The Magnetic Properties of Copper(II) 3- and 4-Substituted Benzoate Adducts with Quinoline and 4-Methylquinoline

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Synopsis. Various copper(II) 3- and 4-substituted and 3,5-disubstituted benzoate adducts with quinoline and 4-methylquinoline have been prepared, and characterized by means of magnetic susceptibility and IR spectroscopy measurements. The variation of their magnetic moments is discussed in terms of the acidities of their parent acids and the resonance effects of 4-substituents.

Most copper(II) carboxylates have bridged dinuclear structures and exhibit strong antiferromagnetic coupling between the pairs of copper(II) ions. With the intention of elucidating the mechanism of the spin-exchange coupling, an attempt has been made to relate the strength of the coupling to the acidity of the parent carboxylic acid.[1-3] While such a correlation has been confirmed for various alkanoate series,[3-5] it remains obscure for arenecarboxylates.[6-8] This is supposed to reflect the versatility of coordination polymerism in arenecarboxylates.[9,10] Besides, their magnetic properties may also be affected by the steric and resonance effects of substituents, as would be expected from the Hammett equation.[11] In order to investigate the resonance effects, we have prepared the quinoline (quin) and 4-methylquinoline (4-Mequin) adducts of a series of copper(II) 3- and 4-substituted benzoates with the substituents of CH_3, Cl, NO_2, CF_3, CH_3O, and CN.

The quinoline adducts of copper(II) 4-substituted benzoates, except 4-cyanobenzoate, were prepared according to the general procedure[9] and recrystallized from *N*,*N*-dimethylformamide containing excess quinoline. The remaining compounds were prepared by treating the ethanol solution of appropriate benzoic acid with a chloroform solution of the quinoline adduct of copper(II) propionate. In most cases the fine green crystals precipitated within a few hours; when this was not the case, the mixture was evaporated under reduced pressure. The effective magnetic moments of these compounds (Table 1) were evaluated from the room-temperature magnetic susceptibilities (χ_M) using the equation $\mu_{eff}=2.83[(\chi_M-\chi_{dia}-N\alpha)T]^{1/2}$. The diamagnetic corrections (χ_{dia}) were estimated from Pascal constants[12] and the temperature-independent paramagnetic contribution ($N\alpha$) was taken as 60×10^{-6} (1 emu=$4\pi\times10^{-6}$ m^3). For the quinoline adducts of copper(II) 3-nitrobenzoate and 3,5-dinitrobenzoate, the temperature dependence of their magnetic susceptibilities was measured in the temperature range of 80—300 K in order to confirm their dinuclear structures. The result agreed well with the Bleaney-Bowers equation,[13] using the parameters of $g=2.17$ and $2J=-276$ cm^{-1} for the 3-nitrobenzoate and $g=2.18$ and $2J=-259$ cm^{-1} for the 3,5-dinitrobenzoate. The IR spectra of the solid compounds show bands characteristic of bridging carboxylate due to unsymmetric and symmetric carboxyl stretching vibrations.[14] The magnetic and IR spectral data indicate that the present compounds have a bridged dinuclear structure, similar to that of copper(II) acetate monohydrate.[15,16]

From an analogy to plots for the corresponding alkanoates,[4,5] the room-temperature magnetic moments (in BM) of the present compounds, together with literature data concerning the corresponding pyridine adducts,[7,16] are plotted in Fig. 1 against $pK_a-0.068pK_a'$ values, where pK_a and pK_a' are the acidities of the parent benzoic acid and the conjugate acid of the addend *N*-heteroaromatic donor. The points for the 3-substituted and 3,5-disubstituted benzoates give a straight line which has the same slope as that for the alkanoates:[4]

$$\mu_{eff}=-0.052(pK_a-0.068pK_a'-4.00)+1.37_1. \quad (1)$$

The variation of the singlet-triplet separation energies (e.g. $-2J=280$, 276, and 259 cm^{-1} for the quinoline adducts of benzoate,[17] 3-nitrobenzoate, and 3,5-dinitrobenzoate, respectively, and $-2J=309$, 307, and 292 cm^{-1} for the pyridine adducts of copper(II) 3-methylbenzoate,[7] benzoate,[18] and 3-bromobenzoate,[7] respectively) is consistent with this equation. Similarly, the carboxyl frequencies (in cm^{-1}) for these compounds show systematic shifts against the acidities of the parent benzoic acids ($\tilde{\nu}_{unsym}=1683-15.0(pK_a-0.068pK_a')$ and $\tilde{\nu}_{sym}=1406+4.9(pK_a-0.068pK_a')$). These relationships indicate that the magnetic properties of the 3-substituted and 3,5-disubstituted benzoates are influenced unambiguously by the inductive effects of substituents. On the other

