

Synthesis, Spectral and Thermal Studies, and Crystal Structure of *cis*-Bis(imidazole)bis(picolinato)copper(II) Dihydrate [Cu(pic)₂(im)₂] · 2H₂O

Zerrin Heren^a, Cem Keser^a, C. Cüneyt Ersanlı^b, O. Zafer Yeşilel^c, and Orhan Büyükgüngör^b

^a Ondokuz Mayıs University, Faculty of Arts and Sciences, Department of Chemistry, TR-55139, Kurupelit, Samsun, Turkey

^b Ondokuz Mayıs University, Faculty of Arts and Sciences, Department of Physics, TR-55139, Kurupelit, Samsun, Turkey

^c Eskişehir Osmangazi University, Faculty of Arts and Sciences, Department of Chemistry, TR-26480, Eskişehir, Turkey

Reprint requests to Dr. Z. Heren. E-mail: zheren@omu.edu.tr

Z. Naturforsch. **61b**, 1072 – 1078 (2006); received February 1, 2006

The mixed-ligand picolinato (pic) complex of Cu(II) with imidazole (im), [Cu(pic)₂(im)₂] · 2H₂O, was synthesized and characterized by elemental analysis, magnetic susceptibility, spectral methods (UV/vis and FT-IR), simultaneous TG, DTA techniques, mass spectroscopy, and X-ray diffraction. The complex crystallizes in the monoclinic space group *Cc* with the following unit cell parameters: *a* = 16.381(1), *b* = 9.556(1), *c* = 5.177(1) Å, *β* = 119.074(5)°, *Z* = 4. In the octahedral complex, the picolinato ligands are coordinated to the copper(II) ion as bidentate *N,O*-donors forming chelate rings. The imidazole ligands are *N*-coordinated at *cis* positions. The thermal decomposition pathway of the complex has been studied by the help of thermal analyses data (TG and DTA) and of the mass spectroscopic fragmentation pattern. The volatile products observed in the thermal decomposition process were also observed in the mass spectrometer ionisation process, except for the molecular peak, and it was concluded that the ionisation and thermal decomposition pathways of the complex resemble each other.

Key words: Picolinic Acid, Imidazole, Copper(II) Complex, Thermal Decomposition

Introduction

Pyridinecarboxylic acids and their derivatives are present in many natural products. They are also of special interest to medicinal chemists because of the wide variety of physiological properties displayed by the natural and also many synthetic derivatives [1]. For example, picolinic acid is one of the metabolites of tryptophan [2]. Zinc(II) pyridine 2-carboxylate has healing effects against Herpes Simplex virus [3]. The picolinic acid (pyridine 2-carboxylic acid, pic) is the body's prime natural chelator. The picolinato ligand is able to chelate with metal ions and can display widely varying coordination behaviour function as a multidentate ligand. It is the most efficient chelator for metal cations such as chromium, zinc, manganese, copper, iron and molybdenum when they are in the body. One of the ways to understand chemistry and properties of the picolinic acid is to study the structures of its metal complexes [4–7]. Imidazole is a very important model

molecule since the imidazole ring occurs in a series of biological molecules such as in histidine, in Vitamin B₁₂ and biotin as well as in many chemotherapeutic agents [8].

In this paper, we report the preparation, characterization by FT-IR and UV/vis measurements, thermal analyses data (TG and DTA), mass spectroscopic fragmentation pattern, and crystal structure of the *cis*-bis(imidazole)bis(picolinato)copper(II) dihydrate complex.

Results and Discussion

IR spectra

In the IR spectrum of the complex the broad band at 3435 cm⁻¹ corresponds to the vibration of water molecules. The bands that appear at 3108 and 2992 cm⁻¹ are due the absorption bands of the NH moiety of imidazole. In the IR spectrum of the

free picolinic acid there is a strong absorption band at 1730 cm^{-1} for the COOH group. In the IR spectrum of the Cu(II) complex this absorption band is absent and the band due to the asymmetric stretch $\nu_{\text{asym}}(\text{COO}^-)$ and symmetric stretch $\nu_{\text{sym}}(\text{COO}^-)$ are observed at 1643 and 1353 cm^{-1} , respectively. The difference $\nu_{\text{asym}}(\text{COO}^-)$ and $\nu_{\text{sym}}(\text{COO}^-)$ being 290 can be taken as a proof of unidentate coordination of the carboxylate group to the central atom [9]. This is in good agreement with the results obtained from X-ray diffraction measurements. In the complex, the band at 1595 cm^{-1} can be attributed to the $(\text{C}=\text{N})$ stretching vibration. The M–O stretching vibration of the complex was observed at 455 cm^{-1} .

