ЖУРНАЛ СТРУКТУРНОЙ ХИМИИ

2011. Том 52, № 6 *Ноябрь – декабрь* *С. 1152 – 1156*

КРАТКИЕ СООБЩЕНИЯ

UDC 548.734:541.49:546.562

CRYSTAL STRUCTURE OF NEW MELAMINE BRIDGED POLYMERIC COMPLEX OF COPPER(II)

© 2011 **G.M. Mamoor[1]*, O. Şahin[2]*, Islam Ullah Khan[3], Ejaz[3], O. Büyükgüngör[2]**

[1]*Department of Polymer Engineering, University of Engineering & Technology, Lahore, Pakistan*
[2]*Department of Physics, Faculty of Arts and Sciences, Ondokuz Mayıs University, Samsun, Turkey*
[3]*Department of Chemistry, Materials Chemistry Laboratory, Government College University, Lahore, Pakistan*

Received December, 14, 2010

The new co-crystal copper(II) melamine complex poly[bis(μ-methacrylato)μ-(1,3,5-triazine-2,4,6-triamine)], $C_{19}H_{26}Cu_2N_6O_8$ (**1**) crystallizes in the triclinic *P*-1 space group with $a = 8.9670(2)$ Å, $b = 9.4108(2)$ Å, $c = 15.4476(3)$ Å, $\alpha = 96.6090(10)°$, $\beta = 100.6270(9)°$, $\gamma = 95.5950(10)°$. Each Cu(II) exhibits a pseudooctahedral geometry. Four coplanar carboxylate oxygen atoms coordinated to the Cu(II) ion define the basal plane, whereas the apical position is occupied by one nitrogen atom from the melamine ligand. Here, the carboxylato-bridged two dinuclear copper(II) complexes are linked through melamine giving a 1D alternating chain. The structure of **1** consists of a two-dimensional supramolecular layer constructed by intermolecular N—H…N hydrogen bonds of the melamine ligands from adjacent one-dimensional $[Cu_2(C_4H_5O_2)_4(C_3H_6N_6)]$ chains.

K e y w o r d s: X-ray diffraction analysis, copper(II), carboxylate, melamine.

Much attention has been paid to 1D, 2D and 3D coordination polymers because they can meet the need of functional materials with desired structures and properties [1—5]. One strategy in the design and synthesis of coordination architectures is the building-block approach. Commonly, bi- or multidentate organic ligands containing N [6, 7] or O [8, 9] atoms have ever been used in the construction. In our current work, we have selected an excellent hydrogen donor and hydrogen acceptor—melamine (MA). Containing three nitrogen atoms as part of a six-member aromatic heterocycle and three amino groups at three carbon atoms of the cycle, MA has exhibited diversified hydrogen bonding modes and extremely interesting architectures [10—17]. We report here the structure of a copper(II) complex with direct bonding of melamine to the metal ion.

Experimental. Synthesis. Copper sulphate (0.16 g, 1 mmol) was dissolved in methanol (20 ml) in a 50 ml round bottom flask; sodium azide (0.033 g, 0.5 mmol) was added and refluxed for 15 minutes; melamine (0.252 g, 2 mmol) was added and refluxed for 5 hours. Then methacrylic acid (0.17 ml, 2 mmol) was added and refluxed for 40 minutes; the greenish solution formed was filtered, the filtrate kept for evaporation; green crystals were obtained from solution after five days.

