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Crystal and molecular structure of bis(2,6-dimethanolpyridine)copper(II)niflumate

M. Koman* and M. Melník

Department of Inorganic Chemistry, Slovak Technical University, 812 37 Bratislava, Slovak Republic

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Abstract—Bis(2,6-dimethanolpyridine)copper(II)niflumate has been prepared and studied by single-crystal X-ray diffraction methods at 293(2) K. The complex is noncentrosymmetric, with the two 2,6-dimethanolpyridine molecules symmetrically coordinated to the copper(II) atom in a tridentate chelating manner making up an "all-trans" elongated octahedral arrangement. In consequence of Jahn–Teller distortion, considerable differences are found between them: for one 2,6-pyme ligand Cu—N is 1.919(5), Cu—O 2.210(4) and 2.244(4) Å, while for the other the values are 1.891(5), 2.074(4) and 2.101(4) Å. The data are compared and discussed with those found in familiar CuL_2 compounds with the CuO_4N_2 chromophore. © 1997 Published by Elsevier Science Ltd

Keywords: copper(II); structure; niflumate; 2,6-dimethanolpyridine.

A number of Cu^{II} complexes of bidentate ligands exhibit an elongated octahedral structure of D_{2h} symmetry [1]. There are some complexes of tridentate ligands [2–10] in which each copper(II) atom is surrounded by a pair of tridentate ligands, coordinated by two O and one N donor atoms. The coordination around the copper(II) atoms, with the chromophore CuO_4N_2, is bipyramidally distorted octahedral as a consequence of the Jahn–Teller effect.

This paper deals with the crystal structure of the copper(II) niflumate adduct with 2,6-dimethanolpyridine (2,6-dmpy). The structure agrees with the formula $[Cu(2,6\text{-dmpy})_2](nif)_2$.

The result is of interest in the context of the above anomaly and in regard to the nature of the Jahn–Teller effect in complexes of symmetrical oligodentate ligand systems and is reported in this paper.

EXPERIMENTAL

Preparation of $Cu(2,6\text{-dmpy})_2(nif)_2$

Bis(2,6-dimethanolpyridine)copper(II)niflumate was prepared by reacting a methanol solution of copper(II) niflumate with a methanol solution of 2,6-dimethanolpyridine at an equimolar ratio. The solution was heated, filtered and left to crystallize. The precipitated product was isolated. Crude product was recrystallized from methanol/acetone solution. Fine crystals were isolated and washed with cold methanol. Found: Cu, 7.1; C, 53.5; H, 3.6; N, 9.3. Calc. for $Cu(2,6\text{-dmpy})_2(nif)_2$: Cu, 7.03; C, 53.13; H, 3.8; N, 9.3%.

Crystallography

Data collection and cell refinement were carried out using Syntex $P2_1$ software. Intensity data were corrected to Lorenz and polarization factors using $XP2_1$ [11]. The structure was solved by the heavy atom method with SHELX86 [12] and subsequent Fourier synthesis using SHELXL93 [5]. Anisotropic thermal parameters were refined for all nonhydrogen atoms. Geometrical analyses was performed using SHELXL93 [13]. The structures were drawn using ORTEP [14]. Crystal data and refinement details are summarized in Table 1. Selected interatomic distances and bond angles are given in Table 2.

Supplementary material including refined atom coordinates, calculated hydrogen coordinates ($\times 10^4$) and anisotropic displacement parameters for non-

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* Author to whom correspondence should be addressed.

Table 1. crystal data and structure refinement for [Cu(nif)$_2$(2,6-dmpy)$_2$]

