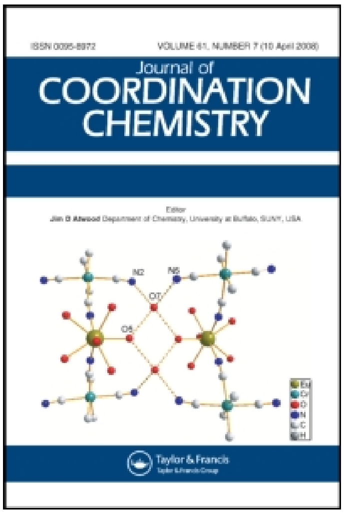

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Crystal structure and properties of a Cu(II) complex with the tridentate Schiff-base ligand, paeonol-(2-aminoethylpiperazine)

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Crystal structure and properties of a Cu(II) complex with the tridentate Schiff-base ligand, paeonol-(2-aminoethylpiperazine)

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A new copper Schiff-base complex $[Cu(C_{15}H_{23}N_3O_2)(NO_3)]NO_3$ was synthesized and characterized by spectroscopic (IR), thermal (TG/DTA) and electrochemical methods. Single crystal X-ray diffraction revealed that the complex is monoclinic, space group *P2(1)/c*, with $a = 23.549(2)$, $b = 6.583(12)$, $c = 12.765(15)$ Å, $\beta = 102.823(2)°$, $V = 1929.4(5)$ Å^3, $Z = 4$, $D_{calcd} = 1.601$ Mg m^{-3}, $F(000) = 964$, goodness-of-fit = 1.034 and $R_1 = 0.0407$. The Cu(II) is four-coordinate with distorted square planar geometry. The structure consists of isolated $[Cu(C_{15}H_{23}N_3O_2)(NO_3)]^+$ and a nitrate, which are further linked to a 3D network by significant N–H ⋯ O, N–H ⋯ N hydrogen bonds and weak O ⋯ Cu interaction.

Keywords: Copper Schiff-base complex; Crystal structure; Electrochemical analysis; 2-Aminoethylpiperazine; Paeonol

1. Introduction

Compounds containing imine (–RC=N–) are known as Schiff bases, usually formed by condensation of primary amine with active carbonyl [1–3]. The chemistry of Schiff bases is of interest for potential applications such as homogeneous or heterogeneous catalysis, magnetism, flexible ligands, etc. [3–9]. Schiff bases accommodate different metals with various coordination modes allowing synthesis of stable complexes with varied stereochemistry. Copper(II) is an important transition metal ion with biological properties, and copper complexes have many properties (e.g. catalytic, redox chemistry, biomimetic behavior), biological activities (e.g. antimicrobial, anti-inflammation, anticonvulsive) and applications (e.g. structural models for copper-containing enzymes, catalysts, pharmaceuticals) [8–16]. We designed a synthetic route trying to prepare a tridentate Schiff base through condensation of 2-aminoethylpiperazine and paeonol in

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methanol, and further to obtain the corresponding copper complex through reaction of the Schiff base and copper nitrate trihydrate (reaction scheme is presented in scheme 1). We could not obtain the solid Schiff base paeonol-(2-aminoethylpiperazine), but only the corresponding mononuclear copper complex. To our knowledge, the title complex is the first 2-aminoethylpiperazine Schiff-base complex. The complex has coordinated and uncoordinated nitrate and a weak O···Cu interaction between adjacent molecules. Herein, we report the synthesis, characterization, crystal structure and electrochemical properties of the title complex.

