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

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The magnetic susceptibilities of the compounds [Cu(bbip)(RO)]X (bbip = 1,3-bis(benzimidazol-2-yl)propane; R = CH_3, C_2H_5; X = NO_3, ClO_4) and related alkoxo-bridged copper(II) compounds were determined over the temperature range 80—300 K. For the dinuclear entities $[Cu(OR)_2Cu']^{2+}$, the strength of the exchange couplings is discussed in terms of the in-plane and out-of-plane tilts of the C–O vector from the bisector of the Cu–O–Cu′ angle.

The structures[1—15] and properties[3—23] of alkoxo-bridged polynuclear compounds have been extensively investigated in order to find a specific structural parameter to which the strength of the exchange couplings can be correlated. As a result, it has become apparent that the exchange couplings involving the alkoxo bridges are affected by many structural parameters concurrently, such as the bridging angle[6,8,11] and the planarity of the bonds about the bridging oxygen atom,[8,10] which are correlated to the couplings in limited members of the alkoxides.[4,5,24]

In a confirmation of such multi-variable correlations, it is important to accumulate reliable magnetic data for structurally characterized compounds. Recently, Bernardinelli et al. carried out an X-ray crystal analysis of [Cu(bbip)(C_2H_5O)](ClO_4)·C_2H_5OH (bbip = 1,3-bis(benzimidazol-2-yl)propane).[15] This compound, being dinuclear with bridging ethoxo ligands and end-capping bbip ligands, is suited for comparative studies on the structures and magnetic properties of alkoxo-bridged compounds. We thus determined the variable-temperature magnetic susceptibilities of this compound along with some related compounds with end-capping *N*-heteroaromatic donors.

Experimental

The alkoxo-bridged compounds having the general formula [Cu(bbip)(RO)]X (R = CH_3, C_2H_5; X = NO_3, ClO_4) were prepared by the procedures reported for [Cu(bbip)(C_2H_5O)](ClO_4)·C_2H_5OH,[15] i.e., through a deprotonation reaction by the amine bbip. Similarly, related compounds, [Cu(NH_2py)$_2$(RO)](NO_3) (NH_2py = 2-aminopyridine; R = CH_3, C_2H_5, C_3H_7, C_4H_9) and [Cu(NH_2py)(pyCH_2CH_2O)]X (pyCH_2CH_2OH = 2-(2-hydroxyethyl)pyridine; X = NO_3, ClO_4), were prepared through a deprotonation reaction by NH_2py.[17,18,23] Analytical data are given in Table 1.

The magnetic susceptibilities were determined over the 80—300 K temperature range, and corrected for diamagnetic contributions using Pascal constants,[25] and for temperature-independent paramagnetism using a value of 0.75×10^{-9} m^3 mol^{-1}. Some samples would tend to be contaminated with hydroxo-bridged species and/or copper(I) species, which may present a serious problem when discussing the magnetic properties. Therefore, the preparations were repeated several times in order to select samples having the best analytical data for susceptibility measurements. The IR spectra of the compounds were recorded using Nujol mulls in the 4000—200 cm^{-1} range.

Results and Discussion

The obtained compounds showed IR bands at 445—455 cm^{-1}, assignable to the Cu–O bond vibrations.[26] Their susceptibility variations with temperature were fitted well to a theoretical equation for a pair of $S=1/2$ spins[27] with parameters of $g=2.08$—2.14 and $-2J=720$—950 cm^{-1} (Table 1), similar to those of the well-characterized alkoxo-bridged copper(II) compounds.[4,5,7—13,16—23] Accordingly, we conclude that the present compounds have alkoxo-bridged dinuclear entities in their crystals, and that we may rule out the possibility of an impurity.

