

STRUCTURAL CHARACTERIZATION OF Cu(bpma)₂ · [BF₄]₂, (bpma: *N*-{[3-(DIMETHOXYMETHYL)PHENYL]METHYLIDE- NE}[DI-(2-PYRIDYL)]METHANAMINE)

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The crystal and molecular structure of a copper complex formulated as Cu(bpma)₂ · [BF₄]₂, (bpma: *N*-{[3-(dimethoxymethyl)phenyl]methylidene}[di-(2-pyridyl)]methanamine) is reported. The ligand results from the reaction of the unmodified carboxaldehyde group of 1,3-benzene-dicarboxaldehyde with the solvent, methanol, giving the acetal. The structure is monomeric and contains the copper cation at a center of symmetry, octahedrally coordinated to two tridentate, symmetry-related bpma ligands. The charge balance is achieved through the inclusion in the structure of (highly disordered) BF₄⁻ counter ions.

Keywords: Copper complexes; Oxidation; Crystal structure

INTRODUCTION

Attempts to duplicate the unusual monophenolase activity of tyrosinase in model systems can be dated from the early work of Brackman and Havinga in the mid-1950s, when simple copper salts were found to be able to mediate phenol hydroxylation reactions [1]. Nevertheless, the most significant insight into the activation of dioxygen comes from the pioneering work by Karlin and co-workers who developed a series of dinuclear Cu(I) complexes derived from *m*-xylyl-tetrapyridyl ligands containing two bis[2-(2-pyridyl)ethyl]amine units, and they succeeded in mimicking the structures and functions of the active sites of hemocyanin and tyrosinase (reversible O₂ binding and aromatic ligand hydroxylation) [2,3]. Casella *et al.* [4] and subsequently others [5], reported similar reactivity by simpler *m*-xylyl-bis(imine)dicopper(I) complexes or their corresponding diamine complexes.

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An interesting feature of the hydroxylation reaction observed in Karlin models, as opposed to the bis(imine) systems, is that the ligand hydroxylation reaction is suppressed when the pyridyl groups on the arms of the xylyl spacer are replaced by other nitrogen heterocycles [6]. In these cases the reaction product corresponds to a four-electron reduction of dioxygen to afford the dihydroxy-copper(II) species. This different behavior is not really understood, and it is likely that both steric and electronic effects play an important role in determining the type of copper/dioxygen intermediate responsible for the hydroxylation of the aromatic ring.

We have reported the oxidation of copper(I) complexes with the binucleating Schiff-base ligands obtained from condensation of benzene-1,3-dicarboxaldehyde and di-(2-pyridyl)methyl amine [7] and the methylated analogue (6-methyl-2-pyridyl)(2'-pyridyl)methyl amine [8]. These *m*-xylyl ligands provide two pyridine nitrogens and one imine nitrogen to each copper ion. Regardless of the type of N-donor, the hydroxylation reaction did not occur, and a bis μ -methoxo- or hydroxo-bridged binuclear copper(II) complex was isolated as product, depending on the solvent used.

Herein we report the molecular structure of the reaction product obtained by oxygenation of a methanolic solution of the copper(I) complex with a ligand with only one side arm (hereafter bpma), derived from the condensation of benzene-1,3-dicarboxaldehyde and (6-methyl-2-pyridyl)(2'-pyridyl)methyl amine, in a 1:1 stoichiometric ratio. The ligand hydroxylation reaction was not observed. Instead, a simple mononuclear copper(II) complex was obtained.

EXPERIMENTAL

HPLC quality methanol was stored over CaSO₄ for several days and freshly distilled before use. (6-methyl-2-pyridyl)(2'-pyridyl) methyl amine was obtained as reported previously [8]. All other reagents and solvents were of commercially available reagent quality.

