

Synthesis and Characterization of Copper(II) Complex Containing 2,2'-dipyridylbenzamide

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Received May 20, 1996

A new copper complex containing 2,2'-dipyridylbenzamide(dpba), $\text{Cu}(\text{dpba})(\text{NO}_3)_2(\text{CH}_3\text{CN})$, has been synthesized and characterized. The crystal structure has been determined. Crystal data: space group $P2_12_12_1$, $Z=8$, $a=13.911(3)$ Å, $b=16.813(3)$ Å, $c=18.932(3)$ Å, $V=4427.9(1)$ Å³ and $R=0.0674$ for 1716 reflections. The copper environment is square pyramidal containing acetonitrile in axial site. Spectroscopic properties has been characterized in solution state. The redox property of the $\text{Cu}(\text{dpba})(\text{NO}_3)_2$ complex is different from that of corresponding copper-dpa complex.

Introduction

There has been much interests in the copper(II) geometry with 4 or 5 coordinated complexes. Especially on the relevance of biological mimic system CuN_2S_2 chromophore, distorted tetrahedral structured copper complexes are attractive in synthetic bioinorganic field.¹⁻² But since sulfur is known to easily reduce copper(II) to copper(I), CuN_2O_2 type complexes are often made instead of sulfur complexes in laboratories. A 2,2'-dipyridylamine (dpa) coordinated complexes are easier to prepare and exhibit higher stability with CuN_2 chromophore.³ We are interested in copper geometry in CuN_2O_2 type complexes containing substituted dpa ligand and oxyanions. The presence of substituent on the ligand changes the geometry and chemical properties of metal complexes as illustrated by many examples from neutral and synthetic system.⁴

In this paper copper(II)-dipyridylbenzamide(dpba) complex has been reported, in which benzoyl group is bonded to the dpa and an amide carbonyl is not intramolecularly coordinated to the copper. The goals of this work are: (1) to synthesize a new copper-dpba complex and characterize structurally and spectroscopically in crystals and solution and (2) to reveal that the presence of benzoyl group in dpba ligand compared to a dpa ligand may affect physical properties in the copper(II) complex.

Experimental

Materials. $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, dpa, benzoyl chloride were purchased and used without further purification. A ligand, dpba was prepared as follows. In a round bottomed flask, dpa (1.758 g, 10 mmol) was dissolved in CH_2Cl_2 . To this solution 1.0 mL of triethylamine (10 mmol) and 1.2 mL of benzoylchloride (10 mmol) were added. The mixture was stirred at room temp. under N_2 atmosphere for 1 day, 10 mL of H_2O was added and extracted with three 50 mL portions of CH_2Cl_2 . Combined organic extracts were washed with saturated NH_4Cl aqueous solution twice and once with water, and dried over MgSO_4 . Removal of solvent gave 2.424 g of yellow solid, which was recrystallized from 40 mL of ethanol

and 2.311 g (83.9%) of crystal was obtained.

To synthesize a new copper(II) complex, the prepared dpba solid 2.750 g (1.0 mmol) was added to a warm 200 mL ethanol solution containing 2.416 g (1.0 mmol) $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$. After stirring about 1 hour blue precipitates were filtered and dried. It was recrystallized in ethanol solution and dried under vacuum. Yield, 82.3%. Anal. for $\text{C}_{17}\text{H}_{13}\text{N}_5\text{O}_7\text{Cu}$ Calcd.: C, 44.11, H, 2.83, N, 15.13. Found: C, 44.45, H, 3.11, N, 15.74%.

Instrumentation

Elemental analysis was carried out by Korea Research Institute of Chemistry. UV/VIS absorption spectra were recorded on a Varian Cary 5 UV-VIS-NIR Spectrophotometer. IR spectra were recorded on a Jasco FT/IR-300E. NMR spectra were recorded on a Varian Unity +300 NMR spectrometer (300 MHz). Cyclic voltammetry was performed under Ar with a BAS VC-500 W Voltammometric Analyzer and computer controlled with 50 w electrochemical software. Tetraethylammonium perchlorate (0.1 M in CH_3CN) was used as a supporting electrolyte. The voltammograms were measured with a platinum working electrode and a Ag/AgCl electrode as the reference. ESR spectra were recorded on a Bruker instruments ESP-300S ESR Spectrometer at the Korea Basic Science Center. For the ESR measurements the complexes were dissolved in CH_3CN and frozen in liquid nitrogen.

