

상자성 구리(II) 화합물의 합성과 그 특성 연구

吳 榮 姬

동의대학교 화학과
(2000. 7. 18 접수)

Synthesis and Characterization of Paramagnetic Copper(II) Complexes

Yunghee Oh*

Department of Chemistry, Donggei University, Pusan 614-714, Korea
(Received July 18, 2000)

요 약. 질산구리와 2,2'-dipyridylbenzylamine(dpb)를 에탄올 용액에서 반응시켜 새로운 구리 착화합물, $\text{Cu}(\text{dpb})(\text{NO}_3)_2$ (1) 를 합성하였다. 아세토니트릴 용액에서 재결정하여 단결정을 얻었으며 XRD법을 이용하여 결정 구조를 확인하였다. 결정은 orthorhombic 형태로서 $P2_1c$ 군에 속하고 그 밖의 자료들은 다음과 같다. $a=12.501(9)\text{\AA}$, $b=9.231(10)\text{\AA}$, $c=17.119(6)\text{\AA}$, $\alpha=90^\circ$, $\beta=107.33(4)^\circ$, $\gamma=90^\circ$, $V=1885.8(2)\text{\AA}^3$, $R_1=0.0647$, $wR_2=0.1866$, $Z=4$. EPR, NMR, UV-VIS, 그리고 IR 등의 분광학적인 확인법에 의하여, 합성된 화합물은 디피리딜아민 유도체를 리간드로 하는 전형적인 상자성 구리(II) 배위 화합물임을 확인하였다.

ABSTRACT. A new copper(II) complex, $\text{Cu}(\text{dpb})(\text{NO}_3)_2(\text{H}_2\text{O})$ (dpb=2,2'-dipyridylbenzylamine) (1) was synthesized from the reaction of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ and dpb in ethanol solution followed by recrystallization in acetonitrile. The structure of 1 was determined by X-ray diffraction methods. The single crystal structure was characterized as follows: space group $P2_1c$, $Z=4$. $a=12.501(9)\text{\AA}$, $b=9.231(10)\text{\AA}$, $c=17.119(6)\text{\AA}$, $\alpha=90^\circ$, $\beta=107.33(4)^\circ$, $\gamma=90^\circ$, $V=1885.8(2)\text{\AA}^3$, $R_1=0.0647$, $wR_2=0.1866$ for 3258 reflections. Compound was a typical paramagnetic copper(II) complex coordinated by 2,2'-dipyridylamine derivative ligand, which was confirmed by EPR, NMR, UV/VIS, and IR spectroscopy.

INTRODUCTION

The coordination chemistry of copper(II) attracts much attention because of its biological relevance and its own interesting coordination chemistry such as geometry, flexible redox property, and oxidation state.¹⁻³ Nowadays, coordination compounds have been known to be useful in constructing molecular information processing systems, particularly by biological self-organizing processes.^{4,5} Especially for this purpose, synthesis, and structural and chemical characterization of copper complexes has been attempted to mimic metalloenzyme.⁶⁻⁸ Recently, we tried to prepared new materials for electric devices. In a series of those compounds, we have prepared copper(II) complexes containing two nitrate ligands and a

2,2'-dipyridylamine(dpa) derivative ligand. The 2,2'-dipyridylamine and its derivatives have been widely used for metal complexes because of their good chelating property, structural flexibility, and feasible reduction property compared with other N,N'-chelating ligand including bipyridine and phenanthroline.⁹⁻¹³

Copper(II) complexes ligated by two nitrate ligands and a N,N'-chelating ligand (L), $\text{CuL}(\text{NO}_3)_2$, are common and some XRD structures have been reported.^{6,14-16} In those complexes, the coordination numbers varied from 4 to 6 according to nitrate ligating properties.

In this paper, copper(II) complex with the dpb and two nitrate ligands is reported. Synthesis and crystal structure characterization are described including stereochemistry of the CuN_2O chromophore. The relation of copper geo-

metry and spectral properties and paramagnetic properties are discussed.

