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Magneto-Structural Correlations in Phenoxo-Bridged Copper(II) Compounds

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The magnetic susceptibilities of compounds [Cu(4-XPhO)$_2$(L)] (4-XPhOH = phenol, 4-nitrophenol, 4-chlorophenol; L = 1,2-diaminoethane, *N,N,N′,N′*-tetramethylethylenediamine) and [Cu(salaz)(RCOO)] (Hsalaz = 8-(2-hydroxyphenyl)-1,5- diazabicyclo[3.2.1]octane; R = CH_3–, C_2H_5–, $(CH_3)_3C$–) were determined over the temperature range of 77—300 K, and compared with those for salicylideneaminato-bridged compounds. The correlation between their structures and exchange-coupling strength were formulated to indicate that the exchange couplings for phenoxo-bridged copper(II) systems were affected not only by the *p* character of the hybrid orbitals on the bridging oxygen atom, but also by the electronic effects of the substituents on the aromatic ring.

A number of experimental and theoretical investigations have been carried out concerning the structures and magnetic properties of O-bridged polynuclear transition metal compounds, such as the hydroxides,[1—3] alkoxides,[1,4] and phenoxides.[5—14] During these studies, the magnetic behaviors of hydroxo- and alkoxo-bridged copper(II) compounds can be inferred, on the whole, in terms of the bridging geometries. Nevertheless, for phenoxo-bridged compounds (structurally-characterized are largely the salicylideneaminato derivatives), attempts to correlate their magnetic properties with the structural parameters, such as the bridging Cu–O–Cu angle,[9,11,14] the planarity of the three bonds attached to the bridging oxygen atoms,[8,12] and/or the dihedral angle between the CuO_2Cu plane and the remaining coordinating plane,[6—8,12] have not been very successful.

One of the causes of the failure may be attributable to the electronic effects of the substituents introduced into the ligand aromatic ring,[13,14] as is well known for dinuclear copper(II) carboxylates.[15] Recently, Calderazzo et al. have reported on the preparation and structure of an unsubstituted-phenoxo bridged copper(II) compound,[16,17] and Ainscough et al. prepared its substituted-phenoxo derivatives with the aim of locating the specific metal-binding site of lactoferrin.[18] More recently, Chiari et al. prepared solvates of a substituted-phenoxo compound, [Cu_2(salaz)$_2$(CH_3COO)$_2$] (Hsalaz = 8-(2-hydroxyphenyl)-1,5- diazabicyclo[3.2.1]octane).[19] These compounds are suited for studying substituent effects by comparing their structures and magnetic properties with those for salicylideneaminato-bridged compounds. We thus prepared these types of phenoxides and determined their variable-temperature magnetic susceptibilities.

Experimental

Compounds of the type [Cu(4-XPhO)$_2$(L)] (4-XPhOH = phenol, 4-nitrophenol, 4-chlorophenol; L = 1,2-diaminoethane, *N,N,N′,N′*-tetramethylethylenediamine) were prepared by methods similar to the reported procedures.[16,18] The appropriate phenol was dissolved in water containing NaOH. The addition of an equimolar of copper(II) acetate monohydrate and an appropriate bidentate *N*-donor in a hot aqueous solution separated dark green or purple materials. Also, compounds of the type [Cu(salaz)(RCOO)] (R = CH_3–, C_2H_5–, $(CH_3)_3C$–), were prepared by methods similar to the reported procedures.[19] Equimolar amounts of appropriate copper(II) carboxylate hydrate and Hsalaz were dissolved in ethanol, and the resulting dark-green solution was allowed to stand at room temperature. Dark-green, crystalline materials slowly separated and were recrystallized from methanol or ethanol. Their magnetic susceptibilities were determined over the temperature range 77—300 K, and corrected for diamagnetic contributions using Pascal constants,[20] and for temperature-independent paramagnetism using a value of 0.75×10^{-9} m^3 mol^{-1}. The infrared spectra of the compounds were recorded using Nujol® mulls in the 4000—650 cm^{-1} range.

