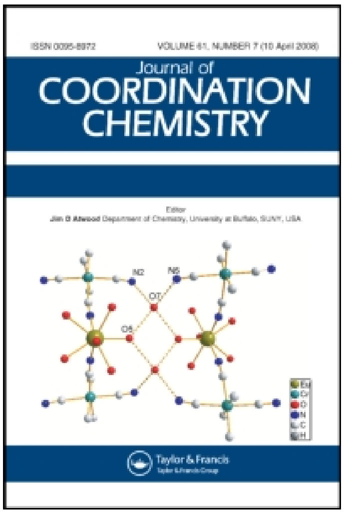

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SPECTRAL AND MAGNETIC STUDY OF COPPER(II) MEFANAMATES: CRYSTAL AND MOLECULAR STRUCTURE OF BIS(MEFANAMATO)DI(N,N-DIETHYLNICOTINAMIDE)DI(AQUA)COPPER(II)

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The synthesis and characterization of Cu(II) mefanamate (mef) compounds of composition $Cu(mef)_2L$ (L = water, caffeine, or methyl-3-pyridylcarbamate) and $Cu(mef)_2L_2$ (L = 3-pyridylcarbinol, nicotinamide, N,N-diethylnicotinamide, 2,6-dimethanol pyridine or nicotine) is reported. Characterizations of the compounds were based on elemental analyses, electronic, infrared and EPR spectra and magnetic susceptibility measurements over a temperature range (80-290 K). The spectral and magnetic properties of $Cu(mef)_2L$ indicate the presence of Cu(II) dimers structurally similar to that of Cu(II) acetate monohydrate. All the $Cu(mef)_2L_2$ compounds possess octahedral stereochemistry about Cu(II) with differing tetragonal distortion.

An X-ray analysis of $Cu(mef)_2(Et_2nia)_2(H_2O)_2$ was carried out, and it featured tetragonal bipyramidal geometry around the Cu(II) atom. The tetragonal plane is created by mefanamate anions bonded to the Cu(II) atom *via* the unidentate carboxylate oxygen atoms [Cu-O(2) = 1.936(3)Å] and the pyridine ring nitrogen atoms of the neutral ligand N,N-diethylnicotinamide [Cu-N(1) = 2.027(3)Å] in *trans*-positions. Axial water molecules [Cu-O(4) = 2.557(3)Å] complete the coordination sphere.

Keywords: copper(II); mefanomate; caffeine; dimers; crystal structure

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INTRODUCTION

The interaction of the Cu(II) atom, which plays a vital role in a number of quite different biological processes, with therapeutically administered drugs is a subject of considerable interest. Fenamates (mefanamic, niflumic and flufenamic acids) constitute an important group of analgesics which are believed to act through inhibition of prostaglandin biosynthesis, like other anti-inflammatory analgesics.[1]

While some Cu(II) niflumates[2] as well as Cu(II) flufenamates[3],[4] were studied, Cu(II) mefanamates were not. In order to better understand other aspects of metal ion—drug interactions, we studied the complexation of mefanamate acid (mefH) [2-{(2,3-dimethylphenyl)-amino} benzoic acid] with Cu(II) as well as its adduct of methyl-3-pyridylcarbamate (mpc), caffeine (caf), 3-pyridylcarbinol—ronicol (ron), nicotinamide (na), N,N—diethylnicotinamide (Et_2na), 2,6-dimethanolpyridine (pyme) and nicotine (nic). The compounds of general formula $Cu(mef)_2L$ (L = H_2O, caf or mpc) and $Cu(mef)_2L_2$ (L = ron, na, Et_2na, pyme or nic) were prepared and studied by spectral and magnetic methods. The derivative $Cu(mef)_2(Et_2nia)_2(H_2O)_2$ was also characterized by X-ray crystallography.

