

catena-Poly[[bis(1*H*-imidazole- κ N³)-copper(II)]- μ -benzene-1,4-dicarboxylato- κ^2 O¹:O⁴]

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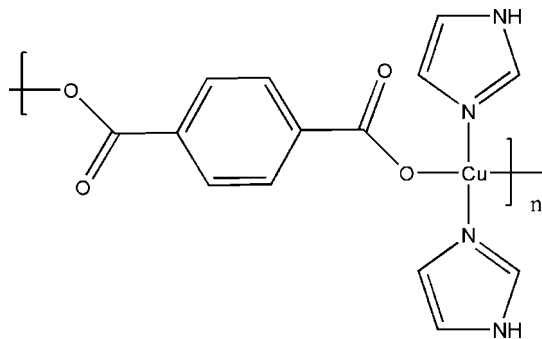
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Key indicators: single-crystal X-ray study; $T = 293$ K; mean $\sigma(\text{C}-\text{C}) = 0.004$ Å; R factor = 0.033; wR factor = 0.085; data-to-parameter ratio = 14.9.

In the title compound, $[\text{Cu}(\text{C}_8\text{H}_4\text{O}_4)(\text{C}_3\text{H}_4\text{N}_2)_2]_n$, the Cu^{II} atom is four-coordinated by two carboxylate O atoms from two different terephthalate ligands and two N atoms from two imidazole ligands in a slightly distorted square-planar coordination environment. Each terephthalate ligand acts as a bis-monodentate ligand that binds two Cu^{II} atoms, thus forming two unique chains extending parallel to $[110]$. The imidazole ligands are attached on both sides of the chains.

Related literature

For general background to ferroelectric metal-organic compounds with framework structures, see: Fu *et al.* (2009); Ye *et al.* (2006); Zhang *et al.* (2008, 2010).



Experimental

Crystal data

$[\text{Cu}(\text{C}_8\text{H}_4\text{O}_4)(\text{C}_3\text{H}_4\text{N}_2)_2]$
 $M_r = 363.82$
Monoclinic, $C2/c$
 $a = 21.435$ (4) Å
 $b = 5.2740$ (11) Å
 $c = 14.164$ (3) Å
 $\beta = 116.65$ (3)°

$V = 1431.1$ (5) Å³
 $Z = 4$
Mo $K\alpha$ radiation
 $\mu = 1.55$ mm⁻¹
 $T = 293$ K
 $0.30 \times 0.25 \times 0.20$ mm

Data collection

Rigaku SCXmini diffractometer
Absorption correction: multi-scan
(*CrystalClear*; Rigaku, 2005)
 $T_{\text{min}} = 0.634$, $T_{\text{max}} = 0.733$

6976 measured reflections
1641 independent reflections
1440 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.048$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.033$
 $wR(F^2) = 0.085$
 $S = 1.08$
1641 reflections
110 parameters

H atoms treated by a mixture of independent and constrained refinement
 $\Delta\rho_{\text{max}} = 0.26$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.32$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

| $D-H\cdots A$ | $D-H$ | $H\cdots A$ | $D\cdots A$ | $D-H\cdots A$ |
|---|----------|-------------|-------------|---------------|
| $\text{N2}-\text{H2A}\cdots\text{O1}^i$ | 0.78 (4) | 2.11 (4) | 2.851 (3) | 157 (4) |

 Symmetry code: (i) $x, -y + 1, z - \frac{1}{2}$.

Data collection: *CrystalClear* (Rigaku, 2005); cell refinement: *CrystalClear*; data reduction: *CrystalClear*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXL97*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: JH2303).

