

Synthesis, Crystal Structure and Property Studies on a Tetrachlorocuprate Salt of an Organic Cation

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Organic-inorganic hybrids provide an exciting opportunity to combine useful attributes of organic and inorganic materials within a single molecular scale composite. Thus, organic-inorganic salts become a relatively large structural family in which a number of interesting magnetic, optical, and electrical phenomena have been observed.¹⁻⁴ Among numerous robust and flexible synthetic strategies to obtain organic-inorganic salts, Orpen and Brammer groups⁴⁻⁶ have used salts of anionic metal complexes with peripheral hydrogen-bond acceptor capability (and no hydrogen-bond donors) in which the relative orientation and location of the ions is controlled at least in part by M-Cl...HN (M=Pt, Pd) hydrogen bonding. This strategy affords diversity through modularity, with a wide variety of ions of various shapes, charges, and properties being available to replace either a cation or an anion. For example, Orpen group explored the consequences on the structures as a result of modifying the geometries of the anion (monatomic Cl⁻, square planar, trigonal bipyramidal, octahedral, and polymeric),⁷⁻⁹ the type and orientation of the ligand hydrogen-bond acceptors,^{10,11} and the location of the cation NH groups.¹² Recently, our group obtained a tetrachlorocuprate salt of an organic cation, [DBPMFH₂]²⁺ [CuCl₄]²⁻·H₂O {DBPMF = 2,7-dibromo-9,9-(4-pyridylmethyl)fluorine}, where Cu-Cl...HN hydrogen bonding helps to form net works and stabilize the molecular structure. Herein, we wish to report the synthesis, crystal

structure, fluorescence and thermal stability of [DBPMFH₂]²⁺ [CuCl₄]²⁻·H₂O.

Crystal structure of the title complex [DBPMFH₂]²⁺ [CuCl₄]²⁻·H₂O crystallizes in orthorhombic system, space group *Pbca*, with lattice parameters *a* = 22.720(4) Å, *b* = 18.070(4) Å, *c* = 27.590(5) Å, *V* = 11327(4) Å³, *Mr* = 731.60 (C₂₅H₂₂Br₂Cl₄CuN₂O), *Z* = 16, *D_c* = 1.716 g/cm³, *μ* = 3.993 mm⁻¹, *F*(000) = 5776, GOF = 0.939, *R*₁ = 0.0592, *wR*₂ = 0.0899. A displacement ellipsoid plot, with the atomic numbering scheme, is shown in Figure 1.

The structure of the title compound contains a pair of crystallographically independent [DBPMFH₂]²⁺ [CuCl₄]²⁻ salts and two water molecules in the asymmetric unit. All of the bond lengths and bond angles in the protonated [DBPMFH₂]²⁺ cation are in the normal range. As for the two independent [CuCl₄]²⁻ anions, both the Cu²⁺ ions adopt obviously distorted tetrahedron conformations. All of the bond angles of Cl-Cu-Cl differ significantly from tetrahedral angle (109.48°) and vary from 94.22(7) to 146.26(8)°. This phenomena can also be found in the similar organic-inorganic salts of bis[cinchoninium tetrachlorocuprate(II)] trihydrate¹³ and bis-dipropylammonium tetrachlorocuprate (II).¹⁴ In the title compound, all of the bond lengths of Cu-Cl [2.2102(18)-2.2735(18) Å] are comparable to the similar organic-inorganic salts cited above.

The most notable structure feature of the title compound is that there are many types of the intramolecular and intermolecular hydrogen bonds, potential weak C-H...Cl (Br), C-H...π intermolecular interactions and π...π stacking interactions between the molecules. Among all of the intermolecular interactions, hydrogen bonds of N-H...Cl-Cu, N-H...O and O-H...Cl-Cu make the two water molecules, two [CuCl₄]²⁻ anions and two [H₂DBPMF]²⁺ cations to form a short chain as shown in Figure 2. In the crystal lattice, these chains are staggered each other to form 3-dimension networks. All of the hydrogen bonds, intermolecular interactions and π...π stacking interactions stabilize the molecular structure.

Fluorescence spectra of the title complex were measured on a F96-fluorospectrophotometer in DMF solution, as shown in Figure 3, which displays a broad emission band with the maximum intensity at λ = 367 nm in the DMF solution upon excitation at λ = 365 nm.

