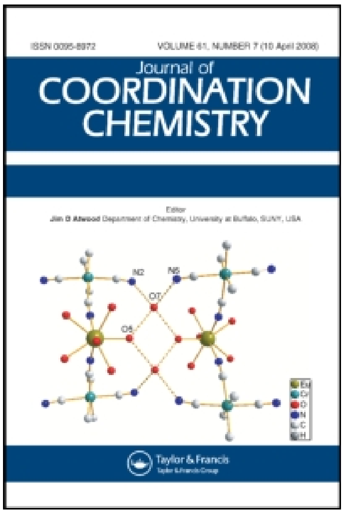

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ESR SPECTRA OF DIMERIC COPPER(II) CARBOXYLATO COMPLEXES WITH THE BIOLOGICALLY IMPORTANT LIGAND NICOTINAMIDE

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NOTE

ESR SPECTRA OF DIMERIC COPPER(II) CARBOXYLATO COMPLEXES WITH THE BIOLOGICALLY IMPORTANT LIGAND NICOTINAMIDE

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ESR studies of dimeric copper(II) carboxylate complexes of the type $Cu(CH_3COO)_2L.2H_2O$ and $Cu(CH_3CH_2COO)_2L$ with the biologically important ligand L = nicotinamide are reported. The spectra show features corresponding to dimeric copper(II) complexes, and which at low temperatures are well resolved. Seven lines from hyperfine splitting A_{z2} (high-field side) and six of seven lines from hyperfine splitting A_{z1} (low-field side) are found. The observed resonances are used to calculate the zero-field splitting parameters D and E. Spin-Hamiltonian and zero-field splitting parameters are used to estimate the antiferromagnetic interaction; for $Cu(CH_3CH_2COO)_2L.2H_2O$ $-2J = 320\ cm^{-1}$ and for $Cu(CH_3CH_2COO)_2L$ $-2J = 332\ cm^{-1}$.

KEY WORDS: Copper(II), dimers, ESR, nicotinamide, antiferromagnetic interactions.

INTRODUCTION

Carboxylatocopper(II) complexes are of interest from both a chemical and biological point of view. Different possible coordinations of the carboxyl group to the central atom lead to the existence of compounds with distinct crystal structures. When the carboxyl group acts as a monodentate ligand, complexes having variously distorted octahedral coordination around the central atom are formed,[1–4] whereas when the carboxyl group is coordinated through both oxygen atoms, complexes of binuclear[5–7] or polymeric structure are formed.[8,9]

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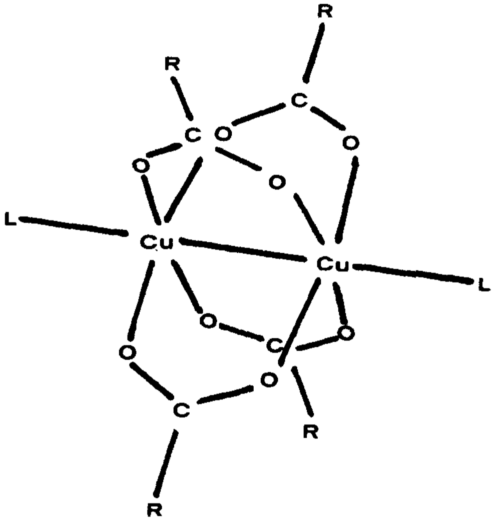

Figure 1 A schematic view of the molecular structure of the binuclear copper(II) carboxylates.

Biologically, copper is the third most abundant transition metal element and plays an important role in the active site of certain electron- and oxygen-carrying metalloproteins.[10] Nicotinamide is an important part of the coenzyme nicotinamide adenine dinucleotide (NAD). NAD dehydrogenates alcohols to aldehydes or ketones or reduces carbonyl groups to alcohols. Nitocinic acid (niacin) is a B vitamin needed for coenzyme synthesis. Its deficiency causes the chronic pellagra. These characteristics suggest that ESR studies[10,11] of copper(II)-nicotinamide complexes may be of interest and therefore we focussed attention on dimeric copper(II) compounds of the general formula $[Cu(RCOO)_2L]_2$ (Figure 1) with L = nicotinamide. In this paper we present a temperature-dependent ESR study of $Cu(CH_3COO)_2nia.2H_2O$ and $Cu(CH_3CH_2COO)_2nia$ (nia = nicotinamide) in the solid state. Spin-Hamiltonian and zero-field splitting parameters are used to estimate antiferromagnetic interactions for both complexes.

