

CRYSTAL STRUCTURES OF Bis(AZIDO)bis(2-MORPHOLIN-4-YLETHYLAMINO)COPPER(II) AND Bis{2,4-DIBROMO-6-[(2-MORPHOLIN-4-YLETHYLIMINO)METHYL]PHENOLATO}COPPER(II)

H.-Y. Liu

UDC 548.73:547.13:546.56

Two new copper(II) complexes $[\text{Cu}(\text{MEA})_2(\text{N}_3)_2]$ (**1**) and $[\text{Cu}(\text{BMP})_2]$ (**2**), where MEA and BMP are 2-morpholin-4-ylethylamine and 2,4-dibromo-6-[(2-morpholin-4-ylethylimino)methyl]phenolate respectively, are prepared and characterized using elemental analysis, FT-IR spectroscopy, and X-ray single crystal diffraction. The crystal of **1** belongs to the triclinic system, space group $P\bar{1}$, with $a = 6.661(2)$ Å, $b = 8.440(3)$ Å, $c = 8.913(3)$ Å, $\alpha = 102.032(3)^\circ$, $\beta = 107.899(2)^\circ$, $\gamma = 98.242(3)^\circ$, $V = 454.6(3)$ Å³, $Z = 1$, $D_c = 1.490$ g/cm³, $R_1 = 0.0226$, and $wR_2 = 0.0564$. The crystal of **2** belongs to the monoclinic system, space group $P2_1/c$, with $a = 7.0707(7)$ Å, $b = 15.438(1)$ Å, $c = 14.227(1)$ Å, $\beta = 96.659(2)^\circ$, $V = 1542.5(3)$ Å³, $Z = 2$, $D_c = 1.821$ g/cm³, $R_1 = 0.0437$, and $wR_2 = 0.1041$. In each complex, the Cu atom is in a square planar coordination. The molecules of **1** are linked through intermolecular N–H···N and N–H···O hydrogen bonds to form layers parallel to the ab plane. The molecules of **2** are linked through intermolecular C–H···Br hydrogen bonds to form a 3D network.

DOI: 10.1134/S0022476614010223

Keywords: X-ray diffraction, copper complex, crystal structure, Schiff base, hydrogen bond.

1,2-Ethylenediamine and its derivatives are a kind of important starting material to synthesize multi-dentate Schiff bases. The complexes derived from diamines and their Schiff base derivatives have attracted much attention in structural and coordination chemistry [1-5]. Copper complexes have received considerable interest in the fields of medicinal chemistry for their antibacterial, antitumor, and antifungal activities [6-8] and materials chemistry [9-11]. As an extension of the work on such complexes, in this paper, two new copper(II) complexes $[\text{Cu}(\text{MEA})_2(\text{N}_3)_2]$ **1** and $[\text{Cu}(\text{BMP})_2]$ **2**, where MEA and BMP are 2-morpholin-4-ylethylamine and 2,4-dibromo-6-[(2-morpholin-4-ylethylimino)methyl]phenolate respectively, were prepared and structurally characterized.

Experimental. Materials and physical measurements. 2-Morpholin-4-ylethylamine and 3,5-dibromosalicylaldehyde were purchased from Lancaster Chemical Company Inc. Copper perchlorate was prepared by the reaction of $\text{Cu}_2(\text{OH})_2\text{CO}_3$ with perchloric acid in distilled water. All other chemicals were of analytical grade. Elemental analyses for C, H, and N were performed using a Perkin-Elmer 240C elemental analyzer. Infrared spectra were recorded on a Nicolet 170SX FT-IR spectrophotometer with KBr pellets in the 4000-400 cm⁻¹ region. Molar conductance measurements were performed in a DDS-11A conductivity meter.

School of Chemistry and Chemical Engineering, Guangdong Pharmaceutical University, Zhongshan, P. R. China; liuhuanyu03@163.com. The text was submitted by the authors in English. *Zhurnal Strukturnoi Khimii*, Vol. 55, No. 1, pp. 139-143, January-February, 2014. Original article submitted August 7, 2012.

