Crystal Structures and Characterization of Copper(II) Complexes of *N,N,N′N′*-Tetrakis(2-pyridylmethyl)-1,2-ethanediamine

Doo Cheon Yoon, Uk Lee,† and Chang Eon Oh*

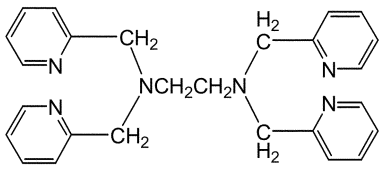
Department of Chemistry, Yeungnam University, Gyongsan 712-749, Korea
†Department of Chemistry, Pukyong National University, Pusan 608-737, Korea
Received February 27, 2004

The structure of $[Cu(tpen)](ClO_4)_2$ (tpen = *N,N,N′,N′*-tetrakis(2-pyridylmethyl)-1,2-ethanediamine) has been identified by X-ray crystallography. The copper(II) ion is surrounded by two amine N atoms and three pyridine N atoms of the ligand, making a distorted trigonal-bipyramid. Among the six potential N donor atoms (two amine N and four pyridine N atoms), only one pyridine N atom remains uncoordinated. We examined structural changes on addition of Cl^- to $[Cu(tpen)]^{2+}$ (**1**). The addition of Cl^- in methanol resulted in the formation of a novel dinuclear copper(II) complex $[Cu_2Cl_2(tpen)](ClO_4)_2 \cdot H_2O$. The structure of the dinuclear complex was verified by X-ray crystallography. Each copper(II) ion in the dinuclear complex showed a distorted square planar geometry with two pyridine N atoms, one amine N atom and one Cl^- ion.

Key Words : Pentadentate copper(II) complex, Dinuclear copper(II) complex, Crystal structure, Tpen

Introduction

N,N,N′,N′-Tetrakis(2-pyridylmethyl)-1,2-ethanediamine (referred to hereafter as tpen) is a hexadentate and useful ligand in analytical, biochemical, and inorganic chemistry.[1]



tpen

The crystallographic studies of types $[M(tpen)]^{n+}$ are well known: M = Co(III),[1,2] Fe(II),[3,4] Fe(III),[5] and Cr(III).[6] These metal complexes are typically mononuclear octahedral, in which the tpen ligand coordinates in a hexadentate manner. However, such geometry in coordination with a hexadentate ligand containing pyridyl arms to the copper(II) ion is not common. For $[Cu(tpen)]^{2+}$, various geometries about the copper(II) ion are possible due to the various bonding modes of the tpen and the d^9 configuration of the copper(II) ion.[7,8] The tpen ligand has been used in the present study to prepare a 6-coordinate copper(II) complex, in which the tpen ligand acts as a hexadentate ligand. However, a 5-coordinate copper(II) complex $[Cu(tpen)]^{2+}$ (**1**), in which the tpen acts as a pentadentate ligand, was obtained. The crystal structure of $[Cu(tpen)](ClO_4)_2$ was identified by X-ray crystallography. The structural characterization of this complex is discussed. We examined structural changes on addition of Cl^- to **1**. The addition of Cl^- in methanol resulted in the formation of a novel dinuclear copper(II) complex $[Cu_2Cl_2(tpen)](ClO_4)_2 \cdot H_2O$, whose structure was also determined by X-ray diffraction. Herein we report the preparation and crystal structures of $[Cu(tpen)](ClO_4)_2$ and $[Cu_2Cl_2(tpen)](ClO_4)_2 \cdot H_2O$.

*Corresponding Author. Tel: +82-53-810-2359; Fax: +82-53-813-4465; e-mail: ceoh@yumail.ac.kr

Experimental Section

Material and physical measurement. All chemicals were purchased from commercial sources and used without further purification. *Caution!* As perchlorate salts of metal complexes are potentially explosive, only a small amount of material should be prepared, and it should be handled with care. The absorption spectra in acetonitrile and in the solid were recorded on a SHIMADZU UV-1601PC UV-visible spectrophotometer at room temperature. The absorption spectrum in solid was obtained by means of a disc. Elemental analyses of carbon, hydrogen, and nitrogen were carried out on a FISONS Elemental analyzer model EA1108.