UV/vis spectra and magnetic susceptibility

The electronic spectrum of the $[\text{Cu}(\text{pic})_2(\text{im})_2] \cdot 2\text{H}_2\text{O}$ in water exhibit a broad absorption band at 642 nm ($\epsilon = 41.0\text{ Lmol}^{-1}\text{cm}^{-1}$) due to the $d-d$ transition and a shoulder at 590 nm ($\epsilon = 25.0\text{ Lmol}^{-1}\text{cm}^{-1}$) assigned to the Jahn-Teller effect. This λ_{max} value was assigned to the ${}^2\text{E}_g \rightarrow {}^2\text{T}_{2g}$ transition. The Δ_0 value for the complex was calculated as $15,576\text{ cm}^{-1}$, since there is only one transition for d^9 complexes [10]. The absorption bands below 300 nm are due to intra-ligand transitions.

The magnetic susceptibility value of the complex is 1.67 BM corresponding to one unpaired electron.

Thermal analysis

Thermal analyses curves of the complex (TG and DTA) are given in Fig. 1. The thermal behaviour of the complex was followed up to $600\text{ }^\circ\text{C}$ in a static air atmosphere. The first stage of the thermal decompo-

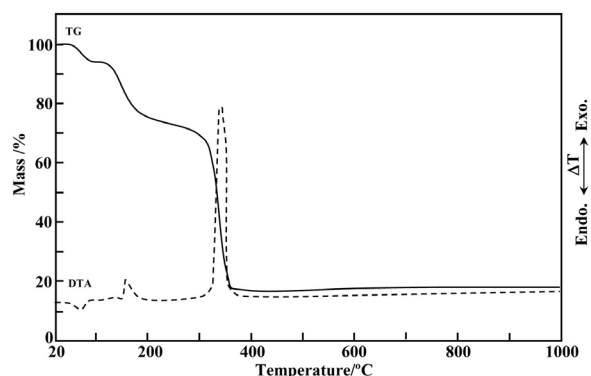


Fig. 1. The TG and DTA curves of the $[\text{Cu}(\text{pic})_2(\text{im})_2] \cdot 2\text{H}_2\text{O}$ complex.

sition starts at $65\text{ }^\circ\text{C}$ with the release of two crystal water molecules associated with an endothermic effect ($\text{DTA}_{\text{max}} 78\text{ }^\circ\text{C}$; found 7.52% ; calcd. 7.50%). The second stage in the $135\text{--}302\text{ }^\circ\text{C}$ temperature range corresponds to the exothermic elimination of two moles of imidazole ligands ($\text{DTA}_{\text{max}} 161\text{ }^\circ\text{C}$). The experimental mass loss of 27.79% agrees well with the calculated mass loss of 28.37% . The decomposition of the two picolinato ligands occurs in the third stage between 305 and $460\text{ }^\circ\text{C}$ with one violently exothermic DTA peak at $347\text{ }^\circ\text{C}$. The final decomposition product CuO, was identified by IR spectroscopy (found 81.67% ; calcd. 83.43%).