TABLE 1. Crystallographic Data and Details of Refinements for the Complexes

Parameters	1	2
Empirical formula	C ₁₂ H ₂₈ CuN ₁₀ O ₂	C ₁₆ H ₁₆ N ₂ NiO ₂
Formula weight	408.0	327.0
Crystal system	Triclinic	Triclinic
Space group	<i>P</i> -1	<i>P</i> -1
Unit cell dimensions <i>a</i> , <i>b</i> , <i>c</i> , Å	6.661(2), 8.440(3), 8.913(3)	9.096(2), 11.351(2), 11.790(2)
α , β , γ , deg	102.032(3), 07.899(2), 98.242(3)	100.947(2), 93.050(2), 109.682(2)
<i>V</i> , Å ³	454.6(3)	1116.3(3)
<i>Z</i>	1	3
<i>D</i> _{calcd} , g·cm ⁻³	1.490	1.459
<i>F</i> (000)	215	510
μ (MoK α), mm ⁻¹	1.231	1.308
Collected/independent/observed reflections	3732/1943/1865	9245/4768/3545
θ range, deg	2.49-27.00	2.3-27.0
<i>R</i> ₁ / <i>wR</i> ₂ [<i>I</i> > 2 σ (<i>I</i>)]	0.0226/0.0564	0.0388/0.0845
<i>R</i> ₁ / <i>wR</i> ₂ (all data)	0.0242/0.0571	
<i>GOOF</i> on <i>F</i> ²	1.054	1.029

Synthesis of the [Cu(MEA)₂(N₃)₂] complex (1). 2-Morpholin-4-ylethylamine (0.130 g, 1 mmol), sodium azide (0.065 g, 1 mmol), and copper perchlorate (0.370 g, 1 mmol) were mixed in methanol (20 ml). The mixture was stirred at ambient temperature for 30 min to give a blue solution. Blue single crystals of **1** suitable for the X-ray analysis were obtained several days later. The yield was 63%. Anal. Calcd. for C₁₂H₂₈CuN₁₀O₂: C, 35.3%; H, 6.9%; N, 34.3%. Found: C, 35.5%; H, 6.9%; N, 34.4%. IR data (KBr; ν , cm⁻¹): 3287 (w), 3241 (w), 3159 (w), 2041 (vs), 1597 (m), 1459 (w), 1446 (w), 1331 (w), 1301 (w), 1271 (w), 1113 (s), 1068 (m), 1035 (w), 1011 (m), 982 (w), 925 (m), 882 (w), 854 (w), 771 (w), 610 (w), 537 (w), 442 (w), 347 (w).

Synthesis of the [Cu(BMP)₂] complex (2). 2-Morpholin-4-ylethylamine (0.130 g, 1 mmol), 3,5-dibromosalicylaldehyde (0.280 g, 1 mmol) were mixed in methanol (20 ml). The mixture was stirred for 30 min at ambient temperature to give a yellow solution. To the above solution a methanolic solution (10 ml) of sodium azide (0.065 g, 1 mmol) and copper perchlorate (0.370 g, 1 mmol) were added with stirring. The final mixture was further stirred at ambient temperature for 30 min to give a blue solution. Blue single crystals of **2** suitable for the X-ray analysis were obtained several days later. The yield was 45%. Anal. Calcd. for C₂₆H₃₀Br₄CuN₄O₄: C, 36.9%; H, 3.6%; N, 6.6%. Found: C, 36.8%; H, 3.5%; N, 6.7%. IR data (KBr; ν , cm⁻¹): 1613 (s), 1456 (m), 1401 (m), 1160 (w), 1110 (w), 856 (w), 777 (w), 707 (w), 586 (w), 530 (w), 445 (w).

X-ray data collection and structure determination. The crystal and instrumental parameters used in the unit cell determination and data collection are summarized in Table 1. Diffraction measurements were made at 298(2) K on a Bruker SMART APEX II X-ray diffractometer using graphite monochromated MoK α radiation in ω scan mode. Unit cell dimensions were determined and refined in the range 2.49 < θ < 27.00° for (**1**) and 1.95 < θ < 28.13° for (**2**). The SMART program [12] was used for the data collection, indexing reflection and determination of lattice parameters, SAINT [12] was used for the integration of the reflection intensity and scaling, and SADABS [13] was used for absorption correction. The structures were solved by the direct method using SHELXS-97 and refined by full-matrix least-squares techniques on *F*² with SHELXL-97 [14, 15]. All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were included in their idealized positions and refined isotropically. Selected bond distances (Å) and angles (deg) for complexes are listed in Table 2. Hydrogen bonding geometries are given in Table 3.