Synthesis of $[Cu(tpen)](ClO_4)_2$. The tpen ligand was prepared as previously reported.[9,10] A solution of the tpen (6.18 g, 14.6 mmol) in methanol (30 cm^3) was added to a solution of copper(II) perchlorate hexahydrate (5.41 g, 14.6 mmol) in methanol (20 cm^3). A green precipitate was formed immediately after mixing. The mixture was stirred for 1 h at room temperature and left overnight. The crude product was filtered and washed twice with water. Recrystallization was carried out by dissolving the crude product in the minimum amount of a 1 : 4 water-acetone mixture. This solution was filtered and left at room temperature for solvent evaporation and precipitation of the pure product, which was isolated as described above. Then a suitable green single crystal for X-ray analysis was obtained. Yield: 8.0 g (79.8%). Analysis calculated for $[Cu(tpen)](ClO_4)_2$: C 45.46, H 4.11, N 12.23%; and found: C 45.51, H 3.97, N 12.00%. λ/nm (ε/$M^{-1} \cdot cm^{-1}$): 686 (163) in acetonitrile;

704 and ~606 (sh) in solid.

Synthesis of $[Cu_2Cl_2(tpen)](ClO_4)_2 \cdot H_2O$. A solution of the tpen (3.18 g, 7.5 mmol) in methanol (15 cm^3) was added to a solution of copper(II) perchlorate hexahydrate (5.56 g, 15.0 mmol) in methanol (20 cm^3). A green precipitate, $[Cu(tpen)](ClO_4)_2$, formed immediately after mixing. An aqueous solution of NaCl (1.17 g, 20 mmol) was added to methanol of the green precipitate. On addition of the aqueous solution of NaCl, this precipitate dissolved. The resulting blue solution was stirred for 8 h at room temperature. After stirring, the mixture was left overnight. The crude product was filtered and washed twice with water. Recrystallization was carried out by dissolving the crude product in the minimum amount of 1 : 5 water-methanol mixture. This solution was filtered and left at room temperature for solvent evaporation and precipitation of the pure product, which was isolated as described above. A suitable blue single crystal for X-ray analysis was formed. Yield: 9.0 g (71.3%). Analysis calculated for $[Cu_2Cl_2(tpen)](ClO_4)_2 \cdot H_2O$: C 37.20, H 3.60, N 10.01%, and found: C 37.51, H 3.53, N 10.02%. λ/nm (ε/$M^{-1} \cdot cm^{-1}$): 675 (327) in acetonitrile.

Crystal structure determination and refinement. A crystal of dimensions $0.38 \times 0.38 \times 0.19$ mm^3 for $[Cu(tpen)](ClO_4)_2$ and one of $0.26 \times 0.18 \times 0.10$ mm^3 for $[Cu_2Cl_2(tpen)](ClO_4)_2 \cdot H_2O$ were selected for X-ray data collection. The data were collected on a STOE STADI4 diffractometer equipped with Mo-Kα radiation (λ = 0.71069 Å) using ω-2θ scan mode at 298(2) K. The data were corrected for Lorentz and polarization effects. Numerical absorption correction based on a series of φ scans was applied. All calculations were carried out with the X-STEP program package.[11] The structures were solved by the direct method. The crystallographic data for $[Cu(tpen)](ClO_4)_2$ and $[Cu_2Cl_2(tpen)](ClO_4)_2 \cdot H_2O$ are summarized in Table 1.

All H atoms bonded to C atoms were included in the structure-factor calculation at idealized positions, and were allowed to ride on their parent atoms with relative isotropic displacement parameters [U_{iso}(H) = 1.2U_{eq}(C)]. The H atoms of the O_w water molecule could not be positioned geometrically or located in the electron density map because a water molecule does not form a definite hydrogen bond. The distance 3.031(6) Å between O_w and O_1 is vague as a hydrogen bond. These H atoms were not included in these calculations (although they are included in the empirical formula).

