

Metal/Semi-Conductivity and Antiferromagnetic Ordering of Fe(III) d spins in (Benzotetrafulvalenothioquinone-1,3-dithiolemethide)₂•FeBr₄

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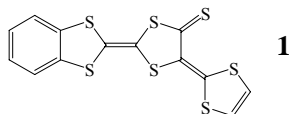
Abstract

A new donor molecule, benzotetrafulvalenothioquinone-1,3-dithiolemethide (**1**) was prepared and electrochemically oxidized in the presence of NEt₄•MX₄ (M = Fe, Ga; X = Cl, Br) to give its charge transfer (CT) salts with MX₄⁻ ions (**1**₂•FeCl₄, **1**₂•GaCl₄, **1**₂•FeBr₄, **1**₂•GaBr₄). These CT salts exhibited considerably high electrical conductivities of 16 - 33 S cm⁻¹ at room temperature. Their electrical conducting properties were metallic above 200 K, but below this temperature became semiconducting behavior with very small activation energies of 4 - 27 meV. Both of the Fe(III) (*S* = 5/2) d spins of FeCl₄⁻ and FeBr₄⁻ ions were subjected to antiferromagnetic interaction, and there was a sign of antiferromagnetic ordering at around 8 K in the FeBr₄⁻ salt.

1. Introduction

Current interest continues to be directed toward molecular/organic magnetic conductors, in which conducting π electrons and local d spins are expected to significantly interact with each other so as to produce unusual electrical conducting and/or magnetic properties. Especially, a great deal of progress has been made so far in several CT salts of π donor molecules with magnetic-metal counteranions, from which paramagnetic superconductivity [1], antiferromagnetic superconductivity [2], metallic ferromagnetism [3] and field-induced ferromagnetic superconductivity [4] emerged. However, simultaneous appearance of novel magnetism and electrical conductivity in the CT salts is not always a result of the interaction between the conducting π electrons and the local d spins involved there. Generally, the π /d interaction is scarcely very weak in all the CT salts except for a λ -type of CT salt of bis(ethylenedithio)tetraselenafulvalene (BETS) with FeCl₄⁻ ion [5], in which significant π /d interaction, however, begins to occur only at low temperatures.

Under the circumstances it is now desired to urgently search for donor molecules other than BETS, which give new salts with magnetic-metal counteranions exhibiting much more increased π /d interaction, by which unprecedented electrical conducting and/or magnetic properties might come out. Very recently, we observed ferromagnetic ordering of Fe(III) d spins of FeBr₄⁻ ions near 1 K through the interaction with the π spins developed on the donor columns in the CT salt of ethylenedithiotetrafulvalenothioquinone-1,3-dithiolemethide with a magnetic FeBr₄⁻ ion [6]. However, this CT salt has problems of metal-to-semiconductor transition near 170 K and very weak π -d interaction. Now, we had much interest in a new donor molecule, **1**, which has a planar and π -donating benzo group in place of an ethylenedithio group. Here are reported the synthesis of CT salts of **1** with Fe(Ga)Cl₄⁻ and Fe(Ga)Br₄⁻ ions, and their crystal structures, and electrical conducting and magnetic properties.



2. Experimental

According to the previous procedure, **1** was prepared using bis-(cyanoethylthio)benzotetrafulvalene as a starting material: overall yield 35%; mp 251 - 252 °C (dec). The **1**₂•MX₄ salts were obtained by an electrochemical oxidation of a chlorobenzene/ethanol (9:1, v:v) solution containing **1** (5 mg) and NEt₄•MX₄ (40 - 80 mg) in a conventional H-shaped cell with Pt electrode at 293 K over 10 days at a constant current of 0.3 μ A. X-Ray diffraction data were collected at 297 K on a Rigaku RAXIS-RAPID imaging plate diffractometer with a graphite-monochromated Mo-K α radiation or on a Rigaku AFC-8 Mercury CCD diffractometer with a confocal X-ray mirror system. Their crystal data were as follows. **1**₂•FeCl₄: monoclinic, space group *P*2₁/*m*, *a* = 7.0447(9), *b* = 34.734(3), *c* = 7.622(1) Å, β = 74.020(3)°, *V* = 1793.0(4) Å³, *R*₁ = 0.041. **1**₂•GaCl₄: monoclinic, space group *P*2₁/*m*, *a* = 7.063(1), *b* = 34.578(7), *c* = 7.607(2) Å, β = 73.83(1)°, *V* = 1784.4(6) Å³, *R*₁ = 0.048.

