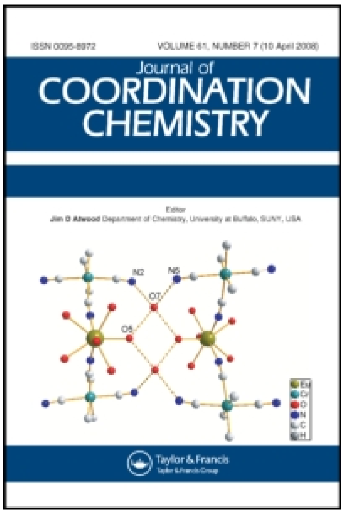

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Synthesis, crystal structure, spectroscopic and electrochemical properties of nickel(II) dipicolinate complex with ethylisonicotinate

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Synthesis, crystal structure, spectroscopic and electrochemical properties of nickel(II) dipicolinate complex with ethylisonicotinate

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The diaqua(ethylisonicotinate)(pyridine-2,6-dicarboxylato)nickel(II) monohydrate complex was synthesized and characterized by spectroscopic (IR, UV/vis), X-ray diffraction and electrochemical methods. The Ni(II) ion is bonded to dipicolinate (dpc) through pyridine N atom and one O atom of each carboxylate group, two aqua ligands and N pyridine atom of ethylisonicotinate (ein), form the distorted octahedral geometry. The molecules are connected via O–H $\cdots$ O hydrogen bonds, forming $R_4^4(12)$ motifs in three dimensional networks. IR and UV-Vis spectroscopies agree with the observed crystal structure. The voltammetric behaviour of the complex was investigated in aqueous solution by square-wave and cyclic voltammetry using a NH_3/NH_4Cl buffer. The square-wave voltammogram of the complex yields three reduction peaks at −0.88, −1.20 and −1.28 V. The irreversible reduction as a shoulder at −1.20 V is due to Ni-dpc-ein complex. The peak at −0.88 V corresponds to irreversible electrode process of Ni(II)-ein complex while the peak at −1.28 V is attributed to the reduction of the coordinated dpc ligands.

Keywords: Nickel(II)-dipicolinate complexes; X-ray crystal structure; UV-Vis; IR; Square-Wave Voltammetry

1. Introduction

Dipicolinic acid (pyridine 2,6-dicarboxylic acid, H_2dpc) is regarded as the key component for the high heat resistance of bacterial spores, owing to its ability to build stabilizing structures with divalent metals [1] and also possesses diverse functional groups and can form bridging hydrogen bonds making it useful for self-assembly [2, 3]. Having potential donor oxygen and nitrogen atoms, dipicolinic acid has attracted interest from inorganic and bioinorganic chemists [4, 5]. Dipicolinates commonly coordinate to transition metals by either carboxylate bridges between metal centers, to form polymeric or dimeric complexes [6, 7], or tridentate (O, N, O′) chelation to one metal ion [8–10]. The dipicolinate ligand with Ni(II) commonly has one or two

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coordination modes. In one coordination mode, a single planar dpc ligand binds in the equatorial plane of a Ni(II) cation and other ligands such as H_2O or pyridine based heterocycles occupy the remaining sites, thereby forming square pyramidal or octahedral coordination geometry [11, 12], or two planar dpc molecules coordinate perpendicularly generating a distorted octahedral coordination geometry [13].

Recently, we initiated crystallographic and spectroscopic characterization of mixed ligand metal dipicolinate complexes in which the dipicolinate acts as a tridentate ligand [14, 15]. As a continuation of these studies, we have now prepared and thoroughly characterized a new Ni(II) complex containing dipicolinate anion together with ethylisonicotinate ligand, $[Ni(dpc)(ein)(H_2O)_2] \cdot H_2O$.