X-Ray diffraction analysis. A greenish crystal suitable for data collection was mounted on glass fibres and data collection was performed on a Bruker SMART APEX II CCD diffractometer with graphite monochromated MoK_α radiation at 296 K. The structures were solved by direct methods using SHELXS-97 and refined by full-matrix least squares methods on F^2 using SHELXL-97 [18] from within the WINGX [19] suite of software. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were located from the electron density difference synthesis and refined isotropically. Crystal data and parameters of the structural experiment are given in Table 1. Atomic coordinates have

* E-mail: mamoorgm@uet.edu.pk, onurs@omu.edu.tr

Table 1

Crystal and Refinement Data for **1**

Molecular formula	$C_{19}H_{26}Cu_2N_6O_8$
Molecular mass	593.54
Crystal system	Triclinic
Space group	*P*-1
Unit cell parameters *a*, *b*, *c*, Å	8.9670(2), 9.4108(2), 15.4476(3)
α, β, γ, deg.	96.609(1), 100.6270(9), 95.595(1)
V, Å^3	1263.25(5)
Z	2
ρ_{calc}, g/cm^3	1.560
T, K	296
Radiation, λ, Å	MoK_α; 0.71073
Crystal size, mm	0.37×0.33×0.32
Color	Green
Crystal shape	Flacks
Reflections measured	23002
$\theta_{min, max}$, deg.	1.4—28.3
Independent reflections	6238 [R_{int} = 0.039]
Parameters refined	320
Final *R* factor [$I > 2\sigma(I)$]	*R*1 = 0.038, *wR*2 = 0.100
R factor (all data)	*R*1 = 0.072, *wR*2 = 0.143
GOOF	1.08
Residual electron density (min / max), e/Å^3	–1.34 / 0.73

been deposited to the Cambridge Structural Database (http://www.ccdc.cam.ac.uk): CCDC 795874. The hydrogen bonds are characterized in Table 3.

Results and discussion. Complex **1** exhibits an alternating chain structure along the [111] direction, which is formed by bridging melamine ligands connecting the $[Cu_2(\mu\text{-}CH_3CH_2CCO_2)_4]$ units. The asymmetric unit consists of $Cu_2(C_4H_5O_2)_4$ together with the melamine ligand (Fig. 1). As shown in Fig. 2, there are two crystallographically independent copper(II) ions, named Cu(1) and Cu(2), that adopt similar coordination environments. Each Cu(II) exhibits a pseudooctahedral geometry. The four coplanar carboxylate oxygen atoms (O(1), O(3), O(2)^i, O(4)^i) coordinated to Cu(1) with practically identical oxygen-to-copper bond lengths (1.958(3)—1.961(3) Å) define the basal plane, whereas the apical position is occupied by one nitrogen atom from the melamine ligand (2.268(3) Å for Cu(1)—N(5)). Similarly, the four carboxylate oxygen atoms (O(5), O(7), O(6)^{ii}, O(8)^{ii}) coordinated to Cu(2) with practically identical

