TABLE III

ELECTRONIC SPECTRA OF M(detsc)$_2$ (M = Ni(II), Pd(II), Pt(II)) IN DICHLOROMETHANE[a]

Complex	d–d band	CT band	Ligand band
Ni(detsc)$_2$	15.4 (1.99)	24.8 (3.78)	29.4 (4.43), 40.8 (4.42)
Pd(detsc)$_2$	21.3 (2.52)	27.0 (3.93)	31.9 (4.99), 40.0 (4.44), 42.9 (4.47)
Pt(detsc)$_2$	24.4 (3.40)	27.6 (4.16)	36.6 (4.60), 43.1 (4.39)

[a] Band maxima in kK; log ε values given in parentheses.

It is noted that the spectra of Ni(detsc)$_2$ and Pd(detsc)$_2$ resemble those[9] of the corresponding dedsc complexes, but the position of each band maximum of the detsc complexes somewhat shifts to the blue region compared with the maxima of the dedsc complexes.

The lowest frequency bands (ν_1) may be due to a spin-allowed d-d transition, in view of their ε values. Since M(detsc)$_2$ are formulated as square-planar d^8 complexes, the ν_1 band is assigned to a singlet–singlet transition from d_{xy} to $d_{x^2-y^2}$. The ν_1 of Ni(detsc)$_2$ occurs at 15.4 kK, which is higher in frequency than that of Ni(dedsc)$_2$ (14.8 kK[9]), while lower than that of Ni(dedtc)$_2$ (15.8 kK[9]). A similar trend is observed in the palladium complexes: 20.6,[9] 21.3, and 22.6[9] kK for the dedsc, detsc, and dedtc complexes, respectively. The ligand field strength of detsc is therefore intermediate between dedsc and dedtc.

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Electron Paramagnetic Resonance Spectrum of Binuclear Copper *n*-Butyrate Monohydrate[1a]

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Since the definitive work of Bleaney and Bowers on the anomalous magnetic properties of copper acetate monohydrate,[2] numerous dimeric copper compounds have been synthesized and largely characterized by magnetic susceptibility and optical spectroscopy.[3] Measurements of zero-field splitting parameters by electron paramagnetic resonance (epr) spectroscopy[4] have often been hampered by inability to grow suitable single crystals. Recently, the epr spectra of randomly oriented triplet-state molecules in powdered samples of copper alkanoates[5-7] and frozen solutions of copper and vanadyl dimers have been successfully analyzed.[8,9]

From a single-crystal study at 24 GHz, the epr parameters of copper butyrate monohydrate, $Cu_2(C_4H_7O_2)_4 \cdot 2H_2O$, have been reported to be $D = 0.35$ cm^{-1}, $g_z = 2.40$, and $g_\perp = 2.04$–2.10.[10] The perpendicular parameters were not well characterized; apparently the spectrum is complicated by the presence of seven independent magnetic units in the crystal having nearly identical parameters. We report here significantly different parameters (an average of the seven units) from a spectral analysis of powdered copper butyrate monohydrate at 77°K. Our values are $|D| = 0.333 \pm 0.005$ cm^{-1}, $|E| = 0.011 \pm 0.003$ cm^{-1}, $g_z = 2.342 \pm 0.005$, and $g_\perp\,[=(g_x + g_y)/2] = 2.063 \pm 0.008$.[11] This study provides conclusive evidence for a rhombic component in the crystalline field.

Results and Discussion

Spectra were collected by standard procedures on a Varian V-4502 spectrometer operating at X band. The marked temperature dependence of the spectrum is shown in Figure 1. From the reported singlet–triplet separation ($-J$) of 339 cm^{-1} [12] we estimate that 37% of the dimers are in the paramagnetic triplet state at 298°K compared to 0.5% at 77°K. The sharp lines around 3300 G are due to a monomer impurity of about 0.01%; monomer lines have been observed for several other binuclear systems. The splitting around 4500 G (H_{x2} and H_{y2}) arises from a rhombic distortion in the crystalline field of the Cu^{2+} ion.

