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PREPARATION AND MOLECULAR STRUCTURE OF 2-BENZYLAMINOPYRIDINE COPPER(I) COMPLEX

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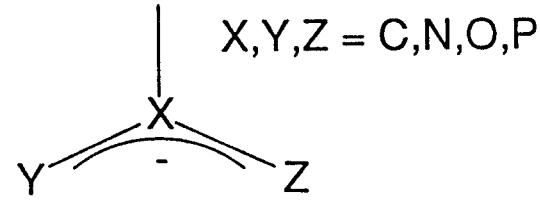
Abstract

2-Benzylaminopyridine (HBAP) reacts with NaH in THF and generates the sodium salt (NaBAP). Further reaction of $[Cu(TMEDA)_2]$ $[CuCl_2]$ with one equivalent of this ligand in THF leads to the formation of a dimeric Cu(I) complex, $[Cu\ (BAP)]_2 . H_2O$. The molecular structure has been determined by using a single-crystal *X*-ray diffraction method. The yellow compound crystallizes in the monoclinic space group $P2_1/c$ with four molecules per unit cell. The unit cell dimensions are a = 8.090(4), b = 11.220(7), c = 22.412(8)Å with β=91.31(3)°. The final R value is 0.065 for 3859 reflections measured. Coordination number around each copper is two (nearly linear). The Cu ... Cu distance is 2.4558(16)Å.

Introduction

Copper(I) stereochemistry is dictated by ligand steric and electron effects [1-4]. The three-center anionic chelating ligands have a remarkable ability for enforcing dimeric, trimeric, and tetrameric aggregation and in some cases with short Cu-Cu contacts in copper(I) complexes [5-14]. Very short metal-metal bonds have also been found in the chemistry of divalent transition metals in the presence of two or more anionic bridging ligands which have the characteristic three-center chelating geometry and the four-pi electron configuration of an allylic system (Scheme I) [15-22].

Reaction of $[Cu(TMEDA)_2]$ $[CuCl_2]$ or CuCl with a series of bidentate amides possessing a three center chelating geometry has resulted in the formation of dinuclear complexes [23]. In this research project, complex of 2-benzylamino-pyridine with $[Cu(TMEDA)_2]$ $[CuCl_2]$ has been prepared and investigated by a single-crystal *X*-ray diffraction.



Scheme I

Keywords: Preparation; 2-Benzylaminopyridine copper(I) complex; Molecular structure; Copper-copper interaction

Experimental Section

All manipulations were carried out under a purified nitrogen atmosphere in a Schlenk apparatus. All solvents and N, N, N′, N′-tetramethylethylene-diamine, TMEDA, were dried and distilled by standard method before using. Infrared spectrum was recorded on a Perkin-Elmer 393 instrument from Nujol mull prepared in a dry-box.

Preparation of Complex

To a stirred 100 ml THF solution of 2-benzylaminopyridine (2.00 g, 10.86 mmol) was added excess of sodium hydride. The reactants were heated gently for approximately 2 h and afforded a light yellow but cloudy suspension which was subsequently filtered to reveal a light yellow clear solution. To this solution was added one equivalent of Cu(I) in the form of [Cu(TMEDA)$_2$] [CuCl$_2$] (2.34 g, 5.44 mmol) producing some yellow microcrystalline material. Following several recrystallizations in THF, flat yellow crystals suitable for *X*-ray diffraction were produced (yield ≈ 70%). IR (Nujol mull, KBr, cm^{-1}):

[Nujol: 3000-2865 (vs), 1455 (s), 1375 (s) 1345 (w, sh)]. 1610 (s), 1527 (m), 1490 (s), 1340 (s), 1325 (w), 1297 (s), 1252 (s), 1205 (vw), 1175 (w), 1160 (s), 1120 (m), 1075 (vw), 1055 (m), 1010 (m), 965 (vw), 910 (vw), 890 (w), 820 (w), 810 (vw), 795 (vw), 753 (s), 743 (s), 725 (m), 690 (s).

Data Collection and Reduction

A yellow crystal of $Cu_2N_4C_{24}H_{22}O$ having approximate dimensions of 0.20×0.20×0.20 mm was mounted on a glass fiber. All measurements were made on a Rigaku AFC6S diffractometer with graphite monochromated Mo-*K*α radiation and 12 kW rotating anode generator, using the θ/2θ scan mode. Absorption corrections were made. Cell dimensions were obtained from 24 reflections with 2θ angle in the range of 40.00-50.00 degrees. This compound crystallizes in the monoclinic space group of $P2_1/c$ symmetry. The unit cell and crystal data are reported in Table 1.