2. Experimental

2.1. *General method*

All chemical reagents were analytical grade commercial products. Solvents were purified by conventional methods. The optical absorption spectra of the title complex were recorded at room temperature in DMF on a CINTRA 20 UV-VIS spectrometer between 200 and 900 nm. The IR spectra were recorded on a Jasco 430 FT/IR spectrometer using KBr pellets and operating in the 4000–400 cm^{-1} range. A three-electrode potentiostatic control system (EG&G PARC 303 A SMDE) with a static mercury working electrode, a $Ag | AgCl | KCl_{sat}$ reference electrode and a platinum auxiliary electrode was used in the voltammetric experiments. The potential scan was generated by means of an EG&G PAR 384 B Polarographic Analyzer. The recording of current-potential curves was obtained by a Houston Instruments DMP-40 plotter connected to the polarography. Stock solutions of the complex were prepared in triply distilled and deionized water, and used immediately. 0.1 M NH_3/NH_4Cl buffer (pH 8.71) was used as supporting electrolyte. Prior to the voltammetric experiments, solution within the electrochemical cell was deaerated by purging with pure nitrogen gas for 10 min, and during measurements a stream of nitrogen gas was passed over the solution. The voltammograms were obtained by using equilibrium time of 5 s and a drop size of medium at ambient temperature. The range of potentials from −0.1 to −1.9 V was selected unless stated otherwise.

2.2. *Synthesis of $[Ni(dpc)(ein)(H_2O)_2] \cdot H_2O$*

To ethanol/water (30 mL, ca 1 : 1 v/v) containing $NiCl_2 \cdot 6H_2O$ (1 mmol; 0.238 g) and disodium dipicolinate (1 mmol; 0.211 g), ein (1 mmol; 0.151 g) was added slowly with continuous stirring. The resulting solutions were refluxed for 1 h and then filtered. The green filtrates were allowed about two weeks at room temperature, and then the green crystals of title complex suitable for X-ray diffraction analyses were collected.

2.3. *X-ray crystallography*

A suitable single crystal was mounted on a glass fiber and data collection was performed on a STOE IPDS(II) image plate detector using Mo-Kα radiation

Table 1. Crystal data and structure refinement for $[Ni(dpc)(ein)(H_2O)_2] \cdot H_2O$.

Formula	$C_{15}H_{18}N_2O_9Ni$
Formula weight	429.0
Temperature (K)	297(2)
Radiation, λ (Mo-Kα)	0.7107
Crystal system	Monoclinic
Space group	$P21/c$
Unit cell dimensions (Å, °)	
a	13.2115(7)
b	18.1269(7)
c	7.0650(4)
β	90.800(4)
Volume (Å^3)	1691.79(15)
Z	4
Calculated density (g cm^{-3})	1.684
μ (mm^{-1})	1.202
F(000)	888
Crystal size (mm^3)	$0.14 \times 0.44 \times 0.68$
θ range (°)	1.91–28.03
Index ranges	$-16 \leq h \leq 16$ $-22 \leq k \leq 20$ $-8 \leq l \leq 8$
Reflections collected	28728
Independent reflections	3331 [$R_{(int)} = 0.029$]
Reflections observed [$I \geq 2\sigma(I)$]	3029
Absorption correction	Integration
Refinement method	Full-matrix least-squares on F^2
Data/restrains/parameters	3331/3/266
Goodness-of-fit on F^2	1.053
Final R indices [$I \geq 2\sigma(I)$]	0.025
R indices (all data)	0.029
Largest diff. peak and hole (e Å^{-3})	0.23, −0.45

($\lambda = 0.71019$ Å) at 298 K. Details of the crystal structure are given in table 1. Data collection: Stoe X-AREA [16]. Cell refinement: Stoe X-AREA [16]. Data reduction: Stoe X-RED [16]. The structure was solved by direct-methods using SHELXS-97 [17] and anisotropic displacement parameters were applied to non-hydrogen atoms in a full-matrix least-squares refinement based on F^2 using SHELXL-97 [17]. All carbon hydrogens were positioned geometrically and refined by a riding model with U_{iso} 1.2 times that of attached atoms and remaining hydrogen atoms were found by Fourier difference. Molecular drawings were obtained using ORTEP-III [18].

3. Results and discussion

3.1. *Crystal structure*

Figure 1 shows the numbering scheme of the title complex and selected bond distances and angles are listed in table 2.

