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Magnetic and Spectral Properties of Dimeric Copper(II) Phenylpropynoate Complexes

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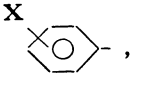
Dimeric copper(II) phenylpropynoate adducts $[Cu(Ph\text{-}C{\equiv}C\text{-}COO)_2 \cdot L]_2$, where L=benzonitrile, 3,5-dichloropyridine, dimethyl sulfoxide and triphenylphosphine oxide, have been synthesized in order to study the influence of the C≡C group linked to the COO group upon the extent of antiferromagnetic interaction between the two metal ions. Magnetic susceptibility measurements between 80 and 300 K show that the singlet-triplet separation ($-2J$) ranges from 283 to 318 cm^{-1}. The magnetic behavior of the non-adduct compound $Cu(Ph\text{-}C{\equiv}C\text{-}COO)_2$ is interpreted by taking an inter-dimer interaction into consideration.

The relation between the magnetism of copper(II) carboxylate dimers, $[Cu(RCOO)_2 \cdot L]_2$, and their structures or the physicochemical nature of R is still subject to much disputation.[1,2] It was previously shown that the antiferromagnetic interaction in $[Cu(RCOO)_2 \cdot L]_2$ complexes tends to increase as the group R becomes a stronger electron donor.[3,4] Thus, in a number of series of dimeric copper(II) carboxylates, the singlet-triplet separation ($-2J$, a measure of the magnetic interaction) increases as the pK_a of the parent acid RCOOH increases.[3,4] However, there exist a few exceptions to the postulated dependence of $-2J$ upon pK_a; for example, while pK_a of trifluoroacetic acid is lower than that of trichloroacetic acid, the $-2J$ found for $[Cu(F_3CCOO)_2(quinoline)]_2$ (310 cm^{-1})[5] is much higher than that found for $[Cu(Cl_3CCOO)_2(2\text{-chloropyridine})]_2$ (217 cm^{-1}).[6] Recently, Doedens *et al.*[7] have pointed out that, in the series of dimeric copper(II) carboxylate adducts with R=H, CH_3, CF_3, CCl_3, and CBr_3, the $-2J$ decreases as the polarizability of the group R increases. However, recent finding of a very large antiferromagnetic interaction, more than 1000 cm^{-1} in $-2J$, in $[Cu(Ph_3MCOO)_2 \cdot L]_2$ (Ph=phenyl and M=Si and Ge) with the very large polarizability of Ph_3M does not stand for the Doedens' indication.[8] These facts suggest the importance of studying the influence of R on the magnetism of $[Cu(RCOO)_2 \cdot L]_2$ from a variety of viewpoints. Under the situation, we have decided to see the influence of unsaturated systems directly linked to the COO group on magnetism in dimeric copper(II) carboxylates. There are three types of such unsaturated systems: (A)  , (B) >C=C<, (C) -C≡C-. Copper(II) carboxylate dimers containing the unsaturated group of type A, *i.e.*, copper(II) arenecarboxylate dimers tend to show lower values of $-2J$ than the related copper(II) alkanoate dimers.[4] Magnetic studies on dimeric copper(II) carboxylates with the unsaturated systems of type B are limited at present. A typical structural and magnetic study in this series is on $[Cu(CH_3CH{=}CHCOO)_2(quinoline)]_2$ which showed a normal value of $-2J$ (333 cm^{-1}).[9] For copper(II) carboxylate dimers with the unsaturated system of type C, no magnetic study has appeared up to date. Based on such a situation, in the present study, six copper(II) phenylpropynoate complexes, $Cu(Ph\text{-}C{\equiv}C\text{-}COO)_2 \cdot 3H_2O$, $Cu(Ph\text{-}C{\equiv}C\text{-}COO)_2$, and $Cu(Ph\text{-}C{\equiv}C\text{-}COO)_2 \cdot L$, where L=benzonitrile (PhCN), 3,5-dichloropyridine (3,5-Cl_2py), dimethyl sulfoxide (DMSO) and triphenylphosphine oxide (Ph_3PO), were prepared and characterized by means of magnetic susceptibility and electronic spectrum measurements. The magnetic properties of $Cu(Ph\text{-}C{\equiv}C\text{-}COO)_2 \cdot L$ complexes were compared with those reported for several other dimeric copper(II) carboxylates. For the sake of discussion, the dimethyl sulfoxide adduct of copper(II) acetate, $Cu(CH_3COO)_2(DMSO)$, was also prepared and investigated.

