Magnetic Properties of Copper(II) Complexes of Phenylboronic Acid

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Synopsis. The magnetic susceptibilities of copper (II) phenylboronate obey the Bleaney-Bowers equation for dinuclear clusters. The exchange integral within the dinuclear copper(II) phenylboronate, J/k, is equal to -195 K. The structures for hydrolysis products of copper(II) phenylboronate are presumed to contain copper(II) phenylboronate dinuclear units connected together by diborate bridges.

Some copper(II) complexes of benzoic acid have copper(II) acetate-type dinuclear structures with strong antiferromagnetic coupling between the copper(II) ions of a pair.[1] It has been proposed that superexchange interaction predominates in the coupling of these compounds. The degree of superexchange depends to a great extent on the electronic structure of the bridging ligands. Although phenylboronic acid is a much weaker acid($pK_a=8.86$)[2] than benzoic acid($pK_a=4.18$),[3] both are isoelectronic. So copper(II) complexes of phenylboronic acid may also have a similar structure to that of copper(II) acetate monohydrate.[4]

The complex $Cu(PhBO_2H)_2(py)_2$ was obtained by concentrating a pyridine solution of phenylboronic acid and anhydrous copper(II) acetate. This pyridine adduct was warmed on a water bath to convert it into $Cu(PhBO_2H)_2$. When $Cu(PhBO_2H)_2$ is allowed to stand for a few days in air, it is partly hydrolysed into $Cu(PhBO_2H)_{3/2}(B_2O_5H_2)_{1/4}$. If the pyridine solution of this complex is concentrated gently on a water bath, the crystalline $Cu(PhBO_2H)_{4/3}(B_2O_5H_2)_{1/3}$ is obtained.

The magnetic susceptibilities of these complexes were measured at room temperature by the Gouy method. Their effective magnetic moments were calculated from expression 1:

$$\mu_{eff} = 2.83\sqrt{(\chi_A - N\alpha)\cdot T}, \quad (1)$$

where χ_A is the molar magnetic susceptibility corrected for the diamagnetism of all the atoms in the compounds by the use of Pascal's constants,[5] and $N\alpha$ is the temperature-independent paramagnetism per gram-ion of Cu(II). The $N\alpha$ was assumed to be 60×10^{-6} cgsu.† The results are given in Table 1. For $Cu(PhBO_2H)_2$, the magnetic measurement was made over the temperature range 80—300 K. The cryomagnetic data could be fitted well to the Bleaney-Bowers equation 2[6] for isotropic exchange in a copper-(II) dimer:

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

where J is the exchange integral and g is the average g factor. The best fit yields $J/k=-195$ K and $g=2.15$ (Fig. 1). These results suggest the existence of dinuclear clusters in crystals. The values are almost the same as $J/k=-225$ K and $g=2.18$ for copper(II) benzoate.[7] This suggests that this compound has a copper(II) acetate-type of dinuclear structure, as shown in Fig. 2 A.

† The value of the molar magnetic susceptibility in $m^3\,mol^{-1}$(SI) can be obtained by multiplying the value in $cm^3\,mol^{-1}$(cgs) by $4\pi\times10^{-6}$.

Table 1. Analytical data and effective magnetic moments at 17 °C

Compound	Cu (%) Found	Cu (%) Calcd	μ_{eff}[a] BM
$Cu(PhBO_2H)_2$	20.8	20.8	1.43
$Cu(PhBO_2H)_2(py)_2$	13.7	13.7	1.79
$Cu(PhBO_2H)_{3/2}(B_2O_5H_2)_{1/4}$	23.4	23.5	1.36
$Cu(PhBO_2H)_{4/3}(B_2O_5H_2)_{1/3}$	24.5	24.5	1.33

a) 1 BM $=9.27\times10^{-24}$ Am^2.