We can see some trends in Table 1. Although the singlet–triplet separation values ($-2J$) are rather insensitive to a replacement of counter anions or end-capping ligands, they are sensitive to the replacement of alkyl substituents. For example, the $-2J$ values are quite similar between the nitrate (**1**) and perchlorate (**2**), and thus between the bbip and NH_2py compounds (**2** and **5**). On the other hand, the $-2J$ values are substantially smaller in the methoxides than in the other alkoxides. Furthermore, the pyridylethoxides (**9** and **10**) show the strongest antiferromagnetic couplings among these alkoxides. This is not unexpected, because the strength of the exchange couplings for aminoalkoxo-bridged compounds[21,22] shows a critical dependence upon the size of the ring containing the bridging oxygen atom. Apparently, these trends can not be attributed to a variation in the electron densities at the bridges.[16,17]

From an analogy with the bridging-angle (ψ) dependencies of the exchange constants (in cm^{-1}) for oxo-bridged iron(III)[28] and fluoro-bridged manganese(III) compounds:[29]

$$J=-22[\cos^2(\psi)-0.03]. \qquad (1)$$

Table 1. Analytical Data and Singlet–Triplet Separations

Compound		Found (Calcd)/%				$-2J$
		Cu	C	H	N	cm^{-1}
$Cu(bbip)(CH_3O)(ClO_4)\cdot H_2O$	**(1)**	12.95	43.8	4.28	11.4	730
		(13.01)	(44.3)	(4.33)	(11.5)	
$Cu(bbip)(CH_3O)(NO_3)\cdot H_2O$	**(2)**	14.04	47.8	4.64	15.6	720
		(14.09)	(47.9)	(4.69)	(15.5)	
$Cu(bbip)(C_2H_5O)(ClO_4)\cdot C_2H_5OH$	**(3)**	12.03	47.4	5.11	10.9	890
		(11.98)	(47.6)	(5.13)	(10.6)	
$Cu(bbip)(C_2H_5O)(NO_3)\cdot H_2O$	**(4)**	13.64	48.7	4.93	14.9	830
		(13.67)	(49.1)	(4.99)	(15.1)	
$Cu(NH_2py)_2(CH_3O)(NO_3)$	**(5)**	18.45	38.1	4.34	20.2	720
		(18.43)	(38.3)	(4.38)	(20.3)	
$Cu(NH_2py)_2(C_2H_5O)(NO_3)$	**(6)**	17.66	39.8	4.81	19.5	775
		(17.71)	(40.2)	(4.77)	(19.5)	
$Cu(NH_2py)_2(C_3H_7O)(NO_3)$	**(7)**	16.97	41.7	5.12	19.1	770
		(17.04)	(41.9)	(5.14)	(18.8)	
$Cu(NH_2py)_2(C_4H_9O)(NO_3)$	**(8)**	16.41	43.1	5.43	18.3	770
		(16.42)	(43.5)	(5.47)	(18.1)	
$Cu(NH_2py)(pyCH_2CH_2O)(NO_3)$	**(9)**	18.53	41.8	4.11	16.3	950
		(18.59)	(42.2)	(4.13)	(16.4)	
$Cu(NH_2py)(pyCH_2CH_2O)(ClO_4)$	**(10)**	16.78	38.1	3.75	10.7	960
		(16.76)	(38.0)	(3.72)	(11.1)	

Hatfield, Hodgson, and co-workers demonstrated a linear relationship between the exchange constants and the bridging angles for a series of hydroxo-bridged copper(II) compounds,[19,20] and naturally suggested a similar relationship for alkoxo-bridged systems. However, it soon became apparent that most alkoxo-bridged copper(II) compounds did not show a significant difference in the bridging angles, compared with the variation in the exchange constants.

Alternatively, Kida et al., based on spectral studies of dinuclear copper(II) compounds, claimed that the primary factor influencing the exchange coupling of the alkoxo-bridged entity, $[M(OR)_2M']^{2+}$, was the planarity of the three bonds attached to the bridging oxygen atom, as measured by the dihedral angle (θ) between the C–O vector and the MOM′ plane[10,30] or by the solid angle formed by the C–O, M–O, and M′–O vectors.[26] The θ dependence of the exchange constants (in cm^{-1}) was successfully formulated for alkoxo-bridged chromium(III) compounds (Fig. 1):[31]