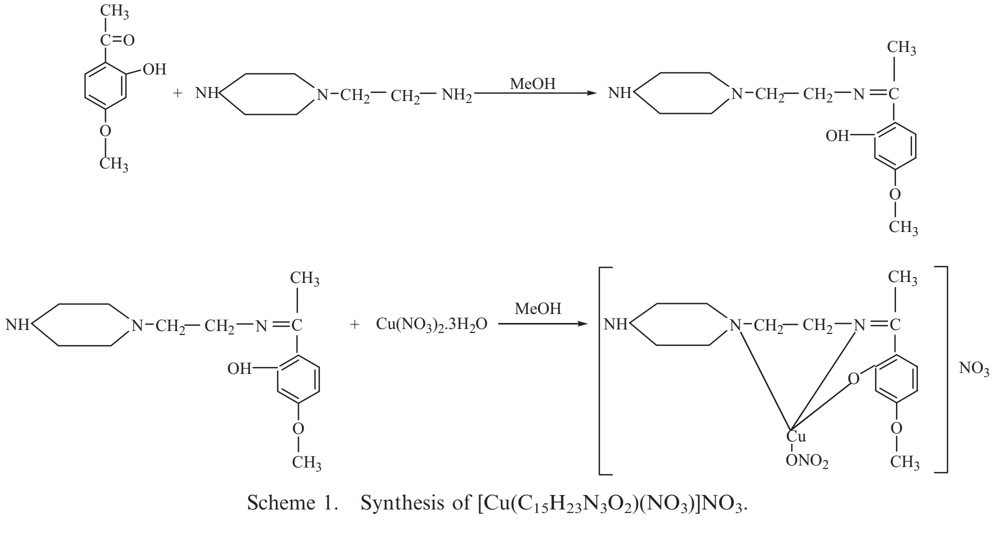
2. Experimental

2.1. *Synthesis of [Cu(C$_{15}$H$_{23}$N$_3$O$_2$)(NO$_3$)]NO$_3$*

A solution of 2-aminoethylpiperazine (0.026 g, 0.2 mmol) in 10 mL anhydrous methanol was added dropwise to the solution of paeonol (0.033 g, 0.2 mmol) in 10 mL anhydrous methanol, then the mixture solution was heated under reflux about 2.5 h, turning yellow. To the yellow solution, after cooling to 40°C, a solution of $Cu(NO_3)_2 \cdot 3H_2O$ (0.048 g, 0.02 mmol) in 8 mL anhydrous methanol was added. The resulting purple solution was continuously stirred for 1.5 h, filtered, and the filtrate left to stand at room temperature. On slow evaporation of the filtrate for 4 days, deep purple block-shape single crystals suitable for X-ray analysis were collected, washed with 5 mL anhydrous methanol, and dried in vacuum. Yield: 74.8%. m.p. 265–268°C (dec.). Anal. Calcd for $C_{15}H_{23}CuN_5O_8$ (%): C, 38.75; H, 4.99; N, 15.06. Found: C, 38.87; H, 5.12; N, 14.93; IR spectra exhibited a complicated pattern of bands in the range 4000–450 cm^{-1}; 3440 cm^{-1} $\nu(OH)$; 1591 cm^{-1} $\nu(C{=}N)$, 1384, 851 cm^{-1} $\nu(NO_3^-)$, 1180 cm^{-1} $\nu(CN)$, 749 cm^{-1} $\nu(NH)$.

2.2. *X-ray crystallography*

Diffraction data for a crystal of dimensions $0.52 \times 0.40 \times 0.15\,mm^3$ were collected on a BRUKER SMART CCD diffractometer with graphite monochromated Mo-Kα



Scheme 1. Synthesis of [Cu(C$_{15}$H$_{23}$N$_3$O$_2$)(NO$_3$)]NO$_3$.

(λ=0.71073 Å) radiation by using the ω-2θ scan technique ($2.66 \le \theta \le 25.01^\circ$) at 298(2) K. The crystal structure was solved by direct methods and Fourier synthesis (SHELXS-97) [17], refined by full-matrix least-squares techniques on F^2 with the program SHELXL-97 [18]. The non-hydrogen atoms were refined anisotropically and hydrogen atoms were added according to theoretical models. A summary of crystallographic data and refinement parameters is given in table 1.

2.3. *Reagents and instrumentation*

All chemicals were purchased from commercial sources of reagent grade and used as received without further purification. Elemental analyses (C, H, N) were determined with a Perkin–Elmer 240c instrument. IR spectra were recorded on a Spectrum One BFT-IR spectrophotometer using KBr pellets in the range 4000–450 cm^{-1}. Thermal analyses were performed on a METTLER TOLEDO TGA/SDTA 851^e. Electrochemical experiments were carried out with a CHI 660A electrochemistry workstation (CHI USA) connected to a Pentium 200 MHz PC.