Empirical formula	$C_{40}H_{34}CuF_6N_6O_8$
Formula weight	904.27
Temperature (K)	293(2)
Wavelength (Å)	0.71073
Crystal system	Triclinic
Space group	$P\bar{1}$
Unit-cell dimensions	a = 11.376(2) Å, α = 80.45(3)°
	b = 13.389(3) Å, β = 78.43(3)°
	c = 13.460(3) Å, γ = 74.02(3)°
Volume (Å^3)	1917.5(7)
Z	2
Density (calculated) (Mg m^{-3})	1.566
Absorption coefficient (mm^{-1})	0.662
F(000)	926
Crystal size (mm)	0.20 × 0.30 × 0.60
θ range for data collection (°)	1.56–25.10
Index ranges	$0/h/13$, $-15/k/15$, $-15/l/16$
Reflections collected	7165
Independent reflections	6787 (R_{int} = 0.0667)
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	6776/0/550
Goodness-of-fit on F^2	0.529
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0514, wR_2 = 0.1389
R indices (all data)	R_1 = 0.1515, wR_2 = 0.2201
Largest difference peak and hole (eÅ^{-3})	0.590 and −0.860

Table 2. Selected bond lengths (Å) and angles (°) for [Cu(nif)$_2$(2,6-dmpy)$_2$]

Cu(1)—N(2)	1.891(5)	Cu(1)—N(1)	1.919(5)
Cu(1)—O(3)	2.074(4)	Cu(1)—O(4)	2.101(4)
Cu(1)—O(2)	2.210(4)	Cu(1)—O(1)	2.244(4)
O(3)—C(14)	1.409(8)	O(4)—C(13)	1.407(8)
O(1)—C(6)	1.387(8)	N(2)—C(8)	1.333(8)
N(2)—C(12)	1.337(8)	O(2)—C(7)	1.376(8)
N(1)—C(1)	1.331(8)	N(1)—C(5)	1.340(7)
C(5)—C(7)	1.486(9)	C(1)—C(6)	1.515(9)
C(12)—C(14)	1.491(9)	C(8)—C(13)	1.491(9)
N(2)—Cu(1)—N(1)	173.8(2)	N(2)—Cu(1)—O(3)	81.3(2)
N(1)—Cu(1)—O(3)	94.0(2)	N(2)—Cu(1)—O(4)	79.6(2)
N(1)—Cu(1)—O(4)	105.2(2)	O(3)—Cu(1)—O(4)	160.7(2)
N(2)—Cu(1)—O(2)	98.1(2)	N(1)—Cu(1)—O(2)	78.4(2)
O(3)—Cu(1)—O(2)	96.7(2)	O(4)—Cu(1)—O(2)	89.1(2)
N(2)—Cu(1)—O(1)	105.3(2)	N(1)—Cu(1)—O(1)	78.6(2)
O(3)—Cu(1)—O(1)	90.2(2)	O(4)—Cu(1)—O(1)	91.8(2)
O(2)—Cu(1)—O(1)	156.4(2)	C(14)—O(3)—Cu(1)	112.0(4)
C(6)—O(1)—Cu(1)	105.8(4)	C(8)—N(2)—C(12)	120.0(6)
C(8)—N(2)—Cu(1)	120.6(4)	C(12)—N(2)—Cu(1)	119.1(4)
C(7)—O(2)—Cu(1)	110.0(4)	C(1)—N(1)—C(5)	120.0(6)
C(1)—N(1)—Cu(1)	119.3(4)	C(5)—N(1)—Cu(1)	120.4(5)
N(1)—C(5)—C(7)	115.8(6)	N(1)—C(1)—C(6)	115.5(6)
N(2)—C(12)—C(14)	115.2(6)	N(2)—C(8)—C(13)	115.1(6)
O(3)—C(14)—C(12)	111.5(5)	O(1)—C(6)—C(1)	112.0(6)
O(2)—C(7)—C(5)	112.5(5)	O(4)—C(13)—C(8)	110.8(6)

hydrogen atoms (Å × 10^3) have been deposited at the Cambridge Crystallographic Data Centre. Observed and calculated structural factors are available on request from the correspondence author.