$$J=-33[\cos^4\theta/(1+2.3\sin^2\theta)^2-0.03]. \qquad (2)$$

Nevertheless, the θ dependence of the exchange constants for alkoxo-bridged copper(II) systems is not clear, because of the existence of some exceptions. For example, the dihedral angle ($\theta=16.6°$) in compound (**1**) is much larger than 3.7° in $[Cu(Et_2NC_2H_4O)]Br$,[1,2] whereas the coupling determined for the former ($J=-445$ cm^{-1}) is rather stronger than that for the latter (-410 cm^{-1}). This deviation, being much greater than the limits of the experimental error (±10 cm^{-1}), seems to be attributable to the in-plane tilt of the C–O vector in $[Cu(Et_2NC_2H_4O)]Br$ from the bisector of the Cu–O–Cu′ angle (the angles C–O–Cu and C–O–Cu′ are 117° and 138°, respectively).

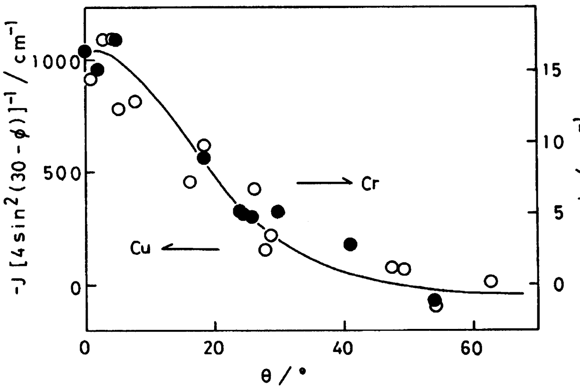

Fig. 1. Planarity dependence of the exchange couplings for alkoxo-bridged copper(II) compounds (○) and chromium(III) compounds (●).

It is well known that the strength of superexchange couplings is influenced by the *p* character of hybrid orbitals on the bridging atom; the mutual relation can be understood based on the Goodenough–Kanamori rule.[32] For alkoxo-bridged systems, the *p* character must depend on three geometrical parameters, i.e., the bridging angle (ψ), the dihedral angle (θ), and the azimuthal angle (ϕ) in Fig. 2, in terms of which the spatial arrangement of bonds in an XY_3-type molecule is represented. Therefore, we may assume that the exchange constants for alkoxo-bridged copper(II) compounds, which mostly have comparable bridging angles (Cu–O–Cu′) and coordination bond lengths (Cu–O), are correlatable to the parameters θ and ϕ.

In order to modify Eq. 2 for alkoxo-bridged copper(II) compounds, we furthermore assumed that the ϕ and θ dependencies of the exchange constants are similar to Eqs. 1 and 2, respectively, as follows:

$$J=-3520\sin^2(30-\phi)[\cos^4\theta/(1+2.3\sin^2\theta)^2-0.03]. \qquad (3)$$

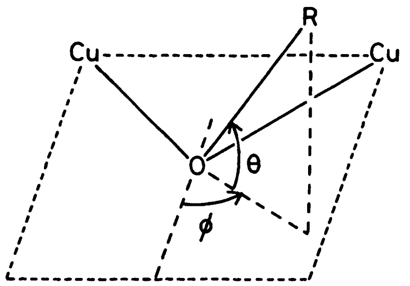

Fig. 2. Coordinate systems for alkoxo bridges.

This expression is consistent with ab initio MO calculations on methoxo-bridged copper(II) compounds.[33,34] Figure 1 well reproduces the planarity dependence of the exchange constants for the present compound together with other alkoxo-bridged copper(II) compounds in which the coordination geometries of copper(II) ions are essentially square-planar, tetragonal pyramidal, or octahedral. The agreement may be improved to some degree by introducing other correction terms, e.g., those for the bridging angle, coordination bond length, coordination geometry, and/or basicity of alkoxo ligand; the available data, however, are insufficient to justify the refinement.

In conclusion, it was confirmed that the primary factor influencing the exchange couplings for alkoxo-bridged copper(II) systems is the *p* character of the hybrid orbitals on the bridging oxygen atom, the *p* character being measured by the in-plane and out-of-plane tilts of the R–O vector from the bisector of the Cu–O–Cu′ angle, and perhaps also by the bridging angle. This has been taken as evidence for a σ pathway for the dominant exchange couplings.

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