3. Results and discussion

3.1. *IR spectra*

Though the condensation of 2-aminoethylpiperazine and paeonol was carried out many times, solid Schiff-base product was not isolated. Therefore, IR spectra of paeonol and

Table 1. Crystal data and structure refinement details for $[Cu(C_{15}H_{23}N_3O_2)(NO_3)]NO_3$.

Formula	$C_{15}H_{23}CuN_5O_8$
M	464.92
Color	Deep purple
Temperature (K)	298(2)
Wavelength (Å)	0.71073
Radiation	Mo-Kα
Crystal system	Monoclinic
Space group	$P2(1)/c$
Unit cell dimensions (Å, °)	
a	23.549(2)
b	6.583(12)
c	12.765(15)
β	102.823(2)
V (Å^3)	1929.4(5)
Z	4
D_{calcd} ($Mg\,m^{-3}$)	1.601
Absorption coefficient (mm^{-1})	1.187
$F(000)$	964
θ Range for data collection (°)	2.66 to 25.01
Reflections collected/unique	9334 3382 [$R(int) = 0.0450$]
Completeness to $2\theta = 25.01$	99.5%
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	3382/0/264
Goodness-of-fit on F^2	1.034
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0407$, $wR_2 = 0.0864$
R indices (all data)	$R_1 = 0.0689$, $wR_2 = 0.1021$
Largest diff. peak and hole (e Å^{-3})	0.397 and −0.424

the copper complex were recorded. The IR spectrum of paeonol shows a strong band at 1620 cm^{-1}, attributable to ν(C=O). The broad band at 3430 cm^{-1} is assigned to ν(OH). In the IR spectrum of the title complex, ν(OH) shifts to 3440 cm^{-1}, indicating that OH takes part in the coordination to the metal ion. The peaks at 1180 and 749 cm^{-1} attribute to the ν(CN) and ν(NH), respectively, and those at 1384 and 851 cm^{-1} to $\nu(NO_3^-)$, suggesting the presence of piperazine and nitrate in the complex. A new strong peak at 1591 cm^{-1} assigned to ν(C=N), together with the absence of $\nu(NH_2)$ and the disappearance of ν(C=O), provide evidence for the formation of Schiff base.

3.2. *Crystal structure*

The molecular structure and atom-numbering schemes for $[Cu(C_{15}H_{23}N_3O_2)(NO_3)]NO_3$ is shown in figure 1 and selected bond lengths and angles are given in table 2. The packing diagram in the unit cell is shown in figure 2. The molecular structure consists of isolated $[Cu(C_{15}H_{23}N_3O_2)(NO_3)]^+$ and nitrate. There are coordinated and uncoordinated nitrates in the complex. The N(1)–C(2) bond length of 1.300(4) Å is much shorter than the N(1)–C(10) of 1.480(4) Å which is in the range for typical C–N single bonds, 1.47 ~ 1.50 Å. With the strong absorption at 1591 cm^{-1} in the IR assigned to imine, indicates that N(1)–C(2) is a double bond and the Schiff base

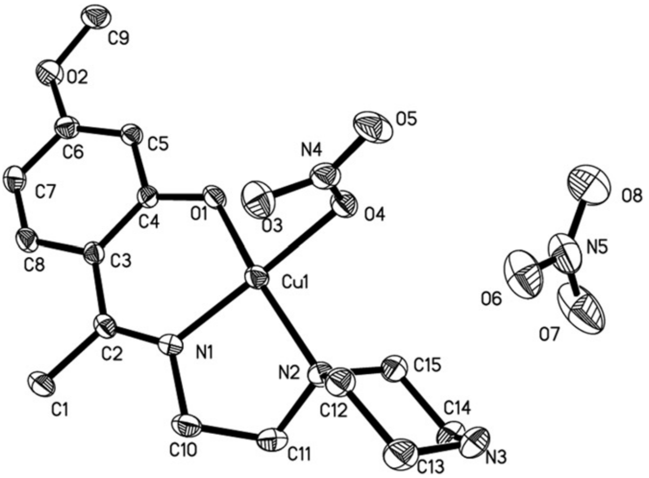


Figure 1. Molecular structure of $[Cu(C_{15}H_{23}N_3O_2)(NO_3)]NO_3$ with atom numbering scheme.