Results and Discussion

The IR spectra of the obtained phenoxides showed sharp bands at ca. 1250—1280 cm^{-1} assignable to the C–O stretching of phenoxo groups.[17,21,22] The temperature dependence of the magnetic susceptibilities for compounds (**1**)—(**3**) exhibited Curie–Weiss behaviors over the range of 77—300 K; the obtained Weiss constants (−10 to −18 K) indicate the existence of rather small antiferromagnetic interactions among the copper(II) ions. As in a structurally-characterized compound (**1**),[16] the copper(II) ions in (**2**) and (**3**) were presumed to be bridged by a pair of phenoxo group to form dinuclear structures, and their susceptibilities were simulated using the Bleaney–Bowers equations[23] with parameters of $J = -34$ and $g = 2.11$ for (**1**), $J = -20$ and $g = 2.12$ for (**2**), and $J = -34$ and $g = 2.11$ for (**3**) (Table 1). These values are almost the same, indicating that the replacements of H in

Table 1. Analytical Data, Singlet–Triplet Separations, and Vibrational Frequencies

Compound		Found (Calcd)/%				J	ν_{C-O}
		Cu	C	H	N	cm^{-1}	cm^{-1}
$Cu(en)(C_6H_5O)_2 \cdot C_6H_5OH$	(**1**)	15.75 (15.73)	59.4 (59.5)	5.97 (5.99)	6.91 (6.93)	−34	1280
$Cu(tmen)(4\text{-}NO_2C_6H_4O)_2$	(**2**)	13.95 (13.94)	47.4 (47.4)	5.30 (5.31)	12.27 (12.29)	−20	1275
$Cu(tmen)(4\text{-}ClC_6H_4O)_2 \cdot H_2O$	(**3**)	15.02 (15.03)	45.4 (45.4)	4.78 (4.77)	6.61 (6.63)	−34	1280
$Cu(salaz)(CH_3COO) \cdot CH_3OH$	(**4**)	17.75 (17.76)	50.5 (50.3)	6.21 (6.20)	7.79 (7.83)	−188	1270
$Cu(salaz)(CH_3COO) \cdot C_2H_5OH$	(**5**)	17.03 (17.09)	51.5 (51.7)	6.51 (6.50)	7.49 (7.53)	−153	1245
$Cu(salaz)(C_2H_5COO) \cdot C_2H_5OH$	(**6**)	16.45 (16.46)	52.7 (52.9)	6.81 (6.79)	7.27 (7.26)	−162	1255
$Cu(salaz)((CH_3)_3CCOO) \cdot C_2H_5OH$	(**7**)	15.39 (15.35)	55.3 (55.1)	7.31 (7.30)	6.79 (6.77)	−175	1255

(**1**) by NO_2 or Cl in (**2**) or (**3**) do not modify the magnetic properties significantly. Maybe the resonance effects due to the substituents compensate for the increases in the acidities of the ligands (vide infra).

The susceptibilities for compounds (**4**)—(**7**) were also simulated using the Bleaney–Bowers equation, indicating that these compounds have dinuclear structures. $J=-188$ cm^{-1} and $g=2.18$ obtained for (**4**) and $J=-153$ cm^{-1} and $g=2.18$ for (**5**), being consistent with those studied by Chiari et al. (-210 and -182 cm^{-1}),[19] confirmed that these compounds have very strong antiferromagnetic couplings between the copper(II) ions. Similarly, $J=-162$ cm^{-1} and $g=2.17$ were obtained for (**6**), and $J=-175$ cm^{-1} and $g=2.17$ for (**7**). The J values of compounds (**4**)—(**7**) are almost the same, indicating a structural resemblance of the phenoxo-bridged moieties.

We had previously pointed out that the exchange coupling strength for a series of alkoxo-bridged copper(II) compounds was successfully correlatable with the three geometrical parameters around the bridging oxygen atom, i.e., the bridging angle (ψ), the dihedral angle (θ), and the azimuthal angle (ϕ):[4]

$$J \propto 1 - 733\cos^2\psi[\cos^2\theta/(1-0.7\sin^2\theta)^2]\sin^2(30-\phi). \quad (1)$$

The mutual relation can be understood based on the Goodenough–Kanamori rule.[24] Taking into account the small differences in the coordination-bond lengths (R in Å) of the alkoxo ligands[25] and distortions of the environments around the copper(II) ions from planarity,[26] we can modify the expression as follows (J in cm^{-1}):

$$J=55(R/2.00)^{-12}\cos^2\tau\{1-733\cos^2\psi[\cos^2\theta/(1-0.7\sin^2\theta)^2] \times \sin^2(30-\phi)\}, \quad (2)$$

where τ is the dihedral angle between the CuO_2 plane and the remaining coordinating plane;[6–8,12] the τ-dependence was roughly estimated by considering the change in the d character of hybrid orbitals on the copper atoms.