EXPERIMENTAL

$Cu(CH_3COO)_2nia.2H_2O$ was prepared by reacting a methanolic solution of $Cu(CH_3COO)_2.2H_2O$ and an methanolic solution of nicotinamide at a mole ratio of 1:1. The solution was filtered after 2 hours and left to crystallize. The green product that precipitated was isolated, washed with methanol and dried at room temperature. $Cu(CH_3CH_2COO)_2nia$ was prepared by reacting a methanolic solution of $Cu(CH_3CH_2COO)_2.2H_2O$ and a methanolic solution of nicotinamide at a mole ratio of 1:1. The solution was filtered and left to crystallize. The green product that precipitated was isolated, washed with cold methanol and dried at room temperature. The crude product was recrystallized from hot methanol to yield green crystals. The compositions of the substances obtained were confirmed by chemical analysis.

ESR spectra were recorded using a Bruker SRC 200D spectrometer operating at the X-band in the temperature range 100–300 K.

RESULTS AND DISCUSSION

ESR spectra of $Cu(CH_3COO)_2nia.2H_2O$ and $Cu(CH_3CH_2COO)_2nia$ in the temperature range 100–295 K are in Figures 2 and 3, respectively. They are typical of the triplet state of dimeric copper(II) compounds and the spin Hamiltonian is given by equation (1),[12]

$$\hat{H} = \beta B.g.\hat{S} + D\left[\hat{S}_z^2 - \frac{1}{3}S(S+1)\right] + E(\hat{S}_x^2 - \hat{S}_y^2) \qquad (1)$$

where D and E are the zero-field splitting parameters, x, y and z are the principal coordinate axes fixed with respect to the Cu-Cu bond and other symbols have their usual meaning.[12]

For powders, it is of course impossible to align the magnetic field along any given direction and the observed spectrum reflects the sum of all possible orientations. It has been shown that sharp discontinuities in the curve occur at values of the resonance field (see ref.[13]). Consequently we may calculate g_x, g_y, g_z, D and E.

It is also known from the angular dependence of field position and transition probability for dimers, that for $D < 1/2\,h\nu$, the contribution to the spectra from forbidden transitions will not be negligible,[14,15] whereas for $D > 1/2\,h\nu$, B_{x1}, B_{y1} and $\Delta M = \pm 2$ are no longer observed and the powder spectrum will consist of only four lines (if, in addition, $E = 0$, the spectrum will consist of only three lines). The ESR spectra of $Cu(CH_3COO)_2nia.2H_2O$ above 200 K exhibit three features at 172 G, 4796 G and 5957 G (room temperature; Table 1), whereas the ESR spectra of $Cu(CH_3CH_2COO)_2nia$ show three features above 180 K at 193 G, 4785 G and 5989 G (room temperature; Table 2). The line corresponding to $B_{\perp 2}$ is in the case of $Cu(CH_3COO)_2nia.2H_2O$ split below 200 K (B_{x2} and B_{y2}), showing that E is non-zero, but small. A similar situation is observed in the case of $Cu(CH_3CH_2COO)_2nia$, but the splitting is more significant. This splitting is almost certainly due to the lack of axial symmetry.

The resonance lines (usually observed with relatively high intensity)[7] at about 3200 G are very small, even at lower temperatures. This indicates a very small amount of nondimeric or monomeric copper(II) ions. From Figures 2 and 3 it is clear that additional lines appear. These are undoubtedly due to the hyperfine interaction of the unpaired electrons with the copper nuclei in the dimer unit. The absorption showed very well resolved six of seven line hyperfine splitting A_{z1} (low-field side) and well resolved seven line hyperfine splitting A_{z2} (high-field side) arising from coupling of the electron with two equivalent copper nuclei ($I = 3/2$).

As previously mentioned, dimeric copper(II) carboxylate complexes show strong antiferromagnetic interaction.[11,16,17] The spin Hamiltonian parameter D involves the sum of terms arising from the exchange intraction and the dipole-dipole interaction, and is given by equation (2).

$$D = -\frac{J}{8}\left[\frac{1}{4}(g_{\parallel} - 2)^2 - (g_{\perp} - 2)^2\right] - \left[g_{\parallel}^2 - \frac{1}{2}g_{\perp}^2\right]\beta/r^3 \qquad (2)$$

Figure 2 ESR spectra $Cu(CH_3COO)_2nia.2H_2O$ at a—293 K, b—150 K, c—100 K.

