



Crystal Structure of A Novel Binuclear Cu (II) Schiff Base Complex: [Bis ((E)-(2-(dimethylamino)ethylimino)methyl)phenolato]bis[μ-(acetato)]Copper(II)

Iran Sheikhshoae*, Hojatollah Khabbazadeh, Nasim Setoodeh

Shahid Bahonar University of Kerman, Kerman, Iran

ABSTRACT

In the crystal structure of the title centrosymmetric dimer, $[Cu_2(C_{26}H_{36}N_4O_6)]$ (1), the Cu(II) atom has an almost perfect square-pyramidal geometry. The Cu (II) ion is coordinated by N_2O donor atoms of the salen based tri dentate Schiff base ligand and, the two O atoms of two acetate groups. The present study demonstrates a novel example of binuclear copper (II) complex with two tri dentate salen ligands and two bridged acetate groups. The independent part of the complex is shown in figure. In the structure of the title compound, each Cu(II) ion is coordinated with two nitrogen atoms (N(1) and N(2)) and one oxygen atom (O1) from tridentate salen ligand and one oxygen of the acetate group, forming $[OAC]CuL$ unit. To complete the coordination sphere around the copper atom, two of these units dimerism over the oxygen atom of acetate group to form a Centro symmetric molecule. In the planar $Cu_2 O_2$ core, each copper atom displays a distorted square-pyramidal geometry. Crystal data for complex at 120 K: monoclinic, space group $P 21/n$, $a = 11.0102$ (9) °, $b = 8.2177$ (7) °, $c = 15.4288$ (12) °, $\beta = 103.041$ (2), $V = 1359.97$ (19) Å³, $Z = 2$, $R = 0.048$.

Keywords: Copper (II), Schiff base complex, Tridentate ligand, Transition metal complex, X-ray structure determination.

INTRODUCTION

Aromatic Schiff bases, especially those derived from reaction of salicylic aldehydes with amines (salen-type Schiff bases), form complexes with a variety of metal ions [1-5]. Among the various possible applications of these complexes [6, 7], their nonlinear optical properties for the design of materials in modern communication technology [8-10].

In the other hand recently, interest has grown in the chemistry of high nuclearity copper (II) complexes draw from their utility in the molecular design of magnetic material and models for the active sites of metallo enzymes [11-13]. Bridged dinuclear copper (II) complexes have been the subject of continuing interest for chemists because of their magneto-structural properties [14, 15]. The present study demonstrates a novel example of dinuclear copper (II) Schiff base complex with two tri dentate ligand and two acetate bridge. The molecular structure of the title molecule is illustrated in Fig. 1. It is a novel binuclear Schiff base copper (II) complex, with the Cu(II) ion having a N_2O_2 square pyramidal geometry.

EXPERIMENTAL SECTION

Materials and Instruments

$Cu(CH_3COO)_2 \cdot 2H_2O$, N, N-dimethylethane-1,2-diamine, MeOH and CH_2Cl_2 were purchased from Merck and used without

further purification. IR spectra were recorded on a Bruker FT-IR Tensor 27 spectrometer (KBr pellets, 4000-400 cm⁻¹).

Synthesis of Complex (1)

Dicopper complex [Cu₂ (L) 2(CH₃COO)₂] was prepared by the reaction of (2 mmol) 2-((E)-(2-(dimethylamino)ethylimino)methyl)phenol (L) [16,17] and (1 mmol) Cu(CH₃COO)₂·2H₂O were allowed to reflux in MeOH (20 ml) for 2 h. The solution turned dark green. The solution was filtered after cooling, and the filtrate allowed evaporating slowly at room temperature. The green solid products were separated by filtration, purified by crystallization from CH₂Cl₂ and resulted in the formation of green crystals of the title complex, after few days. m. p. 185-187° C, Yield 88%.