RESULTS AND DISCUSSION

The structure determination establishes the complex to be $[Cu(2,6\text{-dmpy})_2](nif)_2$. The complex species present comprises copper(II) coordinated by a pair of 2,6-dimethanolpyridine ligands with no niflumate anions in the primary coordination sphere. The complex species contains no crystallography imposed symmetry elements and together with the niflumate anions makes up the asymmetric unit (Fig. 1). Within each 2,6-dimethanolpyridine ligand the internal geometry and that involving the copper(II) is consistent between each half, however, the two ligands differ considerably in their individual mode of interaction with the copper(II), ligand "A" being much more lightly bound than ligand "B". The Cu—L bond distances for the "A" ligand are: Cu—N(2) 1.891(5), Cu—O(3) 2.074(4) and Cu—O(4) 2.101(4) Å; while for the "B" ligand the values are: Cu—N(1) 1.919(5), Cu—O(2) 2.210(4) and Cu—O(1) 2.244(4) Å. In consequence, the geometry of the ligands also differ in terms of the angles. The mean values of the five-membered metallocyclic rings, O—Cu—N bond angles, are 80.5(2)° for the "A" ligand and 78.5(2)° for the "B" ligand. The O—Cu—O bond angle follows this trend, with the values of 160.7(2)° for the former and 156.4(2)° for the latter.

Whereas copper(II) environments have been well studied in an environment of unidentate or three bidentate ligands [1], studies of symmetrical systems involving two tridentate ligand are relatively few. In Table 3 are summarized structural data for such species with the CuO_4N_2 chromophore. From the data in Table 3 we can see that there are two derivatives [8,9] in which the length of the four coordination in the same plane are longer than those of the other two coordination bonds. Such a structure is termed a "compressed" distorted octahedral. In all remaining derivatives (Table 3) distorted (elongated) octahedral coordination takes place.

The mean Cu—L bond distances for the Cu—N_{eq}, Cu—N_{ax}, Cu—O_{eq} and Cu—O_{ap} are: 2.01, 1.945, 2.20 and 2.41 Å. The mean value of the five-membered metallocyclic ring is 79.0°.

There are two examples [5,9] which contain two crystallographically independent molecules in one crystal, differing by a degree of distortion (Cu—L bond distances and L—Cu—L bond angles). These are typical examples of distortion isomerism [15].