Results and discussion. Single crystals of the complexes are stable at ambient temperature and soluble in methanol, ethanol, and acetonitrile. The molar conductivity measurements of the complexes in DMSO at a concentration of 10⁻³ mol/l

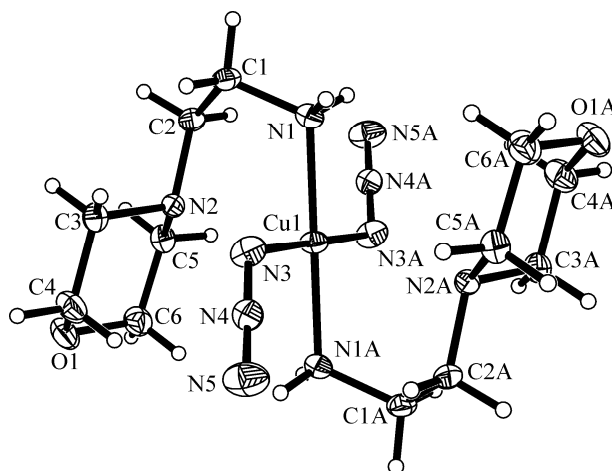
TABLE 2. Selected Bond Lengths (Å) and Angles (deg) for the Complexes

	1		2	
Cu1–N1	2.015(1)	Cu1–O1	1.909(2)	
N1–Cu1–N1A	180	O1–Cu1–O1A	180	
N1–Cu1–N3	86.9(1)	O1–Cu1–N1	91.3(1)	
Cu1–N3	2.022(1)	Cu1–N1	1.996(3)	
N1–Cu1–N3A	93.1(1)	O1–Cu1–N1A	88.7(1)	
N3–Cu1–N3A	180	N1–Cu1–N1A	180	

TABLE 3. Hydrogen Bonding Geometry for the Complexes (Å, deg)

<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>
1				
N1–H1B···N4 ⁱ	0.90	2.61	3.094(2)	115
N1–H1B···O1 ⁱⁱ	0.90	2.30	3.052(2)	140
N1–H1A···N5 ⁱⁱⁱ	0.90	2.30	3.157(2)	159
2				
C8–H8B···O1 ⁱ	0.97	2.31	2.808(2)	111
C9–H9B···Br1 ^{iv}	0.07	2.86	3.789(2)	162
C12–H12A···O2 ^v	0.97	2.56	3.381(2)	143

Symmetry codes: (i) 1–*x*, 1–*y*, 1–*z*; (ii) *x*, 1+*y*, *z*; (iii) –*x*, 1–*y*, 1–*z*; (iv) 1+*x*, 3/2–*y*, –1/2+*z*; (v) –*x*, 2–*y*, 1–*z*.

**Fig. 1.** ORTEP view of (**1**) with 30% thermal ellipsoids and the atom numbering scheme. Atoms labeled with the suffix A are at the symmetry position 1–*x*, 1–*y*, 1–*z*.

suggest that the complexes are non-electrolyte, with conductance values of 45 Ω^{–1}·cm²·mol^{–1} for **1** and 23 Ω^{–1}·cm²·mol^{–1} for **2** respectively [16].

Structure description of the complexes. The molecular structure of **1** is shown in Fig. 1. The complex possesses a crystallographic inversion center symmetry with the Cu atom located at the inversion center. The Cu atom is coordinated by two N atoms from two MEA ligands and two N atoms from two azide ligands, forming a square planar geometry. The Cu–N bond lengths are comparable to those observed in similar copper(II) complexes [17, 18]. As expected, the morpholine rings adopt a *chair* conformation to minimize the steric effects. In the crystal structure of **1**, the molecules are linked through intermolecular N–H···N and N–H···O hydrogen bonds to form layers parallel to the *ab* plane (Fig. 2).

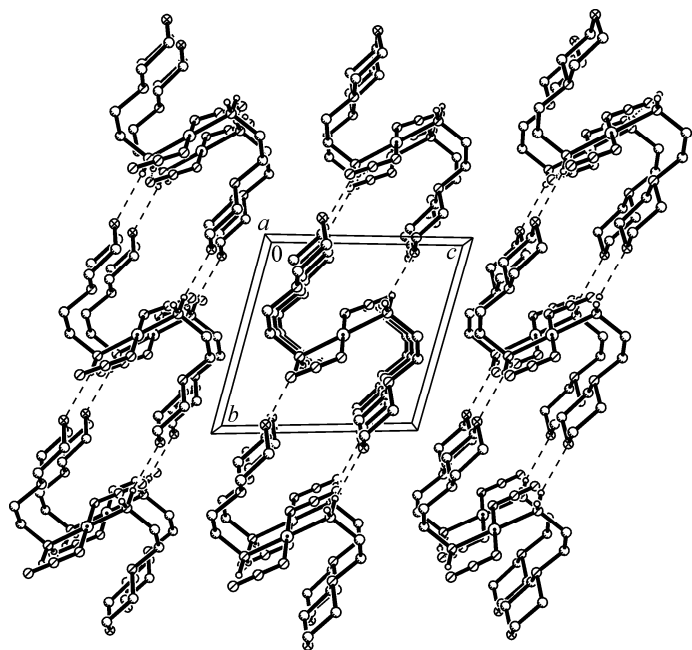


Fig. 2. Molecular packing structure of (1). Hydrogen bonds are drawn as dashed lines.