Table 1. Crystallographic data for $[Cu(tpen)](ClO_4)_2$ and $[Cu_2Cl_2(tpen)](ClO_4)_2 \cdot H_2O$

	$[Cu(tpen)](ClO_4)_2$	$[Cu_2Cl_2(tpen)](ClO_4)_2 \cdot H_2O$
Formula	$C_{26}H_{28}Cl_2CuN_6O_8$	$C_{26}H_{30}Cl_4Cu_2N_6O_9$
FW	686.98	839.44
Crystal system	*Monoclinic*	*Monoclinic*
Space group	*C2/c*	*P2₁/n*
a, Å	37.338(6)	13.267(2)
b, Å	9.748(1)	20.562(3)
c, Å	15.884(2)	12.463(5)
β, deg	95.96(2)	108.637(2)
Z	8	4
V, Å^3	5750(1)	3222(2)
ρ_{calc}, Mg/m^3	1.587	1.731
θ range, deg.	2.16-27.52	1.90-27.48
Measured reflections	6611	7350
No. of parameters	388	425
I > 2σ	4528	5990
GOF	1.124	1.082
μ, mm^{-1}	1.006	1.713
*R*1 ($I > 2\sigma(I)$)	0.0636	0.0430
Rw ($I > 2\sigma(I)$)	0.1348	0.0996
$\Delta\rho_{max}$ and $\Delta\rho_{min}$, eÅ^{-3}	0.83, -0.57	0.85, -0.62

Results and Discussion

An ORTEP drawing of **1** is shown in Figure 1. The complex has a distorted trigonal-bipyramidal geometry about the copper(II) ion, which is coordinated to two amine N atoms and three pyridine N atoms of the tpen. One (N6) out of the six potential N donor atoms in the ligand is not coordinated. Complex **1** shows as two-band visible spectrum in solid, with the intensity of the lower-energy band being significantly higher than the intensity of the higher-energy shoulder (Figure 2). This spectral pattern is characteristic of distorted trigonal-bipyramidal copper(II) complexes.[12,13]

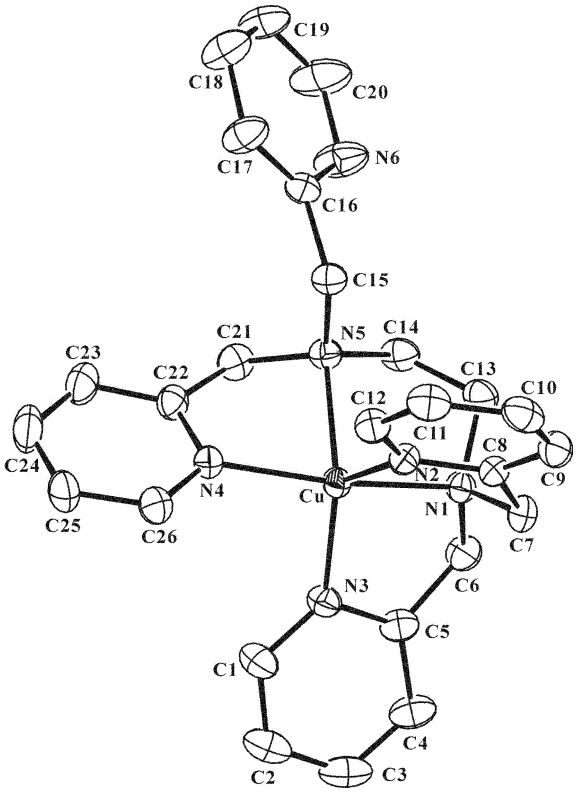


Figure 1. An ORTEP drawing of **1** with the atom numbering; displacement ellipsoids are drawn at the 30% probability level and H atoms have been omitted for clarity.

