



A new two-dimensional coordination polymer: Poly[[bis(μ -chlorido) tris (μ - iso-nicotinate- κ 4 N:N':O,O') copper(II)] tris(μ -iso-nicotinate- κ 3O:N:O)(diaqua) copper(II)].

R. G. Abuhmaiera	Chemistry Department, University of Tripoli, Tripoli-Libya.
R.M. El-mehdawi	Chemistry Department, University of Tripoli, Tripoli-Libya.
M.M. Ben Younes	Chemistry Department, University of Tripoli, Tripoli-Libya.
F. A. Treish	Chemistry Department, University of Tripoli, Tripoli-Libya.
M.N. El-kaheli	Chemistry Department, University of Tripoli, Tripoli-Libya.
Jorg Daniels	lnstitute fur Anorganische Chemi, Universitat Bonn, Gerhard-Domagk-Str. 1,53121, Bonn, Germany.
Johannes Beck	lnstitute fur Anorganische Chemi, Universitat Bonn, Gerhard-Domagk-Str. 1,53121, Bonn, Germany.

ABSTRACT

The new title two-dimensional coordination polymer $[Cu_2Cl(C_6H_4NO_2)_3(H_2O)_2]_n$ (1), consists of an asymmetric unit which contains two crystallographically independent copper (II) centers { [bis(μ -Cl) (μ -C₆H₅NO₂- κ 4N:N':O,O')₃Cu(II)] and [(μ -C₆H₅NO₂- κ 3O:N:O)₃(H₂O)₂Cu(II)] } for Cu₂ and Cu₁ respectively} bridged by iso-nicotinate (L) anion." The bridged L coordinated as a monodentate through O-atom of the carboxylate group to Cu₁, while the N-atom coordinated to Cu₂. The Cu₂ adopts a distorted octahedral geometry formed by two N-atoms from two different L anions, carboxylate oxygen atoms as a chelate from another L anion, and two chloride atoms. Cu₁ adopts a highly distorted square pyramidal by two monodentate carboxylate oxygen atoms from two different L ligands, N-atom from another ligand L and two oxygen atoms from two coordinated water molecules. There is a π - π interactions between neighboring pyridine rings within the same 2D framework. Hydrogen bonds are present in the crystal structure.

KEYWORDS : Copper Chloride; Iso-nicotinic acid; Two-dimension; Coordination polymer; Crystal structure.

1. INTRODUCTION

In the last few years, 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. A number of unique networks have been obtained by reactions between transition metal ions and rationally designed organic ligands [1-6]. 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 ligands. Moreover, recently, intense research activities have been directed toward, the development of porous frameworks including assembly of coordination complexes and organic molecules into extended motif, held together by strong metal-ligand bonding or by very weak bonding forces [7-9], and their useful properties applicable to various fields, such as size-selection sorption, gas storage, host-guest recognition and catalysis [10-14]. There are few structures in the literature of dinuclear copper (II) complexes in which the copper centers are linked by a single bridging atom. Pyridinecarboxylic acids and their derivatives possess very interesting pharmaceutical properties and constitute an important group of anthelmintics and vitamins [15]. We selected iso-nicotinic acid as building blocks to construct 2D framework due to the diversity of binding modes of the carboxyl group and aromatic ring containing nitrogen atom also, in this view, copper(II) ion is very promising, 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 else by a change in coordination number as an alternative means of lifting the degeneracy of unequally occupied d-orbitals. As we expected, when we reacted copper (II) ions with iso-nicotinic acid in presence of sodium azide by conventional reflux method, new two-dimensional polymer containing an open framework was obtained. In the absence of sodium azide or presence of sodium hydroxide different compounds with different colors were formed. Herein, we report the syntheses and crystal structure of the title compound (1).

2. EXPERIMENTAL DETAILS

2.1 Materials

All starting materials were commercial products and were supplied from Aldrich Company.

2.2 Synthesis and crystallization

The title complex (1) was prepared by refluxing a solution of iso-nicotinic acid (0.05g, 4.0×10^{-4} mmol) and NaN₃ (0.030g, 6.0×10^{-4} mmol) in 10ml H₂O was added to a solution of CuCl₂·6H₂O (0.13g, 5.0×10^{-4} mmol) in 16 ml methanol for 2hrs. The resulting turbid solution was allowed to cool to ambient temperature. It was filtered off and slowly evaporated at ambient temperature. Blue crystals of (1) in 35% yield, were obtained within one week.