References

- Fu, D.-W., Ge, J.-Z., Dai, J., Ye, H.-Y. & Qu, Z.-R. (2009). *Inorg. Chem. Commun.* **12**, 994–997.
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supplementary materials

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catena-Poly[[bis(1H-imidazole- κ N³)copper(II)]- μ -benzene-1,4-dicarboxylato- κ^2 O¹:O⁴]

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Comment

Dielectric constant measurements of compounds as a function of temperature is the basic method to find potential ferroelectric phase change materials (Fu *et al.*, 2009; Ye *et al.*, 2006; Zhang *et al.*, 2008; Zhang *et al.*, 2010). Unfortunately, the study carried out on the title compound indicated that the permittivity is temperature-independent, suggesting that there may be no dielectric disuniformity between 80 K to 350 K (m.p. 393–381 K). In this report the crystal structure of the title compound is reported.

An *ORTEP* diagram showing the structure of the title compound with the symmetry related fragments and atom-numbering scheme is shown in Fig. 1. The Cu(II) atom, with an inversion center, adopts a distorted octahedral geometry comprising two nitrogen atoms of two pyrazole ligands [Cu1–N1 = 1.9859 (19) Å] and two oxygen atoms of two different tp ligands [Cu1–O1 = 1.9408 (14) Å]. The N2O2 moiety defines the equatorial plane of the octahedron. In the equatorial plane, the angles between the *cis*-positioned atoms are close to 90° and those of the transpositioned atoms are identical to 180° since the Cu atom resides at the inversion center.

Experimental

An aqueous solution of imidazole (1.64 g, 20 mmol) and terephthalic acid (10 mmol) was treated with CuCl₂ (1.35 g, 10 mmol). After the mixture was churned for a few minutes, slow evaporation of the resulting solution yielded blue crystals after a few days.

Refinement

All H atoms were placed in geometrically idealized positions and constrained to ride on their parent atoms except H2A with C–H = 0.93 Å, with $U_{\text{iso}}(\text{H}) = 1.2 U_{\text{iso}}(\text{C})$.

Figures

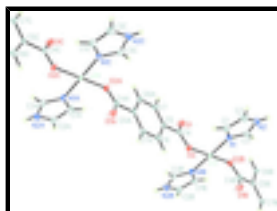


Fig. 1. The molecular structure of the title compound, showing the atomic numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. Symmetry codes for A: 1 - x, 2 - y, 2 - z. Symmetry codes for B: 1.5 - x, 1.5 - y, 2 - z. Symmetry codes for C: 0.5 - x, 2.5 - y, 2 - z.

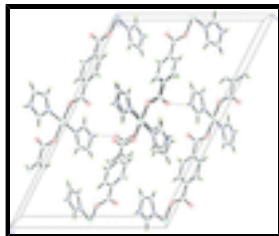


Fig. 2. A view of the packing of the title compound, stacking along the *b* axis. Dashed lines indicate hydrogen bonds.

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Crystal data

| | |
|--|---|
| [Cu(C ₈ H ₄ O ₄)(C ₃ H ₄ N ₂) ₂] | $Z = 4$ |
| $M_r = 363.82$ | $F(000) = 740$ |
| Monoclinic, $C2/c$ | $D_x = 1.689 \text{ Mg m}^{-3}$ |
| Hall symbol: $-C 2yc$ | Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$ |
| $a = 21.435 (4) \text{ \AA}$ | $\theta = 2.8\text{--}27.5^\circ$ |
| $b = 5.2740 (11) \text{ \AA}$ | $\mu = 1.55 \text{ mm}^{-1}$ |
| $c = 14.164 (3) \text{ \AA}$ | $T = 293 \text{ K}$ |
| $\beta = 116.65 (3)^\circ$ | Block, blue |
| $V = 1431.1 (5) \text{ \AA}^3$ | $0.30 \times 0.25 \times 0.20 \text{ mm}$ |

Data collection

| | |
|---|--|
| Rigaku SCXmini diffractometer | 1641 independent reflections |
| Radiation source: fine-focus sealed tube graphite | 1440 reflections with $I > 2\sigma(I)$ |
| CCD_Profile_fitting scans | $R_{\text{int}} = 0.048$ |
| Absorption correction: multi-scan (<i>CrystalClear</i> ; Rigaku, 2005) | $\theta_{\text{max}} = 27.5^\circ$, $\theta_{\text{min}} = 4.0^\circ$ |
| $T_{\text{min}} = 0.634$, $T_{\text{max}} = 0.733$ | $h = -27 \rightarrow 27$ |
| 6976 measured reflections | $k = -6 \rightarrow 6$ |
| | $l = -18 \rightarrow 18$ |

