



Synthesis and crystal structure of inorganic-organic hybrids of Cu(II) complexes of malonic acid

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ABSTRACT A two new copper(II) complexes, $2[\text{Cu}(\text{phen})(\text{mal})\text{H}_2\text{O}] \cdot 1.5 \text{H}_2\text{O}$ (**1**) and $[\text{Cu}(\text{bipy})(\text{mal})\text{H}_2\text{O}] \cdot \text{H}_2\text{O}$ (**2**) (where, phen=1, 10-phenanthroline, bipy=2,2'-bipyridine, mal= malonic acid) have been synthesized and the molecular structure of the compounds have been confirmed by single crystal X-ray diffraction technique. In both the complexes, the Cu(II) ion displays a five coordinated-geometry where the Cu atom is coordinated by two nitrogen atoms of one 1,10-phenanthroline/2,2'-bipyridine ligand, two oxygen atoms of one malonate anion and one oxygen atom of a coordinated water molecule forming a slightly distorted square pyramidal geometry. The title compounds **1** and **2** crystallized in the triclinic system, space group P-1. The crystal structures are stabilized and strengthened by intermolecular O—H...O hydrogen bonds involving both the coordinated and uncoordinated water molecules and weak C—H...O interactions.

KEYWORDS : phenanthroline, bipyridine, copper, malonic acid, X-ray structure.

1. Introduction

Supramolecular systems based on coordination compounds have received much attention because of their potential use as sensors, probes, photonic devices, and catalysts and in host-guest chemistry [1]. Construction of organic inorganic hybrid materials is of interest for interesting framework structures and a variety of applications [2-7]. Bipyridine and its homologous such as phenanthroline as well as substituted phenanthrolines are widely used in the formation of metal complexes [8] for their potential applications in electrochemistry, analytical chemistry, biochemistry as a substitute for amino acid side group [9,10]. These ligands due to their chelating nature in metal complexes convincing control the aggregation behaviour by effectively chelating around the metal centre. In this regard some of the substituted bipyridine and phenanthroline like ligands have been studied [11, 12]. Among the copper complexes explored so far, attention has been mainly focused on the copper(II) complexes of 1,10-phenanthroline ligand due to their high nucleolytic efficiency [13] and numerous biological activities such as antitumor [14], anticandida [15] and antimicrobial [16,17] activities, etc., These complexes have also been widely utilized as foot printing agents of both proteins and DNA [18] probes of the dimensions of the minor groove of duplex structures [19] and identifiers of transcription start sites [20]. It has also been demonstrated to be an efficient antibacterial and also as an antiplaque agent. The crystal structure of malonate-bridged hexamethylenetetramine coordination polymers containing Mn(II) and Cu(II), malonate-based copper(II) coordination compounds [21], copper complex of bis [(2-aminoethyl)aminomethyl] malonate [22], $[\text{Cu}(\text{mal})(\text{bipym})\cdot\text{H}_2\text{O}]$ [23], $[\text{Cu}_2(\text{mal})_2(\text{H}_2\text{O})_2(4,4'\text{-bipy})]$ [24], $[\text{Cu}_2(\text{mal})_2(\text{H}_2\text{O})_2(2,4\text{-bipy})_2]\cdot 2\text{H}_2\text{O}$ [25], $\{(\text{H}_2\text{bpe})[\text{Cu}(\text{mal})_2]\}_n\cdot 4n\text{H}_2\text{O}$ [bpe=bis(4-pyridyl)-ethylene] [26] have been reported in the literature. Phen can easily form π - π interactions among their aromatic moieties, which are either intra or intermolecular [27-29].

2. Experimental section

Preparation

An aqueous solution of copper acetate monohydrate $[\text{Cu}(\text{OAc})_2\cdot\text{H}_2\text{O}]$ (49.7 mg in 5ml water) was added to a methanolic solution of malonic acid (26 mg in 10ml methanol). The mixture was stirred in a magnetic stirrer for 20 minutes. Then 1, 10-phenanthroline/ 2,2'-bipyridine (49.8/ 39 mg dissolved in 15ml methanol) was added dropwise to this mixture. The resultant solution was again stirred at room temperature for another 40 - 60 minutes and then kept as such. After four days dark blue coloured crystals were obtained from their respective solutions. (CCDC deposit Numbers: 1010125 for **1** and 1020237 for **2**)

3. X-ray data collection

For the compound **1** and **2**, the X-ray data were collected using BRUKER SMART APEXII CCD [30] diffractometer with a graphite monochromated MoK α radiation. The absorption correction was performed by multi scan method [31].