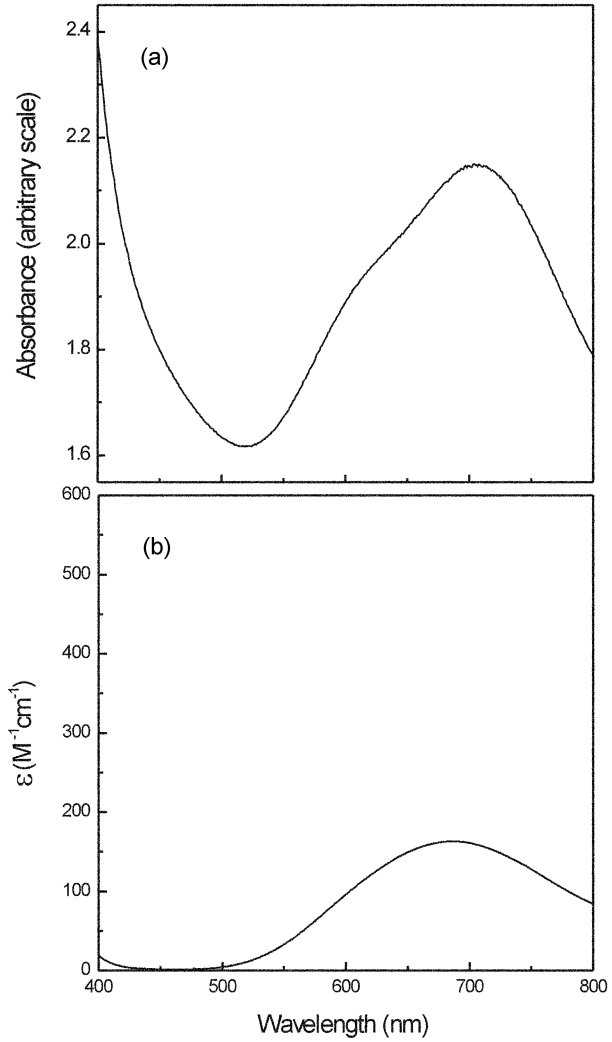


Figure 2. The absorption spectra of **1** in solid (a) and in acetonitrile (b).

Selected bond lengths and angles for **1** are listed in Table 2. In Table 2, the bond angles in the equatorial plane are distorted from the ideal trigonal angle of 120° with one small angle of 104.2(1)° (N2-Cu-N5) between the Cu-N_{am} bond and the equatorial Cu-N_{py} bond and two large angles of 125.9(2)° (N2-Cu-N3) and 127.2(2)° (N3-Cu-N5) between the Cu-N_{py} bonds. The N1-Cu-N2, N1-Cu-N3, and N4-Cu-N5 angles for the picolylamine groups are in the range from 82.0(2)° to 83.5(2)°, and the N1-Cu-N5 angle for the ethane-1,2-diamine group is 87.2(2)°. The N-Cu-N angles for the picolylamine groups are smaller than that for the ethane-1,2-diamine group. This may be due to rigid picolylamine groups. Also, due to the puckering of the ethane-1,2-diamine ring, the angle (N1-Cu-N5) for the ethane-1,2-diamine group is closer to the ideal angle of 90° than those for the picolylamine groups. The copper(II) ion in **1** is displaced by 0.2 Å from the trigonal plane towards the apical N4 atom. In the crystal structure of **1**, there seems to be strain in spite of the coordination number of 5, this conclusion is derived from the observation that the N2-Cu-N5 angle (104.2(1)°) is significantly deviated from the ideal trigonal angle of 120°,

