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Magnetic Studies on the Dissociation Equilibria of Dinuclear Nickel(II) Alkanoates in Non-Aqueous Solutions

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Dinuclear nickel(II) alkanoates, [$Ni_2(RCOO)_4(quin)_2$] (R=$C_2H_5CH(CH_3)$–, $C_2H_5C(CH_3)_2$–, and $(C_3H_7)_2CH$–; quin= quinoline), were prepared, and then characterized by means of magnetic-susceptibility and IR spectroscopy. The equilibria between the mono- and dinuclear species in mixed acetone–benzene, mixed ethanol–benzene, and mixed tetrahydrofuran–benzene solution are discussed in terms of the donor number of acetone, ethanol, and tetrahydrofuran and in terms of the Ni–O bond strength. By comparing the Ni–O and Cu–O bond strengths, the exchange-coupling strength through the carboxylate bridges between the nickel(II) ions was estimated from that between copper(II) ions.

A number of experimental and theoretical studies have been carried out concerning the structures and magnetic behaviors of polynuclear transition metal carboxylates. Particular interest has recently been focused on nickel(II) carboxylate adducts with *N*-heteroaromatic donors because of their unusual magnetic properties; the variable-temperature magnetic susceptibilities could not be well fitted to the Van Vleck equation,[1—4] although X-ray examinations confirmed the copper(II) acetate-type dinuclear structures of the molecules.[3,5,6]

Previously, we demonstrated that an extend Van Vleck equation containing a temperature-dependent coupling parameter ($J+aJ/kT$) was able to reproduce the magnetic susceptibilities of the benzoate derivatives.[4] We ascribed such a phenomenon to Kittel's exchange magnetostriction,[7] assuming a weak σ-bond formation between the nickel(II) ions;[2,4] actually, smaller room-temperature magnetic moments occur in these compounds with shorter Ni–Ni distances.[3,5,6]

If this assumption is correct, there should be two exchange coupling pathways, i.e., through the bridging carboxylate (J_{Ni}) and the Ni–Ni σ-bond (J_{Ni-Ni}). To separate the antiferromagnetic contributions into those from individual pathways, information about the dissociation equilibria of the compounds in solutions seems to be useful, because the former is closely related to the nature of the Ni–O bonds. We thus determined the magnetic susceptibilities of the nickel(II) alkanoate adducts with quinoline in non-aqueous solutions. For this purpose, we selected a series of quinoline adducts of nickel(II) DL-2-methylbutyrate, 2,2-dimethylbutyrate, and 2-propylpentanoate, which have a varying bulkiness of the alkyl substituents, and higher solubilities, rather than other nickel(II) carboxylate derivatives.

Experimental

The nickel(II) alkanoates, [$Ni_2(RCOO)_4(quin)_2$] (R = $C_2H_5CH(CH_3)$–, $C_2H_5C(CH_3)_2$–, and $(C_3H_7)_2CH$–; quin = quinoline), were prepared by procedures similar to those of Novotortsev et al.[1] and of Hirashima et al.[3] Appropriate nickel(II) alkanoate hydrate was suspended in ethanol and a stoichiometric amount of quinoline was added. The solution was allowed to evaporate to dryness on a water bath, and the residue was extracted with benzene. Concentration of the solution on a water bath was followed by the addition of a small amount of cyclohexane yielded green crystals **1**—**3** (Table 1).

The magnetic susceptibilities were measured using a Gouy balance at 20 °C for compounds **1**—**3** in the solid state and in pyridine, tetrahydrofuran, ethanol, acetone, benzene, chloroform, cyclohexane, mixed acetone–benzene, mixed ethanol–benzene, and mixed tetrahydrofuran–benzene solutions at Ni concentrations of 0.10 mol dm^{-3}, except for compound **1** in acetone and cyclohexane. For compound **1** in acetone and cyclohexane solutions, the susceptibilities were measured at Ni concentrations of 0.02 mol dm^{-3} because of its low solubilities. Benzene, tetrahydrofuran, and cyclohexane, chloroform, and acetone solvents were dried over sodium wire, diphosphorus pentaoxide, and anhydrous potassium carbonate, respectively, and were distilled immediately before use.

For calculating the effective magnetic moment per nickel(II) ion, the susceptibility date were corrected for diamagnetic contributions using Pascal constants,[8] and for temperature-independent paramagnetism using a value of 2.5×10^{-9} m^3 mol^{-1}.[9] For solid samples, the variable-temperature susceptibilities were also determined over 80—300 K, and their IR spectra were recorded using Nujol® mulls in the 4000—600 cm^{-1} range.

Results and Discussion

Solid sample **1**—**3** showed magnetic moments of 1.73—1.76 BM at room temperature, comparable to those for well-characterized dinuclear nickel(II) carboxylates (practically the same as those of the quinoline adducts of 2,2-dimethylpropionate[1] and 2-ethylbutyrate,[3] and slightly lower than those of the benzoate derivatives (1.93—2.06 BM)[4]). Furthermore, they exhibited COO stretching bands at 1635—1625 and 1425—1415 cm^{-1}, characteristic of bridging carboxylate groups. These magnetic and IR spectral data are consistent with the presence of dinuclear units in the crystals.