X-ray Crystallography

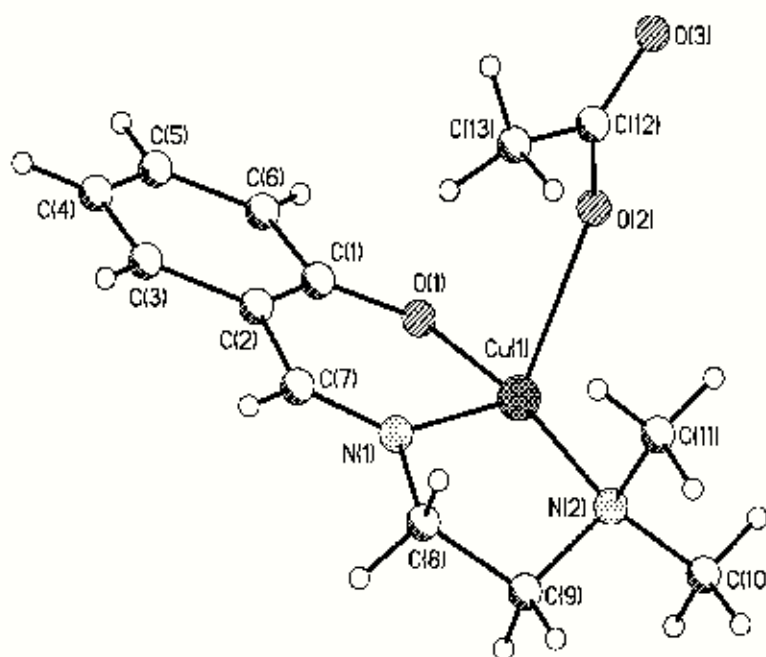
X-ray structure analysis of suitable single crystals was carried out on a Bruker [18], Smart 1000 CCD area detector (Mo Kα radiation, graphic monochromator, λ = 0.71073 Å, at 120 K). The crystal structure of this compound was solved by direct methods (SHELXTL-97) [19] and refined by full-matrix least squares on F² using the program SHELXL-97. Refinement of F² against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F², conventional R-factors R are based on F, with F set to zero for negative F². The threshold expression of F² > s (F²) is used only for calculating R_{int} etc. and is not relevant to the choice of reflections for refinement. R-factors based on F² are statistically about twice as large as those based on F, and R-factors based on all data will be even larger [20]. Crystallographic data and processing parameters are given in Table 1.

RESULTS AND DISCUSSION

The reaction of two mole (2 mmol) 2-((E)-(2-(dimethylamino) ethylimino)methyl)phenol and 1 mol Cu(CH₃COO)₂·2H₂O in MeOH under reflux condition leads to the complex [Cu₂(C₂₆H₃₆N₄O₆)] (1), Fig. 1.

Crystal Structure

Compound (1) crystallizes in monoclinic space group P21/n. Figure 1 illustrates the principle structural features of complex 1, It is a novel binuclear Schiff base copper(II) complex, with the Cu(II) ion having a N₂O₂ square-pyramidal geometry. Selected bond lengths and bond angles are listed in Table 2. In this complex acetate ligands acts as bridged ligand, Fig. 2, the central copper atoms are bonded to the five atoms. The Cu-O and Cu-N bond distances Cu(1)-O(1) 1.9285 Å, Cu(1)-N(1) 1.9503 Å Cu(1)-O(2) 1.9655 Å Cu(1)-N(2) 2.0917 Å, Cu(1)-O(2) 2.3653 Å. The packing of compound (1) is shown in Fig. 3.



