

ON METALLIC BEHAVIOR OF THE TETRAMERIZED SALT, (DMET)<sub>2</sub>ReO<sub>4</sub>

Kazuya SAITO, Yoshimitsu ISHIKAWA, Masayoshi ISHIBASHI,  
Koichi KIKUCHI, Keiji KOBAYASHI,\* and Isao IKEMOTO  
*Department of Chemistry, Faculty of Science,  
Tokyo Metropolitan University, Setagaya, Tokyo 158, JAPAN*  
*\*Department of Chemistry, College of Arts and Sciences,  
The University of Tokyo, Meguro, Tokyo 153, JAPAN*

## ABSTRACT

The crystal structure of (DMET)<sub>2</sub>ReO<sub>4</sub> was solved, and the resistivity and the thermoelectric power were measured. The crystal has columnar structure. In the column the large tetramerization was detected. The resistivity under the normal pressure has seemingly metallic temperature dependence above ca. 295 K. The thermoelectric power is essentially constant above 200 K and no anomaly was detected at 295 K. The apparent inconsistency between the structure and the metallic behavior in the resistivity was discussed.

## INTRODUCTION

DMET is the first of the unsymmetrical donors of which radical salt(s) show the superconductivity. The molecule consists of halves of TMTSF and BEDT-TTF molecules. The wide variety in crystal structure and physical properties has been demonstrated in the DMET family. The family has been classified into 5 groups on the basis of the shape of anion and electrical properties.<sup>1</sup> Each group has the characteristic crystal structure.<sup>2</sup> According to the classification scheme, the title compound seems to belong to group 2 because the shape of the anion has the tetrahedral symmetry. No direct confirmation of the prospect, however, has been made so far. The situation prompted us to study the crystal structure and electrical properties of (DMET)<sub>2</sub>ReO<sub>4</sub>.

## EXPERIMENTAL

The X-ray data were collected on a crystal (0.21 x 0.13 x 0.03 mm<sup>3</sup>) using a four-circle diffractometer and monochromated MoK $\alpha$  radiation. Crystal data: triclinic,  $P\bar{1}$ ,  $a = 6.715(1)$ ,  $b = 14.486(2)$ ,  $c = 15.867(2)$  Å,  $\alpha = 101.94(1)$ ,  $\beta = 90.05(1)$ ,  $\gamma = 78.43(1)^\circ$ ,  $Z = 2$ ,  $T = 297$  K,  $R = 0.074$  for 4391 reflections.

The resistance was measured of some samples using the AC (20 Hz) four-probe method at constant current of 10  $\mu$ A. The thermoelectric power was measured of some samples by the method described elsewhere.<sup>3</sup> The measurements under pressures were performed in a pressure-cell of clamp type.

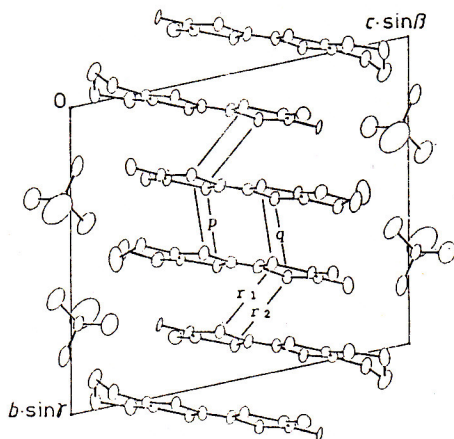


Fig. 1. Crystal structure. Solid lines indicate short interatomic contacts.

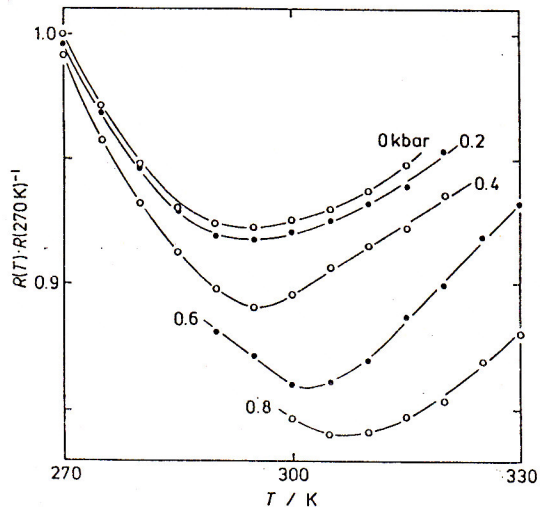


Fig. 2. Resistivity.

