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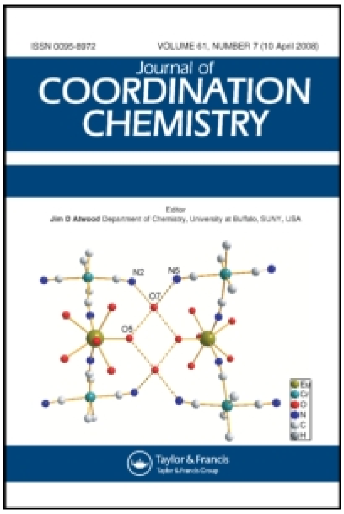

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SPECTRAL AND MAGNETIC PROPERTIES OF COPPER(II) NIFLUMATE COMPOUNDS WITH HETEROCYCLIC N-DONOR LIGANDS

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Copper(II) niflumates (nif) with heterocyclic N-donor ligands (L) have been synthesized and characterized by elemental analysis, IR, electronic and EPR spectroscopy. A dimeric structure is proposed for Cu(nif)$_2$nic, similar to that of Cu(CH$_3$COO)$_2\cdot$H$_2$O. For Cu(nif)$_2$L$_2$, (where L = nia, Et$_2$nia or caf) a *pseudo*-octahedral environment about the copper(II) atom is proposed, in which both nif and L groups participate. For Cu(nif)$_2$(2,6-dmpy)$_2$ an earlier x-ray structure indicated a non-centrosymmetric structure with uncoordinated niflumate anions. In the present work substantial differences between this complex and the other three complexes are observed.

Keywords: Copper(II); niflumate; EPR; spectra

INTRODUCTION

The interaction of copper(II) atoms with drugs administered for therapeutic reasons is a matter of considerable interest. Niflumic acid is part of an important group of analgesics which are believed to act through inhibition of prostaglandin biosynthesis in a manner similar to that of other anti-inflammatory agents.[1] It is known that some drugs act *via* chelation[2] or *via* the inhibition of metalloenzymes.[3] On the basis of spectral and magnetic properties of copper(II) niflumate, a polymeric structure with tetragonal bipyramidal geometry around the copper(II) atom was proposed.[4]

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In order to better understand some aspects of metal-ion drug interactions, we have investigated the complexation of copper(II) niflumate with nicotinamide (nia), N,N-diethylnicotinamide (Et_2nia), 2,6-dimethanol pyridine (2,6-dmpy), caffeine (caf) and nicotine (nic).

EXPERIMENTAL

Cu(nif)$_2$ was prepared as described by Melnik *et al.*[4] Cu(nif)$_2$nic was prepared by treating nic with Cu(nif)$_2$ in an equimolar ratio in hot methanol. The resulting solution was filtered and the filtrate left to stand at room temperature, allowing fine green crystals to precipitate out. These were filtered and washed with cold methanol and dried at room temperature.

Compounds of composition Cu(nif)$_2$L$_2$ were prepared by adding excess L to a methanol solution of copper(II) niflumate. The fine microcrystals produced on standing were separated, washed and dried as described above.

Elemental analyses for the copper(II) niflumate derivatives are given in Table I. Copper was determined by EDTA titration. The analyses of C, H and N were carried out using a Carlo Erba 1108 microanalyser.

Electronic spectra in the region 10–28 kK were measured with a Perkin-Elmer 450 spectrophotometer. IR spectra in the region 400–3600 cm^{-1} were measured with a Beckmann IR 10 spectrometer. In both cases, nujol suspension techniques were used. The EPR spectra of powdered samples were obtained using a Varian E-4 spectrophotometer at room temperature.

