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CHARACTERIZATION AND CRYSTAL STRUCTURE STUDY OF A NEW Cu(II) COMPLEX OF PYRIDINE-2,6-DICARBOXYLIC ACID AND ANILINE CONTAINING A WATER CLUSTER

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A new monoclinic Cu(II) salt complex $(C_6H_6N)_2^+[Cu(2,6\text{-dipico})_2]^{2-}\cdot 6H_2O$, (2,6-dipico = = pyridine-2,6-dicarboxylic acid) is synthesized and characterised by CHN analyses, IR, UV-Vis, magnetic susceptibility measurements, and single crystal X-ray crystallography. The structure contains two pyridine-2,6-dicarboxylate species as tridentate ligands with protonated aniline acting as a counter cation and six uncoordinated water molecules. The complex crystallizes in the monoclinic space group $C2/c$ with unit cell parameters $a = 20.9393(4)$ Å, $b =$ $= 7.94330(10)$ Å, $c = 19.9093(4)$ Å, V(Å^3) = 2932.32(9), $Z = 4$. Crystal packing is stabilized by N—H...O, O—H...O intermolecular hydrogen bonds and weak $\pi...\pi$ interactions. The water molecules are trapped by a cooperative association of coordination interactions forming water clusters as well as by a hydrogen bond to the Cu (II) complex.

Keywords: pyridine-2,6-dicarboxylate complex, monoclinic, octahedral, copper(II) complex, water cluster, crystal structure.

INTRODUCTION

Pyridine-2,6-dicarboxylic acid (2,6-dipico) is known to form a stable chelate with metal ions and oxometal cations and also can display widely varying coordination demeanour functioning as a bidentate, tridentate, meridian or bridging ligand [1, 2]. It is a versatile N—O-chelating agent with limited steric hindrance and can further provide the ability to form polymeric complexes through the bridging coordination of carboxylates under suitable conditions [3]. 2,6-dipico can stabilize unusual oxidation states by forming bridging hydrogen bonds due to its functional groups [4] and also can act as a unique ligand due to its ability to form strong covalent bonds.

Metal carboxylate complexes are extensively studied [5—13] and reviewed [14]. The carboxylate ligand can have different binding modes and each of them may play a role in the formation of a supramolecular assembly [15—17]. Compounds having multiple carboxylic acid groups are good synthons for supramolecular architectures and coordination polymers [7—10]. Metal complexes of pyridine carboxylic acid and some of their derivatives have also been used as model systems for the design of new metallopharmaceutical compounds [16]. A large number of proton transfer compounds have been constructed by the 2,6-dipico ligand [5—9]. Water clusters have also been the focus of related and intense research activity [6—10]. They have been grouped into three classes: discrete water clusters, polymeric water clusters, and metal—water clusters [9—15]. The structural elucidation of discrete and polymeric water clusters provides detailed knowledge of hydrogen bonding and their fluctuations determined by the properties of bulk water. Metal—water clusters are not only involved with hydrogen bonding interactions between water molecules, but also with the coordination bonds between metal atoms and water clusters. In this regard, the design and synthesis of metal—water clusters have become more relevant than those of discrete or polymeric clusters.

2,6-dipico has also become one of the more suitable ligands for modeling potential pharmacologically active compounds because of its low toxicity and amphophilic nature [18]. In the present study, we have successfully designed and synthesized a monomeric copper(II) salt complex with the 2,6-dipico ligand containing discrete water clusters and characterized it by FT-IR, UV, CHN-analyses and magnetic susceptibility measurements as well as by single crystal X-ray crystallography.

EXPERIMENTAL

Materials. All the chemicals in this study were analytical grade and used as received. As a caution, perchlorate salts in presence of organic materials are potentially explosive. Although no problems were encountered in this work, such compounds should be prepared in small amounts and handled with care.

Physical measurements. Elemental analyses (carbon, hydrogen, and nitrogen) were performed on a Perkin-Elmer 2400—II elemental analyzer. Infrared spectra were recorded on a Perkin-Elmer FTIR spectrometer in the range 4000—400 cm^{-1} using KBr pellets. The absorption spectroscopy measurements were performed using a SHIMADZU UV-VISIBLE 2450 spectrophotometer at 298 K. Magnetic susceptibility measurements were performed using a Sherwood magnetic susceptibility balance (M.S.D) with copper sulfate pentahydrate as the standard at room temperature. Diamagnetic corrections were made using Pascal′s constants.