Crystallographic Analysis

Blue crystals suitable for XRD were grown by a slow evaporation of solvent from the saturated acetonitrile solution. A crystal of copper-dpba complex having approximate dimensions of $0.70 \times 0.50 \times 0.10$ mm was mounted on a glass fiber. Preliminary examination and data collection were performed with Mo $K\alpha$ radiation ($\lambda=0.71069$ 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, using the setting angles of 18 reflections in the range $8 < \theta < 12$, measured by the computer controlled diagonal slit method of centering.

Table 1. Crystal Data and Structure Refinement for Cu(dpba)(NO₃)₂(CH₃CN)

Empirical formula	C ₁₉ H ₁₆ CuN ₆ O ₇
Formula weight	503.92
Temperature	293(2) K
Wavelength	0.71069 Å
Crystal system	Orthorhombic
Space group	<i>P</i> 2 ₁ 2 ₁ 2 ₁
Unit cell dimensions	a = 13.911(3) Å b = 16.813(3) Å c = 18.932(3) Å
Volume	4428.1(1) Å ³
Z	8
Density (calculated)	1.503 g/cm ³
Absorption coefficient	1.039 mm ⁻¹
F(000)	2032
Crystal size	0.70 × 0.50 × 0.10 mm
Theta range for data collection	2.15 to 20.00 deg.
Index ranges	0 ≤ h ≤ 13, 0 ≤ k ≤ 16, 0 ≤ l ≤ 18
Reflections collected	1716
Independent reflections	1716 [R(int) = 0.0000]
Refinement method	Full-matrix least-squares on F ²
Data/restraints/parameters	1715/0/298
Goodness-of-fit on F ²	1.056
Final R indices [I > 2σ(I)]	R ₁ = 0.0674, wR ₂ = 0.1386
R indices (all data)	R ₁ = 0.1045, wR ₂ = 0.1677

The orthorhombic cell parameters are: a = 13.911(3), b = 16.813(3), c = 18.932(3) Å.

The data were collected at a temperature of 298 K using the 2θ/ω scan technique. The scan rate varied from 2.4 to 2.7 deg/min (in ω). The variable scan rate allows rapid data collection for intense reflections where a fast scan rate is used and assures good counting statistics for weak reflections where a slow scan rate is used. Data were collected to a maximum 2θ of 40.0°. The scan range (in deg.) was determined as a function of θ to correct for the separation of the Kα doublet.

A total of 1716 reflections were collected, of which 1716 were unique. Lorentz and polarization corrections were applied to the data. No absorption correction was applied to the data. An extinction correction was not necessary. There were no systematic absences. The structure was solved by direct method using SHELXS-86 and refined by full-matrix least-squares.⁵⁻⁶ All non-hydrogen atoms were refined anisotropically; hydrogen atoms were fixed on a geometrically ideal positions with 1.2 times isotropic temperature factors of the attached non-hydrogen atoms.

Details on crystal and intensity data are given in Table 1.

Results and Discussion

Crystal structure. Crystals suitable for the XRD were recrystallized in acetonitrile and the solvent molecule was coordinated to copper(II) in axial position. The copper environment is 5-coordinated with a formula of Cu(dpba)(NO₃)₂

Table 2. Atomic Coordinates (×10⁴) and Equivalent Isotropic Displacement Parameters (Å² × 10³). U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor

	x	y	z	U(eq)
Cu1	2510(1)	2620(1)	1379(1)	49(1)
N1	2058(6)	1884(5)	2137(4)	40(2)
C5	2332(8)	1110(7)	2177(6)	36(3)
C4	2059(9)	609(7)	2690(7)	58(4)
C3	1475(10)	884(10)	3214(7)	72(4)
C2	1140(9)	1670(10)	3206(7)	72(4)
C1	1465(9)	2151(6)	2663(7)	54(4)
N3	2365(6)	1693(6)	703(5)	44(2)
C6	2584(9)	943(7)	905(6)	44(3)
C7	2424(10)	314(6)	462(6)	55(3)
C8	2048(9)	436(10)	-201(8)	72(4)
C9	1846(10)	1194(11)	-419(7)	72(4)
C10	1997(9)	1795(7)	65(8)	65(4)
N2	2964(7)	875(5)	1605(5)	35(2)
C12	4195(7)	403(7)	2414(6)	36(3)
C13	4314(9)	1034(6)	2886(7)	53(3)
C14	4716(10)	914(9)	3541(7)	70(4)
C15	5054(9)	164(12)	3725(7)	81(5)
C16	4953(10)	-465(8)	3258(9)	73(4)
C17	4571(9)	-340(7)	2611(7)	59(4)
C11	3842(9)	491(7)	1696(7)	45(3)
O1	4256(6)	238(5)	1180(4)	66(3)
N4	3229(11)	3405(6)	2566(7)	65(3)
O2	2636(7)	3512(4)	2067(5)	62(2)
O3	3878(8)	2897(6)	2474(5)	92(3)
O4	3196(9)	3789(6)	3111(5)	117(4)
N5	3993(12)	3073(9)	526(7)	83(4)
O5	3120(8)	3282(5)	656(5)	70(3)
O6	4301(7)	2508(7)	879(6)	95(3)
O7	4463(10)	3449(8)	120(6)	143(5)
N6	1043(8)	3151(6)	1057(6)	76(4)
C18	374(10)	3432(7)	797(7)	58(4)
C19	-463(9)	3778(7)	474(6)	75(4)

