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Syntheses and Properties of Dinuclear Copper(II) Complexes with 2,6-Bis[bis(2-pyridylmethyl)aminomethyl]-4-methylphenol

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The dinucleating ligand, 2,6-bis[bis(2-pyridylmethyl)aminomethyl]-4-methylphenol](Hbpmp), formed two types of dinuclear copper(II) complexes, $[Cu_2(bpmp)X_2]^{n+}$($X=Cl^-$, N_3^- py(pyridine), or Him(imidazole), and $n=1$ or 3), and $[Cu_2(bpmp)X]^{2+}$($X=CH_3COO^-$ or im$^-$). On the basis of the dinucleating nature of the ligand (bpmp), the elemental analyses and the conductivity measurements in acetonitrile, it is concluded that the complexes have dimeric unit of $[Cu_2(bpmp)X_2]^{n+}$ or $[Cu_2(bpmp)X]^{2+}$. In $[Cu_2(bpmp)X_2]^{n+}$ type complexes, two copper(II) ions are linked only by a single phenolate bridge. Magnetic susceptibilities of those complexes obey Curie-Weiss law in the temperature range 80—300 K with the Weiss constants ≈ -4 K, indicating that weak antiferromagnetic interactions are present in these complexes. In $[Cu_2[bpmp)X]^{2+}$ type complexes, however, two copper(II) ions are bridged by phenolate and acetate, or phenolate and imidazolate. Cryomagnetic measurements of the acetato and the imidazolato complexes showed antiferromagnetic interactions with the $-2J$ values of 82 and 66 cm^{-1}, respectively. All the complexes exhibited absorption bands at 20000—22000 cm^{-1} except for the azido complex. The origin of those bands are discussed.

Various types of quinquedentate and septidentate dinucleating ligands (L) such as Schiff-bases derived from 2,6-diformyl-4-methylphenol and various amines, 2,6-bis[bis[2-(2-pyridyl)ethyl]aminomethyl]-4-methylphenol (Hbpep), *etc.*, have been designed.[1–6] Dinuclear copper(II) complexes with those ligands are of current interest as models for the active sites of type III coppers such as hemocyanin, tyrosinase, and multicopper oxidases. General formula of those complexes is $[Cu_2(L)X]^{2+}$, in which two copper ions are linked by two bridging groups, *viz.*, phenolate or alkoxide, and additional bridging ligand (X) ($X=OH^-$, Cl^-, N_3^-, $C_3H_3N_2^-$ (pyrazolate), CH_3COO^-, *etc.*).

In the previous studies,[7–9] however, we found that the dinucleating ligand, 2,6-bis[bis(2-pyridylmethyl)-aminomethyl]-4-methylphenol (Hbpmp) forms new type of five-coordinate dinuclear cobalt(II) complexes, $[Co_2(bpmp)X_2]^+$ ($X=Cl^-$, Br^-, NCS^-, and N_3^-), in which two cobalt(II) ions are linked only by a single phenolate bridge. In those complexes, two vacant coordination sites (the sixth coordination sites) are positioned in close proximity and some of the complexes react reversibly with molecular oxygen to form μ-peroxo complexes. Such type of dinuclear copper(II) complexes bridged only by a single phenolate group is rare and attractive for studying interactions with various molecules such as hydrogen peroxide, ascorbic acid, *etc.*, with two copper(II) ions. Therefore, we have undertaken to prepare such type of dinuclear copper(II) complexes with bpmp, $[Cu_2(bpmp)X_2]^{n+}$. This paper deals with the preparations, and magnetic and electronic properties of those complexes. $[Cu_2(bpmp)X]^{2+}$ type complexes in which X acts as bridging ligand are also reported, where X represents CH_3COO^- or im$^-$ (imidazolate).

Experimental

Preparation. The dinucleating ligand, Hbpmp, was prepared according to the literature.[7)]

$[Cu_2(bpmp)(py)_2](ClO_4)_3\cdot 2H_2O$. Pyridine (1.5 mmol) was added to a solution of $Cu(ClO_4)_2\cdot 6H_2O$ (1 mmol) and Hbpmp (0.5 mmol) in methanol (50 cm^3) with stirring. The blue crystals deposited were filtered, washed with ethanol, and dried *in vacuo*.

