Inorg. Chem. **2002**, *41*, 6956–6958

Inorganic Chemistry
Communication

Intramolecular “Aryl–Metal Chelate Ring” *π*,*π*-Interactions as Structural Evidence for Metalloaromaticity in (Aromatic α,α′-Diimine)–Copper(II) Chelates: Molecular and Crystal Structure of Aqua(1,10-phenanthroline)(2-benzylmalonato)copper(II) Three-hydrate

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Received September 5, 2002

By reaction of $Cu_2CO_3(OH)_2$, 2-benzylmalonic acid (H_2Bzmal), and 1,10-phenanthroline (phen), $[Cu(Bzmal)(phen)(H_2O)]\cdot 3H_2O$ (compound **1**) has been obtained and characterized by thermal, spectral, magnetic, and X-ray diffraction methods. The molecular structure of **1** is remarkably similar to that of $[Cu(Bzmal)(bipy)(H_2O)]\cdot 2H_2O$ (compound **2**, bipy = 2,2′-bipyridine). In both complexes, the aryl(Bzmal) ring produces an unexpected *π*,*π*-stacking interaction with the Cu(II)–(aromatic α,α′-diimine) chelate ring, at an average distance $d_{\pi-\pi}$ of 3.40 Å, involving roughly parallel and smoothly slipped rings. This insight is discussed as new structural evidence for metalloaromaticity of Cu(II)–(aromatic α,α′-diimine) chelate rings. Interestingly, **1** recognizes itself by a weak intermolecular *π*,*π*-stacking interaction between aryl(Bzmal) ligands to give pairs of complex molecules. In contrast, there is an intermolecular pyridyl–pyridyl *π*,*π*-stacking interaction also forming pairs of complex molecules in **2**.

Aromatic ring−ring or *π*,*π*-stacking interactions are intra- and/or intermolecular forces, which play relevant roles in molecular recognition processes, supramolecular chemistry, and biological systems. In this broad context, an interesting account for *π*,*π*-stacking interactions in metal complexes having aromatic N-donor ligands has been recently reported by Ch. Janiak[1]. In this connection, structural studies on Cu(II)−dicarboxylato complexes having suitable N-heterocyclic auxiliary ligands have proved the contribution of both hydrogen bonding and aromatic ring−ring stacking interactions to the crystal building. Structural comparisons on copper(II)−malonato complexes where the referred stackings are[2] or are not[3] presented reveal the influence of the *π*-acceptor character of the N-heterocyclic ligand (such as 2,2′-bipyridine[2a] (2,2′-bipy) or 1,10-phenanthroline[2c,d] (phen) and closely related ones[2b,e]) on the copper(II)−O(carboxyl) bond lengths. These findings strongly suggest an active electronic delocalization within the metal−N-heterocyclic chelate ring in such a way that it could exhibit some degree of “metalloaromaticity”. This is a classic concept recently reviewed and improved by H. Masui.[4] The increasing interest in this subject arises from its usefulness as a unifying approach for the reactivity, magnetic and/or spectral properties, and structure of so-called “metalloaromatic compounds”. Resonance energy stabilization, spectral and/or magnetic measurements, and various molecular structural parameters are considered the most suitable criteria for assessing the degree of aromaticity in appropriate compounds.[4]

We are interested in ternary mixed-ligand copper(II) complexes where one or more ligands have aromatic rings and could display intra- and/or intermolecular *π*,*π*-interactions.[5−8] In such context, we considered the possibility of obtaining (2-benzylmalonato)−copper(II) complexes with,

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10.1021/ic026004h CCC: $22.00

for example, 2,2′-bipy or phen as auxiliary ligands. After that, we knew that the crystal structure of [Cu(Bzmal)(2,2′-bipy)(H_2O)]•2H_2O (hereafter compound **2**) had been recently reported by Guan et al.,[9] who pointed out that "the intermolecular stacking in this compound differs from that in other reports", but apparently, the possibilities of metalloaromaticity in the Cu(II)−2,2′-bipy chelate ring were not taken into account. Consequently, we synthesized and characterized the title compound (hereafter compound **1**), we have succeeded in solving its crystal structure, and we used the CCDC deposited structural data of compound **2** for structural comparisons with our results. [Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Center CCDC No. 192100 for the title compound **1**. Data for **1** in CIF format are available as Supporting Information. Structural files and additional information on the physical properties of this compound could be obtained from the deposited data or supplied by the authors upon request.]