4. Structure solution and refinement

The data were reduced by using the program SAINT [30] and empirical absorption corrections were done by using the SADABS [30]. The structures were solved by direct methods using SHELXS-97 [33] and subsequent Fourier analyses, refined anisotropically by full-matrix least-squares method using SHELXL-97 [32]. The crystal data and details of structural determination are listed in Table. 1A for compound **1** and Table. 1B for compound **2**.

5. Results and discussion

The ORTEP views of the compounds are shown in Figure 1A & 1B. In (**1**) two crystallographically independent Cu(II) complex molecules are found. The asymmetric unit contains two complex molecules and three uncoordinated water molecules. In each unit a bidentate malonate anion, one 1,10-phenanthroline molecule and a coordinate water molecule coordinated with Cu(II) ion to form a square pyramidal environment. The bond angles around the Cu(II) centres ($\angle \text{N1B—Cu2—O3B}=172.53(6)^\circ$ and $\angle \text{N1A—Cu1—O3A}=168.60(6)^\circ$) are slightly larger than the second-largest ones ($\alpha: \angle \text{N2B—Cu2—O1B}=164.03(7)^\circ$ and $\alpha: \angle \text{N2A—Cu1—O1A}=164.81(7)^\circ$) (Table. 2A). Atoms O1A, O3A, N1A and N2A/ O1B, O3B, N1B and N2B consist of a square planar geometry with some deviation from perfect square plane. The apical positions are occupied by O1W and O2W respectively. The Cu1—O1W/ Cu2—O2W lengths are 2.263(2) and 2.292(2) Å in the two molecules, slightly shorter than the value of 2.332 (4) Å observed for Cu—O water Å in the complex $[\text{Cu}(\text{Hdapsox})(\text{H}_2\text{O})](\text{ClO}_4)$ where H₂dapsox is 2',2'-(2,6-pyridinediyl)diethylidene) dioxamohydrazide [35] but similar to that observed in the complex $[\text{Cu}(\text{mal})_2(\text{IX})(\text{H}_2\text{O})_2]_n$ [36] where IX is 1,4-bis(imidazole-1-yl-methylene)benzene) (2.277 Å).

In complex **2**, as illustrated in Figure 1B, the Cu(II) atom exhibits a slightly distorted square pyramidal coordination sphere, defined by two oxygen of one bidentate malonate anion, a 2,2'-bipyridine and a water molecule. Two nitrogen atoms from bipy ligand and O atoms from malonate dianion forming the equatorial plane and apical position is occupied by water molecule.

Although the base of the pyramid is planar, the bond angles deviate from the ideal value of 90° (Table 2B). The present complex is monomeric near copper metal centre. The complex molecule has an approximate plane of symmetry passing through atoms Cu1 and O1W bisecting the N2—Cu1—N4 (80.97) and O1—Cu1—O3 (93.05). The Cu—N distances are unequal $[\text{Cu1—N2}= 2.0022 \text{ \AA}$ and $\text{Cu1—N4} 1.9956 \text{ \AA}]$ while Cu-O distances $[\text{Cu1—O1}= 1.9239 \text{ \AA}$ and $\text{Cu1—O3} 1.9375 \text{ \AA}]$. These distances are somewhat longer than reported values.

6. Hydrogen bonding

In complex **1**, the malonate ligand sustained two deprotonated carboxylate groups leading to a dinegative charge on the ligand. Two

symmetry related malonate anions are bridged by adjacent uncoordinated oxygen atoms of three water molecules via O—H...O hydrogen bonds forming a ring with graph set notation $R^2_1(18)$ as shown in Fig 2. One of the uncoordinated water molecule O5W (H5W) interacts with malonate oxygens O3B and O4B forming a ring with graph set notation $R^2_1(4)$. O4W uncoordinated water molecule acts as a donor (H3W) to O2W while the same O4W acts as an acceptor to O5W water molecule (H6W) (Table 3A). These uncoordinated water molecules play a major role in extending these supramolecular architectures. Further the crystal structure is stabilised by weak C—H...O hydrogen bonding interactions Fig 3.