$[Cu_2(bpmp)(Him)_2](ClO_4)_3\cdot H_2O$. Imidazole (1.5 mmol) was added to a hot methanol solution (50 cm^3) of $Cu(ClO_4)_2\cdot 6H_2O$ (1 mmol) and Hbpmp (0.5 mmol) with stirring to give blue oil. The resulting oil was dissolved in 50 cm^3 of methanol on heating to give violet solution. On cooling, the blue crystals formed were collected by filtration, washed with ethanol, and air dried *in vacuo*.

$[Cu_2(bpmp)(N_3)_2]ClO_4$. A solution of sodium azide (1.5 mmol) in water was added to a solution of $Cu(ClO_4)_2\cdot 6H_2O$ (1 mmol) and Hbpmp (0.5 mmol) in 50 cm^3 of CH_3CN and CH_3OH mixture (1:1). The resulting brown solution was filtered and the filtrate was allowed to stand overnight to give brown crystals, which were collected by filtration, washed with ethanol and dried *in vacuo*.

$[Cu_2(bpmp)Cl_2]ClO_4\cdot CH_3OH\cdot H_2O$. A solution of NaCl (1.5 mmol) in water was added to a solution of $Cu(ClO_4)_2\cdot 6H_2O$ (1 mmol) and Hbpmp (0.5 mmol) in 50 cm^3 of aqueous methanol (1:1). The resulting brown solution was allowed to stand overnight to give blue grey crystals, which were collected by filtration, washed with ethanol, and dried *in vacuo*.

$[Cu_2(bpmp)(CH_3COO)](ClO_4)_2$. Sodium acetate (0.05 mmol) was added to a solution of $Cu(ClO_4)_2\cdot 6H_2O$ (1 mmol) and Hbpmp (0.05 mmol) in methanol (30 cm^3). To the resulting brown solution was added 50 cm^3 of ethanol to give brown crystals, which were collected by filtration, washed with ethanol, and dried *in vacuo*.

$[Cu_2(bpmp)im](ClO_4)_2\cdot 1.5CH_3CN$. A solution of CH_3ONa (1 mmol) in methanol (5 cm^3) was added to a solution of $Cu(ClO_4)_2\cdot 6H_2O$ (1 mmol), Hbpmp (0.5 mmol), and Him (0.5 mmol) in acetonitrile (30 cm^3) to give a dark brown solution. Addition of ethanol to the brown solution gave brown crystals, which were collected by filtration, washed with ethanol, and dried *in vacuo*.

Measurements. The electronic spectra in solution and in solid were obtained with a Hitachi EPS-3T recording spectrophotometer and infrared spectra were recorded with a Hitachi 295 spectrophotometer by means of KBr disk. Magnetic susceptibilities were measured by Faraday method in the temperature range 80—300 K. Diamagnetic correction was made using Pascal's constants.[10)] Molar conductivities of the complexes were determined in acetonitrile solution (10^{-3} mol dm^{-3}) at 25 °C.

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Results and Discussion

[Cu_2(bpmp)X_2]$^{n+}$ Type Complexes. As was mentioned before, dinucleating ligands (L) such as bpep have been shown to form [Cu_2(L)X]$^{2+}$ type complexes. However, the addition of NaX to a mixture of Hbpmp and $Cu(ClO_4)_2 \cdot 6H_2O$ gave a new type of dinuclear complexes, [Cu_2(bpmp)X_2]$^+$ (X=Cl^- and N_3^-).

The infrared spectra of [Cu_2(bpmp)X_2]ClO_4 complexes indicated the presence of uncoordinated perchlorate ions because no splitting of the ν(Cl–O) bands was observed definitely. The azido complex exhibited a single strong ν_{asymm} (N_3) band at 2038 cm^{-1}, suggesting that each azide ion coordinates to copper(II) ion in a similar way. In addition, the molar conductivities of those complexes indicated the presence of 1:1 electrolytes in acetonitrile (Table 1).[11] Those observations imply that the complexes have dimeric unit of [Cu_2(bpmp)X_2]$^+$ in which each X^- ion coordinates to copper(II) ion and two copper(II) ions are linked only by a single phenolate bridge as was found for the corresponding dinuclear cobalt(II) complexes.[9] A possible structure of [Cu_2(bpmp)X_2]$^+$ type complexes is given in Fig. 1.

The addition of such bases as pyridine or imidazole to a mixture of Hbpmp and $Cu(ClO_4)_2 \cdot 6H_2O$ in methanol also afforded [Cu_2(bpmp)X_2]$^{3+}$ type complexes. The infrared spectra and molar conductivities also suggested that the complexes have dimeric unit of [Cu_2(bpmp)X_2]$^{3+}$ in which two copper(II) ions are bridged only by a single phenolate.