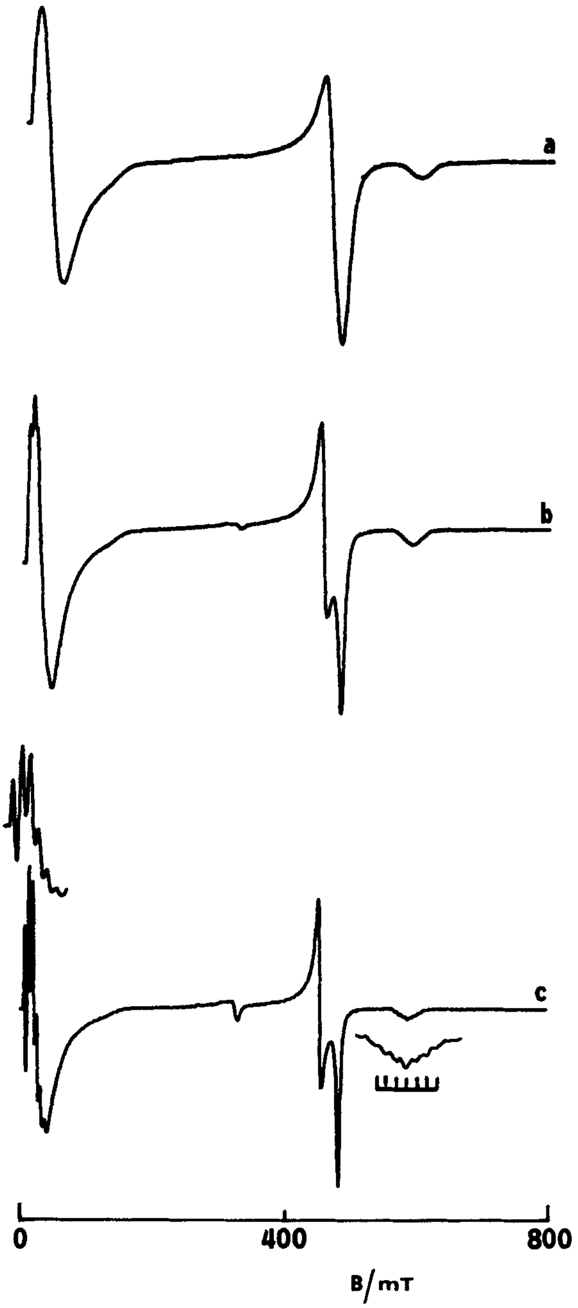

Figure 3 ESR spectra of Cu(CH_3CH_2COO)$_2$nia at a—293 K, b—150 K, c—100 K.

Table 1 Observed ESR data for $Cu(CH_3COO)_2nia.2H_2O$*

T**	B_{z1}	B_{x2} $B_\perp$	B_{y2}	B_{z2} $B_\parallel$	A_{z1}	A_{z2}	g_x g_{xy}	g_y	g_z $g_\parallel$	$\|D\|$	$\|E\|$	$-J$
K	Gauss									cm^{-1}		
297	172	4796		5957			2.006		2.318	0.332		160
150	172	4538	4796	5914	64	64	2.065	2.058	2.335	0.332	0.007	168
100	172	4538	4796	5914	64	64	2.065	2.058	2.335	0.332	0.007	168

*Mononuclear impurities: $g_{iso} = 2.092$ (297, 150, 100 K). **Temperature.

Table 2 Observed ESR data for $Cu(CH_3CH_2COO)_2nia$*

T**	B_{z1}	B_{x2} $B_\perp$	B_{y2}	B_{z2} $B_\parallel$	A_{z1}	A_{z2}	g_x g_{xy}	g_y	g_z $g_\parallel$	$\|D\|$	$\|E\|$	$-J$
K	Gauss									cm^{-1}		
297	193	4785		5989			2.015		2.315	0,334		166
150	193	4516	4828	5914	53		2.068	2.060	2.345	0.334	0.008	161
100	193	4516	4828	5914	53	64	2.068	2.060	2.345	0.334	0.008	161

*Mononuclear impurities: $g_{iso} = 2.092$ (297, 150, 100 K). **Temperature.

The zero-field splitting parameter D, was determined experimentally (Tables 1 and 2) and was assumed to be positive. X-Ray analysis has shown that the Cu-Cu distance in $Cu(CH_3COO)_2nia.2H_2O$ is 2.644Å[18] and in $Cu(CH_3CH_2COO)_2nia$ is 2.635Å.[19]

Exchange parameters for both complexes calculated from (2) are summarized in Tables 1 and 2. The $-2J$ values are 320 cm^{-1} ($Cu(CH_3COO)_2nia.2H_2O$, room temperature) and 332 cm^{-1} ($Cu(CH_3CH_2COO)_2nia$, room temperature), respectively. Thus we may assume that nicotinamide is not very strong electron donor.

ESR measurements of single crystals are in progress using the general method of Byrn and Strouse.[20,21]

Acknowledgements

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