One-Dimensional Anionic Metal-Organic Chain Generated from (Tetraphenylphosphonium)₂benzoquinonediiminedisulfonate and CuI

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The title compound, (C₂₄H₂₀P)₂(C₆H₄N₂O₆S₂)CuI·0.34H₂O, was obtained by the slow evaporation of a solvent from an acetonitrile solution containing a mixture of (PPh₄)₂N,N'-disulfobenzoquinonediimine and CuI. The structure consists of a one-dimensional metal-organic framework of the dianion and CuI. The anionic chains are surrounded by relatively large counter-cations, and are thus well isolated from each other.

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N,N'-Dicyanoquinonediimines (DCNQI, Fig. 1) are one of the most well-known electron acceptors. They have provided conducting charge-transfer (CT) complexes and radical anion salts, which have attracted worldwide interest.¹ For example, (DMeDCNQI)₂Cu (Fig. 1) shows an unusual reentrant metal-insulator-metal transition. These types of salts are usually prepared *via* an electrochemical method. Alternatively, they may be obtained by chemical reactions of DMeDCNQI with CuI in organic solvents, in which the DMeDCNQI acceptor is reduced by the CuI.² Recently, we prepared a new anionic acceptor, N,N'-disulfobenzoquinone diimines [dsqi (**1**)], which has two -SO₃⁻ groups instead of the two -CN groups of DCNQI. **1** is a dianion and also an electron acceptor, by virtue of the -SO₃⁻ groups and an acceptor part, the quinodiimine skeleton. This anion has been used as the counteranion of a BEDT-TTF-based CT salt [BEDT-TTF = bis(ethylenedithio)tetrathiafulvalene].³ However, until now no attempt was made to prepare its Cu complex, which we report in this paper.

Fig. 1 Structures of DMeDCNQI, DCNQI, the anion **1**, and the title compound **3**.

The tetraphenylphosphonium salt of dianion **1**, (PPh₄)₂**1** (**2**), was prepared according to our previously reported method.³ After 5 mg of **2** and 1 mg of CuI were mixed in CH₃CN (20 ml), the solvent was allowed to slowly evaporate from a 50 ml beaker at room temperature, yielding black block crystals at the bottom of the container. X-ray diffraction data were collected at ambient temperature. The asymmetric unit of the black crystal (**3**) has two PPh₄ cations: two halves of **1** (**1A** and **1B** in Fig. 2), one CuI and 0.34 of a water molecule.⁴ There is a Cu-I covalent bond. The Cu atom is also coordinated by two N atoms of the crystallographically independent two halves of the dianions (**1**). Furthermore, one O atom of each sulfo group of the independent two halves of **1** is close to CuI with Cu1-O1 = 2.644(4) Å and Cu1-O6 = 2.751(4) Å, which is slightly shorter

Table 1 Crystal and experimental data

Chemical formula: C ₅₄ H _{44.68} CuIN ₂ O _{6.34} P ₂ S ₂	
Formula weight = 1139.59	
T = 299 K	
Crystal system: monoclinic	Space group: P2 ₁ /c
a = 16.7521(19) Å	
b = 13.8506(16) Å	β = 97.146(3)°
c = 22.607(3) Å	
V = 5204.8(11) Å ³	Z = 4
D _x = 1.454 g/cm ³	
Radiation: Mo Kα (λ = 0.71073 Å)	
μ(Mo Kα) = 1.206 mm ⁻¹	F(0 0 0) = 2309.60
Crystal size = 0.17 × 0.1 × 0.1 mm ³	
No. of reflections collected = 45936	
No. of independent reflections = 11695	
θ range for data collection: 3.45 to 60.62°	
Data/Restraints/Parameters = 11695/0/624	
Goodness-of-fit on F ² = 1.111	
R indices [I > 2σ(I)]: R1 = 0.0590, wR2 = 0.1437	
R indices [all data]: R1 = 0.0833, wR2 = 0.1624	
(Δ/σ) _{max} = 0.000	
(Δρ) _{max} = 0.880 e Å ⁻³	(Δρ) _{min} = -0.870 e Å ⁻³
Measurement: Rigaku Mercury2/MicroMax-007HF/VariMax system	
Program system: CrystalStructure 4.0	
Structure determination: SIR92	
CCDC number: 957019	

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Fig. 2 View of the one-dimensional chain in **3** consisting of **1**, CuI and H₂O with the atomic numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

Fig. 3 Crystal structure of **3**. Displacement ellipsoids are drawn at the 50% probability level.

than that of the van der Waals distance of 2.92 Å. Thus, the geometry about the Cu atom is a tricoordinated arrangement, as shown in Fig. 2. Each dianion is located about a center of symmetry, and is connected *via* CuI to form one-dimensional anionic chains (Fig. 3). Each chain is surrounded and isolated by PPh₄ cations (Fig. 3).