EXPERIMENTAL

Materials. Reagents used for the synthesis, $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, dpa, NaH, benzyl chloride, MgSO_4 , and solvents were purchased and used without further purification.

Instrumentation. Elemental analyses and EPR measurements were carried out by Korea Basic Science Institute. NMR spectra were recorded on a Varian Unity 1300 NMR spectrometer, and UV-VIS absorption spectra were measured on a Shimadzu UV-VIS Spectrophotometer UV-240. IR spectra were recorded on a Jasco FT-IR-300E with a KBr disk.

Preparation. The dpb ligand was synthesized in a

modified route of the literature method.^{6,16} In a round bottom flask, dpa 20 mmol (3.6 g) was dissolved in 20 ml DMF and added NaI 24 mmol (0.96 g) with stirring. After one hour-stirring benzyl chloride was added 24 mmol (2.85 ml). The reaction mixture was stirred under dry nitrogen atmosphere at room temperature for 1 day. Distilled water (20 ml) was added to the solution followed by extraction with three 50 ml portions of ethylacetate. The extracts were washed with distilled water and dried over magnesium sulfate for one night. The solvent was evaporated under reduced pressure. A 10 ml diethylether was added to the brown oily residue and kept in a refrigerator overnight. The precipitates were filtered, washed with cold diethylether, and dried under vacuum. The white powder was recrystallized in acetonitrile (yield 71%), mp 83.2 °C. Anal. for $\text{C}_{13}\text{H}_{11}\text{N}_3\text{O}$

Table 1. Crystal data and structure refinement parameters for $\text{Cu}(\text{dpb})(\text{NO}_3)_2$

Crystal Data	
$\text{Cu}(\text{NO}_3)_2(\text{dpb}) \cdot 5\text{H}_2\text{O}$	Monoclinic
fw=448.88	$P2_1c$
$a=12.501(9)\text{\AA}$	$Z=4$
$b=9.231(10)\text{\AA}$	$d_{\text{calc}}=1.581\text{ Kg m}^{-3}$
$c=17.119(6)\text{\AA}$	$V=1885.8(15)\text{\AA}^3$
$\alpha=90.00^\circ$	$F(000)=916$
$\beta=107.33(4)^\circ$	$T=293(2)\text{ K}$
$\gamma=90.00^\circ$	$0.1 \times 0.5 \times 0.9\text{ mm}$
$\mu=1.204\text{ mm}^{-1}$	Blue Cube
Radiation: Mo $K\alpha$ ($\lambda=0.71070\text{\AA}$)	
Cell parameters from 25 reflections ($2.49^\circ \theta$ 24.99)	
Data Collection	
Enraf-Nonius CAD4 Diffractometer	$\theta_{\text{max}}=24.99^\circ$
$\omega/2\theta$ scans	$h=0 \rightarrow 14$
Absorption correction: none	$k=0 \rightarrow 10$
3259 measured reflections	$l=-20 \rightarrow 19$
3258 independent reflections	3 standard reflections
2283 observed reflections [$I \geq 2\sigma(I)$]	frequency: 60 seconds
	intensity decay: $\pm 3.0\%$
Refinement	
Refinement on F_o^2	$W=1/[\sigma^2(F_o^2)+(0.0840P)^2+6.1376P]$
Final $R=0.0008$	where $P=(F_o^2+2F_c^2)/3$
$\omega R=0.1692$	$\Delta\rho_{\text{max}}=0.886\text{ e\AA}^{-3}$
$S=1.117$	$\Delta\rho_{\text{min}}=-1.262\text{ e\AA}^{-3}$
3258 reflections [$I \geq 2\sigma(I)$]	Atomic scattering factors from
278 parameters	International Tables For X-ray
$(\Delta\sigma)_{\text{max}}=0.981$	Crystallography Vol. C

Calcd: C, 78.15; H, 5.79; N, 16.08. Found: C, 78.09; H, 5.80; N, 16.12%.