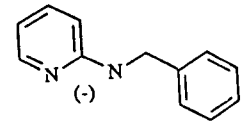
Structure Determination and Refinement

Data were collected at -160°C. The structure was solved by direct method. The non-hydrogen atoms were refined anisotropically. Hydrogen atom positions were calculated but not refined. The final cycles of full-matrix least-squares refinement was based on the number of observed reflections with $I > 2.5\sigma(I)$ and corresponding parameters. The final R value ($R = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$) was 0.065 ($R_w$ = 0.058) for 3859 reflections measured. Fractional atomic coordinates for non-hydrogen atoms are given in Table 2. Anisotropic thermal parameters for non-hydrogen atoms, the hydrogen atom parameters and distances are available.

Results and Discussion

The crystal consists of [Cu(BAP)]$_2$. H$_2$O complex, illustrated in Figure 1. This complex is a dimeric molecule in which anions of 2-benzylaminopyridine

Table 1. Crystal data for [Cu(BAP)]$_2$.H$_2$O; HBAP=2-benzylaminopyridine*

Empirical Formula	$C_{24}H_{22}Cu_2N_4O$
Formula Weight	509.6
Crystal Dimensions (mm)	0.20×0.20×0.20
Crystal System	Monoclinic
Lattice Parameters	a = 8.090(4) Å b = 11.220(7) Å c = 22.412(8) Å β = 91.31(3)° V = 2033.7(18) Å^3
Space Group	$P2_1/c$
Z	4
D_{calc} (g/cm^3)	1.664
R, R_w	0.065, 0.058
* BAP = 	

are linked through linearly coordinated copper atoms to form eight member rings. Stereoview of the packing of [Cu(BAP)]$_2$. H$_2$O in the unit cell is given in Figure 2. Selected bond distances and angles are given in Table 3. The average copper-nitrogen bond distances in [Cu(BAP)]$_2$. H$_2$O is 1.890 Å which is similar to the copper-nitrogen bond distance in [Cu(DPT)]$_2$ (Cu-N bond distance is 1.897Å; HDPT = 1,3-diphenyltriazene) [23]. The average N-Cu-N bond angle is 175.8° in [Cu(BAP)]$_2$. H$_2$O which is close to N-Cu-N bond angle in [Cu(DPT)]$_2$ (172.7°). The Cu ... Cu distances are 2.456(2)Å and 2.447(2)Å in [Cu(BAP)]$_2$. H$_2$O and [Cu(DPT)]$_2$ complexes respectively which are shorter than those which exist in metallic copper (2.56 Å). In these complexes, the short Cu...Cu distances may be imposed by the bridging ligands. The short Cu...Cu distances in various Cu aggregates, ranging from 2.38 Å which is nearly 0.2 Å shorter than the Cu...Cu distances in metallic copper to about 2.8 Å, raise the question of whether significant direct Cu...Cu bonding occurs. The Cu...Cu distances in [Cu(BAP)$_2$]. H$_2$O and [Cu(DPT)]$_2$ indicate strong Cu...Cu interactions. The assignment of any direct or otherwise unusual bonding character between the copper atoms may be premature and

Table 2. Fractional atomic coordinates and Biso for $[Cu(BAP)]_2 . H_2O$ complex*