In complex 2, there is a O—H...O bond found between the coordinated water molecule and un-coordinated water molecule (O1W—H1W...O2W= 2.851Å, 177°). The other H atom (H2W) interacts with malonate Oxygen O4 atom through O—H...O bond. (2.793 Å, 175°). Two oppositely running copper complex molecules are interconnected by uncoordinated water molecule via O—H...O hydrogen bonds forming a supramolecular ladder (Fig. 4). C4 atom of bipyridine (H4) interacts with O1W water molecule through C—H...O hydrogen bonds (Table 3B). Two such oppositely running molecules interact via a pair of C—H...O bonds forming a cage like structure as shown in Fig 5.

7. Conclusion

Copper + malonic acid complexed with phenanthroline/2,2'-bipyridine have been synthesized and characterized by X-ray crystallography. The malonate ligand sustained two deprotonated carboxylate groups leading to a dinegative charge on the ligand. Here Cu(II) ions adopts distorted square pyramidal geometries. This is of interest in the design of metallo-organic hybrid frameworks, crystal engineering, biomolecular recognitions etc.

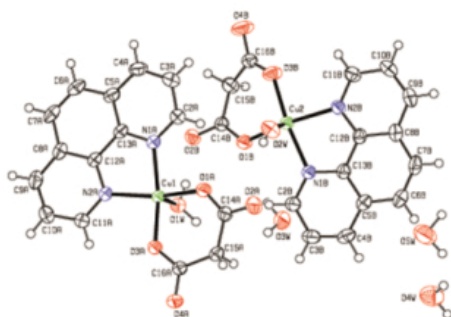


Fig 1A. ORTEP view of the title compound (I) showing 50% probability displacement ellipsoids.

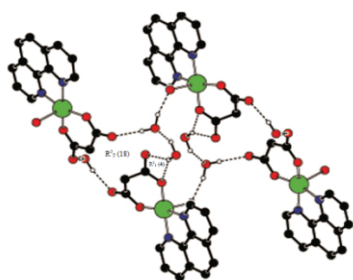


Fig 2. A packing view of O—H...O interactions forming a loop (I)

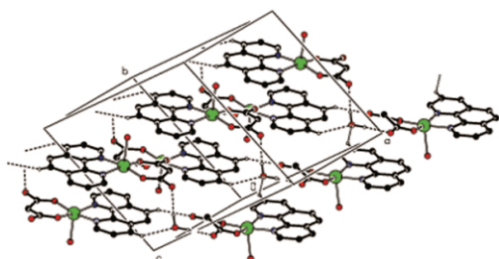


Fig 3. A view of the two-dimensional layer constructed by O—H...O and C—H...O hydrogen bonding interactions.

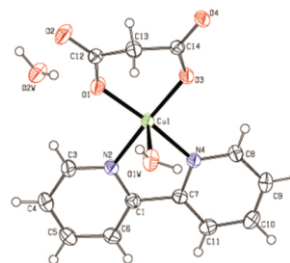


Fig1B. ORTEP view of the title compound (2) showing 50% probability displacement ellipsoids.

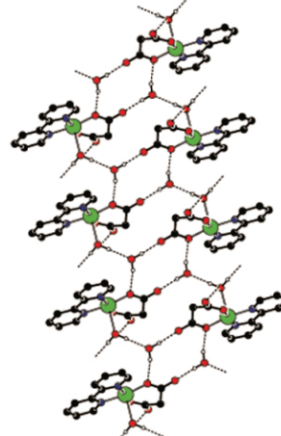


Fig 4. A View of supramolecular ladder of title compound (II).

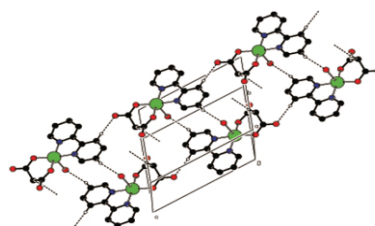


Fig 5. A pair of C—H...O hydrogen bonds forming a cage in compound (II)

Table 1A - Crystal Data and Details of the Structure Determination for compound 1 & 2