EXPERIMENTAL

Preparation

A sodium mefanamate solution was prepared from an aqueous solution of NaOH (0.01 mol) by addition of niflumic acid (0.01 mol), following by boiling. The partially evaporated solution was filtered hot and the filtrate placed in a refrigerator. White sodium mefanamate which slowly precipitated, was isolated and dried at room temperature. The Cu(II) mefanamate monohydrate was prepared by reaction of a solution of sodium mefanamate (0.01 mol, pH adjusted to 4.5-5.0 using the free acid) with an aqueous solution of Cu(II) sulphate in the mol ratio 2:1. The solution was boiled, filtered, and left to crystallize in a refrigerator. The pale green product that precipitated was washed with cold water and dried at room temperature.

The Cu(II) mefanamates of composition $Cu(mef)_2L$ were prepared by treating L with $Cu(mef)_2(H_2O)$ in an equimolar ratio in hot methanol/acetone. The resulting solutions were filtered and the filtrate left to stand at room temperature, allowing fine green microcrystals to precipitate. These were filtered off, washed with cold methanol and dried in a vacuum desiccator over P_2O_5. The compounds are stable in air at ambient temperature.

TABLE I Elemental analyses of bis(mefanamato)copper(II) compounds

Compound[a]	*Calculated (Found) (%)*		
	C	*H*	*N*
$Cu(mef)_2 \cdot H_2O$	61.4	5.37	4.98
	(64.3)	(5.5)	(4.78)
$Cu(mef)_2(mpc)$	63.82	5.21	8.05
	(64.0)	(5.0)	(8.06)
$Cu(mef)_2(cof)$	61.18	5.18	11.38
	(62.0)	(5.1)	(11.33)
$Cu(mef)_2(ron)_2$	66.18	5.55	7.35
	(65.7)	(5.7)	(7.38)
$Cu(mef)_2(na)_2$	63.98	5.11	10.66
	(63.1)	(5.15)	(10.7)
$Cu(mef)_2(Et_2nia)_2(H_2O)_2$	64.2	6.45	8.98
	(63.9)	(6.5)	(8.91)
$Cu(mef)_2(pyme)_2$	64.26	5.63	6.81
	(64.3)	(5.5)	(6.65)
$Cu(mef)_2(nic)_2$	69.14	6.5	9.68
	(69.0)	(6.6)	(9.7)

[a] mef = mefanamate; mpc = methyl-3-pyridylcarbamate; cof = coffeine; ron = 3-pyridylcarbinol (ronicol); na = nicotinamide; Et_2na = N,N-diethylnicotinamide; pyme = 2,6-dimethanolpyridine; nic = nicotine.

Compounds of composition $Cu(mef)_2L_2$ were prepared by adding L in excess to a methanol/acetone solution of $Cu(mef)_2H_2O$. The fine microcrystals produced on standing were prepared, washed and dried as described above.

Crystals of $Cu(mef)_2(Et_2nia)_2(H_2O)_2$ suitable for structural determination were obtained by recrystallizing the crude product from acetone.

Elemental analyses for the Cu(II) mefanamate derivatives are given in Table I.

Spectroscopic Studies

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 an IR 10 spectrometer. In both cases, Nujol suspension techniques were used. The EPR spectra of powder samples were obtained using a Varian Model E4 Spectrometer at room temperature. Spectral data are given in Table II and Table IV.

Magnetic Studies

Magnetic susceptibilities of powdered samples were determined at different temperatures on a Gouy Balance (Newport Instrument Ltd.) standardized against

TABLE II Spectral data for $Cu(mef)_2L$

L	*IR* $\nu_{(C=N)}$ $\nu_{as}(COO^-)$ $\nu_s(COO^-)$ (cm^{-1})	*Electronic spectra* ν_{max}, kK Band I	Band II	*EPR* $g_\perp$ $\langle g \rangle$	$g_\parallel$ $\lvert D \rvert$, cm^{-1}
H_2O	— 1625s 1410m	14.8	27.5sh	2.084 2.188	2.396 0.325
cof	1605s 1622s 1390s	14.3	28.0sh	2.080 2.178	2.376 0.348
mpc	1635s 1620s 1385m	13.6	27.7sh	2.075 2.172	2.365 0.366

s = strong; m = medium; sh = shoulder

TABLE III Magnetic data[a] for $Cu(mef)_2L$

	$\Delta \times 10^6$ $(cm^3 \cdot mol^{-1})^b$	$\chi_M^{corr} \times 10^6$ $(cm^3 \cdot mol^{-1})^c$	μ_{eff} (B.M.)	$-2J$ (cm^{-1})
H_2O	−301	900	1.46	290
mpc	−355.5	850	1.42	310
cof	−377	890	1.45	350