The present dinucleating ligand (bpmp) contains two tripodal parts ($N(CH_2py)_2(CH_2C_6H_5O^-)$). It is known that the tripod ligands which form three five-membered chelate rings tend to enforce trigonal bipyramidal copper(II) complexes with an additional unidentate ligand.[12] In general, trigonal bipyramidal copper(II) complexes show a band with a high energy shoulder in the d-d region.[13] However, [Cu_2(bpmp)Cl_2]$^+$ shows a band at *ca.* 14000 cm^{-1} with a low energy shoulder at ≈10000 cm^{-1} both in solid and acetonitrile (Fig. 2 and Table 2). This spectral pattern is indicative of a square pyramidal or a distorted square pyramidal structure about copper(II) ion.[13] An additional band is observed at 20000—22000 cm^{-1} both in solid and in acetonitrile. The complexes containing phenolate group(s) have been shown to display

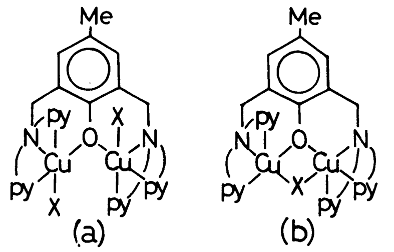

Fig. 1. Possible structures of [Cu_2(bpmp)X_2]$^{n+}$ (a) and [Cu_2(bpmp)X]$^{2+}$ (b) type complexes.

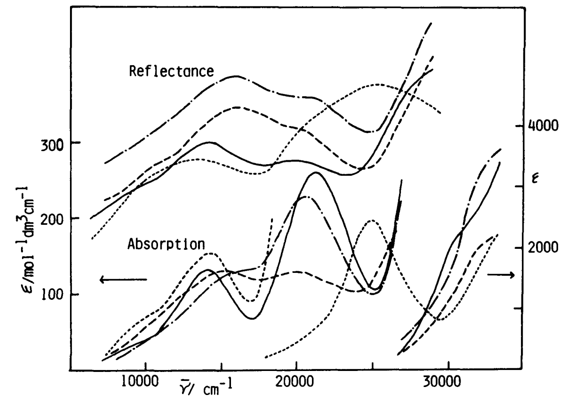

Fig. 2. Reflectance and absorption spectra of [Cu_2(bpmp)Cl_2]$ClO_4 \cdot CH_3OH \cdot H_2O$ (——), [Cu_2(bpmp)(N_3)$_2$]ClO_4 (------), [Cu_2(bpmp)(py)$_2$]$(ClO_4)_3 \cdot 2H_2O$ (----), and [Cu_2(bpmp)(Him)$_2$]$(ClO_4)_3 \cdot H_2O$ (—·—).

TABLE 1. ELEMENTAL ANALYSES AND MOLAR CONDUCTIVITIES OF COMPLEXES

Complex	Found(Calcd) (%)			Molar conductivity
	C	H	N	Ω^{-2} cm^2 mol^{-1}
[Cu_2(bpmp)Cl_2]$ClO_4 \cdot CH_3OH \cdot H_2O$	46.62(46.56)	4.32(4.48)	9.68(9.58)	154
[Cu_2(bpmp) (N_3)$_2$]ClO_4	47.00(47.17)	4.32(3.96)	20.13(20.00)	131
[Cu_2(bpmp) (py)$_2$] $(ClO_4)_3 \cdot 2H_2O$	45.00(44.94)	3.91(4.12)	9.62(9.75)	432
[Cu_2(bpmp) (Him)$_2$] $(ClO_4)_3 \cdot H_2O$	42.26(42.23)	3.89(3.91)	12.62(12.63)	374
[Cu_2(bpmp) (CH_3COO)] $(ClO_4)_2$	45.81(45.96)	4.09(3.97)	9.17(9.19)	272
[Cu_2(bpmp) (im)] $(ClO_4)_2 \cdot 1.5CH_3CN$	47.88(47.59)	4.36(4.15)	13.46(13.52)	229