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RESULTS AND DISCUSSION

The IR spectrum of Cu(nif)$_2$nic shows the carboxylate stretching frequencies $\nu_{as}(COO^-)$ at 1685 cm^{-1} and $\nu_s(COO^-)$ at 1460 cm^{-1}. The positions of

TABLE I Elemental analysis of bis(niflumato)copper(II) compounds

Compound[a]	*Calculated (Found) %*			
	Cu	*C*	*H*	*N*
Cu(nif)$_2$(nic)$_2$	8.1 (7.9)	54.8 (55.0)	3.8 (4.0)	10.7 (10.8)
Cu(nif)$_2$(nia)$_2$	7.3 (7.5)	52.9 (52.5)	3.24 (3.1)	12.9 (12.8)
Cu(nif)$_2$(Et$_2$nia)$_2$	6.5 (6.5)	56.3 (56.4)	4.5 (4.5)	11.4 (11.4)
Cu(nif)$_2$(2,6-dmpy)$_2$	7.0 (7.1)	53.1 (53.3)	3.8 (3.65)	9.3 (9.3)
Cu(nif)$_2$(caf)$_2$	6.3 (6.5)	49.7 (48.9)	3.6 (3.55)	16.6 (16.5)

[a] nif = niflumate; nic = nicotine; nia = nicotinamide; Et_2nia = N,N-diethylnicotinamide; 2,6-dmpy = 2,6-dimethanol pyridine; caf = caffeine.

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the bands, as well as the difference in frequency, are characteristic of dimeric copper(II) carboxylate compounds.[5] The stretching vibration of the C=N bond in the pyridine ring appears at $1590\,\mathrm{cm}^{-1}$, and on complexation a shift to higher frequencies is observed.[6] In Cu(nif)$_2$nic this shift to about $1615\,\mathrm{cm}^{-1}$ may suggest bond formation by the copper(II) atom to the pyridine ring nitrogen, thereby increasing the dipolar contribution of C=N in the heterocyclic ring.[7]

The electronic spectrum of Cu(nif)$_2$(nic) shows a band at 14.5 kK, which was identified as a *d–d* transition of the copper(II), and a shoulder at 27.0 kK. The shoulder is characteristic of the bridging system with an antiferromagnetic interaction.[8]

The EPR spectrum of Cu(nif)$_2$nic at room temperature contained the typical absorption bands of an axially symmetric dimeric species.[9] The EPR spectrum is shown in Figure 1. The spectrum of the powder at room temperature shows absorptions at both low and high fields (Hz$_1$ and Hz$_2$, respectively) with an asymmetric absorption near 4500 G (H_{T2}). One absorption (H_{T1}) is missing because $|D| > h\nu$ at the X-band frequency used. The spectrum can be interpreted using a spin Hamiltonian for axial symmetry,

$$H = g_{\|}\beta H_z S_z + g_{\perp}(H_x S_x + H_y S_y) + D(S_z^2 + 2/3)$$

where $S = 1$ for the thermally accessible triplet state and the other symbols have their usual meaning. The value obtained for the spin Hamiltonian parameters are: $g_{\perp} = 2.066$; $g_{\|} = 2.360$; $g_{\mathrm{av}} = 2.164$ and $|D| = 0.360\,\mathrm{cm}^{-1}$. The $|D|$ value of about $0.3\,\mathrm{cm}^{-1}$ is large compared to the magnetic quantities (approximately 3.00 G), but small compared to vibrational frequencies. The values are comparable to those found in dimeric copper carboxylates.[10] On the basis of spectral properties it is proposed that the molecule is a dimeric

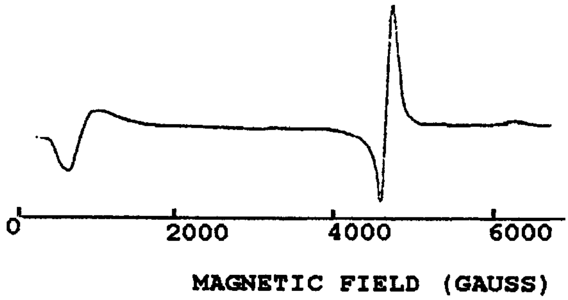

FIGURE 1 EPR spectrum of Cu(nif)$_2$nic.

unit, [Cu(nif)$_2$nic]$_2$, with square-pyramidal geometry at each copper center. The two copper atoms are bridged by four carboxylate moieties of the niflumate ligands, with apical sites occupied by nic.