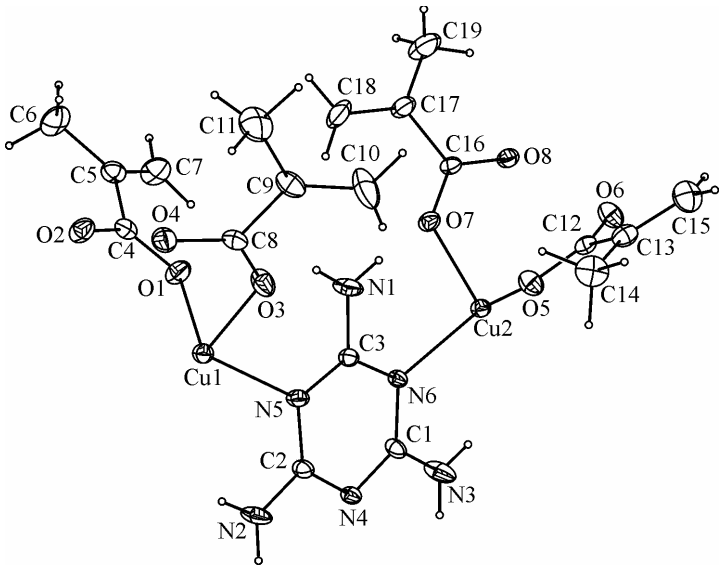

Fig. 1. Independent part of the structure of $C_{19}H_{26}Cu_2N_6O_8$

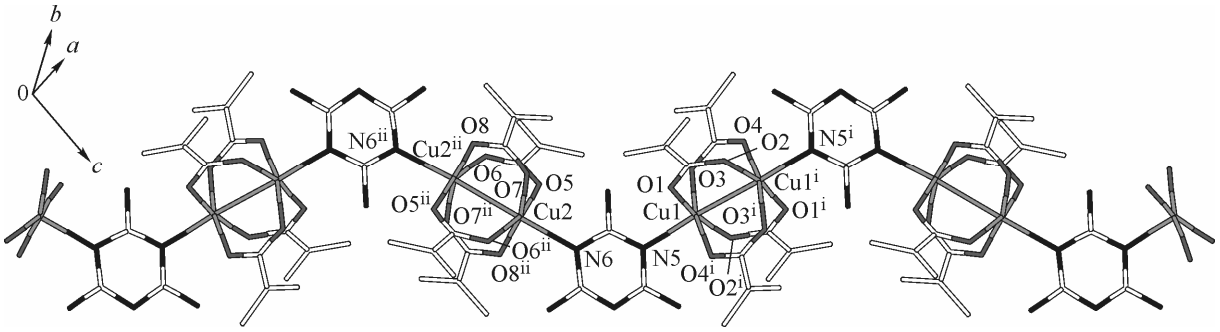

Fig. 2. View of part of the crystal structure of **1**, showing the formation of a coordination polymer chain parallel to the [111] direction. For the sake of clarity, all H atoms have been omitted. (Symmetry operations as in Table 2)

oxygen-to-copper bond lengths (1.957(3)—1.971(2) Å) build the basal plane, whereas the other nitrogen atom from the melamine ligand occupies the axial position (2.312(2) Å for Cu(2)—N(6)). The average value of the copper- to-carboxylate oxygen bond distances lies within the range of similar bonds with other carboxylate (1.92—2.16 Å) [20—24]. The values of O(1)—Cu(1)—O(3) and O(5)—Cu(2)—O(7) bond angles (88.62(13) and 89.48(12)° respectively) reflect the pseudooctahedral surrounding at Cu(1) and Cu(2). Each methylacrylate group similarly adopts bidentate bridging syn—syn modes and connects Cu(1) and Cu(2) together to form a $[Cu_2(\mu\text{-}CH_3CH_2CCO_2)_4]$ paddle-wheel cage. The Cu(1)—$Cu(1)^i$ and Cu(2)—$Cu(2)^{ii}$ separations are 2.6702(7) and 2.7048(7) Å in the dinuclear Cu