TABLE 2. ELECTRONIC SPECTRAL DATA

Complex	Reflectance spectra $\tilde{\nu}/10^3$ cm^{-1}			Absorption spectra[a] $\tilde{\nu}/10^3$ cm^{-1} (ε/mol^{-1} dm^3 cm^{-1})		
[Cu_2(bpmp)Cl_2]$ClO_4 \cdot CH_3OH \cdot H_2O$	10^s	13.9	19.6	10^s	14.2(131)	21.3(258)
[Cu_2(bpmp) (N_3)$_2$]ClO_4		$13.2^{b)}$	25.0	10^s	14.3(153)	24.9(2450)
[Cu_2(bpmp) (py)$_2$] $(ClO_4)_3 \cdot 2H_2O$	11^s	15.9	20.0^s		15.3(130)	20.0(129)
[Cu_2(bpmp) (Him)$_2$] $(ClO_4)_3 \cdot H_2O$		15.7	21.3		$15.4(137)^s$	20.5(230)
[Cu_2(bpmp) (CH_3COO)] $(ClO_4)_2$	9.6^s	15.3	21.7	11.6(110)	13.5(110)	22.4(319)
[Cu_2(bpmp) (im)] $(ClO_4)_2 \cdot 1.5CH_3CN$	11.8		20.6	11.7(209)	$14.3(180)^s$	21.5(329)

a) In acetonitrile. b) Broad band. s : Shoulder.

Table 3. Magnetic data of complexes

Complex	μ_{eff}/BM		θ/K	$-2J$/cm^{-1}	g	$N\alpha/10^{-6}$ cgs mol^{-1} a)
	80 K	297 K				
$[Cu_2(bpmp)Cl_2]ClO_4 \cdot CH_3OH \cdot H_2O$	1.84	1.87	−4			
$[Cu_2(bpmp)(N_3)_2]ClO_4$	1.78	1.81	−5			
$[Cu_2(bpmp)(py)_2](ClO_4)_3 \cdot 2H_2O$	1.80	1.83	−4			
$[Cu_2(bpmp)(Him)_2](ClO_4)_3 \cdot H_2O$	1.79	1.83	−5			
$[Cu_2(bpmp)(CH_3COO)](ClO_4)_2$	1.32	1.75		82	2.05	80
$[Cu_2(bpmp)(im)](ClO_4)_2 \cdot 1.5CH_3CN$	1.43	1.75		66	2.05	60

a) cgs mol^{-1}×4π×10^{-6}→m^3 mol^{-1}.

phenolate (Opπ) to copper(II) ($d_{x^2-y^2}$) charge-transfer (CT) bands in the visible or the near-ultraviolet region.[5,6,14,15] It is unlikely that the band is ascribed to the d-d transitions since such a (distorted) square pyramidal complex with ClN_3O donor set would not exhibit the d-d band at such high energy. It is also unlikey that chloride (pπ) to copper CT transitions occur at such low energy; chloride to copper CT transitions would be expected to occur at about 30000 cm^{-1}.[16] Therefore, we believe that the band at 20000—22000 cm^{-1} is ascribed to phenolate to copper CT transition. A shoulder observed at 30000 cm^{-1} is assigned to chloride to copper CT transitions.

The azido complex exhibits a broad band at 13000 cm^{-1} in the reflectnace spectrum, while in the absorption spectrum, this band is resolved into a single band and a low energy shoulder. This spectral pattern is also indicative of a (distorted) square pyramidal structure. An intense band (ε=2500 mol^{-1}dm^3 cm^{-1}) is observed at 25000 cm^{-1}. This band is assigned to azide to copper CT transitions. Phenolate to copper CT transition may be hidden under this intense band.

The pyridine and the imidazole complexes exhibit the d-d band maxima at 15000—16000 cm^{-1} in the reflectance spectra, which are shifted to blue (1000—2000 cm^{-1}) compared with those of the chloro and the azido complexes. These blue shifts of the d-d band maxima of the former two complexes are attributed to the stronger ligand field strengths of pyridine and imidazole. The pyridine and the imidazole complexes show bands at 20000—21000 cm^{-1}. We tentatively assigned those bands to phenolate to copper CT transitions. If these assignments are correct, the energies of phenolate to copper CT transitions of $[Cu_2(bpmp)X_2]^{n+}$ type complexes are much lower than that of $[Cu_2(bpep)N_3]^{2+}$ (26000 cm^{-1}). This shift of the CT transition energies may be attributed to the geometries of the Cu-O-Cu moieties.[17]

Sakurai *et al.*[18] reported that $[Cu_2(tba)_2pcp]^{3+}$ (tba=tris(2-benzimidazolylmethyl)amine and pcp=4-chlorophenolate) in which two copper(II) ions are bridged only by a single phenolate group shows a reduced magnetic moment (1.7 BM††) at room temperature in acetone. However, magnetic property of this complex has not been fully investigated. The magnetic susceptibilities of the present complexes obey Curie-Weiss law in the temperature range 80—300 K with Weiss constants of −4— −5 K (Fig. 3 and Table 3). This implies that, although antiferromagnetic interactions are present between two copper(II) ions, they are very weak. Thus in these complexes, phenolic oxygens are not good mediator for antiferromagnetic superexchange pathway. In order to discuss their magnetisms more fully, precise structure data are necessary.

