

Synthesis, Crystal Structure and Spectroscopic Characterization of a Copper(II) Complex Coordinated by 2,2'-Dipyridylstearylamine

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A new ligand containing the long aliphatic hydrocarbon chain, dipyridylstearylamine (dps) and its copper(II) complex, $\text{Cu}(\text{dps})(\text{NO}_3)_2$ have been prepared. The copper complex was characterized structurally and spectroscopically. The XRD crystal structure of the copper complex reveals that copper is octahedrally coordinated by dps and two nitrate ligands. The nitrate groups ligate asymmetrically to the copper. Crystal data are $P1\bar{1}2$, $a=8.249(2)$, $b=10.416(3)$, $c=20.915(4)$ Å, $\alpha=86.54(2)$, $\beta=84.026(2)$, $\gamma=72.32(2)^\circ$, $V=1702.7(7)$ Å³, $Z=2$, $\lambda(\text{Mo K}\alpha)=0.71073$ Å, $\mu=0.689$ mm⁻¹, $T=293(2)$ K, $R=0.0560$ for 3529 reflections. The dps and the copper complex are stable in the air and the copper complex exhibits features of typical of other copper(II) complexes containing dipyridylamine-based ligand.

Keywords : Copper, Stearyl, Dipyridylamine, Crystal structure.

Introduction

Transition metal complexes with an organic spacer may yield interesting structures with different sizes and shapes.¹ Hence, synthesis and characterization of one-, two- and three dimensional hybrid materials of transition metals with organic groups has become a promising topic in material, electronic, and crystal engineering research areas. Such complexes show potential applications as materials for liquid crystals^{2,3} or non-linear optics,^{4,5} surfactants,⁶ electrical conductivity⁷ and molecular recognition,⁸ etc.

New design of such molecules with hybrid or organic long chain may be made possible with known crystal structural data. There are some crystal structural reports for inorganic/organic complexes with shapes of ladders, brick walls, and molecular bilayers, etc.¹ However, few structures of transition metal complexes with long alkyl chain have been reported.^{9,10}

In our lab we have attempted to synthesize new materials for electronic devices. In a series of those compounds, we have prepared copper complexes containing the 2,2'-dipyridylamine (dpa) derivative ligand. The 2,2'-dipyridylamine ligand and its derivatives are desirable for new architectural design of metal complexes because of their good chelating property, structural flexibility, and feasible reduction potential compared with other chelating ligands including bipyridine and phenanthroline.¹¹⁻¹³

In this paper we have described (1) the synthesis of dpa derivative, 2,2'-dipyridylstearylamine ligand (dps) ligand and its copper(II) complex, $\text{Cu}(\text{dps})(\text{NO}_3)_2$, (2) the XRD crystal structure of the complex, and (3) the characterization of the solution and solid state properties by spectroscopic methods.

Experimental Section

Materials. $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, dipyridylamine (dpa), NaH and stearyl chloride were purchased and used without further purification. All the experiments were performed under N_2 atmosphere.

dps: dpa (3.6 g) was dissolved in 20 mL of DMF in a schlenk tube followed by an addition of 0.96 g of NaH. After H_2 gas was evolved, 7.08 g of stearyl chloride was added to the solution. The solution was refluxed for 2 hours. The reaction mixture was cooled and 20 mL ethyl acetate was added, followed by extraction with ethyl acetate. The ethyl acetate layer was dried over MgSO_4 for one day, and evaporated. To the remaining brown oily solution was added ether and the solution was kept in the refrigerator. The yellow powder was filtered, washed with cold ether and dried in a vacuum oven. Yield 71%. ¹H NMR (in CDCl_3 , δ ppm): 0.91 (3H, t, CH_3), 1.29 (32H, s, 16 CH_2), 4.20 (4H, t, 2 CH_2), 6.87-8.37 (8H, m, heteroaromatic H). Anal. for $\text{C}_{28}\text{H}_{45}\text{N}_3$ Calcd.: C, 77.24, H, 10.64, N, 9.90%. Found: C, 77.22, H, 10.09, N, 9.50%.

$\text{Cu}(\text{dps})(\text{NO}_3)_2$: To an ethanol solution of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (2.42 g), was added the dps ligand (4.34 g) in ethanol solution under N_2 atmosphere. The reaction mixture was stirred for an hour and kept in the air for one day. Blue needle crystals precipitated and were recrystallized in acetonitrile. Yield 55%. ¹H NMR (in CDCl_3 , δ ppm): 0.92 (3H, t, CH_3), 1.33 (20H, s, 10 CH_2). Anal. for $\text{C}_{28}\text{H}_{45}\text{N}_3\text{Cu}$ Calcd.: C, 55.24, H, 7.41, N, 12.88%. Found: C, 54.87, H, 7.56, N, 12.53%.