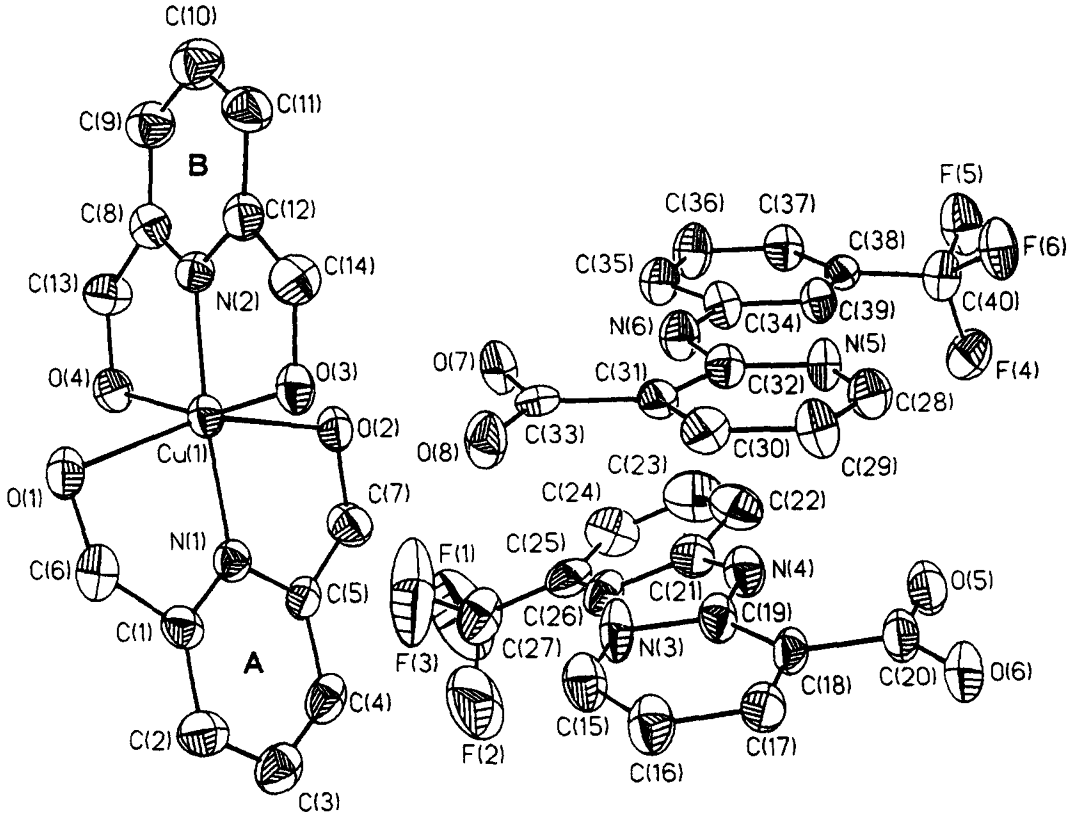

Fig. 1. ORTEP plot of $[Cu(2,6\text{-dmpy})_2](nif)_2$ with thermal ellipsoids at the 40% probability level.

Table 3. Summary of the structural data for CuL_2 compounds with the CuO_4N_2 chromophore[a]

Compound (color)	Cryst. cl. Space group *Z*	*a* (Å) *b* (Å) *c* (Å)	α (°) β (°) γ (°)	Chromo-phore		Cu—L[b] (Å)		L—Cu—L[b] (°)	Ref.
$Cu(2,6\text{-dmpy})_2(nif)_2$	m	20.901(5)		CuO_4N_2	N_{eq}	1.983(4,20)	N_{eq},N_{eq}	83.5(1)[c]	
(green)	*C*2/*c*	7.439(2)	114.59(3)		O_{eq}	2.015(3,25)	O_{eq},N_{eq}	94.1(1,4)	
	8	18.708(4)			O_{ax}	2.481(3,8)		172.3(1,2.9)	This work
							$O_{ax}N_{eq}$	91.6(1,3.7)	
								131.5(1,3.5)	
							O_{ax},O_{eq}	55.7(1,8)[c]	
							O_{eq},O_{eq}	89.2(1)	
							O_{ax},O_{ax}	123.8(1)	
$Cu(degly)_2$	m	9.73(2)		CuO_4N_2	N_{eq}	2.14		Not given	[2]
(blue)	$P2_1/b$	7.07(2)			O_{eq}	1.90			
	2	12.22(3)	111		O_{ax}	2.41			
$[Cu(bcmgly)_2]\cdot 2H_2O$	m	6.845(1)		CuO_4N_2	O_{eq}	1.954(2) × 2	O_{eq},O_{eq}	180	[3]
(pale blue)	$P2_1/c$	14.095(4)	91.95(2)		N_{eq}	2.062(2) × 2	O_{eq},N_{eq}	86.11(9)[c]	
	2	9.427(3)			O_{ax}	2.321(2) × 2	O_{eq},O_{ax}	86.8(1)	
							N_{eq},O_{ax}	77.97(9)[c]	
$[Cu(npac)_2]\cdot 2H_2O$	m	8.636(2)		CuO_4N_2	N_{eq}	2.071(2) × 2	O_{eq},N_{eq}	85.3(1)[c]	[4]
(not given)	$P2_1/c$	14.361(4)	94.78(2)		O_{eq}	1.939(2) × 2	N_{eq},O_{ax}	90.9(1)[c]	
	2	9.247(2)			O_{ax}	2.416(2) × 2	O_{eq},O_{ax}	88.5(1)	
$[Cu(Hpydca)_2]\cdot 3H_2O$[d]	m	14.74(1)		CuO_4N_2	N_{eq}	1.947(11,48)	O_{eq},N_{eq}	100.5(3,6)	[5]
(blue)	*Pc*	10.30(1)	123.9(1)		O_{eq}	2.051(8,7)		79.6(4,3)[c]	
	4	13.77(1)			O_{ax}	2.349(9,27)	O_{ax},N_{eq}	103.8(4,1.2)	
								77.1(4)[c]	
							O_{eq},O_{ax}	92.5(3,3.0)	
								75.4(3)[c]	
							O_{ax},O_{ax}	152.4(3)	
							N_{eq},N_{eq}	179.1(4)	
							O_{eq},O_{eq}	159.1(3)	
				CuO_4N_2	N_{eq}	1.952(12,50)	O_{eq},N_{eq}	80.0(4,6)[c]	
					O_{eq}	2.026(10,7)		108.0(4,2)	
					O_{ax}	2.389(11,63)	O_{ax},N_{eq}	107.1(4)	
								75.0(4,1.0)[c]	
							O_{ax},O_{eq}	92.6(4,8)	
							O_{ax},O_{ax}	150.0(4)	
							N_{eq},N_{eq}	176.9(4)	
							O_{eq},O_{eq}	160.0(4)	