Copper complex was synthesized from the ethanol solution (30 ml) containing the dpb 10 mmol (2.61 g) and equimolar $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (2.42 g) by stirring at room temperature for 1 h. The reaction mixture was kept for 1 day, and the blue precipitates were filtered. The solid was dried and recrystallized in the acetonitrile solution (65%). Anal. for $\text{C}_{11}\text{H}_{15}\text{N}_5\text{O}_6\text{Cu}$ Calcd.: C, 45.49; H, 3.34; N, 15.61. Found: C, 45.45; H, 3.47; N, 15.71%.

Crystallographic analysis. Single crystal for XRD measurement was grown by the slow evaporation of solvent from the saturated acetonitrile solution and heptane. The crystal was not stable in air and was sealed in the capillary tube. The blue cubic crystal of $\text{C}_{11}\text{H}_{15}\text{N}_5\text{O}_6\text{CuCH}_3\text{CN}$ having approximate dimensions of $0.1 \times 0.5 \times 0.9$ mm was used for data collection. Preliminary examination and data collection were performed with Mo $\text{K}\alpha$ radiation ($\lambda=0.71070\text{\AA}$) on an Enraf-Nonius CAD-4 diffractometer equipped with a graphite crystal. 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 $2\theta/\omega$ scan technique. Data were collected to a maximum 2θ of 25.0° . A total of 3258 reflections were collected. Lorentz and polarization corrections were applied to the data. No absorption correction was applied for the crystal. The structure was solved by direct method with SHELXL-97 and refined by full-matrix least-squares.^{17,18}

The crystal data and refinement parameters are given in Table 1. Final positional and thermal parameters are given in Table 2.

RESULTS AND DISCUSSION

The reaction of dpb with benzyl chloride afforded an amine ligand, dpb. The amine reacted with copper salt in ethanol resulting in a new copper-dpb complex as shown in Scheme 1.

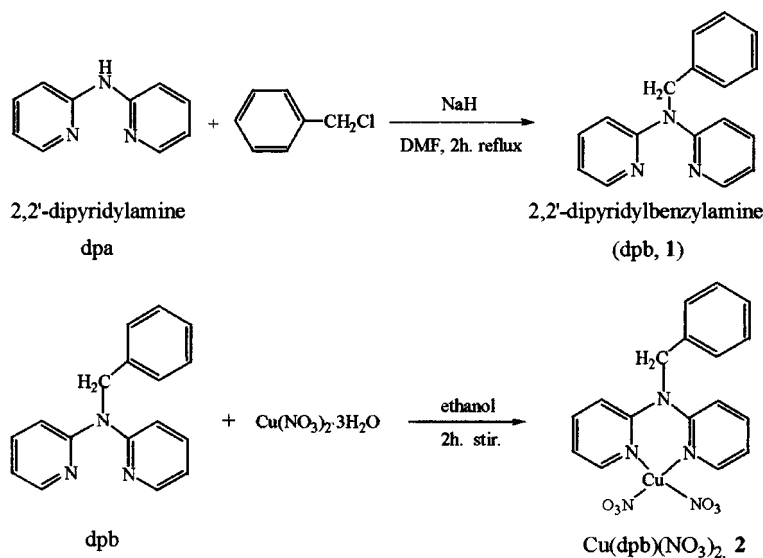
As the copper complex is paramagnetic, proton signals of the dipyriddy ring were not found in proton nmr spectrum. Even phenyl protons of the benzyl group locating far from the paramagnetic copper center could not be observed. In EPR spectrum, the signal at $g=2.18$ was

