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Synthesis and Crystal Structure of [Cu(*N*-salicylidene-3-aminopyridine)$_2$]$_n$Constructed from Unsymmetric Bridging Ligand with Two Dissimilar Metal-Binding Sites

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Synthesis and characterization of novel coordination polymer, [Cu(salapy)$_2$]$_n$ (Hsalapy = *N*-salicylidene-3-aminopyridine), having the 2-D thick layer structure is reported.

Keywords: crystal engineering; coordination polymer; Cu(II) ion; schiff base type ligand; 2-D layer

INTRODUCTION

Crystal engineering of metal-ligand extended systems comprised of metal ions and bridging ligands toward advanced materials has been a subject of current research interest. The choice of a suitable bridging ligand is critical for construction of such inorganic/organic hybrid systems. The most extensively employed bridging units have been 4,4'-bipyridine and its derivatives, which afford various 1-D, 2-D, and 3-D structures.[1] On the other hand, extended networks containing unsymmetric bridging ligands have been strictly limited compared with those having symmetric bridges. An unsymmetric ligand with two dissimilar metal-binding sites is of particular interest because two interaction sites for metal ions could provide a new network topology. To synthesize such a new metal-ligand extended system, we chose *N*-salicylidene-3-aminopyridine (Hsalapy) as an unsymmetric bridging ligand, which contains the two types of metal coordination sites, i.e. bidentate 'salicylaldehyde' and the monodentate 'pyridyl'. In this paper, the synthesis and crystal structure of a novel 2-D thick extended system of salapy is described.

EXPERIMENTAL SECTION

Preparation of compound

Ligand : Hsalapy was prepared according to the literature method.[2]

Synthesis of $[Cu(salapy)_2]_n$: An ethanol solution (10 mL) of Hsalapy (0.99 g, 5.0 mmol) was added to a hot ethanol solution (30 mL) of $Cu(CH_3COO)_2 \cdot H_2O$ (0.50 g, 2.5 mmol). The obtained dark-green powder was collected by filtration, washed with ethanol, and dried *in vacuo* for 2 hours. Yield: 1.07 g (2.35 mmol, 94%) Anal. Calcd for $C_{24}H_{18}CuN_4O_2$: C, 62.94; H, 3.96; N, 12.23. Found: C, 62.51; H, 4.24; N, 11.86.

X-Ray Structure Determination : All measurements were made on a Rigaku AFC7R diffractometer with graphite monochromated Mo-Kα radiation and a 12 kW rotating anode generator. The unit cell constant was obtained from a least-squares refinement using the setting angles of 25 carefully centered reflections with 2θ values in the range of $26.14\ ^\circ < 2\theta < 29.97\ ^\circ$. The structure was solved by the direct method using the SIR92 program[3] and expanded using Fourier techniques.[4] The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. The final refinements were carried out using full-matrix least-squares techniques with non-hydrogen atoms. All calculations were performed using the TEXSAN crystallographic software package[5] of Molecular Structure Corporation.

TABLE 1 Crystallographic Data

Formula	$C_{24}H_{18}CuN_4O_2$
Formula weight	457.98
Crystal system	monoclinic
Space group	$P2_1/c$ (No.14)
a/Å	12.313(7)
b/Å	7.298(5)
c/Å	12.575(4)
β/deg	114.15(3)
V/Å^3	1031.1(8)
Z	2
T/°C	23
R[a]	0.037
R_w[b,c]	0.032
Reflections measured	2665
Independent reflections	1322

[a] $R = \Sigma||Fo| - |Fc||/S|Fo|$. [b] $R_W = [(\Sigma w(|Fo| - |Fc|)^2/\Sigma wFo^2)]^{1/2}$. [c] $w = 1/[\sigma^2(Fc)]$.

RESULTS AND DISCUSSION

Crystal structure : An ORTEP view around a Cu(II) center is shown in FIGURE 1 with numbering scheme, where the metal ion is on the crystallographic inversion center. The Cu center is based on an elongated octahedral environment with two nitrogen atoms and two oxygen atoms of the bidentate schiff base parts of salapy$^-$ in the basal plane, and two pyridine nitrogen donors of salapy$^-$ in the axial sites. The trans N-Cu-N and O-Cu-O bond angles are crystallographically 180 °, whereas cis N-Cu-O and N-Cu-N bond are almost 90 °.

Two salapy$^-$ ligands bind in a trans form. The schiff base sites of

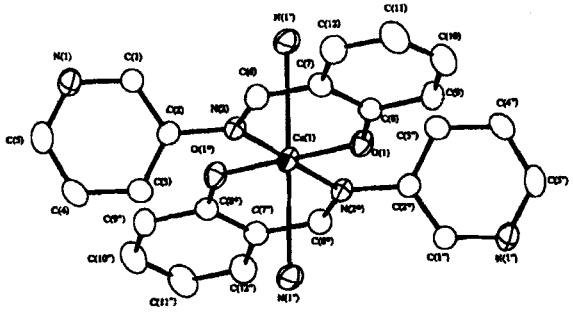

FIGURE 1 ORTEP Drawing of a Cu center at the 30 % probability level.

salapy$^-$ ligands coordinate to the Cu(II) ions in a chelating fashion [Cu-O = 1.900(2) Å and Cu-N = 2.021(3) Å], while the remaining axial coordination sites of Cu(II) are weakly coordinated by the pyridine sites

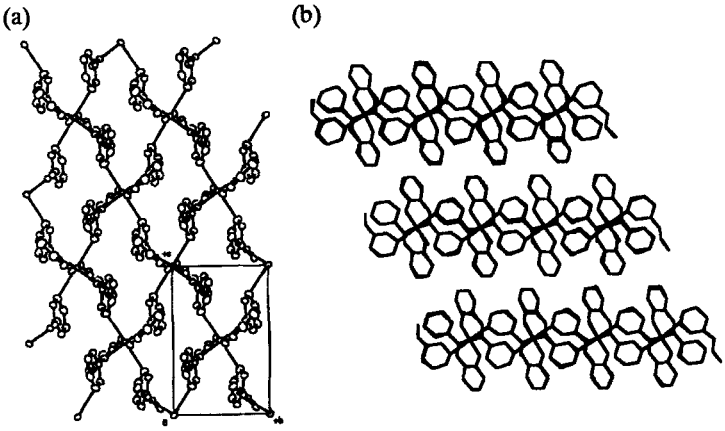

FIGURE 2 (a) The 2-D sheet network in the *bc*-plane. (b) The stacking form of 2-D sheets.

of the neighboring salapy⁻ ligand [2.693(3) Å], resulting in the formation of a 2-D network with *ca.* 11 Å thick in the *bc*-plane as shown in FIGURE 2(a). These 2-D networks stack along the *a*-axis [FIGURE 2(b)] and no significant interaction is observed between the sheets.

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