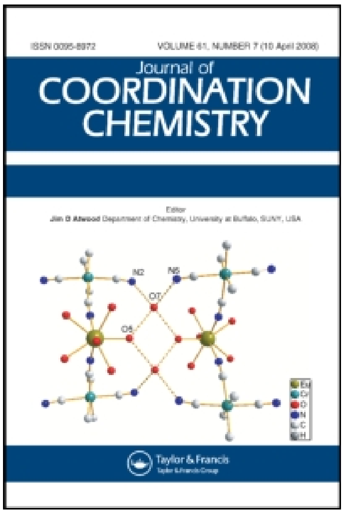

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SYNTHESIS AND CRYSTAL STRUCTURE OF A POLYMERIC 1,2,4,5-BENZENETETRACARBOXYLATO COMPLEX OF Cu(II) WITH IMIDAZOLE, $Cu_2(C_{10}H_2O_8)(C_3H_4N_2)_6(H_2O)_4 \cdot 4H_2O$

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SYNTHESIS AND CRYSTAL STRUCTURE OF A POLYMERIC 1,2,4,5-BENZENETETRACARBOXYLATO COMPLEX OF Cu(II) WITH IMIDAZOLE, $Cu_2(C_{10}H_2O_8)(C_3H_4N_2)_6(H_2O)_4 \cdot 4H_2O$

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The title complex, $Cu_2(C_{10}H_2O_8)(C_3H_4N_2)_6(H_2O)_4 \cdot 4H_2O$, consists of polymeric copper(II) complex anions and discrete copper(II) complex cations. Benzenetetracarboxyl anions bridge copper(II) atoms coordinated to water and imidazole groups to form the anionic polymeric chains along the *a* axis, while discrete copper(II) complex cations involving four imidazole and two water ligands are packed between parallel polymeric anionic chains, an extensive H-bonding network linking complex cations and anions.

Keywords: Copper(II); Crystal structure; Polymeric, 1,2,4,5-benzenetetracarboxyl acid; Imidazole

INTRODUCTION

Owing to its fundamental importance, the study of polynuclear complexes has been an active field of coordination chemistry in recent years [1, 2]. Structural investigations of transition metal complexes bridged by aromatic molecules have been continuing in our laboratory for several years with the

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*Corresponding author.

aim of studying the magnetic behaviour of these complexes in relation to their structures [3]. Owing to the possible coordination capability of the four carboxyl groups, the 1,2,4,5-benzenetetracarboxylate anion (BTC) has recently been used as a bridging ligand to synthesize a series of multinuclear copper complexes [2, 4]. Through different coordination modes of the carboxyl groups, a series of interesting and varied BTC complexes has been synthesized, among which polymeric complexes with linear or three dimensional network structures have been reported [5–7]. As a part of this research, we present here the unusual polymeric structure of the title complex.

EXPERIMENTAL

About 5 mmol (1.27 g) of 1,2,4,5-benzenetetracarboxylic acid was slowly added to 20 cm^3 of an aqueous solution of NaOH (0.80 g, 20 mmol) with stirring (pH = 7.0). Copper(II) sulfate pentahydrate (2.52 g, 10 mmol) was dissolved in 20 cm^3 of water and mixed with the above solution at room temperature. Imidazole (2.04 g, 30 mmol) was then slowly added to above mixture at room temperature with stirring until all the imidazole had dissolved. The mixture was filtered and 1.5 cm^3 of methanol was added to the filtrate to obtain well-shaped crystals. Deep blue, single crystals were obtained after standing the solution for thirty days. *Anal.* Calc. for $C_{28}H_{42}N_{12}O_{16}Cu_2$(%): C, 36.16; H, 4.52; N, 18.08. Found: C, 36.23; H, 4.52; N, 19.12. The IR spectrum of the complex was recorded with a Shimadzu IR-470 spectrophotometer (4000–400 cm^{-1}) using a powdered sample spread on a KBr plate.

Crystal Structure Determination

A blue, prismatic crystal of the title complex with approximate dimensions 0.45 × 0.55 × 0.48 mm was mounted on a glass fibre X-ray diffraction intensity data were collected on a Bruker P4 AXS diffractometer up to a 2θ value of 60.0° with graphite–monochromatized MoKα radiation ($\lambda = 0.71069$ Å) by the $\theta - 2\theta$ scan technique at 293 K. A total of 5384 independent reflections was collected, of which 4967 reflections were considered as observed [$I > 2\sigma(I)$] and used for the structure determination. Usual Lp and empirical adsorption corrections were applied [8].

The crystal structure was solved by the Patterson method followed by Fourier syntheses. Structure refinement was carried out by full-matrix least-squares procedures using the SHELEXTL program package [9]. H atoms were located in a difference Fourier map, and coordinates and thermal parameters were fixed during structure refinement. Anisotropic refinement including all the non-H atoms converged to agreement factors $R=0.030$ and $R_w=0.089$. Atomic scattering factors were taken from International Tables for X-ray Crystallography [10].