2.3 Crystal Structure determination and refinement of the title complex

Suitable blue single crystals of the title complex were obtained by slow evaporation of the solvent at ambient temperature. A crystal of the size 0.17 x 0.13 x 0.07 mm was selected for data collection. Data were collected on Bruker–Nonius Kappa CCD diffractometer at 123 (2) K using graphite monochromated Mo- κ radiation ($\lambda=0.71073$ Å). The structure was solved by direct methods using SHELXS-97 [16], and refined using full matrix least-squares based on F^2 using SHELXL-97 [17]. Non-hydrogen atoms were refined anisotropically. All hydrogen atoms were located by difference Fourier synthesis and refined isotropically. Further details regarding the data collection, crystal and final refinement parameters are found in Table (1). Additional material available from the Cambridge Crystallographic Data Center comprises thermal parameters and remaining bond distances and angles (CCDC No. 898044). These data can be obtained free of charge from The Cambridge Crystallographic Data Center (CCDC), 12 Union Road, Cambridge CB2 1EZ, UK (fax +44(0)1223-336033; e-mail: deposit@ccdc.cam.ac.uk).

Crystal data.**Table 1.** Crystal data and structure refinement details for the complex

Empirical formula	$C_{18}H_{16}ClCu_2N_3O_{11.05}$
Formula weight	613.66
Temperature	123 K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group (No.)	$C2/c$
Unit cell parameters	$a = 24.2172(3)$ Å $b = 17.6947(2)$ Å, $\beta = 106.8473(7)^\circ$ $c = 12.0011(1)$ Å
Cell volume	$4921.94(9)$ Å ³
Z	8
ρ_c	1.693 Mg m ⁻³
μ	1.90 mm ⁻¹
F(000)	2527
Crystal size	$0.17 \times 0.13 \times 0.07$ mm
θ range for data collection	$2.91 - 33.142^\circ$
Index ranges	$-37 \leq h \leq 37, -27 \leq k \leq 27, -18 \leq l \leq 18$
Reflections collected	99959
Largest difference peak and hole	0.261 and -0.223 Å ⁻³
Independent reflections	9384 [R(int) = 0.056]
Data / restraints / parameters	9384 / 1 / 370
Goodness-of-fit on F^2	1.02
R indices	[$I > 2\sigma(I)$] R1 = 0.0353, wR2 = 0.0801
R indices (all data)	R1 = 0.0622, wR2 = 0.0917

3. RESULTS AND DISCUSSION

The new title coordination polymer $[Cu_2(C_6H_4NO_2)_3Cl(H_2O)]_n$ (**1**) indicates that the repeat unit contains two asymmetric copper(II) atoms, three **L** anions, two coordination water molecules, and one chloride atom (Figure 1). In (**1**) Cu2 is six coordinate, surrounded by two nitrogen atoms provided by two **L** ligands (N1, N2), two chloride atoms (Cl1, Cl1ⁱⁱⁱ), and two oxygen atoms

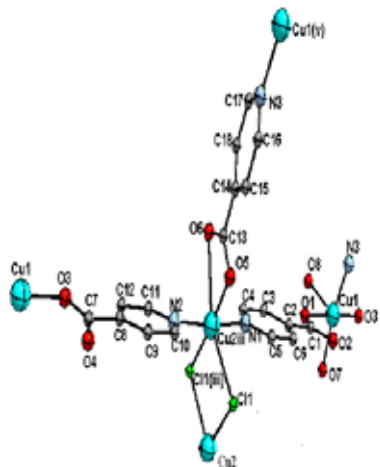


Figure 1. Molecular structure for the title compound (**1**) with the atomic numbering scheme. Displacement ellipsoids are plotted at the 50 % probability level. Hydrogen atoms are omitted for clarity. Symmetry codes: (i) $x, y+1, z$; (ii) $-x+1/2, y+1/2, -z+1/2$; (iii) $-x, y, -z+1/2$; (iv) $x, y-1, z$; (v) $-x+1/2, y-1/2, -z+1/2$.