Single crystal X-ray structural analysis shows that the compound consists of a neutral $[Ni(dpc)(ein)(H_2O)_2]$ unit and one solvent water molecule. The dpc anion, with its two carboxylate groups in ortho positions with respect to the pyridine nitrogen atoms, is potentially tridentate. In the complex, the Ni(II) ion is hexa-coordinated by two

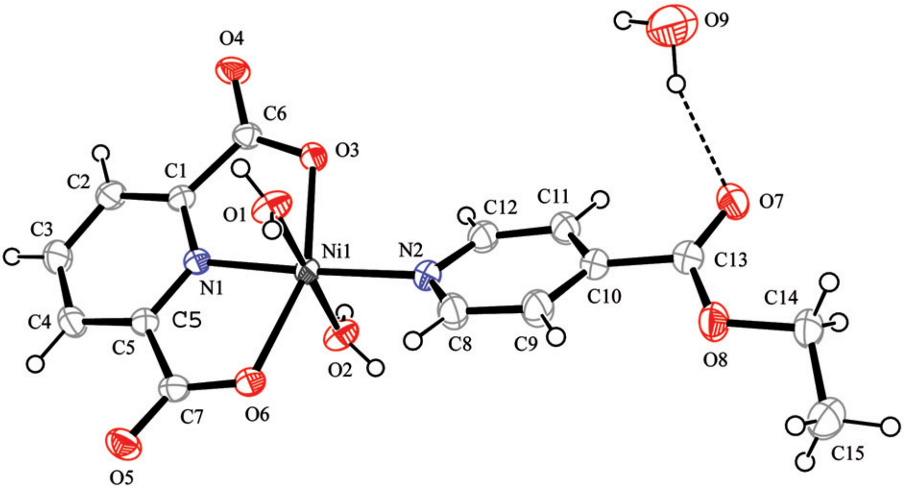

Figure 1. The molecular structure of nickel(II) complex, showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 40% probability level and H atoms are shown as small spheres of arbitrary radii.

Table 2. Interatomic bond distances (Å) and angles (°) around the Ni1(II) ion.

O1–Ni1:	2.088(1)	O2–Ni1:	2.103(1)	O3–Ni1:	2.131(1)
O6–Ni1:	2.131(1)	N1–Ni1:	1.959(1)	N2–Ni1:	2.028(1)
O2–Ni1–O1:	177.54(6)	O2–Ni1–N1:	89.22(6)	O1–Ni1–N1:	91.76(6)
O1–Ni1–N2:	90.15(6)	O2–Ni1–N2:	89.04(6)	N1–Ni1–N2:	175.55(6)
N2–Ni1–O6:	105.38(5)	O1–Ni1–O6:	89.28(5)	O2–Ni1–O6:	88.69(5)
N2– Ni1–O3:	97.57(5)	O1–Ni1–O3:	88.45(5)	O2–Ni1–O3:	93.96(5)

Hydrogen-bonding interactions (Å, °)

D–H···A	D–A	H···A	D···A	D–H···A
O9–H9A···O7	0.937	2.064	2.930	153.15
O9–H9B···O5^{i}	0.957	2.095	2.975	152.31
O1–H1A···O5^{ii}	0.867	1.855	2.714	170.46
O1–H1B···O3^{iii}	0.783	2.051	2.820	167.14
O2–H2A···O6^{iv}	0.806	2.015	2.794	162.57
O2–H2B···O4^{v}	0.808	1.991	2.789	169.01

Symmetry codes: (i) $-x+1$, $y+1/2$, $-z+1/2$; (ii) $-x+1$, $-y$, $-z$; (iii) x, $-y+1/2$, $z-1/2$; (iv) $-x+1$, $-y$, $-z+1$; (v) x, $-y+1/2$, $z+1/2$.