## RESULTS AND DISCUSSION

The crystal structure is shown in Fig. 1. The structure is columnar and distinct from those of  $\text{BF}_4$  and  $\text{ClO}_4$  salts. The molecules alternately stack along the  $b$  axis and the basic period of the crystal lattice contains four molecules. Although the intercolumnar contacts are similar to those observed in other DMET salts, the intracolumnar contacts have a remarkable feature; the short contacts are confined within a unit cell. Since the periodicity of 4 molecules corresponds to  $2k_F$  distortion, the crystal should be semiconducting, irrespective of the magnitude of electron correlation.

The resistivity under pressures are shown in Fig. 2. Under the normal pressure, the salt is seemingly metallic above ca. 295 K. The "transition temperature" shifts upward on applying moderate pressure. The behavior of the resistivity is in contradiction with the crystal structure as described above.

The thermoelectric power under 0.2 kbar is plotted in Fig. 3. There is nothing anomalous at 295 K where the minimum of the resistivity appears. This demonstrates that the salt is not metallic at the microscopic level. The thermoelectric power under the normal pressure is shown in Fig. 4

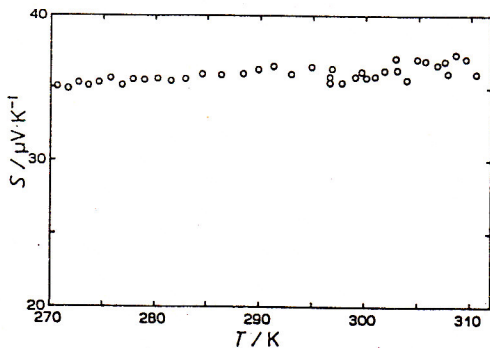


Fig. 3. Thermoelectric power under 0.2 kbar.

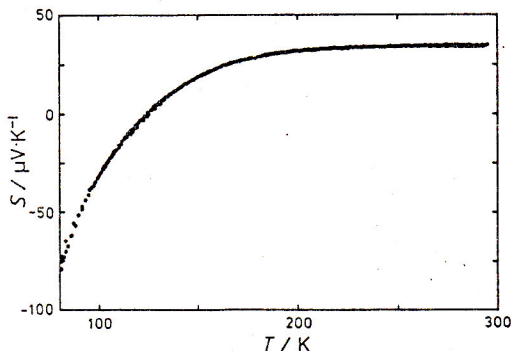


Fig. 4. Thermoelectric power under the normal pressure.

in the wider temperature region. Above ca. 200 K the value is almost independent of temperature. On lowering temperature, the thermoelectric power gradually decreases, passes zero at about 140 K, and decreases more rapidly.

The situation very resembles that in  $(\text{TMTTF})_2\text{ClO}_4$ ,<sup>4</sup> where the apparent "metallic" behavior was attributed to the rather strong temperature dependence in the mobility of charge carriers. The temperature dependence is generally written as  $T^{a-0.5} \exp(-E_a/T)$ , where  $a$  is the exponent characterizing the scattering mechanism of the carrier and  $E_a$  an activation energy.  $a$  and  $E_a$  were determined as 2.0 and 470 K, respectively, from the present results. It is well-known that the simple electron scattering by phonon gives the value 2 for  $a$ . Thus, the values are within a reasonable range. Namely,  $(\text{DMET})_2\text{ReO}_4$  is intrinsically semiconducting and the apparent metallic behavior is due to the temperature dependence in the mobility of the carriers.

Concerning the temperature-independent thermoelectric power, it is likely that the effect of electron correlation plays an important role. It is well-known that the thermoelectric power is independent of temperature when the ratio between the on-site Coulomb repulsion and the transfer integral is sufficiently large. The expected value is 60  $\mu\text{V}/\text{K}$  for the quarter-filled hole band. The observed value is smaller than the expected, but not too small.

There remains a problem, that is why the thermoelectric power changes the sign below 140 K. Similar behavior was reported for  $(\text{TMTTF})_2\text{ClO}_4$ .<sup>4</sup> In that case, the negative thermoelectric power was attributed to some defects. The same explanation may be possible for the present case.

In conclusion,  $(\text{DMET})_2\text{ReO}_4$  has tetramerized structure distinct from any other radical salts of DMET, and it is characterized by a rather strong electron correlation. The seemingly metallic behavior in the resistivity is attributed to the small band-gap and the temperature dependence of the carrier.

#### REFERENCES

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