

This article was downloaded by:

On: 23 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



## Journal of Coordination Chemistry

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713455674>

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

Marián Valko<sup>a</sup>; Rodney F. Bilton<sup>a</sup>; Harry Morris<sup>a</sup>; Milan Melnik<sup>b</sup>

<sup>a</sup> School of Physical and Chemical Sciences, and School of Biomolecular Sciences, Liverpool J.M. University, Liverpool, U.K. <sup>b</sup> Department of Chemistry, York University, Ontario, Canada

**To cite this Article** Valko, Marián , Bilton, Rodney F. , Morris, Harry and Melnik, Milan(1993) 'ESR SPECTRA OF DIMERIC COPPER(II) CARBOXYLATO COMPLEXES WITH THE BIOLOGICALLY IMPORTANT LIGAND NICOTINAMIDE', *Journal of Coordination Chemistry*, 29: 4, 257 – 263

**To link to this Article:** DOI: 10.1080/00958979308037431

**URL:** <http://dx.doi.org/10.1080/00958979308037431>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

## NOTE

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

MARIÁN VALKO,\* RODNEY F. BILTON, HARRY MORRIS

*School of Physical and Chemical Sciences, and School of Biomolecular Sciences,  
Liverpool J.M. University, Byrom Street, Liverpool L3 3AF, U.K.*

and MILAN MELNIK

*Department of Chemistry, York University, North York, Ontario M37 1P3, Canada*

*(Received September 29 1992)*

ESR studies of dimeric copper(II) carboxylate complexes of the type  $\text{Cu}(\text{CH}_3\text{COO})_2\text{L}\cdot 2\text{H}_2\text{O}$  and  $\text{Cu}(\text{CH}_3\text{CH}_2\text{COO})_2\text{L}$  with the biologically important ligand  $\text{L} = \text{nicotinamide}$  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  $\text{Cu}(\text{CH}_3\text{CH}_2\text{COO})_2\text{L}\cdot 2\text{H}_2\text{O} - 2J = 320 \text{ cm}^{-1}$  and for  $\text{Cu}(\text{CH}_3\text{CH}_2\text{COO})_2\text{L} - 2J = 332 \text{ cm}^{-1}$ .

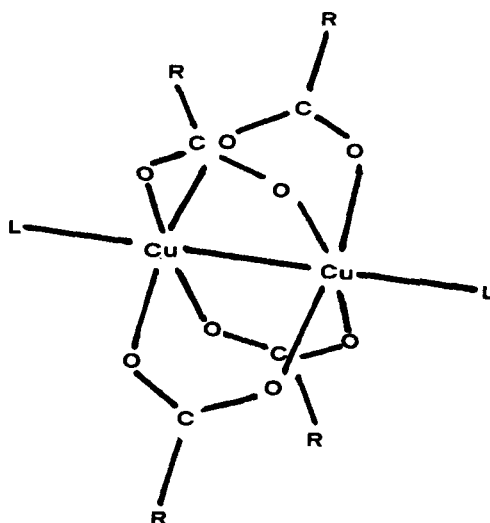
KEY WORDS: Copper(II), dimers, ESR, nicotinamide, antiferromagnetic interactions.

## 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,<sup>1–4</sup> whereas when the carboxyl group is coordinated through both oxygen atoms, complexes of binuclear<sup>5–7</sup> or polymeric structure are formed.<sup>8,9</sup>

---

\* Author for correspondence.



**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.<sup>10</sup> 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. Nicotinic acid (niacin) is a B vitamin needed for coenzyme synthesis. Its deficiency causes the chronic pellagra. These characteristics suggest that ESR studies<sup>10,11</sup> of copper(II)-nicotinamide complexes may be of interest and therefore we focussed attention on dimeric copper(II) compounds of the general formula  $[\text{Cu}(\text{RCOO})_2\text{L}]_2$  (Figure 1) with  $\text{L} = \text{nicotinamide}$ . In this paper we present a temperature-dependent ESR study of  $\text{Cu}(\text{CH}_3\text{COO})_2\text{nia}\cdot 2\text{H}_2\text{O}$  and  $\text{Cu}(\text{CH}_3\text{CH}_2\text{COO})_2\text{nia}$  ( $\text{nia} = \text{nicotinamide}$ ) in the solid state. Spin-Hamiltonian and zero-field splitting parameters are used to estimate antiferromagnetic interactions for both complexes.