Synthesis

A solution of the Schiff-base ligand was obtained by refluxing the amine (2 mmol) with benzene-1,3-dicarboxaldehyde (2 mmol) in methanol (10 cm³) for 30 min. The solution was degassed and 4 mmol of Cu(acetonitrile)₄ClO₄, as a saturated acetonitrile solution, was added. The resulting solution was allowed to react with atmospheric oxygen. The solution turns green-blue and the crystals that separated with time were filtered, washed with cold methanol, and dried.

Anal. Calcd. for Cu(C₄₄H₄₆N₆O₄)(BF₄)₂(%): C, 54.6; H, 4.0; N, 8.9; Cu, 6.8. Found: C, 55.06; H, 4.03; N, 8.76; Cu, 6.62.

Caution: Perchlorate salts are potentially explosive!

Measurements

The C, H, N elemental analyses were performed on Fison-Carlo Erba EA 108 instrument at CEPEDQ (University of Chile). X-ray structure determination was made on a Bruker Smart Apex diffractometer with a graphite-monochromated Mo K α source ($\lambda = 0.71073 \text{ \AA}$).

X-ray Diffraction

A highly redundant data set was collected at room temperature up to a 2θ max. of ca. 58° and a 0.3° separation between frames. Data integration was performed using SAINT and a multi-scan absorption correction was applied using SADABS, both programs in the diffractometer package. The structure was solved by direct methods and difference Fourier synthesis, and refined by the least-squares method on F^2 with anisotropic displacement parameters for non-H atoms. Hydrogen atoms were placed at their calculated positions and allowed to ride on their host carbons both in coordinates and in thermal parameters. Those corresponding to terminal methyl groups were allowed to rotate as well. All calculations to solve the structure, refine the model proposed and obtain derived results were carried out with the computer programs SHELXS97 and SHELXL97 [9] and SHELXTL/PC [10]. Full use of the CCDC package was also made for searching in the CSD Database [11]. A summary of crystallographic and refinement data is presented in Table I, while Table II shows relevant interatomic distances and angles.

RESULTS AND DISCUSSION

Reactions of 1,3-benzene-dicarboxaldehyde with primary amines afford the corresponding Schiff bases. Under the experimental conditions employed (1:1 stoichiometric ratio) we expected to obtain the base resulting from condensation of only one

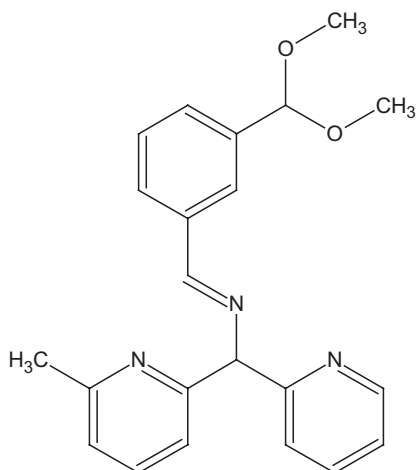
TABLE I Crystal and structure refinement data

Empirical formula	C ₄₄ H ₄₆ B ₂ CuF ₈ N ₆ O ₄
Formula weight	960.02
Crystal system, space group	Monoclinic, $P2_1/n$
Z	4
Temperature (K)	293(2)
Wavelength (Å)	0.71073
<i>a</i> (Å)	10.1472(10)
<i>b</i> (Å)	16.8938(17)
<i>c</i> (Å)	13.6234(14)
(°)	104.968(2)
Volume (Å ³)	2256.1(4)
Calculated density (g/cm ³)	1.413
Absorption coefficient (mm ⁻¹)	0.566
<i>F</i> (000)	990
Crystal size (mm ³)	0.21 × 0.16 × 0.14
θ range (°)	1.96 to 27.99
Index ranges	$-13 \leq h \leq 13$, $-22 \leq k \leq 22$, $-17 \leq l \leq 17$
Reflections collected	18414
Independent reflections	5090 ($R_{\text{int}} = 0.062$)
Completeness to θ max. (%)	99.8
Absorption correction	Empirical (SADABS)
Max. and min. transmission	0.91 and 0.89
Data parameters	5090/324
Refinement method	Full-matrix least-squares on F^2
Final <i>R</i> indices [$I > 2\sigma(I)$]	$R1^a = 0.0594$, $wR2^b = 0.1548$
<i>R</i> indices (all data)	$R1^a = 0.1560$, $wR2^b = 0.2000$
Goodness-of-fit on F^2	$S^c = 0.811$
Largest diff. peak and hole (e Å ⁻³)	0.526 and -0.246