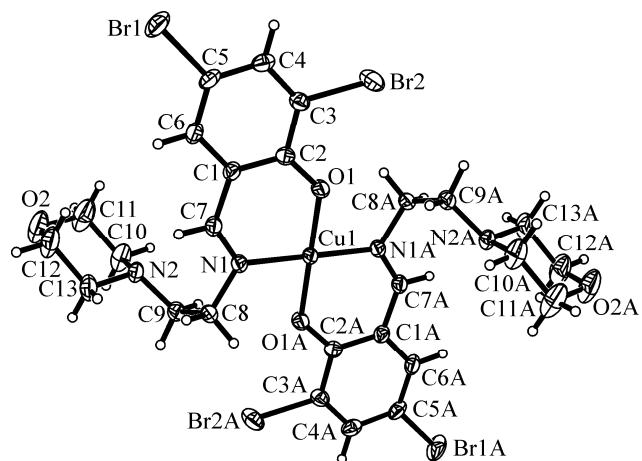


Fig. 3. ORTEP view of (2) with 30% thermal ellipsoids and the atom numbering scheme. Atoms labeled with the suffix A are at the symmetry position $1-x, 1-y, 1-z$.

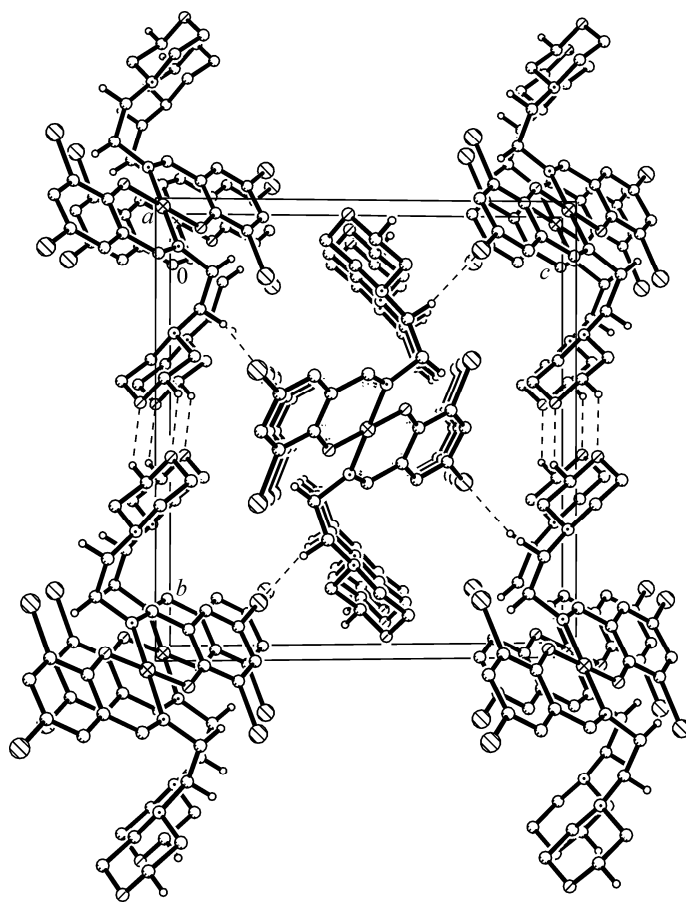


Fig. 4. Molecular packing structure of (2). Hydrogen bonds are drawn as dashed lines.

The molecular structure of **2** is shown in Fig. 3. The complex possesses a crystallographic inversion center of symmetry with the Cu atom located at the inversion center. The Cu atom is coordinated by two phenolate O and two imine N atoms from two Schiff base ligands BMP, forming a square planar geometry. The Cu–N and Cu–O bond lengths are comparable to those observed in similar copper(II) complexes with Schiff bases [19, 20]. As expected, the morpholine rings adopt a *chair* conformation to minimize the steric effects. In the crystal structure of **2**, molecules are linked through intermolecular C–H···Br hydrogen bonds to form a 3D network (Fig. 4).