[a] There are more than 12 data points between the two experimental temperature limits (80-293 K) [b] Diamagnetic correction [c] Data at 293 K

mercury tetrathiocyanatocobaltate(II).[5] The molar susceptibilities were corrected for diamagnetism using Pascal's constants.[6] The effective magnetic moments were calculated using the following expression1

$$\mu_{eff} = 2.83(\chi_M{}^{corr} \cdot T)^{0.5}$$

Magnetic data are given in Table III and Table V.

Structure Determination

Data collection and cell refinement were carried out using Kuma (1991) KM4 diffractometer software.[7] Intensity data were corrected for Lorenz and polarization factors. The structure was solved by the heavy atom method with SHELX86,[8] and subsequent Fourier synthesis using SHELXL93.[9] Anisotropic thermal parameters were refined for all nonhydrogen atoms. Geometrical analysis was performed using SHELXL93.[9] The structures were drawn using

TABLE IV Spectral data for $Cu(mef)_2L_2$

L	*IR* $\nu_{(C=N)}$ $\nu_{as}(COO^-)$ $\nu_s(COO^-)$ (cm^{-1})	*Electronic spectra* ν_{max}, kK Band I	Band II	EPR $g_\perp$	$g_\parallel$	$\langle g \rangle$
ron	1604m 1613s 1380m	13.5	22.5sh	2.07	2.34	2.16
na	1602s 1615s 1375m	15.4	23sh	2.06	2.31	2.15
Et_2na	1620m 1695s 1580m 1414s	14.7	23sh	2.055	2.32	2.14
pyme	1609s 1677s 1647s 1464m	13.2	23.5sh			2.145
nic	1612m 1680s 1565m 1415s	16.5b	23sh	2.06	2.30	2.14

TABLE V Magnetic data[a] for $Cu(mef)_2L_2$

	magnetic data[a] $\Delta \times 10^6$ $(cm^3 \cdot mol^{-1})$[b]	$\chi_M^{corr} \times 10^6$ $(cm^3 \cdot mol^{-1})$[c]	μ_{eff} (B.M.)[c]	C $(cm^3 \cdot mol^{-1})$	θ (K)
ron	−421.5	1530	1.91	0.470	−10.5
na	−424	1400	1.85	0.435	−10.0
Et_2na	−499.8	1490	1.87	0.507	−12.0
pyme	−444	1510	1.90	0.450	−6.2
nic	−512	1440	1.87	0.507	−9.5

There are more than 12 data points between the two experimental temperature limits (80-293 K) [b]Diamagnetic correction [c]Data at 293 K

TABLE VI Crystal data and structure refinement for Cu(mef)$_2$ (Et$_2$nia)$_2$ (H$_2$0)$_2$

Identification code	lm
Empirical formula	$C_{50}H_{60}CuN_6O_8$
Formula weight	936.58
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	monoclinic
Space group	$P2_1/n$
Unit cell dimensions	a = 7.946(2) Å α = 90°
	b = 10.423(2) Å β = 95.03(3)°
	c = 28.732(6) Å γ = 90°
Volume	2370.5(9) Å^3
Z	2
Density (calculated)	1.312 Mg/m^3
Absorption coefficient	0.521 mm^{-1}
F(000)	990
Crystal size	0.55 × 0.40 × 0.25 mm
θ range for data collection	1.42 to 25.04°
Index ranges	0\\$h$\\9, 0\\$k$\\12, −34\\$l$\\34
Reflections collected	4521
Independent reflections	4210 (R_{int} = 0.0220)
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	4168/0/295
Goodness-of-fit on F^2	1.014
Final R indices [I > 2 σ I)]	$R1$ = 0.0585, wR2 = 0.1436
R indices (all data)	$R1$ = 0.1106, wR2 = 0.1992
Largest diff. peak and hole	0.517 and −0.426 eÅ^{-3}

ORTEP.[10] The final parameters after refinement are summarized in Table VI. Selected bond distances and angles are in Table VII.

