Magnetic Properties of Cobalt(II) and Nickel(II) Benzoate Adducts with Quinoline Analogues

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Synopsis. Various cobalt(II) and nickel(II) 3-substituted benzoate adducts with quinoline, 4-methylquinoline, and quinoxaline were prepared. They were then characterized by means of magnetic susceptibility and IR spectroscopy. The variation in their magnetic moments is discussed in terms of the basicities of the benzoate ligands as well as the coordinate-bond lengths between the benzoate oxygen and metal atoms. For the nickel(II) compounds, the formation of weak nickel(II)–nickel(II) bonding is suggested.

Many transition metal carboxylates have carboxylate-bridged dinuclear structures, and exhibit strong antiferromagnetic couplings between pairs of metal ions. It has been recognized that the spin-exchange couplings in such copper(II),[1-4] nickel(II),[5,6] cobalt(II),[7-12] and manganese(II)[13,14] carboxylates operate predominantly by superexchange through the bridging carboxylate ligands, whereas coupling in the chromium(II) analogues is the result of a quadruple bond between two chromium(II) ions.[15] However, the strength of the couplings in these carboxylates, except in the copper(II) carboxylates, remains obscure, since the temperature dependence of their magnetic susceptibilities, thus far studied,[5,6,11,16] shows appreciable deviations from the Van Vleck equation.[17] This obscurity might be clarified by comparative studies of the magnetic properties of dinuclear copper(II), nickel(II), and cobalt(II) compounds. We thus prepared cobalt(II) and nickel(II) 3-substituted benzoate adducts with quinoline (quin), 4-methylquinoline (4-Mequin), and quinoxaline (quix), and then studied their magnetic properties.

The compounds were prepared by methods similar to those of Catterick and Thornton[10] and of Bencini et al.[5]

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

Compound		Found (Calcd)/%				μ_{eff}/BM
		M	C	H	N	
$Co(3\text{-}CH_3C_6H_4COO)_2\cdot quin$	(1)	12.88 (12.86)	65.5 (65.5)	4.63 (4.62)	3.05 (3.06)	4.17
$Co(3\text{-}CH_3C_6H_4COO)_2\cdot 4\text{-Mequin}$	(2)	12.51 (12.48)	66.1 (66.1)	4.93 (4.91)	2.97 (2.96)	4.23
$Co(C_6H_5COO)_2\cdot 4\text{-Mequin}$	(3)	13.28 (13.26)	64.8 (64.9)	4.33 (4.31)	3.13 (3.15)	4.23
$Co(C_6H_5COO)_2\cdot quix$	(4)	13.69 (13.66)	61.2 (61.3)	3.75 (3.74)	6.50 (6.49)	4.14
$Co(3\text{-}ClC_6H_4COO)_2\cdot 4\text{-Mequin}$	(5)	11.51 (11.48)	56.1 (56.2)	3.36 (3.34)	2.71 (2.73)	4.27
$Co(3\text{-}BrC_6H_4COO)_2\cdot quin$	(6)	10.04 (10.02)	46.7 (47.0)	2.58 (2.57)	2.32 (2.38)	4.21
$Co(3\text{-}BrC_6H_4COO)_2\cdot 4\text{-Mequin}$	(7)	9.82 (9.79)	47.8 (47.9)	2.87 (2.85)	2.34 (2.33)	4.25
$Co(3\text{-}CH_3OC_6H_4COO)_2\cdot 4\text{-Mequin}$	(8)	11.71 (11.68)	61.9 (61.9)	4.62 (4.60)	2.76 (2.78)	4.25
$Ni(3\text{-}CH_3C_6H_4COO)_2\cdot quin$	(9)	12.76 (12.81)	65.5 (65.5)	4.63 (4.62)	3.10 (3.06)	1.93
$Ni(3\text{-}CH_3C_6H_4COO)_2\cdot 4\text{-Mequin}$	(10)	12.13 (12.43)	66.0 (66.1)	4.97 (4.91)	2.93 (2.97)	2.02
$Ni(C_6H_5COO)_2\cdot 4\text{-Mequin}$	(11)	13.52 (13.22)	64.9 (64.9)	4.29 (4.31)	3.13 (3.15)	1.96
$Ni(3\text{-}ClC_6H_4COO)_2\cdot quin\cdot 1/2C_6H_6$	(12)	10.97 (10.91)	58.0 (58.0)	3.35 (3.37)	2.59 (2.60)	2.05
$Ni(3\text{-}ClC_6H_4COO)_2\cdot 4\text{-Mequin}\cdot 3/2C_6H_6$	(13)	9.29 (9.31)	62.9 (62.9)	4.08 (4.16)	2.19 (2.22)	2.04
$Ni(3\text{-}BrC_6H_4COO)_2\cdot quin$	(14)	9.87 (9.98)	47.0 (47.0)	2.58 (2.57)	2.37 (2.38)	2.04
$Ni(3\text{-}BrC_6H_4COO)_2\cdot 4\text{-Mequin}\cdot C_6H_6$	(15)	8.55 (8.63)	53.0 (53.0)	3.38 (3.41)	2.06 (2.06)	2.00
$Ni(3\text{-}CH_3OC_6H_4COO)_2\cdot 4\text{-Mequin}$	(16)	11.72 (11.64)	61.8 (61.9)	4.58 (4.60)	2.81 (2.78)	1.99
$Ni(3\text{-}NO_2C_6H_4COO)_2\cdot quin$	(17)	11.10 (11.29)	53.1 (53.1)	2.87 (2.91)	8.05 (8.08)	2.06