T a b l e 2

Bond Lengths (*d*, Å) *and Bond Angles* (ω, deg.) *for* **1**

Bond	*d*	Bond	*d*	Bond	*d*
Cu(1)—N(5)	2.268(3)	$O(2)^i$—Cu(1)	1.961(3)	O(6)—C(12)	1.259(4)
Cu(1)—O(1)	1.958(3)	$O(4)^i$—Cu(1)	1.958(3)	O(7)—C(16)	1.252(4)
Cu(1)—O(3)	1.960(2)	$O(6)^{ii}$—Cu(2)	1.957(3)	O(8)—C(16)	1.253(4)
Cu(2)—N(6)	2.312(2)	$O(8)^{ii}$—Cu(2)	1.966(2)	Cu(1)—$Cu(1)^i$	2.6702(7)
Cu(2)—O(5)	1.962(5)	O(1)—C(4)	1.250(4)	Cu(2)—$Cu(2)^{ii}$	2.7048(7)
Cu(2)—O(7)	1.971(2)	O(2)—C(4)	1.259(4)	O(5)—C(12)	1.250(4)
O(3)—C(8)	1.255(4)	O(4)—C(8)	1.252(4)		
Bond angle	ω	Bond angle	ω	Bond angle	ω
O(1)—Cu(1)—$O(4)^i$	89.80(12)	O(1)—Cu(1)—$Cu(1)^i$	84.65(7)	$O(8)^{ii}$—Cu(2)—O(7)	165.60(10)
O(1)—Cu(1)—O(3)	88.62(13)	$O(4)^i$—Cu(1)—$Cu(1)^i$	83.04(8)	$O(6)^{ii}$—Cu(2)—N(6)	98.21(10)
$O(4)^i$—Cu(1)—O(3)	166.76(10)	O(3)—Cu(1)—$Cu(1)^i$	83.73(7)	O(5)—Cu(2)—N(6)	95.90(10)
O(1)—Cu(1)—$O(2)^i$	166.89(10)	$O(2)^i$—Cu(1)—$Cu(1)^i$	82.25(8)	$O(8)^{ii}$—Cu(2)—N(6)	96.99(10)
$O(4)^i$—Cu(1)—$O(2)^i$	88.50(12)	N(5)—Cu(1)—$Cu(1)^i$	176.29(8)	O(7)—Cu(2)—N(6)	97.40(10)
O(3)—Cu(1)—$O(2)^i$	90.07(12)	$O(6)^{ii}$—Cu(2)—O(5)	165.89(10)	$O(6)^{ii}$—Cu(2)—$Cu(2)^{ii}$	83.38(7)
O(1)—Cu(1)—N(5)	99.04(11)	$O(6)^{ii}$—Cu(2)—$O(8)^{ii}$	89.69(12)	O(5)—Cu(2)—$Cu(2)^{ii}$	82.51(7)
$O(4)^i$—Cu(1)—N(5)	96.50(11)	O(5)—Cu(2)—$O(8)^{ii}$	88.29(12)	$O(8)^{ii}$—Cu(2)—$Cu(2)^{ii}$	82.81(7)
O(3)—Cu(1)—N(5)	96.74(10)	$O(6)^{ii}$—Cu(2)—O(7)	89.02(12)	O(7)—Cu(2)—$Cu(2)^{ii}$	82.79(7)
$O(2)^i$—Cu(1)—N(5)	94.07(10)	O(5)—Cu(2)—O(7)	89.48(12)	N(6)—Cu(2)—$Cu(2)^{ii}$	178.40(8)

Symmetry operations: (i) 2–*x*, 2–*y*, 1–*z*; (ii) 1–*x*, 1–*y*, –*z*.

Table 3

Parameters of Hydrogen Bonds for **1**

D—H…A	*d*(D—H)	*d*(H…A)	∠DHA	*d*(D…A)	Symmetry operations
N(1)—H(1A)…O(3)	0.86	2.26	143.2	2.992(4)	*x*, *y*, *z*
N(1)—H(1A)…O(1)	0.86	2.56	130.5	3.186(4)	*x*, *y*, *z*
N(1)—H(1B)…O(7)	0.86	2.07	152.1	2.855(4)	*x*, *y*, *z*
N(2)—H(2A)…N(4)	0.86	2.21	174.3	3.065(4)	–*x*+1, –*y*+1, –*z*+1
N(2)—H(2B)…O(2)	0.86	2.29	138.6	2.987(5)	–*x*+2, –*y*+2, –*z*+1
N(2)—H(2B)…O(4)	0.86	2.38	131.5	3.024(5)	–*x*+2, –*y*+2, –*z*+1
N(3)—H(3B)…O(8)	0.86	2.08	144.3	2.823(4)	–*x*+1, –*y*+1, –*z*

cage, which is shorter than the Van der Waals distances for two copper atoms (2.86 Å) and slightly longer than the Cu—Cu single bond distance (2.55 Å). Each melamine ligand makes these paddle-wheel cages connected axially to form the one-dimensional chain by N(5) and N(6) atoms. The melamine ligand is practically planar, the largest deviation from the mean plane being 0.0438(33) Å for the N(5) atom respectively. The selected bond lengths and angles are given in Table 2.