Refinement

| | |
|---------------------------------|--|
| Refinement on F^2 | Secondary atom site location: difference Fourier map |
| Least-squares matrix: full | Hydrogen site location: inferred from neighbouring sites |
| $R[F^2 > 2\sigma(F^2)] = 0.033$ | H atoms treated by a mixture of independent and constrained refinement |
| $wR(F^2) = 0.085$ | $w = 1/[\sigma^2(F_o^2) + (0.040P)^2 + 0.9748P]$ |
| $S = 1.08$ | where $P = (F_o^2 + 2F_c^2)/3$ |
| 1641 reflections | $(\Delta/\sigma)_{\text{max}} < 0.001$ |
| 110 parameters | $\Delta\rho_{\text{max}} = 0.26 \text{ e \AA}^{-3}$ |
| 0 restraints | $\Delta\rho_{\text{min}} = -0.32 \text{ e \AA}^{-3}$ |
| | Extinction correction: <i>SHELXL97</i> (Sheldrick, 2008) |

Primary atom site location: structure-invariant direct methods Extinction coefficient: 0

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R -factor wR and goodness of fit S are based on F^2 , conventional R -factors R are based on F , with F set to zero for negative F^2 . The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R -factors(gt) *etc.* and is not relevant to the choice of reflections for refinement. R -factors based on F^2 are statistically about twice as large as those based on F , and R -factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

| | <i>x</i> | <i>y</i> | <i>z</i> | $U_{\text{iso}}^*/U_{\text{eq}}$ |
|-----|--------------|------------|--------------|----------------------------------|
| C1 | 0.37485 (12) | 0.7554 (5) | 0.82142 (19) | 0.0385 (5) |
| H1 | 0.3432 | 0.8726 | 0.8240 | 0.046* |
| C2 | 0.35883 (15) | 0.5594 (5) | 0.7531 (2) | 0.0460 (6) |
| H2 | 0.3148 | 0.5180 | 0.7002 | 0.055* |
| C3 | 0.47038 (14) | 0.5553 (5) | 0.8563 (2) | 0.0387 (6) |
| H3 | 0.5170 | 0.5067 | 0.8866 | 0.046* |
| C4 | 0.38692 (10) | 1.0497 (4) | 1.04391 (18) | 0.0269 (5) |
| C5 | 0.31559 (10) | 1.1531 (4) | 1.02048 (16) | 0.0249 (4) |
| C6 | 0.29077 (11) | 1.3731 (4) | 0.96075 (18) | 0.0303 (5) |
| H6 | 0.3179 | 1.4565 | 0.9344 | 0.036* |
| C7 | 0.27444 (12) | 1.0321 (4) | 1.05946 (19) | 0.0301 (5) |
| H7 | 0.2908 | 0.8856 | 1.0997 | 0.036* |
| N1 | 0.44579 (9) | 0.7532 (3) | 0.88681 (14) | 0.0303 (4) |
| N2 | 0.41890 (14) | 0.4355 (5) | 0.77617 (19) | 0.0447 (6) |
| O1 | 0.41430 (8) | 0.8830 (3) | 1.11055 (14) | 0.0426 (4) |
| O2 | 0.41356 (7) | 1.1465 (3) | 0.98747 (12) | 0.0306 (3) |
| Cu1 | 0.5000 | 1.0000 | 1.0000 | 0.02373 (14) |
| H2A | 0.4238 (19) | 0.322 (7) | 0.744 (3) | 0.074 (11)* |