Supplementary material including non-hydrogen and hydrogen atomic coordinates (×10^4), anisotropic displacement parameters for nonhydrogen atoms [Å × 10^3] have been deposited at the Cambridge Crystallographic Data Centre. Observed and calculated structural factors are available on request from M.M..

RESULTS AND DISCUSSION

The IR spectra of the compounds are very complex. The IR spectra of hydrates Cu(mef)$_2$H$_2$O and Cu(mef)$_2$(Et$_2$na)$_2$(H$_2$O)$_2$ show a strong absorption bands at 3328 and 3438 cm^{-1} for the former and at 3300 and 3500 cm^{-1} for the latter. These frequencies correspond to the antisymmetric and symmetric OH stretches and confirm the presence of water in the compounds. These were absent from the spectra of all the other compounds in the study. Each compound showed carboxylate stretching frequencies $\nu_s(COO^-)$ and $\nu_{as}(COO^-)$, and the data are

TABLE VII Selected bond lengths [Å] and angles [°] for $Cu(mef)_2(Et_2nia)_2(H_2O)_2$

Cu(1)-O(2)	1.936(3)	Cu(1)-O(4)	2.557(3)
Cu(1)-N(1)	2.027(3)	O(1)-C(6)	1.228(5)
N(1)-C(1)	1.329(5)	N(1)-C(5)	1.337(5)
N(2)-C(6)	1.323(5)	N(2)-C(7)	1.462(6)
N(2)-C(9)	1.477(5)	O(3)-C(11)	1.244(5)
O(2)-C(11)	1.264(5)	C(17)-N(3)	1.367(6)
N(3)-C(18)	1.394(6)		
O(2)#1-Cu(1)-O(2)	180.0	O(2)#1-Cu(1)-N(1)	88.14(12)
O(2)-Cu(1)-N(1)	91.86(12)	O(2)#1-Cu(1)-N(1)#1	91.86(12)
O(2)-Cu(1)-N(1)#1	88.14(12)	N(1)-Cu(1)-N(1)#1	180.0
C(1)-N(1)-C(5)	118.4(3)	C(1)-N(1)-Cu(1)	120.0(3)
C(5)-N(1)-Cu(1)	121.6(3)	N(1)-C(5)-C(4)	122.8(4)
C(6)-N(2)-C(7)	126.8(4)	C(6)-N(2)-C(9)	118.0(4)
C(7)-N(2)-C(9)	114.8(3)	O(1)-C(6)-N(2)	122.5(4)
O(1)-C(6)-C(4)	116.5(3)	N(2)-C(6)-C(4)	121.0(4)
N(1)-C(1)-C(2)	122.7(4)	N(2)-C(7)-C(8)	111.7(5)
N(2)-C(9)-C(10)	113.7(4)	C(11)-O(2)-Cu(1)	126.3(3)
O(3)-C(11)-O(2)	123.8(4)	O(3)-C(11)-C(12)	120.9(4)
O(2)-C(11)-C(12)	115.3(4)	N(3)-C(17)-C(12)	120.4(4)
N(3)-C(17)-C(16)	121.9(4)	C(17)-N(3)-C(18)	126.3(4)
C(23)-C(18)-N(3)	118.6(5)	N(3)-C(18)-C(19)	119.4(5)