	x	y	z	Biso
CU1	0.66445(12)	0.16657(9)	0.20707 (4)	1.71 (4)
CU2	0.83539(12)	0.08690(9)	0.28979 (4)	1.72 (4)
O1	0.3348 (12)	0.1660 (9)	0.2910 (4)	1.43(17)
O2	0.1662 (12)	0.0853 (9)	0.2075 (4)	1.09(16)
N1	0.5522 (8)	0.2541 (7)	0.2649 (3)	2.2 (3)
N2	0.7115 (8)	0.1792 (6)	0.3439 (3)	1.71(24)
N3	0.7862 (8)	0.0717 (6)	0.1532 (3)	1.77(25)
N4	0.9505 (9)	0.0016 (6)	0.2316 (3)	2.1 (3)
C1	0.5929 (9)	0.2573 (7)	0.3219 (3)	1.6 (3)
C2	0.5184 (11)	0.3380 (8)	0.3651 (4)	2.3 (3)
C3	0.5629 (11)	0.3299 (8)	0.4246 (4)	2.2 (3)
C4	0.6750 (10)	0.2448 (8)	0.4447 (3)	1.9 (3)
C5	0.7473 (10)	0.1720 (7)	0.4022 (3)	1.6 (3)
C6	0.4181 (11)	0.3311 (8)	0.2430 (3)	2.2 (3)
C7	0.3824 (7)	0.3025 (5)	0.17748(16)	2.0 (3)
C8	0.2979 (7)	0.1984 (4)	0.16168(18)	2.0 (3)
C9	0.2675 (7)	0.1715 (4)	0.10165(21)	2.4 (3)
C10	0.3216 (7)	0.2488 (5)	0.05742(15)	2.0 (3)
C11	0.4061 (7)	0.3529 (5)	0.07322(20)	2.6 (4)
C12	0.4365 (7)	0.3798 (4)	0.13325(23)	2.7 (4)
C13	0.9068 (10)	-0.0033 (7)	0.1749 (3)	1.7 (3)
C14	0.9814 (10)	-0.0833 (8)	0.1320 (4)	2.0 (3)
C15	0.9338 (11)	-0.0802 (8)	0.0725 (4)	2.2 (3)
C16	0.8150 (10)	0.0032 (8)	0.0527 (4)	2.0 (3)
C17	0.7452 (10)	0.0750 (7)	0.0946 (3)	1.9 (3)
C18	1.0870 (10)	-0.0731 (8)	0.2534 (3)	2.1 (3)
C19	1.1192 (7)	-0.0453 (5)	0.31901(16)	2.3 (3)
C20	1.0657 (7)	-0.1258 (4)	0.36191(23)	2.6 (4)
C21	1.0896 (8)	-0.1004 (5)	0.42243(20)	2.5 (4)
C22	1.1670 (8)	0.0054 (5)	0.44005(16)	2.7 (4)
C23	1.2205 (7)	0.0858 (4)	0.39714(22)	2.8 (4)
C24	1.1966 (7)	0.0605 (4)	0.33662(20)	1.8 (3)

* Biso is the mean of the principal axes of the thermal ellipsoid.

Table 3. Selected bond distances (Å) and angles (deg) for $[Cu(BAP)]_2 . H_2O$. Estimated standard deviations are given in parentheses.

Cu(1) - Cu(2) = 2.4558 (16)	
Cu(1) - N(1) = 1.877(7)	Cu(1) - N(3) = 1.901(6)
Cu(2) - N(2) = 1.899(6)	Cu(2) - N(4) = 1.881(7)
N(1) - C(1) = 1.311(10)	N(2) - C(1) = 1.383(10)
N(4) - C(13) = 1.313(10)	N(3) - C(13) = 1.368(11)
Cu(2)-Cu(1)-N(1)=86.68(23)	Cu(2)-Cu(1)-N(3)= 89.11(22)
Cu(1)-Cu(2)-N(4)=86.61(22)	Cu(1)-Cu(2)-N(2)=89.30(21)
N(1)-Cu(1)-N(3)=175.7(3)	N(2) - Cu(2) - N(4) = 175.9(3)
N(1) - C(1) - N(2) = 119.2(7)	N(3) - C(13) - N(4) = 119.4(7)