from a carboxylate group of another neighboring **L** anion forming a (4+1+1) coordination polyhedron, which can be described as a distorted octahedral (Figure 1). The bridging chlorides connect two Cu2 atoms resulting in a Cu_2Cl_2 binuclear unit. The coordination sphere around Cu1 is penta-coordinate square pyramidal with a distortion caused by (4+1) elongation. The basal plane with central Cu1 is formed by one N-atom (N3) of an **L** ligand, two carboxylate O-atoms (O1, O3) from two different **L** ligands, and one O-atom (O7) by an aqua molecule, the apical site was occupied by an O-atom (O8) of another aqua molecule. The geometry around Cu2

in (**1**) is hexa-coordinate octahedral with a distortion caused by a (4+1+1) elongation. The equatorial plane was occupied by two N-atoms (N1, N2) from two **L** ligands, carboxylate O-atom (O5) from another **L** ligand and the fourth position was occupied by Cl1 atom which bridges Cu2 and Cuⁱⁱⁱ(2) in (1) [symmetry code: (iii) – $x, y, -z + 0.5$], the axial sites are occupied by carboxylate O-atom (O6) from different ligand **L** and Cl-atom (Clⁱⁱⁱ(1)). The most notable feature of the structure is the semi-bridging chloride ligand coordinate to Cu2 in the equatorial plane and more weakly to Cuⁱⁱⁱ(2) in the axial position, leading to an acute angle at the chloride: Cu2–Cl1 2.2775(5) Å, Cu2–Clⁱⁱⁱ(1) 2.7048(4) Å and Cu2–Cl1–Cuⁱⁱⁱ(2) 87.422(13)° with a dihedral angle Clⁱⁱⁱ(1)–Cu2–Cl–Cuⁱⁱⁱ(2) 2.49°, the long Cu2–Clⁱⁱⁱ(1) bond, which is considered shorter than those reported by Powell [18], has the effect of making the halide and the carboxylate- O6 occupy the axial positions, so the effect of the halide bridge is to reduce the Cu2----Cuⁱⁱⁱ(2) separation to 3.457 Å compared with other di-copper complex reported by El-mehdawi [19]. Selected bond distances and angles around the copper atoms are shown in (Table 2). The inter-layer distance between Cu1 and Cuⁱⁱⁱ(1) is 4.906 Å. The bond distances around copper(II) atoms are all different, for Cu2, the Cu–O length vary from 1.994 to 2.627 Å, but Cu1–O lengths falls in the range of 1.963 to 2.213 Å comparable with those of similar coordination. For Cu–N bond lengths, all fall in the normal range.

Table 2: Selected bond lengths (Å) and angles (°) of the title compound.

Bond lengths					
Cu1–O1	1.9632(12)	Cu1–O3 ⁱⁱ	1.9648(12)	Cu1–O7	1.9852(13)
O1–N3 ^a	2.0119(14)	Cu1–O8	2.2133(14)	Cu2–O5	1.9944(12)
Cu2–N2	2.0067(15)	Cu2–N1	2.0150(15)	Cu2–Cl1	2.2775(4)
Cu2–Cl1 ⁱⁱⁱ	2.7049(4)	Cu2–O6	2.6271(13)		
Bond angles					
O1–Cu1–O3 ⁱⁱ	176.80(5)	O1–Cu1–O7	87.95(5)	O3 ⁱⁱ –Cu1–O7	89.14(6)
O1–Cu1–N3 ^a	91.32(6)	O3 ⁱⁱ –Cu1–N3 ^a	91.82(6)	O7–Cu1–N3 ^a	166.18(6)
O1–Cu1–O8	86.54(5)	O3 ⁱⁱ –Cu1–O8	92.51(5)	O7–Cu1–O8	97.17(5)
N3 ^a –Cu1–O8	96.57(6)	O5–Cu2–N2	88.17(5)	O5–Cu2–N1	89.99(5)
N2–Cu2–N1	174.30(6)	O5–Cu2–Cl1	174.72(4)	N2–Cu2–Cl1	90.48(4)
N1–Cu2–Cl1	90.87(4)	O5–Cu2–Cl1 ⁱⁱⁱ	92.68(4)	N2–Cu2–Cl1 ⁱⁱⁱ	94.35(4)
N1–Cu2–Cl1 ⁱⁱⁱ	91.12(4)	Cl1–Cu2–Cl1 ⁱⁱⁱ	92.511(14)	Cu2–Cl1–Cu2 ⁱⁱⁱ	87.422(14)

Symmetry codes: (i) $x, y+1, z$; (ii) $-x+1/2, y+1/2, -z+1/2$; (iii) $-x, y, -z+1/2$; (iv) $x, y-1, z$; (v) $-x+1/2, y-1/2, -z+1/2$.