In (DMeDCNQI)₂Cu, the DMeDCNQI anions form uniform stacks along the crystallographic *c*-axis, which are interlinked *via* Cu atoms that are coordinated tetrahedrally by cyano groups to form a three-dimensional conducting network. Moreover, the observation of satellite reflections due to the *c*-axis having three-folded symmetry indicates that each Cu has a partial charge of +4/3, and therefore DMeDCNQI also has a partial charge of -2/3. Thus, an electron transfer occurs from Cu to DMeDCNQI, and the resulting electrons are delocalized across the whole crystal. Partial oxidation/reduction plays a crucial role in the salt's high conductivity.⁵ Similarly, compound **3** should be electrically conductive through the one-dimensional chain if Cu is in a partial oxidation state. An electrical resistivity measurement was performed by the conventional two-probe method. The observed resistivity at room temperature is more than 10⁶ Ω cm, which indicates that compound **3** is an insulator. Moreover no any satellite reflections and/or diffuse strikes were observed. These results suggest that Cu is not partially oxidized.

There are two possibilities: (a) Cu has a charge of +1 and the quinonediimine skeleton is neutral (the charge of **1** is -2); (b) Cu has a charge of +2 and the quinonediimine skeleton is charged -1 (the charge of **1** is -3). We attempted to determine

Table 2 Selected bond distances (Å)

I1-Cu1	2.5881(6)	Cu1-N1	1.936(3)
Cu1-N2	1.973(3)	S1-N1	1.743(4)
S2-N2	1.733(4)		

Table 3 Bond lengths (Å) of quinonediimine skeletons of **1** in (PPh₄)₂ **1** and **3**

Bond (See Fig. 1)	2 (PPh ₄) ₂ 1	1A	3 1B
A	1.335(3)	1.359(6)	1.340(5)
B	1.460(4)	1.447(6)*	1.448(6)*
C	1.291(3)	1.322(5)	1.320(5)

*Average of two bond lengths.

the oxidation state of Cu by analyzing the bond lengths between Cu and its ligands. However, there seems to be no simple relations between atomic charge and bond lengths.⁶ We also tried to compare the bond lengths of the quinonediimine skeleton before and after the complex formation. If **1** in compound **3** has one more electron from Cu(I), bond A and bond C will become longer and bond B will become shorter than those in (PPh₄)₂**1** (**2**) (Fig. 1). Table 3 gives the average bond lengths of the quinonediimine skeletons of **2** and **3**. Actually, bonds A and C of **3** become longer and B becomes shorter than those of **2**.³ However, we can also consider whether the bond length difference is caused by the electron transfer, or by an effect of electron donation from each lone pair of N atoms of the diimine to Cu. We can say that (a) Cu(I) and **1**²⁻ are both diamagnetic and (b) Cu(II) and **1**³⁻ are both paramagnetic. We therefore measured the ESR spectrum of a single crystal of **3** at room temperature. The compound has no significant ESR signal, which suggests that compound **3** is diamagnetic, and no reduction of the dianionic acceptor **1** by CuI is observed. In other words, CuI has a +1 charge, and the quinonediimine skeleton in **3** is neutral. However, dianion **1** is such a strong acceptor³ that **1** not being reduced by CuI is unexpected; further investigation is now in progress.

References

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4. The O7 water molecule is partially occupied [Occ = 0.340(15)], although there is no obvious crystallographic reason (*e.g.* symmetry generated short contacts) as to why this should be the case. When we analyzed the data without the water molecule, 1.6 e/Å² of Fourier peak was observed. Based on short O7...O6 contacts of 3.145(16) Å, the water molecule probably takes part in the -O-H...O₃S-hydrogen bond. Another short contact with a carbon atom of a benzene ring of PPh₄⁺ of 3.130(15) Å was also observed. Since water H atoms could not be found, one H atom must be located on the line between O7 and O6 and the other H atom was tentatively located as being far from the benzene rings.
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