

Synthesis and Structure of Tetraploid (Imidazole) Copper(II) Terephthalate , [Cu(Im)₄] (teph)

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The crystal structure of [Cu(Im)₄] (teph) (Im = imidazole , teph = terephthalate) has been determined by X-ray crystallography. It crystallizes in the triclinic system , space group $P\bar{1}$ with cell dimensions of $a = 0.8035(16)$ nm , $b = 0.84269(17)$ nm , $c = 0.88967(18)$ nm , $\alpha = 76.90(3)^\circ$, $\beta = 68.95(3)^\circ$, $\gamma = 75.94(3)^\circ$, and $Z = 1$. Its structure of the title compound is composed of discrete monomeric molecule of [Cu(Im)₄] (teph). The copper(II) ions have a square plane geometry with the CuN₄ chromophore.

Keywords copper(II) complexes , terephthalate , imidazole , X-ray

Introduction

Imidazole is of considerable interest as a ligand which presents in many biological systems (for example in the histidyl residue of proteins) providing a potential binding site for metal ions . Imidazole as an unidentate ligand can form complexes with metal ions through its tertiary nitrogen atom . Some complexes of imidazole and its derivatives with transition-metal ions have been reported.¹⁻⁴

The preparation of the complexes of copper(II) carboxylate with a variety of basic ligands and their magnetic and spectral properties have been reported.^{5,6} But the number of ternary copper(II) complexes containing carboxylate and other basic ligands is , however , quite limited.⁷ The complexes of copper(II) with carboxylate and imidazole ligands have been studied as models for copper proteins that contain both functionalities in the side chain .⁸⁻¹⁰ In addition , some of these copper(II) complexes were found to exhibit a variety of pharmacological activity¹¹ and super oxide dismutase activity.¹² Because copper(II) terephthalate has a lower solubility in major solvent , the copper(II) complexes containing terephthalate and other basic ligands have not been reported . In this paper , the synthesis and crystal structure of the title compound are described .

Experimental

All chemicals were of analytical reagent grade and used directly without further purification . Copper(II) terephthalate was prepared by mixing aqueous solutions of copper(II) sulfate and terephthalic acid disodium salt according to the reported method.¹³ To a warm solution of imidazole (1.0 g , 15 mmol) in H₂O (50 mL) , 1.0 g of Cu[*p*-Ph(COO)₂] · 2H₂O (3.8 mmol) was added with stirring and the mixture was refluxed for 30 min . The blue solution was filtered and the filtrate was left to stand undisturbed . Upon slow evaporation at room temperature , a blue crystalline solid appeared several weeks later and was separated by filtration . The C , H and N contents were determined using a Carlo Erba 1106 elemental analyser (Anal . calcd for C₂₀H₂₀N₈O₄Cu₁ : C 48.0 , H 4.0 , N 22.4 ; found C 48.3 , H 4.1 , N 22.1). The IR spectrum was recorded on a Nicolet 510P FT-IR spectrometer using KBr pellets and the UV spectrum was obtained using Varian Cary 50 probe UV-visible spectrophotometer .

A summary of the key crystallographic information is given in Table 1 . The selected crystal of [Cu(Im)₄] (teph) was mounted on a Nonius CAD4 diffractometer . Reflection data and reflections for the unit cell determination were measured at 20 °C using Mo K α radiation ($\lambda = 0.071073$ nm) with a graphite monochromator . The technique used was ω -scan with θ limits 12.94°—23.04° for the complex . Absorption correction was made with psi-scans . The structure was solved by direct method and refined by full-matrix least-squares method on F^2_{obs} by using the SHELXTL¹⁴ software package . All non-H atoms were anisotropically refined . The hydrogen atoms were geometrically fixed and allowed to ride on the parent atoms to which they are attached . The final conventional data are $R = 0.0239$ and $wR = 0.0575$ for 1164 reflections with $I > 2\sigma(I)$; $w = 1/\sqrt{\sigma^2(F_o^2) + (0.0000P)^2 + 0.1512P}$ where $P = [F_o^2 + 2(F_c^2)]/3$. The molecular graphics were created by using SHELXTL . Atomic scattering factors and