As expected the apical Cu1–O8 bond distance (2.213(1) Å) is significantly longer than the remaining four distances in the Cu1 coordination polyhedron (Table 2). The weak apical bond reflects a weak axial contact, as expected for Jahn-Teller sensitive copper (II) complexes. A short Cu1----O2 contact of 2.895 Å which is only slightly shorter than the sum of the Van der Waals radii (2.92 Å), should also be mentioned [20]. Since the O8–Cu1–O2 angle is 164.99° so, we can consider the coordination geometry about Cu1 is between a (4+1) distorted square pyramidal and a (4+1+1) distorted octahedral environment. Cu2 displays an octahedral geometry with four short bonds in the equatorial sites including two N-atoms one chloride atom and a chelating carboxylate-O atom and a longer axial contact of 2.627(1) Å for Cu2–O6 from the chelating carboxyl group that already coordinated to Cu2 through O5. The chelate O5–Cu–O6 angle [55.58(5)°] is similar to those reported by Rogan [21] and have strong impact on the distortion of the octahedron due to the constrain imposed by chelation. The other axial site was occupied by Cl1 with long Cu–Cl bond distance of 2.7048(4) Å. The ligand **L** acts as a bidentate bridge, linking Cu2 through N-atom and Cu1 through carboxylate O-atom also, as a tridentate ligand chelating Cu2 through carboxylate O-atoms and Cu1 through N-atom. The hydrogen atoms of the guest disordered water or methanol molecules were not located.

Further analysis of the packing structure of the title complex reveal that this structure contains intermolecular hydrogen bonds between one of the coordinated water molecules of one layer and the oxygen atoms of the carboxylate group of another layer results in the formation of a 3D structure (Table 3). Also, extensive hydrogen bonding occurs between unbound disordered solvent in the cavities and the O-atoms of the carboxylate groups. It appears that O9/ O11/ O12 are closely spaced sites of an oxygen atom that could be donating an H-bond to O6. Since their occupancies nearly add up to 1, these could be refined as one

water oxygen with large thermal ellipsoid. Similarly it appears that O8 is donating an H-bond to O10/O15, which may be treated as another water oxygen. Owing to the poor refinement of the molecules within the cavities it is not so easy to define correct interactions of the rest of molecules in the cavities with metal framework.

Table 3. Hydrogen-bond geometry (Å, °)

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
O7—H7A...O2 ⁱⁱⁱ	0.72(2)	2.027(4)	2.785	167.04
O7—H7B...O4 ^{vii}	0.84(2)	1.846(9)	2.686	177.27
O8—H8A...O2	1.03(4)	1.785(2)	2.813	173.80

Symmetry code: (iii) $-x, y, 0.5-z$; (vii) $-x, -1+y, 0.5-z$.