Molecules of **1** are linked into sheets by a combination of N—H…O and N—H…N hydrogen bonds (Table 3). Within the selected asymmetric unit, intramolecular N—H…O hydrogen bonds produce S(6) motifs [25]. Similarly, intermolecular N(2)—H(2B)…O(2), N(2)—H(2B)…O(4) and N(3)—H(3B)…O(8) hydrogen bonds produce R_1^1 (6) rings. The N(2) atom in the molecule at (*x*, *y*, *z*) acts as a hydrogen-bond donor (via H(2A)) to the N(4) atom in the molecule at (–*x*+1, –*y*+1, –*z*+1), so forming a centrosymmetric R_2^2 (8) rings. The combination of intermolecular N—H…N hydrogen bonds and $[Cu_2(C_4H_5O_2)_4(C_3H_6N_6)]$ chains generates a two-dimensional supramolecular layer (Fig. 3).

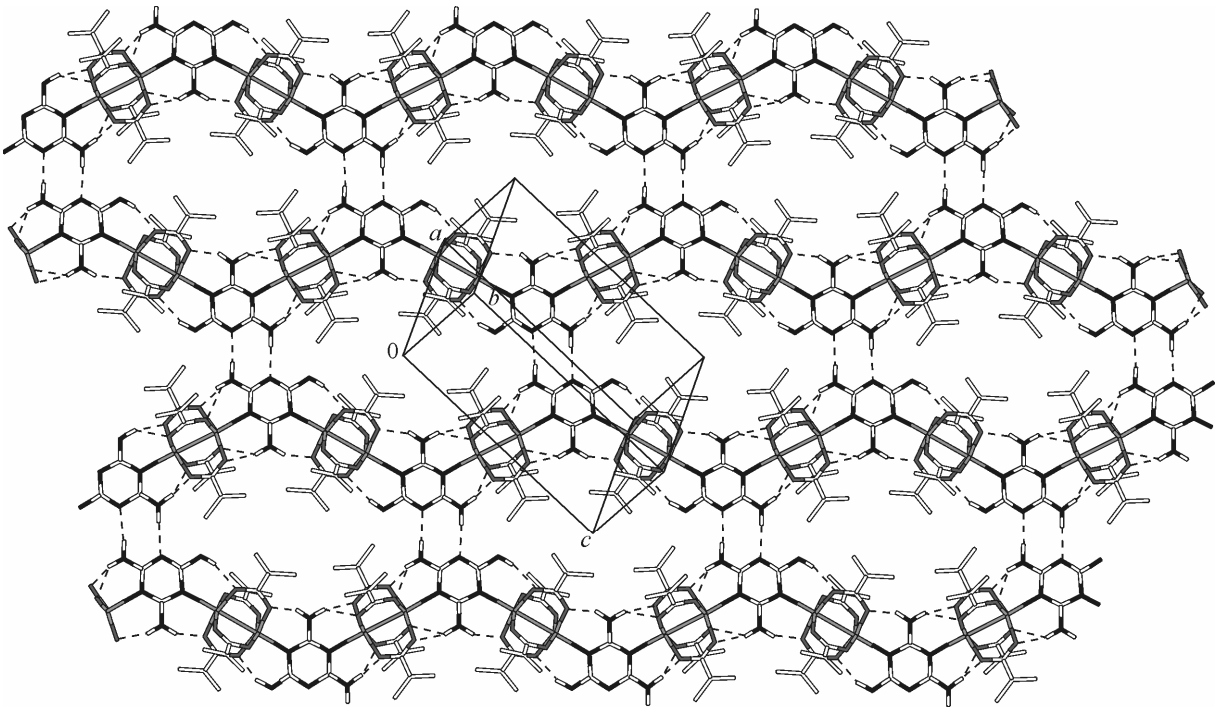

Fig. 3. Part of the crystal structure of **1**, showing the formation of R_1^1 (6) and R_2^2 (8) rings. H atoms not involved in these interactions have been omitted for clarity