Instrumentation. Elemental Analyses were carried out by Korea Basic Science Institute. UV/VIS spectra were recorded on a Varian Cary 5 UV-VIS-NIR Spectrophotometer and IR were recorded on an Jasco FT/IR-300E. Protein NMR spectra (300 MHz) were measured on a Varian Unity +300 NMR spectrometer.

Crystallographic Analysis. Blue crystals for the single

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crystal study were grown by slow evaporation of solvent from an acetonitrile and heptane solution. The crystals were needle shaped. The crystal lattice is not stable in the air, and the crystal was sealed in a capillary tube. The selected crystal of the copper complex had a dimension of $0.30 \times 0.30 \times 0.40$ mm. Preliminary examination and data collection were performed with Mo $K\alpha$ radiation ($\lambda=0.71073$ Å) on an Enraf-Nonius CAD-4 computer controlled kappa axis diffractometer equipped with a graphite crystal incident beam monochromator. Cell constants and an orientation matrix for data collection were obtained from least-squares refinement.

The data were collected at a temperature of 293 K using the θ/ω scan technique. Data were collected to a maximum 2θ of 25.0° .

A total of 4659 reflections were collected. Lorentz and polarization corrections were applied to the data and psi scan was applied for absorption correction. The structure was solved by direct methods using SHELXS-97 and refined by full-matrix least-squares.¹⁴

The crystal data and refinement parameters are given in Table 1.

Table 1. Crystal Data and Refinement Parameters for Cu(dps)(NO₃)₂

Crystal Data	
Cu(dps)(NO ₃) ₂ ·CH ₃ CN	Triclinic
$f_w = 652.28$	P_1
$a = 8.249(2)$ Å	$Z = 2$
$b = 10.416(3)$ Å	$d_{\text{calc}} = 1.266$ Kg m^{-3}
$c = 20.915(4)$ Å	$V = 1702.7(7)$ Å ³
$\alpha = 86.54(2)^\circ$	$F(0\ 0\ 0) = 688$
$\beta = 84.26(2)^\circ$	$T = 293(2)$ K
$\gamma = 72.32(2)^\circ$	$0.3 \times 0.3 \times 0.4$ mm
$\mu = 0.689$ mm ⁻¹	Blue Cube
Radiation : Mo $K\alpha$ ($\lambda=0.71073$ Å)	
Cell parameters from 25 reflections	
Data Collection	
Enraf-Nonius CAD-4 Diffractometer	$\theta_{\text{max}} = 25.0^\circ$
$\omega/2\theta$ scans	$h = 0 \rightarrow 9$
Absorption correction : none	$k = -11 \rightarrow 11$
4661 measured reflections	$l = -24 \rightarrow 24$
4659 independent reflections	3 standard reflections
3529 observed reflections [$I \geq 2\sigma(I)$]	frequency : 60 seconds
	intensity decay : < 3.0%
Refinement	
Refinement on F_o^2	$w=1/$ $[\sigma^2(F_o^2)+(0.1322P)^2+1.5843P]$
Final $R = 0.0560$	where $P = (F_o^2 + 2F_c^2)/3$
$\omega R = 0.1509$	$\Delta\rho_{\text{max}} = 0.621$ eA ⁻³
$S = 1.060$	$\Delta\rho_{\text{min}} = -0.840$ eA ⁻³
3529 reflections [$I \geq 2\sigma(I)$]	Atomic scattering factors from
409 parameters	International Tables For X-ray
$(\Delta/\sigma)_{\text{max}} = 0.986$	Crystallography Vol. C

Results and Discussion

Synthesis. The dps ligand was prepared from the reaction of dpa and stearyl chloride in ethanol solution. Because of the lower reactivity of the stearyl chloride, the reaction conditions were more vigorous temperature and reaction time compared to those with a simple acyl halide chain. The dps was stable and soluble in ether, dichloromethane, ethanol and chloroform.

