

1-(4-Chlorobenzyl)pyridinium bis(maleonitriledithiolato)cuprate(III)

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Key indicators

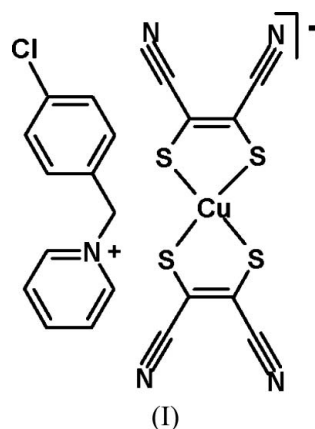
Single-crystal X-ray study
T = 293 K
Mean $\sigma(\text{C}-\text{C}) = 0.004 \text{ \AA}$
R factor = 0.034
wR factor = 0.090
Data-to-parameter ratio = 18.8For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.In the title complex, $(\text{C}_{12}\text{H}_{11}\text{ClN})[\text{Cu}(\text{C}_4\text{N}_2\text{S}_2)_2]$, both anions and cations form segregated and regular columnar stacks.

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Comment

Some charge-transfer salts with their cations and anions packed in segregated stacks exhibit unusual properties in magnetism and conductivity (Gama *et al.*, 1992; Coomber *et al.*, 1996; Kawamura *et al.*, 1997; Ren *et al.*, 2002; Xie *et al.*, 2002, 2003). In our previous studies, benzylpyridinium derivatives have been employed as the counter-cation of $[\text{M}(\text{mnt})_2]^-$ ions ($M = \text{Ni}^{3+}$ or Pt^{3+} ; $\text{mnt}^{2-} =$ maleonitriledithiolate) in the preparation of a series of compounds with segregated stacks displaying magnetic transitions (Ren *et al.*, 2002, 2004, 2005, 2006; Xie *et al.*, 2002, 2003). Although all compounds exhibit the same structural features at room temperature, with the anions regularly stacked in columns, magneto-structural transitions were observed only for some compounds while others displayed magnetic transitions that did not affect the molecular assembly. In the former, the magnetic transition is associated with the dimerization of the regular magnetic anionic stacks, a process similar to a spin-Peierls transition.



In the title compound, (I) (Fig. 1), the $[\text{Cu}(\text{mnt})_2]^-$ anion has a square-planar geometry. The Cu—S bond lengths range from 2.1740 (7) to 2.1865 (7) Å (Table 1). The cation adopts a conformation in which the benzene and pyridine rings are almost perpendicular to the reference plane (N5, C14, C15), making angles of 83.0 (2) and 86.63 (17)°, respectively. The benzene ring makes a dihedral angle of 65.88 (9)° with the pyridine ring. The anions and cations stack into segregated columns along the *c*-axis direction, as shown in Fig. 2, with the metal ions uniformly spaced along the columns. The

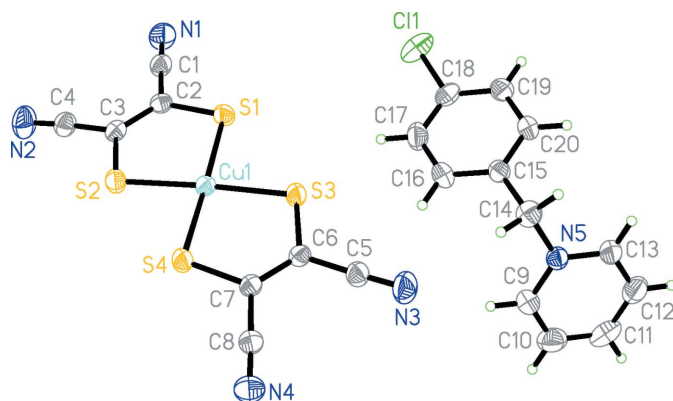


Figure 1
The asymmetric unit of complex (I), showing 30% probability displacement ellipsoids and the atom-numbering scheme.