X-ray crystallography. The crystal structure of the salt complex was determined on a Bruker SMART APEX-II CCD diffractometer with MoK_α radiation ($\lambda = 0.71073$ Å) at 296(2) K and scan mode in the range $2.79 < \theta < 28.32°$ using SMART and SAINT software. An empirical absorption correction (SADABS) was applied to the raw data. The structure was solved by direct methods and refined by full-matrix least squares on F^2 with the SHELXTL-97 (Sheldrick-2008) program package. All of the non-hydrogen atoms were refined with anisotropic temperature factors. The calculations were performed with SHELXTL-97 [19]. Crystallographic details of the data collection and structure refinement are summarized in Table 1. Selected bond lengths and bond angles are given in Table 2. Hydrogen bonding distances and angles are listed in Table 3. The crystallographic data (CIF file) of complex has been deposited at the Cambridge Crystallographic Data Centre (CCDC), UK.CCDC No. 822823.

Synthesis of the complex. Pyridine 2,6-dicarboxylic acid (0.334 g, 2 mmol) was dissolved in 20 ml of ethanol; to it aniline (0.186 g, 2 mmol) in 10 ml of ethanol was added. The resulting solution was stirred for an hour at 60 °C. The straw colored solution was then cooled to room temperature. To the straw colored solution, copper perchlorate hexahydrate (0.354 g, 1 mmol) in 15 ml of ethanol was added dropwise with constant stirring. The resulting blue colored solution was stirred magnetically at 60 °C for two hours. The solution was then cooled at room temperature, filtered and the filtrate was kept for slow evaporation. Pale blue, block shaped crystals suitable for single crystal X-ray diffraction studies formed after 14 days.

Anal. Calcd. for $C_{26}H_{34}CuN_4O_{14}$: C 45.28; H 4.80; Cu 9.44; N 8.18. Found C 45.25; H 4.97; Cu 9.21; N 8.12 %.

RESULTS AND DISCUSSION

UV-Vis spectra. The UV-Vis spectra of $(C_6H_8N)_2^+[Cu(2,6\text{-dipico})_2]^{2-}\cdot 6H_2O$ were recorded in methanol and show a peak near 594 nm, which may be assigned to a $^2E_g \rightarrow {}^2T_{2g}$ transition that is generally observed for octahedral complexes of Cu(II) [20]. The peaks observed at 329 nm may be assigned to LMCT transitions.

Table 1

Crystal data and structure refinement for $(C_6H_8N)_2^+[Cu(2,6\text{-dipico})_2]^{2-}\cdot 6H_2O$

Empirical formula	$C_{26}H_{34}CuN_4O_{14}$
Formula weight	690.11
Temperature, K	296(2)
Wavelength, Å	0.71073
Crystal system	Monoclinic
Space group	*C*2/*c*
Unit cell dimensions *a*, *b*, *c*, Å; β, deg.	20.9393(4), 7.94330(10), 19.9093(4); 117.686(2)
Volume, Å^3	2932.32(9)
Z	4
Density (calculated), g/cm^3	1.563
Absorption coefficient, mm^{-1}	0.823
F(000)	1436
Crystal size, mm	0.34×0.25×0.21
Crystal color / habit	Pale blue / block
Theta range for data collection, deg.	2.79 to 28.32°
Index ranges	$-23 \le h \le 27$, $-10 \le k \le 10$, $-26 \le l \le 26$
Reflections collected	14210
Independent reflections	3614 [*R*(int) = 0.0544]
Completeness to θ = 25.00°	99.3 %
Absorption correction	Multi-scan / sadabs
Max. and min. transmission	0.8461 and 0.7672
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3614 / 12 / 231
Goodness-of-fit on F^2	1.083
Final *R* indices [$I > 2\sigma(I)$]	*R*1 = 0.0291, *wR*2 = 0.0825
R indices (all data)	*R*1 = 0.0326, *wR*2 = 0.0844
Largest diff. peak and hole, e/Å^{-3}	0.356 and –0.420

Table 2

Selected bond lengths (Å) *and angles* (deg.) *for* $(C_6H_8N)_2^+[Cu(2,6\text{-dipico})_2]^{2-}\cdot 6H_2O$

