The Magnetic Properties of the 2-Pyridone Adducts of Copper(II) Benzoates and Related Copper(II) Compounds

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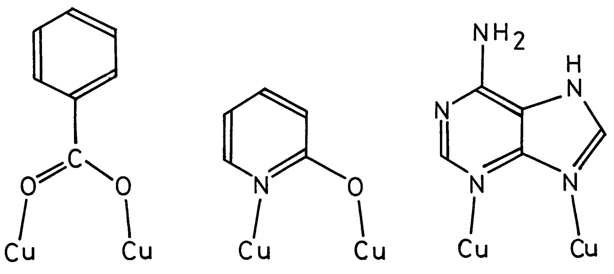
Synopsis. The 2-pyridone adducts of copper(II) benzoate, copper(II) 2-pyridinolate, and bis(adenine)copper(II) sulfate were prepared, and then characterized by means of magnetic susceptibility and IR spectroscopy. Their magnetic properties were correlated with the basicities and coordinate-bond lengths of the bridging ligands.

Like copper(II) alkanoates, most copper(II) benzoate,[1] copper(II) 2-pyridinolate,[2,3] copper(II) pyrrolo[2,3-*b*]pyridinate,[4] and bis(adenine)copper(II) compounds[5,6] may have dinuclear structures similar to that of copper(II) acetate monohydrate.[7,8] Through the bridging ligands between the copper(II) ions, superexchange couplings operate, and the room-temperature magnetic moments vary with the strength of the spin-exchange couplings (the Bleaney–Bowers equation).[1–6] Naturally, the magnetic moments or the strength of the spin-exchange couplings for these dinuclear compounds have been discussed with reference to the basicity of the bridging ligands (pK_{a1} or pK_{a2}).[9,10] On the other hand, for series of transition metal oxides and fluorides, a correlation between the strength of the spin-exchange couplings and the coordinate-bond lengths has been proposed,[11,12] and rationalized with an exchange perturbation treatment of cation–anion–cation in a three-center, four-electron model.[13] Also, in copper(II) acetate-type dinuclear compounds, the coordinate-bond length must play a role in determining the strength of the superexchange couplings. In order to investigate concurrently the basicity and bond length dependence, we prepared some 2-pyridone adducts of copper(II) benzoates, copper(II) 2-pyridinolates, and bis(adenine)-copper(II) sulfate, and measured their magnetic susceptibilities at room temperature.

The adducts were prepared by heating the hydrates of copper(II) acetate, copper(II) 3- and 5-substituted benzoates, and bis(adenine)copper(II) sulfate with excesses of molten 2-pyridones for 30 min (mp 107, 165, and 185 °C for 2-pyridone and 5-chloro- and 5-nitro-2-pyridones, respectively). The excess 2-pyridones were removed by sublimation.[3] The effective magnetic moments were evaluated from the magnetic susceptibilities, which were corrected for the diamagnetic contribution using the Pascal constants[14] and for temperature-independent paramagnetism using the value 60×10^{-6} emu mol^{-1} (1 emu=$4\pi \times 10^{-6}$ m^3). The IR spectra of the solid compounds were recorded using nujol mulls in the 4000—600 cm^{-1} range.

The obtained compounds show magnetic moments of 1.25—1.45 BM, similar to those of well-characterized dinuclear copper(II) compounds.[8–10,15] All of the benzoates show COO stretching bands of ca. 1675—1615 and 1435—1405 cm^{-1}, characteristic of bridging carboxylate anions.[16] The magnetic and IR spectral data indicate that the present compounds have copper(II) acetate-type dinuclear structures with 2-pyridones occupying the axial positions (Fig. 1). Although the 2/3 adducts have structures with a partial lack of axial ligands, their magnetic moments are assumed to be practically the same as those of the monoadducts.