Spectroscopic data for the Cu(nif)$_2$L$_2$ complexes are given in Table II. The IR spectra of the Cu(nif)$_2$L$_2$ compounds are complex. Each compound showed the carboxylate stretching frequencies ν_{as} and ν_s as indicated in Table II together with the stretching vibrations of the C=N bond. Except for Cu(nif)$_2$(2,6-dmpy)$_2$ the carboxylate stretching frequencies are below 1700 cm^{-1}, indicating coordination of the niflumate group to the copper(II) atom. In a previous x-ray analysis of the (2,6-dmpy) derivative[11] it was observed that the carboxylate groups are not coordinated to copper(II), which is reconfirmed by the present IR data. This complex is non-centrosymmetric with two 2,6-dmpy molecules symmetrically coordinated to the copper(II) atom in a tridentate chelating manner, giving an "all-*trans*" elongated octahedral arrangement with no niflumate anions in the primary coordination sphere. Due to Jahn–Teller distortion, considerable differences were found between the two 2,6-dmpy ligands. For one of them the Cu–N

TABLE II Spectral data for Cu(nif)$_2$L$_2$

L	*IR* (cm^{-1}) ν(C=N) ν_{as}(COO$^-$) ν_s(COO$^-$)	*Electronic spectra*		*EPR*		
		$\nu_{(max)}$ kK		$g_\perp$	$g_\parallel$	g_{av}
nia	1608 (m) 1695 (s) 1635 (s) 1462 (m) 1377 (m)	14.8	23.5 sh	2.080	2.307	2.155
Et$_2$nia	1610 (m) 1635 (s) 1495 (s) 1460 (s) 1421 (s)	15.0 sh 18.3	23.5 sh	2.075	2.305	2.152
2,6-dmpy	1598 (m) 1520 (s) 1773 (s) 1719 (s) 1460 (w) 1377 (m)	13.3		g_1 2.078 g_2 2.120 g_3 2.285		2.161
caf	1605 (m) 1695 (s) 1652 (s) 1420 (m) 1400 (m)	12.5 sh 15.4		2.072	2.265	2.136

s = strong; m = medium; sh = shoulder.

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bond distance is 191.5 (5), while in the other the value is 189.1 (5) pm. Similarly the Cu–O values are, respectively, 221.0 (4) and 224.4 (4) pm for the first, 207.4 (4) and 210.1 (4) pm for the second.[11]

For all four complexes the electronic spectra indicate variations in the *d–d* bands of the copper(II), with no 27 kK component associated with the antiferromagnetic bridging interaction.

The EPR spectra of the Cu(nif)$_2$L$_2$ derivatives in powder form showed an axial-type spectrum for L = nia, Et$_2$nia or caf. For L = 2,6-dmpy, as expected from the x-ray structure,[11] the EPR spectrum differs from the others. It is a *pseudo*-rhombic type, with *g* values given in Table II. These values are typical for compounds with tetragonal distortion around the Cu(II) atom.

In summary, on the basis of the spectral data, a dimeric structure is proposed for Cu(nif)$_2$nic similar to that of $Cu(CH_3COO)_2 \cdot H_2O$.[12] In [Cu(2,6-dmpy)$_2$](nif)$_2$ the six coordination sites about the copper(II) atom are occupied by the two tridentate 2,6-dmpy molecules with no niflumate ligands in the primary coordination sphere. For Cu(nif)$_2$L$_2$ (L = nia, Et$_2$nia or caf) the spectroscopic data suggest a *pseudo*-octahedral environment about the copper(II) atom, with both the nif and L ligands coordinated.

Acknowledgments

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