Their effective magnetic moments (Table 1) were evaluated from the molar magnetic susceptibilities (χ) using the equation $\mu_{eff}=798[(\chi-N\alpha)T]^{1/2}$. The temperature-independent paramagnetic contribution ($N\alpha$) was taken to be 6.3×10^{-9} m^3 mol^{-1} for cobalt(II) ion and 2.5×10^{-9} m^3 mol^{-1} for nickel(II) ion. The Pascal constants[18] were used to correct for the diamagnetic contributions. For the cobalt(II) and nickel(II) benzoate adducts with quinoline, the variation with the temperature of their magnetic susceptibilities was determined over the temperature range 80—300 K. The IR spectra of the solid compounds were recorded using nujol mulls in the 4000—600 cm^{-1} range for confirmation of bridging carboxylate anions.[3,19]

It was affirmed that the strength of a superexchange coupling is affected by the basicity and coordination geometry of the intervening ligand. For example, the room-temperature magnetic moments (in BM) of dinuclear copper(II) 3-substituted benzoates are approximated by the following equation:[4]

$$\mu_{eff}=\mu_{mono}[1-65\times R^{-12}(pK_{al}-0.068pK_a'+23.0)]. \quad (1)$$

Here, K_{al} and K_a' are the acid constants of the conjugate cation acid of the bridging benzoate and axial ligands; R is the coordinate-bond length (in Å) between the benzoate oxygen and copper atoms. $\mu_{mono}=1.95$ BM is the effective magnetic moment for a magnetically dilute copper(II) system with tetragonal pyramidal coordination. The exchange parameters for a series of manganese(II), cobalt(II), and nickel(II) oxides and fluorides were also correlated with their coordinate-bond lengths, being approximated by a power law, $J\propto R^{-12}$.[20,21] Then, if the couplings in the present cobalt(II) and nickel(II) benzoates are operating in mechanisms similar to that in the dinuclear copper(II) benzoates, i.e., unpaired electrons in the $d_{x^2-y^2}$ orbitals delocalize mainly into the σ-bonding systems of the carboxylate groups, Eq. 1 is also applicable to their magnetic moments by substituting the relevant values for μ_{mono}. The pK_a dependence is compared in Fig. 1 between the magnetic moments of the present compounds, together with some literature data,[9-12] and Eq. 1. The points for the cobalt(II) compounds give a straight line with a slope of -0.053 BM; it agrees well with Eq. 1 when the following parameters are used: $\mu_{mono}=5.00$ BM and $R=2.053$ Å.[7,8] Similar systematic shifts were observed in plots of the COO stretching frequencies against the basicities and coordinate-bond lengths.[3,19] On the other hand, the magnetic moments of these nickel(II) compounds are appreciably lower than the values calculated by Eq. 1 using the parameters of $\mu_{mono}=3.20$ BM and $R=2.014$ Å.[6,22] This discrepancy suggests that other demagnetization mechanism may be cooperative in the nickel(II) compounds.

