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A one dimensional coordination polymer: poly{[[(u-dcpdaa-K4-O1:O2:O3:O4)(MeOH)2 Copper(II)]bis[(aquo)(dcpdaa-K4-O1:O2:O3:N1)Copper(II)]] dihydrate}

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ABSTRACT

The new title one-dimensional homo-trinuclear Cu3 coordination polymer {[Cu3(HL2)2(H2O)2(CH3OH)1.18)]. 2H2 O}n (1) was isolated as a green solid by heating a mixture of 2,5-(bis(dicarboxyphenyl)diacetic acid amine (dcpdaa) with Cu (NO3)2 in methanol in the presence of NaOH. The coordination polymer has been characterized by FTIR and X-ray single crystal diffraction. It consists of two dependent Copper (II) centers were linked by a six-coordinate Cu (II) ion through the carboxylic oxygen ligands o HL3-. The two dependent Cu (II) centers, features two very similar pyramidal with CuNO4 chromophores. Three-dimensional metal-organic framework were constructed via H-bonding of the terminal non-bonded carboxylic group of the ligand with lattice water molecules.

KEYWORDS: *Homo-trinuclear; 2,5-dicarboxydiacetic acid amine; coordination polymer ؛one-dimensional; octahedral.*

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INTRODUCTION

In the last decade, much research on metal -organic framework has mostly focused on coordination polymer with rigid organic ligands containing either N or O-atom donors or both [1,2,3,4,5]. Flexible Polycarboxylate ligands present very rich coordination chemistry, because of their ability to bridge transition metal ions generating various polynuclear complexes also, acts as good hydrogen bond acceptors capable of assembling supramolecular structures [6,7,8]. It is known that assembly of coordination networks is not only controlled by the geometry of metal ions but also determined by the nature of the ligand. By choosing appropriate multidentate carboxylate ligands you can obtain the desired polymer. The terminology used to describe porosity, which is often assumed in metal-organic frameworks, seems inappropriate in which the included solvent molecules cannot be removed without lose of framework integrity [9]. It seems now approved that a MOF should exhibit 3D structure with some degree of porosity, which have many application areas such gas storage, drug delivery, optics and catalysis [10,11,12]. Due to the flexible nature of copper (II) coordination sphere, assisted by the Jahn-Teller effect which can be realized either by distortion of an octahedral geometry to give a 4+1+1 bonding, or square pyramidal to give a 4+1 bonding or else by a change in coordination number as an alternative means of lifting the degeneracy of unequally occupied d-orbitals. Due to the various bridging modes of the carboxylate ligands such as syn-syn, syn-anti and anti-anti configuration, which provide a means for efficiently transmitting magnetic information in paramagnetic metal ions, so copper is the best choice [13]. Herein, we report the synthesis and crystal structure of the title compound.

MATERIALS AND METHODS

MATERIALS AND MEASUREMENTS

2,5-(bis(dicarboxyphenyl)diacetic acid amine (dcpdaa) was prepared using previously described method [14]. All other chemicals used were of reagent grade BDH or Aldrich. All reactions were performed under atmospheric pressure. Fourier Transform Infrared Spectroscopy (FTIR) spectra were recorded at room temperature with a Bruker IFS-2 5OPUS/IR (Bruker Analytic Gmbhg, Hanau, Germany) over 400 to 4000cm-1 range with reflections of 4 cm-1.

SYNTHESIS OF {[CU3(HL2)2(H2O)2(CH3OH)1.18)]. 2H2O}N (1)

The title complex was prepared by heating a mixture of 2,5-(bis(dicarboxyphenyl))diacetic acid amine (H4L) (0.34 m mol, 0.10 g) in (1ml H2O + 9 ml MeOH + few drops of Et3N) with Cu (ClO4)2. 6H2O (0.48 m mol, 0.10 g) in (1ml H2O + 9 ml MeOH) Green solution was formed, , the solution was changed to a dark- green precipitate after half an hour. By filtration and dissolving the green solid in H2O, block light-blue crystals suitable for analysis were obtained within one week. The title complex (1) was characterized by X-ray diffraction and by FTIR (cm-1). 3336br, 3054br, 1613 m, 1598m, 1563m, 1457s, 1274 s, 997s, 904m, 823s, 762s, 734s, 704s

CRYSTAL STRUCTURE DETERMINATION AND REFINEMENT OF THE TITLE COMPLEX.

Crystal structure data for complex (1) were collected from a single crystal sample, which was mounted on a loop fiber using a Bruker Venture diffractometer equipped with a photon III CMOS detector, a Helios MX optics and kappa goniometer (λ Cu Kα = 1.34139 Å). The structure was solved using SHELXT 2015 (Sheldrick et al., 2008) [15] and for computing structure refinement by (Bourhis 2015) [16] and for computing molecular graphic and molecular materials by Olex2, 1.5 (Dolomanov et al. 2009) [17]. (CIF files are available from the Cambridge Crystallographic Data Center (CSD Code 2219536).