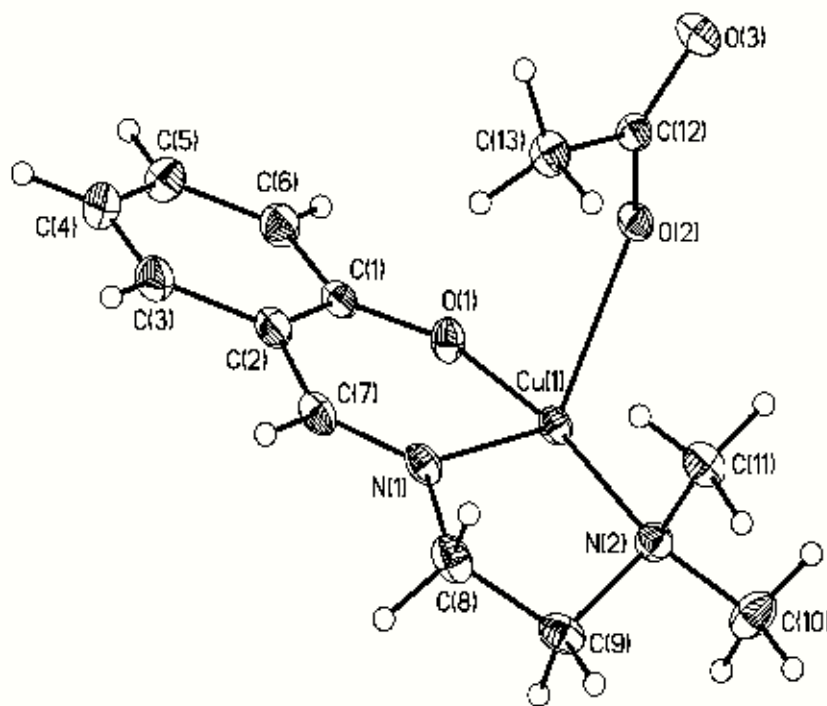


Fig. 1 General view of the independent part of the complex (1) in representation of atoms via thermal ellipsoids at 50% probability level.

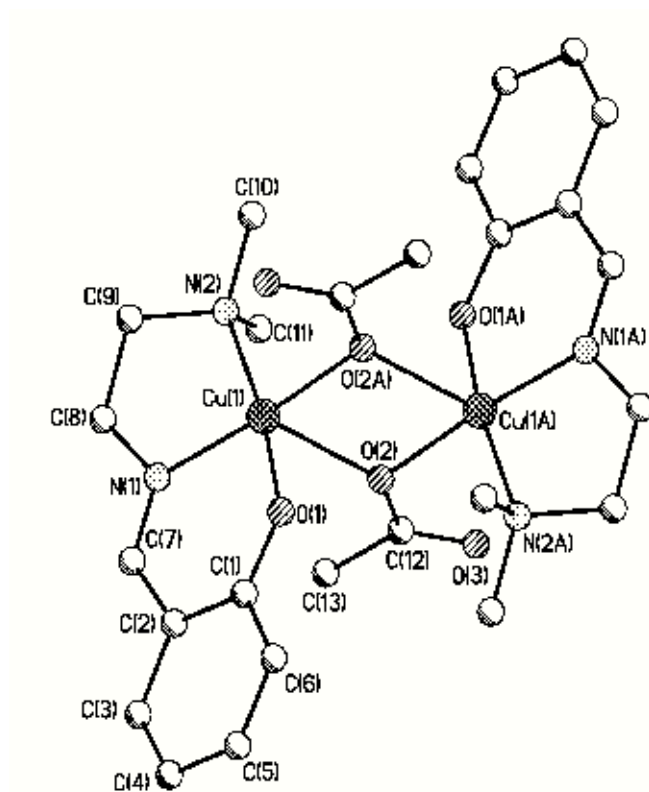


Fig. 2 General view of the molecule of the complex (1). The hydrogen atoms are omitted for clarity

