Synthesis, Spectral and Thermal Studies, and Crystal Structure of *cis*-Bis(4-methylimidazole)bis(picolinato)copper(II) $[Cu(pic)_2(4\text{-}MeIm)_2]$

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The mixed-ligand picolinato (pic) complex of Cu(II) with 4-methylimidazole (4-MeIm), $[Cu(pic)_2(4\text{-}MeIm)_2]$, was synthesized and characterized by elemental analysis, magnetic susceptibility, spectroscopic methods (UV/vis and FT-IR) and X-ray diffraction. In the slightly distorted octahedral *cis*-bis(4-methylimidazole)bis(picolinato)copper(II) complex, the pic ligands are coordinated to the Cu(II) ion as bidentate N,O-donors forming chelate rings. The 4-MeIm ligands are *N*-coordinated in *cis* positions. The complex crystallizes in the triclinic space group $P1$ with unit cell parameters $a = 9.204(5)$, $b = 9.498(5)$, $c = 13.095(5)$ Å, $\alpha = 90.395(5)$, $\beta = 101.687(5)$, $\gamma = 112.291(5)^\circ$ and $Z = 2$. Hydrogen bondings and C-H$\cdots\pi$ interactions occur between picolinato and methylimidazole ligands of neighboring complex molecules. The thermal decomposition of the complex is described.

Key words: Copper(II) Complex, 4-Methylimidazole, Picolinic Acid, Thermal Decomposition

Introduction

Pyridinecarboxylic acids and their derivatives are present in many natural products. They are 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]. Picolinic acid (pyridine 2-carboxylic acid, pic) is the body's prime natural chelator. The picolinato ligand is able to chelate metal ions and can display widely varying coordination modes as a multidentate ligand. It is the most efficient chelator for metal ions such as chromium, zinc, manganese, copper, iron and molybdenum in body fluids. Chromium picolinate favors the function of insulin, regulating blood sugar, diminishing cholesterol and fat and increasing muscle mass. It increases and regulates the secretion of insulin, such that glucose is better used and the amino acids are better absorbed [3, 4]. Zinc picolinate has a healing effect against Herpes Simplex virus [5]. One of the ways to understand the chemistry and properties of picolinic acid is to study the structures of its metal complexes [4 – 7]. Imidazole derivatives are very important model molecules since the imidazole ring occurs in a series of biological molecules such as in histidine, in Vitamin B_{12} and biotin as well as in many chemotherapic agents [8].

In this paper, we describe the preparation and the characterization by FT-IR and electronic measurements, thermal analyses data (TG and DTA) and crystal structure determination of the *cis*-bis(4-methylimidazole)bis(picolinato)copper(II) complex.

Results and Discussion

IR spectrum

The IR spectrum of the complex exhibits a medium intensity and broad band in the 3093 – 2960 cm^{-1} region which can be attributed to the N-H stretching vibration of 4-MeIm. The strong and broad bands appearing in the 1632 – 1381 cm^{-1} region are attributed to the asymmetric and symmetric stretching vibrations of the coordinated carboxylate groups of the picolinato ligand. Such absorptions have already been reported and the positions of these bands have been well described in text books and articles [9 – 11]. Separation between asymmetric and symmet-

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ric stretching frequencies of 251 cm^{-1} is in agreement with a monodentate coordination mode for the carboxylate groups [9]. This is in good agreement with the results obtained from X-ray diffraction measurements. In the complex, the band at 1567 cm^{-1} can be attributed to the (–C=N–) stretching vibration. The M–O stretching vibration of the complex is observed at 419 cm^{-1}.

UV/vis spectrum and magnetic susceptibility

The electronic spectrum of $[Cu(pic)_2(4\text{-MeIm})_2]$ in water exhibits a broad absorption band at 641 nm ($\varepsilon = 42.0$ $Lmol^{-1}cm^{-1}$) due to a *d*-*d* transition. This λ_{max} value was assigned to the $^2E_g \rightarrow ^2T_{2g}$ transition. The $\Delta_o$value for the complex was calculated as 15,600 cm^{-1}, since there is only one transition for d^9 complexes [12]. The absorption bands below 300 nm are due to intra-ligand transitions.

The magnetic susceptibility value of the complex is $\mu_{eff} = 1.79$ BM corresponding to one unpaired electron.