Table 1: Crystal data and structure refinement of complex 1.

Empirical formula		$C_{24}H_{20}Cu_3N_2O_{18}$. 1.184($CH_4O$) 4($H_2O$)
Formula weight		925.07
Temperature		150.0(2)K
Crystal system		Monoclinic
Space group		*P2₁/c*
	a	8.900(3)(2) Å
	b	23.3385(8) Å
	c	8.0751(13) Å
β		90 °
Volume		2119.83(6) $Å^3$
Z		4
$P_{calc}g/cm^3$		1.759
μ		14.646 mm^{-1}
F(000)		1136.0
Crystal size		0.22 × 0.12 × 0.11 mm^3
Radiation		Cu Kα (λ = 1.54184)
2Θ range for data collection/°		10.026 to 133.24
Index ranges		$-17 \leq h \leq 17, -13 \leq k \leq 13, -12 \leq l \leq 15$
Reflections collected		14652
Independent reflections		1867 [R_{int} = 0.0534, R_{sigma} = 0.0254]
Data/restraints/parameters		1867/0/143
Goodness-of-fit on F^2		1.097
Final R indexes [I>=2σ (I)]		R_1 = 0.0433, wR_2 = 0.1075
Final R indexes [all data]		R_1 = 0.0522, wR_2 = 0.1206
Largest diff. peak/hole / e $Å^{-3}$		0.81/-0.54

RESULTS AND DISCUSSION

crystallizes in the mono-clinic space group P21/c. Details of the x-ray data collection of 1 are summarized in (Table 1) and selected bond lengths and angles are listed in (Table 2). The homo tri-nuclear Cu3 coordination polymer (Figure 1a) was synthesized by the reaction between, Copper (II) perchlorate and H4 L as a ligand (Scheme 1) and characterized by FTIR and X-ray single crystal diffraction.

$$H_4L + Cu\ (ClO_4)_2.6H_2O \longrightarrow \{[Cu_3(HL_2)_2(H_2O)_2(CH_3OH)_{1.18})].2H_2O\}_n$$

Scheme 1

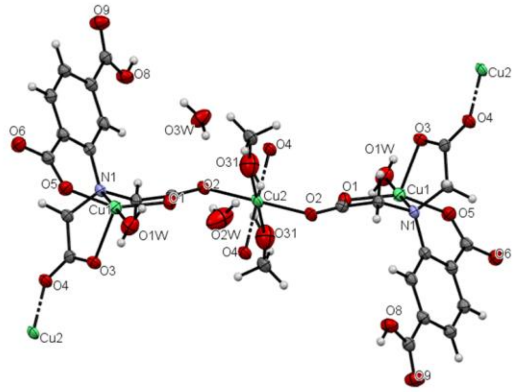


Figure 1. (a) Crystal Structure of the Coordination Polymer (1)

The title coordination polymer is built from a three Cu(II) ions and a tetra-dentate HL3- as a skeleton ligands (Scheme 2) and two H2O molecules in the crystal lattice. The crystal packing structure (figure 1b) is reinforced by hydrogen bonds between non-protonated and protonated carboxylate groups and the lattice water molecules.

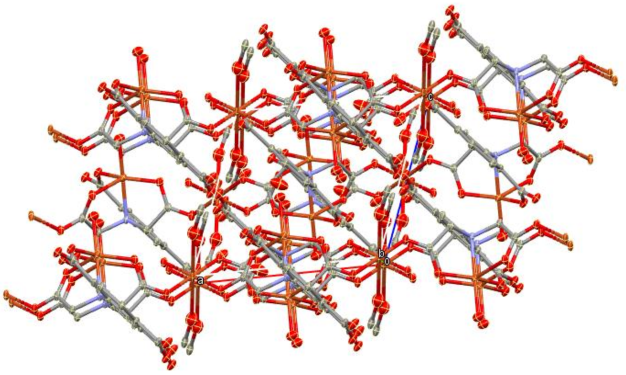
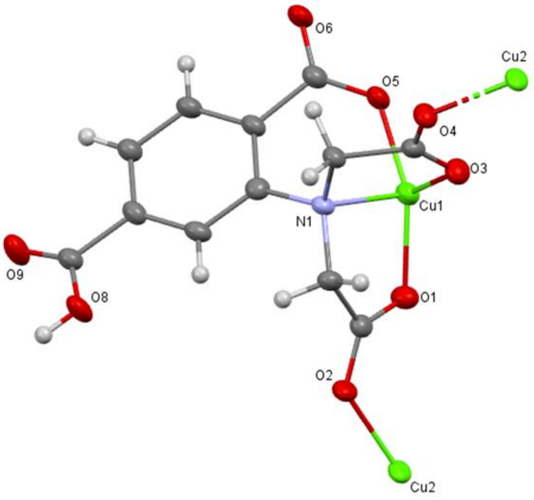