Table 2. Selected bond lengths (Å) and angles (°) for $[Cu(C_{15}H_{23}N_3O_2)(NO_3)]NO_3$.

Cu(1)–O(1)	1.864(2)	Cu(1)–O(4)	2.026(2)
Cu(1)–N(1)	1.922(3)	Cu(1)–N(2)	2.048(3)
N(1)–C(2)	1.300(4)	N(1)–C(10)	1.480(4)
O(1)–Cu(1)–N(1)	95.45(11)	O(1)–Cu(1)–O(4)	89.19(10)
N(1)–Cu(1)–O(4)	168.30(12)	O(1)–Cu(1)–N(2)	164.18(11)
N(1)–Cu(1)–N(2)	87.03(12)	O(4)–Cu(1)–N(2)	91.43(11)
C(2)–N(1)–C(10)	121.9(3)	N(1)–C(2)–C(3)	121.9(3)

paeonol-(2-aminoethylpiperazine) formed. The C–N lengths are slightly longer than those of uncoordinated C=N and C–N single bond of paeonol-organic amine Schiff base [19, 20], further proving coordination of the Schiff-base with copper. The X-ray analysis revealed that Cu(II) is four-coordinated to a piperazine nitrogen [N(2)], an imine nitrogen [N(1)], a phenolic oxygen [O(1)] from the Schiff base and an oxygen [O(4)] from coordinated nitrate. The coordination geometry around Cu(1) approaches distorted square planar. The Cu(1)–N(1), Cu(1)–N(2), Cu(1)–O(1) and Cu(1)–O(4) distances are 1.922(3), 2.048(3), 1.864(2) and 2.026(2) Å, respectively, comparable with those of other copper complexes [21, 22]. The bond angles of O(1)–Cu(1)–N(1), O(1)–Cu(1)–O(4), N(1)–Cu(1)–N(2) and O(4)–Cu(1)–N(2) are, respectively, 95.45(11), 89.19(10), 87.03(12) and 91.43(11)°, whose summation is near 360°, but that of N(1)–Cu(1)–O(4) and O(1)–Cu(1)–N(2) are 168.31(11) and 164.19(11)°, much smaller than the ideal value of 180°. From the bond angles, it can be concluded that Cu(1), N(1), N(2), O(1) and O(4) atoms are not planar, and the best-square plane through these atoms shows deviations of 0.0295, 0.2281, −0.2328, −0.2441 and 0.2191 Å, respectively. The phenyl ring can be considered almost coplanar, with mean deviation from the plane of 0.0046 Å. Piperazine can be regarded as three moieties: plane A composed of N(2)–C(12)–C(15), ring B composed of C(12)–C(13)–C(14)–C(15) and plane C composed of N(3)–C(13)–C(14). Ring B can be considered as almost coplanar with mean deviation from the plane of 0.0058 Å, and N(2) and N(3) lie above or below the mean plane by −0.6501 and 0.6549 Å with respect to one another. Furthermore the dihedral angles among the three planes are 48.4° for A and B, 52.7° for B and C and 4.3° for A and C, respectively. Consequently, A and C are almost parallel and the piperazine ring adopts the stable chair conformation, not the boat conformation [22, 23].

There are two types of hydrogen bonding and a weak interaction between oxygen and Cu, O···Cu. The O(7), O(6) and nitrogen N(5) of uncoordinated nitrate are

