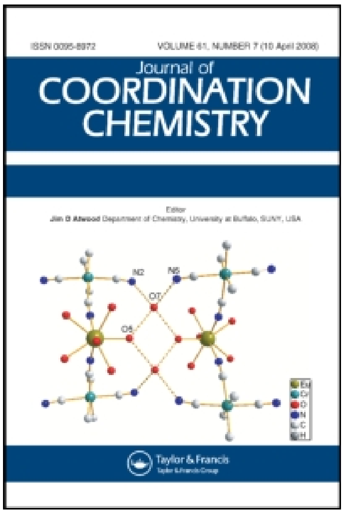

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Synthesis and crystal structure of tetra(imidazole) copper(II) terephthalate

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The molecular structure of tetra(imidazole)copper(II) terephthalate was determined by single-crystal X-ray diffraction methods. The complex is triclinic, space group $P\bar{1}$, with $a = 8.0299(6)$, $b = 8.4180(7)$, $c = 8.8992(4)$ Å, $\alpha = 77.122(3)$, $\beta = 68.898(3)$, $\gamma = 76.116(2)°$, $V = 538.59(7)$ Å^3. The Cu(II) atom is located on an inversion center and assumes tetragonally elongated octahedral coordination geometry, with an axial Cu–O(carboxyl) bond distance of 2.682(2) Å. The terephthalate dianion is located on another inversion center and bridges neighboring Cu(II) atoms to form polymeric chains. IR spectra of the complex are consistent with the crystal structure.

Keywords: Copper(II) complex; Crystal structure; Jahn–Teller distortion; Imidazole; Terephthalate

1. Introduction

Jahn–Teller distortion of Cu(II) complexes is well known [1]. In most Cu(II) complexes, axial bonds are usually longer than those in the equatorial coordination plane by about 0.2 to 0.6 Å [2]. In some Cu(II) complexes of carboxylate ligands, (O1–C–O2), the ligands coordinate as chelates with one Cu–O distance longer than the other [3–5]. In tetra(imidazole)copper(II) terephthalate, a long axial distance of 2.682(2) Å is observed between Cu and the carboxyl oxygen atoms, and the bond is considered to be fairly weak for this class of complex.

2. Experimental

2.1. *Synthesis*

All reagents were commercially available and of analytical grade. An ethanol solution (5 cm^3) of imidazole (2 mmol) was mixed with an aqueous solution (5 cm^3) of

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$CuCl_2 \cdot 2H_2O$ (1 mmol), and the mixture refluxed for 1 h. After the addition of an aqueous solution (8 cm^3) of terephthalic acid (1 mmol) and Na_2CO_3 (2 mmol), the mixture was again refluxed for 1 h. The solution was cooled to room temperature and filtered. Blue, single crystals of tetra(imidazole)copper(II) terephthalate were obtained during 3 weeks. C, H and N content analyses were carried out on a Carlo-Erba 1160 instrument. Anal. Calcd. for $C_{20}H_{20}CuN_8O_4$(%): C, 48.00; N, 22.41; H, 4.03; Found: C, 48.35; N, 21.62; H, 3.98. IR spectra were recorded (KBr pellets) in the 4000–400 cm^{-1} range using a Nicolet 5DX FTIR spectrophotometer.

2.2. *Crystal structure determination*

X-ray diffraction intensities of a single crystal were collected on a Rigaku RAXIS-RAPID diffractometer at room temperature. The structure was solved by direct methods [6] followed by Fourier syntheses using Sir92. Structure refinement was performed by full-matrix least-squares procedures using SHELX-97 on F^2 [7]. Hydrogen atoms of lattice water molecules were located in a difference Fourier map and included in the structure factors calculation with fixed positional parameters and isotropic displacement parameters of 0.08 Å^2. Other H atoms were placed in calculated positions, with C–H = 0.93 Å and N–H = 0.86 Å, and were included in the final cycles of refinement in riding mode with $U_{iso}(H) = 1.2U_{eq}$ of the carrier atoms.

Crystal data and refinement conditions are summarized in table 1. Final fractional atomic coordinates and equivalent isotropic thermal parameters for the non-H atoms are listed in table 2. Full lists of crystallographic data have been deposited at the Cambridge Crystallographic Data Centre with deposition number CCDC 253588.

3. Results and discussion

3.1. *Crystal structure*

The molecular structure of the title complex is shown in figure 1. The Cu atom is located on an inversion center and is surrounded by four imidazole molecules and two terephthalate dianions with tetragonally elongated octahedral coordination geometry (table 3). The Cu–O1 distance of 2.682(2) Å in the axial direction is longer than the sum (2.04 Å) of covalent radii of Cu and O atoms by 0.64 Å, showing appreciable Jahn–Teller distortion. This Cu–O1 distance is comparable to that found [2.683(2) Å] in the salicylato–Cu(II) complex [3] and is considered to constitute a fairly weak bond between Cu(II) and a carboxylate ligand.