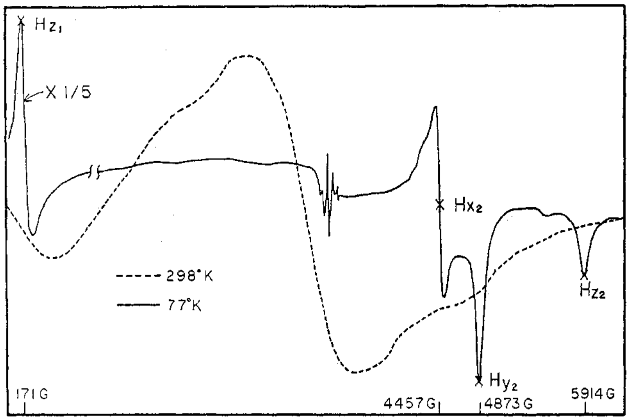

Figure 1.—First-derivative X-band epr spectrum of powdered copper butyrate monohydrate at 298 and 77°K. Both spectra have comparable signal levels. × 1/5 denotes a signal level one-fifth as large as that used in the rest of the spectrum. Principal resonance fields are indicated by ×. H_0 = 3342.2 G.

These spectra are governed by the usual $S = 1$ spin Hamiltonian[2]

$$\mathcal{H} = \beta \mathbf{H}\cdot\mathbf{g}\cdot\mathbf{S} + D(S_z^2 - {}^2\!/_3) + E(S_x^2 - S_y^2) \qquad (1)$$

where D and E are the zero-field splitting parameters. Here we have omitted the metal hyperfine terms since they only serve to broaden the principal resonance features. Assuming that the principal axes of the D and g tensors coincide, a full-matrix calculation of the energy levels[13] gives six principal resonance fields ($\Delta M_s = \pm 1$)

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of which only four are observed at X band for copper butyrate, *viz.*

$$H_{x2}^2 = (g_e/g_x)^2(H_0 + D' - E')(H_0 - 2E') \quad (2)$$

$$H_{y2}^2 = (g_e/g_y)^2(H_0 + D' + E')(H_0 + 2E') \quad (3)$$

$$H_{z1}^2 = (g_e/g_z)^2[(H_0 - D')^2 - E'^2] \quad (4)$$

$$H_{z2}^2 = (g_e/g_z)^2[(H_0 + D')^2 - E'^2] \quad (5a)$$

where $H_0 = \hbar\omega_0/g_e\beta$, $D' = D/g_e\beta$, $E' = E/g_e\beta$, and $g_e = 2.0023$. Since $(H_0 + D')^2 \gg E'^2$, eq 5a can be replaced by (5b) to good accuracy. Combining eq 4 and 5a, we obtain

$$H_{z2} \simeq (g_e/g_z)(H_0 + D') \quad (5b)$$

after rearrangement

$$D' = (g_z/g_e)^2(H_{z2}^2 - H_{z1}^2)/4H_0 \quad (6)$$

By setting $g_x = g_y = g_\perp$, we now have four unknowns (D', E', g_z, $g_\perp$) and four resonance fields (H_{x2}, H_{y2}, H_{z1}, H_{z2}). The parameters were determined by an iterative procedure beginning with eq 5b and 6 (yielding D' and g_z), then using eq 4 (yielding an initial E'), and finally using eq 2 and 3 (yielding final E' and $g_\perp$). The final parameters checked with eq 2–5a well within the stated errors.[11]

We obtain reliable parameters, particularly D and g_z, by this procedure. The fractional error in E is given by $|\delta E/E| \simeq (H_{x2}^2 + H_{y2}^2)(g_x - g_y)/2(H_{y2}^2 - H_{x2}^2) = 5.6(g_x - g_y)$. Of all the alkanoates the acetate has the largest known rhombic component in $g_\perp$ ($g_x - g_y = 0.040$).[14] The axial symmetry approximation in g perhaps introduces 20–30% error in E while the error introduced in $g_\perp$ [$= (g_x + g_y)/2$] is small, ±0.002.