Table 2. Fractional coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) of $\text{Cu}(\text{dpb})(\text{NO}_3)_2$

	x	y	z	U(eq)
Cu	6230(1)	2541(1)	7163(1)	36(1)
N1	5183(3)	2979(5)	6074(3)	35(1)
N2	7468(4)	3186(5)	6745(3)	39(1)
N3	6541(4)	2040(5)	5523(3)	39(1)
N4	4654(4)	624(5)	7288(3)	50(1)
N5	7843(4)	993(6)	8313(3)	48(1)
O1	4979(4)	1871(5)	7565(3)	54(1)
O2	3892(4)	48(5)	7491(3)	71(1)
O3	5109(5)	21(5)	6837(3)	76(2)
O4	7264(4)	2136(5)	8265(2)	57(1)
O5	8477(4)	647(6)	8982(3)	68(1)
O6	7745(7)	298(7)	7706(3)	107(2)
C1	5476(5)	2655(5)	5400(3)	38(1)
C2	4768(5)	2945(7)	4631(4)	50(1)
C3	3737(6)	3559(7)	4548(4)	58(2)
C4	3450(5)	3894(7)	5250(4)	57(2)
C5	4196(4)	3590(6)	5994(4)	44(1)
C6	7483(4)	2772(6)	6000(3)	40(1)
C7	8388(5)	3092(7)	5718(4)	52(2)
C8	9272(6)	3863(7)	6206(5)	63(2)
C9	9249(5)	4317(8)	6969(5)	64(2)
C10	8328(5)	3960(7)	7213(4)	54(2)
C11	6666(5)	1114(7)	4846(3)	50(2)
C12	7580(6)	22(7)	5122(4)	56(2)
C13	7858(7)	-616(8)	5878(4)	72(2)
C14	8706(8)	-1658(10)	6092(7)	96(3)
C15	9249(9)	-2050(12)	5539(11)	128(5)
C16	8943(10)	-1438(13)	4790(10)	130(5)

observed, which was similar to that of the corresponding dps copper(II) complex, $g=2.10$. In the IR spectra of the copper complex, C-N stretching at 1324 cm^{-1} , and nitrate ligand at $1473, 1384, 1302, 1020\text{ cm}^{-1}$ were observed, which was comparable to those of the known compounds^{6,16}. Absorption bands due to d-d electronic transition were observed at 394 and 655 nm showing the similar results to those of previously reported corresponding 2,2'-dipyridylbenzamide(dpba)⁶, 2,2'-dipyridylacetamide(dpaa)¹⁶, and 2,2'-dipyridylstearylamine (dps)¹⁹ copper(II) complex. The spectroscopic measurements are presented in Table 3.

As shown in Fig. 1 and Fig. 2, copper is coordinated by dpb, two nitrate ligand, and axial nitrate oxygen, exhibiting a square pyramidal structure. The twist angle between N1CuN2 plane and O1CuO4 plane is almost 0° .



Scheme 1.

Table 3. UV/VIS and IR spectral data of Cu(II) complexes coordinated by 2,2'-Dipyridylamine derivative

Complexes	UV VIS. λ_{max} in nm (ϵ , $\text{dm}^3 \text{cm}^{-1} \text{mol}^{-1}$) ^a	IR. ν in cm^{-1} ^b
$\text{Cu}(\text{dpb})(\text{NO}_3)_2$ ^c	298(340) 394(29) 655(24)	ν_{as} . 1324 ν_{sym} . 1475, 1384, 1302, 1020
$\text{Cu}(\text{dpba})(\text{NO}_3)_2$ ^d	274(13300) 651(65)	ν_{as} . 1685 ν_{as} . 1328 ν_{sym} . 1473, 1384, 1305, 1020
$\text{Cu}(\text{dpaa})(\text{NO}_3)_2(\text{H}_2\text{O})$ ^e	200(31200) 656(71)	ν_{as} . 1687 ν_{as} . 1327 ν_{sym} . 1473, 1380, 1304, 1010
$\text{Cu}(\text{dps})(\text{NO}_3)_2$ ^f	388(104) 630(82)	ν_{as} . 2910, 2854 ν_{as} . 1321 ν_{sym} . 1485, 1367, 1302, 1095