Experimental

Syntheses. $Cu(Ph\text{-}C{\equiv}C\text{-}COO)_2 \cdot 3H_2O$: Phenylpropynoic acid (12 mmol) was dissolved in 0.25 M sodium hydroxide (100 ml) and the resulting solution was filtered. The solution was neutralized with dilute nitric acid using phenolphthalein as an indicator. When a solution of copper(II) nitrate trihydrate (6 mmol) in water (25 ml) was added to the above solution with stirring, blue crystals precipitated. The crystals were collected, washed repeatedly with water and air-dried at room temperature.

$Cu(Ph\text{-}C{\equiv}C\text{-}COO)_2 \cdot L$: L=PhCN or DMSO: The mixture of $Cu(Ph\text{-}C{\equiv}C\text{-}COO)_2 \cdot 3H_2O$ (1 mmol) and L (5 mmol) in chloroform (60 ml) was stirred for *ca.* 1/2 h at room temperature. The resulting solution was filtered and then concentrated to one-third of its volume. When petroleum ether was added to the solution, green crystals precipitated. The crystals were collected, washed with petroleum ether and dried *in vacuo* at room temperature. L=3,5-Cl_2py or Ph_3PO: A solution of L (1 mmol) in acetone (10 ml) was added to a solution of $Cu(Ph\text{-}C{\equiv}C\text{-}COO)_2 \cdot 3H_2O$ (1 mmol) in acetone (30 ml). The separated green crystals were collected, washed with a 1:2 acetone-petroleum ether mixture and dried *in vacuo* at room temperature.

$Cu(Ph\text{-}C{\equiv}C\text{-}COO)_2$: This non-adduct compound was obtained by dehydrating the hydrate complex at *ca.* 80 °C.

$Cu(CH_3COO)_2(DMSO)$: The mixture of anhydrous copper(II) acetate (5 mmol) and DMSO (13 mmol) in ehanol (70 ml) was heated with stirring for *ca.* 6 h. The

resulting solution was filtered and then allowed to stand overnight at *ca.* 5 °C in a refrigerator. The separated green crystals were collected, washed with benzene and dried *in vacuo* at room temperature.

The results of the elemental analyses are given in Table 1.

Physical Measurements. Magnetic susceptibilities in the temperature range of 80—300 K were determined by the Faraday method. Pascal's constants[10] were used for diamagnetic corrections. The value of 60×10^{-6} cgs emu mol^{-1} (1 cgs emu $mol^{-1}=4\pi\times10^{-6}$ m^3 mol^{-1}) for the temperature-independent paramagnetism ($N\alpha$) per gram ion of copper(II) was used throughout the present study. The cryomagnetic data of $Cu(Ph-C\equiv C-COO)_2 \cdot 3H_2O$ were analyzed in terms of Curie-Weiss law of the form,

$$\chi_A = \frac{Ng^2\beta^2}{4k(T-\theta)} + N\alpha, \quad (1)$$

where θ is Weiss constant and the other symbols have their usual meanings. Plots of χ_A *vs.* T and of $(\chi_A - N\alpha)^{-1}$ *vs.* T are shown in Fig. 1. The cryomagnetic data of the adduct complexes, $Cu(Ph-C\equiv C-COO)_2 \cdot L$, were fitted to the modified Bleaney-Bowers equation (2),

$$\chi_A = \frac{Ng^2\beta^2}{3k(T-\theta')}\left[1+\frac{1}{3}\exp\left(\frac{-2J}{kT}\right)\right]^{-1}\cdot(1-P) + \frac{Ng_i^2\beta^2}{4kT}\cdot P + N\alpha, \quad (2)$$

where P is the mole fraction of the noncoupled copper(II) impurity, g_i is the average g factor for the impurity and θ' represents the Weiss constant for inter-cluster interaction. A fixed value of 2.2 was used for g_i throughout this study. The best-fit parameters, $-2J$, g, P, and θ', were obtained by a nonlinear least-squares fitting procedure. The quality of fit was estimated by means of a discrepancy index, σ_{dis},

$$\sigma_{dis} = \left[\frac{\Sigma(\chi_{obsd}-\chi_{calcd})^2}{\Sigma\chi_{obsd}^2}\right]^{1/2}. \quad (3)$$

The thermal magnetic data are shown in Figs. 2 and 3 as plots of χ_A *vs.* T. The values of $-2J$, g, P, θ', and σ_{dis} are summarized in Table 2.

IR spectra were recorded on a Hitachi 260-10 IR Spectrophotometer as Nujol mulls.