Analysis of the mass spectrum

The mass spectrum of any substance mainly reveals the most delicate and fragile points present in the structure of a molecule. It was assumed that the thermal process somewhat resembles the ionisation process [11,12]. For this purposes, the mass spectrum of $[\text{Cu}(\text{pic})_2(\text{im})_2] \cdot 2\text{H}_2\text{O}$ complex was recorded to establish a relation between the thermal and ionisation process to formulate more appropriately the thermal decomposition pathway. The mass spectrum was recorded by the FAB technique. It is not very complicated and only a few major peaks appeared in significant quantities. No molecular ion peak was observed. Absence of the molecular peak may indicate that almost all of the molecular ion is decomposed in the ionization process. The peak observed at $m/z = 445$ possibly corresponds to the $[\text{Cu}(\text{pic})_2(\text{im})_2]$ molecule produced by the loss of two moles of water molecules in the ionisation process. The peaks observed at $m/z = 375$ and 307 values may correspond to the species $[\text{Cu}(\text{pic})_2(\text{im})]$ and $[\text{Cu}(\text{pic})_2]$, respectively. Formation of these fragments in the thermal process may also be proved by the thermal analysis data, since $[\text{Cu}(\text{pic})_2]$ was observed after the loss of water molecules at $65\text{--}128\text{ }^\circ\text{C}$ (found 7.52% ; calcd. 7.50%) and of two moles of imidazole ligands at $135\text{--}302\text{ }^\circ\text{C}$ (found 27.79% ; calcd. 28.37%). An intermediate compound is formed from $[\text{Cu}(\text{pic})_2(\text{im})]$ by the release of one mole CO_2 as observed in the mass spectrum at $m/z = 331$. This may confirm that a picolinato ligand is thermally decomposed by the release of CO_2 . The observed ionisation products resemble the products predicted by the thermal analysis results. The decomposition products observed in the ionisation process are given in Fig. 2.