Symmetry transformations used to generate equivalent atoms: #1 −x, −y, −z

given in Table II and Table IV. The positions of bands are characteristic of Cu(II) carboxylate compounds. The stretching vibration of the C = N of the heterocyclic ring appears at around 1590 cm^{-1}, and on complexation a shift to higher frequencies is observed. In the present examples this shift (to about 1610 cm^{-1}, Table II and Table III) may suggest bond formation by the metal atom to the heterocyclic ring nitrogen atom, thereby increasing the dipolar contribution of $C = N^+$ in the heterocyclic ring.[11] The electronic spectra of the compounds of composition $Cu(mef)_2L$ (Table II) each showed a band at about ≈14.0 kK (band I) which was identified as $d - d$ transitions of the Cu(II), and a shoulder at 27.5 kK (band II). The shoulder (band II) is characteristic of a bridging system with an antiferromagnetic interaction.[12] There is correspondence between the two bands, both maxima showing a blue shift of essentially the same magnitude, which indicates differing degrees of distortion about the Cu(II) atom.

The temperature susceptibility data for all $Cu(mef)_2L$ compounds can be described by the equation:

$$\chi_M^{corr} = \frac{g^2N\beta^2}{3\,k\,T}\;\frac{1}{1 + 1/3\,\exp^{-J/kT}} + N\cdot\alpha$$

where $-2J$ is the exchange coupling constant, and the other symbols have the usual meaning. The energy separations ($-2J$) (Table III) between the triplet and singlet states are similar to those of other related Cu(II) carboxylates.[12]

The EPR spectra obtained for the powdered samples of $Cu(mef)_2L$ at room temperature contained the typical absorption bands of an axially symmetric binuclear species.[13] The spectra show absorptions at low and high fields (Hz_1 and Hz_2, respectively), with an asymmetrical absorption near 4500 G (H_T2). One absorption (H_T1) is missing because $|D| > h\nu$ at the X-band frequency used. The spectra can be interpreted using a spin Hamiltonian for axial symmetry

$$H = g_{\|}\beta H_Z S_Z + g_{\perp}(H_X S_X + H_Y S_Y) + D(S^2_Z + 2/3)$$

where $S = 1$ for the thermally accessible triple state and the other symbols have their usual meaning. The values obtained for the spin Hamiltonian parameters are given in Table III. The $|D|$ values of about 0.3 cm^{-1} are large compared to the magnetic quantities (approximately 3.00 G), but are small compared to vibrational frequencies. The values are comparable to those found in binuclear Cu(II) carboxylates.[14] From the foregoing it may be reasonably supposed that $Cu(mef)_2L$ derivatives possess binuclear structures $[Cu_2(mef)_4L_2]$ with a distorted square pyramidal configuration around each Cu(II) atom. Each of these is coordinated to four carboxylate oxygen atoms of the mefanamate anions (in plane) and a donor atom of L (oxygen for H_2O, nitrogen for npc or caf) at the apex.

The solid state electronic spectra of $Cu(mef)_2L_2$ (Table V) exhibit a broad ligand field band with a maximum between 13.2-16.5 kK and a charge-transfer band at about 23.0 kK for all five compounds. This type of $d - d$ spectrum is typical for tetragonal arrangements around Cu(II) and corresponds to electron transfer from the one—electron orbital ground state, $d_{x^2-y^2}$.

Magnetic susceptibility measurements of polycrystalline samples of $Cu(mef)_2L_2$ between 80 and 295 K obey the Curie-Weiss law

$$\chi_M^{corr} = C/(T - \theta)$$

where the Curie constant $C = Ng^2\beta^2S(S + 1)/3k$ for $S = 1/2$. The values of μ_{eff} are slightly dependent on temperature. Since all $Cu(mef)_2L_2$ compounds possess negative Weiss constants (Table V), a weak antiferromagnetic interaction may occur.

EPR spectra of the powdered $Cu(mef)_2L_2$ samples are of two types. The ron, na, Et_2na and nic derivatives are axial, the remaining pyme derivative is isotropic (Table IV). The axial type have $g_{\|} > g_{\perp}$, which points to a structure with a value of the effective spin $S = 1/2$ and a basic state $d_{X^2-Y^2}$. All of the compounds possess octahedral stereochemistry with differing degrees of tetragonal distortion around the Cu(II) atom.