Thermal analysis

Thermal analysis curves of the complex (TG and DTA) are given in Fig. 1. The thermal behavior of the complex was followed up to 600 °C in a static air atmosphere. The complex is thermally stable up to 167 °C. The decomposition begins with melting at 172 °C (DTA peak) and reveals a 25.8% mass loss between 167 and 290 °C. At this stage the elimination of the 4-methylimidazole ligands and the decomposition of the picolinato ligands with release of CO_2 proceed. The IR spectrum of the intermediate product obtained in this step showed that the picolinato ligand indeed has decomposed with release of CO_2. A good agreement between the experimental and calculated values was observed for the mass loss (found 25.8%; calcd. 26.8%). The strong exothermic peak at 340 °C is associated with the burning of the organic residue (found Cu 81.8; calcd. 83.2%). The final decomposition product CuO was identified by IR spectroscopy.

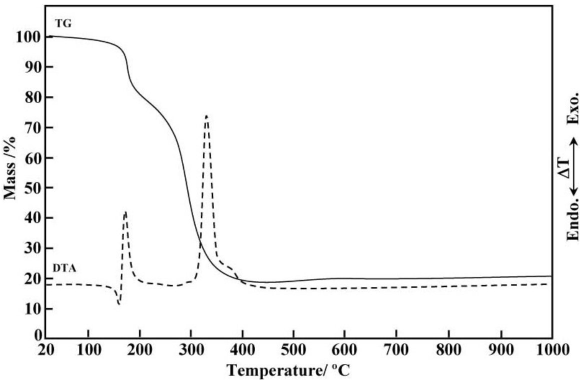

Fig. 1. The TG and DTA curves of $[Cu(pic)_2(4\text{-MeIm})_2]$.

Crystallography

π-π Stacking between aromatic rings is correlated with the electron-transfer process in some biological systems [13]. Several metal complexes are known to incorporate imidazole rings [14]. The crystal structure of the copper(II) complex shows no π-π stacking between imidazole rings.

The molecular structure is shown in Fig. 2 and the crystallographic data are summarized in Table 1. Tables 2 and 3 list bond lengths and angles and hydrogen-bonding parameters. The Cu(II) atom has a slightly distorted octahedral coordination geometry formed by 4-methylimidazole and picolinato ligands (Table 2). The Cu-O bond lengths of Cu1-O1 = 2.325(1), Cu1-O3 = 2.307(1) Å are in reasonable agreement with the values found in [15]. As shown in Table 2, the lengths of the Cu-N bonds [2.000(2) and 2.069(2) Å] are similar to other values reported in the literature [16]. The coordination of copper(II) clearly shows the geometrical pattern typi-

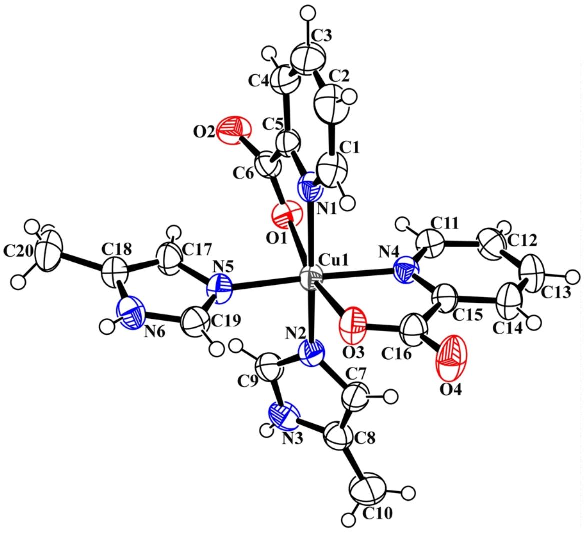

Fig. 2. A view of the copper coordination, with the atom labeling scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

Table 1. Crystal data and structure refinement parameters for $[\mathrm{Cu(pic)_2(4\text{-}MeIm)_2}]$.

Formula	$C_{20}H_{20}N_6O_4Cu$
Color	blue
Molecular weight	471.96
Temperature (K)	296
Wavelength (Å)	0.71069 Mo-K_α
Crystal system	triclinic
Space group	$P\bar{1}$
Unit cell dimensions	
a (Å)	9.204(5)
b (Å)	9.498(5)
c (Å)	13.095(5)
α (°)	90.395(5)
β (°)	101.687(5)
γ (°)	112.291(5)
Volume (Å^3)	1032.8(9)
Z	2
Calculated density (Mgm^{-3})	1.518
μ (mm^{-1})	1.098
Crystal size (mm)	$0.52 \times 0.48 \times 0.33$
Θ Range for data collection	2.3 – 28.0°
Index ranges	
h	$-11 \rightarrow 11$
k	$-11 \rightarrow 11$
l	$-14 \rightarrow 16$
Reflections collected	14918
Independent reflections	3717 ($R_{\mathrm{int}} = 0.025$)
Reflections observed ($\geq 2\sigma$)	4051
Absorption correction	integration
Max. and min. Transmission	0.594 and 0.704
Refinement method	F^2
w	$1/[2\sigma(F_o{}^2) + (0.0325P)^2 + 0.3985P]$ where $P = (F_o{}^2 + 2F_c{}^2)/3$
Goodness-of-fit on F^2	1.03
$R[F^2 \geq 2\sigma(F^2)]$	0.025
$wR(F^2)$	0.066
Largest diff. peak and hole (e Å^{-3})	0.24, −0.33