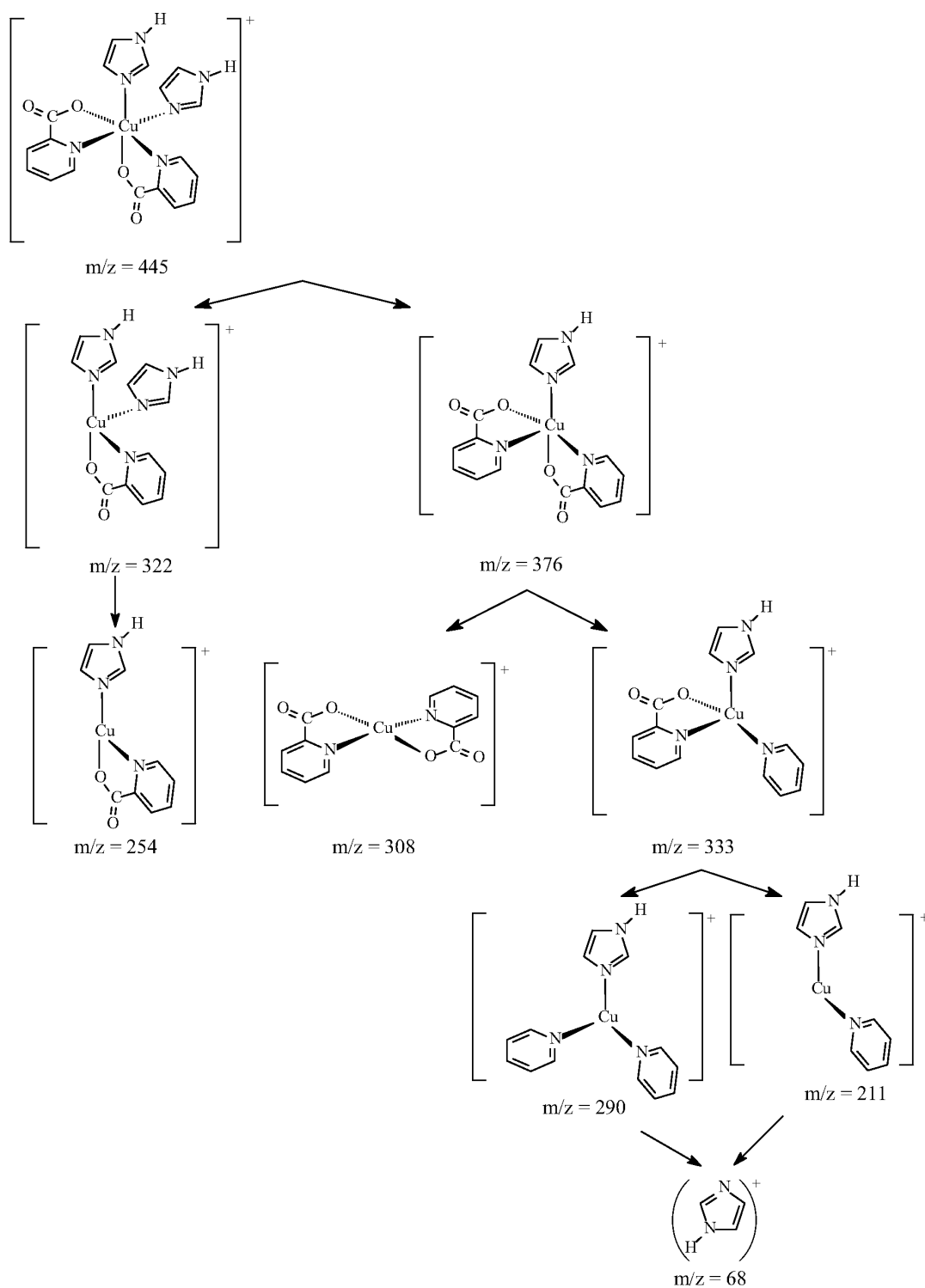


Fig. 2. Mass spectral fragmentation pattern of the $[\text{Cu}(\text{pic})_2(\text{im})_2] \cdot 2\text{H}_2\text{O}$ complex.

Table 1. Crystal data and structure refinement parameters for [Cu(pic)₂(im)₂] · 2H₂O.

Formula	C ₁₈ H ₂₀ N ₆ O ₆ Cu
Colour	blue
Molecular weight	479.94
Temperature (K)	296
Wavelength (Å)	0.71073 Mo-K α
Crystal system	monoclinic
Space group	<i>Cc</i>
Unit cell dimensions	
<i>a</i> (Å)	16.381(1)
<i>b</i> (Å)	9.556(1)
<i>c</i> (Å)	15.177(1)
β (°)	119.074 (5)
Volume (Å ³)	2076.3 (3)
<i>Z</i>	4
<i>D</i> _{calc} (Mgm ⁻³)	1.535
μ (mm ⁻¹)	1.100
Crystal size (mm ⁻³)	0.42 × 0.31 × 0.22
Θ Range for data collection	1.5–26.9°
Flack's <i>x</i> parameter [21]	0.02(2)
Index ranges	
<i>h</i>	–21 → 21
<i>k</i>	–12 → 12
<i>l</i>	–19 → 17
Reflections collected	6614
Independent reflections	2454 (<i>R</i> _{int} = 0.002)
Reflections observed (> 2 σ)	4249
Absorption correction	integration
Max. and min. Transmission	0.767 and 0.875
Refinement method	<i>F</i> ²
<i>w</i>	1/[2 σ (<i>F</i> _o ²) + (0.1041 <i>P</i>) ²] where <i>P</i> = (<i>F</i> _o ² + 2 <i>F</i> _c ²)/3
Goodness-of-fit on <i>F</i> ²	0.91
Final <i>R</i> indices [<i>F</i> ² > 2 σ (<i>F</i> ²)]	<i>R</i> ₁ = 0.057, <i>R</i> ₁ (all data) = 0.092
<i>wR</i> (<i>F</i> ²)	<i>wR</i> ₂ = 0.133, <i>wR</i> ₂ (all data) = 0.168
Largest difference peak and hole (e Å ⁻³)	–0.76 to 0.91
CCDC deposition no.	CCDC 286619

Table 2. Selected bond lengths (Å) and bond angles (°) for [Cu(pic)₂(im)₂] · 2H₂O.

Cu(1)–N(1)	2.022(4)	Cu(1)–O(1)	2.320(4)
Cu(1)–N(3)	1.988(6)	Cu(1)–O(2)	2.257(4)
Cu(1)–N(4)	2.095(4)	C(9)–O(1)	1.279(9)
Cu(1)–N(5)	1.999(9)	C(9)–O(3)	1.241(7)
		C(15)–O(2)	1.234(7)
		C(15)–O(4)	1.248(7)
N(1)–Cu(1)–N(4)	172.5(2)	N(5)–Cu(1)–N(4)	88.9(3)
N(3)–Cu(1)–N(1)	88.7(3)	N(3)–Cu(1)–O(2)	93.8(2)
N(3)–Cu(1)–N(4)	91.2(3)	N(5)–Cu(1)–O(2)	89.7(3)
N(3)–Cu(1)–N(5)	176.3(3)	N(4)–Cu(1)–O(2)	76.4(2)
N(5)–Cu(1)–N(1)	91.7(3)	N(4)–Cu(1)–O(1)	91.5(2)

Crystallography

The structure of the title complex, [Cu(pic)₂(im)₂] · 2H₂O, is shown in Fig. 3 and the crystallo-

Table 3. Hydrogen bonding geometry (Å, °).