A new copper(II) complex was made from dps and a copper salt, Cu(NO₃)₂, in ethanol solution. The copper(II) com-

Table 2. Atomic Coordinates ($\times 10^4$) and Isotropic Thermal Parameters ($\text{Å}^2 \times 10^3$) for Cu(dps)(NO₃)₂

	x	y	z	*U (eq)
Cu(1)	6668(7)	9278(7)	1366(3)	46.4(3)
N(1)	8566(6)	7714(5)	1602(2)	57.1(12)
N(2)	8310(5)	10222(5)	1045(2)	48.1(14)
N(3)	9925(6)	9212(6)	1916(3)	62.7(14)
N(4)	4469(6)	11395(5)	1879(3)	52.3(12)
N(5)	4654(6)	8095(5)	938(3)	61.3(13)
O(1)	4729(4)	10958(4)	1303(2)	55.0(10)
O(2)	5430(6)	10736(5)	2274(2)	74.5(13)
O(3)	3265(6)	12402(4)	2004(3)	75.5(13)
O(4)	4957(5)	8273(4)	1511(2)	58.4(10)
O(5)	3522(7)	7591(6)	862(3)	94.8(17)
O(6)	5508(6)	8463(5)	486(2)	75.3(13)
C(1)	9880(7)	7884(6)	1877(3)	59.7(16)
C(2)	11173(8)	6784(8)	2111(3)	74(2)
C(3)	11074(11)	5519(8)	2053(4)	85(2)
C(4)	9790(11)	5335(8)	1755(4)	87(2)
C(5)	8548(9)	6428(7)	1541(4)	75.4(19)
C(6)	9696(6)	10075(6)	1376(3)	54.1(15)
C(7)	10854(7)	10764(8)	1144(4)	69.0(19)
C(8)	10579(9)	11582(8)	601(4)	78(2)
C(9)	9142(9)	11707(7)	271(4)	68.2(17)
C(10)	8061(7)	11013(6)	520(3)	56.5(15)
C(11)	10884(8)	9494(8)	2418(4)	80(2)
C(12)	10102(9)	10777(9)	2719(4)	87(2)
C(13)	11140(8)	11045(7)	3235(3)	69.4(18)
C(14)	10600(7)	12479(7)	3393(3)	56.9(15)
C(15)	11724(8)	12864(7)	3841(3)	60.2(16)
C(16)	11197(8)	14375(6)	3951(3)	57.8(15)
C(17)	12270(8)	14792(6)	4388(3)	57.4(15)
C(18)	11766(8)	16291(6)	4484(3)	56.2(14)
C(19)	12810(8)	16735(6)	4928(3)	61.3(16)
C(20)	12258(8)	18233(6)	5028(3)	60.6(16)
C(21)	13295(8)	18664(6)	5500(3)	64.6(17)
C(22)	12719(8)	20146(6)	5626(3)	64.4(16)
C(23)	13746(9)	20585(6)	6089(3)	66.9(17)
C(24)	13138(9)	22051(7)	6221(3)	67.5(17)
C(25)	14205(9)	22526(6)	6643(3)	64.0(16)
C(26)	13601(8)	24024(6)	6747(4)	66.2(17)
C(27)	14662(9)	24509(7)	7174(4)	72.5(19)
C(28)	14011(12)	26009(8)	7259(5)	10.4(3)

plex, $\text{Cu}(\text{dps})(\text{NO}_3)_2$ was soluble in ethanol, acetonitrile and water much like similar copper complexes coordinated by dipyridylamine (dpa) derivatives.¹⁵ In aqueous solution, two nitrate ligands are easily replaced by water molecules and the complex goes to an ionic species, which is typical with dpa-based Cu(II) complexes.¹⁵ We can take advantage of the amphiphilic characteristics of the complex for LB films and liquid crystals, and the application of the complex for this purpose is being studied.

Crystal Structure. We are interested in the copper(II) geometry in the complex containing long a hydrocarbon chain and two nitrate ligands. Atomic coordinates for the crystal are given in Table 2. Selected bond distances and angles are shown in Tables 3 and 4, respectively. As presented in Figure 1, hydrocarbon chains are extended straight from a head group in the molecule (coordinated copper site). Figure 2 shows the crystal packing. Two nitrate ligands coordinate to copper asymmetrically with bond distances of 1.99 and 2.45 Å. The N1, N2, O1, O4 coordinating atoms can be imagined as a basal plane of the octahedral structure and the O2 and O5 atoms occupy the axial position, with weak interaction to the metal. Weak interaction of this asymmetric coordination has been found in a copper(II) complex with the nitrate ligand¹⁶ and the long distances between Cu(II)-O are known for other copper complexes.¹⁷⁻¹⁹ Therefore the geometry of this six coordinated copper complex is pseudo-octahedral. The twist angle between the N1-Cu-N2 and O2-Cu-O4 plane is 28.5° and the angle for O1-Cu-O2, O4-Cu-O5 are 56.9° and 56.7°, which are similar to reported chelating nitrate ligands.²⁰ The other bond distances and angles coincide with known Cu(II) complexes.¹⁵