For phenoxo-bridged copper(II) compounds, the exchange-coupling strength must be expressed similarly as

$$J=A(R/2.00)^{-12}\cos^2\tau\{1+B\cos^2\psi[\cos^2\theta/(1-0.7\sin^2\theta)^2] \times \sin^2(30-\phi)\}. \quad (3)$$

Fitting parameters $A=55$ and $B=-569$ were obtained by substituting the relevant values for R, τ, ψ, θ, and ϕ of various salicylidenaminato-bridged copper(II) compounds.[5–14] In order to demonstrate the bridging-angle dependence graphically, the J^{cor} values (i.e., $\theta=0$, $\phi=0$, $\tau=0$, and $R=2.00$ Å) are plotted against the bridging angles in Fig. 1, where

$$J^{cor}=[J(R/2.00)^{12}/\cos^2\tau-55]/4[\cos^2\theta/(1-0.7\sin^2\theta)^2] \times \sin^2(30-\phi)+55. \quad (4)$$

Figure 1 well reproduces the bridging-angle dependence of the exchange constants for the copper(II) compounds, together with those for the nickel(II) compounds ($6.1\times J$).[27] Similarly, the C–O stretching vibrations for these compounds show systematic shifts against the bridging angles (Fig. 2); the agreement may be improved to some degree by introducing other correction terms. The higher frequencies are re-

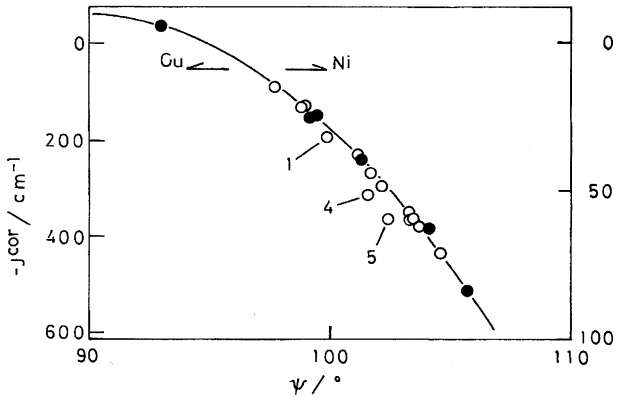

Fig. 1. Bridging-angle dependence of the exchange couplings for phenoxo-bridged copper(II) compounds (○) and nickel(II) compounds (●). The solid curve represents Eq. 3 in the text.

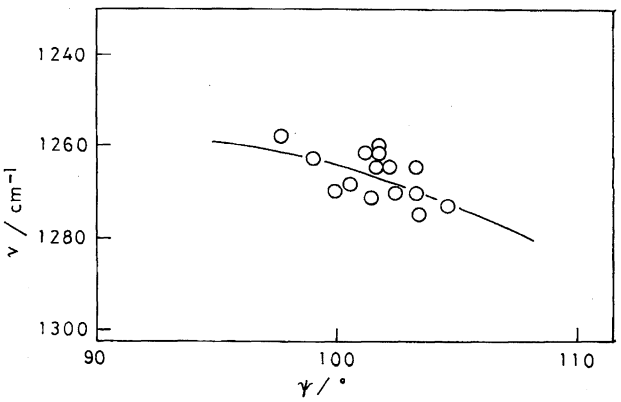

Fig. 2. Bridging-angle dependence of the C–O stretching frequencies of phenoxo groups.

garded as having a lower p character in analogy with the correlation involving C–H stretching modes for hydrocarbons.[21] Hence, it was confirmed that the primary factor influencing the exchange couplings for phenoxo-bridged copper(II) systems was the p character of hybrid orbitals on the bridging oxygen atom as for alkoxo-bridged copper(II) systems. In addition, it was found that the exchange couplings for compounds (**1**), (**4**), and (**5**) deviated from the correlation for salicylidenaminato-bridged copper(II) compounds. Chiari et al. first pointed out such deviations, and attributed them to the weak axial bonds;[19] the axial ligand effect on the magnetic properties of dinuclear copper(II) carboxylate compounds, however, makes such a hypothesis very unlikely.[28,29]