1₂•FeBr₄: monoclinic, space group *P*2₁/*m*, *a* = 7.063(3), *b* = 35.514(12), *c* = 7.661(3) Å, β = 105.673(1)°, *V* = 1850.3(11) Å³, *R*₁ = 0.050. **1**₂•GaBr₄: monoclinic, space group *P*2₁/*m*, *a* = 7.073(2), *b* = 35.602(7), *c* = 7.661(2) Å, β = 106.0624(10)°, *V* = 1853.8(7) Å³, *R*₁ = 0.043. Electrical conductivity measurement was performed on the single crystals using a four-probe method. The static magnetic susceptibility was measured between 1.8 and 300 K using the microcrystals of **1**₂•FeCl₄ and **1**₂•FeBr₄ under an applied field of 1 kOe on a SQUID susceptometer (MPMSXL, Quantum Design).

3. Results and Discussion

The crystal structures of **1**₂•FeCl₄ and **1**₂•FeBr₄ projected down to *bc* and *ab* planes are shown in Fig. 1 and Fig. 2, respectively. The GaCl₄⁻ and GaBr₄⁻ salts have almost the same crystal structures to those of the corresponding FeCl₄⁻ and FeBr₄⁻ salts. In both of **1**₂•Fe(Ga)Cl₄ and **1**₂•Fe(Ga)Br₄, **1** molecules are stacked in almost the same manner to form a one-dimensional column, in which the neighboring **1** molecules have comparatively effective overlap and the interplanar distances are almost equal (3.49 - 3.50 Å) and comparable to " π -cloud thickness". In addition, there are several contacts through the S atoms of the tetrathiaethylene moieties and C=S groups of **1** molecules between the neighboring columns. It should be noted that the Fe(Ga)Cl₄⁻ and Fe(Ga)Br₄⁻ salts have almost the same **1**-stacked column and layer structures in spite of different sizes of Fe(Ga)Cl₄⁻ and Fe(Ga)Br₄⁻ ions, which only bring about marked change in the distance between the layers (4.55 - 4.59 Å for **1**₂•Fe(Ga)Cl₄, and 5.00 - 5.05 Å for **1**₂•Fe(Ga)Br₄).

The Fe(Ga)Cl₄⁻ and Fe(Ga)Br₄⁻ ions are arranged in a square lattice between the neighboring layers of **1** molecules. The Cl•••Cl and Br•••Br contact distances between the neighboring Fe(Ga)Cl₄⁻ ions are 4.28 and 4.38 Å, and between the neighboring Fe(Ga)Br₄⁻ ions are 4.10 and 4.26 Å, respectively, which are longer than the sum of van der Waals radii (vwr) of two Cl atoms (3.60 Å) and two Br atoms (3.90 Å). The Cl and Br atoms of these ions have also contacts with the S atoms of 1,3-dithiole groups in **1**. The Cl•••S contact distances are 3.34 and 3.76 Å, and one is shorter but the other is longer than the sum of vwr of Cl and S atoms

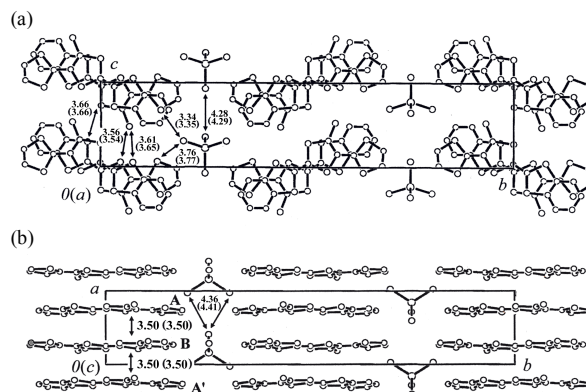


Fig. 1. The crystal structure of **1**₂•FeCl₄ projected to (a) *bc* and (b) *ab* planes