^aIn acetonitrile, 24.5 °C. ^bKBr pellet ^cThis work. dpb-2,2'-dipyridylbenzylamine

^dRef 4. dpba-2,2'-dipyridylbenzamide

^eRef 9. dpaa-2,2'-dipyridylacetamide

^fRef 12. dps-2,2'-dipyridylstearoylamine

and so the CuN_2O_2 basal plane is an exact square plane. A typical interesting feature of the copper complex containing 2,2'-dipyridylamine derivative is known to be a formation of pocket because N-substituted group is almost perpendicular to the dipyridyl plane. (in Fig. 2).^{6,16} The dpb-copper complex exhibits the same structure.

Distances of copper and pyridyl nitrogens are 1.974(4) and 1.980(4) and those of Cu-O with the nitrate ligand 1.979(4) and 1.986(4)Å, while Cu-O with axial nitrate in

neighboring atom, (O2a), is 2.404(5)Å, which is longer than those of Cu-O in equatorial sites. These results are similar to those of the corresponding dpba complex⁶ and 2,2'-dipyridylamine(dpa) 2,2'-dipyridylamine(dpa) or bipyridine complexes^{11,20-23} Two nitrate ligands are monodentately coordinated to the copper resulting in a 5-coordinated environment for copper geometry. The bond distances of N-O in nitrate ligand, N4-O1 and N5-O4, are longer than other nitrogen and noncoordinated oxy-

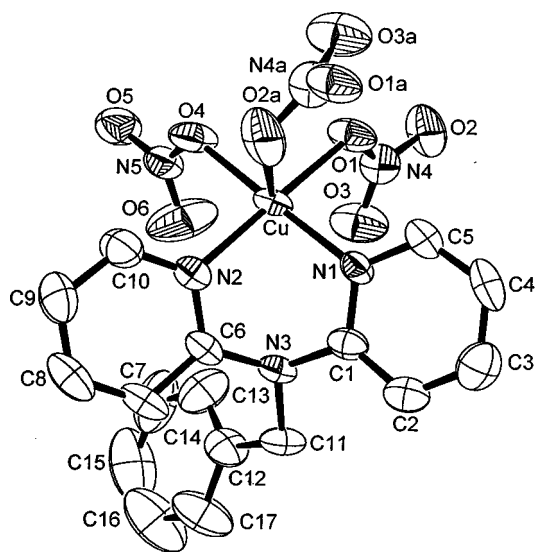


Fig. 1. ORTEP plot of the $\text{Cu}(\text{dpb})(\text{NO}_3)_2$ showing the atom-labeling scheme (all hydrogens are omitted).

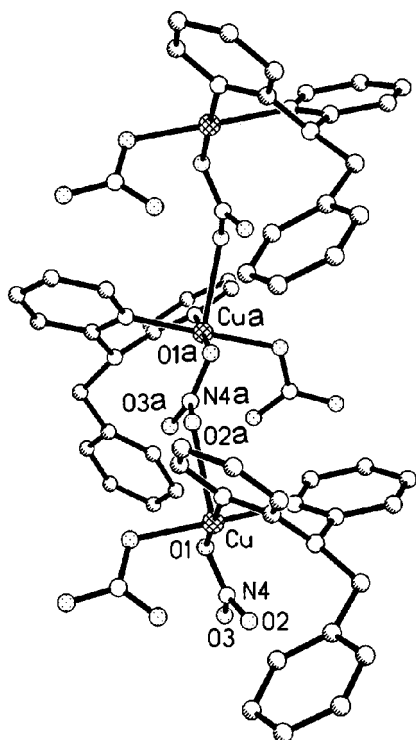


Fig. 2. A view of $\text{Cu}(\text{dpb})(\text{NO}_3)_2$ with axial coordinations of neighboring atoms.

gen distances. Selected bond lengths are presented in Table 4.