^a $R1 = \sum ||F_o| - |F_c|| / \sum |F_o|$; ^b $wR2 = [\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]]^{1/2}$; ^c $S = [\sum [w(F_o^2 - F_c^2)^2] / (n-p)]^{1/2}$.

TABLE II Interatomic bond lengths (Å) and angles (°)

Cu(1)–N(1)	1.981(4)	N(1)#1–Cu(1)–N(1)	180
Cu(1)–N(2)	2.105(3)	N(1)–Cu(1)–N(2)	87.33(14)
Cu(1)–N(3)	2.409(3)	N(2)#1–Cu(1)–N(2)	180
		N(1)–Cu(1)–N(3)	77.81(13)
		N(3)#1–Cu(1)–N(3)	180
		N(2)–Cu(1)–N(3)	74.89(13)

Symmetry code: #1 $-x, -y + 1, -z$.

carboxaldehyde group, with the second one unchanged. A solution of the Schiff base was allowed to react with $\text{Cu}(\text{AN})_4\text{BF}_4$ in methanol and was then exposed to dioxygen. The resulting copper(I) complex was expected to be tricoordinated. Karlin *et al.* [12] reported the reactivity of a mononuclear tricoordinated copper(I) complex with the ligand di-[2-(2-pyridyl)ethyl]-benzylamine in comparison to the corresponding binuclear copper(I) complex with the parent ligand 1,3-bis-di-[(2-(2-pyridyl)ethyl)-amino-methyl] benzene, which affords aromatic hydroxylation upon reaction with oxygen. In the former case only a binuclear copper(II) complex, formulated as an oxo-bridged compound, was isolated. In the presence of small amounts of water this complex is transformed into the bis hydroxy-bridged compound. Other mononuclear copper(I) complexes react similarly. In our case, hydroxylation of the xylyl moieties does not occur and the isolated copper (II) complex, herein reported, is a simple mononuclear copper(II) compound containing a ligand that results from the reaction of the unmodified carboxaldehyde group with the solvent, methanol, giving the acetal. This behavior of carbonyl compounds in the presence of copper complexes is not unusual [13].

The compound crystallizes in the monoclinic space group $P21/c$. The structure is composed of monomeric units of $\text{Cu}(\text{bpma})_2^{2+}$, stabilized by BF_4^- groups acting as counterions. The copper atom is located at a symmetry center, with an octahedral environment defined by the tridentate bite of two symmetry-related bpma ligands (see Fig. 1). The latter bind through their pyridine nitrogens acting as basal ligands