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1. REPORT DATE JUL 2004	2. REPORT TYPE N/A	3. DATES COVERED -	
4. TITLE AND SUBTITLE Metal/Semi-Conductivity and Antiferromagnetic Ordering of Fe(III) d spins in (Benzotetrathiafulvalenothioquinone-1,3-dithiolemethide)2FeBr4		5a. CONTRACT NUMBER	
		5b. GRANT NUMBER	
		5c. PROGRAM ELEMENT NUMBER	
6. AUTHOR(S)		5d. PROJECT NUMBER	
		5e. TASK NUMBER	
		5f. WORK UNIT NUMBER	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) AOARD/AFOSR Unit 45002 APO AP 96337-5002		8. PERFORMING ORGANIZATION REPORT NUMBER	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)		10. SPONSOR/MONITOR'S ACRONYM(S)	
		11. SPONSOR/MONITOR'S REPORT NUMBER(S)	
12. DISTRIBUTION/AVAILABILITY STATEMENT Approved for public release, distribution unlimited			
13. SUPPLEMENTARY NOTES Proceedings of the International Conference for the Science and Technology of Synthetic Metals (ICSM 2004). Held in New South Wales, Australia on Jun 28- July 2 2004. Copyrighted: Government Purpose Rights License. See also ADM001811.			
14. ABSTRACT			
15. SUBJECT TERMS			
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT UU
a. REPORT unclassified	b. ABSTRACT unclassified	c. THIS PAGE unclassified	
			18. NUMBER OF PAGES 2
			19a. NAME OF RESPONSIBLE PERSON

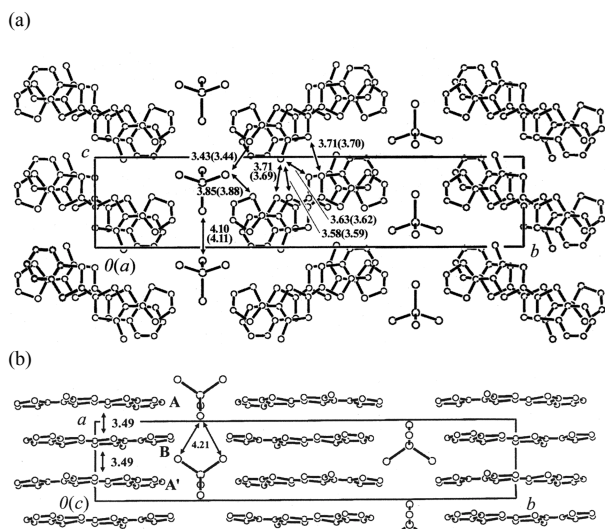


Fig. 2. The crystal structure of $\mathbf{I}_2 \cdot \text{FeBr}_4$ projected to (a) bc and (b) ab planes

(3.65 Å). On the other hand, the $\text{Br} \cdots \text{S}$ contacts have distances of 3.43 and 3.85 Å, and one is shorter than the sum of radii of Br and S atoms (3.80 Å), and the other is comparable to the value.

Electrical conductivity results of $\mathbf{I}_2 \cdot \text{FeCl}_4$, $\mathbf{I}_2 \cdot \text{GaCl}_4$, $\mathbf{I}_2 \cdot \text{FeBr}_4$ and $\mathbf{I}_2 \cdot \text{GaBr}_4$ are summarized in Table 1. As expected from the uniform and effective stacking of \mathbf{I} 's with one positive charge per two molecules, all the CT salts exhibited good electrical conductivities (σ 's) at room temperature (σ_{RT} 's), which are the highest among CT salts of several derivatives of \mathbf{I} so far obtained. From the temperature dependence of σ , metallic behavior was only recognized in the higher temperature region than 208 - 270 K, and below the temperature it changed to be semiconducting with very small activation energy of < 30 meV. Supposedly, this metal-to-semiconductor transition occurring at considerably high temperatures reflects one-dimensional character of the \mathbf{I} -stacked columns.

Table 1. Electrical conducting properties of $\mathbf{I}_2 \cdot \text{Fe}(\text{Ga})\text{Cl}_4$ and $\mathbf{I}_2 \cdot \text{Fe}(\text{Ga})\text{Br}_4$.