D–H...A	D–H	H...A	D...A	D–H...A
O5–H5A...O1	0.920(10)	1.984(14)	2.876(7)	163.1(6)
O6–H6B...O5	0.91(5)	2.41(5)	2.972(12)	119(5)
C10–H10...O1	0.93	2.60	3.197(8)	122.9
N2–H2N...O6 ⁱ	0.86	1.99	2.833(8)	164.9
O5–H5B...N6 ⁱⁱ	0.923(10)	2.27(5)	2.797(9)	116(4)
O6–H6A...O4 ⁱⁱⁱ	0.915(10)	2.106(16)	2.792(6)	130.9(15)
N6–H6N...O5 ^{iv}	0.86	1.98	2.797(9)	158.1
C3–H3...O4 ^v	0.93	2.49	3.200(8)	133.3

Symmetry codes: ⁱ 1/2 + *x*, *y* – 1/2, *z*; ⁱⁱ *x* – 1/2, 1/2 – *y*, *z* – 1/2; ⁱⁱⁱ *x* – 1/2, *y* – 1/2, *z*; ^{iv} 1/2 + *x*, 1/2 – *y*, 1/2 + *z*; ^v *x*, *y* – 1, *z*.

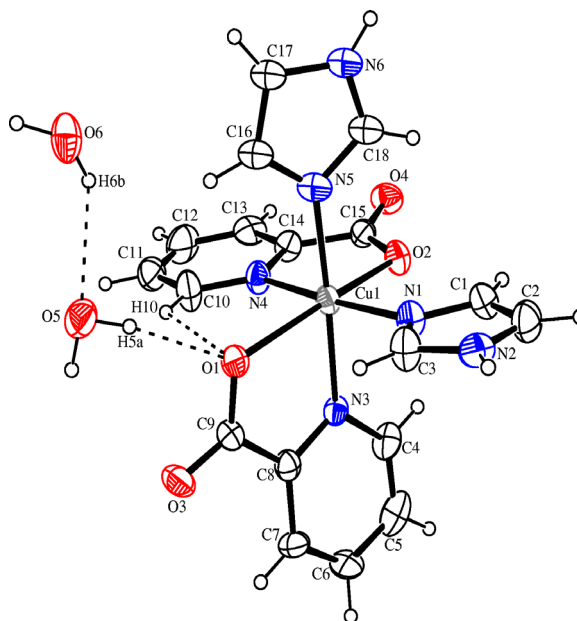


Fig. 3. A view of the copper coordination, with the atom labeling scheme. Displacement ellipsoids are drawn at the 50% probability level.

graphic data are summarized in Table 1. Tables 2 and 3 list bond lengths and angles and hydrogen-bonding geometries. The Cu(II) ion has a slightly distorted octahedral coordination geometry comprised of the two atoms N3 and N4, two carboxylate O atoms from deprotonated bidentate picolinate ligands, and two tertiary N atoms from imidazole molecules. Atoms N3 and O1 and N4 and O2 are bonded to Cu1 to form two five-membered chelate ring [N3–Cu1 = 1.988(6) and O1–Cu1 = 2.320(4) Å; N4–Cu1 = 2.095(4) and O2–Cu1 = 2.257(4) Å]. The imidazole atom N1 [Cu1–N1 = 2.022(4) Å] is in an equatorial position and the imidazole atom N5 [Cu1–N5 = 1.999(9) Å] in an apical position of the Cu(II) coordination octahedron.