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

Compound		Found (Calcd)/%				μ_{eff}
		Ni	C	H	N	BM
$[Ni\{CH_3CH_2C(CH_3)_2COO\}_2(quin)]$	(**1**)	14.04 (14.04)	60.2 (60.3)	6.99 (6.99)	3.35 (3.35)	1.76
$[Ni\{CH_3CH_2CH(CH_3)COO\}_2(quin)]$	(**2**)	15.03 (15.05)	58.3 (58.5)	4.49 (4.46)	3.58 (3.59)	1.74
$[Ni\{(CH_3CH_2CH_2)_2CHCOO\}_2(quin)]$	(**3**)	12.37 (12.38)	63.2 (63.3)	7.88 (7.86)	2.95 (2.95)	1.76

The variable-temperature susceptibilities were simulated by the extended Van Vleck equations for a pair of exchange-coupled $S=1$ spins[4)] when the following parameters were used: $g=2.25$ (fixed) and $J=-109$ cm^{-1} and $a=39$ cm^{-1} for **1**, $J=-108$ cm^{-1} and $a=39$ cm^{-1} for **2**, and $J=-106$ cm^{-1} and $a=38$ cm^{-1} for **3**. The obtained J values are slightly more negative than -85 cm^{-1} for the corresponding benzoates;[4)] the difference may be interpreted, at least in part, in terms of the basicities of the carboxylate ligands and the resonance effect of the phenyl group.[10)]

The magnetic susceptibilities of compounds **1**—**3** in solutions depend upon the kind of solvents in which they are dissolved (Table 2). For benzene, chloroform, and cyclohexane solutions, the evaluated magnetic moments are practically the same as those of the solids, indicating the presence of dinuclear units similar to those in the crystals; also, there is no significant long-range intermolecular coupling present in the crystals.

In contrast, for pyridine, tetrahydrofuran, ethanol, and acetone solutions, the magnetic moments are practically the same as those of mononuclear nickel(II) species, indicating that the dinuclear species undergo dissociative processes in the donor solvents. Actually, we can isolate mononuclear species by concentrating pyridine solutions, such as $[Ni(RCOO)_2(py)_2]$ ($R=CH_3$–, C_2H_5–, C_3H_7–; 3.04—3.18 BM)[11)] and $[Ni(RCOO)_2(quin)(py)]$ ($R=(C_2H_5)_2CH$–, $(CH_3)_3C$–, $C_2H_5C(CH_3)_2$–; 3.13—3.15 BM).

Such a behavior parallels that found for the copper(II) carboxylates,[12—14)] although the nickel(II) carboxylate are much more easily solvolized; in the case of the copper(II) carboxylates, the ethanol[12)] and even mixed pyridine–chlorobenzene[13)] solutions contain the dinuclear species in a fairly large portion. This reflects the weakness of the Ni–O bonds relative to the Cu–O bonds (greater importance of the entropy changes), being consistent with the bond distances (Cu–O distance, 1.94—1.98 Å; Ni–O distance, 2.00—2.02 Å)[3,5,6)] and COO stretching vibration bands (1625—1615 and 1420—1410 cm^{-1} for the copper(II) salts; 1635—1625 and 1425—1415 cm^{-1} for the nickel(II) salts) observed for the solid samples.

Table 2. Effective Magnetic Moments at 20 °C in Various Solvents ($c_{Ni}=0.10$ mol dm^{-3}, * $c_{Ni}=0.02$ mol dm^{-3})

Solvent	μ_{eff}/BM		
	(**1**)	(**2**)	(**3**)
Pyridine	3.25	3.26	3.29
Tetrahydrofuran	2.96	2.98	3.13
Ethanol	2.94	2.95	2.94
Acetone	2.9*	2.87	2.92
Benzene	1.77	1.77	1.78
Chloroform	1.78	1.77	1.77
Cyclohexane	1.8*	1.75	1.78
Solid	1.76	1.74	1.76

The dissociation equilibria of dinuclear copper(II) carboxylates in pyridine solutions are well known.[13)] For the purpose of a comparison, we tried to determine the equilibrium constants of compounds **1**—**3** in mixed pyridine–benzene solutions. Unfortunately, the attempts were unsuccessful, because the dinuclear species dissociated almost completely to the mononuclear species. Alternatively, we studied the dissociation equilibria of compounds **1**—**3** in mixed acetone–benzene, mixed ethanol–benzene, and mixed tetrahydrofuran–benzene solutions.