Cu1—N1	1.927(11)	N1—Cu1—N1#1	179.32(6)	O3—Cu1—O1#1	82.23(4)
Cu1—N1#1	1.928(11)	N1—Cu1—O3	78.48(4)	O3#1—Cu1—O1#1	155.41(4)
Cu1—O3	2.179(11)	N1#1—Cu1—O3	101.09(4)	N1—Cu1—O1	76.93(4)
Cu1—O3#1	2.179(11)	N1—Cu1—O3#1	101.09(4)	N1#1—Cu1—O1	103.50(4)
Cu1—O1#1	2.255(11)	N1#1—Cu1—O3#1	78.48(4)	O3—Cu1—O1	155.41(4)
Cu1—O1	2.255(11)	O3—Cu1—O3#1	102.57(6)	O3#1—Cu1—O1	82.23(4)
		N1—Cu1—O1#1	103.50(4)	O1#1—Cu1—O1	103.54(6)
		N1#1—Cu1—O1#1	76.93(4)		

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

Table 3

Hydrogen bonds for $(C_6H_8N)_2^+[Cu(2,6\text{-dipico})_2]^{2-}\cdot 6H_2O$ (Å *and* deg.)

D—H...A	*d*(D—H)	*d*(H...A)	*d*(D...A)	∠(DHA)
N2—H2NC...O4	0.95(2)	1.79(2)	2.728(2)	169(2)
N2—H2NA...O2 #1	0.94(1)	2.09(2)	3.000(2)	166(2)
N2—H2NB...O5 #2	0.94(1)	1.88(2)	2.814(2)	174(2)
O5—H5WB...O1	0.84(9)	1.92(1)	2.758(2)	168(2)
O5—H5WA...O6 #3	0.84(9)	2.19(1)	3.025(2)	170(2)
O6—H6WB...O7 #4	0.83(9)	1.95(9)	2.782(2)	177(2)
O6—H6WA...O2	0.82(9)	2.01(1)	2.815(2)	168(2)
O7—H7WB...O6 #2	0.84(9)	1.97(1)	2.808(2)	168(2)
O7—H7WA...O3	0.84(9)	1.89(9)	2.741(2)	175(2)

Symmetry transformations used to generate equivalent atoms: #1 *x*+1/2, *y*–1/2, *z*; #2 -*x*+1, *y*–1, –*z*+3/2; #3 –*x*+1/2, *y*–1/2, –*z*+3/2, #4 *x*–1/2, *y*+1/2, *z*.

Magnetic susceptibility measurements. The magnetic susceptibility measurement of the $(C_6H_8N)_2^+[Cu(2,6\text{-dipico})_2]^{2-}\cdot 6H_2O$ salt complex at room temperature was found to be 1.84 BM which is close to the theoretical value of 1.73 BM for Cu (II) octahedral complexes [21—24].

IR spectra. The FTIR spectrum of the synthesized copper salt complex $(C_6H_8N)_2^+[Cu(2,6\text{-dipico})_2]^{2-}\cdot 6H_2O$, was recorded within the 4000—400 cm^{-1} range. Two broad absorption bands at 3251 cm^{-1} and 3328 cm^{-1} are attributed to ν(OH) vibrations of lattice water molecules. In the Cu(II) anion complex, the presence of a $—COO^-$ group is reflected by IR vibrational absorption bands $\nu_{as}(COO^-)$ and $\nu_s(COO^-)$ at 1681 cm^{-1} and 1421 cm^{-1} respectively. The difference between $\nu_{as}(COO^-)$ and $\nu_s(COO^-)$, $\Delta\nu = 260\ cm^{-1}$, suggests a unidentate binding mode of the carboxylate group to the Cu(II) anion. The sharp peak observed at 1261 cm^{-1} may be assigned to the C—N stretching bands for aniline. The ν(Cu—O) and ν(Cu—N) absorption bands appear at 576 cm^{-1} and 408 cm^{-1} [25, 26] respectively.