Crystal Data

$C_{28}H_{42}N_{12}O_{16}Cu_2$, $Mr=929.83$, triclinic, space group $P\bar{1}$, $a=10.034(1)$, $b=10.652(1)$, $c=11.101(1)$ Å, $\alpha=114.74(1)$, $\beta=95.75(1)$, $\gamma=108.45(1)°$, $V=984.2(2)$ Å^3, $Z=1$, $F(000)=482$, $D_c=1.570$ g cm^{-3}, μ(MoKα) = 1.165 cm^{-1}.

RESULTS AND DISCUSSION

Crystal Structure

Final atomic coordinates and thermal parameters are listed in Table I. Selected atomic distances and angles are presented in Table II. The title complex consists of polymeric Cu(II) complex anions and discrete mononuclear Cu(II) complex cations. The structures of the complex anion and cation are illustrated in Figure 1 with the atom numbering scheme. In the complex anion, an octahedral Cu(II) ion is located at a crystallographic inversion centre. Two imidazole and two water molecules coordinate to Cu(II) with normal distances and angles and benzenetetracarboxyl anions bridge adjacent Cu(II) atoms, by a pair of carboxyl groups in the *para* position, to form infinite polymeric chains along the *a* axis. Although the benzentetracarboxyl group acts as a unidentate ligand in the title complex, the Cu(1)—O(1) coordination distance of 2.435(1) Å is about 0.4 Å longer than coordination distances in the equatorial plane as a result of Jahn-Teller distortion. There is no significant difference in coordination distance between imidazole nitrogen atoms and water oxygen atoms. Most coordination bond distances in the present complex range from 1.996(1) to 2.020(1) Å and are comparable to those reported previously [11]. Carboxyl groups display significantly different C—O distances, the longer C—O distance being associated with coordinated O, as expected. The carboxyl groups of the benzenetetracarboxyl group are non-coplanar with the benzene ring, the dihedral angles between the coordinated carboxyl groups and benzene ring and between the uncoordinated carboxyl

TABLE I Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2). U_{eg} is defined as one third of the trace of the orthogonalized U_{ij} tensor

Atom	*x/a*	*y/b*	*z/c*	U_{eq}
Cu1	0.5000	0.0000	0.5000	0.02423 (8)
Cu2	0.0000	0.0000	0.0000	0.02790 (9)
O1	0.27164 (12)	-0.18808 (13)	0.47977 (12)	0.0296 (2)
O2	0.38734 (12)	-0.29374 (14)	0.56366 (14)	0.0333 (3)
O3	0.29661 (15)	-0.48467 (15)	0.73605 (15)	0.0409 (3)
O4	0.29609 (14)	-0.25636 (14)	0.81906 (12)	0.0368 (3)
O5	0.61345 (12)	-0.10637 (13)	0.54889 (12)	0.0288 (2)
O6	-0.15736 (18)	0.06296 (18)	0.14790 (15)	0.0465 (3)
O7	0.90723 (17)	1.05240 (17)	0.39564 (16)	0.0446 (3)
O8	0.80582 (16)	0.79028 (16)	0.42364 (16)	0.0446 (3)
N1	0.52846 (16)	0.12738 (16)	0.70074 (13)	0.0301 (3)
N2	0.58381 (18)	0.21168 (19)	0.92381 (14)	0.0392 (3)
N3	0.02496 (17)	-0.13416 (17)	0.08112 (15)	0.0337 (3)
N4	0.1040 (2)	-0.2028 (2)	0.22503 (17)	0.0430 (4)
N5	0.17749 (15)	0.17283 (16)	0.14256 (14)	0.0312 (3)
N6	0.40270 (18)	0.33875 (19)	0.2373 (2)	0.0500 (4)
C1	0.27484 (15)	-0.28156 (16)	0.52078 (14)	0.0233 (3)
C2	0.24900 (16)	-0.39168 (17)	0.72980 (15)	0.0255 (3)
C3	0.13210 (14)	-0.39049 (15)	0.51505 (14)	0.0215 (3)
C4	0.12301 (15)	-0.44786 (16)	0.60765 (14)	0.0219 (3)
C5	0.00939 (16)	-0.44179 (17)	0.40940 (15)	0.0244 (3)
C6	0.5409 (2)	0.0909 (2)	0.79992 (16)	0.0348 (3)
C7	0.6008 (3)	0.3329 (2)	0.9049 (2)	0.0505 (5)
C8	0.5659 (3)	0.2801 (2)	0.76596 (19)	0.0469 (5)
C9	0.1167 (2)	-0.0908 (2)	0.1968 (2)	0.0402 (4)
C10	-0.0502 (4)	-0.2844 (3)	0.0327 (3)	0.0921 (14)
C11	-0.0027 (5)	-0.3264 (3)	0.1218 (3)	0.0964 (15)
C12	0.3096 (2)	0.2132 (2)	0.1252 (2)	0.0440 (4)
C13	0.3276 (2)	0.3798 (2)	0.3314 (2)	0.0500 (5)
C14	0.1880 (2)	0.2775 (2)	0.27179 (19)	0.0403 (4)