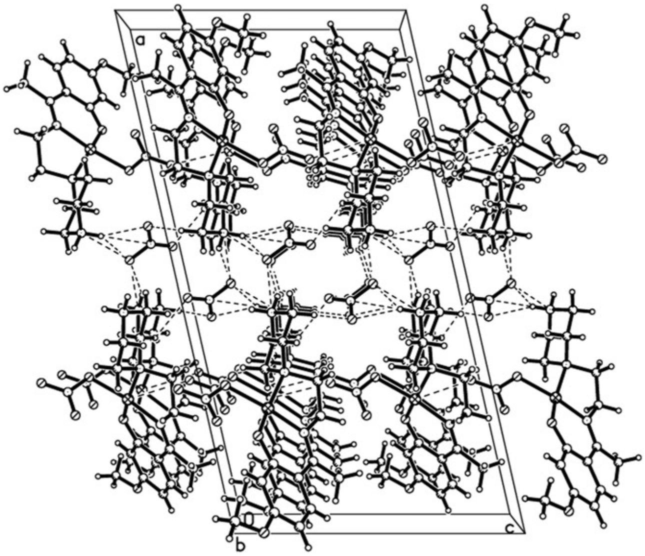


Figure 2. Packing diagram of the title complex.

Table 3. Hydrogen bonding data (Å, °) for the complex.

D–H···A	*d*(D–H)	*d*(H···A)	*d*(D···A)	∠(DHA)
N(3)–H(3A)···N(5)#1	0.900	2.64	3.519(5)	167.3
N(3)–H(3A)···O(7)#1	0.900	1.94	2.754(5)	150.0
N(3)–H(3B)···N(5)	0.900	2.53	3.411(6)	165.4
N(3)–H(3B)···O(7)	0.900	2.15	2.907(5)	141.4
N(3)–H(3B)···O(6)	0.900	2.16	3.018(5)	158.0

Symmetry transformations used to generate equivalent atoms; #1: $-x+1$, $y+1/2$, $-z+3/2$.

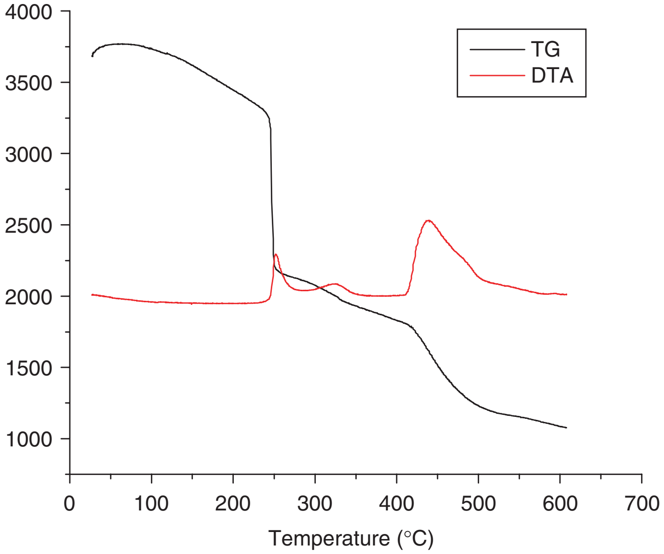


Figure 3. The TG-DTA curves of the title complex.

hydrogen bonded to N(3) of piperazine, forming intramolecular hydrogen bonds: N(3)–H(3B)···O(7), N(3)–H(3B)···O(6) and N(3)–H(3B)···N(5), and intermolecular hydrogen bonds: N(3)–H(3A)···O(7) and N(3)–H(3A)···N(5). The interaction between N(3) and N(5) may be hardly classified as hydrogen bond since the H···N distances (H(3A)···N(5) 2.635 Å, H(3B)···N(5) 2.523 Å) are too long and close to the sum of the corresponding van der Waals radii [24]. Detailed data for the hydrogen bonds are given in table 3. Besides these H-bonds, weak intermolecular interaction exists between Cu(II) of $[Cu(C_{15}H_{23}N_3O_2)(NO_3)]^+$ and O(5) of coordinated nitrate group among adjacent molecules; the Cu···O distance is 3.175 Å, longer than Cu–O coordinated bond length. The above-mentioned interactions form the 3D supramolecular structure, as shown in figure 2.