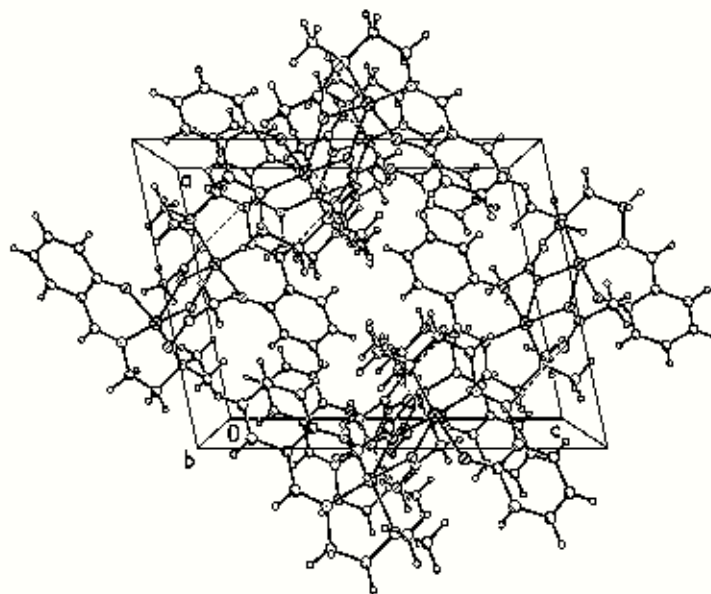


Fig. 3 Fragment of the crystal packing of the compound (1) along the crystallographic axis b.

Table 1 Crystallographic data of complex (1)

Empirical formula	C ₂₆ H ₃₆ Cu ₂ N ₄ O ₆
Formula weight	627.67
Temperature	120(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	P 21/n
Unit cell dimensions	a = 11.0102(9) Å α = 90°. b = 8.2177(7) Å β = 103.041(2)°. c = 15.4288(12) Å γ = 90°
Volume	1359.97(19) Å ³
Z	2
Density (calculated)	1.533 Mg/m ³
Absorption coefficient	1.611 mm ⁻¹
F(000)	652
Final R indices [for 3053 rfln with I>2σ(I)]	R1 = 0.0374, wR2 = 0.0901
R indices (all data)	R1 = 0.0442, wR2 = 0.0943
Largest diff. peak and hole	1.376 and -0.469 e. Å ⁻³

Table 2. Some of bond lengths [Å] and angles [°] of complex (1)

Bond	Bbond lengths [Å]	Angles [°]			
Cu(1)-O(1)	1.9285(14)	O(1)-Cu(1)-N(1)	91.25(7)	C(11)-N(2)-C(9)	110.21(16)
Cu(1)-N(1)	1.9503(17)	O(1)-Cu(1)-O(2)#1	88.61(6)	C(10)-N(2)-Cu(1)	114.84(13)
Cu(1)-O(2)#1	1.9655(14)	N(1)-Cu(1)-O(2)#1	173.80(6)	C(11)-N(2)-Cu(1)	111.45(13)
Cu(1)-N(2)	2.0917(17)	O(1)-Cu(1)-N(2)	171.39(6)	C(9)-N(2)-Cu(1)	102.37(13)
N(1)-C(8)	1.479(3)	N(1)-Cu(1)-N(2)	83.58(7)	C(1)-O(1)-Cu(1)	127.76(13)
N(2)-C(10)	1.481(3)	O(2)#1-Cu(1)-N(2)	95.79(6)	C(12)-O(2)-Cu(1)#1	113.68(12)
N(2)-C(11)	1.484(3)	O(1)-Cu(1)-O(2)	89.19(6)	C(12)-O(2)-Cu(1)	143.67(12)
N(2)-C(9)	1.487(3)	N(1)-Cu(1)-O(2)	108.18(6)	Cu(1)#1-O(2)-Cu(1)	101.98(6)
O(1)-C(1)	1.301(2)	O(2)#1-Cu(1)-O(2)	78.02(6)		
O(2)-C(12)	1.294(2)	N(2)-Cu(1)-O(2)	98.94(6)		
O(2)-Cu(1)#1	1.9655(14)	C(7)-N(1)-C(8)	118.33(17)		
C(11)-H(11C)	0.9800	C(7)-N(1)-Cu(1)	126.95(14)		
C(12)-C(13)	1.512(3)	C(8)-N(1)-Cu(1)	114.69(13)		
C(13)-H(13A)	0.9800	C(10)-N(2)-C(11)	108.05(17)		
C(13)-H(13C)	0.9800	C(10)-N(2)-C(9)	109.82(17)		