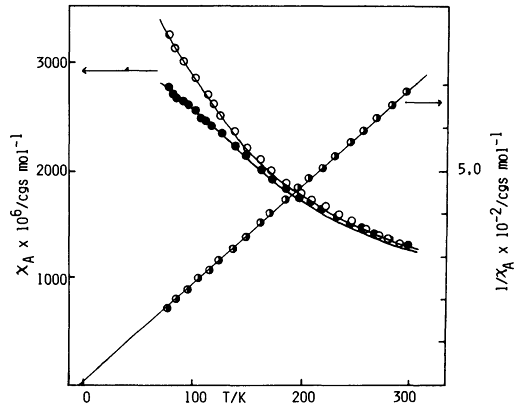

Fig. 3. Temperature dependence of inverse magnetic susceptibilities of $[Cu_2(bpmp)Cl_2]ClO_4 \cdot CH_3OH \cdot H_2O$ (◑), and temperature dependence of magnetic susceptibilities of $[Cu_2(bpmp)(CH_3COO)](ClO_4)_2$ (●) and $[Cu_2(bpmp)im](ClO_4)_2 \cdot 1.5CH_3CN$ (○). Solid curves for $[Cu_2(bpmp)(CH_3COO)](ClO_4)_2$ and $[Cu_2(bpmp)im](ClO_4)_2 \cdot 1.5CH_3CN$ are drawn based on the Eq. 1 using the parameters listed in Table 3.

As was mentioned before, the dinucleating ligand, bpep, forms $[Cu_2(bpep)X]^{2+}$ type complexes [$X=Cl^-$ and N_3^-],[5] whereas bpmp forms $[Cu_2(bpmp)X_2]^+$ type complexes. This suggests that in the bpmp complexes, it is difficult for the binding sites available for linking two copper ions by one atom bridge such as Cl^- to approach in close proximity. Thus the chelate ring size of dinucleating ligand has a significant influence on stereochemistry of dinuclear copper(II) complex. It was attempted to prepare $[Cu_2(bpmp)X]^{2+}$ type complexes containing one atom bridge (X), and $[Cu_2(bpmp)(OH)](ClO_4)_2$ was obtained (*vide infra*).

$[Cu_2(bpmp)X]^{2+}$ Type Complexes. The addition of NaOH to a mixture of Hbpmp and $Cu(ClO_4)_2 \cdot 6H_2O$ in aqueous acetonitrile afforded green powder. The elemental analysis of the green powder is in agreement with $[Cu_2(bpmp)(OH)](ClO_4)_2$. Although magnetic susceptibility data over temperature range 80—300 K suggested that antiferromagnetic interaction is present in this complex, the data could not be explained on the basis of the Bleaney-Bowers equation.[19] The preparation of the complex was repeated several times

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†† 1 BM=0.9273×10^{-23} JT^{-1}.

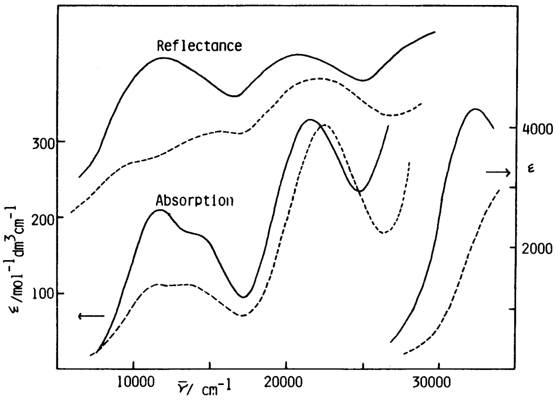

Fig. 4. Reflectance and absorption spectra of [Cu_2-(bpmp)im](ClO_4)$_2$·1.5CH_3CN (——) and [Cu_2(bpmp)-(CH_3COO)](ClO_4)$_2$ (----).

under various conditions. However, magnetic susceptibilities of those complexes were found to be highly dependent on the preparative conditions. Thus, in this experiment, magnetically pure [Cu_2(bpmp)(OH)]-(ClO_4)$_2$ could not be obtained.