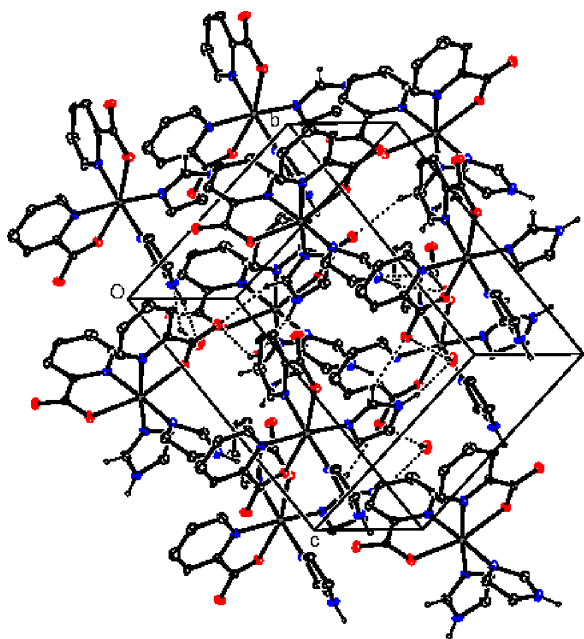


Fig. 4. The packing of the $[\text{Cu}(\text{pic})_2(\text{im})_2] \cdot 2\text{H}_2\text{O}$ complex with the unit cell.

The C–O bond lengths are in the range 1.234(7)–1.279(9) Å, which is comparable with those in similar Cu(II) complexes [13]. However, in the Co(II) [13], Ni(II) [14] and Mg(II) [15] complexes, the carboxylate group is asymmetric [C–O = 1.223(3)–1.278(2), 1.248(2)–1.253(2) and 1.243(2)–1.262(2) Å, respectively].

As shown in Table 1, the lengths of the Cu–N bonds [1.988(6)–2.095(4) Å] are normal, and these distances are similar to other values reported in the literature [16]. The coordination of copper(II) clearly shows the geometrical pattern typical for the Jahn–Teller effect. The Cu1–N3 and Cu1–N4 distances are shorter than the Cu1–O1 and Cu1–O2 distances, and this results in the formation of an octahedral geometry elongated along the N atoms. The Jahn–Teller effect is also observed in the electronic spectra. This effect is common for analogous metal complexes, such as [17] [Cu1–N3 = 2.007(3) and Cu1–O1 = 2.383(3) Å] and [18] [Cu1–N2 = 2.006(2) and Cu1–O3 = 2.390(2) Å].

The title compound contains two pyridine rings and two imidazole rings. For simplicity, the four rings will be called A, B, C and D, corresponding to N3/C4–C8, N4/C10–C14, N1/N2/C1–C3 and N5/N6/C16–C18, respectively. The dihedral angles between the planes of the rings are A/C = 85.36(31), A/D = 23.99(44),

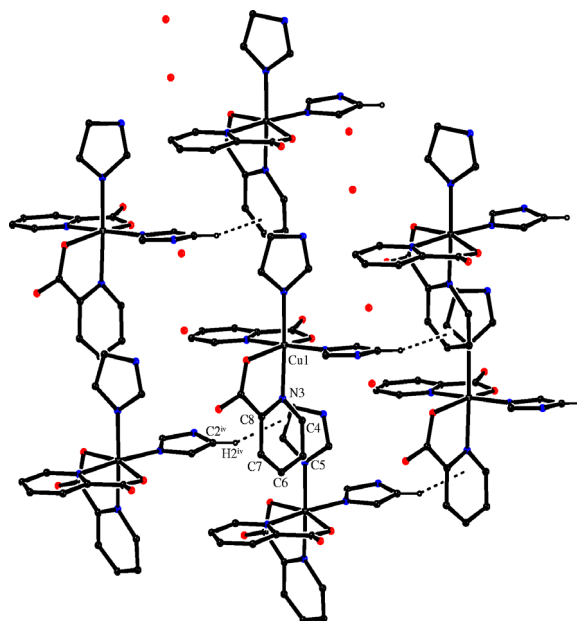


Fig. 5. The C–H... π interactions of the molecules.

B/C = 2.96(40) and B/D = 89.17(36)°. The two imidazole rings are individually planar, with r.m.s. deviations of 0.0095 and 0.0004 Å, and the maximum deviations from these planes are –0.0086(62) Å for atom C3 and 0.0005(5) Å for atom C18. These planes are approximately perpendicular, with a dihedral angle of 86.46(41)°, in agreement with those previously reported for other imidazole and picolinate ligands containing Cu(II) complexes [19, 20]. The crystal packing of the title complex is formed by intermolecular N–H...O, O–H...O, O–H...N, and C–H...O hydrogen bondings (Table 3, Fig. 4) and π -ring interaction (Fig. 5). For the C2–H2...CgA (CgA with symmetry code: $x + 1/2, 1/2 - y, 1/2 + z$ is the centroid of N3/C4–C8) π -ring contact, the distance between atom H2 and the centre of ring A (CgA) is 2.92 Å, and the C2–H2...CgA angle is 132.7°.