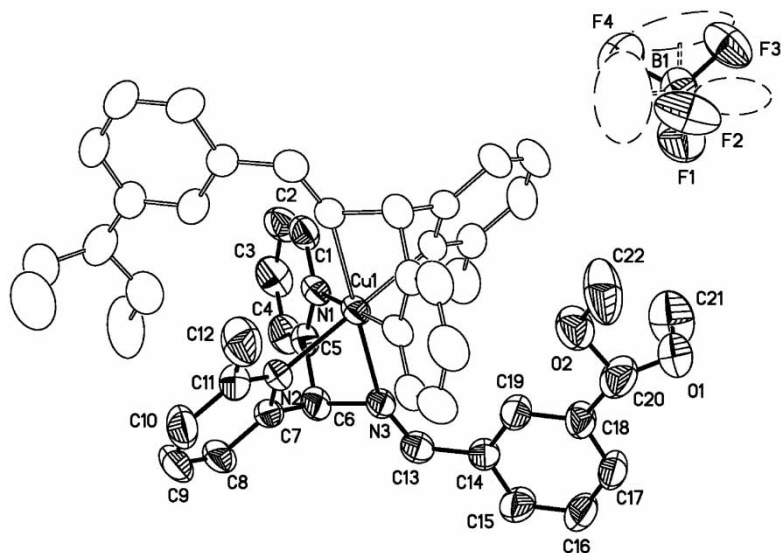


FIGURE 1 Molecular diagram (XP in SHELXTL-PC¹⁰) of the monomeric unit. Displacement ellipsoids drawn at 40% level.

[Cu(1)–N(1): 1.981(4) Å, Cu(1)–N(2): 2.105(3) Å], while the N-imino occupies the apical sites [Cu(1)–N(3): 2.409(3) Å]; all are normal coordination distances for copper complexes with similar ligands (see, for example, ref. [7]). By symmetry considerations the octahedral base is perfectly planar and embeds all five atoms defining it [N(1), N(2), N(1'), N(2'), Cu(1); $(-x, 1-y, -z)$]. The flexibility of the ligand also allows for a rather regular geometry of the base [N(1)–Cu(1)–N(2): 87.33(14), 92.67(14)°]. The chelating restrictions, however, show up in the severe deviation of the N(3)–Cu(1) apical axis from the vertical, which amounts to as much as 19.2(1)°. In spite of these restraints, however, the polyhedron exhibits a typical Jahn–Teller distorted geometry: a search in the CSD showed some 50 cases of similar centrosymmetrical CuN₆ cores with minimum, medium and maximum bond lengths averaging 2.02(3), 2.05(4) and 2.42(13) Å, respectively, values which compare fairly well with the ones herein reported.

Bond distances and angles in the bpma ligand have the expected values; the double bond therein is quite definite [N(3)=C(13), 1.263(6) Å] without any trace of delocalization, as reported in some related ligands complexed to copper, *viz.* dibromo-2[*N*-(2-pyridylmethyl)iminomethyl-pyridine]copper(II) [14]. The ligand displays a degree of angular symmetry, with the benzyl group almost bisecting the angle defined by the pyridine rings (actual values: 55.3(3), 57.0(3)°), and all three planar groups oriented in such a way as to have a common intercept, nearly coincident with the C(6)···Cu(1) line. Thus, when viewed along this direction, the group of planes suggests an approximate sixfold local symmetry (see Fig. 2). The tridentate character of the ligand leads to formation of six metalocycles in the structure which share the same copper cation. Though only three of them are independent (the other three being their centrosymmetric images) the whole ensemble bears an extra *pseudo* mirror plane of symmetry which halves the six-membered cycle [Cu(1)–N(1)–C(5)–C(6)–C(7)–N(2)] through Cu(1) and C(6), thus giving this loop an almost perfect boat conformation (Fig. 1) and

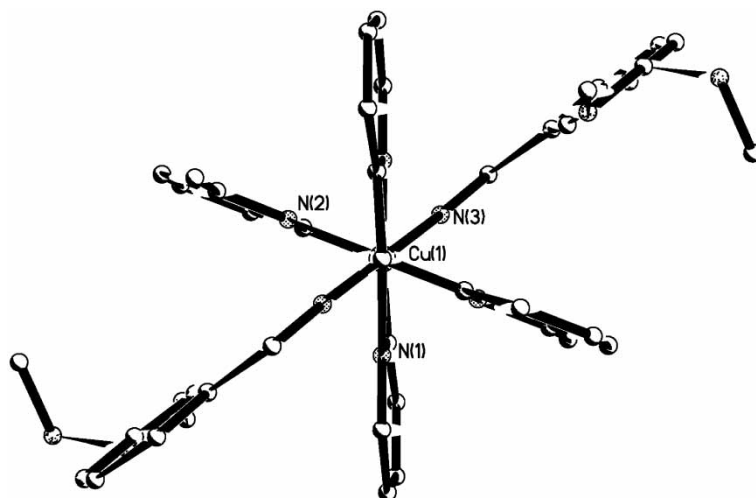


FIGURE 2 View of the monomeric unit down the C(6)···Cu(1) line, showing the symmetric disposition of the bpa planes.