Compound	1	2
CCDC deposition numbers	1010125	1020237
Formula	$2(C_{13}H_{12}CuN_2O_5) \cdot 3(H_2O)$	$(C_{13}H_{12}CuN_2O_5) \cdot (H_2O)$
Formula Weight	780.67	357.81
Crystal System	Triclinic	Triclinic
Space group	P-1 (No. 2)	P-1 (No. 2)
a, b, c [Å]	11.539(5) 11.731(5) 12.500(5)	7.133(5) 10.399(5)
10.707(5)		
alpha, beta, gamma [°]	92.153(5) 105.422(5) 109.169(5)	105.841(5)
104.615(5) 105.193(5)		
V [Å ³]	1526.2	691.0(7)
Z	2	2
D(calc) [g/cm ³]	1.699	1.72
Mu(MoKa) [/mm]	1.471	1.613
F(000)	798	366
Crystal Size [mm]	0.21 x 0.16 x 0.17	0.20 x 0.15 x 0.10
Temperature (K)	293(2)	293(2)
Radiation [Å]	MoKa 0.71073	MoKa 0.71073
Theta Min-Max [°]	1.71, 26.50	2.11, 26.89
Dataset	-14; 14; -14; 14; -15; 15	-8; 8; -13; 13; -13;
13		
Tot., Uniq. Data, R(int)	22977, 6288, 0.024	10067, 2892, 0.032
Observed data [I > 2.0 σ (I)]	5704	2717
Nref, Npar	6288, 479	8412, 375
R, wR2, S	0.0253, 0.0702, 1.027	0.0247, 0.0656, 1.099
$w = 1/[\sigma^2(F_o^2) + (0.0581P)^2]$	where $P = (F_o^2 + 2F_c^2)/3$	where
$P = (F_o^2 + 2F_c^2)/3$		
Min. and Max. Resd. Dens. [e/Å ³]	-0.427, 0.467	-0.365, 0.41

Table 2A. Selected bond lengths (Å) and bond angles (°) for compound 1

Cu1-O1A	1.9087(15)	N2A-C12A	1.355(3)
Cu1-O1W	2.2628(17)	N2A-C11A	1.322(2)
Cu1-O3A	1.9216(17)	N1B-C2B	1.320(3)
Cu1-N1A	2.0174(18)	N1B-C13B	1.354(2)
Cu1-N2A	2.0251(18)	N2B-C11B	1.327(3)
Cu2-N2B	2.0272(17)	N2B-C12B	1.356(3)
Cu2-O2W	2.292(2)	Cu2-O3B	1.904(2)
Cu2-O1B	1.9256(15)	Cu2-N1B	1.9908(19)
N1A-C13A	1.358(2)	N1A-C2A	1.320(2)
O1A-Cu1-O1W	99.24(6)	C2A-N1A-C13A	118.30(16)
O1A-Cu1-O3A	94.74(6)	Cu1-N1A-C13A	112.74(11)
O1A-Cu1-N1A	89.32(6)	Cu1-N1A-C2A	128.90(14)
O1A-Cu1-N2A	164.81(7)	Cu1-N2A-C12A	112.60(11)
O1W-Cu1-O3A	93.73(6)	Cu1-N2A-C11A	129.31(14)
O1W-Cu1-N1A	96.13(6)	N1A-C2A-C3A	122.24(19)
O1W-Cu1-N2A	93.75(6)	C2B-N1B-C13B	118.82(17)
O3A-Cu1-N1A	168.60(6)	Cu2-N1B-C2B	128.09(14)
O3A-Cu1-N2A	92.23(6)	Cu2-N1B-C13B	113.00(12)
N1A-Cu1-N2A	81.45(6)	Cu2-N2B-C12B	111.87(11)
O2W-Cu2-O3B	96.27(7)	Cu2-N2B-C11B	129.77(14)
O2W-Cu2-N1B	85.87(7)	O2W-Cu2-N2B	94.40(6)
O3B-Cu2-N1B	172.53(6)	N1B-Cu2-N2B	81.85(6)
O1B-Cu2-O2W	100.00(6)	O1B-Cu2-O3B	94.39(6)
O1B-Cu2-N1B	92.27(7)	O1B-Cu2-N2B	164.03(7)
Cu1-O1A-C14A	129.33(12)	Cu1-O3A-C16A	127.76(11)
Cu2-O1B-C14B	126.30(13)	Cu2-O3B-C16B	129.77(14)
Cu2-O2W-H2O	121(3)	N2A-C11A-C10A	122.4(2)
N2A-C12A-C8A	123.31(16)	N2A-C12A-C13A	116.43(15)
N1A-C13A-C12A	116.38(16)	N1A-C13A-C5A	123.30(16)
O1A-C14A-O2A	121.79(18)	N1B-C2B-C3B	121.99(19)
O2A-C14A-C15A	117.24(18)	O1A-C14A-C15A	120.96(16)
O3A-C16A-O4A	121.98(16)	O3A-C16A-C15A	121.71(17)
O4A-C16A-C15A	116.31(18)	N2B-C12B-C13B	116.27(15)
N1B-C13B-C5B	123.24(17)	N1B-C13B-C12B	116.53(17)
O1B-C14B-O2B	122.56(17)	O2B-C14B-C15B	117.80(16)
O1B-C14B-C15B	119.62(15)	O3B-C16B-O4B	121.31(19)

