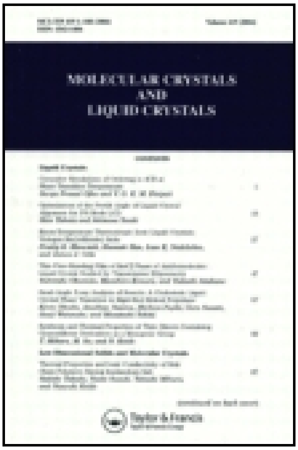

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# Structural, Spectroscopic and Magnetic Properties of Charge-Transfercomplex, (TMTSF)[Cr($Cl_4$SQ)$_2$($Cl_4$Cat)]· 0.5$CH_2Cl_2$

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# Structural, Spectroscopic and Magnetic Properties of Charge-Transfercomplex, (TMTSF)[Cr($Cl_4SQ)_2(Cl_4Cat)$]• $0.5CH_2Cl_2$

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A complex (TMTSF)[Cr($Cl_4SQ)_2(Cl_4Cat)$](1)•$0.5CH_2Cl_2$ (SQ = semiquinonate; Cat = catecholate, TMTSF = tetramethyltetraselenafulvalene) has been synthesized and characterized. **1**•$0.5CH_2Cl_2$ crystallizes in the monoclinic, space group $P2_1/n$ with $a = 12.472(3)$ Å, $b = 17.451(4)$ Å, $c = 18.815(5)$ Å, $\beta = 101.80(2)°$ and $V = 4008(1)$ Å$^3$. **1**•$0.5CH_2Cl_2$ contains a paramagnetic TMTSF$^+$ cation and an unprecedented anion [Cr($Cl_4SQ)_2(Cl_4Cat)$]$^-$ as a result of one-electron redox reaction between TMTSF and Cr($Cl_4SQ)_3$. Structure of **1**•$0.5CH_2Cl_2$ consists of dimerized TMTSF$^+$cation, (TMTSF$^+)_2$ and one dimensionally stacked [Cr($Cl_4SQ)_2(Cl_4Cat)$]$^-$ anions. **1** behaves as a semiconductor, and its magnetic susceptibility obeys a Curie-Weiss law in the region of 150–300 K.

*Keywords:* chromium; semiquinonate; charge-transfer complex; TTF derivative

## INTRODUCTION

A large number of molecule-based charge-transfer (CT) complexes have been prepared in the searches for molecule-based conductors and magnets. They are exemplified by the well known organic metal TTF-TCNQ and ferromagnet [FeCp*$_2$][TCNE]·MeCN. Recently, more attention has been devoted to the construction of new-type organic/inorganic hybrid materials using paramagnetic anions and conventional organic $\pi$-donors[1]. In the previous studies, small magnetic anions such as $MX_m^{n-}$ were often utilized[2] because of feasible crystal packing with TTF derivatives, while the preparation of CT salts with large magnetic anions is still limited. In this manuscript we report the synthesis, crystal structure and physical properties of a charge-transfer complex (TMTSF)[Cr(Cl$_4$SQ)$_2$(Cl$_4$Cat)] (**1**)·0.5CH$_2$Cl$_2$ containing a paramagnetic dioxolene chromium complex.

## EXPERIMENTAL SECTION

### Preparation

Cr(Cl$_4$SQ)$_3$·4C$_6$H$_6$ was prepared by the procedure described previously[3]. Single crystals of **1**·0.5CH$_2$Cl$_2$ were grown up from a layered solution with a CS$_2$ solution of Cr(Cl$_4$SQ)·4C$_6$H$_6$ (0.2 mmol) and a CH$_2$Cl$_2$ solution of TMTSF (0.2 mmol). Dark green cubic crystals were obtained after 2 weeks. The crystals were unstable because the solvent came out on exposure to air.

Anal. Calcd for $C_{28.5}H_{13}O_6Cl_{12}CrSe_4$: C, 26.74; H, 1.02. Found: C, 26.69; H, 1.14. IR (KBr pellet): 1541m, 1471m, 1437m, 1377w, 1329s, 1259s, 1116s, 981s, 920w, 796s, 739w, 690s, 576m, 493s cm$^{-1}$.

## Physical Measurements

Absorption spectra were recorded on a Hitachi U-3500 spectrophotometer. EPR spectra were recorded on powders at X-band frequency with a JOEL RE-3X spectrometer operating 9.0-9.5 GHz. Magnetic susceptibility data were recorded over the temperature range 2-300 K at 1 T with a superconducting quantum interference device (SQUID) susceptometer (Quantum Design, San Diego, CA). Magnetic susceptibility data were corrected by subtracting temperature independent terms from experimental data. Electrical resistivity of a compacted pellet was measured by a conventional two-probe method.