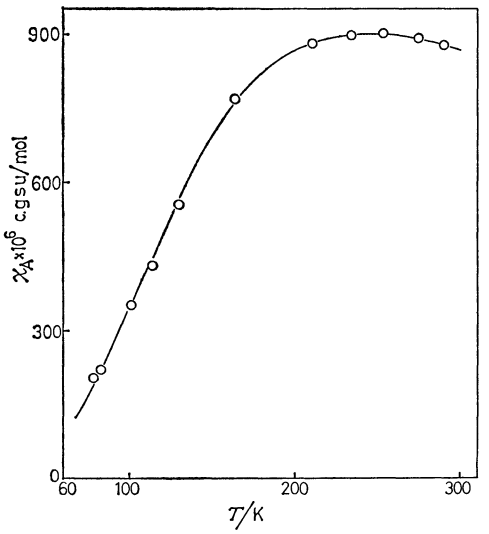

Fig. 1. Observed and calculated magnetic susceptibilities of $Cu(PhBO_2H)_2$: ○, experimental; solid curve, calculated by Eq. 2 with $J/k=-195$ K, $g=2.15$, and $N\alpha=60\times10^{-6}$ cgsu.

On the basis of the analytical data and the reactivity of phenylboronic acid, we assumed that the hydrolysis products, $Cu(PhBO_2H)_{3/2}(B_2O_5H_2)_{1/4}$ and $Cu(PhBO_2H)_{4/3}(B_2O_5H_2)_{1/3}$, have the B and C types of bridging structure shown in Fig. 2, respectively.

Since the magnitude of J should be proportional to the number of bridging ligands involved in the superexchange interaction,[8] the mean exchange integrals for these hydrolysis products can be predicted from Eq. 3 by assuming that no magnetic interaction operates through the >B–O–B< bridge between the dimers:

$$J = \frac{2n+2}{n}J_{PhBO_2H} + \frac{2n-2}{n}J_{B_2O_5H_2} \quad (n=2 \text{ and } 3), \quad (3)$$

where the J_{PhBO_2H} and $J_{B_2O_5H_2}$ are the exchange integrals per single phenylboronate and diborate bridge,

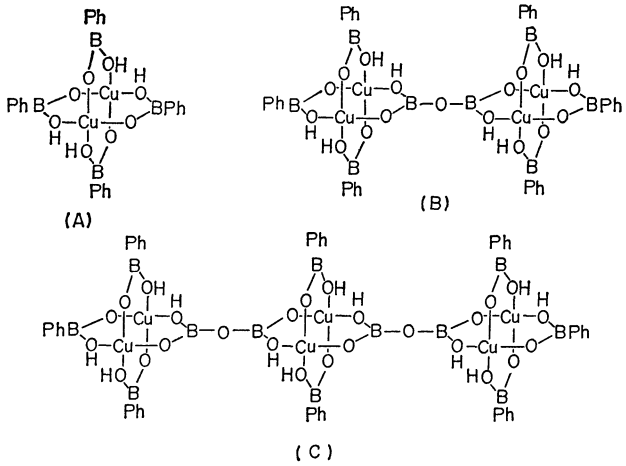

Fig. 2. Schematic representations of probable structure.
(A): $Cu(PhBO_2H)_2$, (B): $Cu(PhBO_2H)_{3/2}(B_2O_5H_2)_{1/4}$, (C): $Cu(PhBO_2H)_{4/3}(B_2O_5H_2)_{1/3}$.

respectively. The observed magnetic moments of hydrolysis products are the same as the calculated ones (for $n=2$ and 3, 1.36 and 1.33 BM respectively) from the mean exchange integrals obtained with $J_{PhBO_2H}/k=-49$ K (a quarter of the J/k value evaluated by use of Eq. 2) and $J_{B_2O_5H_2}/k=-73$ K.[9,10] This close agreement supports the validity of the postulated structure of hydrolysis products.

The magnitude of superexchange interaction depends to a great extent on the electronic structure of the bridging ligand. Our result, where the J/k value of $Cu(PhBO_2H)_2$ is nearly equal to the value of $Cu(PhCO_2)_2$, can be explained by the isoelectronicity of the ligands. The other result, where the antiferromagnetic interaction operates more strongly in the hydrolysis products than in $Cu(PhBO_2H)_2$, can be explained by considering that diborate groups promote the migration of positive holes to a greater extent than phenylboronate groups.

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