Inorg. Chem. **2008**, *47*, 7074−7076

Inorganic Chemistry
Communication

$Fe_2OCl_6^{2-}$ Salt Formed by Electrochemical Oxidation of Ethylenedioxytetrathiafulvalenoquinone-1,3-dithiolemethide in the Presence of $FeCl_4^-$ Ion with a Silicon Wafer Electrode

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Received April 11, 2008

Electrochemical oxidation of a bent donor molecule, ethylenedioxytetrathiafulvalenoquinone-1,3-dithiolmethide (**2**), in chlorobenzene (PhCl)/ethanol containing NBu_4FeCl_4 as a supporting electrolyte is performed using an undoped silicon wafer electrode. Black crystals of $\mathbf{2}_6 \cdot Fe_2OCl_6 \cdot 2PhCl$ are obtained that have a different molecular formula from that of $\mathbf{2}_2 \cdot FeCl_4$ crystals obtained previously using a platinum rod electrode. The new crystal has a structure composed of alternately stacked layers of **2** molecules and $Fe_2OCl_6^{2-}$ ions, whose Fe−O−Fe bond is completely linear and for which the geometry around the Fe atom is almost tetrahedral. The electrical resistivity decreases with temperature until ca. 200 K, but below this temperature, it gently increases. The magnetic susceptibility (χ_p) observed can be described by the sum of χ_p obeying a Curie−Weiss law for the impurity spins and of χ_p obeying a dimer model with a spin-exchange integral ($J \sim -180$ K) in each $Fe_2OCl_6^{2-}$ ion, which is also weakly coupled to neighboring $Fe_2OCl_6^{2-}$ ions through an additional exchange interaction.

Molecular and magnetic conductors are usually based on charge-transfer (CT) salts produced by electrochemical oxidations of π-donor molecules in the presence of supporting electrolytes of tetraalkylammonium salts with magnetic or nonmagnetic counteranions.[1] In general, the above electrochemical oxidations are performed using electrodes made of metals such as platinum and gold, on whose surface CT salt crystals are grown. The use of semiconducting silicon wafer electrodes also yields CT salt crystals, but very rarely wirelike crystals of micro- and nanosizes are produced on the surface of silicon wafers.[2]

Very recently, we performed electrochemical oxidation of a bent donor molecule, ethylenedithiotetrathiafulvalenoquinone-1,3-dithiolmethide (**1**), in the presence of NBu_4FeCl_4 using a silicon wafer electrode, whose (001)-oriented surface was coated with a multilamellar structure of phospholipid molecules, and we observed the formation of nanowires (thickness = 10−25 nm) of $\mathbf{1}_4 \cdot 2FeCl_4$.[3] This suggests that such a multilamellar structure can serve as a nanoscale reaction space for efficiently producing nanowires of CT salts for molecular and magnetic conductors. The electrical conducting property of $\mathbf{1}_4 \cdot 2FeCl_4$ nanowires still has not been elucidated. Metallic conductivity cannot be predicted based on the bulk crystals, which have a low room-temperature electrical conductivity and a small-gap semiconducting property.[4] Because the ethylenedioxy derivative of **1** (**2**) is a bent donor molecule suitable for producing CT salts exhibiting metallic conductivity,[5,6] whether nanowires of **2**-based CT salts can also be produced using a phospholipid-modified silicon wafer electrode and whether the electrical conductivity is metallic or small-gap semiconducting as expected are of much interest. Prior to the study, we

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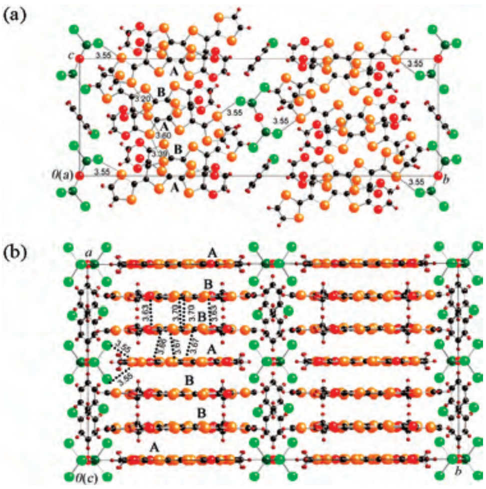
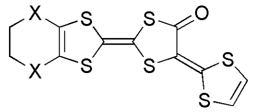