oxygens of dpc dianion [Ni1–O_{dpc} = 2.088(1)–2.103(1) Å] and two nitrogens from dpc [Ni1–N_{dpc} = 1.959(1) Å] and ein [Ni1–N_{ein} = 2.028(1) Å] composing the basal plane, and two aqua ligands occupying the axial sites [Ni1–O_{aqua} = 2.131(1) Å], adopting a distorted octahedron (figure 1). The Ni(II) lies 0.005(5) Å out of the basal plane, distorted from a square by the double chelate formed by dpc. The fact that the Ni1–N_{dpc} distance is significantly shorter than Ni1–N_{ein} distance indicates that N1 is the strongest donor site, since two carboxylate groups in ortho positions enhance the basicity of this atom. The Ni1–N_{dpc} and Ni1–O_{dpc} bond distances in the title complex are slightly different from the corresponding distances reported for $[Ni(Hdpc)_2] \cdot 3H_2O$ [Ni–N = 1.966(3) Å; Ni–O = 2.098(2)–2.099(2) Å] [19], $[Ni(dpc)(H_2O)_2]$ [Ni–N = 1.903(3) Å; Ni–O = 2.005(2)–2.006(2) Å] [11], $[Ni(nit2Py)(dpc)(H_2O)] \cdot (MeOH) \cdot (H_2O)$

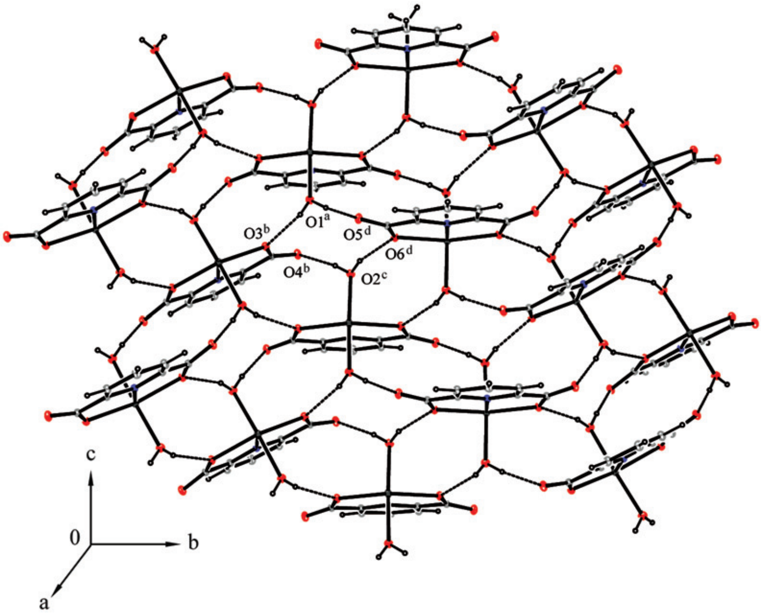

Figure 2. A partial view of the packing of nickel(II) complex, showing hydrogen-bond interactions as dashed lines (ein ligands were omitted for the clarity). *Symmetry code* (*a*) $1-x$, $0.5+y$, $1.5-z$; (*b*) $-x$, $-y$, $-z$; (*c*) $1-x$, $0.5+y$, $0.5-z$; (*d*) x, $0.5-z$, $0.5+z$.

[Ni–N = 1.965(4) Å; Ni–O = 2.083(3)–2.113(3) Å] [12] [nit2Py: 2-(2′-pyridyl)-4,4,5,5-tetramethylimidazoline-1-oxyl-3-oxide, MeOH: methanol], [Ni(bta)$_3$(dpc)] [Ni–N = 1.992(5) Å; Ni–O = 2.112(1)–2.180(1) Å] [20] [bta: benzo-trizole], [Ni(cyclam)(H$_2$O)$_2$][Ni(dpc)$_2$] · 2.5H$_2$O [Ni–N = 1.931(3) Å; Ni–O = 2.132(2)–2.146(2) Å] [13] [cyclam: 1,4,8,11-tetraazacyclotetradecane]. The Ni–O$_{\text{aqua}}$ distances are slightly different from those found in [Ni(dpc)(H$_2$O)$_2$] [Ni–O = 1.971(2)–2.150(3) Å] and [Ni(nit2Py)(dpc)(H$_2$O)]·(MeOH) · (H$_2$O) [Ni–O = 2.080(3) Å], probably due to the hydrogen bonding interactions between the aqua and acceptor groups. The dpc chelate angles are 78.47(5)° and 78.67(5)°, comparable to those found in other dipicolinate-metal complexes [21, 22]. The pyridine ring of the dpc anion in the title complex is essentially planar and two carboxylate groups are not significantly displaced from the mean planes of this ring [torsion angle is 171.15(2)° for O6/C7/C5/C4 and 169.87(16)° for C2/C1/C6/O3]. The dihedral angle between the mean pyridine planes of dpc and ein is 29.73(7)°.