	σ_{RT} (S cm^{-1})	M - I transition temperature (K)	activation energy (meV)
$\mathbf{I}_2 \cdot \text{FeCl}_4$	19	232	5 - 18
$\mathbf{I}_2 \cdot \text{GaCl}_4$	18	208	8 - 27
$\mathbf{I}_2 \cdot \text{FeBr}_4$	33	268	4 - 18
$\mathbf{I}_2 \cdot \text{GaBr}_4$	16	270	13

The temperature dependence of paramagnetic susceptibility (χ_p) was investigated in the temperature range of 1.8 - 300 K for $\mathbf{I}_2 \cdot \text{FeCl}_4$ and $\mathbf{I}_2 \cdot \text{FeBr}_4$. As shown in Figure 3, there is marked difference in the $\chi_p - T$ behavior between the two salts. Thus, for $\mathbf{I}_2 \cdot \text{FeCl}_4$ the χ_p simply increased with lowering the temperature from 300 K. The $\chi_p - T$ behavior can be well reproduced by giving $C = 4.54 \text{ emu K mol}^{-1}$, $\theta = -4.3 \text{ K}$ to an equation of $\chi_p = C/(T - \theta)$, where C is Curie constant, θ Weiss temperature. The C obtained is very close to the value (4.46 emu K mol^{-1}) calculated as Fe(III) d spin entity with $S = 5/2$ and $g = 2.0179$. The θ value is very small and negative, indicating that very weak antiferromagnetic interaction preferentially occurs between the Fe(III) d spins of FeCl_4^- ions. On the other hand, for $\mathbf{I}_2 \cdot \text{FeBr}_4$ the χ_p also increased with lowering the temperature from 300 K, but the increasing degree was very small compared to that for $\mathbf{I}_2 \cdot \text{FeCl}_4$. In addition, a peak appeared at ca. 8 K and below the temperature the χ_p reversely decreased with

lowering the temperature. In the temperature range of 8 - 300 K the χ_p well obeyed an equation as above with $C = 4.56 \text{ emu K mol}^{-1}$, $\theta = -16.1 \text{ K}$. Judging from this large and negative θ value, the interaction between the Fe(III) d spins of FeBr_4^- ions is fairly stronger than that of the FeCl_4^- salt. This can be well understood by considering the X-ray structure result as above that much closer contacts occur between the Br atom of FeBr_4^- ion and the S atoms in the 1,3-dithiole rings. Supposedly, at low temperatures such a one-dimensional antiferromagnetic interaction can furthermore extend to become two- and/or three-dimensional, eventually giving rise to antiferromagnetic ordering of the Fe(III) d spins of FeBr_4^- ions below 8 K.

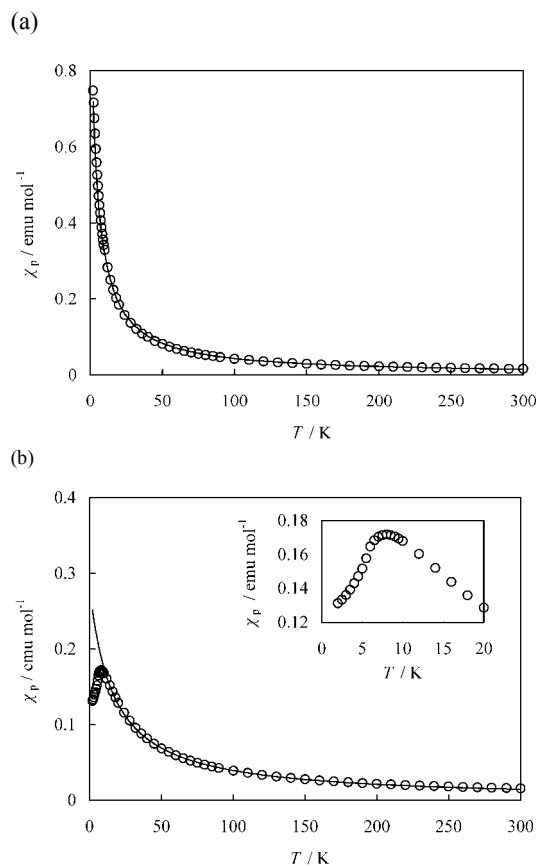


Fig. 3. Temperature dependence of χ_p in (a) $\mathbf{I}_2 \cdot \text{FeCl}_4$ and (b) $\mathbf{I}_2 \cdot \text{FeBr}_4$.

4. Conclusions

It was shown that \mathbf{I} is superior to its related donor molecules in the formation of uniform and effective conducting columns and also in such stronger π -d interaction with a magnetic FeBr_4^- ion as to possibly bring about antiferromagnetic ordering near 8 K due to the conducting π electrons or the π spins on the \mathbf{I} -stacked columns.

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