Compound **1** was prepared by reaction of $Cu_2CO_3(OH)_2$ (221 mg, 1 mmol, Aldrich) and H_2Bzmal (388 mg, 2 mmol, Aldrich) in water (150 mL) in a Kitasato flask, with heating ($T < 50$ °C) and stirring under reduced pressure (to remove the CO_2, byproduct), followed by the addition of phen (360 mg, 2 mmol). The solution was stirred and heated at 60 °C for 30 min more, left to cool, and slowly filtered (without vacuum) on a crystallization device. Slow evaporation at room temperature produced many well-shaped crystals of compound **1**. Plate or needles crystals could be observed, but an X-ray diffraction study confirmed that there was only one solid phase: yield 864 mg (85%). Analytical data[10] were consistent with a formula as Cu(Bzmal)(phen)•4H_2O, and our crystallographic results[11] revealed that only one water molecule was bound to the metal atom.

The asymmetric unit of compound **1** consists of one complex molecule (Figure 1) and three noncoordinated water molecules. A comparison of metal coordination parameters and copper(II)−malonato chelate ring conformation in compounds **1** and **2** (Table 1) reveals the most remarkable similarities of their internal geometries. In both complexes, the metal atom exhibits an elongated square pyramidal geometry (SP), and the Cu(II)−malonato-like ring exhibits a slightly distorted, puckered boat conformation. The SP coordination is rather common in Cu(II)−malonato complexes,[2,3,12] particularly in mixed-ligand copper(II) complexes with malonato and a N-heterocyclic[2,9] or N-aliphatic amines as secondary ligand.[12]

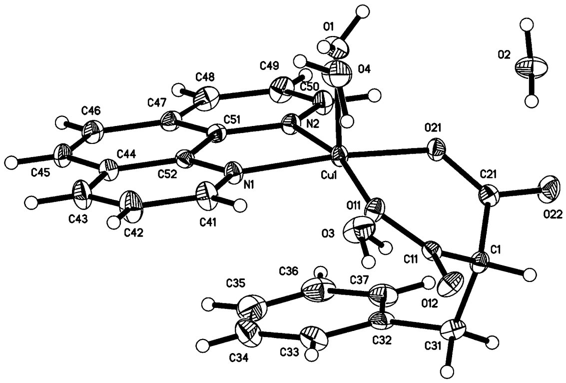

Figure 1. Complex molecule of [Cu(Bzmal)(phen)(H_2O)]•3H_2O (compound **1**). Bond lengths (Å): Cu(1)−O(11) 1.922(2), Cu(1)−O(21) 1.918(2), Cu(1)−N(1) 2.011(2), Cu(1)−N(2) 2.011(2), Cu(1)−O(1) 2.235(2). Trans angles (deg): N(1)−Cu(1)−O(21) 170.0(8), N(2)−Cu(1)−O(11) 165.1(8).

Table 1. Comparison of Structural Data for Compounds **1** and **2**

	1	**2**
Cu(II) coordination type	4 + 1	4 + 1
Cu−O(carboxyl) bond (Å)	1.918(2)	1.915(2)
Cu−O(carboxyl) bond (Å)	1.922(2)	1.928(2)
Cu−N(heterocyclic) bond (Å)	2.011(2)	1.998(2)
Cu−N(heterocyclic) bond (Å)	2.011(2)	2.007(2)
Cu−O(W) apical bond (Å)	2.235(2)	2.245(2)
trigonal distortion, τ (%)[a]	8.2	10.9
tetragonality, T	0.88	0.87
Atom deviats. from basal plane (MBP, Å)	±0.05(1)	±0.07(1)
Cu(II) displacement from MBP (Å)	0.190(1)	0.220(1)
"Cu−malonate" conformation	puckered boat	puckered boat

[a] $\tau = 100(\theta - \varphi)/60$, with θ and φ being the trans coordination angles.