Experimental Section

Materials and measurements

All chemicals used were analytical reagent grade products. Imidazole was obtained from Merck. Picolinic acid was purchased from ACROS Organics.

The magnetic susceptibility measurement at r.t. was performed using a Sherwood Scientific MXI model Gouy magnetic balance. The UV/vis spectrum was obtained for the aqueous solution of the complex (10^{-3} M) with a Unicam UV2 spectrometer in the range 900–190 nm. The IR

spectrum was recorded in the 4000–400 cm^{-1} region with a Mattson 1000 FT-IR spectrometer using KBr pellets. A TG8110 thermal analyzer was used to record simultaneous TG and DTA curves in static air atmosphere at a heating rate of 10 Kmin^{-1} in the temperature range 20–1000 $^{\circ}\text{C}$ using platinum crucibles. Highly sintered $\alpha\text{-Al}_2\text{O}_3$ was used as a reference and the DTG sensitivity was 0.05 mg s^{-1} . The elemental and mass spectroscopic analysis was carried out at the TÜBİTAK Marmara Research Centre. Mass spectroscopic analysis was performed on a AGILENT 1100 MSD mass spectrometer.

X-ray structure determination

Data collection was performed on a STOE IPDS-II image plate detector using Mo- $\text{K}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$). Intensity data were collected in the θ range 1.5–26.9 $^{\circ}$ at 296 K. Details of crystal structures are given in Table 1. Data collection and cell refinement: STOE X-Area [22]. Data reduction: STOE X-RED32 [22]. The structure was solved by direct methods using SHELXS-97 [23]. Anisotropic displacement parameters were applied to non-hydrogen atoms in a full-matrix least-squares refinement based on F^2 using SHELXL-97 [23]. All hydrogen atoms except those bound to O5 and O6 were placed in calculated positions and refined using a riding model, with C–H distances of 0.93 (aromatic), N–H distances of 0.86 \AA and with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C}, \text{N})$. Molecular drawings were obtained using ORTEP-III [24]. Software used to prepare material for publication: WinGX [25].

Preparation of the $[\text{Cu}(\text{pic})_2(\text{im})_2] \cdot 2\text{H}_2\text{O}$

The $[\text{Cu}(\text{pic})_2] \cdot 2\text{H}_2\text{O}$ complex was prepared by the method reported earlier [26]. A solution of im (0.27 g, 4 mmol) in ethanol (10 ml) was added dropwise with stirring to a solution of $[\text{Cu}(\text{pic})_2] \cdot 2\text{H}_2\text{O}$ (0.69 g, 2 mmol) in distilled water (20 ml). The solution was heated to 60 $^{\circ}\text{C}$ in a temperature-controlled bath and stirred for 6 h. The reaction mixture was then cooled to r.t. The blue crystals formed were filtered and washed with 10 ml of cold distilled water and ethanol and dried in *air*. UV/vis (H_2O): $\lambda_{\text{max}}(\lg \epsilon) = 642 \text{ nm}$ (3.71). – IR (KBr): $\tilde{\nu} = 3435 \text{ cm}^{-1}$ (OH), 1643, 1353, 1595, 455. – MS (ES, 35 eV): m/z (%) = 445 $[\text{Cu}(\text{pic})_2(\text{im})_2]^+$, 375 (68) $[\text{Cu}(\text{pic})_2(\text{im})_2 - (\text{im})]^+$. – $\text{C}_{18}\text{H}_{20}\text{N}_6\text{O}_6\text{Cu}$ (479.9): calcd. C 45.05, H 4.17, N 17.52; found C 45.01, H 4.22, N 17.28.

Supplementary Data

Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as the supplementary publication No. CCDC 286619. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk).

Acknowledgements

The authors wish to acknowledge the Faculty of Arts and Sciences, Ondokuz Mayıs University, Turkey, for the use of the STOE IPDS-II diffractometer (purchased under grant F.279 of the University Research Fund).