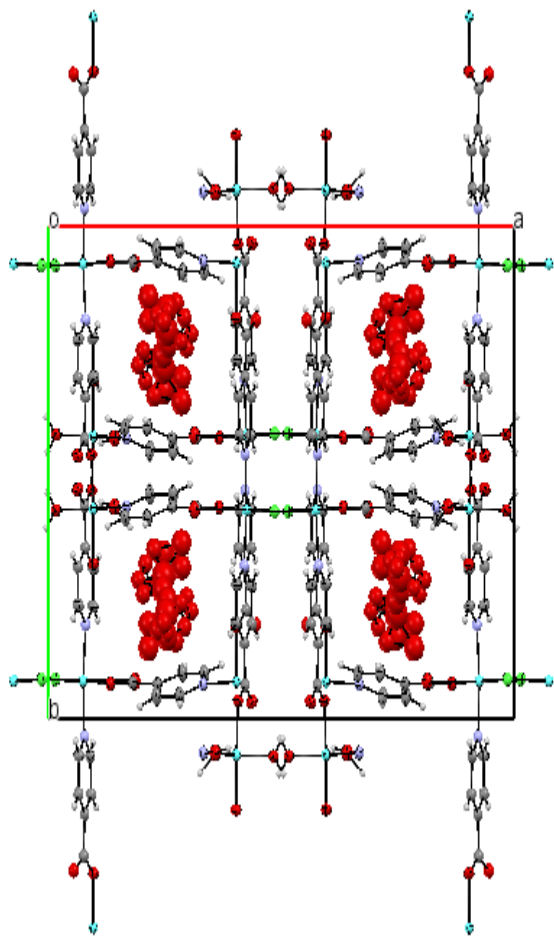


Figure 2. A view of the crystal packing down the *c* axes for the title compound

The two dimensional networks stack parallel to each other at an interplanar distance of 9.0 Å. This interplanar space is filled by the L moieties from the bimetallic units of two adjacent networks (Figure 3). In particular the L groups belonging to superposed bimetallic units enables π - π stacking of pyridine rings between layers. The shortest distances between C atoms of neighbouring pyridyl rings are 3.6263(3) Å for C9...C12ⁱⁱⁱ and 3.6948(3) Å for C3...C6ⁱⁱⁱ [symmetry code: (iii) $-x, y, 0.5-z$], with corresponding Cg...Cgⁱⁱⁱ separations between pyridine rings 3.7092(3) and 3.7309(4) Å, respectively. The interplanar distances: Cg(4) \rightarrow Cg(4)(ii) = 3.6948(11) Å, Cg(5) \rightarrow Cg(5)(ii) 3.6112(10) Å, [symmetry code: (ii) $0.5-x, 0.5+y, 0.5-z$]. These values indicate that there is a pronounced slippage between the stacked rings.

The important feature of the title polymer is that each repeated unit, there exist an open framework which containing highly disordered, unbound solvent molecules that appear to flow freely through the void spaces of the well-defined framework. The

open framework formed within the (Cu₂L₂)-loops have a size of 7-8.8 Å, along the b-axis, these cavities are stacked and the so-built channels contains disordered solvent molecules. The disordered solvent molecules are not found exactly between the ligand molecules, but below and above the chain. The disordered solvent molecules interact with walls of the cavities through C-H... π interactions.

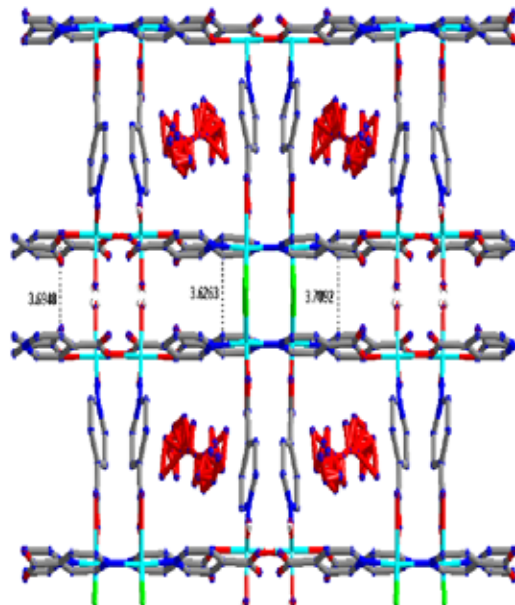


Figure 3. A projection of the title complex along the *c* axes, showing the crystal

Packing, π - π interactions and an open framework contains disordered oxygen atoms of unbound solvent.

4. CONCLUSION

In summary, we have synthesized one new two dimensional coordination polymer, which is stabilized by H-bonding and π - π stacking. The geometry around the copper (II) centers are controlled by the iso-nicotinate and chloride ligands. The two dimensional networks are extended into 3D supramolecular structure via hydrogen bonding between one of the coordinated water molecules and the oxygen atom of the carboxyl group of another molecule. The disordered unbound solvent occupied an open framework. The open framework was used through the text instead of porous, generally has been conceded as an adequate description of materials unbound solvent molecules that appears to flow freely.

