group (B) complexes is considerably smaller than those found in $Cu_2(C_2H_5COO)_4$ ($-2J=300$ cm^{-1})[27] and $Cu_2(ClCH_2COO)_4(\alpha\text{-pic})_2$ ($-2J=322$ cm^{-1}).[24] Such a decrease in magnetic interaction can

Table 4. Comparison of $-2J$ values determined for phenolic oxygen-bridged binuclear copper(II) complexes with salicylideneamines

Complex	$-2J$, cm^{-1}	Structure type
Cu(Sal·N-CH_3)Cl (brown form)[a]	242[a] 292[b]	Pseudo-tetrahedral[c]
Cu(Sal·N-sec·C_4H_9)Cl	320[c]	Pseudo-tetrahedral[c]
Cu(Sal·N-$CH_2CH_2CH_2OH$)Cl·DMF	518[d]	Square-pyramidal[d]
Cu(Sal·N-*p*-tol)NO_3·DMF	528[e]	Square-pyramidal[e]
Cu(Sal·N-*p*-Clph)NO_3·DMF	516[e]	Square-pyramidal[e]
Cu(Sal·N-*p*-tol)HCOO·DMF	498[f]	Square-pyramidal[f]
Cu(Sal·N-*p*-Clph)HCOO·DMF	514[f]	Square-pyramidal[f]
Cu(Sal·N-$CH_2CH_2CH_2OH$)Cl	504[d]	Trigonal bipyramidal with some distortion[g]
Cu(Sal·N-CH_3)Cl (yellow-orange form)[a]	580[a]	Trigonal bipyramidal[d]
Cu(Sal·N-*p*-NO_2ph)Cl	563[d]	Trigonal bipyramidal[d]

a) Ref. 31. b) Ref. 1. c) Ref. 25. d) Ref. 2. e) Ref. 5. f) Present work. g) Ref. 32.

be explained in terms of a decrease in the number of the bridging carboxylate groups through which superexchange interaction is operative, from four in these dimeric copper(II) carboxylates[23,28] to two in the Group (B) complexes. (2) The degree of antiferromagnetic interaction in the Group (B) complexes is apparently reduced according as the number of the substituted chlorine atoms on the acetate group is increased; the order of decrease in $-2J$ is $\mathrm{Cu(Sal{\cdot}N\text{-}R)C_2H_5COO} >$ $\mathrm{Cu(Sal{\cdot}N\text{-}R)ClCH_2COO} >$ $\mathrm{Cu(Sal{\cdot}N\text{-}R)Cl_2CHCOO}$. This is the same as the order of decrease in the ligand-field transition energies observed for these complexes (*cf.* Table 3 and Fig. 5); *i.e.*, there exists a good linear relation between the $-2J$ and $\nu_{\max}$ values. The effect of the chloro-substituent on the magnetic and spectral properties may be attributed to the electron-withdrawing nature of the substituent; *i.e.*, the electron-withdrawing effect causes a decrease in the overlap between the metal-ion orbitals and the orbitals of the bridging carboxylate oxygen atoms and, hence, leads to a weaker magnetic interaction and a lower ligand-field band energy. However, the same type of polar effect of the substituents does not appear in the dimeric copper(II) carboxylates as in $\mathrm{Cu_2(F_3CCOO)_4(quinoline)_2}$ ($-2J=310\ \mathrm{cm^{-1}}$),[13] $\mathrm{Cu_2(ClCH_2COO)_4(\alpha\text{-pic})}$ ($-2J=322\ \mathrm{cm^{-1}}$),[24] and $\mathrm{Cu_2(CH_3COO)_4(py)_2}$ ($-2J=325\ \mathrm{cm^{-1}}$).[29] These complexes all show almost the same magnitude of $-2J$ values regardless of the nature of the substituents. Therefore, there must exist some different conditions in these two types of complexes which make the II-type complexes more sensitive to substitution than the IV-type compounds. The insensitivity of the IV complexes to substitution seems to be linked to the rigid framework of the dimer structure, composed of four carboxylate bridges. This is apparent in the Cu–O–C–O–Cu superexchange path length, which is almost the same for these adduct complexes, *ca.* 6.45 Å.[13,28,30] Such an extremely inflexible path length may lead to constancy in the magnitude of superexchange interaction. On the other hand, the II-type complexes, whose dimer structure is constructed by connecting a pair of copper(II) ions with two carboxylate bridges, is more flexible than that of the IV complexes; thus, it should be more sensitive to any change upon substitution. The different sensitivities could cause the different electronic states in these flexible and inflexible dimer systems, leading to the observed difference in the magnetic interaction. Another probable explanation can perhaps be given in terms of the steric effect of substituents. The flexible framework of the II complexes is considered to be more sensitive to any type of steric conditions than the inflexible framework of the IV compounds. Such steric conditions may come from the repulsion force between the electronegative halogen atoms on the adjacent dimeric molecules or some others. At present, it is difficult to decide which reason is the more important for the observed substituent effect. However, the authors hope that their observation of the effect will lead to the resolution of the unsolved problems regarding the magnetic interaction in copper(II) carboxylate systems.

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