On the other hand, the acetate-bridged complex, [Cu_2(bpmp)(CH_3COO)](ClO_4)$_2$, was easily obtained by mixing Hbpmp, $Cu(ClO_4)_2 \cdot 6H_2O$, and CH_3COONa in methanol. The infrared spectrum showed that $\Delta\tilde{\nu}(\tilde{\nu}_{\mathrm{asymm}}(CO_2^-)-\tilde{\nu}_{\mathrm{symm}}(CO_2^-))$ is $\approx$120 cm^{-1}, suggesting that the acetate ion acts as bridging ligand in syn-syn configuration.[20] The reflectance spectrum exhibits three bands at 9600, 15300, and 21700 cm^{-1} (Fig. 4). The former two bands are assigned to the d-d bands and this spectral pattern suggests a (distorted) square pyramidal coordination geometry about copper(II). The absorption spectrum is different from the reflectance spectrum, implying that the structural change occurs in acetonitrile. The band at 21700 cm^{-1} can be assigned to phenolate to copper CT transition and/or bridging acetate to copper CT transition, since dimeric copper(II) acetate monohydrate shows carboxylate to copper CT transition in this region.[21]

Such dinuclear copper(II) complexes with acetate bridge in syn-syn configuration and additional bridging ligand are rare.[3,4] Reed *et al.*[4] reported that [Cu_2(L-Et)(CH_3COO)](ClO_4)$_2$ (L-Et=1,3-bis[bis(1-ethylbenzimidazole-2-ylmethyl)amino]-2-propanolate) is essentially spin free. However, the present complex showed demagnetization by spin-pairing. Magnetic susceptibility data can be explained on the basis of the Bleaney-Bowers equation,

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

where the symbols have their usual meanings. The $-2J$, g, and $N\alpha$ values were determined by the best fit of the χ_A values to the Bleaney-Bowers equation (1) (Fig. 3 and Table 3). The $-2J$ value thus obtained is 82 cm^{-1}, indicating that antiferromagnetic interaction is present between two copper(II) ions.

In the course of the preparation of [Cu_2(bpmp)(Him)$_2$]-(ClO_4)$_3$ (blue crystals) in acetonitrile, very small amount of brown crystals were obtained as a byproduct. The elemental analysis showed that the brown compound has a chemical composition of [Cu_2(bpmp)(im)](ClO_4)$_2$·1.5CH_3CN. This brown compound was easily prepared by the method described in the experimental section. Since the complex contains imidazolate and phenolate anions, the imidazolate and phenolate are expected to act as bridging ligands. The conductivity measurement indicated the presence of a 2:1 electrolyte in acetonitrile. This implies that the complex has a dimeric unit, [Cu_2(bpmp)im]$^{2+}$, in acetonitrile.

The complex shows a single band at 11800 cm^{-1} in the reflectance spectrum, whereas in the absorption spectrum this band is resolved into a band and a high energy shoulder. As was mentioned before, trigonal bipyramidal complexes show a band with a high energy shoulder and the energies of the main bands are much lower than those of square pyramidal complexes with the same donor sets. Thus the electronic spectra both in solid and in acetonitrile suggest that the complex adopts a trigonl bipyramidal structure. The complex also exhibits a band at 21500 cm^{-1} both in solid and in acetonitrile. This band is assigned to imidazolate (pπ) to copper(d_{z^2}) or less probably to phenolate to copper(d_{z^2}) CT transition. The magnetic susceptibilities were measured in the temperature range 80—300 K. The experimental data can be well explained on the basis of the Bleaney-Bowers equation (Fig. 3). This supports that the complex has a dinuclear unit with an imidazolate bridge. The $-2J$ value obtained is 66 cm^{-1}, indicating the presence of antiferromagnetic interaction between two copper(II) ions. Since the complex is trigonal bipyramidal, the magnetic d orbital (d_{z^2}) seems to interact mainly with the bridging imidazolate and only weakly with bridging phenolate which is in the equatorial plane. Therefore, it is probable that the bridging imidazolate provides the major superexchange pathway for the antiferromagnetic interaction between copper(II) ions. The magnitude of the antiferromagnetic interaction for the present complex is comparable to those of the imidazolate-bridged dinuclear copper(II) complexes so far reported.[22]

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