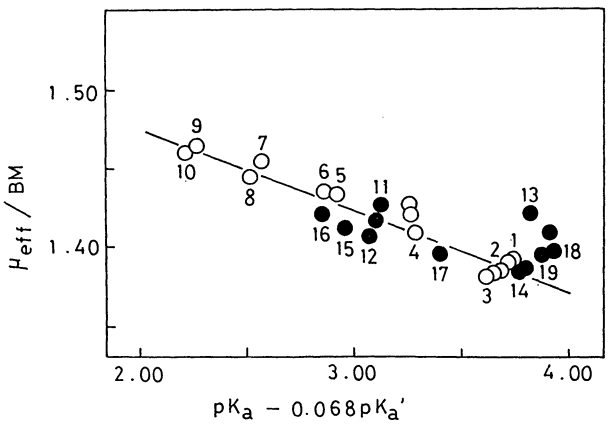

Fig. 1. The magnetic moments at 20 °C plotted against the acidities of the ligands for the copper(II) 3-substituted (○) and 4-substituted (●) benzoate adducts with pyridine, quinoline, and 4-methylquinoline.

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

Compound		Found(Calcd)/%				μ_{eff}/BM
		Cu	C	H	N	
$Cu(3\text{-}CH_3C_6H_4COO)_2 \cdot quin$	(1)	13.85 (13.73)	64.37 (64.86)	4.65 (4.57)	2.96 (3.03)	1.39
$Cu(3\text{-}CH_3C_6H_4COO)_2 \cdot 4\text{-}Mequin$	(2)	13.52 (13.32)	65.34 (65.47)	4.74 (4.86)	2.87 (2.94)	1.39
$Cu(C_6H_5COO)_2 \cdot 4\text{-}Mequin$	(3)	14.17 (14.15)	63.89 (64.21)	4.15 (4.27)	3.06 (3.12)	1.38
$Cu(3\text{-}ClC_6H_4COO)_2 \cdot quin$	(4)	12.62 (12.61)	54.67 (54.83)	2.98 (3.00)	2.70 (2.78)	1.41
$Cu(3\text{-}NO_2C_6H_4COO)_2 \cdot quin$	(5)	11.87 (12.11)	52.48 (52.63)	2.81 (2.88)	7.89 (8.00)	1.43
$Cu(3\text{-}NO_2C_6H_4COO)_2 \cdot 4\text{-}Mequin$	(6)	11.45 (11.79)	53.31 (53.49)	3.11 (3.18)	7.65 (7.80)	1.44
$Cu(3,5\text{-}Cl_2C_6H_3COO)_2 \cdot quin$	(7)	11.10 (11.10)	47.82 (48.24)	2.46 (2.29)	2.35 (2.45)	1.46
$Cu(3,5\text{-}Cl_2C_6H_3COO)_2 \cdot 4\text{-}Mequin$	(8)	11.04 (10.83)	48.93 (49.13)	2.51 (2.58)	2.32 (2.39)	1.44
$Cu[3,5\text{-}(NO_2)_2C_6H_3COO]_2 \cdot quin \cdot CHCl_3$	(9)	8.89 (8.65)	39.13 (39.26)	1.89 (1.92)	9.47 (9.54)	1.46
$Cu[3,5\text{-}(NO_2)_2C_6H_3COO]_2 \cdot 4\text{-}Mequin \cdot CHCl_3$	(10)	8.64 (8.49)	39.98 (40.13)	2.30 (2.15)	9.33 (9.36)	1.46
$Cu(4\text{-}CF_3C_6H_4COO)_2 \cdot quin$	(11)	11.45 (11.13)	52.63 (52.59)	2.67 (2.65)	2.55 (2.45)	1.43
$Cu(4\text{-}CF_3C_6H_4COO)_2 \cdot 4\text{-}Mequin$	(12)	10.87 (10.86)	53.48 (53.39)	2.97 (2.93)	2.43 (2.39)	1.41
$Cu(4\text{-}CH_3C_6H_4COO)_2 \cdot quin$	(13)	13.62 (13.73)	65.04 (64.86)	4.61 (4.57)	3.27 (3.03)	1.40
$Cu(4\text{-}CH_3C_6H_4COO)_2 \cdot 4\text{-}Mequin$	(14)	13.19 (13.32)	65.59 (65.47)	4.93 (4.86)	2.99 (2.94)	1.38
$Cu(4\text{-}NCC_6H_4COO)_2 \cdot 4\text{-}Mequin \cdot C_2H_5OH$	(15)	11.96 (11.66)	61.33 (61.70)	3.97 (4.25)	7.79 (7.71)	1.42
$Cu(4\text{-}NO_2C_6H_4COO)_2 \cdot 4\text{-}Mequin$	(16)	11.88 (11.79)	53.57 (53.49)	3.31 (3.18)	7.85 (7.80)	1.43
$Cu(4\text{-}ClC_6H_4COO)_2 \cdot 4\text{-}Mequin$	(17)	11.99 (12.27)	55.88 (55.67)	3.45 (3.31)	2.85 (2.70)	1.41
$Cu(4\text{-}CH_3OC_6H_4COO)_2 \cdot quin \cdot (CH_3)_2NCHO$	(18)	11.47 (11.19)	60.70 (59.20)	4.80 (4.97)	4.75 (4.93)	1.40
$Cu(4\text{-}CH_3OC_6H_4COO)_2 \cdot 4\text{-}Mequin$	(19)	12.36 (12.48)	61.53 (61.35)	4.59 (4.55)	2.83 (2.75)	1.40