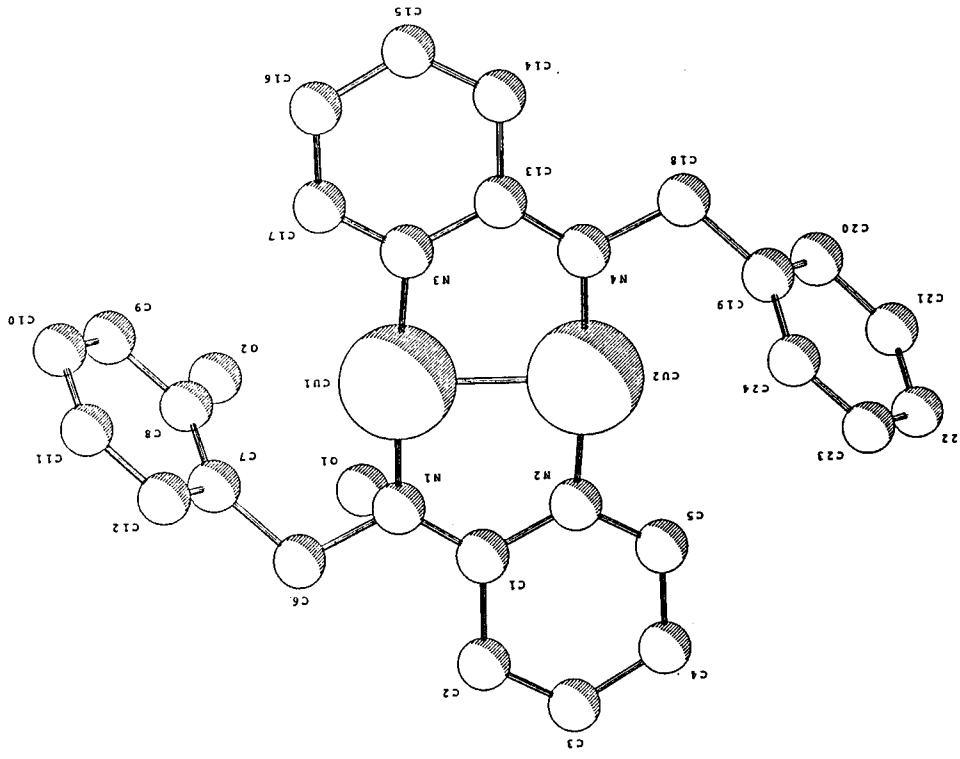


Figure 1. Molecular structure of $[Cu(BAP)]_2 . H_2O$; HBAP = 2-benzylaminopyridine

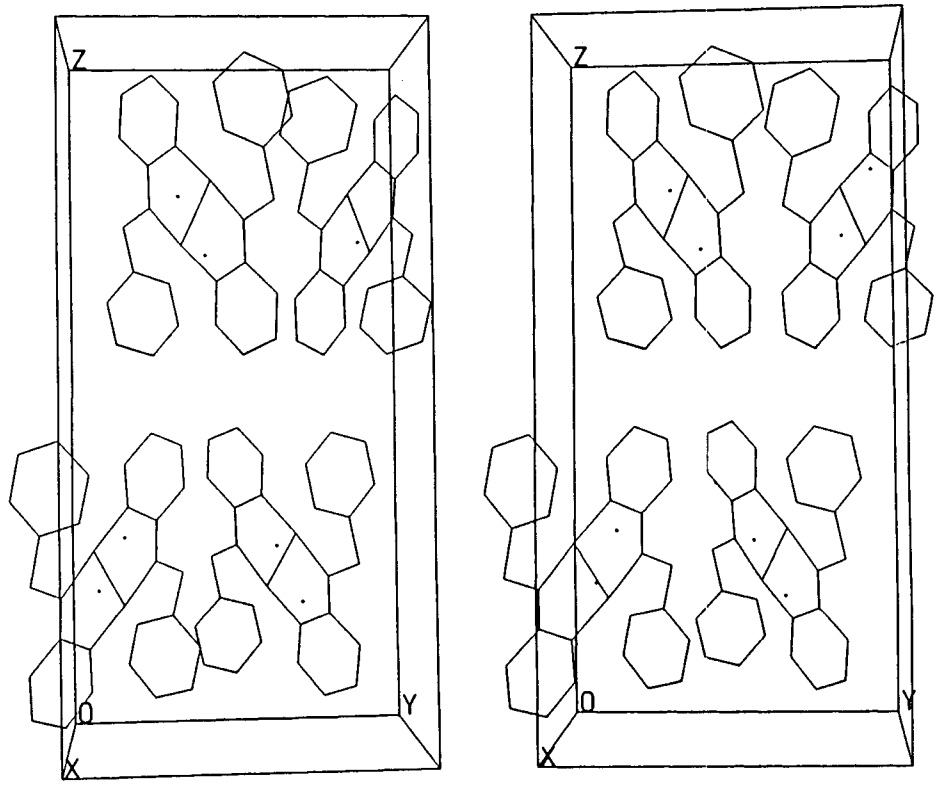


Figure 2. Stereoview of the packing of $[Cu(BAP)]_2 . H_2O$ complex in the unit cell

unjustified. Molecular orbital calculations were made for several representative systems [24, 25]. The results indicate that direct Cu...Cu bonding is at best weak, and possibly negligible.

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