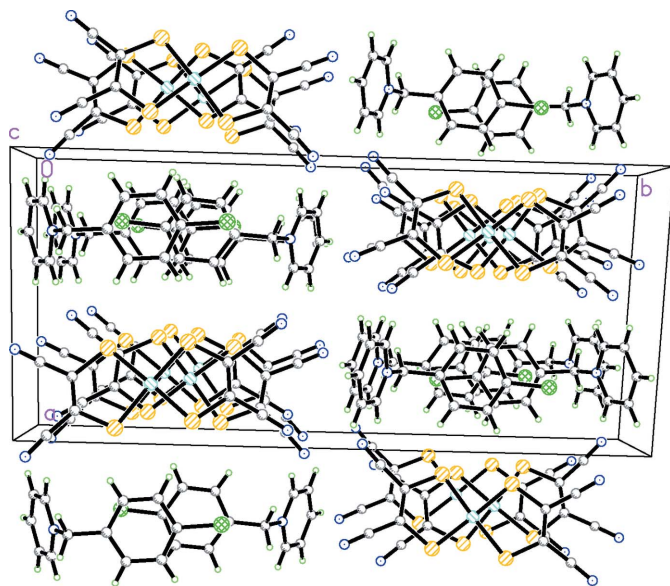


Figure 2
The packing of the anions and cations, projected along the *c* axis.

$\text{Cu1} \cdots \text{Cu1}^i$ [symmetry code: (i) $x, \frac{1}{2} - y, -\frac{1}{2} + z$] distance is 3.9411 (7) Å, and the centroid-to-centroid distance between adjacent overlapping benzene rings is 4.1731 (12) Å.

Experimental

Disodium maleonitriledithiolate (Na_2mnt) was prepared following a literature procedure (Davison *et al.*, 1967). 1-(4-Chlorobenzyl)pyridinium chloride was prepared by reacting 4-chlorobenzyl chloride with 1.5 equivalents of pyridine in refluxing acetone for 4 h. The resulting white microcrystalline product was filtered, washed with acetone and diethyl ether, and dried in a vacuum (yield *ca* 82%). $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, Na_2mnt and 1-(4-chlorobenzyl)pyridinium chloride (equivalent molar ratio 1:2:2) were mixed in water; the brown precipitated product was separated, washed with water and then dissolved in a little MeCN. Iodine (1.5 molar equivalents) was added to the solution with stirring. Five times the resulting volume of MeOH was then added and the mixture allowed to stand for 24 h. The

resulting microcrystals were separated, washed with MeOH and dried in a vacuum, (yield approximately 40%). A saturated MeCN solution of (I) was placed in a refrigerator at 277 K for 5 d, and single crystals of (I) suitable for structure analysis were obtained.

Crystal data

$(\text{C}_{12}\text{H}_{11}\text{ClN})[\text{Cu}(\text{C}_4\text{N}_2\text{S}_2)_2]$
 $M_r = 548.57$
Monoclinic, $P2_1/c$
 $a = 12.084$ (2) Å
 $b = 26.171$ (5) Å
 $c = 7.4355$ (15) Å
 $\beta = 102.57$ (3)°
 $V = 2295.0$ (8) Å³

$Z = 4$
 $D_x = 1.588$ Mg m⁻³
Mo $K\alpha$ radiation
 $\mu = 1.45$ mm⁻¹
 $T = 293$ (2) K
Block, brown
 $0.25 \times 0.15 \times 0.10$ mm

Data collection

Bruker SMART CCD area-detector diffractometer
 φ and ω scans
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)
 $T_{\min} = 0.76$, $T_{\max} = 0.87$

22178 measured reflections
5255 independent reflections
3855 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.032$
 $\theta_{\max} = 27.5^\circ$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.034$
 $wR(F^2) = 0.091$
 $S = 1.04$
5255 reflections
280 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0438P)^2 + 0.4985P]$
where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 0.46$ e Å⁻³
 $\Delta\rho_{\min} = -0.33$ e Å⁻³

Table 1

Selected bond lengths (Å).

Cu1—S4	2.1740 (7)	Cu1—S3	2.1783 (8)
Cu1—S2	2.1765 (8)	Cu1—S1	2.1865 (7)

All H atoms were placed in geometrically calculated positions ($\text{C—H} = 0.93$ and 0.97 Å), and refined as riding, with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$.

Data collection: SMART (Siemens, 1996); cell refinement: SMART; data reduction: SAINT (Siemens, 1996); program(s) used to solve structure: SHELXS97 (Sheldrick, 1997a); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997a); molecular graphics: SHELXTL (Sheldrick, 1997b); software used to prepare material for publication: SHELXL97.

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