Table 2. Selected bond lengths and angles for **1** and **2**

Complex	Bond length (Å)		Bond angle (deg)	
1				
	Cu-N(1)	2.005(4)	N(4)-Cu-N(1)	167.3(2)
	Cu-N(2)	2.084(4)	N(4)-Cu-N(3)	97.7(2)
	Cu-N(3)	2.028(4)	N(1)-Cu-N(3)	83.5(2)
	Cu-N(4)	1.972(4)	N(4)-Cu-N(2)	106.0(2)
	Cu-N(5)	2.148(4)	N(1)-Cu-N(2)	83.1(2)
			N(3)-Cu-N(2)	125.9(2)
			N(4)-Cu-N(5)	82.0(2)
			N(1)-Cu-N(5)	87.2(2)
			N(3)-Cu-N(5)	127.2(2)
			N(2)-Cu-N(5)	104.2(1)
2				
	Cu(1)-N(1)	1.972(3)	N(1)-Cu(1)-N(2)	81.7(1)
	Cu(1)-N(2)	2.061(2)	N(3)-Cu(1)-N(2)	82.3(1)
	Cu(1)-N(3)	1.974(3)	N(1)-Cu(1)-Cl(1)	99.0(1)
	Cu(1)-Cl(1)	2.265(1)	N(3)-Cu(1)-Cl(1)	97.3(1)
	Cu(2)-N(4)	2.047(2)	N(5)-Cu(2)-N(4)	81.5(1)
	Cu(2)-N(5)	1.996(3)	N(6)-Cu(2)-N(4)	81.0(1)
	Cu(2)-N(6)	2.002(3)	N(5)-Cu(2)-Cl(2)	98.0(1)
	Cu(2)-Cl(2)	2.245(1)	N(6)-Cu(2)-Cl(2)	98.9(1)

and the axial N atoms (N1 and N4) are severely tilted from the ideal axial positions.

In Table 2, Cu-N distances are in the range 1.972(4)-2.148(4) Å. The distance of Cu-N5 having one uncoordinating pyridine N6 atom is 2.148(4) Å, which is the longest among Cu-N distances. The bond lengths of axial Cu-N (N1 and N4) bonds are slightly shorter than those of the equatorial Cu-N (N2, N3, and N5) bonds, in agreement with the result found in the pentachlorocuprate(II) anion.[14] This axial contraction may be due to rigid tpen, and not the influence of the d^9 electronic distribution on the coordination geometry.

The absorption spectrum of pentadentate complex **1** in

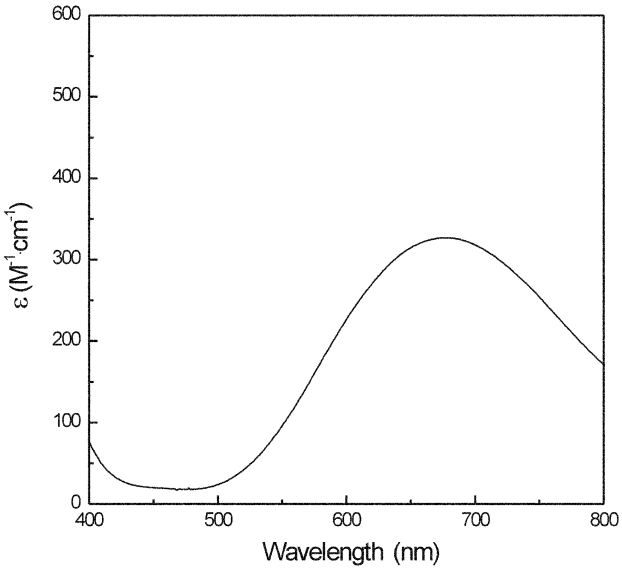
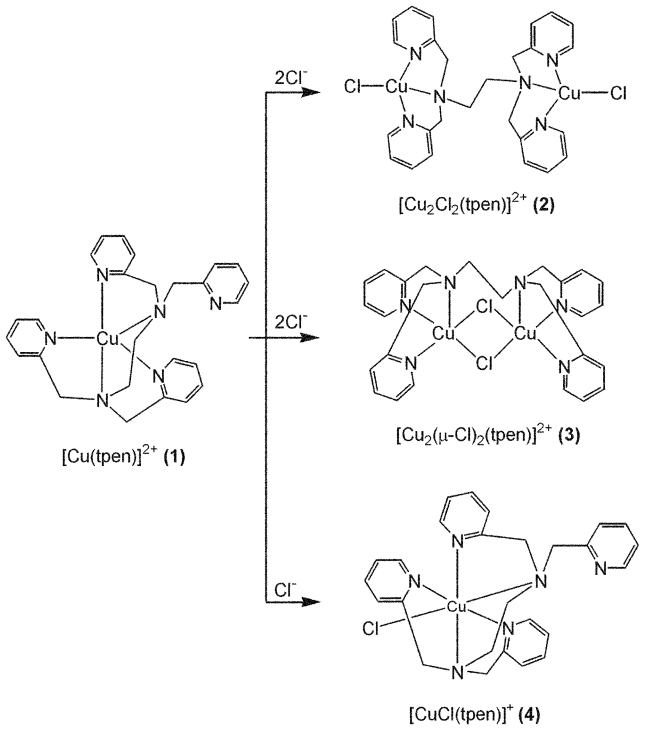