Kato and Muto examined the magnetic properties and electronic spectra of salicylidenaminato-bridged and pyridine N-oxide-bridged copper(II) compounds, and plotted the data on 2-dimensional diagrams with the magnetic moments at 25 °C (μ_{eff} in BM) on the abscissa and d–d band positions ($\nu_{\max}$ in cm^{-1}) on the ordinate.[29] The observed linear relationship ($\mu_{\mathrm{eff}}=-1.50+2.4\times10^{-4}\nu_{\max}$) was interpreted in terms of the mechanism that an increase in tetrahedrality accompanying a decrease in the Cu–O–Cu angles leads to a decrease in the exchange couplings, being consistent with Eq. 3. Another relationship ($\mu_{\mathrm{eff}}=2.24-1.5\times10^{-4}\nu_{\max}$), the variation with the substituent positions on the aromatic ring, i.e., μ_{eff}(o-substituted) < μ_{eff}(p-substituted) < μ_{eff}(m-substituted)≈μ_{eff}(unsubstituted), indicates that the exchange couplings are also affected by the electronic effects of the substituents; the resonance involving the *ortho* and *para* substituents strengthens the negative charge on the oxygen atom developed by the inductive effect. Furthermore, Yokoi et al. have shown that the equilibrium constants between the monomer and dimer species of the bis(salicylideneaminato)-copper(II) compounds in toluene solutions are affected by the resonance effects of the substituents.[30] These facts suggest that the above-mentioned deviation of compounds (**1**), (**4**), and (**5**) is attributable to the resonance effects by the substituents.

We can quantitatively estimate the electronic effects in phenoxo-bridged compounds by comparing the magneto-structural correlations among the O-bridged compounds, i.e., hydroxo-, alkoxo-, and phenoxo-bridged compounds. Comparing Eqs. 2 and 3 with the expression for hydroxo-bridged compounds (assuming that $\theta=0$ and $\phi=0$),[2,3]

$$J = 55(R/2.00)^{-12}\cos^2\tau\{1-290\cos^2\psi[\cos^2\theta/(1-0.7\sin^2\theta)^2]\sin^2(30-\phi)\}, \quad (5)$$

the strength of the exchange coupling for O-bridged compounds may be formulated generally as follows:

$$J = 55(R/2.00)^{-12}\cos^2\tau\{1-(ApK_a+BpK_\pi+C)\times\cos^2\psi[\cos^2\theta/(1-0.7\sin^2\theta)^2]\sin^2(30-\phi)\}, \quad (6)$$

where pK_π is the correction term for the resonance effect by a substituent on the bridging group and pK_a is the acidity of the parent bridging ligand (pK_a=15.5, 10, and 14 for alcohol, phenol, and water, respectively).

Swain and Lupton have proposed that the substituent constants predicting the substituent effects on any kind of physical properties may be expressed as $fF+rR$, where F and R are the field and resonance constants, and where f and r are weighting factors independent of the particular substituent.[31] The correction term for the resonance effect has already been estimated to be ca. $pK_\pi=48.0(R-0.38F)$, i.e., −5.67, −6.00, and 0 for the alkyl, o-iminophenyl, and hydrogen substituents, respectively.[32] Fitting parameters A=34.1, B=−69.2, and C=−187 were obtained by substituting the relevant values for pK_π and pK_a. Thus, the strength of the exchange coupling for O-bridged compounds is formulated as

$$J = 55(R/2.00)^{-12}\cos^2\tau\{1-34.1(pK_a-2.03pK_\pi-5.50)\times\cos^2\psi[\cos^2\theta/(1-0.7\sin^2\theta)^2]\sin^2(30-\phi)\}. \quad (7)$$

As mentioned above, the exchange couplings of the copper(II) compounds bridged by unsubstituted phenoxo and 2-alkylphenoxo ligands are more negative than that expected from the Eq. 3 (Fig. 1). We can anticipate their coupling strength, by substituting −6.77 and −7.38 for pK_π in Eq. 7, as J=−33 for (**1**), J=−186 cm^{-1} for (**4**), and J=−151 cm^{-1} for (**5**), which agree well with those determined or refined in this work. In conclusion, it was confirmed that the primary factor influencing the exchange couplings for phenoxo-bridged copper(II) systems is the p character of the hybrid orbitals on the bridging oxygen atom, the p character being measured by the bridging angle and the in-plane and out-of-plane tilts of the Ph–O vector from the bisector of the Cu–O–Cu′ angle. In addition, it was found that the exchange couplings were also affected by the electronic effects of the substituents on the aromatic ring.

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