- [1] K. A. Idriss, M. S. Saleh, H. Sedaira, M. M. Sleim, E. Y. Hashem, *Monatsh. Chem.* **122**, 507 (1991).
- [2] R. Song, K. M. Kim, Y. S. Sohn, *Inorg. Chim. Acta* **292**, 238 (1999).
- [3] T. L. Varadinova, P. R. Bontehev, C. K. Nachev, S. A. Shiskov, *J. Chemother.* **5**, 3 (1993).
- [4] N. E. Chakov, R. A. Collins, J. B. Vincent, *Polyhedron* **22**, 2891 (1999).
- [5] R. March, W. Clegg, R. A. Coxall, L. Cucurull-Sánchez, L. Lezama, T. Rojo, P. González-Duarte, *Inorg. Chim. Acta* **353**, 129 (2003).
- [6] S. L. Jain, P. Bhattacharya, H. L. Milton, A. M. Z. Slawin, J. D. Woollins, *Inorg. Chem. Comm.* **7**, 423 (2004).
- [7] S. Basu, S.-M. Peng, G.-H. Lee, S. Bhattacharya, *Polyhedron* **24**, 157 (2005).
- [8] R. M. Achelson, *Introduction to the Chemistry of Heterocyclic Compounds*, Wiley, New York (1986).
- [9] K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, p. 232, Wiley & Sons, New York (1986).
- [10] D. Sutton, *Electrostatic Energy Level Diagrams and the Spectra of Octahedral Complexes*. In *Electronic Spectra of Transition Metal Complexes*, p. 115, McGraw-Hill, London (1968).
- [11] M. Rehakova, K. Jesenak, S. Nagyova, R. Kubinec, S. Cuvanov, V. S. Fajnor, *J. Therm. Anal. Cal.* **76**, 139 (2004).
- [12] D. Czakis-Sulikowska, A. Czyłkowska, *J. Therm. Anal. Cal.* **76**, 543 (2004).
- [13] H. Icbudak, H. Ölmez, O. Z. Yesilel, F. Arslan, P. Naumov, G. Jovanovski, A. R. Ibrahim, A. Usman, H. K. Fun, S. Chantrapromma, S. W. Ng, *J. Mol. Struct.* **657**, 255 (2003).
- [14] I. Ucar, A. Bulut, O. Z. Yesilel, H. Ölmez, O. Büyükgüngör, *Acta Crystallogr.* **C60**, m563 (2004).
- [15] I. Mutikainen, R. Hamalaitainen, M. Klinga, O. Orama, U. Turpeinen, *Acta Crystallogr.* **C52**, 2480 (1996).
- [16] H.-Y. Wang, S.-J. Liu, R.-J. Wang, C.-C. Su, *Acta Crystallogr.* **C59**, m512 (2003).
- [17] C.-S. Gu, S. Gao, L.-H. Huo, H. Zhao, J.-G. Zhao, *Acta Crystallogr.* **E60**, m1852 (2004).
- [18] M. Bhar, M. Chaudhury, E. R. T. Tiekink, *Acta Crystallogr.* **E57**, m305 (2001).

- [19] J. G. Díaz, J. Kožíšek, M. Fronc, A. Gatial, I. Svoboda, V. Langer, *Acta Crystallogr.* **C61**, m180 (2005).
- [20] L. Wang, D.-H. Zhou, J.-P. Zhang, *Acta Crystallogr.* **E61**, m958 (2005).
- [21] H. D. Flack, *Acta Crystallogr.* **A39**, 876 (1983).
- [22] Stoe & Cie, X-Area (version 1.18) and X-RED32 (version 1.04). Stoe & Cie, Darmstadt, Germany (2002).
- [23] G. M. Sheldrick, SHELXS-97 and SHELXL-97. Program for Crystal Structure Refinement, University of Göttingen, Germany (1997).
- [24] M. N. Burnett, C. K. Johnson, ORTEP-III. Report ORNL-6895. OAK Ridge National Laboratory, Tennessee, U.S.A. (1996).
- [25] L. J. Farrugia, WinGX Suite for Single Crystal Small Molecule Crystallography, *J. Appl. Crystallogr.* **32**, 837 (1999).
- [26] R. Faure, H. Loiseleur, G. Thomas-David, *Acta Crystallogr.* **B29**, 1890 (1973).