Symmetry transformations used to generate equivalent atoms: #1 -x+1, -y+1, -z

Table 3. Atomic coordinates (104) and equivalent isotropic displacement parameters (Å² × 10³) for complex (1)*U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.*

	X	Y	Z	U(eq)
Cu(1)	6078(1)	4655(1)	948(1)	15(1)
N(1)	6793(2)	5562(2)	2121(1)	17(1)
N(2)	7631(2)	5729(2)	611(1)	17(1)
O(1)	4825(1)	3509(2)	1403(1)	18(1)
O(2)	4521(1)	6461(2)	195(1)	16(1)
O(3)	3207(1)	8455(2)	-370(1)	23(1)
C(1)	4494(2)	3757(2)	2150(1)	17(1)
C(2)	5137(2)	4808(2)	2838(1)	19(1)
C(3)	4699(2)	4983(3)	3635(2)	24(1)
C(4)	3676(2)	4156(3)	3763(2)	27(1)
C(5)	3050(2)	3096(3)	3094(2)	25(1)
C(6)	3444(2)	2895(3)	2316(1)	22(1)
C(7)	6287(2)	5597(2)	2797(1)	19(1)
C(8)	8032(2)	6324(3)	2208(1)	22(1)
C(9)	8580(2)	5665(3)	1465(2)	23(1)
C(10)	8102(2)	4866(3)	-91(2)	26(1)
C(11)	7378(2)	7443(3)	324(1)	22(1)
C(12)	4058(2)	7902(2)	223(1)	16(1)
C(13)	4628(2)	8923(3)	1027(1)	20(1)

Table 4. Anisotropic displacement parameters (Å² × 10³) for complex (1)*The anisotropic displacement factor exponent takes the form: -2π²[h²a*²U11+...+2hka*b*U12]*

	U11	U22	U33	U23	U13	U12
Cu(1)	15(1)	15(1)	13(1)	-1(1)	0(1)	-2(1)
N(1)	17(1)	16(1)	15(10)	0(1)	-2(1)	-3(1)
N(2)	15(10)	19(1)	18(1)	-1(1)	3(1)	-2(10)
O(1)	20(1)	20(1)	14(1)	-1(1)	3(1)	-4(1)
O(2)	17(10)	15(1)	15(1)	-1(1)	1(1)	0(1)
O(3)	23(1)	22(1)	21(1)	2(1)	-2(1)	3(1)
C(1)	17(1)	17(1)	15(1)	2(1)	0(1)	3(1)
C(2)	20(1)	19(1)	16(1)	1(1)	1(1)	2(1)
C(3)	26(1)	27(1)	17(1)	-2(1)	3(1)	5(1)
C(4)	28(1)	34(1)	20(1)	1(1)	8(1)	6(1)
C(5)	22(1)	30(1)	25(1)	4(1)	8(1)	1(1)
C(6)	21(1)	24(10)	20(1)	0(1)	3(1)	0(1)
C(7)	23(1)	16(10)	15(1)	-1(1)	-1(1)	1(1)
C(8)	20(1)	24(1)	18(1)	1(1)	-3(1)	-8(1)
C(9)	15(1)	24(1)	25(1)	1(1)	-3(1)	-1(1)
C(10)	20(1)	31(1)	29(1)	-8(1)	10(1)	-6(1)
C(11)	21(1)	20(1)	22(1)	3(1)	1(1)	-2(1)
C(12)	15(1)	17(1)	17(1)	1(1)	4(1)	0(1)
C(13)	23(1)	18(1)	19(1)	-4(1)	3(1)	-2(1)

Supplementary Material

Complete bond lengths and angles, co-ordinates and displacement parameters have been Deposited at Cambridge Crystallography Data Center. Supplementary data are available from the CCDC, 12 Union Road, Cambridge CB2 IEZ, UK (FAX: 44 (1223)336-033; E-mail: deposit@ccdc.cam.ac.uk) on request, quoting the deposition number 793210 for C₂₆H₃₆Cu₂N₄O₆.