We now examine the zero-field splitting parameter D in some detail. The magnetic dipole interaction D_{dd} and the pseudo dipolar term D_{pseudo} both contribute to the experimental D value, $|D_{\text{exptl}} \simeq D_{\text{dd}} + D_{\text{pseudo}}|$. For several vanadyl and copper dimers the magnetic dipole interaction dominates[8,9] ($D_{\text{exptl}} \simeq D_{\text{dd}}$) whereas the opposite is true for the copper chloride–pyridine *N*-oxides[15] ($D_{\text{exptl}} \simeq D_{\text{pseudo}}$); the copper alkanoates are intermediate.

At the short Cu–Cu distance (2.64 Å) of copper acetate,[16] a reasonable calculation of D_{dd} must take some account of the spin-density distributions on each half of the dimer. Using a covalent model which places 5% of the spin density on each of the four in-plane oxygen atoms and the remaining spin at four points representing the copper $d_{x^2-y^2}$ orbital (see ref 9 for a similar calculation), we estimate $D_{\text{dd}} \simeq -0.12\ \text{cm}^{-1}$ for the alkanoates. This value is considerably smaller than the previous estimate of $-0.20\ \text{cm}^{-1}$ based on a simple two-center calculation.[9,17]

The pseudo dipolar term is given approximately by the relationship[2]

$$D_{\text{pseudo}} \simeq -J'[(g_z - 2.002)^2/4 - (g_\perp - 2.002)^2]/8$$

where J' is an "average" exchange interaction, unknown in magnitude and sign, of excited electronic states. For copper butyrate we estimate D_{pseudo} to be $+0.45$ or $-0.21\ \text{cm}^{-1}$ depending on the relative sign of D_{exptl} and D_{dd} ($D_{\text{pseudo}} \simeq 0.12 \pm 0.33\ \text{cm}^{-1}$). The corresponding approximate J' values are $-140\ \text{cm}^{-1}$ (antiferromagnetic) or $+65\ \text{cm}^{-1}$ (ferromagnetic) compared to the antiferromagnetic exchange interaction, $J = -339\ \text{cm}^{-1}$, of the ground state.[12] Reduction in magnitude of excited-state exchange interactions relative to the ground-state value has also been noted for the copper chloride–pyridine *N*-oxide complexes.[15]

Literature D_{exptl} values for the acetate,[14] propionate,[7] butyrate,[10] benzoate,[6] monochloroacetate–2.5-water,[18] and monochloroacetate monohydrate[10] all fall in the narrow range 0.327–0.350 cm^{-1} (except for the cyanoacetate[5] with $D_{\text{exptl}} = 0.39 \pm 0.01\ \text{cm}^{-1}$). Within experimental error, assuming a common J' value ($-140\ \text{cm}^{-1}$) and $D_{\text{dd}} = -0.12\ \text{cm}^{-1}$, variations in g of the respective compounds can readily account for the differences in D_{exptl}. g_z values range from 2.34 to 2.40, and $g_\perp$ values, from 2.06 to 2.08. Note that variations in g should have a more pronounced effect on D_{pseudo} than on D_{dd}.

Differences in the rhombic component of the crystalline field are evidenced by variations in E from $<0.001\ \text{cm}^{-1}$ for the propionate[7] to $0.0147 \pm 0.0003\ \text{cm}^{-1}$ for the benzoate.[6] The acetate[14] and butyrate are intermediate with $E = 0.007 \pm 0.003$ and $0.011 \pm 0.003\ \text{cm}^{-1}$, respectively. Several other carboxylates have been studied by Lewis, *et al.*[19]

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The Kinetics of Interaction of Nickel(II) and Cobalt(II) with Bis(2-pyridylmethyl)amine

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The general features of the mechanism of formation of complexes of transition metal ions in aqueous medium have been thoroughly discussed.[1-4] More recently, determinations have been made of some of the more subtle effects in the formation process arising from variations in the ligand which replaces the coordinated water of the metal ion. Chelate ring size is important if coordinated water is sufficiently labile;[5,6] substitution

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