REFERENCES

1. Stang P. J, Olenyuk B. Self-assembly and molecular architecture: Coordination as the π motif in design of supramolecular metallacyclic polygons and polyhydra. *Acc. Chem. Res.*, 1997;30: 502-518 . | 2. Aakeroy C. B. & Seddon. K. R. The hydrogen bond and crystal engineering. *Chem. Soc. Rev.*, 1993, 22, 397-407 . | 3. Munakata M, Wu L. P, Kurods-Sowa T. The Silver-Alkene Interaction as a π Supramolecular Syntho; Divinylbenzene-based Assemblies. *Adv. Inorg. Chem.*, | 1999; 46: 173-303 . | 4. Robinson F. & Zaworotko M. J. Triple interpenetration in $\text{Ag}[\text{4,4-bipyridine}]\text{NO}_3$ A π cationic polymer with a three-dimensional motif generated by self-assembly of T-shape | building blocks *J. Am. Chem. Soc. Commun.*, 1995; 23: 2413-2414 | 5. Fujita M, Kwon Y. J, Ogura S. Preparation, clathration ability, and catalysis of a two- π dimensional square network material composed of cadmium(II) and 4,4'-bipyridine. *J. Am. Chem. Soc.*, 1994;116; 1151-1152. | 6. Hargman D , Zubieta C , Rose D, Zubieta J, Haushalter R. C. Diaqua bis(hydrogen | tartarato)copper(II)dehydrate. *Angew. Chem., Int. Ed. Eng.*, 1997;35:873-876. | 7. Li H, Laine A , Keefe M. O, Yaghi O. M. Supertetrahedral sulfide crystals with giant π cavities and channels. *Science.*,1999; 283: 1145-1147 . | 8. Chen B, Eddaoudi M, Hyde S. T, Keefe M. O, Yaghi O. M. Interwoven metal- π organic framework on a periodic minimal surface with extra-large pores. *Science.*, | 2001;291:1021-1023. | 9. Seo R, Ishizuka T, Abdel-Aziz A. A. M. & Kunieda T. Versatile chiral synthons for π 1,2-diamines: (4S,5S)- and (4R,5R)-4,5-dimethoxy-2-imidazolidinones, *Tetrahedron Lett.*,2001; 42:6353-6355 . | 10. Eddaoudi M, Moler DB, Li H, Chen B, Reineke TM, O'Keefe M, Yaghi OM. | Modular chemistry: Secondary building units as a basis for the design of highly π porous and robust metal-organic carboxylate frameworks. *Acc Chem Res*, 2001, 34: | 319-330 | 11. Janiak C. Engineering coordination polymers towards applications. *Dalton trans.*, | 2003;2781-2804. | 12. Kesanli, B. & Lin, W. Chiral porous coordination networks: rational design and π applications in enantioselective processes. *Coord. Chem. Rev.* 2003; 246:305-326. | 13. Rowsell J. L. C, Millward A. R, Park K. S. & Yaghi O. M. Hydrogen sorption in π functionalized metal-organic frameworks. *J. Am. Chem. Soc.*,2004; 126: 5666-5667. | 14. Robin A. Y. & Fromm K. M. Coordination Polymer Networks with O- and N- π Donors: What they are, why and how they are made. *Coord. Chem. Rev.*, 2006; 250: | 2127-2157. | 15. Zhang H, Zhou T, Grishin N.N. Crystal structures of E. coli nicotinate Mononu- π cleotide adenyltransferase and its complex with deamido-NAD. *Structure* ., | 2002;10: 69-79. | 16. Sheldrick G. M. (1997). SHELXL97, Program for Crystal Structure Refinement |, University of Gottingen. | 17. G. M. Sheldrick. (1997). SHELXL97, Program for Crystal Structure Solution, | University of Gottingen.SHELX , Sheldrick, G. M., *Acta Cryst.*, 2008; A64: 112. | 18. Powell A, Laborda S, Cle'rac R, Christopher E. A. Intra and Intermolecular π Magnetic Interactions in a Series of Dinuclear Cu(II)/hxta Complexes (H5hxta = π N,N'-(2-hydroxy-1,3-xylene)-bis-(N-carboxymethylglycine): Correlation of π Magnetic Properties with Geometry. *Inorg.Chem.*,2004;43:5931-5943. | 19. El-mehdawi R.M, El-kaheili M. N, Abuhmaiera R. G , Ben Younes M. M ,Treish F | A, Guerri A, Bazzicalupi C. Poly[[π 4-benzene-1,3,5-tricarboxylato- π π 4O1:O1:O2:O3]bis(2,2-bipyridine- π 2N,N.) π (π 2-hydroxido)dicopper(II)] [trihydrate]. *Acta Cryst.*, 2014; E70: m270-m271. | 20. Bondi A. Van der Waals Volumes and Radii. *J. Phys. Chem.*, 1964;68: 441-451. | 21. Rogan J, Poleti D. & Karanovic L. catena-Poly[[π (di-2-pyridylamine- 2N2,N2')- π | copper(II)]- π benzene-1,3-dicarboxyl- π ato- 3O1,O1':O3] mono-hydrate], a zigzag π coordination polymer with strong -inter-ac-tions. *Acta Cryst.*, 2011; C67: m230- | m233. |