Curiously, compounds **1** and **2** have short Cu−O(carboxyl) distances, in the range of those of other Cu/malonato/bidentate N-heterocycle complexes[3−7] (1.885(2)−1.932(2) Å). These data strongly suggest an electron delocalization effect within the nearly planar copper(II)−(aromatic α,α′-diimine) chelate ring. In contrast, the Cu−O(carboxyl) bond lengths in *catena*-poly[aqua(benzimidazole)(μ-malonato)]-copper(II)[3a] are 1.953(3) and 1.970(3) Å, respectively, in the usual range of copper(II)−malonato complexes without bidentate N-heterocyclic ligands (1.93−1.98(2) Å). Unexpectedly, we also appreciate that in **1** and **2** the conformational flexibility of the benzyl arm enables the stacking of its "aromatic Bzmal ring" and the corresponding Cu−(aromatic α,α′-diimine) chelate ring. As Figure 2 shows, such intramolecular stacks occur in a roughly "face-to-face" manner (a strict "face-to-face" stack is very unusual and is not possible between rings of different sizes[1]). To assess the implication of such chelate rings in π,π-stacking interactions, we decide to include this ring in the analysis of short ring interactions with the program PLATON.[13] Relevant structural

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(10) Analytical data (%). Needle crystals: C 52.19, H 5.52, N 5.70. Plate crystals: C 52.11, H 5.05, N 5.62. Calcd for $C_{22}H_{24}CuN_2O_8$: C 52.02, H 4.79, N 5.51.

(11) Crystal data: sky-blue plate crystal; empirical formula, $C_{22}H_{24}CuN_2O_8$; fw, 507.97; $T = 208(2)$ K; monoclinic system, space group $P2_1/c$. Unit cell: $a = 9.214(6)$ Å, $b = 13.454(1)$ Å, and $c = 18.738(2)$ Å; $\beta = 102.98°$; $V = 2267.7$ Å^3. $Z = 4$. $F(000)$ 1052. Calcd density 1.488 Mg m^{-3}. $\mu = 1.014$ mm^{-1}. GOF on $F^2 = 1.025$. Final $R = 0.039$, $R_w = 0.096$ [$I > 2\sigma(I)$].

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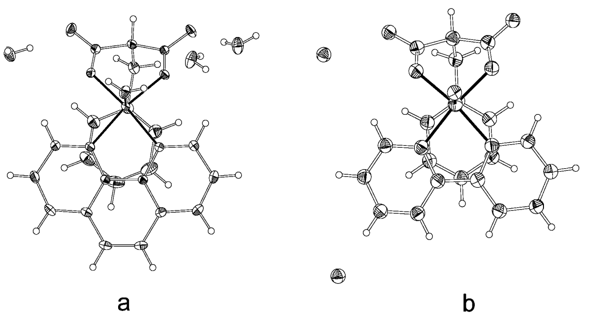

Figure 2. Asymmetric unit of compound **1** (a) and compound **2** (b), showing the roughly "face-to-face" stacking of the aryl moiety of Bzmal ligand and the Cu(II)−(aromatic α,α′-diimine) chelate ring.

Table 2. Intramolecular "Aryl−Metal Chelate Ring" and Intermolecular π,π-Stacking Parameters for Compounds **1** and **2**

stacking params	**1**	**2**
	Intramolecular Chelate/Aryl Ring	
av $d(\pi-\pi)$ Å	3.38	3.41
$d(c_1-c_2)$ Å/α deg	3.49/2.1	3.51/8.2
$d(\perp c_1-P(2))$ Å/β deg	3.39/15.5	3.37/10.7
$d(\perp c_2-P(1))$ Å/γ deg	3.36/13.9	3.45/16.4
	Intermolecular	
	benzyl/benzyl	pyridyl/pyridyl
av $d(\pi-\pi)$ Å	3.33	3.36
$d(c_1-c_2)$ Å/α deg	4.23/0.02	3.88/0.03
$d(\perp c_1-P(2))$ Å/β deg	3.43/36.0	3.40/28.8
$d(\perp c_2-P(1))$ Å/γ deg	3.43/36.0	3.40/28.8