Figure 3. The absorption spectrum of **2** in acetonitrile.



Scheme 1. The structures of possible compound produced from the reaction between **1** and Cl^- ion.

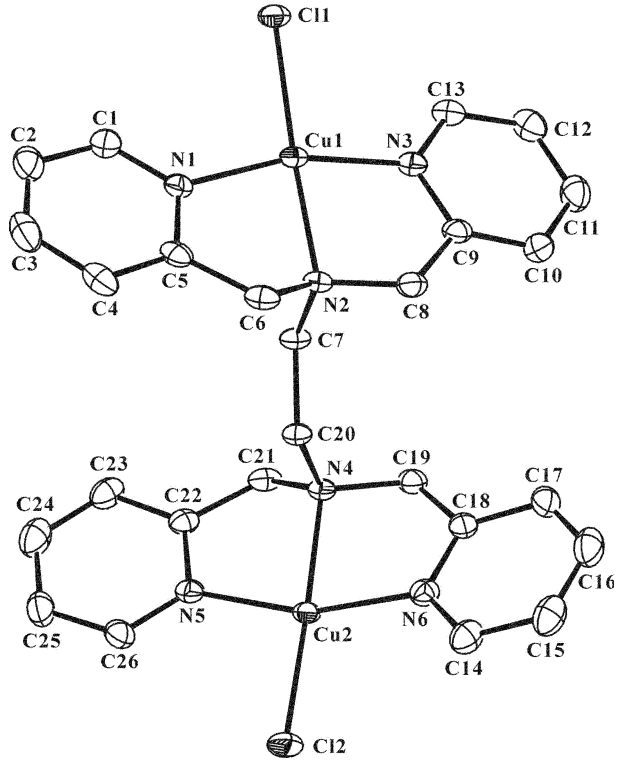


Figure 4. An ORTEP drawing of **2** with the atom numbering; displacement ellipsoids are drawn at the 30% probability level and H atoms have been omitted for clarity.

acetonitrile, as compared with the absorption spectrum in solid, changed in the shape and position of band maxima (Figure 2). Only the lower-energy band remained, and the higher-energy shoulder disappeared. This difference in spectral shapes between "in solid" and "in solution" is ascribed to a geometrical transformation. Because a solvent molecule, acetonitrile, in solution affects the geometry of **1**, it would be interesting to investigate whether a substituent such as Cl^- can affect the structure of complex **1**. The absorption spectrum of the product obtained after addition of Cl^- was measured in acetonitrile (Figure 3). The position of band maxima of the product related to **1** moved toward higher energy with the retention of the shapes of band maxima of two compounds. This indicates that **1** transformed to some other entity. The structures of possible products are shown in Scheme 1. The dinuclear complex, $[Cu_2Cl_2(tpen)]^{2+}$ (**2**), is the only product found from among three possible complexes. Two other complexes, $[Cu_2(\mu\text{-}Cl)_2(tpen)]^{2+}$ (**3**) and $[CuCl(tpen)]^+$ (**4**), were not observed. The structure of **2** was confirmed by X-ray crystallography. An ORTEP drawing of **2** is shown in Figure 4. This dinuclear complex has a distorted square-planar geometry, and each copper(II) ion is surrounded by two pyridine N atoms, one amine N atom and one Cl^- ion. Selected bond lengths and angles for **2** are summarized in Table 2. The square planar angles in between the copper(II) ion and the equatorial coordinating atoms are in the range of 81.7(1)° to 99.0(1)° for Cu1 and of 81.0(1)° to 98.9(1)° for Cu2. They deviate from the ideal square planar angle of 90°. In addition, the four equatorial coordinating atoms (3N and Cl^-) about each copper(II) ion are nearly coplanar, and the copper(II) ions are displaced by 0.05 Å for Cu1 and 0.07 Å for Cu2 from each planes, respectively.