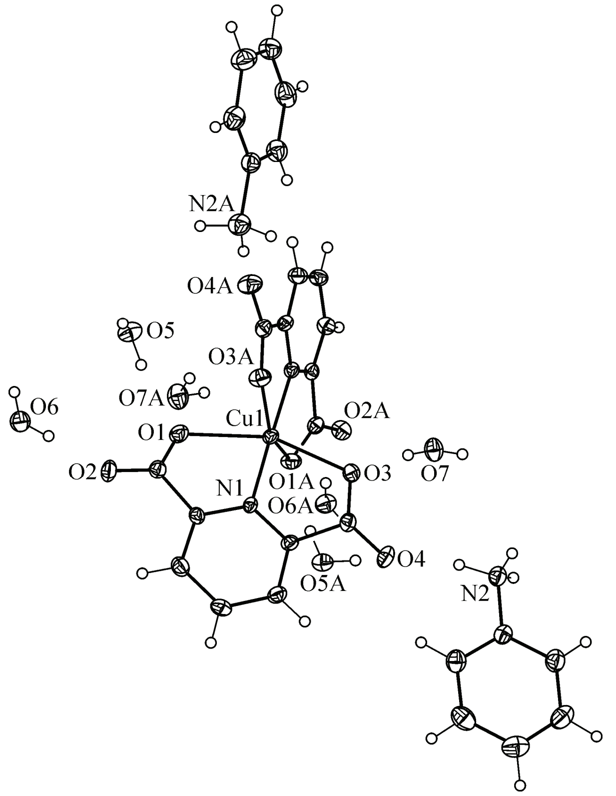

Fig. 1. Molecular structure of $(C_6H_8N)_2^+[Cu(2,6\text{-dipico})_2]^{2-}\cdot 6H_2O$ with 50 % ellipsoidal probability, showing the atom numbering scheme

X-ray crystallography. The crystal structure of the synthesized monomeric copper(II) salt complex having the molecular formula $(C_6H_8N)_2^+[Cu(2,6\text{-dipico})_2]^{2-}\cdot 6H_2O$ with its atom numbering scheme is shown in Fig. 1. Selected bond lengths, bond angles and hydrogen bonding geometry are given in Tables 2 and 3. Crystallographic analysis reveals that the complex consists of a discrete $[Cu(2,6\text{-dipico})_2]^{2-}$ anion, two protonated aniline cations, and six crystal water molecules. The crystal structure shows that the Cu(II) ion is coordinated by tridentate 2,6-dipico ligands through two oxygen atoms from two carboxylate groups and the nitrogen atom from a pyridine ring. Four carboxylate oxygen atoms (O1, O3, O1A, and O3A) from 2,6-dipico comprise the equatorial plane, while the nitrogen atoms from the dipico ligands (N1 and N1A) occupy axial positions, with Cu1—N1 and Cu1—N1A having the same bond length of 1.927(6) Å. The four oxygen atoms (O1, O3, O1A, and O3A) from the two pyridine 2, 6-dicarboxylic acid ligands, after deprotonation, occupy the equatorial positions in a distorted horizontal square plane along with the metal ion (Cu1). The carboxylate groups are nearly coplanar with the pyridine ring and the C—O distances in the 2,6-dipic anion also display some variability, depending on their environment. An interesting structural feature of the salt complex is that the Cu—O bond lengths (Cu1—O1 and Cu1—O1A = 2.255(5) Å; Cu1—O3 and Cu1—O3A = 2.179(2) Å) are longer than the two Cu—N bond lengths (Cu1—N1 and Cu1—N2 = 1.927(6) Å), which can be attributed to the Jahn—Teller effect [27]. This indicates that the Cu (II) ion forms a t_{2g}^{6}; $d_{(x^2-y^2)^2}$, $d_{(z^2)^1(e_g^3)}$ configuration, resulting in shielding of the Cu(II) nucleus along the *X* and *Y* axis as compared to the *Z* axis. In addition, it can be seen that the oxygen atoms form a flattened tetrahedron around the copper ion, as evidenced by the O3A—Cu1—O1A and O3—Cu1—O1 angles (155.41(4)°) which are greater than 150°. The crystal structure of the title salt complex shows that two aniline ions are not coordinated to the metal ion and act solely as cations. The N1A—Cu1—N1 bond angle (179.32(6)°) also indicates that one of the two pyridine-2,6-dicarboxylate groups lies over the other in nearly perpendicular fashion (Fig. 1). The distorted nature of the complex is further supported by the bond lengths and angles listed in Table 2.

The four oxygen atoms (O1, O3, O1A, and O3A) bonded to Cu1, from the two pyridine-2,6-dicarboxylic acid ligands, after deprotonation, act as anions and contribute four negative charges. The two $(C_6H_8N)^+$ ions, which act as cations, contribute two positive charges, while the charge on Cu1 may be assumed to be +2, providing a charge balanced formula. Crystal packing is stabilized by N—H...O, O—H...O intermolecular hydrogen bonds and weak π...π stacking interactions. The crystallized water molecules and two $(C_6H_8N)^+$ cations are directly involved with the intermolecular hydrogen bonding to the carboxyl oxygen atoms O1, O2, O3, and O4 of the 2,6-dipico ligand, forming water clusters. The π...π stacking interactions (centroid — centroid distance = 3.9561(9) Å) are observed between the pyridine rings of the 2,6-dipico group and the benzyl ring of the aniline and carboxylate groups