It is notable that the carboxyl group coordinates to the Cu(II) atom in the unusual *anti*-configuration, with a large Cu–O1–C7 angle of 158.1(2)°. A search of the Cambridge Structure Database [8] indicates that this is the only reported Cu(II) complex with a benzoate (or derivative) ligand in the *anti*-configuration. The coordination of the carboxyl groups results in closer crystal packing of complex units than does the *syn*-coordination. The larger Cu–O1–C7 bond angle implies poor overlap of atomic orbitals of Cu and O1 atoms.

The terephthalate dianion is located on another inversion center, the carboxyl group making a dihedral angle of 20.7(3)° with the benzene ring. Each terephthalate bridges two neighboring Cu(II) atoms to form polymeric chains along the $[10\bar{1}]$ direction.

Table 1. Crystal data and structure refinement details for the complex.

Empirical formula	$Cu(C_3H_4N_2)_4(C_8H_4O_4)$
M	499.98
Crystal size (mm)	$0.40 \times 0.38 \times 0.26$
Temperature (K)	295
Wavelength (Å)	0.71073
Crystal system	Triclinic
Space group	$P\bar{1}$
Unit cell dimensions (Å, °)	$a = 8.0299(6)$ $b = 8.4180(7)$ $c = 8.8992(4)$ $\alpha = 77.122(3)$ $\beta = 68.898(3)$ $\gamma = 76.116(2)$
V (Å^3)	538.59(7)
Z	1
Density (calculated) (g cm^{-3})	1.541
Absorption coefficient (mm^{-1})	0.530
$F(000)$	129
θ range for data collection (°)	2.5 to 25.2
Reflections collected	4032
Independent reflections	1924
Observed reflections $[I > 2\sigma(I)]$	1829
Parameters	151
Goodness-of-fit on F^2	1.15
Final R indices $[I > 2\sigma(I)]$	$R_1 = 0.030$, $wR_2 = 0.076$
R indices (all data)	$R_1 = 0.032$, $wR_2 = 0.077$
Largest diff. peak and hole (e Å^{-3})	0.26 and −0.27

Table 2. Atomic coordinates and equivalent isotropic displacement parameters for the non-hydrogen atoms. U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

	x/a	y/b	Z/c	U_{eq} (Å^2)
Cu	0.5	0.5	0.5	0.0390(1)
O1	0.7224(2)	0.6669(2)	0.2443(2)	0.0596(6)
O2	0.9283(2)	0.8151(2)	0.0808(2)	0.0545(6)
N1	0.6705(2)	0.5112(2)	0.6186(2)	0.0326(5)
N2	0.8859(3)	0.4379(3)	0.7291(3)	0.0609(8)
N3	0.6619(2)	0.2968(2)	0.4154(2)	0.0351(5)
N4	0.8589(2)	0.1390(2)	0.2445(2)	0.0441(6)
C1	0.6542(3)	0.6244(3)	0.7138(4)	0.0611(9)
C2	0.7865(4)	0.5794(4)	0.7819(4)	0.0722(11)
C3	0.8136(3)	0.4015(3)	0.6318(3)	0.0452(7)
C4	0.7832(3)	0.2934(3)	0.2694(3)	0.0398(7)
C5	0.7827(3)	0.0363(3)	0.3805(3)	0.0504(8)
C6	0.6614(3)	0.1345(3)	0.4866(3)	0.0443(7)
C7	0.7707(3)	0.7823(2)	0.1347(2)	0.0372(6)
C8	0.6314(2)	0.8961(2)	0.0627(2)	0.0291(5)
C9	0.4752(3)	0.8423(2)	0.0781(2)	0.0352(6)
C10	0.6558(3)	1.0549(2)	−0.0167(2)	0.0350(6)

Adjacent chains are linked by hydrogen bonds between carboxyl groups and imidazole ligands (table 4) to form a three-dimensional supramolecular structure. C–H$\cdots\pi$ interactions occur between neighboring aromatic rings as shown in figure 1. The H1$\cdots$Cg(N3^{i}-ring) (Cg denotes the centroid of the ring) distance and the