For several series of dinuclear copper(II) compounds,[9,10] it has been reported that the room-temperature magnetic moments decrease linearly with the basicities of the bridging ligands. In order to demonstrate the linear correlation for the present compounds, their magnetic moments (in BM), together with literature data regarding related copper(II) com-



(a) (b) (c)

Fig. 1. Bonding arrangements in dinuclear copper(II) benzoate (a), copper(II) 2-pyridinolate (b), and bis(adenine)copper(II) (c) compounds.

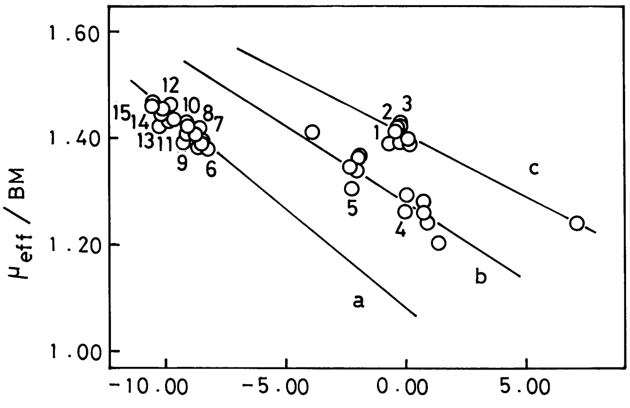


Fig. 2. Magnetic moments at 20 °C for copper(II) benzoate (a), copper(II) 2-pyridinolate (b), and bis(adenine)copper(II) (c) compounds plotted against the acidities of the ligands.

Table 1. Analytical Data and Effective Magnetic Moments at 20 °C

Compound		Found (Calcd)/%				μ_{eff}/BM
		Cu	C	H	N	
$CuSO_4(Haden)_2 \cdot PyOH \cdot H_2O$	**(1)**	11.86 (11.70)	32.70 (33.18)	3.05 (3.16)	28.10 (28.38)	1.41
$CuSO_4(Haden)_2(5\text{-}ClPyOH)_{2/3}$	**(2)**	12.26 (12.31)	30.98 (31.02)	2.50 (2.47)	28.88 (28.94)	1.42
$CuSO_4(Haden)_2 \cdot 5\text{-}NO_2PyOH$	**(3)**	11.16 (11.15)	31.44 (31.61)	2.50 (2.48)	29.36 (29.49)	1.43
$Cu(5\text{-}ClpyO)_2 \cdot 5\text{-}ClPyOH$	**(4)**	14.31 (14.12)	39.98 (40.02)	2.23 (2.24)	9.31 (9.33)	1.26
$Cu(5\text{-}NO_2pyO)_2 \cdot 5\text{-}NO_2PyOH$	**(5)**	12.93 (13.19)	37.29 (37.39)	2.03 (2.09)	17.43 (17.44)	1.31
$Cu(C_6H_5COO)_2 \cdot PyOH$	**(6)**	15.77 (15.85)	56.95 (56.93)	3.78 (3.77)	3.51 (3.49)	1.38
$Cu(3\text{-}ClC_6H_4COO)_2 \cdot PyOH$	**(7)**	13.65 (13.53)	48.59 (48.58)	2.80 (2.79)	2.99 (2.98)	1.41
$Cu(3\text{-}ClC_6H_4COO)_2(5\text{-}ClPyOH)_{2/3}$	**(8)**	13.71 (13.78)	45.18 (45.16)	2.35 (2.33)	2.01 (2.03)	1.40
$Cu(3\text{-}NO_2C_6H_4COO)_2 \cdot 5\text{-}ClPyOH$	**(9)**	12.19 (12.10)	43.45 (43.44)	2.31 (2.30)	8.02 (8.00)	1.39
$Cu(3\text{-}NO_2C_6H_4COO)_2(5\text{-}NO_2PyOH)_{2/3}$	**(10)**	13.08 (12.99)	42.58 (42.56)	2.22 (2.20)	9.52 (9.54)	1.43
$Cu(3,5\text{-}Cl_2C_6H_3COO)_2(PyOH)_{2/3}$	**(11)**	12.68 (12.53)	41.13 (41.07)	1.89 (1.86)	1.83 (1.84)	1.43
$Cu(3,5\text{-}Cl_2C_6H_3COO)_2(5\text{-}ClPyOH)_{2/3}$	**(12)**	11.98 (11.99)	39.31 (39.29)	1.66 (1.65)	1.74 (1.76)	1.46
$Cu[3,5\text{-}(NO_2)_2C_6H_3COO]_2(PyOH)_{4/3}$	**(13)**	10.30 (10.37)	40.55 (40.52)	2.09 (2.08)	12.23 (12.20)	1.42
$Cu[3,5\text{-}(NO_2)_2C_6H_3COO]_2 \cdot 5\text{-}ClPyOH$	**(14)**	10.53 (10.33)	37.13 (37.09)	1.65 (1.64)	11.40 (11.38)	1.44
$Cu[3,5\text{-}(NO_2)_2C_6H_3COO]_2(5\text{-}NO_2PyOH)_{4/3}$	**(15)**	9.51 (9.45)	36.91 (36.91)	1.73 (1.70)	13.96 (13.88)	1.44

