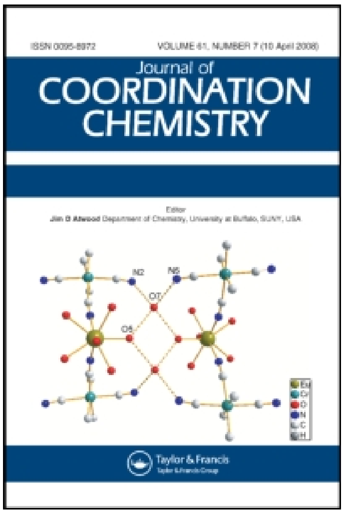

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STRUCTURE, SPECTRAL AND MAGNETIC BEHAVIOURS OF COPPER(NIFLUMATO)$_2$(N,N-DIETHYLNICOTINAMIDE)$_2$

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STRUCTURE, SPECTRAL AND MAGNETIC BEHAVIOURS OF COPPER(NIFLUMATO)$_2$(N,N-DIETHYLNICOTINAMIDE)$_2$

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The green Cu(nif)$_2$(denc)$_2$ (nif = niflumate, denc = diethylnicotinamide) crystallizes in the triclinic system, space group *P*-1 with unit cell parameters: a = 7.984(2)Å, b = 12.270(2)Å, c = 12.904(3)Å, α = 75.23(3)°, β = 71.22(3)°, γ = 72.04(3)° and Z = 2. The final R value for 5325 independent reflections is equal to 0.0455. The structure is centrosymmetric. The Cu(II) atom is *pseudo*-octahedrally *trans*-coordinated by four carboxylic O atoms of two niflumate anions, Cu-O bond distances being 1.955(2) (2×) and 2.643(2)Å (2×), and by two N atoms from two N,N-diethyl- nicotinamide ligands, Cu - N bond distance is 2.007(3)Å (2×).

An EPR spectrum of the complex is of the axial type with $g_{\parallel} > g_{\perp}$ and S = 1/2. Magnetic data of the complex obey the Curie-Weiss law with a small positive value of the Weiss constant (6.6K) indicating a weak ferromagnetic interaction.

Keywords: copper(II); niflumate; crystal structure; magnetism

INTRODUCTION

Solvated Cu(II) carboxylates have been the subject of numerous investigations[1]. Different coordination modes of the carboxyl group lead to formation of mononuclear, binuclear or polynuclear structures. Copper(II) niflumate, together with the 3-pyridylcarbinol adduct, have been characterized by spectroscopic and magnetic methods[2]. It was found that while Cu(nif)$_2$ (nif = niflumate) is polymeric, Cu(nif)$_2$(3-pycar)$_2$ (3-pycar = 3-pyridylcarbinol) is monomeric.

N,N-diethylnicotinamide (denc) as a ligand in Cu(II) carboxylates was studied in the structures $Cu_2(acetate)_4(denc)_2$[3] and $Cu(4\text{-}OHC_6H_4COO)_2.\ (denc)_2$[4]. In both compounds N,N-diethylnicotinamide is a monodentate nitrogen bonded ligand. The crystal structure of $Cu(nif)_2(denc)_2$ as well as spectral and magnetic properties, are presented in this paper.

EXPERIMENTAL

Preparation of $Cu(nif)_2(denc)_2$

Cu(II) niflumate was prepared as described earlier[2]. The N,N - diethylnicotinamide adduct was prepared by adding the ligand (denc, 0.025 mol) to 100 cm^3 of a methanolic suspension of $Cu(nif)_2$ (3.43g-0.01 mol). After heating to boiling, a solution was obtained which was left to cool and stand at room temperature. The green product that precipitated was isolated and washed with cold methanol and dried at room temperature. The crude product was recrystallized from hot methanol to yield green crystals. Anal. Calcd for $Cu(nif)_2(denc)_2$ (%): Cu, 12.96; C, 56.25; H, 4.52; N, 11.40. Found: Cu, 13.0; C, 56; H, 4.48; N, 11.42.

Spectroscopic Studies

An electronic spectrum in the region 10 to 28 kK was measured with a Perkin-Elmer 450 Spectrophotometer using a Nujol suspension. EPR spectra of microcrystalline samples were run on a Varian Model E4 Spectrometer at room temperature and at 77K.