Figure 1. Views of the crystal structure of $\mathbf{2}_6\cdot Fe_2OCl_6\cdot 2PhCl$ along the (a) *a* and (b) *c* axes.

investigated the electrochemical oxidation of **2** in chlorobenzene (PhCl)/ethanol (EtOH) containing NBu_4FeCl_4 using an undoped silicon wafer electrode. A CT salt with a molecular formula of $\mathbf{2}_6\cdot Fe_2OCl_6\cdot 2PhCl$ was obtained, in which the counteranion is not a $FeCl_4^-$ ion from the supporting electrolyte but a $Fe_2OCl_6^{2-}$ ion newly produced from the $FeCl_4^-$ ion. The $Fe_2OCl_6^{2-}$ ion, with a unique linear Fe−O−Fe bridge, was not produced using a platinum electrode but only using a silicon wafer electrode. This Communication reports the crystal structure and zero-gap semiconductor-like electrical conducting property of $\mathbf{2}_6\cdot Fe_2OCl_6\cdot 2PhCl$ and the significant interaction between the Fe^{III} ($S = {}^5/_2$) d spins in each $Fe_2OCl_6^{2-}$ ion as well as in the neighboring $Fe_2OCl_6^{2-}$ ions.



1: X = S, **2**: X = O

An undoped (100)-oriented silicon wafer purchased from Siltronix (diameter = 2 in.; thickness = 275 μm) was cut into 5 × 20 mm^2 pieces. Each piece was dipped in 3% HF/H_2O for 1 min, rinsed with distilled H_2O, and dried in air. Using this silicon wafer electrode, the electrochemical oxidation of **2** was carried out with a constant current of 0.1 μA at room temperature in PhCl/EtOH (9:1, v/v) containing a supporting electrolyte of NBu_4FeCl_4. After ca. 1 month, several pieces of black crystals with a molecular formula of $\mathbf{2}_6\cdot Fe_2OCl_6\cdot 2PhCl$[7] grew on the surface of the silicon wafer electrode.

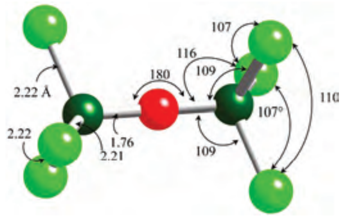


Figure 2. Molecular structure of the $Fe_2OCl_6^{2-}$ ion.

The views of the crystal structure along the *a* and *c* axes are shown in parts a and b of Figure 1. The crystal is composed of alternating donor layers of **2** molecules and layers of $Fe_2OCl_6^{2-}$ ions and PhCl molecules in a 1:2 ratio. In each donor layer, two crystallographically independent **2** molecules (**A** and **B**) are two-dimensionally stacked in an ···**ABBA**··· fashion. The molecule **A** seems to have a completely planar molecular skeleton, including the ethylenedioxy ring. This is due to a mirror plane being present on the molecule. In contrast, the molecular skeleton of the **B** molecule, including two O atoms in the ethylenedioxy ring, is almost planar, but the ethylene group is greatly distorted with a dihedral angle of 34.3°. There are close top and bottom contacts between **A** and **B** and between **B** molecules and also close side-by-side contacts between **A** and between **B** molecules, as evidenced by S···S distances shorter than twice the van der Waals (vdW) radius of sulfur (3.70 Å).[8]