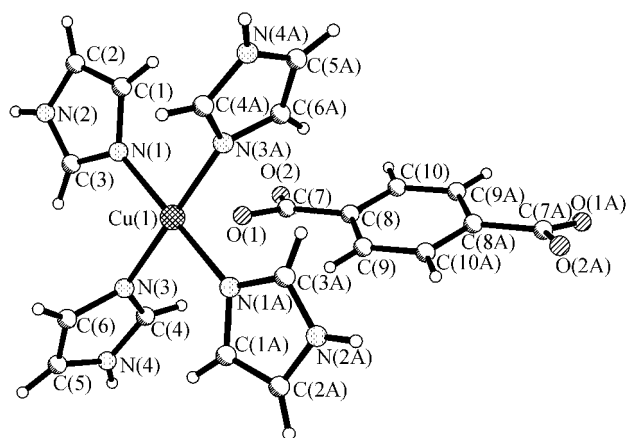
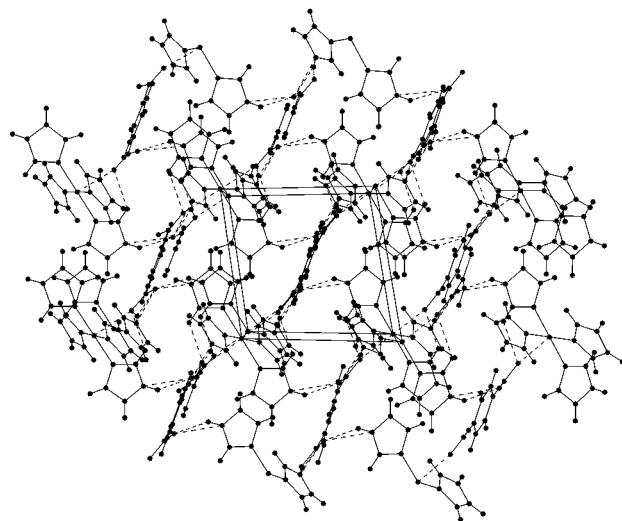
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Table 1 Summary of crystallographic results for $[\text{Cu}(\text{Im})_4](\text{teph})$

Formula	$\text{C}_{20}\text{H}_{20}\text{N}_8\text{O}_4\text{Cu}$
Formula weight	499.98
Color	Blue
Crystal system	Triclinic
Space group	$P\bar{1}$
a (nm)	0.80356(16)
b (nm)	0.84269(17)
c (nm)	0.88967(18)
α ($^\circ$)	76.90(3)
β ($^\circ$)	68.95(3)
γ ($^\circ$)	75.94(3)
V (nm^3)	0.53889(19)
Z	1
D_{calcd} ($\text{g}\cdot\text{cm}^{-3}$)	1.5406
μ (cm^{-1})	10.594
$F(000)$	257.0
Crystal size (mm^3)	0.24 \times 0.20 \times 0.20
Radiation	Mo $K\alpha$ ($\lambda = 0.071073$ nm)
Temp. (K)	293
θ Range ($^\circ$)	12.94—23.04
$-H, h/-k, k/-l, l$	-8, 8/-9, 0/-9, 9
Reflections collected	1228
Independent reflections	1164
Absorption correction	psi-scan
No. restraints	0
No. parameters	151
GOF	1.118
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0239, wR_2 = 0.0575$
R indices (all data)	$R_1 = 0.0266, wR_2 = 0.0601$
Largest peak and hole ($\text{e}\cdot\text{nm}^{-3}$)	161 and -143

**Fig. 1** Molecular structure for $[\text{Cu}(\text{Im})_4](\text{teph})$ with the atomic numbering scheme.**Fig. 2** A view of the crystal packing down the x -axis for $[\text{Cu}(\text{Im})_4](\text{teph})$.

anomalous dispersion correction were taken from International Table for X-Ray Crystallography.¹⁵

Results and discussion

X-Ray crystal structure of title compound

The X-ray structure of the complex $[\text{Cu}(\text{Im})_4](\text{teph})$ is built up of discrete monomeric molecules. Fig. 1 shows a perspective view of the title compound with atomic numbering scheme and Fig. 2 a perspective view of the crystal packing in the unit cell. Table 2 contains atomic positions and equivalent temperature factors for non-hydrogen atoms. Selected bond lengths and angles and hydrogen bond distances are presented in Tables 3 and 4.