Magnetic Studies

Magnetic susceptibilities of powdered samples were determined at different temperatures on a Gouy Balance (Newport Instrument Ltd.) standardized against tetrathiocyanatocobaltate(II)[5]. The molar susceptibilities were corrected for diamagnetism using Pascal's constants[6]. The effective magnetic moments were calculated using the following expression:

$$\mu_{eff} = 2.83(X_M^{corr}.T)^{1/2}$$

Structure Determination

Data collection and cell refinement were carried out using Kuma (1991) KM4 diffractometer software[7]. Intensity data were corrected for Lorenz and polar-

TABLE 1 Crystal data and structure refinement for [Cu(nif)2(denc)2]

Empirical formula	$C_{48}H_{46}Cu_1F_6N_6O_6$
Formula weight	490.22
Temperature	291(2) K
Wavelength	0.71069 Å
Crystal system	triclinic
Space group	P-1
Unit cell dimensions	$a = 7.984(2)$ Å $\alpha = 75.23(3)^\circ$
	$b = 12.270(2)$ Å $\beta = 71.22(3)^\circ$
	$c = 12.904(3)$ Å $\gamma = 72.04(3)^\circ$
Volume	1121.4(4) Å^3
Z	2
Density (calculated)	1.452 Mg/m^3
Density (measured)	1.46 Mg/m^3
Absorption coefficient	0.569 mm ^{1}
F(000)	507
Crystal size	0.25 × 0.30 × 0.30 mm
θ range for data collection	2.23 to 28.05°
Index ranges	$0\backslash h\backslash 9, -14\backslash k\backslash 16, -15\backslash l\backslash 16$
Reflections collected	5325
Independent reflections	5325 ($R_{int} = 0.0842$)
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	4047/0/331
Goodness-of-fit on F^2	1.096
Final R indices [I > 2r(I)]	$R1 = 0.0455$, wR2 = 0.1269
R indices (all data)	$R1 = 0.0455$, wR2 = 0.1269
Extinction coefficient	0.004(2)
Largest diff. peak and hole	0.739 and −0.547 eÅ^{-3}

ization 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 analyses was performed using SHELXL93[9]. The structures were drawn using ORTEP[10]. The final parameters after refinement are summarized in Table I.

Supplementary material including calculated hydrogen coordinates ($\times 10^4$), anisotropic displacement parameters for nonhydrogen atoms [Å × 10^3] and observed and calculated structure factors are available on request from M.K.

RESULTS AND DISCUSSION

The solid state electronic spectrum of $Cu(nif)_2(denc)_2$ exhibits a broad ligand field band with a maximum at 18.5 kK, a shoulder at about 12.7 kK and a change transfer band at about 23.5 kK. This type of *d-d* spectrum is typical for tetragonal arrangements around Cu(II), coresponding to electron transfers from the one-electron orbital ground state $d_{x^2}-y$.

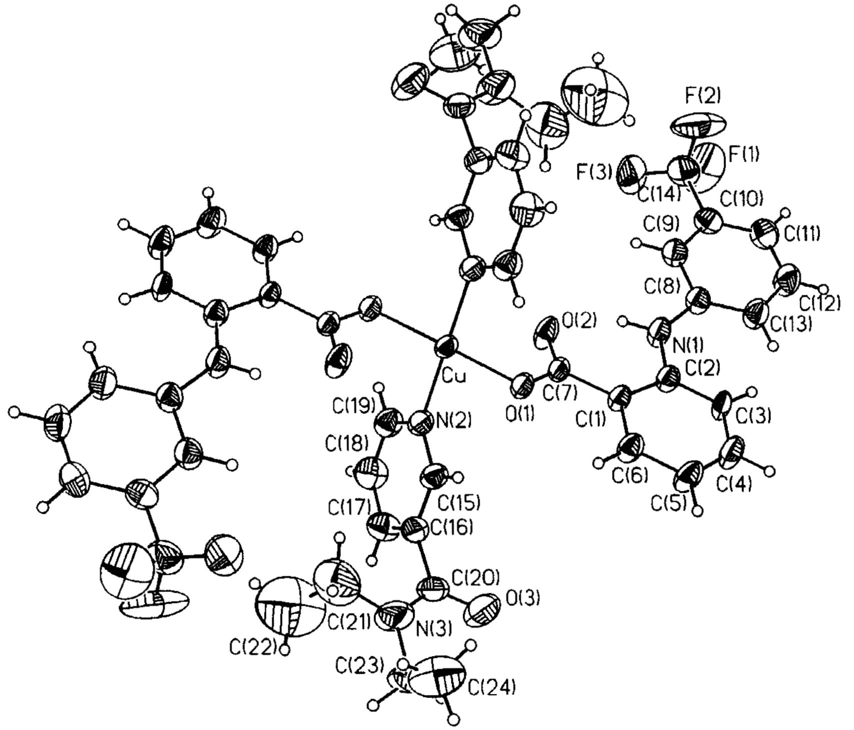

FIGURE 1 An ORTEP plot of $Cu(nif)_2(denc)_2$ with thermal ellipsoids shown at the 50% probability level.

The nearest Cu-Cu distances in the unit cell of $Cu(nif)_2(denc)_2$ are 7.984(3)Å. The structure of the complex is such that the Cu(II) atom is effectively shielded by niflumate and N,N-diethylnicotinamide molecules.