$[Cu(purp)_2]\cdot 7.6H_2O$	tr	12.187(4)	73.57(3)	CuO_4N_2	N_{eq}	1.997(6,24)	N_{eq},O_{eq}	81.9(2)[c]	[6]
(not given)	$P\bar{1}$	11.889(5)	83.72(3)		O_{eq}	2.026(7,3)		90.0(3,8.1)	
	2	10.447(3)	75.09(2)		O_{ax}	2.296(5,7)	N_{eq},N_{eq}	179.0(7)	
							N_{eq},O_{ax}	76.8(2,2)[c]	
								103.3(2,1.2)	
							O_{eq},O_{eq}	164.2(2)	
							O_{eq},O_{ax}	91.8(2,1.3)	
							O_{ax},O_{ax}	153.5(2)	
$K_2[Cu(idac)_2\cdot H_2O$	m	15.53(3)		CuO_4N_2	N_{eq}	1.97(2) × 2		Not given	[7]
(not given)	$B2/b$	13.17(3)			O_{eq}	1.95(2) × 2			
	4	6.28(3)	95.5(5)		O_{ax}	2.43(2) × 2			
$K_2[Cu(pydca)_2]\cdot 7H_2O$	or	20.823(5)		CuO_4N_2	O_{eq}	2.189(5,29)	O_{eq},O_{eq}	87.9(3,2.5)	[8]
(not given)	$Pnna$	13.398(5)			N_{ax}	1.936(5)		154.7(3)	
	4	8.183(3)					O_{eq},N_{ax}	77.6(2,3)[c]	
							N_{ax},N_{ax}	173.7(3)	
$[Cu(pydca)(Hpycda)]\cdot H_2O$[d]	m	14.76(9)		CuO_4N_2	O_{eq}	2.06(1,1)	N_{ax},O_{eq}	78.2(4,2.7)[c]	[9]
(not given)	Pc	10.27(3)	124.0(1)			2.315(1,50)	N_{ax},N_{ax}	179.5(7)	
	4	13.76(8)			N_{ax}	1.93(1,5)	O_{eq},O_{eq}	92.3(4,2.3)	
								156.5(4,3.7)	
				CuO_4N_2	O_{eq}	2.02(1,1)	N_{ax},O_{eq}	77.5(5,4.3)[c]	
						2.375(2,75)	N_{ax},N_{ax}	177.1(5)	
					N_{ax}	1.97(1,5)	O_{eq},O_{eq}	92.5(9,3.0)	
								155.0(5,5.5)	
$[Cu(mdac)_2]\cdot (ClO_4)_2$	m	6.183(2)		CuO_4N_2	O_{eq}	1.952(2) × 2	O_{eq},N_{eq}	85.5(1)[c]	[10]
(not given)	$P2_1/c$	17.617(4)	110.2(1)		N_{eq}	2.021(2) × 2	O_{eq},O_{ax}	91.1(1)	
	2	8.900(2)			O_{ax}	2.471(3) × 2	N_{eq},O_{ax}	71.7(1)[c]	

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degly = diethanolglycinate; bcmgly = *N,N*-bis(carboxymethyl)glycinate; npac = nitrolodi(*β*-propionamide)monoacetate; Hpydca = Hydrogen-pyridine-2,6-dicarboxylate; purp = purpurate; idac = iminodiacetate; pydac = pyridine-2,6-dicarboxylate; mdac = iminodiacetamide.

[a] Where more than one chemically equivalent distance or angle are present the mean values are tabulated. The first number in parentheses is the e.s.d.s and the second is a maximum deviation from the mean value.

[b] The chemical identity of the coordinated atom is specified in these columns.

[c] The five-membered metallocyclic ring.

[d] There are two crystallographically independent molecules.

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