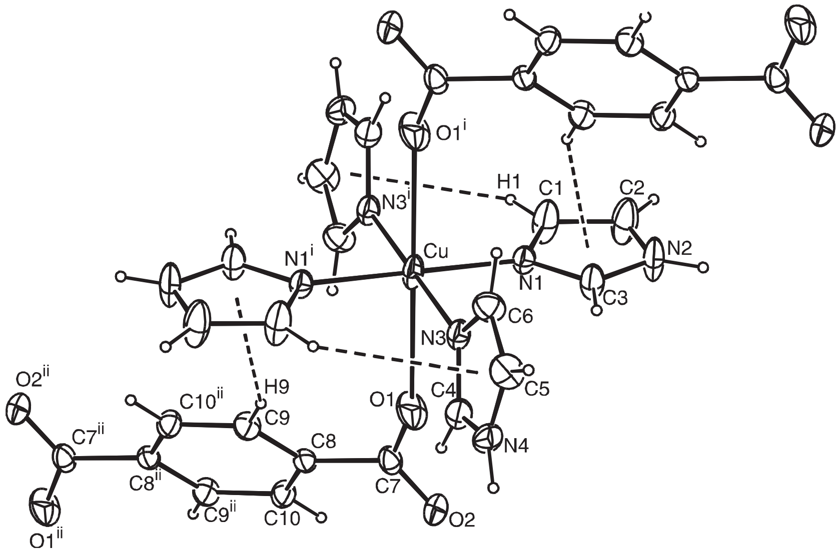

Figure 1. The molecular structure of the complex drawn with 30% probability displacement ellipsoids, showing the atom numbering scheme. Symmetric codes used are (i): $1-x$, $1-y$, $1-z$; (ii): $1-x$, $2-y$, $-z$.

Table 3. Selected bond lengths (Å) and angles (°) for the title complex.

Cu–O1	2.682(2)	Cu–N1	2.036(2)
Cu–N3	1.996(2)	O1–C7	1.238(2)
O2–C7	1.257(3)	N1–C1	1.365(3)
N1–C3	1.314(3)	N2–C2	1.342(4)
N2–C3	1.321(4)	N3–C4	1.315(3)
N3–C6	1.372(3)	N4–C4	1.327(3)
N4–C5	1.357(3)	C1–C2	1.344(5)
C5–C6	1.350(4)	C7–C8	1.519(3)
C8–C9	1.385(3)	C8–C10	1.389(2)
C9–C10^{ii}	1.386(3)		
O1–Cu–N1	84.56(6)	O1–Cu–N3	85.51(6)
N1–Cu–N3	90.05(7)	Cu–O1–C7	158.2(2)
Cu–N1–C1	128.4(2)	Cu–N1–C3	127.1(2)

Symmetry code used is (ii): $1-x$, $2-y$, $-z$.

Table 4. Hydrogen-bonding parameters (Å,°).

D–H···A	D–H	H···A	D···A	D–H–A
N2–H2···O1^{iii}	0.86	2.34	3.137(3)	155
N2–H2···O2^{iii}	0.86	2.14	2.883(3)	145
N4–H4A···O2^{iv}	0.86	2.03	2.776(2)	145

Symmetry codes used are (iii): $2-x$, $1-y$, $1-z$; (iv): $2-x$, $1-y$, $-z$.

C1–H1–Cg(N3^{i}-ring) angle are 2.80 Å and 131°, respectively. The H9···Cg(N1^{i}-ring) distance and C9–H9–Cg(N1^{i}-ring) angle are 2.86 Å and 153°, respectively. Although π–π stacking between aromatic rings is commonly observed in metal complexes of unsaturated ligands, this is not the case in the present complex.

3.2. *IR spectra*

IR spectra of the complex are consistent with the crystal structure. Stretching vibrations of the carboxyl group are observed at 1587 [ν_{as}(coo)] and 1371 cm^{-1} [ν_s(coo)]. The $\Delta\nu$ value of 216 cm^{-1} agrees with the monodentate coordination mode of the carboxyl group [9].

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References

[1] H.A. Jahn, E. Teller, *Proc. R. Soc., Ser.* A **161**, 220 (1937).
[2] B.J. Hathaway, D.E. Bulling, *Coord. Chem. Rev.* **5**, 143 (1970).
[3] H. Li, D.-J. Xu, *Acta Cryst.* C61, M19 (2005).
[4] E.G. Bakalbassis, A. Terzis, *Inorg. Chim. Acta* **218**, 167 (1994).
[5] J. Cano, G. De Munno, J.L. Sanz, R. Ruiz, J. Faus, F. Lloret, M. Julve, A. Caneschi, *J. Chem. Soc., Dalton Trans.* 1915 (1997).
[6] A. Altomare, G. Cascarano, C. Giacovazzo, A. Guagliardi, *J. Appl. Cryst.* **26**, 343 (1993).
[7] G.M. Sheldrick, *SHELX-97: Program for Crystal Structure Refinement*, University of Göttingen, Germany (1997).
[8] F.H. Allen, *Acta Cryst.* **B58**, 380 (2002).
[9] K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, John Wiley and Sons, New York (1978).