parameters[1] are listed in Table 2. As far as concerns regarding the intramolecular stacking, it should be noted that the angle (α) between planes of the Cu−(aromatic α,α′-diimine) chelate ring and the aryl(Bzmal) ligand has a lower value in **1** (2.1°) than in the closely related **2** (8.2°) despite the similar centroid−centroid distances ($d_{c-c} = 3.50 \pm 1$ Å). In both cases, it should be emphasized that the slipping angles β and γ (defined by the vector c_1-c_2 and the normal to plane P(1) or P(2) from c_2 and c_1, respectively) have reasonably low values.

Without doubt, the most interesting observation is that both molecules exhibit similar intramolecular stacking parameters and they are appropriate enough to consider that effective "metal chelate ring/aromatic ring" π,π-stacking interaction is operative. By far, it is clear that the metalloaromaticity in Cu−(aromatic α,α′-diimine) chelate rings seems to have been structurally proved and perhaps would promote further experimental or theoretical approximations[4] by other researchers. On the other hand, data of Table 2 and Figure 3a reveal that compound **1** displays a weak intermolecular π,π-stacking interaction between aryl(Bzmal) rings from adjacent molecules, but no phen−phen stack is observed. In addition, compound **2** exhibits an intermolecular pyridyl−pyridyl π,π-stacking (Figure 3b). In both compounds, such intermolecular interactions form pairs of molecules (Figure 3) which act as building blocks with noncoordinated water molecules in a 3D hydrogen bonded network.

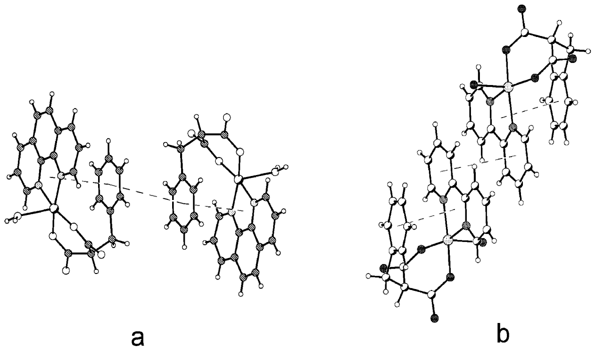

Figure 3. Intramolecular "aryl−metal chelate ring" and intermolecular "benzyl−benzyl" or "pyridyl−pyridyl" π,π-stacking interactions in compounds **1** (a) and **2** (b). Dashed lines link the centroids of two rings involved in each stacking interaction.

Compound **1** loses part of the water in air-dry flow and decomposes as $[Cu(Bzmal)(phen)(H_2O)]\cdot 1.28H_2O$ in four steps. The first corresponds to all remaining water, the next two give CuO(phen), and the last leaves CuO as residue. The FT-IR spectrum has expected bands for water, Bzmal, and phen. Electronic (ν_{max} 15.5 kK) and ESR spectra ($g_{\parallel}$ 2.18, $g_{\perp}$ 2.06) agree well with misaligned $CuN_2O_2 + O$ chromophores in the crystal. The compound follows a Curie−Weiss-like behavior (80−300 K, $C = 0.44$, $\theta = 4.34$, $\mu_{Cu} = 1.87$ μ_B).

To our knowledge the intramolecular π,π-stacking of the aryl(Bzmal) and Cu−(aromatic α,α′-diimines) chelate rings represents new structural evidence of the metalloaromaticity. In addition, compounds **1** and **2** display different molecular patterns to recognize themselves and build the crystal packing. Interestingly, the referred intra- and intermolecular π,π-stacking interactions coexist with an extensive 3D hydrogen bonding network.

Acknowledgment. We are grateful to the DGI (MCYT, Spain) for financial support (Research Project BQU2002-04523-C02-01/02). D.Ch.-L. is gratefully indebted to the AECI (MAE, Spain) for a Ph. Doctoral grant.

Supporting Information Available: Crystallographic data for **1** in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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