On the other hand, each counteranion layer contains $Fe_2OCl_6^{2-}$ ions and PhCl molecules arranged as $\cdots(Fe_2OCl_6^{2-})(PhCl)(PhCl)\cdots$ along the *a* axis and $\cdots(Fe_2OCl_6^{2-})(PhCl)\cdots$ along the *c* axis on the *ac* plane. As shown in Figure 2, the $Fe_2OCl_6^{2-}$ ion has a completely linear Fe−O−Fe bridge. This linear geometry is very rare, although a few examples have previously been reported, but an orientational disorder has been recognized, except for one Fe−O−Fe bridge.[9] The observed Fe−O distance is 1.76 Å, comparable to the values reported so far. Two $FeCl_3$ moieties are centrosymmetric with respect to the O atom of the Fe−O−Fe bridge. The geometry around the Fe atom is slightly distorted tetrahedral, as seen from the O−Fe−Cl (108.8, 108.8, and 115.5°) and Cl−Fe−Cl (109.9, 107.0, and 107.0°) bond angles. The Fe−Cl bond distances are 2.21−2.22 Å. Each PhCl molecule is disordered such that the Cl atom is located symmetrically to the right and left of a benzene ring in a 1:1 ratio. PhCl molecules with one conformation only are depicted in the figure. Close contacts also occur between $Fe_2OCl_6^{2-}$ ions and **2** molecules. The contact distance between the chlorine atoms of the $Fe_2OCl_6^{2-}$ ion and the sulfur atom on the 1,3-dithiol ring of **A** is 3.55 Å, which is somewhat shorter than the sum (3.65 Å) of chlorine and sulfur atoms' vdW radii.[8]

There are four kinds of top and bottom contacts and two kinds of side-by-side contacts experienced by neighboring **2** molecules. The overlap integrals (*S*) of the contacts are calculated by an extended Hückel molecular orbital (MO) method. A comparison of the *S* values shows that the top and bottom contact between **A** and **B** has a larger overlap than that between **B** molecules. On the other hand, the overlap of side-by-side contact is larger between **A** molecules

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(7) Crystal data for $\mathbf{2}_6\cdot Fe_2OCl_6\cdot 2PhCl$: $C_{19.5}H_{11.5}O_{4.75}S_9Cl_2Fe_{0.5}$, M = 709.17, orthorhombic, a = 20.687(7) Å, b = 39.282(14) Å, c = 12.764(4) Å, V = 10372(6) Å^3, T = 293 K, space group *Cmca*, Z = 16, μ(Mo Kα) = 12.755 cm^{-1}, 42 864 reflections measured (R_{int} = 0.072), 7656 unique, of which 4139 were used in all calculations [$F^2 > 2.00\sigma(F^2)$]. The final R and R_w were 0.065 and 0.076, respectively.

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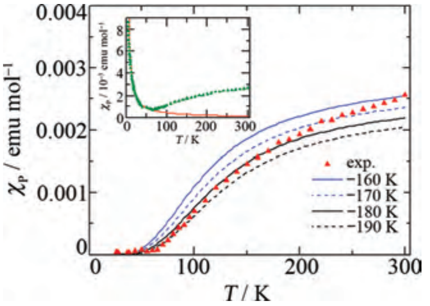

Figure 3. Temperature dependences of paramagnetic susceptibility (χ_P) in the temperature range of 5−300 K: (green ▲) observed data due to the impurity and d spins and (red line) a contribution of the impurity spins obeying a Curie−Weiss law ($C = 0.05$ emu K mol^{-1} and $\theta = +3$ K) (inset) and (red ▲) a contribution due to the d spins and $\chi_\mathrm{P}-T$ curves with $J = -160$ K (blue —), −170 K (blue - - -), −180 K (black —), and −190 K (black - - -) in a dimer model.

than between **B** molecules. On the basis of these S values, the band dispersion and Fermi surface were calculated by a tight-binding method. Because each donor layer contains 12 **2** molecules in the unit cell, the band dispersion calculated for their highest occupied molecular orbitals consists of 12 branches. These branches are degenerated into 6 branches along the MZ and XM lines and into 3 branches at the M point (k_a/2, 0, k_c/2) because of the symmetry of the space group (*Cmca*). From the 6:2 ratio of the **2** molecule and the $Fe_2OCl_6^{2-}$ ion, a total of 6 **2** molecules possesses a net charge of 1+, so the energy band has a $^5/_6$-filled electronic state. Accordingly, the Fermi level (E_F) locates on the degenerated position, and no Fermi surface is observed even though there is no band gap at E_F, suggesting a zero-gap semiconducting property for this salt.