Table 4. Selected bond distances (Å) in the $\text{Cu}(\text{dpb})(\text{NO}_3)_2$

Cu-N1	1.974(4)	N5-O4	1.268(6)
Cu-O4	1.979(4)	O2-Cu	2.404(5)
Cu-N2	1.980(4)	C1-C2	1.376(8)
Cu-O1	1.986(4)	C2-C3	1.376(9)
Cu-O2a	2.404(5)	C3-C4	1.387(9)
N1-C5	1.325(7)	C4-C5	1.365(9)
N1-C1	1.346(7)	C6-C7	1.388(7)
N2-C10	1.340(8)	C7-C8	1.369(10)
N2-C6	1.337(7)	C8-C9	1.380(10)
N3-C6	1.392(7)	C9-C10	1.376(9)
N3-C1	1.404(7)	C11-C12	1.491(9)
N3-C11	1.484(7)	C12-C17	1.369(9)
N4-O3	1.221(7)	C12-C13	1.369(10)
N4-O2	1.229(6)	C13-C14	1.397(12)
N4-O1	1.265(6)	C14-C15	1.368(16)
N5-O6	1.196(7)	C15-C16	1.349(18)
N5-O5	1.225(6)	C16-C17	1.373(14)

Table 5. Selected bond angles (deg) in the $\text{Cu}(\text{dpb})(\text{NO}_3)_2$

N1-Cu-O4	178.7(2)	N4-O2-Cu	126.7(4)
N1-Cu-N2	88.1(2)	N5-O4-Cu	114.6(4)
N1-Cu-O1	91.2(2)	N1-C1-C2	121.0(5)
O4-Cu-O1	88.2(2)	N1-C1-N3	116.7(5)
N2-Cu-O1	179.0(2)	C2-C1-N3	122.2(5)
N1-Cu-O2	87.9(2)	C3-C2-C1	119.6(6)
O4-Cu-O2	91.1(2)	C2-C3-C4	118.6(6)
N2-Cu-O2	85.0(2)	C2-C3-C4	118.6(6)
O1-Cu-O2	95.8(2)	C5-C4-C3	118.8(5)
C5-N1-C1	119.2(5)	N1-C5-C4	122.7(5)
C5-N1-Cu	121.3(4)	N2-C6-C7	121.1(6)
C1-N1-Cu	119.4(4)	N2-C6-N3	116.7(4)
C10-N2-C6	119.0(5)	C7-C6-N3	122.2(5)
C10-N2-O	121.3(4)	C8-C7-C6	119.4(6)
C6-N2-Cu	119.6(4)	C7-C8-C9	119.7(6)
C6-N-C1	119.4(4)	C10-C9-C8	118.0(6)
C6-N3-C11	118.1(4)	N2-C10-C9	122.8(6)
C1-N3-C11	115.5(4)	N3-C11-C12	113.0(5)
O3-N4-O2	121.9(6)	C17-C12-C13	119.3(8)
O3-N4-O1	119.6(5)	C17-C12-C11	117.6(7)
O2-N4-O1	118.5(5)	C13-C12-C11	123.0(6)
O6-N5-O	122.9(6)	C12-C13-C14	120.2(9)
O6-N5-4	118.8(5)	C15-C14-C13	119.7(1)
O5-N5O4	118.4(5)	C16-C15-C14	119.2(1)
N4-O-Cu	110.6(3)	C15-C16-C17	121.9(1)
C12-C17-C16	119.7(1)		

The bite angle of the dpb ligand N1-Cu-N3 is 88.1°. In the corresponding dpba and dpaa copper(II) complexes.

these value were 86.9° and 88.1° respectively. They are comparable to those of the dpa copper complexes (86° to 96°).²⁴⁻²⁶ Selected bond angles are listed in Table 5.