rendering the other two [Cu(1)–N(1)–C(5)–C(6)–N(3) and Cu(1)–N(2)–C(7)–C(6)–N(3)] almost perfect mirror images of one another. The conformation of the latter five-membered cycles is that of an envelope, with the common N(3) protruding outwards and the remaining four in each group being fairly planar, with mean deviations of 0.03 and 0.01 Å, respectively. The N–Cu–N bite angle in the three independent metallocycles adheres closely to the mean values found in a comprehensive literature survey by Melnik *et al.* [15]; thus, for the five-membered cycles the corresponding angles in the present structure are 74.89(13) and 77.81(13)° as compared to a mean (span) of 78.0(–5.0, +2.5)° [15], and for the six-membered one, 87.33(14) against 90.2(–4.8, +6.3)°.

Finally, the structure is stabilized by one independent, severely disordered BF_4^- unit (two units per each copper atom lying at a center of symmetry with multiplicity 0.5), thus providing charge balance.

The fact that the bulky acetal branch of the bpa ligand is not involved in coordination causes it to spread outwards in such a way as to “push” neighboring monomers away. As a result the whole structure is loosely packed, with non-interacting monomers being some distance from each other. This is confirmed by the low value for the calculated density (1.413 g cm^{–3}, against 1.55–1.70 g cm^{–3} in related copper compounds with similar ligands, and in the lower 15th percentile of the whole population of non-polymeric, “copper-only” complexes reported in the CSD. Figure 3 shows a packing view of the structure down the *a* axis where wide channels can be seen running vertically, centered at the cell midpoint and corners and where the completely isolated counterions are embedded. A search for eventual voids in the structure amenable to solvent inclusion was fruitless.

Besides the obvious Coulombian interactions due to the ionic character of the compound, there are some weak C–H···X contacts stabilizing the structure, which are presented in Table III and to which we refer for the symmetry codes involved. The first three interactions shown link the reference molecule to two different neighbors (symm. codes #1, #2; X: O, N); the remaining ten link it to four different BF_4^- units

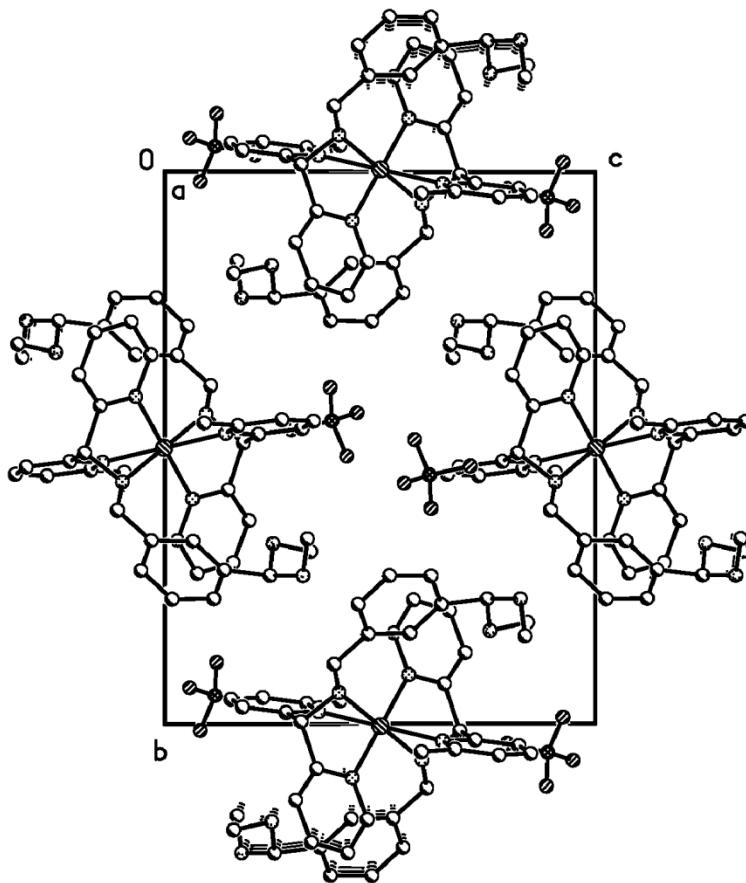
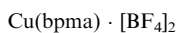