Spectral Characterization. As the copper(II) complex is

Table 4. Selected Bond Angles (°) in the $\text{Cu}(\text{dps})(\text{NO}_3)_2$

N2-Cu-N1	89.4(2)	C17-C18-C19	115.3(5)
N2-Cu-O4	168.55(18)	C18-C19-C20	114.4(5)
N1-Cu-O4	93.5(2)	C19-C20-C21	113.7(5)
N2-Cu-O1	91.57(17)	C22-C21-C20	114.5(5)
N1-Cu-O1	168.95(19)	C21-C22-C23	114.9(5)
O4-Cu-O1	87.74(17)	C24-C23-C22	114.3(6)
N1-C1-N3	116.9(5)	C23-C24-C25	115.3(6)
N1-C1-C2	121.9(6)	C24-C25-C26	114.2(5)
N3-C1-C2	121.2(6)	C27-C26-C25	114.6(5)
C3-C2-C1	118.6(7)	C28-C27-C26	112.4(6)
C4-C3-C2	119.9(7)	C1-N1-C5	117.2(5)
C3-C4-C5	119.7(8)	C1-N1-Cu	120.5(4)
N1-C5-C4	122.6(7)	C5-N1-Cu	122.1(4)
N2-C6-N3	118.7(5)	C10-N2-C6	120.7(5)
N2-C6-C7	118.2(6)	C10-N2-Cu	120.6(4)
N3-C6-C7	123.1(5)	C6-N2-Cu	118.7(4)
C8-C7-C6	120.5(6)	C6-N3-C1	120.1(5)
C7-C8-C9	119.8(6)	C6-N3-C11	117.4(6)
C10-C9-C8	116.9(7)	C1-N3-C11	117.7(6)
N2-C10-C9	123.8(6)	O3-N4-O2	124.3(5)
C12-C11-N3	114.6(5)	O3-N4-O1	118.7(5)
C11-C12-C13	113.3(6)	O2-N4-O1	116.9(4)
C14-C13-C12	111.6(6)	O5-N5-O6	123.2(6)
C13-C14-C15	114.8(5)	O5-N5-O4	119.1(6)
C14-C15-C16	112.9(5)	O6-N5-O4	117.7(5)
C17-C16-C15	114.5(5)	N5-O4-Cu	103.1(3)
C18-C17-C16	114.2(5)	N1S-C1S-C2S	149.2(16)

Table 3. Selected Bond Distances (Å) in the $\text{Cu}(\text{dps})(\text{NO}_3)_2$

Cu-N2	1.949(5)	C14-C15	1.530(7)
Cu-N1	1.964(5)	C15-C16	1.526(9)
Cu-O4	1.989(4)	C16-C17	1.500(8)
Cu-O1	1.988(4)	C17-C18	1.509(8)
C1-N1	1.337(8)	C18-C19	1.507(8)
C1-N3	1.402(8)	C19-C20	1.508(8)
C1-C2	1.409(8)	C20-C21	1.536(8)
C2-C3	1.359(11)	C21-C22	1.503(9)
C3-C4	1.348(12)	C22-C23	1.522(9)
C4-C5	1.367(9)	C23-C24	1.489(9)
C5-N1	1.358(8)	C24-C25	1.507(9)
C6-N2	1.360(7)	C25-C26	1.508(9)
C6-N3	1.392(8)	C26-C27	1.516(9)
C6-C7	1.394(9)	C27-C28	1.505(10)
C7-C8	1.373(10)	N4-O3	1.226(6)
C8-C9	1.400(10)	N4-O2	1.231(6)
C9-C10	1.358(9)	N4-O1	1.287(6)
C10-N2	1.326(8)	N5-O5	1.229(6)
C11-C12	1.448(10)	N5-O6	1.234(7)
C11-N3	1.469(7)	N5-O4	1.284(7)
C12-C13	1.529(8)	N1S-C1S	1.59(5)
C13-C14	1.471(9)	C1S-C2S	2.05(3)