Table 2. Selected bond lengths (Å) and bond angles (°) for $[\mathrm{Cu(pic)_2(4\text{-}MeIm)_2}]$.

Cu(1)–N(1)	2.069(2)	Cu(1)–O(3)	2.307(1)
Cu(1)–N(2)	2.000(2)	C(9)–N(2)	1.318(2)
Cu(1)–N(4)	2.052(2)	C(19)–N(5)	1.314(2)
Cu(1)–N(5)	2.015(2)	C(7)–C(8)	1.350(3)
Cu(1)–O(1)	2.325(1)	C(17)–C(18)	1.351(3)
N(2)–Cu(1)–N(5)	92.0(1)	N(1)–Cu(1)–O(3)	94.0(1)
N(2)–Cu(1)–N(4)	90.2(1)	N(2)–Cu(1)–O(1)	93.4(1)
N(5)–Cu(1)–N(4)	172.0(1)	N(5)–Cu(1)–O(1)	91.8(1)
N(5)–Cu(1)–N(1)	90.4(1)	N(4)–Cu(1)–O(1)	95.7(1)
N(4)–Cu(1)–N(1)	88.9(1)	N(1)–Cu(1)–O(1)	75.9(1)
N(2)–Cu(1)–O(3)	96.4(1)	O(3)–Cu(1)–O(1)	167.1(1)
N(5)–Cu(1)–O(3)	96.3(1)		

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

D–H···A	D–H	H···A	D···A	D–H···A
N3–H3N···O2$^{\mathrm{i}}$	0.74(2)	2.01(2)	2.750(2)	171(2)
N6–H6N···O4$^{\mathrm{ii}}$	0.76(3)	1.98(3)	2.744(2)	177(3)

Symmetry codes: $^{\mathrm{i}}$ $1-x$, $1-y$, $-z$; $^{\mathrm{ii}}$ $1-x$, $1-y$, $1-z$.

cal for the Jahn-Teller effect. The Cu1-N1 and Cu1-N4 distances are shorter than the Cu1-O1 and Cu1-O3 distances, and this results in the formation of a distorted octahedral geometry elongated along the N atoms. This effect is usually observed for analogous compounds, such as *catena*-poly[[(1,10-phenanthroline-$\kappa^2 N,N'$)copper(II)]-μ-4-carboxyimidazole-5-carboxylato(2-)-$\kappa^4 N,O:N',O'$] [17] [Cu1-N3 = 2.007(3) and Cu1-O1 = 2.383(3) Å] and chloro(methylpicolinato-N,O)(picolinato-N,O)copper(II) [18] [Cu1-N2 = 2.006(2) and Cu1-O3 = 2.390(2) Å].

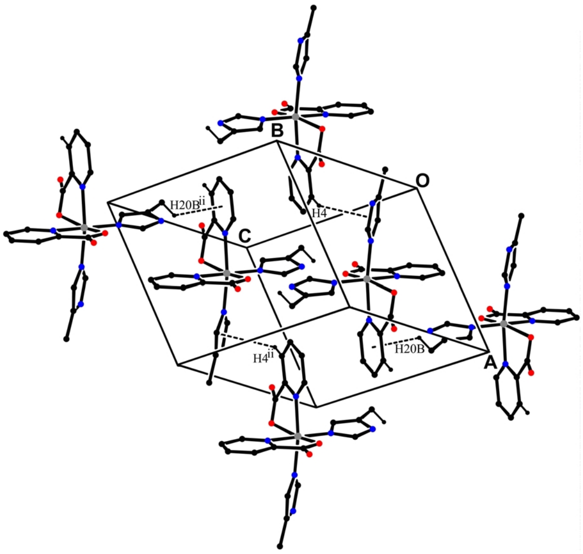

Fig. 3. Diagram of the C–H···π interactions (dashed lines). H atoms not involved in C–H···π interactions have been omitted for clarity [symmetry code: $^{\mathrm{ii}}$ $1-x$, $1-y$, $1-z$].