## EXPERIMENTAL

$\text{Cu}(\text{CH}_3\text{COO})_2\text{nia}\cdot 2\text{H}_2\text{O}$  was prepared by reacting a methanolic solution of  $\text{Cu}(\text{CH}_3\text{COO})_2\cdot 2\text{H}_2\text{O}$  and a 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.  $\text{Cu}(\text{CH}_3\text{CH}_2\text{COO})_2\text{nia}$  was prepared by reacting a methanolic solution of  $\text{Cu}(\text{CH}_3\text{CH}_2\text{COO})_2\cdot 2\text{H}_2\text{O}$  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  $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$  and  $\text{Cu}(\text{CH}_3\text{CH}_2\text{COO})_2 \cdot \text{nia}$  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),<sup>12</sup>

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

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.<sup>12</sup>

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.<sup>13</sup>). 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,<sup>14,15</sup> 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  $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$  above 200 K exhibit three features at 172 G, 4796 G and 5957 G (room temperature; Table 1), whereas the ESR spectra of  $\text{Cu}(\text{CH}_3\text{CH}_2\text{COO})_2 \cdot \text{nia}$  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  $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$  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  $\text{Cu}(\text{CH}_3\text{CH}_2\text{COO})_2 \cdot \text{nia}$ , 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)<sup>7</sup> 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.<sup>11,16,17</sup> The spin Hamiltonian parameter D involves the sum of terms arising from the exchange interaction and the dipole-dipole interaction, and is given by equation (2).

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



Figure 2 ESR spectra  $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{nia} \cdot 2\text{H}_2\text{O}$  at a—293 K, b—150 K, c—100 K.

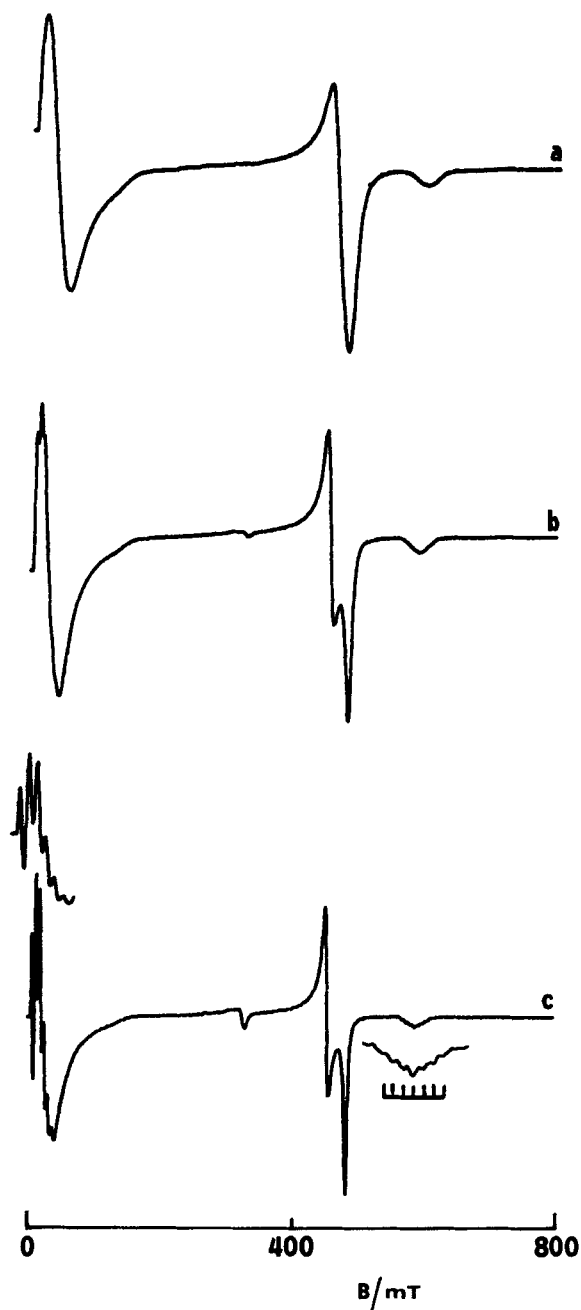


Figure 3 ESR spectra of  $\text{Cu}(\text{CH}_3\text{CH}_2\text{COO})_2.nia$  at a—293 K, b—150 K, c—100 K.