TABLE II Selected bond distances (Å) and angles (°)

Cu1—N1	1.9962 (13)	Cu1—O5	2.0202 (12)
Cu1—O1	2.4350 (11)	Cu2—N5	1.9967 (14)
Cu2—N3	2.0432 (15)	Cu2—O6	2.4304 (15)
O1—C1	1.2635 (19)	O2—C1	1.2468 (19)
O3—C2	1.251 (2)	O4—C2	1.2499 (19)
C1—C3	1.5067 (19)	C2—C4	1.5145 (19)
N1—Cu1—N1$^{\#1}$	180.0	N1—Cu1—O5$^{\#1}$	91.27 (5)
N1—Cu1—O5	88.73 (5)	O5$^{\#1}$—Cu1—O5	180.0
N1—Cu1—O1$^{\#1}$	87.71 (5)	O5—Cu1—O1$^{\#1}$	89.28 (4)
N1—Cu1—O1	92.29 (5)	O5—Cu1—O1	90.72 (4)
O1$^{\#1}$—Cu1—O1	180.0	N5—Cu2—N3	90.67 (6)
N5—Cu2—O6	92.23 (6)	N3—Cu2—O6	87.83 (6)
C1—O1—Cu1	119.41 (9)	C6—N1—Cu1	128.01 (12)
C8—N1—Cu1	125.38 (12)	C9—N3—Cu2	126.41 (13)
C10—N3—Cu2	129.31 (14)	C12—N5—Cu2	125.29 (13)
C14—N5—Cu2	128.64 (13)	O2—C1—O1	125.26 (13)

Symmetry transformation used to generate equivalent atoms: #1: $-x+1$, $-y$, $-z+1$.

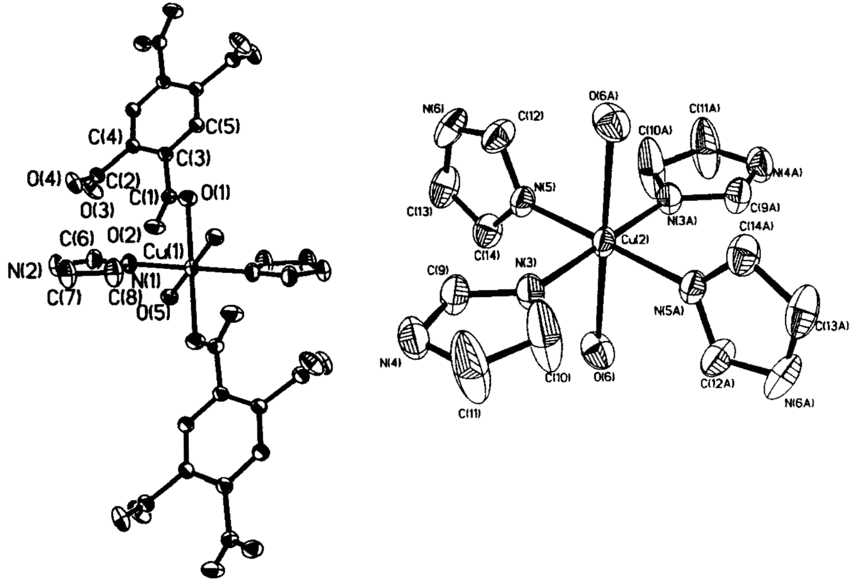

FIGURE 1 The structures of complex anion (left) and cation (right) showing 30% probability displacement ellipsoids; H atoms are omitted for clarity.

group and benzene ring being 32.2° and 64.2°, respectively. The plane C(1)—O(1)—Cu(1) is non-coplanar with the benzene ring as well; the dihedral angle is 29.2°.

In the complex cation, the octahedral Cu(II) ion also is located at a crystallographic inversion centre and is coordinated by four imidazole N atoms and two water molecules with *trans* configuration. The Cu(2)—O(6) distance of 2.430(2) Å is also about 0.4 Å longer than coordination distances in the equatorial plane. All imidazole molecules have normal geometric parameters.

The crystal structure consists of parallel polymeric chains of anions, discrete complex cations and crystalline water molecules. The complex cations are packed between the polymeric chains and linked to them through H-bonds between imidazole N atoms, coordinated water molecules of the complex cations and uncoordinated carboxyl groups of the polymeric anions. Extensive H-bonding network also exists between complexes and crystalline water molecules (supplementary material).

Infrared Spectrum

Carboxyl group stretches were observed at 1615 [$\nu(C{=}O)$] and 1370 cm^{-1} [$\nu(C{-}O)$] in the title complex, in agreement with values reported previously [3]. The $\Delta\nu$ value [$\nu(C{=}O) - \nu(C{-}O)$] of 245 cm^{-1} suggests unidentate coordination of the carboxyl group [12, 13], also in agreement with the crystal structure.

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Supplementary Material

Full lists of crystallographic data are available from the authors upon request.

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