Conclusion

We prepared a 5-coordinate copper(II) complex $[Cu(tpen)](ClO_4)_2$ from copper(II) perchlorate hexahydrate and the tpen in methanol. In complex **1**, the tpen ligand acts as a pentadentate ligand. In addition, we found the effect of the Cl^- on the structure of the mononuclear 5-coordinate complex **1**. The Cl^- addition to **1** brought about structural change, which gave a novel dinuclear copper(II) complex **2**, in which each copper(II) ion has a distorted square-planar geometry.

Supplementary material. Crystallographic data for the structures reported here have been deposited with the Cambridge Crystallographic Data Centre (Deposition Nos. CCDC-214894 for $[Cu(tpen)](ClO_4)_2$ and CCDC-214895 for $[Cu_2Cl_2(tpen)](ClO_4)_2 \cdot H_2O$. The data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).

References

1. Mandel, J. B.; Douglas, B. E. *Inorg. Chim. Acta* **1989**, *55*, 155.
2. Mandel, J. B.; Maricondi, C.; Douglas, B. E. *Inorg. Chem.* **1988**, *27*, 2990.
3. Chang, H. R.; McCusker, J. K.; Toftlund, H.; Wilson, S. R.; Trautwein, A. X.; Winkler, H.; Hendrickson, D. N. *J. Am. Chem.*

Soc. **1990**, *112*, 6814.
4. Toftlund, H.; Andersen, S. Y. *Acta Chem. Scand.* **1981**, *A35*, 575.
5. Duelund, L.; Hazell, R.; McKenzie, C. J.; Nielsen, L. P.; Toftlund, H. *J. Chem. Soc. Dalton Trans.* **2001**, 152.
6. Erikson, J.; Goodson, P.; Hazell, A.; Hodgson, D. J.; Michelsen, K.; Mönsted, O.; Rasmussen, J. C.; Toftlund, H. *Acta Chem. Scand.* **1999**, *33*, 1083.
7. Lee, Y. M.; Kim, Y. K.; Jung, H. C.; Kim, Y. I.; Choi, S. N. *Bull. Korean Chem. Soc.* **2002**, *23*, 404.
8. Ganjali, M. R.; Emami, M.; Masoud, S. N. *Bull. Korean Chem. Soc.* **2002**, *23*, 1394.
9. Yoon, D. C.; Oh, C. E.; Lee, U. *Acta Cryst.* **2002**, *E58*, m113.
10. Hirayama, N.; Iimuro, S.; Kubono, K.; Kokusen, H.; Honjo, T. *Talanta* **1996**, *43*, 621.
11. *STOE. STADI4, X-RED and X-SHAPE. X-Ray Structure Evalutation Package*; STOE-Cie Gmbh, Hilpertstrasse 10, D64295: Darmstadt, Germany, 1996.
12. Rybak-Akimova, E. V.; Nazarenko, A. Y.; Chen, L.; Krieger, P. W.; Herrera, A. M.; Tarasov, V. V.; Robinson, P. D. *Inorg. Chim. Acta* **2001**, *324*, 1.
13. Hathaway, B. J. *Comprehensive Coordination Chemistry*; Pergamon Press: Oxford, 1987; vol. 5, p 533.
14. Anderson, O. P. *Inorg. Chem.* **1975**, *14*, 730.