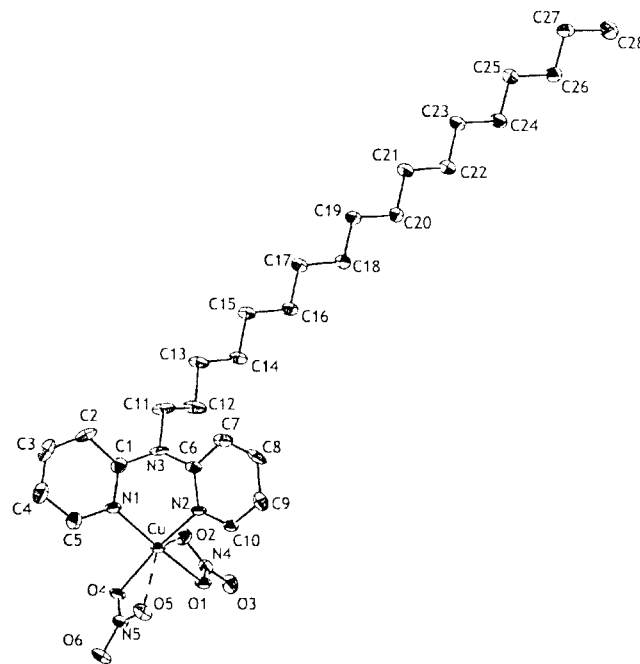


Figure 1. ORTEP Drawing of $\text{Cu}(\text{dps})(\text{NO}_3)_2$ with Atomic Labeling Scheme.

paramagnetic, nmr bands are broader compared to diamagnetic compounds. Stearyl proton signals were found at 0.92 ppm, and 1.33 ppm for the methyl and methylene protons,

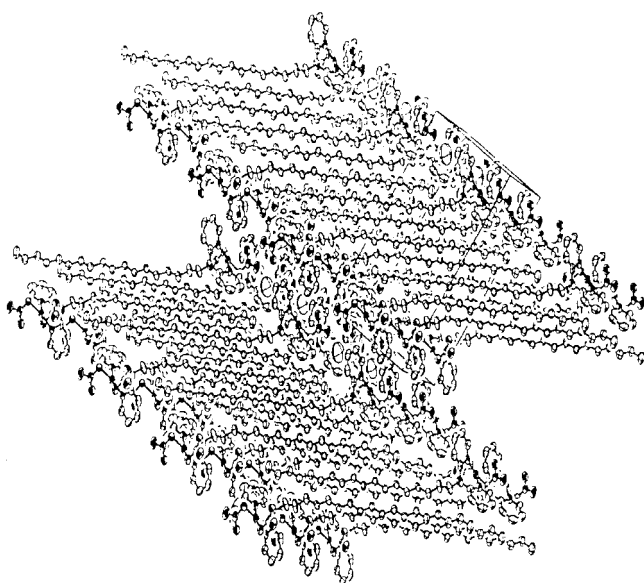


Figure 2. View Showing the Crystal Packing of $\text{Cu(dps)(NO}_3)_2$ Molecules.

Table 5. UV/VIS and IR Spectral Data of Cu(II) Complexes

Complexes	UV/VIS, λ_{max} in nm (ϵ , $\text{dm}^3\text{cm}^{-1}\text{mol}^{-1}$) ^a	IR, ν in cm^{-1} , ^b
$\text{Cu(dps)(NO}_3)_2$	388 (104)	$\nu_{\text{C-H}}$, 2910, 2854
	630 (82)	$\nu_{\text{C-N}}$, 1321
		ν_{NO_3} , 1485, 1367, 1302, 1095

^aIn acetonitrile, 24.5 °C, ^bKBr pellet

respectively. According to the integration data, 10 methylene proton signals of the stearyl group were observed. Being affected by the paramagnetic copper center, nmr resonances for the other stearyl methylene protons and dipyriddy ring protons located close to the copper could not be found. In the optical absorption spectra in acetonitrile, λ_{max} were found at 388 nm and 630 nm for $d \rightarrow d$ transitions. In IR spectra, absorptions due to the nitrate ligands were observed at 1485, 1367, 1302 and 1095 cm^{-1} . Table 5 represents the spectral data for $\text{Cu(dps)(NO}_3)_2$. Results were comparable with those observed in the related copper(II) complexes containing the 2,2'-dipyridylamine-based ligand.¹⁵

Conclusion

Air stable dipyriddy stearylamine and its copper(II) complex were synthesized and characterized. The crystal structure of $\text{Cu(dps)(NO}_3)_2$ shows that copper is octahedrally coordinated by two nitrogen atoms of dps and two oxygen atoms from each of the nitrate ligands. Bidentate nitrate ligates asymmetrically to the copper center. The copper

complex shows typical structural features as compared to known copper(II) complexes containing the dipyriddyamine-based ligand.

Supplementary Information Available. Tables giving details of X-ray data collection parameters, crystal data and structure refinement, atomic coordinates and equivalent isotropic displacement parameters, bond lengths and angles, anisotropic displacement parameters, hydrogen coordinates and isotropic displacement parameters are available.

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