The EPR spectra obtained for $Cu(nif)_2(denc)_2$ at room temperature and at 77K are of axial type[11]. Spin Hamiltonian parameters at room temperature (at 77K) are: $g_{\perp} = 2.075(2)(2.072(2))$; $g_{\parallel} = 2.274(2)(2.279(2))$. This indicates that the unpaired electron is in the antibonding Ψ_{big} molecular orbital, clearly demonstrating an elongated bipyramidal coordination around Cu(II), in agreement with X-ray data.

The value of μ_{eff} is slightly dependent on temperature (1.85 B.M. at 295 K and 1.87 B.M. at 80 K).

Magnetic susceptibility measurements of a polycrystalline sample of the compound between 80 and 295 K obey the Curie-Weiss law

$$X_M^{corr} = C(T - \Phi)$$

TABLE II Atomic coordinates [× 10^4] and equivalent isotropic displacement parameters [Å^2 × 10^3] for [Cu(nif)2(denc)2]. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	*y*	*z*	*U(eq)*
Cu	0	0	0	31(1)
O(1)	−2048(2)	−632(2)	144(2)	36(1)
O(2)	56(3)	−2235(2)	470(2)	47(1)
O(3)	−2971(4)	486(2)	−3786(3)	75(1)
N(1)	−969(3)	−4237(2)	1098(2)	42(1)
N(2)	522(3)	218(2)	−1659(2)	36(1)
N(3)	−3024(5)	2352(3)	−3954(3)	80(1)
C(1)	−2797(3)	−2415(2)	384(2)	32(1)
C(2)	−2502(3)	−3632(2)	748(2)	35(1)
C(3)	−3691(3)	−4209(2)	772(2)	35(1)
C(4)	−5187(4)	−3612(3)	445(3)	48(1)
C(5)	−5601(4)	−2437(3)	82(3)	47(1)
C(6)	−4375(3)	−1830(2)	50(2)	39(1)
C(7)	−1495(3)	−1742(2)	337(2)	32(1)
C(8)	−471(4)	−5375(2)	1642(2)	37(1)
C(9)	1085(4)	−5658(2)	2027(2)	41(1)
C(10)	1708(4)	−6768(2)	2562(2)	42(1)
C(11)	817(5)	−7625(3)	2741(3)	52(1)
C(12)	−732(5)	−7339(3)	2369(3)	59(1)
C(13)	−1384(4)	−6240(2)	1829(3)	50(1)
C(14)	3356(5)	−7037(3)	2986(3)	57(1)
C(15)	−881(4)	584(2)	−2121(2)	39(1)
C(16)	−663(4)	839(2)	−3253(2)	41(1)
C(17)	1095(5)	653(3)	−3939(3)	55(1)
C(18)	2549(5)	267(3)	−3467(3)	56(1)
C(19)	2220(4)	78(2)	−2337(3)	44(1)
C(20)	−2320(4)	1222(3)	−3698(2)	47(1)
C(21)	−2504(8)	3292(5)	−3597(5)	105(2)
C(22)	−1441(10)	3761(9)	−4553(3)	194(5)
C(23)	−4601(6)	2748(4)	−4428(3)	81(1)
C(24)	−6375(8)	3101(6)	−3580(5)	108(2)
F(1)	4334(12)	−8082(7)	2850(12)	119(4)
F(2)	2875(16)	−7026(13)	4027(8)	120(5)
F(3)	4336(10)	−6355(8)	2476(9)	99(3)

where the Curie constant is $C = Ng^2\beta^2S(S + 1)3K$ with $S = 1/2$.

The best values of the Curie (C) and Weiss (Φ) constants are 0.36 and 6.6 K, respectively. The small positive Weiss constant indicates a weak ferromagnetic interaction.

The structure consists of relatively isolated centrosymmetric [Cu(nif)$_2$(denc)$_2$] units Figure 1. Coordinates and equivalent isotropic thermal parameters of nonhydrogen atoms are given in Table II. Selected bond distances and angles are in Table III. The approximately square planar *trans*-coordination of the Cu(II)

TABLE III Selected bond lengths [Å] and angles [°] for [Cu(nif)2(denc)2].