Their magnetic moments (μ_{eff}) were determined at 20 °C in the concentration range $c_L=0$—4 mol dm^{-3} ($L=CH_3COCH_3$, C_2H_5OH, and C_4H_8O). The marked dependence of the magnetic moments on the L concentrations provides direct evidence for equilibria among species differing in the number of nickel(II) ions (Fig. 1); we assumed equilibria similar to those for copper(II) carboxylate derivatives;[13)]

$$[Ni_2(RCOO)_4(quin)_2]+2L \rightleftharpoons 2[Ni(RCOO)_2(quin)(L)]. \quad (1)$$

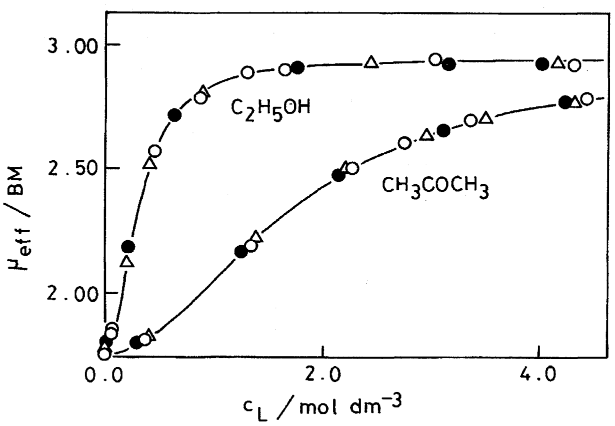

Fig. 1. Magnetic moments of compounds **1** (○), **2** (●), and **3** (△) at 20 °C in mixed benzene–acetone and mixed benzene–ethanol solutions ($c_{Ni}=0.01$ mol dm^{-3}) are plotted against the acetone and ethanol concentrations.

To simulate the experimental μ_{eff} vs. c_L plots, we furthermore assumed that the magnetic moments of the di- and mononuclear species are 1.75 BM (values of crystalline samples) and 2.94 BM (values of very dilute solutions), respectively. The curves correspond to the dissociation equilibria (Eq. 1), where $K' = [\mathrm{Ni(RCOO)_2(quin)(L)}]^2/[\mathrm{Ni_2(RCOO)_4(quin)_2}][\mathrm{L}]^2 = 0.043$, 0.32, and 0.31 $\mathrm{mol\,dm^{-3}}$ for the $\mathrm{L=CH_3COCH_3}$, $\mathrm{C_2H_5OH}$, and $\mathrm{C_4H_8O}$ systems, respectively.

Figure 1 shows no difference in the curves for compounds **1**—**3**, indicating that the equilibria remain practically unperturbed by a steric hindrance due to the bulkiness of the alkyl substituents. The solvolyses may thus be discussed in terms of the donor numbers (DN) of the solvents,[15] being formulated as a linear equation,

$$\log K' = 0.29 \times \mathrm{DN} - 6.3, \tag{2}$$

for the present nickel(II) alkanoates in ethanol, tetrahydrofuran, and acetone (DN=20.0, 20.0, and 17.0, respectively).

Substituting 33.1 (DN of pyridine), we can anticipate the equilibrium constant of the compounds in pyridine solutions to be $\log K' = 3.3$ (as described above, the equilibria lies so far to the right). A comparison of this value with -2.7 for the copper(II) analogues in pyridine solution[13] indicates that copper(II) ions are bridged more strongly than nickel(II) ions, by roughly a factor of $(3.3+2.7)/2 \approx 3.0$; the solvolysis in pyridine results in the dissociation of four M–O bonds and the formation of two M–N bonds. The factor obtained for the methanol solutions is rather less reliable, but of the same order.[16]

Since the carboxylate ligand is a typical 'hard base', we may correlate the magnetic properties of carboxylate compounds with the M–O bond strength; for example, in some series of dinuclear copper(II), nickel(II), and cobalt(II) carboxylates, the magnetic moment tends to increase as the $\mathrm{p}K_\mathrm{a}$ value of the parent acid decreases.[4,17] Taking into account the number of unpaired electrons on each magnetic center (comparing the S^2J values), we can estimate the exchange couplings through the bridging carboxylate (J_{Ni}) from $J_{\mathrm{Cu}} = -150\ \mathrm{cm^{-1}}$ for the copper(II) analogues, to be approximately $(1/4)J_{\mathrm{Cu}}/3.0 = -13\ \mathrm{cm^{-1}}$. The ratio ($J_{\mathrm{Cu}}/J_{\mathrm{Ni}} \approx 12$) is consistent with those observed for oxalato-bridged[18] and phenoxo-bridged[19] compounds, and strongly supports this estimation. In conclusion, the exchange couplings through the bridging carboxylate and direct Ni–Ni σ-bond pathways (the average for three compounds) have been evaluated to be on the order of $J_{\mathrm{Ni}} \approx -13\ \mathrm{cm^{-1}}$ and $J_{\mathrm{Ni\text{-}Ni}} = J(1+a/kT) - J_{\mathrm{Ni}} \approx -95 - 108a/kT\ \mathrm{cm^{-1}}$, respectively.

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