As shown in figure 3, the DTA curve has three exothermal peaks during decomposition and the TG curve three corresponding weight loss steps. The first weight loss is 52.73% in the range 100–300°C, attributed to loss of uncoordinated nitrate anion and parts of the tridentate Schiff-base ligand: piperazine ring and the methoxylbenzene (Calcd 53.56%). Upon further heating, a weight loss of 24.73% is

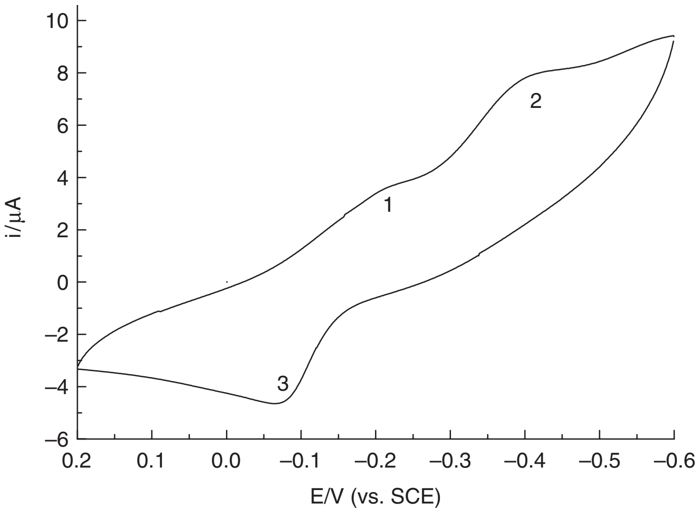


Figure 4. Cyclic voltammogram of the title complex.

observed between 300 and 550°C, consistent with loss of the residue of ligand [–CH_2–CH_2–N=C(CH_3)–] and coordinated nitrate ion (NO_3) (Calcd. 28.18%), and during heating, the nitrate ion was ionized. A total weight loss of 79.1% is observed in the range of 27 and 608°C, leaving residue of copper oxide.

Electrochemical behavior has been examined by cyclic voltammetry (CV). A conventional three-electrode electrochemical system was used for all electrochemical experiments, consisting of a working electrode, a platinum wire auxiliary electrode and a saturated calomel reference electrode (SCE). A glassy carbon disk electrode (GCE) of surface area $0.071\,\mathrm{cm}^2$ was used as the working electrode. All potentials reported are versus SCE. The bare GCE was polished successively with 1.0 and 0.3 μm aluminum oxide powder on chamois leather. Then, it was rinsed with doubly distilled water and sonicated in ethanol and doubly distilled water for 5 min. Cyclic voltammograms for $1 \times 10^{-4}\,\mathrm{mol\,L^{-1}}$ of the title complex in aqueous solution containing 0.2 M phosphate buffer as supporting electrolyte were recorded by scanning from −0.6 V to 0.2 V at a scan rate of $10\,\mathrm{mV\,s^{-1}}$. As shown in figure 4, there are three peaks. The cathodic peak 1 and anodic peak 3 consist of a pair of redox peaks, which can be attributed to $Cu^{2+} \rightleftharpoons Cu^{+}$, exhibiting a quasi-reversible process [3, 25, 26]. The potential for the pair of redox peaks is $E_{pa} = -0.065\,\mathrm{V}$, $E_{pc} = -0.2\,\mathrm{V}$, and the half-wave potential is located at $E_{1/2} = -0.1325\,\mathrm{V}$, the difference between the peaks is 0.135 V, and the peak current ratio I_{pa}/I_{pc} is 6.09. Cathodic peak 2 is a single peak, attributed to $Cu^{+} \rightharpoonup Cu^{0}$, exhibiting an irreversible process [3, 25, 26] with $E_{pc} = -0.395\,\mathrm{V}$, $I_{pc} = 1.5\,\mu\mathrm{A}$.