Atomic displacement parameters (\AA^2)

| | U^{11} | U^{22} | U^{33} | U^{12} | U^{13} | U^{23} |
|----|-------------|-------------|-------------|--------------|-------------|--------------|
| C1 | 0.0315 (12) | 0.0408 (13) | 0.0383 (13) | 0.0008 (10) | 0.0112 (10) | -0.0025 (11) |
| C2 | 0.0446 (16) | 0.0497 (15) | 0.0364 (14) | -0.0083 (12) | 0.0118 (12) | -0.0049 (11) |
| C3 | 0.0433 (14) | 0.0348 (12) | 0.0468 (15) | 0.0008 (10) | 0.0281 (12) | -0.0052 (10) |
| C4 | 0.0204 (10) | 0.0273 (10) | 0.0356 (12) | 0.0022 (8) | 0.0149 (9) | -0.0036 (8) |
| C5 | 0.0185 (9) | 0.0276 (10) | 0.0313 (11) | 0.0029 (7) | 0.0136 (8) | -0.0019 (8) |
| C6 | 0.0234 (10) | 0.0324 (11) | 0.0412 (12) | 0.0028 (9) | 0.0200 (9) | 0.0061 (10) |
| C7 | 0.0252 (11) | 0.0280 (11) | 0.0411 (13) | 0.0065 (8) | 0.0184 (10) | 0.0076 (9) |
| N1 | 0.0278 (9) | 0.0327 (9) | 0.0348 (10) | 0.0012 (7) | 0.0179 (8) | -0.0024 (8) |
| N2 | 0.0651 (16) | 0.0371 (11) | 0.0443 (13) | -0.0095 (11) | 0.0354 (12) | -0.0117 (10) |

supplementary materials

| | | | | | | |
|-----|------------|-------------|-------------|--------------|--------------|--------------|
| O1 | 0.0308 (8) | 0.0477 (10) | 0.0555 (11) | 0.0185 (8) | 0.0248 (8) | 0.0186 (9) |
| O2 | 0.0226 (7) | 0.0345 (8) | 0.0408 (9) | 0.0066 (6) | 0.0197 (7) | 0.0009 (7) |
| Cu1 | 0.0187 (2) | 0.0272 (2) | 0.0299 (2) | 0.00423 (13) | 0.01502 (16) | 0.00013 (14) |

Geometric parameters (\AA , $^\circ$)

| | | | |
|------------------------|-------------|--|-------------|
| C1—C2 | 1.351 (4) | C5—C7 | 1.388 (3) |
| C1—N1 | 1.381 (3) | C5—C6 | 1.393 (3) |
| C1—H1 | 0.9300 | C6—C7 ⁱ | 1.388 (3) |
| C2—N2 | 1.347 (4) | C6—H6 | 0.9300 |
| C2—H2 | 0.9300 | C7—C6 ⁱ | 1.388 (3) |
| C3—N1 | 1.326 (3) | C7—H7 | 0.9300 |
| C3—N2 | 1.335 (4) | N1—Cu1 | 1.9857 (19) |
| C3—H3 | 0.9300 | N2—H2A | 0.78 (4) |
| C4—O1 | 1.229 (3) | O2—Cu1 | 1.9408 (14) |
| C4—O2 | 1.279 (3) | Cu1—O2 ⁱⁱ | 1.9408 (14) |
| C4—C5 | 1.513 (3) | Cu1—N1 ⁱⁱ | 1.9857 (19) |
| C2—C1—N1 | 108.9 (2) | C5—C6—H6 | 120.0 |
| C2—C1—H1 | 125.5 | C6 ⁱ —C7—C5 | 120.9 (2) |
| N1—C1—H1 | 125.5 | C6 ⁱ —C7—H7 | 119.6 |
| N2—C2—C1 | 106.8 (2) | C5—C7—H7 | 119.6 |
| N2—C2—H2 | 126.6 | C3—N1—C1 | 105.5 (2) |
| C1—C2—H2 | 126.6 | C3—N1—Cu1 | 127.21 (17) |
| N1—C3—N2 | 110.6 (2) | C1—N1—Cu1 | 127.28 (15) |
| N1—C3—H3 | 124.7 | C3—N2—C2 | 108.2 (2) |
| N2—C3—H3 | 124.7 | C3—N2—H2A | 125 (3) |
| O1—C4—O2 | 124.91 (19) | C2—N2—H2A | 126 (3) |
| O1—C4—C5 | 120.90 (19) | C4—O2—Cu1 | 117.36 (13) |
| O2—C4—C5 | 114.17 (18) | O2 ⁱⁱ —Cu1—O2 | 180.000 (1) |
| C7—C5—C6 | 119.12 (18) | O2 ⁱⁱ —Cu1—N1 | 90.10 (7) |
| C7—C5—C4 | 120.45 (19) | O2—Cu1—N1 | 89.90 (7) |
| C6—C5—C4 | 120.42 (18) | O2 ⁱⁱ —Cu1—N1 ⁱⁱ | 89.90 (7) |
| C7 ⁱ —C6—C5 | 120.00 (19) | O2—Cu1—N1 ⁱⁱ | 90.10 (7) |
| C7 ⁱ —C6—H6 | 120.0 | N1—Cu1—N1 ⁱⁱ | 180.0 |