The electrical resistivity (ρ) at room temperature measured on a single crystal was ca. 1 Ω cm, which decreased very slightly with temperature until ca. 200 K, but below 200 K, it gently increased with a very small activation energy of ca. 40 meV. This electrical conducting property observed reflects that of a zero-gap semiconductor predicted by the above band structure calculation above 200 K. However, below 200 K, some structural change, such as charge ordering, brought about insulation. A SQUID measurement was performed on the microcrystal in the temperature range of 1.9−300 K under a magnetic field of 3 T. The inset to Figure 3 shows the temperature dependence of paramagnetic susceptibility (χ_P).[10] χ_P gradually decreased with decreasing temperature from 300 K until ca. 50 K. However, below 50 K, χ_P sharply increased with decreasing temperature. The observed $\chi_\mathrm{P}-T$ behavior can be reproduced considerably well by considering contributions of both impurity spins, obeying a Curie−Weiss law with Curie constant $C = 0.05$ emu K mol^{-1} and Weiss temperature $\theta = +3$ K, and Fe$^{\mathrm{III}}$ ($S = {}^5/_2$) d spins, obeying a dimer model[11] with a spin-exchange integral ($J \sim -180$ K) in each $Fe_2OCl_6^{2-}$ ion (see Figure 3). The J value in the present $Fe_2OCl_6^{2-}$ ion is comparable with that (−191 K) in the known $Fe_2OCl_6^{2-}$ ion with a linear Fe−O−Fe bridge.[9] Nevertheless, the fit between the observed and $J = -180$ K curves in the $\chi_\mathrm{P}-T$ plot is still not good. This probably is due to an additional exchange interaction between the d spins of neighboring $Fe_2OCl_6^{2-}$ ions. The further analysis using an antiferromagnetic Heisenberg alternating-linear-chain model with two kinds of J values[12] is now in progress.

The present CT salt obtained using a silicon wafer electrode does not use a counteranion of NBu_4FeCl_4 but rather the $Fe_2OCl_6^{2-}$ ion, with which the supporting electrolyte is not contaminated at all. On the basis of the previous report that the reaction of two $FeCl_4^-$ ions with one molecule of sodium trimethylsiloxide gives one $Fe_2OCl_6^{2-}$ ion in good yield,[13] the conversion from $FeCl_4^-$ to $Fe_2OCl_6^{2-}$ ions on silicon wafer anode is assumed to proceed according to the following reaction scheme: Some Si atoms in the dangling bond state on the surface of silicon wafer are electrochemically oxidized to siloxides (Si−O$^-$) in the presence of a small amount of H_2O in the EtOH used, and Si−O$^-$ participates in the reaction between two $FeCl_4^-$ ions to produce one $Fe_2OCl_6^{2-}$ ion and regenerate Si−O$^-$ by reaction with H_2O. The $Fe_2OCl_6^{2-}$ ions produced on the silicon wafer anode combine with neutral and oxidized **2** molecules also residing on the anode to preferentially make crystals of the present CT salt rather than crystals of the $FeCl_4^-$ salt. The formation of $Fe_2OCl_6^{2-}$ ions does not occur on the platinum rode anode, so a semiconducting silicon wafer can be characterized as an electrode different from the usual metal electrodes in the electrochemical reactions.

Acknowledgment. This work was supported by a Grant-in-Aid for Scientific Research (Grant 19350073) from the Ministry of Education, Culture, Sports, Science and Technology of Japan. We thank Prof. Hiroki Nakano (University of Hyogo) for his advice on magnetic data analyses.

Supporting Information Available: X-ray crystallographic file for $\mathbf{2}_6\cdot Fe_2OCl_6\cdot 2PhCl$ in CIF format, overlap integrals between neighboring donor molecules, band dispersion and Fermi surfaces of each donor layer calculated by an extended Hückel MO method, the temperature dependence of resistivity, and the conversion scheme from $FeCl_4^-$ to $Fe_2OCl_6^{2-}$ ions. This material is available free of charge via the Internet at http://pubs.acs.org.

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(10) The χ_P value is obtained with emu per mole of $\mathbf{2}_6\cdot Fe_2OCl_6\cdot 2PhCl$.

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