Reflectance spectra were recorded on a Hitachi Recording Spectrophotometer 323.

Results and Discussion

The magnetic susceptibility data of $Cu(Ph-C\equiv C-$

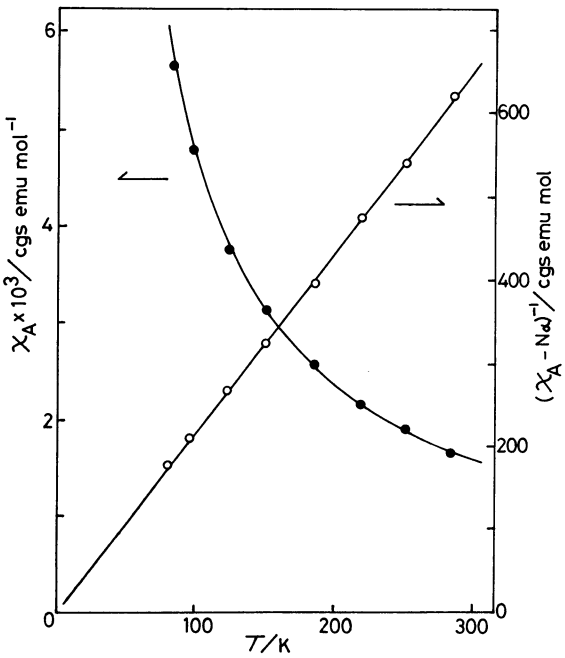


Fig. 1. Temperature dependence of magnetic susceptibilities (●, χ_A; ○, $(\chi_A - N\alpha)^{-1}$) of $Cu(Ph-C\equiv C-COO)_2 \cdot 3H_2O$.
The solid curve and line were obtained as described in the text.

Table 1. Analytical data

Complex	Found(Calcd) (%)			
	C	H	N	Cu
$Cu(Ph-C\equiv C-COO)_2 \cdot 3H_2O$	52.82 (53.00)	3.97 (3.95)		15.49 (15.58)
$Cu(Ph-C\equiv C-COO)_2$	60.96 (61.10)	2.85 (2.85)		18.14 (17.96)
$Cu(Ph-C\equiv C-COO)_2(PhCN)$	65.22 (65.71)	3.38 (3.31)	2.95 (3.06)	13.92 (13.90)
$Cu(Ph-C\equiv C-COO)_2(3,5\text{-}Cl_2py)$	55.32 (55.05)	2.53 (2.61)	2.61 (2.79)	12.57 (12.66)
$Cu(Ph-C\equiv C-COO)_2(DMSO)$	55.47 (55.61)	3.94 (3.73)		14.80 (14.71)
$Cu(Ph-C\equiv C-COO)_2(Ph_3PO)$	68.34 (68.40)	3.86 (3.98)		10.02 (10.05)
$Cu(CH_3COO)_2(DMSO)$	27.81 (27.74)	4.66 (4.65)		24.45 (24.46)

Table 2. Magnetic parameters

Complex	$\frac{-2J}{cm^{-1}}$	g	$P\times10^2$	$\frac{\theta'}{K}$	$\sigma_{dis}\times10^3$
$Cu(Ph\text{-}C\equiv C\text{-}COO)_2(PhCN)$	318	2.27_1	0.20	0	4.15
$Cu(Ph\text{-}C\equiv C\text{-}COO)_2(3,5\text{-}Cl_2py)$	300	2.29_1	1.27	0	6.45
$Cu(Ph\text{-}C\equiv C\text{-}COO)_2(DMSO)$	287	2.26_8	0.48	0	4.96
$Cu(Ph\text{-}C\equiv C\text{-}COO)_2(Ph_3PO)$	283	2.38_4	2.41	0	6.74
$Cu(Ph\text{-}C\equiv C\text{-}COO)_2$	213	2.16_2	7.11	+6.86	5.08
$Cu(CH_3COO)_2(DMSO)$	326	2.25_0	0.32	0	5.66