FIGURE 3 Packing view of a unit cell down the crystallographic *a* axis showing the channels defined by the molecular packing, in turn occupied by the counterions. For clarity, only one of the two disordered halves of each BF₄ unit is shown.

TABLE III Hydrogen bond distances (Å) and angles (°)

<i>D</i> – <i>H</i> ⋯ <i>A</i>	<i>d</i> (<i>D</i> – <i>H</i>)	<i>d</i> (<i>H</i> ⋯ <i>A</i>)	<i>d</i> (<i>D</i> ⋯ <i>A</i>)	∠(<i>DHA</i>)
C(12)–H(12A)⋯N(1)#1	0.96	2.48	3.226(7)	134.5
C(12)–H(12A)⋯N(3)#1	0.96	2.53	3.370(8)	146.4
C(1)–H(1A)⋯O(1)#2	0.93	2.55	3.366(7)	146.2
C(3)–H(3A)⋯F(2')#2	0.93	2.45	3.155(10)	132.3
C(4)–H(4A)⋯F(3')#3	0.93	2.45	3.278(9)	147.7
C(6)–H(6A)⋯F(3)#3	0.98	2.53	3.396(8)	147.5
C(6)–H(6A)⋯F(3')#3	0.98	2.59	3.472(9)	150.0
C(6)–H(6A)⋯F(2')#3	0.98	2.64	3.527(9)	150.3
C(13)–H(13A)⋯F(2')#3	0.93	2.21	3.134(9)	173.4
C(13)–H(13A)⋯F(3)#3	0.93	2.57	3.347(8)	141.1
(10)–H(10A)⋯F(3)#4	0.93	2.30	3.171(9)	155.6
C(10)–H(10A)⋯F(1)#4	0.93	2.60	3.381(6)	142.4
C(16)–H(16A)⋯F(2)#5	0.93	2.44	3.117(7)	129.2

Symmetry transformations used to generate equivalent atoms: #1 $-x, -y+1, -z$; #2 $-x+1/2, y-1/2, -z+1/2$; #3 $x, y, z-1$; #4 $x-1, y, z-1$; #5 $x+1/2, -y+3/2, z-1/2$.

(symm. codes #2 to #5, X: F). A survey in the CSD for similar C–H···FBF₃ contacts gave a mean value of 2.51(12) Å for the H···F distance for some 25 000 cases. The same calculation for the ten H···F contacts quoted in Table III gave 2.48(13) Å, indicating that the interactions are similar to those reported in the literature.

Summarizing: notable progress has been made in the last few years (mainly through the work of Karlin and co-workers) to mimic tyrosinase activity using tailor-made complexes with N-donor ligands; the hydroxylation of the arene ring in these models has been attributed to both electronic and steric effects [3,16,17]. However, in order for this process to occur the aromatic ring must be properly oriented with respect to the copper/oxygen intermediate. In the systems already studied by us [7,8], and in particular the one herein reported, it appears that such requirements are not fulfilled and simple copper(II) complexes are obtained instead.

Acknowledgment

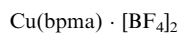
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Supplementary Data

Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 212748. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, fax: (44) 1223 336-033; e-mail: deposit@ccdc.cam.ac.uk.

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