REFERENCES

1. *Yaghi O.M., Li H.L.* // J. Amer. Chem. Soc. – 1996. – **118**. – P. 295.
2. *Batten S.R., Robson R.* // Angew. Chem. Int. Ed. Engl. – 1998. – **37**. – P. 1460.
3. *Wang Q.M., Wu X.T., Zhang W.J. et al.* // Inorg. Chem. – 1999. – **38**. – P. 2223.
4. *Cui C.P., Dai J.C., Du W.X. et al.* // Polyhedron. – 2002. – **21**. – P. 175.
5. *Bi W.H., Sun D.F., Cao R., Hong M.C.* // Acta Crystallogr. – 2002. – **E58**. – P. m324.
6. *Noro S.I., Kitaura R., Kondo M. et al.* // J. Amer. Chem. Soc. – 2002. – **124**. – P. 2568.
7. *Yang L., Tian J.L., Liu Z.Q. et al.* // Chinese J. Struct. Chem. – 2004. – **23**. – P. 510.
8. *Xia S.Q., Hu S.M., Zhang J.J. et al.* // Chinese J. Struct. Chem. – 2004. – **23**. – P. 898.
9. *Bean A., Garcia E., Scott B., Runde W.* // Inong. Chem. – 2004. – **43**. – P. 6145.
10. *Zhang J., Li Z.J., Wen Y.H. et al.* // J. Mol. Struct. – 2004. – **697**. – P. 185.
11. *Ranganathan A., Pedireddi V.R., Rao C.N.R.* // J. Amer. Chem. Soc. – 1999. – **121**. – P. 1752.
12. *Acharya S.N.G., Gopalan R.S., Kulkarni G.U. et al.* // Chem. Commun. – 2000. – P. 1351.
13. *Lange R.F.M., Beijer F.H., Sijbesma R.P. et al.* // Angew. Chem. Int. Ed. – 1997. – **36**. – P. 969.
14. *Zhang Y.G., Li J.M., Nishiura M., Imamoto T.* // Chem. Lett. – 1999. – P. 543.
15. *Mathias J.P., Simanek E.E., Zerkowski J.A. et al.* // J. Amer. Chem. Soc. – 1994. – **116**. – P. 4316.
16. *Sharif M.A., Aghabozorg H., Shokrollahi A. et al.* // Pol. J. Chem. – 2006. – **80**. – P. 847.
17. *Zerkowski J.A., MacDonald J.C., Seto C.T. et al.* // J. Amer. Chem. Soc. – 1994. – **116**. – P. 2382.
18. *Sheldrick G.M.* // Acta Crystallogr. – 2008. – **A64**. – P. 112.
19. *Farrugia L.J.* // J. Apply. Cryst. – 1999. – **32**. – P. 837.
20. *Perez C.R., Sanchiz J., Molina M.H. et al.* // Inorg. Chem. – 2003. – **39**. – P. 1363.
21. *Sanchiz J., Martin Y.R., Perez C.R. et al.* // New. J. Chem. – 2002. – **26**. – P. 1624.
22. *Subramaniam P.S., Dave P.C., Boricha V.P., Srinivas D.* // Polyhedron. – 1998. – **17**. – P. 443.
23. *Chung Y.H., Wei H.H., Liu Y.H. et al.* // Polyhedron. – 1998. – **17**. – P. 449.
24. *Liu T.F., Sun H.L., Gal S. et al.* // Inorg. Chem. – 2003. – **42**. – P. 4792.
25. *Bernstein J., Davis R.E., Shimoni L., Chang N.-L.* // Angew. Chem. Int. Ed. Engl. – 1995. – **34**. – P. 1555.