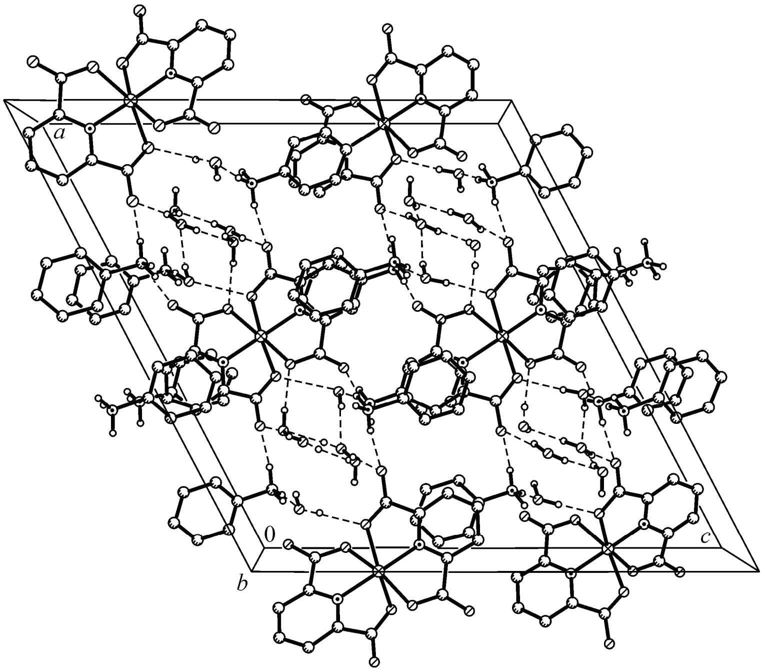

Fig. 2. Packing diagram of the $(C_6H_8N)_2^+[Cu(2,6\text{-dipico})_2]^{2-}\cdot 6H_2O$ salt complex viewed along the *b* axis. Dashed lines indicate N---H...O, O---H...O hydrogen bonds and π—π stacking forming a 2D supramolecular network

(Fig. 2). The strong intermolecular O—H…O and N—H…O hydrogen bonds and weak π…π interactions form a two dimensional supramolecular network complex.

CONCLUSIONS

A new Cu(II) salt complex with pyridine-2,6-dicarboxylic acid and aniline has been synthesized and characterized by analytical, spectroscopic, and crystallographic methods. The structure of the complex exhibits a novel two dimensional network, where pyridine-2,6-dicarboxylic acid acts as a tridentate ligand having N_2O_4 chromophore. In the complex, the Cu(II) atom has a distorted octahedral coordination geometry, created by two N atoms of the pyridine ring and four carboxyl O atoms and an anilinium cation acting as a counterion. The asymmetric unit also contains 6 uncoordinated water molecules. Crystal structures are stabilized by intermolecular N—H…O, O—H…O hydrogen bonds forming water clusters and also by weak π…π interactions between the pyridine rings of the cation.

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Supplementary information. Significant crystallographic data are summarized in Table 1. CCDC No. 822823 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK; e-mail: deposit@ccdc.cam.ac.uk or www.ccdc.cam.ac.uk/data_request/cif.