Analyses of the crystal packing indicate intermolecular O–H · · · O hydrogen bonds, involving the oxygen atoms of aqua ligands and crystal water, carboxylate oxygen atoms of dpc and ein ligands (figure 2) (table 2). In the title complex, extended monomeric moieties produce a 3D supramolecular array in the crystal network. An arbicular hydrogen-bonded synthon consisting of four monomeric units, notated as $R_4^4(12)$ [23], is observed as the basal building block of this 3D pattern. In addition, there is also C–H · · · π interaction between pyridine of ein (CgA) and H11. For the C11–H11 · · · π contact, the distance between H11 and the center of CgA is 2.766 Å, the distance between H11 and the plane of CgA is 2.765 Å, and the C11–H11 · · · CgA angle is 164.58°.

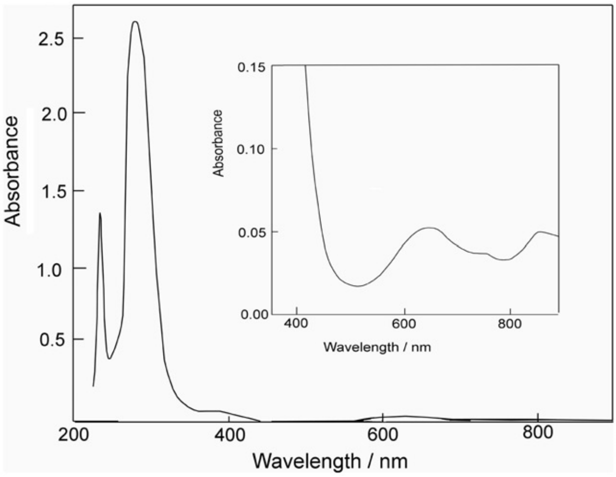

Figure 3. The electronic absorption spectra of (10^{-3} mol L^{-1}) $[Ni(dpc)(ein)(H_2O)_2] \cdot H_2O$ in DMF.

3.2. *Optical absorption and FT-IR investigation*

The electronic absorption spectra of the nickel complex were recorded in DMF (figure 3). In the UV-range two strong absorption peaks were observed at 257 and 270 nm, which can be assigned to intraligand transitions of dpc and ein. In the visible range, three broad peaks were observed at 390, 645 and 855 nm, which can be assigned to spin-allowed d–d transition bands of ${}^3A_{2g} \rightarrow {}^3T_{1g}(P)$, ${}^3A_{2g} \rightarrow {}^3T_{1g}(F)$, ${}^3A_{2g} \rightarrow {}^3T_{2g}$. These transitions are consistent with octahedral geometry [24] and indicate that the solid structure is preserved in solution.

The IR spectra of dipicolinate-containing complexes have characteristic absorption bands. The IR spectrum of the title complex has two distinguishable regions. High energy bands, ranging from 3600 cm^{-1} to 3000 cm^{-1}, have two absorption peaks 3554 and 3278 cm^{-1}, due to ν(O–H) of aqua and crystal water molecules. The weak ν(C–H) vibrations are also observed at 3099, 2998 and 2938 cm^{-1}. In the low energy region, a series of absorption peaks are observed. Strong bands at 1712 and 1643 cm^{-1} are assigned to $\nu(C=O)_{ein}$ and $\nu(C=O)_{dpc}$, respectively, and another strong absorption at 1370 cm^{-1} is due to ν(C–O) vibration. The difference between $\nu(C=O)$ and ν(C–O) of dpc is nearly 300 cm^{-1}, indicating that the carboxyl groups are monodentate [25], in accord with the structure determination. The ring wagging vibrations of the pyridine groups are observed 760 and 728 cm^{-1}. The $\delta_{O\text{–}C\text{–}O}$ in-plane deformation vibration which occurs as a strong sharp band at 701 cm^{-1} in the free H_2dpc, shifts to 698 cm^{-1} in the title complex, as found in the literature [26]. The medium intensity band at 1425 cm^{-1} corresponds to C–H deformation and a strong band centered at 1295 cm^{-1} is attributed to the C–N stretching vibrations [27]. Weak intensity ring stretching is observed at 1571 cm^{-1}.