Figure 4 gives the thermal analysis curve of the title compound. In Figure 4, there are mainly two exothermic peaks,

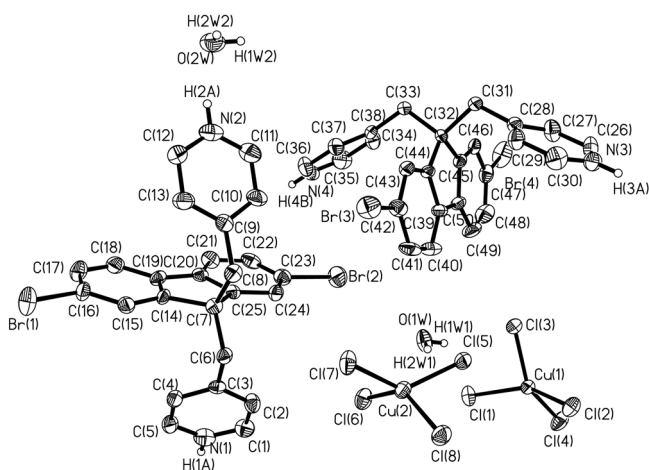


Figure 1. Molecular structure for the title compound with the atomic numbering scheme.

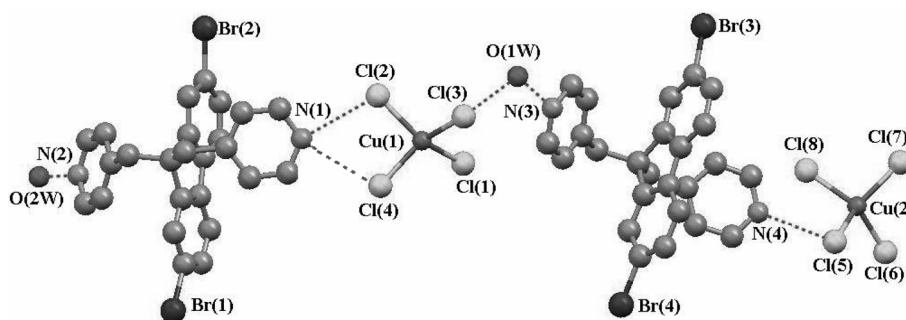


Figure 2. Short chain built through hydrogen bonds for the title compound.

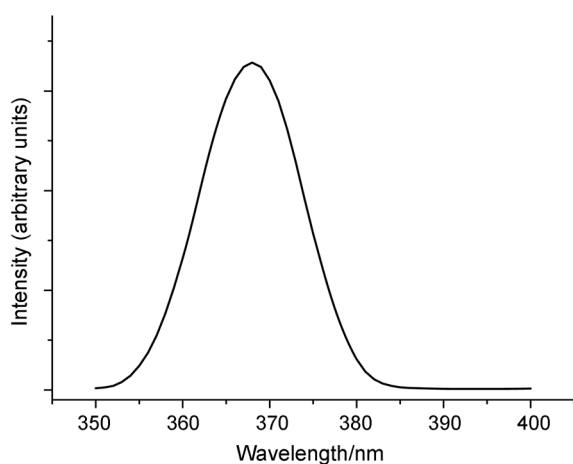


Figure 3. Fluorescence emission spectra of the title compound in DMF solution.

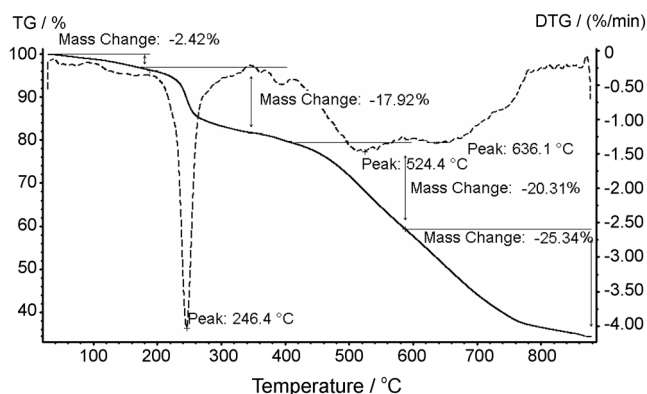


Figure 4. The thermal analysis curve of the title compound.