Supplementary data

Crystallographic data for the structure reported in this article have been deposited with the Cambridge Crystallographic Data Center, CCDC reference number 644454. Copies of these information may be obtained free of charge from: the Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336033; Email: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

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References

[1] E.S. José, R.D. Edward, T.C. Éder. *Carbohydr. Polym.*, **60**, 277 (2005).
[2] L. Shi, H.M. Ge, S.H. Tan, H.Q. Li, Y.C. Song, H.L. Zhu, R.X. Tan. *Eur. J. Med. Chem.*, **42**, 558 (2007).
[3] B.X. Ye, Y. Xu, F. Wang, Y. Fu, M.P. Song. *Inorg. Chem. Commun.*, **8**, 44 (2005).
[4] A. Majumder, G.M. Rosair, A. Mallick, N. Chattopadhyay, S. Mitra. *Polyhedron*, **25**, 1753 (2006).
[5] X.X. Sun, C.M. Qi, S.L. Ma, H.B. Huang, W.X. Zhu, Y.C. Liu. *Inorg. Chem. Commun.*, **9**, 911 (2006).
[6] P.E. Aranha, M.P. Santos, S. Romera, E.R. Dockal. *Polyhedron*, **26**, 1373 (2007).
[7] N. Hossein, S. Javad, H. Arash. *Dyes and Pigments*, **73**, 251 (2007).
[8] L.G. Fa, Z.Y. Nian, L.X. Xun. *Acta Chim. Sinica*, **50**, 473 (1992).
[9] Y.R. Zhang, J.Q. Zhao, L.Q. He, S.M. Zhang. *Chinese J. Inorg. Chem.*, **21**, 1871 (2005).
[10] C. Adihikary, D. Mal, R. Sen, A. Bhattacharjee, P. Gütlich, S. Chaudhuri, S. Koner. *Polyhedron*, **26**, 1658 (2007).
[11] C.P. Pradeep, S. Supriya, P.S. Zacharias, S.K. Das. *Polyhedron*, **25**, 3588 (2006).
[12] A.B. Garcia, F.J.G. Barros, F.J.H. Rolando, F.L. Giles, R.P. Marín. *J. Inorg. Biochem.*, **98**, 15 (2004).
[13] H.Y. Shrivastava, M. Kanthimathi, B.U. Nair. *Biochim. Biophys. Acta*, **1573**, 149 (2002).
[14] J. Sanchiz, C. Kremer, M.H. Torre, G. Facchin, E. Kremer, E.E. Castellano, J. Ellena. *J. Mol. Struct.*, **797**, 179 (2006).
[15] X.Y. Xu, J. Gao, M.Y. Wang, W.X. Ma, H.B. Song, K.P. Wainwright. *J. Coord. Chem.*, **58**, 669 (2005).
[16] G.A.A. Al-hazmi, M.S. El-shahawi, I.M. Gabr, A.A. El-asmy. *J. Coord. Chem.*, **58**, 713 (2005).
[17] G.M. Sheldrick. *SHELXS-97*, Program for X-ray Crystal Structure Refinement, University of Göttingen, Germany (1997).
[18] G.M. Sheldrick. *SHELXL-97*, Program for X-ray Crystal Structure Refinement, University of Göttingen, Germany (1997).
[19] T.T. Xu, J. Gao, X.Y. Xu, S.R. Niu, X.J. Yang, L.D. Lu, X. Wang. *Chinese J. Struct. Chem.*, **25**, 801 (2006).
[20] T.T. Xu, X.Y. Xu, J. Gao, L.L. Liu, S.S. Ni, L.D. Lu, X.J. Yang. *Chinese J. Struct. Chem.*, **25**, 1502 (2006).
[21] Z. Smékal, Z. Trávnícek, J. Mroziński, J. Marek. *Inorg. Chem. Commun.*, **6**, 1395 (2003).
[22] S.S. Massoud, F.A. Mautner. *Inorg. Chem. Commun.*, **7**, 559 (2004).
[23] M. Boiocchi, M. Bonizzoni, L. Fabbrizzi, F. Foti, M. Licchelli, A. Taglietti, M. Zema. *Dalton Trans.*, 653 (2004).
[24] M.D.C. Hernández-Galindo, V. Jancik, M.M. Moya-Cabrera, R.A. Toscano, R. Cea-Olivares. *J. Organomet. Chem.*, **692**, 5295 (2007).
[25] W. Li, C.H. Li, Y.Q. Yang, Y.F. Kuang. *Chinese J. Inorg. Chem.*, **23**, 721 (2007).
[26] J.V. Arenas, I. Lazaro, R. Cruz. *Electrochim. Acta*, **52**, 6106 (2007).