Symmetry codes: (i) $-x+1/2, -y+5/2, -z+2$; (ii) $-x+1, -y+2, -z+2$.

Hydrogen-bond geometry (\AA , $^\circ$)

| $D-H\cdots A$ | $D-H$ | $H\cdots A$ | $D\cdots A$ | $D-H\cdots A$ |
|-----------------------------------|----------|-------------|-------------|---------------|
| N2—H2A \cdots O1 ⁱⁱⁱ | 0.78 (4) | 2.11 (4) | 2.851 (3) | 157 (4) |

Symmetry codes: (iii) $x, -y+1, z-1/2$.

Fig. 1

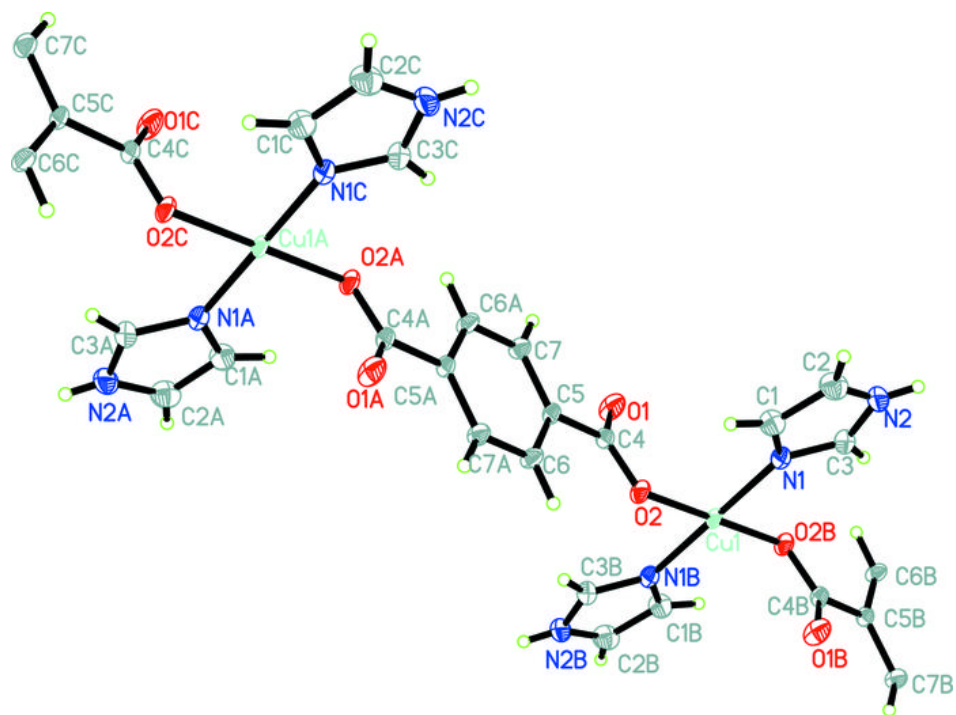


Fig. 2