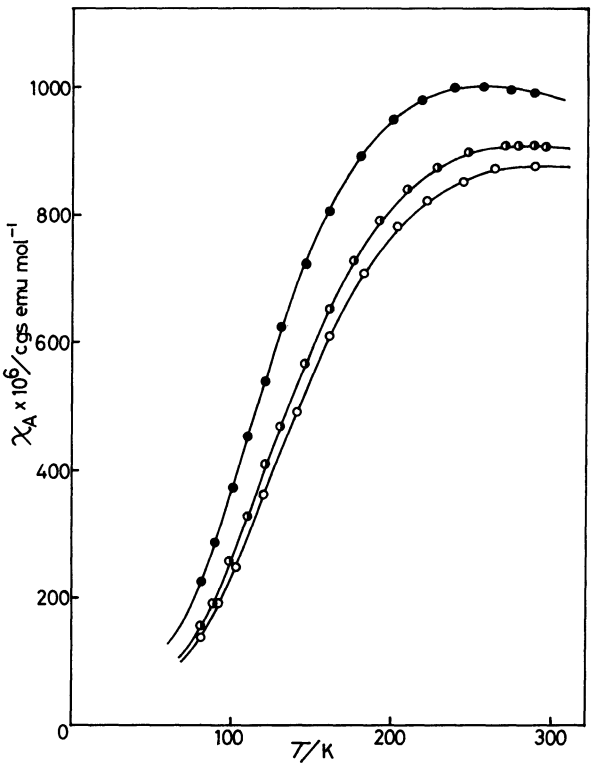


Fig. 2. Temperature dependence of magnetic susceptibilities of $Cu(Ph\text{-}C\equiv C\text{-}COO)_2(DMSO)$ (●), $Cu(Ph\text{-}C\equiv C\text{-}COO)_2(PhCN)$ (◑), and $Cu(CH_3COO)_2(DMSO)$ (○).
The solid curves were obtained as described in the text.

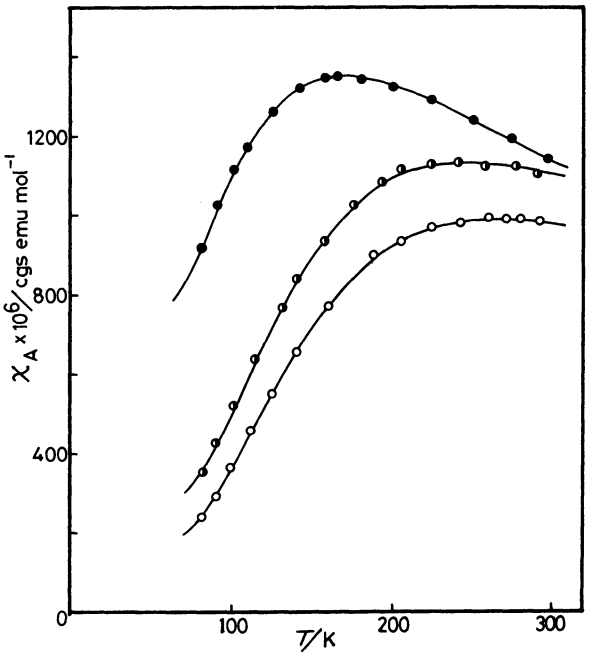


Fig. 3. Temperature dependence of magnetic susceptibilities of $Cu(Ph\text{-}C\equiv C\text{-}COO)_2$ (●), $Cu(Ph\text{-}C\equiv C\text{-}COO)_2(Ph_3PO)$ (◑), and $Cu(Ph\text{-}C\equiv C\text{-}COO)_2(3,5\text{-}Cl_2py)$ (○).
The solid curves were obtained as described in the text.

$COO)_2\cdot 3H_2O$ follow the Curie-Weiss law. The best fit of the experimental data to Eq. 1 yields the values of $g=2.19_9$ and $\theta/K=+2.0$ with $\sigma_{dis}=8.55\times10^{-3}$. The effective magnetic moment at 10 °C calculated from the equation, $\mu_{eff}=2.83[(\chi_A-N\alpha)\cdot T]^{1/2}$, is 1.91 BM (1 BM=$9.27\times10^{-24}$ A m^2). These results indicate that this compound does not have a dimeric structure but may have a monomeric structure, as has copper(II) 2-carboxybenzoate dihydrate[11] (μ_{eff}=1.95 BM at 297 K and $\theta/K=-0.6\pm3.3$),[12] or a polymeric structure, as has copper(II) benzoate trihydrate[13] (μ_{eff}=1.97 BM at 293.4 K and $\theta/K=+40$).[14]