**Table 1** Observed ESR data for  $\text{Cu}(\text{CH}_3\text{COO})_2\text{nia}\cdot 2\text{H}_2\text{O}^*$ 

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									$\text{cm}^{-1}$		
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  $\text{Cu}(\text{CH}_3\text{CH}_2\text{COO})_2\text{nia}^*$ 

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									$\text{cm}^{-1}$		
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  $\text{Cu}(\text{CH}_3\text{COO})_2\text{nia}\cdot 2\text{H}_2\text{O}$  is  $2.644\text{\AA}^{18}$  and in  $\text{Cu}(\text{CH}_3\text{CH}_2\text{COO})_2\text{nia}$  is  $2.635\text{\AA}^{19}$ .

Exchange parameters for both complexes calculated from (2) are summarized in Tables 1 and 2. The  $-2J$  values are  $320\text{ cm}^{-1}$  ( $\text{Cu}(\text{CH}_3\text{COO})_2\text{nia}\cdot 2\text{H}_2\text{O}$ , room temperature) and  $332\text{ cm}^{-1}$  ( $\text{Cu}(\text{CH}_3\text{CH}_2\text{COO})_2\text{nia}$ , 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.<sup>20,21</sup>

### Acknowledgements

This note is based in part on work supported by the Pecess Foundation (U.K.). One of us (M.V.) is indebted to Dr. Rod Bilton and Dr. Harry Morris for their hospitality.

### References

1. M. Valko, M. Melnik, P. Pelikan, F. Valach and M. Mazur, *Chem. Phys. Lett.*, **174**, 591 (1990).
2. M. Valko, P. Pelikan, S. Biskupic and M. Mazur, *Chem. Papers*, **44**, 805 (1990).
3. M. Melnik, L. Macaskova and J. Mrozinsky, *Polyhedron*, **7**, 1745 (1988).
4. M. Melnik, M. Kabesova, F. Valach and J. Gazo, *Finn. Chem. Lett.*, **8** (1974).
5. M. Melnik, *Coord. Chem. Rev.*, **42**, 259 (1982).
6. L. Manojlovi-Muir, *J. Chem. Soc. Chem. Commun.*, 1057 (1967).
7. M. Valko, M. Melnik, H. Morris, R.F. Bilton and P. Pelikan, *Chem. Phys. Lett.*, **183**, 372 (1991).
8. R. Kiriya, H. Ibamoto and K. Matsuo, *Acta Cryst.*, **7**, 482 (1954).
9. H. Koisumi, K. Osaki and T. Watanabe, *J. Phys. Soc. Jpn.*, **18**, 117 (1963).

10. F.A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry*, (John Wiley and Sons, New York, 1980).
11. Y. Saito, *Int. Rev. Phys. Chem.*, **8**, 235 (1989).
12. A. Abragam and B. Bleaney, *Electron Paramagnetic Resonance of Transition Ions*, (Clarendon Press, Oxford, 1970).
13. E. Wasserman, L.C. Snyder and W.A. Yager, *J. Chem. Phys.*, **41**, 1763 (1964).
14. T.D. Smith and J.R. Pilbrow, *Coord. Chem. Rev.*, **13**, 173 (1974).
15. S.S. Eaton, K.M. More, B.M. Sawant and G.R. Eaton, *J. Am. Chem. Soc.*, **105**, 6560 (1983).
16. M. Melnik, Z. Sabova, J. Mrozinsky and A. Szymaszek, *J. Mol. Struct.*, **240**, 285 (1990).
17. M. Valko, M. Melnik, R.F. Bilton and H. Morris, unpublished results.
18. G.V. Cincadze, R.A. Kiguradze, A.N. Snulin and C.S. Mamedov, *Zh. Strukt. Khim.*, **25**, 82 (1984).
19. K. Smolander, M. Macko, M. Valko and M. Melnik, *Acta Chem. Scand.*, **46**, 29 (1992).
20. M.P. Byrn and C.E. Strouse, *J. Magn. Reson.*, **53**, 32 (1983).
21. D. Innis, S.M. Soltis and C.E. Strouse, *J. Am. Chem. Soc.*, **110**, 5644 (1988).