ACKNOWLEDGEMENTS

We are grateful to Shahid-Bahonar University of Kerman Research Council and by the Group of Organometallic Catalysts, Shahid Bahonar University of Kerman for the financial support of this Research.

REFERENCES

- [1] N Hoshino, *Coord. Chem. Rev.*, **1998**, 174, 77-108.
- [2] DA Atwood, MJ Harvey, *Chem. Rev.*, **2001**, 101(1), 37-52.
- [3] PG Cozzi, *Chem Soc Rev.*, **33**, **2004**, 410-421.

-
- [4] N Monad, I Sheikhshoae, A Rezaeifard, H Stoeckli-Evans, *Acta Cryst*, **2009**, 65 (9), m1124-m1125.
- [5] I Sheikhshoae, V Langer, SA Yasreb, *Acta Cryst*, **2011**, E67, m839.
- [6] I Sheikhshoae, A Rezaeifard, N Monadi, S Kaafi, *Polyhedron*, **2009**, 28, 733-738.
- [7] I Sheikhshoae, H Nezamabadipour, *Bull. Chem. Soc. Ethiop.*, **2009**, 23(2), 309-313.
- [8] AP Alivisatos, PF Barbara, AW Castleman, J Chang, DA Dixon, ML Klein, *Adv. Mater.*, **1998**, 10, 1297-1299.
- [9] L Dalton, *Adv. Polym. Sci.*, **2002**, 158, 1-82.
- [10] H Khabazzadeh, I Sheikhshoae, S Saeid-Nia, *Transition Met. Chem.*, **2010**, 35(1), 13-17.
- [11] H Borzel, P Comba, H Pritzkow, *J. Chem. Soc. Chem. Commun.*, **2001**, 97-101.
- [12] SS Chui, SMF Lo, JPH Charmant, AG Orpen, ID Williams, *Science*, **1999**, 283, 1148-1150.
- [13] LK Thompson, SK Mandal, SS Tandon, JN Bridson, MK Park, *Inorg. Chem.*, **1996**, 35, 3117-3125.
- [14] V H Crawford, HW Richardson, JR Wasson, DJ Hodgson, WE Hatfield, *Inorg. Chem.*, **1976**, 15, 2107-2110.
- [15] L Merz, W Haase, *J. Chem. Soc. Dalton Trans.*, **1980**, 875.
- [16] D Gopal, S Rameshwer, M Subrata, S Ramsharan, KB Parimal, *Inorg. Chem.*, **1997**, 26, 323-329.
- [17] PS Subramanian, E Suresh, P Dastidar, *Polyhedron*, **2004**, 23, 2515-2522.
- [18] E Bruker, **1998**, SMART Bruker Molecular Analysis Research Tool, Version 5.059. Bruker AXS, Madison, Wisconsin, USA.
- [19] Bruker, **1999**, SAINTPLUS Data Reduction and Correction Program Version 6.01, Bruker, AXS, Madison, Wisconsin, USA.
- [20] GM Sheldrick, **1998a**, SADABS Version .2.01, Bruker/Siemens Area Detector Absorption Correction Program, Bruker AXS, Madison, Wisconsin, USA. GM Sheldrick, 1998b. SHELXTL v. 5.10, Structure Determination Software Suite, Bruker AXS, Madison, Wisconsin, USA.