The cryomagnetic data observed for the adducts of copper(II) phenylpropynoate prepared in the present study are well represented by Eq. 2 (*cf.* Figs. 2 and 3 and Table 2), indicating that all these adducts have a dimeric structure similar to that found for copper(II) acetate monohydrate.[15] The $-2J$ values of these adducts and those of the corresponding adducts of other dimeric copper(II) carboxylates studied in our laboratory are given in Table 3 along with the pK_a values of their parent carboxylic acids. From Table 3, it can be seen that, in each series of the complexes with the same L, the $-2J$ value decreases as the pK_a value of the parent carboxylic acid becomes smaller. This fact suggests that, in the present phenylpropynoate adducts, the electron-withdrawing nature of the Ph-C≡C group predominantly affects the magnetic interaction. On the other hand, in the present study, the influence of the highly unsaturated

Table 3. Comparison of $-2J$ values for [Cu(RCOO)$_2$·L]$_2$ complexes

R \ L	$-2J$/cm^{-1} PhCN	3,5-Cl$_2$py	DMSO	Ph$_3$PO	p$K_a^{25\,°C}$ of RCOOH[f]
CH_3		349[c]	326[b]	319[e]	4.76
$ClCH_2$	352[a]	340[c]			2.81
Ph-C≡C	318[b]	300[b]	287[b]	283[b]	2.32
Cl_2CH		312[c]			1.29
Cl_3C	224[a]	92[d]			0.08

a) Ref. 23. b) Present work. c) Ref. 22. d) Ref. 24. e) Ref. 25. f) Ref. 26.

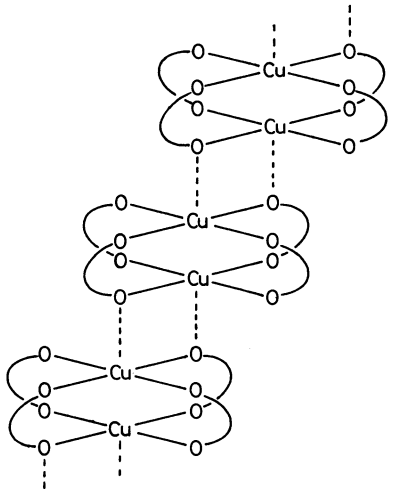


Fig. 4. Schematic representation of polymeric chain structure of copper(II) propionate.[19]

property of the C≡C group directly linked to the COO group on the magnetic interaction could not be detected.

For the non-adduct compound, Cu(Ph-C≡C-COO)$_2$, the best fit of the thermal magnetic data to Eq. 2 gave the value of $-2J$=213 cm^{-1}, a value much lower than those found for the adduct complexes, 283—318 cm^{-1} (*cf.* Table 2 and Fig. 3). Such magnetochemical behavior is in accord with the general trend that, in many dimeric copper(II) carboxylates, the values of $-2J$ for the non-adduct complexes are often lower than those for the corresponding adduct complexes,[4,16] as seen in the case, Cu(C$_2$H$_5$COO)$_2$ (300 cm^{-1})[17]<Cu(C$_2$H$_5$COO)$_2$(py) (350 cm^{-1}).[18] The crystal structure of Cu(C$_2$H$_5$COO)$_2$ is composed of carboxylato-bridged dimers which are linked into one-dimensional polymeric chains by apical Cu-O interaction (*cf.* Fig. 4).[19] Such an apical Cu-O interaction will disturb the superexchange interaction through the carboxylato bridges,[20] leading to the lower value of $-2J$. The low $-2J$ value found for Cu(Ph-C≡C-COO)$_2$, therefore, suggests the presence of apical-to-basal Cu-O-Cu linkages similar to Cu(C$_2$H$_5$COO)$_2$ in this compound. This deduction is further supported by the fact that, among the dimeric compounds in the present study, only the non-adduct compound, Cu(Ph-C≡C-COO)$_2$, showed an appreciably large positive value of θ', θ'/K=+6.86 (*cf.* Table 2). The positive value of θ' is considered to arise from the presence of ferromagnetic spin-spin interaction through the apical-to-basal Cu-O-Cu bonds shown in Fig. 4.