pounds,[4,8–10,15] are plotted in Fig. 2 against the basicities of the bridging ligands ($pK_{a1}-0.068\,pK_a'$), where $-0.068\,pK_a'$ is the correction term for the axial ligation. K_{a1} and K_a' are the acid constants of the conjugate cation acids of the bridging and axial ligands, respectively.[17,18] The points for each series of the copper(II) benzoate, copper(II) 2-pyridinolate, and bis(adenine)copper(II) compounds give a straight line with slopes of $K=-0.037$, -0.029, or -0.023, respectively. The slope obtained for the benzoates is in fair agreement with that ($K=-0.052$) for plots of the magnetic moments of dinuclear copper(II) carboxylates[9] against $pK_{a2}-0.068\,pK_a'$, when the linear relationship for carboxylic acids, $pK_{a1}=1.40\,pK_{a2}-13.8$, is taken into account.[19] Three lines intersect at a point, enabling us to summarize them as

$$\mu_{eff} = 1.94[1 + K(pK_{a1} - 0.068pK_a' + 23.0)]. \qquad (1)$$

The reasonably good correlation for each series confirms that the strength of spin-exchange couplings is undoutedly affected by the basicity of the bridging ligands; the different slopes for the three series indicate that it is also affected by factors other than basicity.

Although the variation in the slopes seems to be attributable to bondings between pairs of copper(II) ions, this is not consistent concerning the trend in copper(II)–copper(II) separations.[1–6] The coordinate-bond lengths of the present bridging ligands are typically Cu–O(1), 1.967(6)—1.981(6) Å and Cu–O(2), 1.950(10)—1.965(6) Å in dinuclear copper(II) benzoates,[1] Cu–N, 2.000(6)—2.015(10) Å and Cu–O, 1.950(10)—1.959(6) Å in dinuclear copper(II) 2-pyridinolates,[2,3] and Cu–N(1), 2.038(6)—2.043(11) Å and Cu–N(2), 2.008(11)—2.012(6) Å in dinuclear bis(adenine)copper(II) compounds,[5,6] respectively. The longer coordinate bond of each bridging ligand is selected for a comparison, because the strength of the superexchange coupling is determined by the weakest bond in the coupling pathway.[10] Apparently, the above-obtained slopes become steeper as the coordinate-bond lengths decrease; the variation in the K's is in good quantitative agreement with the theoretical prediction regarding the distance dependence of the strength of the spin-exchange coupling.[11] The basicity and bond length dependence was collaborated and evaluated separately. These relations suggest that the spin-exchange couplings in the present compounds operate through the sp^2-orbitals more strongly than through the p_π-orbitals of the bridging ligands.

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