3.3. *Electrochemical investigation*

The square-wave voltammogram of 1×10^{-4} M $[Ni(dpc)(ein)(H_2O)_2] \cdot H_2O$ yields, by scanning the potential from −0.6 to −1.9 V, a well-established peak at −1.72 V, and

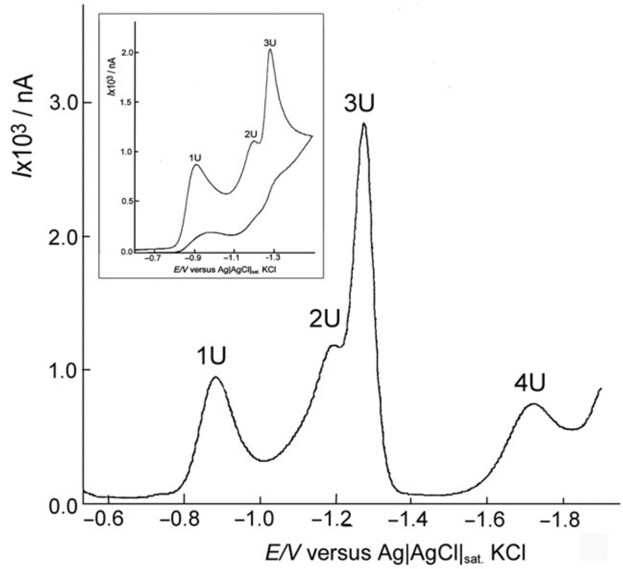

Figure 4. Square-wave voltammograms of 1×10^{-4} M $[Ni(dpc)(ein)(H_2O)_2] \cdot H_2O$ complex at 0.1 M NH_3/NH_4^+ buffer (pH 8.71) supporting electrolyte. 1U, the reduction of Ni(II)-ein complex; 2U, the reduction of $[Ni(dpc)(ein)(H_2O)_2] \cdot H_2O$ complex; 3U, the reduction of coordinated dpc; 4U, catalytic hydrogen wave. Experimental conditions: pulse height, 20 mV; frequency, 100 Hz; drop size, medium; scan rate, 200 mV s^{-1} equilibrium time, 5 s. Inset: Cyclic voltammogram of 1×10^{-4} M $Ni(dpc)_2(ein)_2$ complex at 0.1 M NH_3/NH_4^+ buffer (pH 8.71).

a shoulder at −1.20 V, in addition to peaks at −0.88 and −1.28 V (figure 4). The peak at −1.72 V is due to catalytic hydrogen wave [28]. The shoulder at −1.20 V is different from those of the coordinated dpc (−1.28 V) and the Ni(II)-ein complex (−0.88 V). Thus, the shoulder at −1.20 V may be explained as reduction of Ni(II) in the nickel complex. Although the reduction of the complexed Ni(II) ion with nitrogen containing ligands takes place at more positive potential than that of free Ni(II) ions, the presence of the coordinating carboxylate group in dpc molecule diminishes the positive shift [28]. The appearance of the peak potential of $[Ni(dpc)(ein)(H_2O)_2] \cdot H_2O$ complex (−1.20 V) at a more negative potential than that of Ni(II)-ein complex (−0.88 V) supports complexation of the carboxylate group of dpc.

In the cyclic voltammogram of the $[Ni(dpc)(ein)(H_2O)_2] \cdot H_2O$ at pH 8.71, in the potential range of −0.6 to −1.5 V, three peaks at −0.91 V, −1.21 V and −1.29 V were observed (figure 4). Nevertheless, no peaks were observed in the anodic scan implying that the process is irreversible.