CONCLUSION

A stable new copper(II) complex containing dipyridyl-benzylamine ligand, Cu(dpb)(NO₃)₂, was prepared from Cu(NO₃)₂ and dpb in an ethanol solution. The X-ray crystallographic study revealed that the coordination geometry of CuN₂O₃ chromophore was square pyramidal. The benzyl group was almost perpendicular to the pyridyl plane. The solution spectroscopic properties were consistent with the other reported copper(II) complexes.

Acknowledgement. This work was accomplished by a grant of 1999 academic research fund program in Dongeui University.

REFERENCES

- Murakami, T.; Hatano, M. *Inorg. Chim. Acta* **1986**, *125*, 111.
- Sigel, H.; Martin, R. B. *Chem. Rev.* **1982**, *82*, 385.
- Braga, D.; Grepioni, F.; Desiraju, G. R. *Chem. Rev.* **1998**, *98*, 1375.
- Petty, M. C.; Bryce, M. R.; Bloor, D. Eds.: *An Introduction to Molecular Electronic*, Edward Arnold press: 1995; pp. 348-376.
- Dong, Y.; Layland, R. C.; Smith, M. D.; Pschirer, N. G.; Bunz, U. H. F.; Loye, H. *Inorg. Chem.* **1999**, *38*, 3056.
- Lee, D.; Kim, B.; Oh, Y.; Jahn, M. S.; Chang, W. *Bull. Korean Chem. Soc.* **1996**, *17*, 836.
- Baxter, C. E.; Rodig, O. R.; Schlatter, R. K.; Sinn, E. *Inorg. Chem.* **1979**, *18*, 1918.
- Gauge, E. M.; Geldard, J. F. *Inorg. Chem.* **1978**, *17*, 270.
- Munoz, M. C.; Lazaro, J. M.; Faus, J.; Julve, M. *Acta Cryst.* **1993**, *C49*, 1756.
- Adeltsson, H.; Wamma, K.; Moberg, C. *J. Org. Chem.* **1994**, *59*, 2004.
- Ugozzoli, F.; Lantfred, A. M. M.; Marich, N.; Camus, A. *Inorg. Chim. Acta* **1997**, *256(1)*, 1.
- Jacobson, R. A.; Jensen, W. P. *Inorg. Chim. Acta* **1986**, *114*, 19.
- Jensen, W. P.; Jacobson, R. A. *Inorg. Chim. Acta* **1981**, *49*, 199.
- Rehorek, D.; Witzenhansen, U. *Z. anorg. allg. Chem.* **1978**, *447*, 221.
- Choi, S.; Kwon, M.; Kim, Y.; Bereman, R. D.; Singh, P.; Knight, B. *J. Coord. Chem.* **1995**, *34*, 241.
- Oh, Y.; Ko, Y. *Donggukmonjip*. **1998**, *28(2)*, 291.
- Sheldrick, G. M. *Acta Crystallogr.* **1990**, *A46*, 467.
- Sheldrick, G. M. SHELXL97; University of Göttingen: Germany, **1997**.
- Oh, Y.; Kim, J.; Park, Y.; Chang, W. *Bull. Korean Chem. Soc.* manuscript submitted.
- Ray, N.; Hathaway, B. J. *Acta Crystallogr.* **1978**, *B34*, 3224.
- Ray, N.; Tyagi, S.; Hathaway, B. J. *Acta Crystallogr.* **1972**, *B38*, 1574.
- Nakai, H. *Bull. Chem. Soc. Japan*, **1971**, *44*, 1371.
- Murphy, B. *Acta Crystallogr.* **1978**, *B34*, 3224.
- Aduldecha, S.; Hathaway, B. *Acta Cryst.* **1991**, *C47*, 84.
- Akhter, P.; Hathaway, B. *Acta Cryst.* **1991**, *C47*, 86.
- Lubben, M.; Hage, R.; Meetsma, A.; Byma, K.; Feringa, B. L. *Inorg. Chem.* **1995**, *34*, 2217.