The variable-temperature magnetic susceptibilities of the cobalt(II) and nickel(II) benzoate adducts with quinoline are given in Fig. 2. As was reported,[5,6,11,16] it is difficult to make them fit with the Van Vleck equation for a pair of $S=1$ or $S=3/2$ spins.[17] As the temperature is lowered, the experimental susceptibilities decrease more rapidly than do those calculated by the Van Vleck equation. An obvious way out of this problem is to

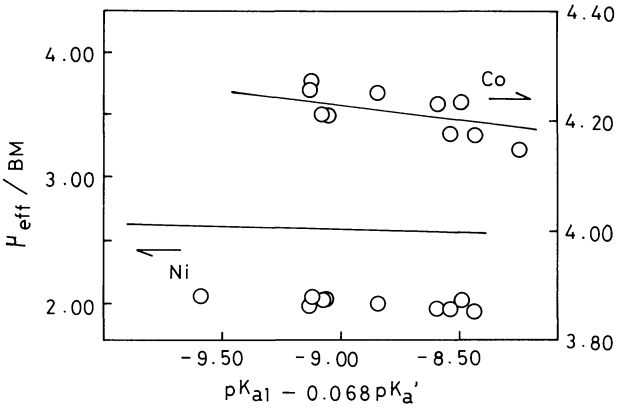

Fig. 1. Magnetic moments at 20°C plotted against the acidities of the ligands for the nickel(II) and cobalt(II) 3-substituted benzoate adducts with quinoline analogues. The solid lines represent Eq. 1.

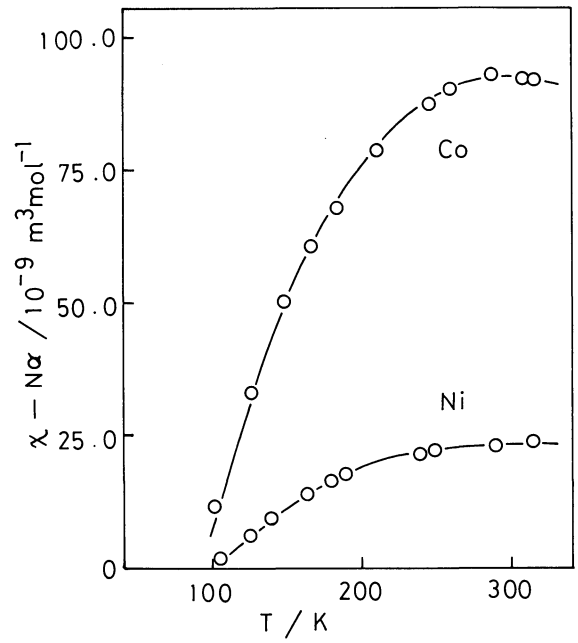

Fig. 2. Observed and calculated magnetic susceptibilities of the nickel(II) and cobalt(II) benzoate adducts with quinoline. The solid curves represent the extended Van Vleck equation.

postulate a temperature dependence of the spin-exchange coupling, which may be written in the form $J+a(J/kT)+b(J/kT)^2+\cdots$. By using the first two terms ($J+aJ/kT$), this extended Van Vleck equation can be satisfactorily fitted to the experimental susceptibilities, yielding $g=2.78$, $J=-20$ cm^{-1}, and $a=160$ cm^{-1} for the cobalt(II) compound and $g=2.27$, $J=-85$ cm^{-1}, and $a=21$ cm^{-1} for the nickel(II) compound. Introducing the higher-order terms improves the agreement; the present data, however, are insufficient to justify this refinement. The $-J$ values for the copper(II), cobalt(II), and manganese(II) benzoate adducts with quinoline (150,[5] 20, and 4[14] cm^{-1}, respectively) are consistent with the common trend in the exchange constants for a series

of structurally analogous transition metal(II) compounds.[23] On the other hand, the $-J$=85 cm^{-1} for this nickel(II) benzoate is appreciably larger than that predicted by the above-mentioned trend. A plausible explanation for this disagreement is the formation of weak nickel(II)–nickel(II) bonding, since the extended lobes of the two d_{z^2} orbitals are properly situated for the overlap with each other.

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