Supplementary data

Crystallographic data (excluding structure factors) for the structure in this paper have been deposited with the Cambridge Crystallographic Data Centre as the supplementary publication no. CCDC 642006. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge, CB12 1EZ, UK, Fax: + 44 1223 366 033, E-mail: deposit@ccdc.ac.uk or on the web www: http://www.ccdc.cam.ac.uk

References

[1] L. Chung, K.S. Rajan, E. Merdinger, G. Grecz. *Biophys. J.*, **11**, 469 (1971).
[2] G. Nardin, L. Randaccio, R.P. Bonomo, E. Rizzarelli. *J. Chem. Soc. Dalton Trans.*, **3**, 369 (1980).
[3] L. Wang, L. Duan, E. Wong, D. Xiao, Y. Li, Y. Lan, L. Xu, C. Hu. *Trans. Metal Chem.*, **29**, 212 (2004).
[4] L.Q. Yang, D.C. Crans, A. Cour, O.P. Anderson, P.M. Kaszynski, M.E. Godzala, L.D. Austin, G.R. Willsky. *Inorg. Chem.*, **41**, 4859 (2002).
[5] E.E. Sileo, M.A. Blesa, G. Rigotti, B.E. Rivero, E.E. *Castellano, Polyhedron*, **15**, 4531 (1996).
[6] C.B. Ma, C.N. Chen, Q.T. Liu, D.Z. Liao, L.C. Li. *Eur. J. Inorg. Chem.*, **6**, 1227 (2003).
[7] M. Ranjbar, H. Aghabozorg, A. Moghimi. *Acta. Cryst.*, **E58**, m304 (2002).
[8] M. Devereux, M. McCann, V. Leon, V. McKee, R.J. Ball. *Polyhedron*, **21**, 1063 (2002).
[9] C. Ma, C. Fan, C. Chen, Q. Liu. *Acta Cryst.*, **C58**, m553 (2002).
[10] M. Koman, M. Melnik, J. Moncol. *Inorg. Chem. Commun.*, **3**, 262 (2000).
[11] Y. Liu, J.M. Dou, D. Wang, X.X. Zhang, L. Zhou. *Acta Cryst.*, **E62**, m2208 (2006).
[12] C.X. Zhang, D.Z. Liao, Z.H. Jiang, S.P. Yan, B. Zhao. *Trans. Met. Chem.*, **28**, 621 (2003).
[13] H. Park, A.J. Lough, J.C. Kim, M.H. Jeong, Y.S. Kang. *Inorg. Chim. Acta* (2007), In press.
[14] I. Uçar, A. Bulut, O. Büyükgüngör. *Acta Cryst.*, **C61**, m479 (2005).
[15] I. Uçar, A. Bulut, A. Karadağ, C. Kazak. *J. Mol. Struct.*, **837**, 38 (2007).
[16] Stoe & Cie X-AREA (Version 1.18) and X-RED (Version 1.04), Stoe & Cie, Darmstadt, Germany (2002).
[17] G.M. Sheldrick. *SHELXL97, Program for the Refinement of Crystal Structures*, University of Göttingen, Germany (1997).
[18] M.N. Burnett, C.K. Johnson. *ORTEPIII. Report ORNL-6895*, Oak Ridge National Laboratory, Tenessee, U.S.A (1996).
[19] L.C. Nathan, T.D. Mai. *J. Chem. Cryst.*, **30**, 509 (2000).
[20] P. Ramadevi, S. Kumaresan, K.W. Muir. *Acta Cryst.*, **E61**, m1749 (2005).
[21] L. Mao, Y. Wang, Y. Qi, M. Cao, C. Hu. *J. Mol. Struct.*, **688**, 197 (2004).
[22] C. Xie, B. Zhang, X. Liu, X. Wang, H. Kou, G. Shen, D. Shen. *Inorg. Chem. Commun.*, **7**, 1037 (2004).
[23] The graph set topological terminology for the analysis of hydrogen bonded network patterns is described in: M.C. Eter. *Acc. Chem. Res.*, **23**, 120 (1990).
[24] A.B.P. Lever. *Inorganic Electronic Spectroscopy*, Elsevier, New York (1968).
[25] S.D. Robinson, M.F. Uttley. *J. Chem. Soc. Dalton Trans.*, **18**, 1912 (1973).
[26] P. Carmona. *Spectrochim. Acta*, **36A**, 705 (1980).
[27] L. Levi, C.E. Hubley. *Anal. Chem.*, **28**, 1591 (1956).
[28] F.G. Banica, E. Diacu. *Collection Czechoslovak Chem. Commun.*, **56**, 140 (1991).