(CH₃CN). Two nitrates are monodentated and the coordination geometry about copper is square pyramidal. Dihedral angle between CuN(1)N(3) plane and CuO(2)O(5) is 7.44°. A plane CuN(1)N(3)O(2)O(5) is almost a square plane. Final position and thermal parameters for Cu(dpba)(NO₃)₂(CH₃CN) are given Table 2. The crystal structure is shown in Fig. 1 and selected bond lengths and angles are presented in Table 3. An interesting feature is that the phenyl plane is unexpectedly bent from dipyridyl plane. As is shown in a side view (Fig. 2) phenyl ring plane is almost normal to the dipyridyl planes. A nice pocket exists with the benzoyl group and nitrate ligands. The other side of copper is occupied with acetonitrile.

Distances of Cu-N(1) and Cu-N(3) in dpba ligand are 1.95 Å, 2.027 Å and of Cu-O(2) and Cu-O(5) in nitrates 1.995, 1.958 Å, respectively. These are in coincidence with other reported copper dipyridylamine(dpa) complexes or bipyridine complexes.⁷⁻⁹ The distance of copper and axial acetonitrile

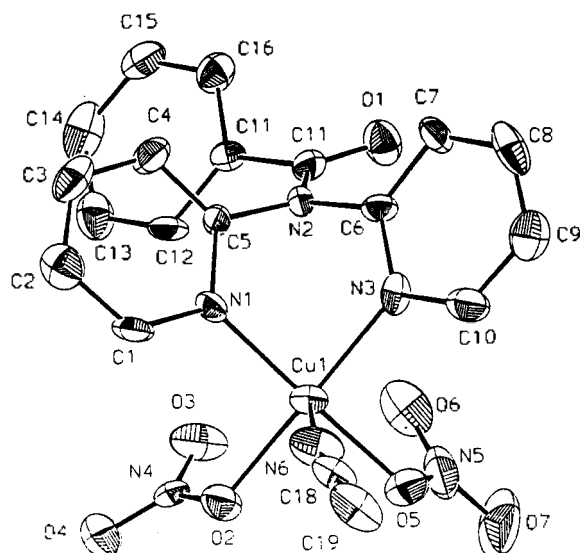


Figure 1. ORTEP plot of the $\text{Cu}(\text{dpba})(\text{NO}_3)_2(\text{CH}_3\text{CN})$ molecule showing the atom-labeling scheme (all hydrogens are omitted).

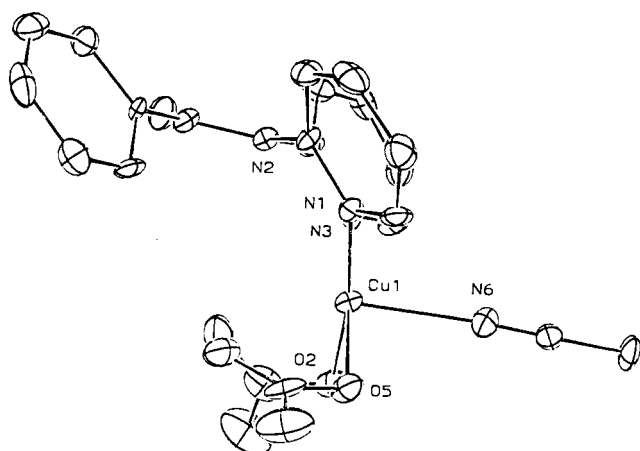


Figure 2. Side view of $\text{Cu}(\text{dpba})(\text{NO}_3)_2(\text{CH}_3\text{CN})$.

nitrogen is 2.310 Å, which is in the range of bond length. Distances of copper and another oxygens in nitrates, Cu-O(6) and Cu-O(3) are longer than normal bond distances with values of 2.672 and 2.853 Å.¹⁰

Solution Spectral Characterization. The solubility of $\text{Cu}(\text{dpba})(\text{NO}_3)_2(\text{CH}_3\text{CN})$ in DMF is extremely large (more than grams/ml), which might be due to a similarity in the structures. It dissolves in acetonitrile or methanol slightly (less than 5×10^{-3} grams/mL). In methanol solution the structure of the Cu-dpba complex may not be coordinated by acetonitrile in contrast to acetonitrile-coordinated in crystal structure and in acetonitrile solution.