REFERENCES

1. *Grossel M.C., Golden C.A., Gomn J.R., Horton P.N., Merket Das, Oszer M.E., Parker R.A.* // Crystallogr. Eng. Commun. – 2001. – **42**. – P. 1 – 4.
2. *Ducommun Y., Helm L., Laurenezy G., Merbach A.* // Inorg. Chim. Acta. – 1989. – **158**. – P. 3 – 4.
3. *Szorcsik A., Nagy L., Sletten J., Szalontai G., Kamu E., Fiore T., Pellerito L., Klman E.* // J. Organomet. Chem. – 2004. – **689**. – P. 1145 – 1154.
4. *Hoff D.L., Tislay D.G., Walton R.A.* // J. Chem. Soc. Dalton Trans. – 1973. – P. 200 – 204.
5. *Aghabozorg H., Sadr-khanlou E., Soleimannejad J., Adams H.* // Acta Crystallogr. – 2007. – **E63**. – P. 1760.
6. *Aghabozorg H., Bahrami Z., Tabatabaie M., Ghadermazi M., Attar Gharamaleki J.* // Acta Crystallogr. – 2007. – **E63**. – P. 2022 – 2023.
7. *Soleimannejad J., Aghabozorg H., Hooshmand S., Ghadermazi M., Attar Gharamaleki J.* // Acta Crystallogr. – 2007. – **E63**. – P. 2389 – 2390.
8. *Sharif M.A., Aghabozorg H., Moghim A.* // Acta Crystallogr. – 2007. – **E63**. – P. 1599 – 1601.
9. *Aghabozorg H., Daneshvar S., Motyeian E., Ghadermazi M.* // J. Attar Gharamaleki, Acta Crystallogr. – 2007. – **E63**. – P. 2468 – 2469.
10. *Aghabozorg H., Sadr-khanlou E.* // Acta Crystallogr. – 2007. – **E63**. – P. 1753.
11. *Aghabozorg H., Sadr-khanlou E., Soleimannejad J., Adams H.* // Acta Crystallogr. – 2007. – **E63**. – P. 1769.
12. *Aghabozorg H., Ghasemikhah P., Ghadermazi M., Soleimannejad J., Adams H.* // Acta Crystallogr. – 2007. – **E63**. – P. 1487 – 1789.
13. *Aghabozorg H., Attar Gharamaleki J., Ghasemikhah P., Ghadermazi M., Soleimannejad J.* // Acta Crystallogr. – 2007. – **E63**. – P. 1710 – 1711.
14. *Aghabozorg H., Manteghi F., Sheshmani S.* // J. Iran. Chem. Soc. – 2008. – **5**. – P. 184 – 227.
15. *Aghabozorg H., Mohamadpanah F., Sadr-khanlou E.* // Anal. Sci. – 2007. – **23**. – P. 139 – 140.
16. *Aghabozorg H., Ramezanipour F., Nakhjavan B., Soleimannejad J., Attar Gharamaleki J.S, Sharif M.A.* // Crystallogr. Res. Technol. – 2007. – P. 1 – 8.
17. *Aghabozorg H., Zabihi F., Ghadermazi M., Attar Gharamaleki J., Sheshmani S.* // Acta Crystallogr. – 2006. – **E62**. – P. 2091 – 2092.
18. *Sakurai H., Koyima Y., YoshiKawa Y., Kawabe K., Yasui H.* // Coord. Chem. Rev. – 2002. – **226**. – P. 187 – 211.
19. *Sheldrick G.M.* SHELXS-97, Program for the Refinement of Crystal Structure, University of Göttingen, Germany, 1997.
20. (a) *Bhubon Singh R.K., Abdul Malik K.M., Ghodsi Mahali S.O., Salah El Fallah Md., Karan, N.K., Mitra S.* // Inorg. Chem. Commn. – 2001. – **4**. – P. 315 – 318. (b) *Hathaway B.J.* // Struct. Bonding. – 1984. – **57**. – P. 55.

21. (a) *Sutapa S., Chirantan R.C., Nirmal K.K., Amitabha D., Samiran M., Bhubon Singh R.K., Volker Gramlich.* // Inorg. Chem. Commn. – 2003. – **6**. – P. 1311 – 1314. (b) *Hartman J.R., Vachet R.W., Pearson W., Wheat R.J., Callahan J.H.* // Inorg. Chim. Acta. – 2003. – **343**. – P. 119 – 132.
22. *Erer H., Yeşilel O.Z., Darcan C., Büyükgüngör O.* // Polyhedron. – 2009. – **28**. – P. 3087 – 3093.
23. *Masouda M.S., El-Enein S.A.A., Ramadan, Goher A.S.* // J. Anal. Applied Pyrolysis. – 2008. – **81**. – P. 45 – 51.
24. *Bottcber A., Elias H., Jiiger E.G., Langfelderova H., Mazur M., Miiller L., Pau1us H., Pelikan P., Rudolph M., Vakol M.* // Inorg. Chem. – 1993. – **32**, N 19. – P. 4131 – 4138.
25. (a) *Samanta B., Joy C., Bhubon Singh R.K., Manas K.S., Batten S.R., Jensen P., Salah El., Fallah M., Mitra S.* // Polyhedron. – 2007. – **26**. – P. 4354 – 4362. (b) *Yang Y., Crans D.C., Miller S.M., Cour A., Anderson O.P., Kaszynski P.M., Godzala M.E., Austin L.D., Willsky G.R.* // Inorg. Chem. – 2002. – **41**, N 19. – P. 4859 – 4871.
26. *Kamal Y., Bradie E.I.* // Monants. Chem. – 2005. – **136**. – S. 1139 – 1155.
27. *Yesilal O.Z., Ilker I., Refat M.S., Ishida H.* // Polyhedron. – 2010. – **29**. – P. 2345 – 2351.