The C≡C stretching vibrations for the non-adduct

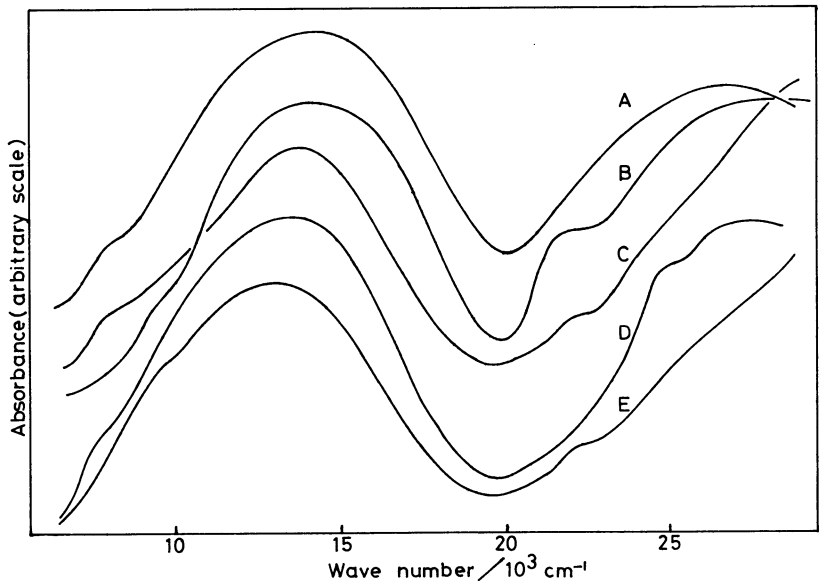


Fig. 5. Reflectance spectra of Cu(CH$_3$COO)$_2$(DMSO) (A), Cu(Ph-C≡C-COO)$_2$(PhCN) (B), Cu(Ph-C≡C-COO)$_2$(3,5-Cl$_2$py) (C), Cu(Ph-C≡C-COO)$_2$(DMSO) (D), and Cu-(Ph-C≡C-COO)$_2$(Ph$_3$PO) (E).

Table 4. Reflectance spectral data

Complex	Band I		New Band		Band II
	$\tilde{\nu}_{max}/10^3$ cm^{-1}				
$Cu(Ph\text{-}C\equiv C\text{-}COO)_2(PhCN)$	14.0	9.5[a]	24.9[a]	22.2[a]	28.3
$Cu(Ph\text{-}C\equiv C\text{-}COO)_2(3,5\text{-}Cl_2py)$	13.8	7.8[a]	24.5[a]		
$Cu(Ph\text{-}C\equiv C\text{-}COO)_2(DMSO)$	13.6	7.8[a]	25.1[a]		28.7
$Cu(Ph\text{-}C\equiv C\text{-}COO)_2(Ph_3PO)$	13.0	8.0[a]	24.5[a]		
$Cu(CH_3COO)_2(DMSO)$	14.2	7.9[a]			26.7

a) Shoulder.

compound (2223 cm^{-1}) and the adduct compounds (2221—2223 cm^{-1}) are almost the same as those for free phenylpropynoic acid (2235, 2200 cm^{-1}). This fact indicates the absence of coordination through the C≡C π system in these dimeric copper(II) compounds.

The reflectance spectra of the present adduct complexes in the range 5000—29400 cm^{-1} show three bands having maxima at 28000—29000 cm^{-1} (so-called Band II), 24000—25000 cm^{-1}, and 13000—14000 cm^{-1} (so-called Band I) with a shoulder at *ca.* 8000 cm^{-1}. The wave numbers of the band maxima ($\tilde{\nu}_{max}$) are listed in Table 4 and their spectral curves are shown in Fig. 5. A remarkable feature of the spectra of these complexes is the appearance of a new band in the range 24000—25000 cm^{-1} which is absent in dimeric copper(II) alkanoate and arenecarboxylate complexes. For comparison, the reflectance spectrum of $Cu(CH_3COO)_2(DMSO)$ ($-2J$=326 cm^{-1}) is given in Fig. 5, which has no such absorption in the 24000—25000 cm^{-1} region. Such a new band has been recently observed for $[Cu(Ph_3GeCOO)_2(DMSO)]_2$ and $[Cu(Me_2PhSiCOO)_2(DMSO)]_2$, where Me=methyl.[8] Since the assignment of d-d bands for dimeric copper(II) carboxylates is still in dispute,[21] finding of such a new band is hoped to serve to elucidate the electronic state of the copper(II) ion in these dimeric systems. From Table 4 and Fig. 5, we can also see that the $\tilde{\nu}_{max}$ value of Band I decreases in the order: PhCN adduct>3,5-Cl_2py adduct>DMSO adduct>Ph_3PO adduct, the order of which is the same as that of the $-2J$ value (*cf.* Table 2). A parallelism exists between the $\tilde{\nu}_{max}$ and $-2J$ values (higher $\tilde{\nu}_{max}$-higher $-2J$). A similar parallelism was previously observed for a series of $[Cu(RCOO)_2\cdot L]_2$ complexes, where R=CH_3, $ClCH_2$, and Cl_2CH, and L=pyridine analogues, and the parallelism was interpreted in terms of the electroneutrality principle.[22]

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