In the electronic spectrum of $\text{Cu}(\text{dpba})(\text{NO}_3)_2(\text{CH}_3\text{CN})$ in acetonitrile, absorption bands at 651 nm ($\epsilon = 65 \text{ M}^{-1} \text{ cm}^{-1}$) and 274 nm ($\epsilon = 13620 \text{ M}^{-1} \text{ cm}^{-1}$) are observed. Only one of the low energy transitions corresponding $d_{x^2-y^2} \rightarrow d_{xy}$ and $d_{x^2-y^2} \rightarrow d_{z^2}$ ¹¹ is observed in the visible region of 900 to 300 nm (Table 4).

In the X-band ESR spectrum in frozen glass of acetonitrile at 77 K for $\text{Cu}(\text{dpba})(\text{NO}_3)_2(\text{CH}_3\text{CN})$, $g_z = 1.98$ and $g_x = 2.32$

Table 3. Bond lengths (Å) and angles (deg)

Cu1-O5	1.958(9)	C9-C10	1.38(2)
Cu1-N1	1.995(9)	N2-C11	1.393(13)
Cu1-O2	1.995(8)	C12-C13	1.396(13)
Cu1-N3	2.027(9)	C12-C17	1.406(14)
Cu1-N6	2.310(12)	C12-C11	1.453(14)
N1-C5	1.358(12)	C13-C14	1.38(2)
N1-C1	1.369(13)	C14-C15	1.39(2)
C4-C5	1.341(13)	C15-C16	1.39(2)
C5-N2	1.449(12)	C16-C17	1.35(2)
C3-C4	1.36(2)	C11-O1	1.211(12)
C2-C3	1.40(2)	N4-O4	1.217(12)
C1-C2	1.38(2)	N4-O3	1.256(13)
N3-C10	1.323(14)	N4-O2	1.266(12)
N3-C6	1.351(12)	N5-O7	1.190(14)
C6-C7	1.368(13)	N5-O6	1.239(14)
C6-N2	1.432(13)	N5-O5	1.29(2)
C7-C8	1.38(2)	N6-C18	1.153(14)
C8-C9	1.37(2)	C18-C19	1.44(2)
O5-Cu1-N1	172.5(4)	C9-C8-C7	119.5(12)
O5-Cu1-O2	89.4(3)	C8-C9-C10	116.8(12)
N1-Cu1-O2	91.4(3)	N3-C10-C9	124.8(12)
O5-Cu1-N3	92.3(4)	C11-N2-C6	118.4(9)
N1-Cu1-N3	86.9(4)	C11-N2-C5	124.5(10)
O2-Cu1-N3	178.4(3)	C6-N2-C5	116.5(9)
O5-Cu1-N6	88.8(4)	C13-C12-C17	117.5(10)
N1-Cu1-N6	98.7(4)	C13-C12-C11	124.2(11)
O2-Cu1-N6	87.7(4)	C17-C12-C11	117.7(11)
N3-Cu1-N6	92.4(4)	C14-C13-C12	121.0(11)
C5-N1-C1	116.2(9)	C13-C14-C15	119.7(13)
C5-N1-Cu1	123.1(8)	C16-C15-C14	119.9(12)
C1-N1-Cu1	120.7(8)	C17-C16-C15	120.0(13)
C4-C5-N1	124.3(10)	C16-C17-C12	121.6(12)
C4-C5-N2	122.8(11)	O1-C11-N2	118.7(11)
N1-C5-N2	112.9(10)	O1-C11-C12	124.0(11)
C3-C4-C5	118.9(12)	N2-C11-C12	117.3(11)
C4-C3-C2	120.7(12)	O4-N4-O3	120.3(14)
C1-C2-C3	116.7(12)	O4-N4-O2	122.2(13)
N1-C1-C2	123.1(11)	O3-N4-O2	117.5(12)
C10-N3-C5	117.8(10)	N4-O2-Cu1	115.9(7)
C10-N3-C1	121.0(9)	O7-N5-O6	125(2)
C6-N3-C1	121.0(7)	O7-N5-O5	120(2)
N3-C6-C7	120.8(11)	O6-N5-O5	115.6(14)
N3-C6-N2	114.8(9)	N5-O5-Cu1	112.8(9)
C7-C6-N2	124.4(11)	C18-N6-Cu1	169.6(12)
C6-C7-C8	120.4(11)	N6-C18-C19	179.6(14)

signals are observed. A hyperfine coupling constant A_{\parallel} is $160 \times 10^4 \text{ cm}^{-1}$, which is occurred with other 4 or 5 coordinated Cu(II) complexes.¹²