The title complex contains two picolinato rings and two imidazole rings. The two imidazole rings are individually planar, with r.m.s. deviations of 0.002 Å, with maximum deviations from these planes of 0.002(2) Å for atom C8 and of 0.003(2) Å for atom C19. These planes are approximately perpendicular, with a dihedral angle of 85.7(1)°. The dihedral angles between the picolinato ring (containing N4) and the imidazole groups are 82.7(1) and 8.0(1)°. The internal geometries are as expected, with the bond lengths N2-C9 [1.318(2) Å], N5-C19 [1.314(2) Å], C7-C8 [1.350(3) Å] and C17-C18 [1.351(3) Å] corresponding to typical double-bond lengths. These values are comparable with those in mixed-ligand imidazole-Cu(II) complexes [19, 20]. The two picolinato rings are individually planar, with r.m.s. deviations of 0.002 and 0.003 Å, and with maximum deviations from these planes of 0.011(2) Å for atom C3 and 0.010(3) Å for atom C13. These planes are approximately perpendicular, with a dihedral angle of 89.0(1)°. The dihedral angles between the picolinato ring (containing N1) and the imidazole groups are 40.3(1) and 86.6(1)°.

The crystal packing of the title complex is formed *via* intermolecular hydrogen bonds and π-ring interactions. Carboxyl atoms O2 and O4 are hydrogen bonded to the picolinato ligands of a neighboring complex molecule (Table 3). A PLATON analysis [21] shows that C-H...π interactions occur between the imidazole and neighboring picolinato rings (Fig. 3); C4-H4...Cg1 = 139(2)° and H4...Cg1 = 2.96(3) Å, where Cg1 denotes the centroid of the N2/N3/C7-C9 ring [symmetry code: (ii) $1-x, 1-y, 1-z$] and C20-H20B...Cg2 = 134(3)° and H20B...Cg2 = 2.82(4) Å, where Cg2 denotes the centroid of the N1/C1-C5 ring [symmetry code: (ii) $1-x$, $1-y$, $1-z$]. No π–π stacking occurs between picolinato rings.

Experimental Section

Materials and measurements

All chemicals used were analytical reagent grade products. 4-Methylimidazole was obtained from Merck. Picolinic acid was purchased from ACROS organics.

Magnetic susceptibility measurements at r. t. were 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 K min^{-1} in the temperature range 20 – 1000 °C using platinum crucibles. Highly sintered α-Al_2O_3 was used as a reference and the DTG sensitivity was 0.05 mg s^{-1}. The elemental analysis was carried out at the TÜBİTAK Marmara Research Centre.

Crystallographic analysis

A blue single crystal suitable for data collection was mounted on a glass fiber and data collection was performed on a STOE IPDS-II diffractometer with graphite monochromated MoK_α radiation (λ = 0.71069 Å) at 296 K. Details of the crystal structure 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] and refined by full-matrix least-squares methods on F^2 using SHELXL-97 [23]. All non-hydrogen atoms were refined with anisotropic parameters. All H atoms were refined isotropically. The refined C-H and N-H bond lengths are in the ranges 0.83(4) – 1.00(4) and 0.74(2) – 0.76(3) Å, respectively. Molecular drawings were obtained using ORTEP-III [24]. Software used to prepare material for publication: WinGX [25].

Crystallographic data (in cif files) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 291470. Copies of this information may be obtained from the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

Preparation of [Cu(pic)$_2$(4-MeIm)$_2$]

The $[Cu(pic)_2]\cdot 2H_2O$ complex was prepared by the method reported earlier [7]. A solution of 4-MeIm (4 mmol) in ethanol (10 cm^3) was added dropwise with stirring to a solution of $[Cu(pic)_2]\cdot 2H_2O$ (2 mmol) in ethanol (20 cm^3). The solution was heated to 50 °C in a temperature-controlled bath and stirred for 4 h. The reaction mixture was then cooled to r. t. The dark blue crystals formed were filtered off and washed with water and dried in air. Crystals suitable for X-ray diffraction were obtained by slow diffusion of absolute ethanol into the filtrate. M. p. 172 °C. – UV/vis (H_2O): $\lambda_\text{max}\,(\lg\varepsilon)$ = 641 nm (3.74). – IR (KBr): $\tilde{\nu}$ = 3093 (N-H), 1632, 1381, 1567, 419 cm^{-1}. – $C_{20}H_{20}N_6O_4Cu$ (471.96): calcd. C 50.90, H 4.24, N 17.81; found C 50.72, H 4.27, N 17.54.

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