hand, the magnetic moments of the present 4-substituted benzoates are rather independent of the acidities of the parent acids (Fig. 1). This discernible trend has already been pointed out for the magnetic properties of the copper(II) 4-substituted benzoate adducts with 1-butanol, since their singlet-triplet separation energies are insensitive to the nature of the substituents.[6] It is plausible that the resonance and inductive effects of 4-substituent[11,19] tend to be cancelled out. For cases where the perturbation on the π-electron density of the carboxyl group may not be disregarded, using $\Delta\mu\pi$ to represent this correction term, we can write

$$\mu_{eff} = -0.052(pK_a - 0.068pK_a' - 4.00) + \Delta\mu\pi + 1.37_1. \quad (2)$$

Previously, we have pointed out that the $\Delta\mu\pi$ term may be correlated with $R-0.38F$,[5] where R and F are the resonance and field constants of Swain and Lupton.[20] The $\Delta\mu\pi$ values evaluated by the use of Eq. 2 are plotted, in Fig. 2, against $R-0.38F$. The apparent linear correlation indicates that the resonance effect takes a role in determining the magnetic

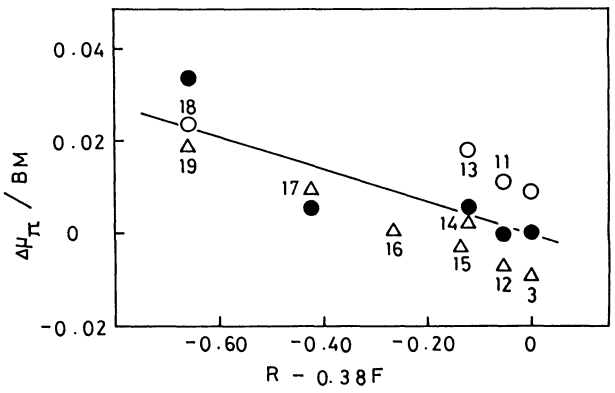

Fig. 2. The correction values $\Delta\mu\pi$ for the 4-substituted benzoate adducts with pyridine (●), quinoline (○), and 4-methylquinoline (△) plotted against the substitutent constants $R-0.38F$.

properties of the 4-substituted benzoates. The magnitude of the resonance effect is estimated to be about $-0.03_5(R-0.38F)$, e.g., 0.00_4, 0.01_5, and 0.02_3 BM for

the CH_3, Cl, and CH_3O substituents, respectively. These values are much smaller than those found in the case of copper(II) (substituted formate)s.[5] This refers perhaps to the torsion between the planes of the carboxylate and phenyl groups (the dihedral angles of 0.2—27.2°),[21-24] in adition to the long separation between the bridging carboxylato and substituent groups.

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