The crystal structure of the complex consists of monomeric $[\text{Cu}(\text{Im})_4]^{2+}$ cations and terephthalate anions linked by electrostatic forces and hydrogen bonds. The coordination model of the copper(II) atom can be described as CuN_4 chromophore. The copper(II) ion has a square

Table 2 Atomic coordinates and equivalent isotropic displacement parameters

Atom	x	y	z	U_{eq}
Cu(1)	1.00000	0.00000	0.00000	0.03913
N(1)	0.82879	-0.01124	-0.11882	0.03277
N(2)	0.61395	0.06103	-0.22887	0.06090
N(3)	0.83785	0.20370	0.08505	0.03542
O(1)	0.77805	-0.16713	0.25490	0.05987
O(2)	0.57209	-0.31458	0.41909	0.05493
O(1)	0.84487	-0.12443	-0.21273	0.06111
O(2)	0.71348	-0.07900	-0.28220	0.07157
O(3)	0.68684	0.09810	-0.13216	0.04486
O(4)	0.71762	0.20643	0.23018	0.03926

plane geometry. Four imidazole molecules are coordinated through its tertiary nitrogen atoms to each copper(II) ion and one terephthalate is out of coordination sphere, in general, balances the charge. The bond distances of $\text{Cu}(1)-\text{N}(1)$ and $\text{Cu}(1)-\text{N}(3)$ of $[\text{Cu}(\text{Im})_4](\text{teph})$

Table 3 Selected bond distances (nm) and bond angles ($^{\circ}$) of the title compound

Cu(1)—N(3)	0.20027(18)	N(2)—C(3)	0.1324(3)
Cu(1)—N(1)	0.20427(16)	N(2)—C(2)	0.1334(4)
N(1)—C(3)	0.1304(3)	N(3)—C(4)	0.1307(3)
N(1)—C(1)	0.1360(3)	N(3)—C(6)	0.1367(3)
N(4)—C(4)	0.1330(3)	N(4)—C(5)	0.1350(4)
C(1)—C(7)	0.1244(3)	C(2)—C(7)	0.1255(3)
N(1)—Cu(1)—N(3A)§1	89.72(7)	C(2)—C(1)—N(1)	109.8(2)
N(1)—Cu(1)—N(1A)§1	180.00(6)	C(3)—N(2)—C(2)	107.5(2)
N(3)—Cu(1)—N(1)	90.28(7)	C(6)—N(3)—Cu(1)	128.66(15)
C(4)—N(3)—Cu(1)	125.09(15)	C(4)—N(4)—C(5)	107.57(19)
C(1)—N(1)—Cu(1)	128.32(14)	N(3)—C(4)—N(4)	110.96(19)
N(1)—C(3)—N(2)	111.9(2)	N(2)—C(2)—C(1)	106.2(2)

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

Table 4 Hydrogen bond distances (nm) of the title compound

D	H	A	Symm	D—H	H...A	D...A	D—H...A
N(2)	H(2A)	C(1)	$1-x, -y, -z$	0.08600	0.23318	0.31364	155.87
N(2)	H(2A)	C(2)	$1-x, -y, -z$	0.08600	0.21381	0.28793	144.10
N(4)	H(4A)	C(2)	$1-x, -y, 1-z$	0.08600	0.20331	0.27805	144.82
C(4)	H(4B)	C(1)	—	0.09300	0.23898	0.30354	126.40

are 0.20427(16) and 0.20027(18) nm, respectively. All parameters are significantly longer than those of octahedral [Cu(Im)₄(OB₂)₂][0.1974(2), 0.1985(2) nm]¹⁶ In the solid state, one carboxyl oxygen atom of terephthalate forms an intramolecule hydrogen bond with the carbon atom of [Cu(Im)₄]²⁺ and an intermolecule hydrogen bond with the carbon atom of another [Cu(Im)₄]²⁺ (Fig. 2),¹⁷ the donor and acceptor distances are C(4)...O(1) 0.30354, N(2)—O(1) ($1-x, -y, -z$) 0.31364, N(2)...O(2) ($1-x, -y, -z$) 0.28793, N(4)...O(2) ($1-x, -y, 1-z$) 0.27805 nm, the whole complexes forming a 3-dimensional network structure.

IR and UV spectra

IR spectrum of the title compound exhibits the characteristic absorption. The most important absorption in the spectrum is the terephthalate antisymmetric carboxyl vibration which appears at 1586 cm⁻¹, and the symmetric carboxyl stretching frequency occurs at 1371 cm⁻¹. The absorption at 3140 cm⁻¹ is the nitrogen-hydrogen vibration of imidazole, $\nu(\text{NH})$, indicating that the coordinated atom with copper(II) is the double bond nitrogen (=N) in imidazole. The UV spectrum shows the terephthalate absorption at 241 nm and the Cu—N complex absorption at 620 nm, suggesting that imidazole forms complex with the copper(II) atom.

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