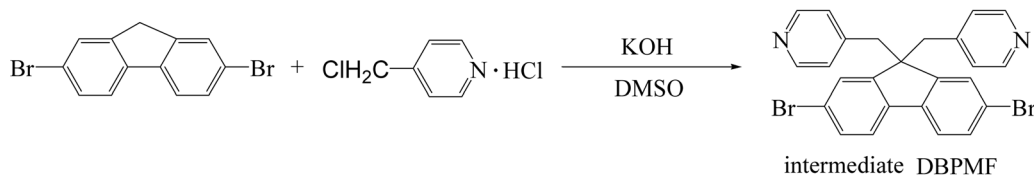
one is a sharp peak at 246.4 °C and another is a continuous broad peak from 524.4 to 636.1 °C, corresponding to two weight-loss processes. The title compound exhibits the first weight loss (20.34%) at 100-360 °C, which is approximately

corresponding to the loss of one water molecule and four Cl atoms (calcd. 21.85%). The second weight loss (45.65%) occurs at 360-820 °C, which is attributed to the loss of $[\text{H}_2\text{DBPMF}]^{2+}$ cation except two Br atoms (calcd. 47.54%). The residue may be CuBr_2 (calcd. 30.61%).

Experimental Section

Preparation of the intermediate 2,7-dibromo-9,9-(4-pyridyl-methyl)fluorene [DBPMF]. The reaction path is shown in Scheme 1. 2,7-Dibromofluorene (0.1 mol) and 4-chloromethyl pyridine hydrochloride (0.2 mol) were mixed in DMSO (70 mL) with stirring at room temperature. Addition of the powders of KOH (0.55 mol) to the resulting mixture produced a viscous solution. After 3 h, the reaction was stopped and the mixtures were poured into 200 mL cool water and stirred fleetly. After filtering and drying, the white products were obtained. Yield: 99%. mp. 136-137 °C. ^1H NMR (400 MHz, DMSO) δ 3.20 (s, 2H), 7.25-7.28 (d, 4H), 7.55-7.57 (d, 2H), 7.53-7.56 (d, 4H), 8.60-8.64 (d, 4H); IR: ν 3329 (vs), 3172 (vs), 3106 (vs), 1672 (vs), 1573 (vs), 1466 (vs), 1425 (s), 1283 (vs), 1028 (s), 1002 (m), 962 (w), 871 (w), 597 (m), 472 (w) cm^{-1} . Found: C, 59.12; H, 3.19; N, 5.38%. Calc. for $\text{C}_{25}\text{H}_{18}\text{Br}_2\text{N}_2$: C, 59.31; H, 3.58; N, 5.54%.

Preparation of $\{[\text{H}_2\text{DBPMF}]^{2+}[\text{CuCl}_4]^{2-} \cdot \text{H}_2\text{O}\}$. To a warm solution of intermediate [DBPMF] [0.51 g, 1.0 mmol] in DMF (50 mL) was added with stirring CuCl_2 (0.16 g, 1.0 mmol) and yellow-green depositions were observed immediately. After two drops of hydrochloric acid [6 mol/L] were added into the mixture, the depositions were dissolved and the solution became to clear yellow-green. The resulting yellow-green solution was filtered, and the filtrate was evaporated at room temperature in air. Three days later, crystals suitable for an X-ray structure determination were obtained. IR: ν 3444 (vs), 3351 (vs), 1617 (m), 1557 (m), 1422 (m), 1224 (w), 1067 (w), 990 (m), 818 (m), 593 (w),



Scheme 1

473 (m) cm^{-1} . Found: C, 40.98; H, 3.19; N, 3.76%. Calc. for $\text{C}_{25}\text{H}_{22}\text{Br}_2\text{Cl}_4\text{CuN}_2\text{O}$: C, 41.04; H, 3.03; N, 3.83%.

Crystal structure determination. The diffraction data were collected on a Enraf-Nonius CAD-4 diffractometer with graphite-monochromated $\text{Mo-K}\alpha$ radiation ($\lambda = 0.71073$ Å, $T = 293$ K). The technique used was ω -scan with limits 1.48 to 28.33°. The structure of the title compound was solved by direct methods and refined by least-squares refinements on F^2 by using the *SHELXTL*¹⁵ software package. All non-hydrogen atoms were anisotropically refined. The hydrogen atom positions were fixed geometrically at calculated distances and allowed to ride on the parent carbon atoms. The weighting scheme, $w = 1/[\sigma^2(F_o^2) + (0.0340 P)^2]$, where $P = (F_o^2 + 2F_c^2)/3$. The molecular graphics were plotted using *SHELXTL*. Atomic scattering factors and anomalous dispersion corrections were taken from *International Tables for X-ray Crystallography*.¹⁶

Crystallographic data for the structure reported here have been deposited with CCDC (Deposition No. CCDC-672341). These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html> or from CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, e-mail: deposit@ccdc.cam.ac.uk.

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