Cu-O(1)	1.955(2)	Cu-N(2)	2.008(2)
O(1)-C(7)	1.280(3)	O(2)-C(7)	1.245(3)
O(3)-C(20)	1.215(4)	N(1)-C(2)	1.370(3)
N(1)-C(8)	1.393(3)	N(2)-C(15)	1.340(3)
N(2)-C(19)	1.343(4)	N(3)-C(20)	1.324(4)
N(3)-C(23)	1.470(4)	N(3)-C(21)	1.550(7)
C(1)-C(6)	1.386(3)	C(1)-C(2)	1.415(3)
C(1)-C(7)	1.494(3)	C(2)-C(3)	1.337(3)
C(3)-C(4)	1.330(4)	C(4)-C(5)	1.368(4)
C(5)-C(6)	1.386(4)	C(8)-C(13)	1.396(4)
C(8)-C(9)	1.398(4)	C(9)-C(10)	1.379(4)
C(10)-C(11)	1.378(4)	C(10)-C(14)	1.498(4)
C(11)-C(12)	1.383(5)	C(12)-C(13)	1.377(4)
C(14)-F(3)	1.239(7)	C(14)-F(2)	1.275(10)
C(14)-F(1)	1.302(8)	C(15)-C(16)	1.377(4)
C(16)-C(17)	1.383(5)	C(16)-C(20)	1.507(4)
C(17)-C(18)	1.383(5)	C(18)-C(19)	1.367(5)
C(21)-C(22)	1.356(7)	C(23)-C(24)	1.502(7)
O(1)-Cu-N(2)	89.03(9)	O(1)#1-Cu-N(2)	90.97(9)
C(7)-O(1)-Cu	107.3(2)	C(2)-N(1)-C(8)	131.4(2)
C(15)-N(2)-C(19)	118.1(2)	C(15)-N(2)-Cu	119.0(2)
C(19)-N(2)-Cu	122.9(2)	C(20)-N(3)-C(23)	119.1(3)
C(20)-N(3)-C(21)	123.4(3)	C(23)-N(3)-C(21)	116.6(3)
C(6)-C(1)-C(2)	117.7(2)	C(6)-C(1)-C(7)	119.0(2)
C(2)-C(1)-C(7)	123.3(2)	C(3)-C(2)-N(1)	118.9(2)
C(3)-C(2)-C(1)	121.8(2)	N(1)-C(2)-C(1)	119.3(2)
C(4)-C(3)-C(2)	118.5(2)	C(3)-C(4)-C(5)	124.3(2)
C(4)-C(5)-C(6)	117.7(3)	C(1)-C(6)-C(5)	120.1(2)
O(2)-C(7)-O(1)	121.6(2)	O(2)-C(7)-C(1)	121.7(2)
O(1)-C(7)-C(1)	116.6(2)	N(1)-C(8)-C(13)	125.8(2)
N(1)-C(8)-C(9)	116.1(2)	C(13)-C(8)-C(9)	118.2(2)
C(10)-C(9)-C(8)	120.6(3)	C(11)-C(10)-C(9)	121.4(3)
C(11)-C(10)-C(14)	119.3(3)	C(9)-C(10)-C(14)	119.3(3)
C(10)-C(11)-C(12)	117.9(3)	C(13)-C(12)-C(11)	122.1(3)
C(12)-C(13)-C(8)	119.9(3)	F(3)-C(14)-F(2)	110.9(8)
F(3)-C(14)-F(1)	107.5(7)	F(2)-C(14)-F(1)	106.8(7)
F(3)-C(14)-C(10)	111.6(4)	F(2)-C(14)-C(10)	110.2(6)
F(1)-C(14)-C(10)	109.6(5)	N(2)-C(15)-C(16)	123.2(3)
C(15)-C(16)-C(17)	118.0(3)	C(15)-C(16)-C(20)	119.5(3)
C(17)-C(16)-C(20)	122.3(3)	C(18)-C(17)-C(16)	119.0(3)
C(19)-C(18)-C(17)	119.5(3)	N(2)-C(19)-C(18)	122.1(3)
O(3)-C(20)-N(3)	123.0(3)	O(3)-C(20)-C(16)	118.9(3)
N(3)-C(20)-C(16)	118.1(3)	C(22)-C(21)-N(3)	103.5(5)
N(3)-C(23)-C(24)	112.6(4)		

Symmetry transformations used to generate equivalent atoms: #1 −x, −y, −z atom in a monomeric unit is formed by two carboxylic O(1) atoms from two anions of niflumate (Cu-O(1) = 1.955(2)Å), and by two nitrogen atoms from N,N-diethylnicotinamide molecules (Cu-N(2) = 2.007(3)Å), completed by two remaining carboxylic oxygen atoms from two niflumate anions (Cu-O(2) = 2.643(2)Å). The strong deformation of the coordination octahedron around the Cu(II) atom is caused by creation of the two four membered metallocyclic rings O(1)-Cu-C(7)-O(2) of 54.88(9)°.

The Cu-N bond distance of 2.007(3)Å is shorter than those found in $Cu_2(acetate)_4(denc)_2$[3] and in $Cu(4\text{-}OHC_6H_4COO)_2(denc)_2$[4] with the mean Cu-N bond distances of 2.175(6) and 2.022(3)Å, respectively.

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