IR spectra. The middle and sharp band at 3208 cm^{−1} in the IR spectrum of **1** is assigned to the N–H vibrations. The intense absorption in the IR spectrum of **1** is assigned to the stretching vibrations of the azide ligands. The strong absorption band at 1606 cm^{−1} in the IR spectrum of **2** is attributed to the azomethine stretching frequencies of the Schiff base ligands.

Supplementary material. CCDC 895550 (1) and 895551 (2) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge through www.ccdc.cam.ac.uk/data_request/cif, or by e-mailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK. Fax: +44(0)1223-336033.

The work was supported by the Guangdong Pharmaceutical University Young Teachers' Fund and the Ten Hundred Thousand Project of the Bureau of Education of Guangdong Province, P. R. China.

REFERENCES

1. A. A. Hoser, W. Schilf, A. S. Chelminiecka, B. Kolodziej, B. Kamiński, E. Grech, and K. Wozniak, *Polyhedron*, **31**, No. 1, 241-248 (2012).
2. H. Y. Liu, G. W. Li, Z. L. Li, J. Y. Wu, and Y. C. Cai, *Russ. J. Coord. Chem.*, **37**, No. 9, 668-673 (2011).
3. Z.-L. You, D.-H. Shi, J.-C. Zhang, Y.-P. Ma, C. Wang, and K. Li, *Inorg. Chim. Acta*, **384**, No. 1, 54-61 (2012).
4. S. K. Dey, M. S. El Fallah, J. Ribas, T. Matsushita, V. Gramlich, and S. Mitra, *Inorg. Chim. Acta*, **357**, No. 5, 1517-1522. (2004)
5. D. Parker, E. S. Davies, C. Wilson, and J. McMaster, *Inorg. Chim. Acta*, **360**, No. 1, 203-211 (2007).
6. G. Murtaza, M. K. Rauf, A. Badshah, M. Ebihara, M. Said, M. Gielen, D. de Vos, E. Dilshad, and B. Mirza, *Eur. J. Med. Chem.*, **48**, No. 1, 26-35 (2012).
7. B. Roopashree, V. Gayathri, and H. Mukund, *J. Coord. Chem.*, **65**, No. 8, 1354-1370 (2012).
8. N. Raman, A. Kulandaisamy, and C. Thangaraja, *Transition Met. Chem.*, **29**, No. 2, 129-135 (2004).
9. L. D. Popov, S. I. Levchenkov, M. A. Kiskin, I. N. Shcherbakov, Y. P. Tupolova, O. V. Maevskii, and V. A. Kogan, *J. Struct. Chem.*, **53**, No. 2, 393-396 (2012).
10. D. Saha, T. Maity, T. Dey, and S. Koner, *Polyhedron*, **35**, No. 1, 55-61 (2012).
11. P. Seppala, E. Colacio, A. J. Mota, and R. Sillanpaa, *Dalton Trans.*, **41**, No. 9, 2648-2658 (2012).
12. Bruker, *SMART and SAINT*, Bruker AXS Inc., Madison, Wisconsin, USA (2002).
13. G. M. Sheldrick, *SADABS*, Univ. Göttingen, Germany (1996).
14. G. M. Sheldrick, *SHELXS-97*, Univ. Göttingen, Germany (1997).
15. G. M. Sheldrick, *SHELXL-97*, Univ. Göttingen, Germany (1997).
16. W. Geary, *Coord. Chem. Rev.*, **7**, Nos. 1/2, 81-122 (1971).
17. Y.-Q. Cui, Z.-L. You, X.-F. Li, X.-L. Wang, Y.-P. Ma, C. Wang, and C.-L. Zhang, *Transition Met. Chem.*, **35**, No. 2, 159-163 (2010).
18. B. Sarkar, M. S. Ray, M. G. B. Drew, C.-Z. Lu, and A. Ghosh, *J. Coord. Chem.*, **60**, No. 20, 2165-2176 (2007).
19. C. Adhikary, D. Mal, K. Okamoto, S. Chaudhuri, and S. Koner, *Polyhedron*, **25**, No. 11, 2191-2197 (2006).
20. M. Zbiri, S. Saha, C. Adhikary, S. Chaudhuri, C. Daul, and S. Koner, *Inorg. Chim. Acta*, **359**, No. 4, 1193-1199 (2006).