Table 2B. Selected bond lengths (Å) and bond angles (°) for compound 2

Cu1-O1	1.9239	Cu1-O1W	2.526
Cu1-O3	1.9375	Cu1-N2	2.0022
Cu1-N4	1.9956	O1-C12	1.2843
O2-C12	1.2206	O3-C14	1.2779
O4-C14	1.2345	N2-C3	1.3375
N2-C1	1.3467	N4-C8	1.3393
N4-C7	1.3501	O1-Cu1-O1W	99.76
O1-Cu1-O3	93.05	N4-C7-C1	114.58
O1-Cu1-N2	90.72	N4-C8-C9	122.03
O1-Cu1-N4	169.51	O1W-Cu1-O3	94.94
O1W-Cu1-N2	90.44	O1W-Cu1-N4	86.78
O2-C12-C13	120.06	O3-Cu1-N2	172.81
O1-C12-C13	117.66	O3-Cu1-N4	94.56
O1-C12-O2	122.26	N2-Cu1-N4	80.97
Cu1-O1-C12	124.46	O3-C14-C13	118.59
Cu1-O3-C14	123.41	O4-C14-C13	117.98
Cu1-N2-C1	115.11	O3-C14-O4	123.42
Cu1-N4-C8	125.64	C1-N2-C3	126.17
C7-N4-C8	119.32	C1-N2-C4	118.71
N2-C1-C7	114.3	Cu1-N4-C7	115.04
N2-C3-C4	122.51	N2-C1-C6	121.92
N4-C7-C11	121.71		

Table 3A. Hydrogen bonding geometry (Å, °) for compound 1

D-H...A	Distance, Å			D-H...A (°)
	D-H	H...A	D...A	
O1W-H1W1...O2B	0.87(2)	1.86(2)	2.720(2)	170(2)
O3W-H1W...O4A	0.92(2)	2.07(2)	2.984(3)	175(2)
O1W-H2W2...O4A	0.90(3)	1.93(3)	2.818(3)	175(2)
O3W-H2W...O2B	0.91(3)	1.92(3)	2.825(3)	171(3)
O4W-H3W...O2W	0.96(5)	1.85(5)	2.768(3)	160(5)
O4W-H4W...O2A	0.88(2)	1.93(3)	2.784(3)	164(3)
O5W-H5W...O3B	0.96(4)	2.42(5)	3.311(3)	155(4)
O5W-H5W...O4B	0.96(4)	2.06(4)	2.915(3)	148(5)
O5W-H6W...O4W	0.95(4)	2.20(3)	2.812(3)	121(3)
O2W-H2O...O2A	0.57(2)	2.43(3)	2.965(3)	159(4)
C4A-H4A...O3W	0.93	2.45	3.268(3)	146
C7A-H7A...O4B	0.93	2.49	3.272(3)	141
C10B-H10B...O3W	0.93	2.46	3.285(3)	149

Table 3B. Hydrogen bonding geometry (Å, °) for compound 2

D-H...A	Distance, Å			D-H...A (°)
	D-H	H...A	D...A	
O1W-H1W...O2W	0.90	1.95	2.8511	177
O1W-H2W...O4	0.90	1.90	2.7934	175
O2W-H3W...O1	0.90	1.98	2.8648	167

O2W-H4W...O2	0.89	1.88	2.7624	173
C3-H3...O1	0.93	2.43	2.9449	115
C4-H4...O1W	0.93	2.53	3.4077	157
C6-H6...O4	0.93	2.46	3.3912	176
C8-H8...O3	0.93	2.54	3.0526	115
C13-H13A...O2W	0.97	2.57	3.5232	166

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