Figure 1. (b) Packing of I, with view along down reciprocal cell axis perpendicular to ab plane

The homo-coordination polymer Cu3, consists of asymmetric unit contains two dependent Cu (II) centers, features two very similar pyramidal Cu1 and Cu3 with CuNO4 chromophores and hexa-coordinate Cu2 with CuO6-chromofore. The five coordinate Cu (II) ions both adopting a (4+1) distorted square-pyramidal environment (t = 0.38 as described by the parameter t = (α - β)/60°, where the trans-angles α = β = 180° for perfectly square-pyramidal and α = 120° and β = 180° for perfectly triagonal-bipyramidal, where β is the largest angle and α the second largest). For complexes that deviate from ideal geometries, the t-parameter will be between 0 and 1 [18]. Each of the five coordinate Cu (II) centers was surrounded by four O-atoms and one N-atom from two carboxylate arms, one phenyl carboxylate group and one water molecule. The basal plane was occupied by three O-atoms and one N-atom (O1, O5, N1 and OW) while the apical site was occupied by O3. As expected for Cu (II) ions in square-pyramidal geometry, the weak apical Cu1---O3 bond distance (2.165 Å) of the ligand is significantly longer than the remaining four distances in the Cu1-coordination polyhedron (Cu1---O1 = 1.966 Å, Cu1---O5 = 1.834 Å, Cu1---OW = 1.92 Å (Figure 1c). This circumstance is characteristic of Jahn - Teller systems. The Cu2 ion which is octahedrally surrounded by 6O-atoms of two methanol molecules in the axial position with a Cu---O distance of 2.51 Å, these two methanol sites were refined to be partially occupied (Table 3) and oxygen-atoms of four ligands occupied the equatorial plane with a mean Cu----O distance 1.50 Å acts as a bridge between Cu1 atoms. The elongation of the axial sites compared with equatorial sites is owing to the Jahn-Teller effect. Each of the HL3- used its non-bonded O-atoms of the carboxylate groups in a syn-anti mode to link the adjacent trinuclear units through binding to the octahedrally Cu2 centers. The intermetallic distance of the two dependent Cu (II) atoms [Cu 1-----Cu 1] of complex 1 through bridging of Cu2-atom is 10.495 Å, and between Cu1-----Cu2 is 5.248 Å. The trinuclear units were linked into a one-dimensional double zig-zag chain (Figure 1d) via H-bonding through the non-bonded terminal carboxylic group, which further construct three-dimensional metal-organic framework.

DISSCUSION

The results of this study showed that comparison of ages in (50) sample therefore cases over 50 years of age were 28% for all cases over50 years. The gender distribution shows that the majority of patients (56.0%) are male, while females make up a significant minority (44.0%. All patients in this sample have a formal diagnosis of chronic kidney disease or kidney failure, indicating that the sample consists entirely of patients with a confirmed diagnosis. The majority of patients (52%) have been recently diagnosed with kidney disease, while about a third (32%) have been living with the condition for an extended period. A smaller proportion (16%) have had kidney disease since birth. The majority of patients (44%) received general anesthesia, followed closely by local anesthesia (32%), and then regional anesthesia (24%). This suggests that general anesthesia is the most commonly used type of anesthesia for patients with kidney disease undergoing surgery, but local and regional anesthesia are also significant options. Only about half of the patients (52.0%) had their anesthesia approach tailored to their kidney function, while nearly half (48.0%) did not. The majority of patients (56.0%) experienced side effects or complications due to anesthesia, which is a significant proportion. Only about half of the patients (48.0%) had their kidney function monitored before and after surgery, while a slight majority (52.0%) did A majority of patients (56.0%) required dialysis or changes to their dialysis schedule after surgery, while a significant proportion (44.0%) did not. This highlights the importance of careful postoperative management for patients with kidney disease. An overwhelming majority (80%) of respondents believe that the patient's renal status is an important factor when planning anesthesia. In terms of pain management, the preferred analgesic for patients with renal failure is Diclofenac [2]. A majority (60%) of respondents believe that Isoflurane is the most suitable inhalational anesthetic for patients with kidney failure. At the end of this research, we reached a very important result, which is the effect of anesthesia on kidney diseases and kidney failure, which is represented by the patient being exposed to monitoring kidney functions through dialysis, changing the treatment regimen, and suffering from acute kidney failure after the operation. The objectives of the study were consistent with the results of this study We note that the current study is consistent with previous studies in its main topic, which is kidney diseases. We differed from the first study in terms of objectives, as we had a set of objectives in our current study, and the previous study had one objective, which was to study the protective effects of omega-3 acids on kidney function [4]. We differed in the method of conducting the study. The method of conducting our current study was by using a questionnaire that was distributed to 50 samples. The questionnaire was divided into two groups, between 25 patients and 25 doctors. The method of the first previous study was through a double randomized trial on 500 patients in stages 3-4 of chronic kidney disease [4]. There was a difference in the results. The results of our current study showed that there was an age comparison in 50 samples, and that the majority of patients were males. All patients had an official diagnosis of the disease.