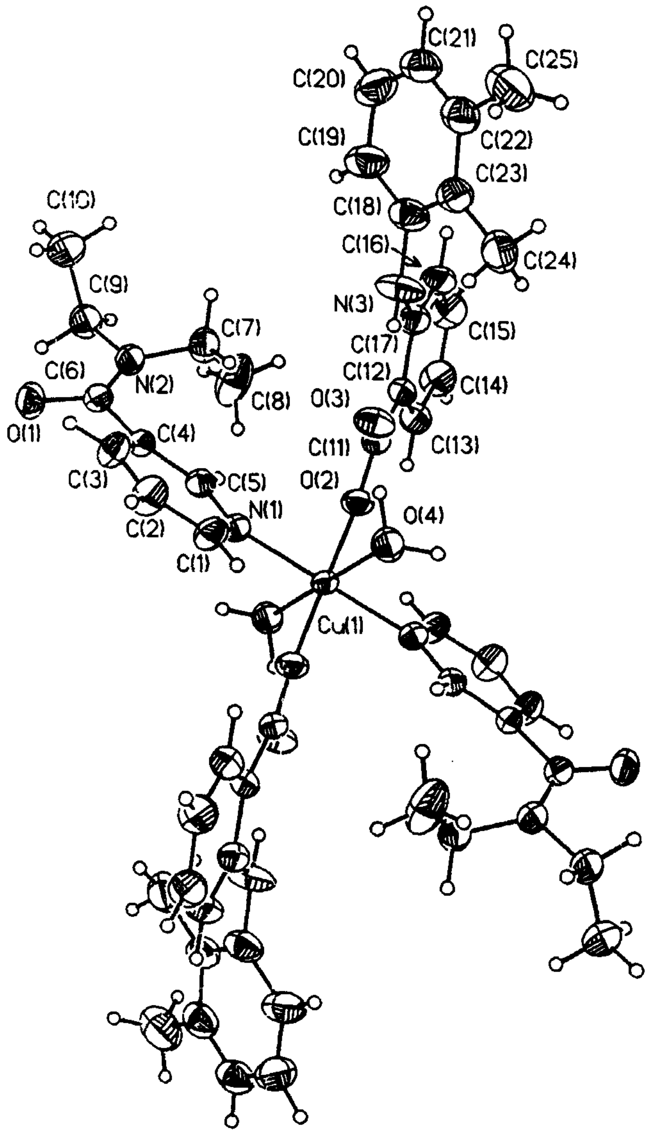

FIGURE 1 An ORTEP plot of $Cu(mef)_2(Et_2nia)_2(H_2O)_2$ with thermal ellipsoids shown at the 50% probability level.

The principal structural features of $Cu(mef)_2(Et_2nia)_2(H_2O)_2$ are illustrated in Figure 1. The coordination environment of the Cu(II) atom is tetragonal bipyramidal. The tetragonal plane is built up by a pair of unidentate mefanamate anions using carboxylate oxygen atoms [Cu-O(2) = 1.936(3)Å] and by a pair of neutral N,N-diethylnicotinamide molecules using pyridine ring nitrogen atoms [Cu-N(1) = 2.027(3)Å] in *trans* positions. The axial positions are occupied by water molecules [Cu-O(4) = 2.557(3)Å]. A similar structure has been found in $Cu(flu)_2(Et_2nia)_2(H_2O)_2$ (flu = flufenamate).[4] The Cu - L bond lengths are 1.961(2)Å (oxygen), 2.001(3)Å (nitrogen) and 2.449(4)Å (H_2O). Both compounds have the same CuO_4N_2 chromophore with a tetragonal bipyramidal geometry, axially elongated as predicted by the Jahn - Teller theorem. The T parameter ($T = R_S/R_L$), indicates the degree of tetragonal distortion about the Cu(II) centers, the value of 0.774 is smaller than that found for $Cu(flu)_2(Et_2nia)_2(H_2O)_2$ (0.809), which indicates a somewhat higher degree of distortion in $Cu(mef)_2(Et_2nia)_2(H_2O)_2$ than in $Cu(flu)_2(Et_2nia)_2(H_2O)_2$.

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