As copper(II) complexes are paramagnetic, nmr measurements are only for proton signals far apart from the copper center. A benzyl proton resonance in CD_3OD is observed at 7.85 ppm. The axial acetonitrile may be deligated in the CD_3OD and is observed at 2.0 ppm as is normal in any

Table 4. UV/VIS and IR Spectral Data for Cu(II) Complexes

Complexes	UV/VIS, λ_{max} in nm (ϵ , $M^{-1}cm^{-1}$) ^a	IR, ν in cm^{-1} , ^b
Cu(dpba)(NO ₃) ₂ (CH ₃ CN)	274(13620)	ν_{CO} , 1685 ν_{C-N} , 1328,
	651(65)	ν_{NO_3} , 1473, 1384, 1305, 1020 ν_{NCH_3} , 2280
Cu(dpa)(NO ₃) ₂	249(24300)	ν_{C-H} , 3320
	297(19900)	ν_{NO_3} , 1477, 1385, 1320, 1020
	316(19000)	
	432(103)	
	709(110)	

^aIn acetonitrile, 25 °C ^bKBr pellet**Table 5.** Cyclic Voltammetric Data for Cu(II) Complexes in CH₃CN (volts)^a

complexes	$E_{1/2}$ ^b	E_{pc}	E_{pa}	ΔE
Cu(dpba)(NO ₃) ₂ (CH ₃ CN)	0.32	-0.07	0.70	0.77
Cu(dpa)(NO ₃) ₂	-0.08	-0.12	-0.03	0.08

^aRef. electrode: Ag/Ag⁺, 0.1 M (C₄H₉)₄NClO₄, working electrode: Pt disk. ^bMid peak potential, ($E_{pc} + E_{pa}$)/2

diamagnetic compounds. The dipyriddy ring proton signals are not observed.

In IR spectrum absorption due to the acetonitrile is observed at 2280 cm^{-1} . Table IV represents the spectral data for Cu(dpba)(NO₃)₂(CH₃CN) and corresponding copper-dpa complex for the comparison.¹³

An interesting feature of the copper-dipyridylbenzamide complex is the observation of Cu(II)/Cu(I) couple redox pattern in cyclic voltammetry. The E_{pc} and E_{pa} values are -0.072 and 0.70 volts, respectively, for Cu(dpba)(NO₃)₂(CH₃CN). A value of ΔE ($E_{pa} - E_{pc}$) is large resulting in a more positive $E_{1/2}$ value. To compare we measured redox potential with the corresponding copper-dipyridylamine (dpa) complex, which is different from the copper-dpba for the absence of the benzoyl ring. Values of E_{pc} and E_{pa} are -0.12 and -0.03 volts for the dpa complex showing small ΔE . The benzoyl group in the amine ligand influences on the observed Cu(II)/Cu(I) redox potential. Some discussion for the large ΔE in the cv data has reported with electronic and steric effect of substituted group on a ligand in Cu(I) complexes.¹⁴ We presumed that benzoyl substitution may affect the redox property because of steric hindrance. Once Cu(II)-dpba complex reduced to Cu(I) corresponding complex, it is hard to come back to Cu(II) complex since the presence of the benzoyl drives a steric hindrance for the converting from Cu(I)-distorted structure to Cu(II)-square pyramidal. The value of $E_{1/2}$

for the dpba complex is more positive than that for the dpa complex. The reduction of Cu(II) is known to be affected by various factors such as the reducing power of the ligand and structural distortion at the copper center.¹⁵ Since the donor atoms for the two complexes may be same in the CH₃CN solvent, the difference of $E_{1/2}$ value comes from the difference of structure rather than the effect of the donor atoms with the same reason for large difference of ΔE . However, we need to get more structural evidences to explain large ΔE in cv results.

Conclusions

From the reaction of Cu(NO₃)₂ and dpba a new copper complex has been synthesized and characterized in crystal and in solution. Coordination geometry around copper is a square pyramid in solid state. The redox property of copper-dpba complex is different from that of dpa complex due to a presence of benzoyl group compared to a dpa ligand. On the relevance of copper coordination chemistry bulky group attachment on the amide carbonyl may give interesting redox result as well as provide an interesting structure.

Supplementary Material Available. Observed and calculated structure factors for Cu(dpba)(NO₃)₂(CH₃CN) are available from one of authors (Y. Oh).

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