Scheme 2. Coordination of HL3- as a tetradentate to Cu 1 atoms

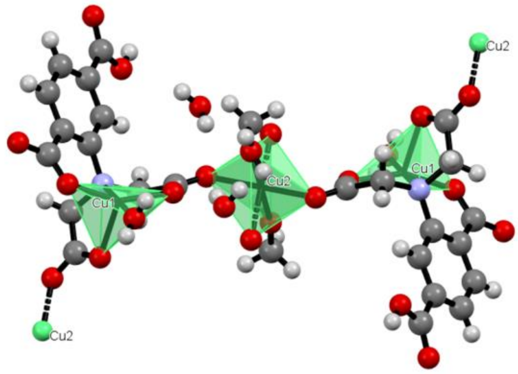


Figure 1. (c) Coordination polymer polyhedron around the Cu atoms.

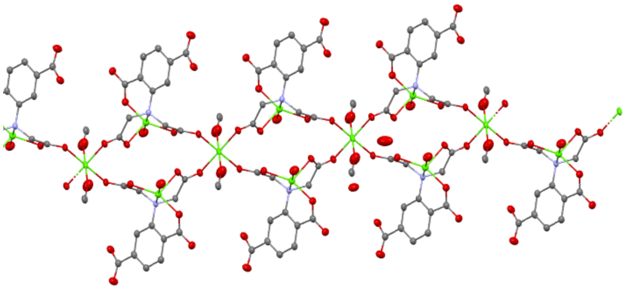


Figure 1. (d) One dimensional double zig-zag chain run along the b-axis.

Table 2 Selected bond distances (Å) and angles (°) for 1

Bond Distances/Å					
Cu1–N1	2.030(4)	Cu1–O1W	1.929(4)	Cu2–O^{3}4	1.953(3)
Cu1-O1	1.966(4)	Cu2 –O^{1}2	1.948(4)		
Cu1-O3	2.164(4)	Cu2–O2	1.948(4)		
Cu1–O5	1.934(4)	Cu2–O^{2}4	1.953(3)		
Bond Angles/°					
N1–Cu1–O3	80.29(16)	O5–Cu1–O1	154.57(16)	O1W–Cu1–O1	93.22(17)
O1–Cu1–N1	86.01(16)	O5–Cu1–O3	97.03(15)	O1W–Cu1–O3	97.71(18)
O1–Cu1–O3	106.97(15)	O1W–Cu1–N1	177.59(17)	O2–Cu2–O4^3	95.38(14)
O5–Cu1–N1	89.95(16)	O4^3–Cu2–O4^2	180.00(17)		

1-X,1-Y,1-Z; 2-1+X,+Y,+Z; 31-X,1-Y,1-Z; 41+X,+Y,+Z for bond angles

Table 3. Atomic Occupancy for Complex 1.

Atom	***Occupancy***	**Atom**	***Occupancy***	**Atom**	***Occupancy***
C13	0.592(14)	H13A	0.592(14)	H13B	0.592(14)
H13C	0.592(14)	O31	0.592(14)	H31	0.592(14)

Table 6. Hydrogen Bonds for Complex 1.

D	H	A	d(D-H)/Å	d(H-A)/Å	d(D-A)/Å	D-H-A/°
O8	H8	O6^1	0.84	1.74	2.550(5)	162.8

1-1+X+Y, -1+Z

CONCLUSION

In this work, we have reported the structure of one-dimensional homo-trinuclear Cu3 coordination polymer. It Consists of two dependent Cu (II) centers, features two very similar pyramidal Cu1 and Cu3 with CuNO4 chromophores and hexa-coordinate Cu2 with CuO6-chromofore. The primary building unit of the title coordination polymer is made of two HL-3 ligands, three Cu(II) ions, two water molecules and 1.18 ethanol molecules. The flexible carboxylate ligands capable of assembling supramolecular structures through it is interactions with lattice water molecules.

ACKNOWLEDGMENT

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