## Crystallographic Data Collection and Refinement of Structure

Crystallographic measurement was made on a Rigaku AFC7R diffractometer with graphite-monochromated Mo K$\alpha$ radiation and a rotating anode generator. A suitable crystal was chosen and mounted in a thin-walled glass capillary with mother liquor. The crystal data of $1 \cdot 0.5CH_2Cl_2$ is as follows; formula: $C_{28.5}H_{13}O_6Cl_{13}CrSe_4$, monoclinic, space group $P2_1/n$ (No. 14), $FW =$

1280.14, $a$ = 12.472(3) Å, $b$ = 17.451(4) Å, $c$ = 18.815(2) Å, $\beta$ = 101.80(2) °, V = 4008(1) Å$^3$, $d_{calc}$ = 2.121 g/cm$^3$, Mo K$\alpha$ radiation, $\lambda$ = 0.71070 Å, 29.53 ° < $2\theta$ < 29.98 °, 9504 reflections were collected, of which 4150 unique reflections ($I_0 > 3\sigma(I_0)$) were used for refinement, converging to R = 0.045 and $R_w$ = 0.033. The structure was solved by a direct method (SIR92). Hydrogen atoms were placed in the calculated positions, but their parameters were not refined. The non-hydrogen atoms were refined anisotropically. The position of the dichloromethane molecule ((C(29), Cl(13), and Cl(14)) was determined from a Fourier map, but not refined.

## RESULTS AND DISCUSSION

Figure 1 shows an ORTEP drawing of **1**·0.5$CH_2Cl_2$ with an atom numbering scheme. The complex has crystallographically independent one TMTSF and one [$Cr(C_6O_2Cl_4)_3$] in a unit cell, together with one dichloromethane solvent molecule. The TMTSF molecule is nearly planar, which is similar to that commonly observed in conducting TMTSF salts such as Bechgaard salts. The intermolecular distances in the TMTSF molecule are compared with those in the TMTSF$^{\delta+}$ salts, and the oxidation state of TMTSF molecule in **1**·0.5$CH_2Cl_2$ is estimated +1. As shown in Figure 2, the TMTSF molecules

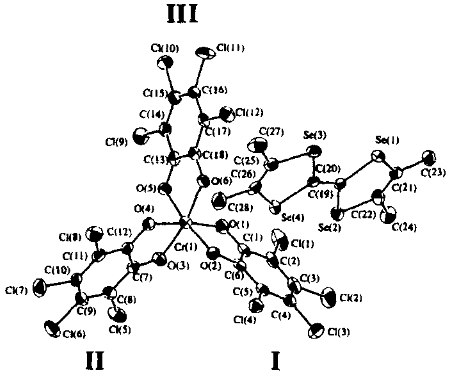

FIGURE 1. ORTEP drawing of **1**·0.5CH$_2$Cl$_2$. Dichloromethane molecule is omitted for clarity. Cr(1)-O(1) 1.921(6), Cr(1)-O(2) 1.930(5), Cr(1)-O(3) 1.948(5), Cr(1)-O(4) 1.954(5), Cr(1)-O(5) 1.972(5), Cr(1)-O(6) 1.956(5), O(1)-C(1) 1.303(9), O(2)-C(6) 1.327(9), O(3)-C(7) 1.293(9), O(4)-C(12) 1.303(9), O(5)-C(13) 1.286(9), O(6)-C(18) 1.289(8), Se(1)-C(19) 1.854(7), Se(1)-C(21) 1.878(9), Se(2)-C(19) 1.883(8), Se(2)-C(20) 1.896(8), C(19)-C(20) 1.381(10) Å.

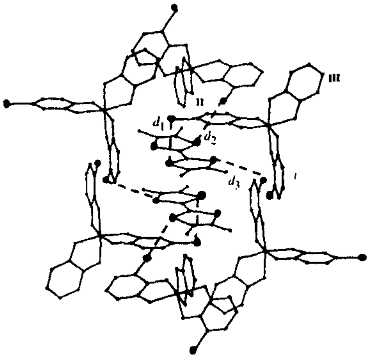

FIGURE 2. Crystal packing structure with short [cation]···[anion] contacts: $d_1$ [Se(2)···Cl(6)] 3.712(3) Å; $d_2$ [Se(3)···Cl(5)] 3.407(3) Å; $d_3$ [Se(1)···Cl(4)] 3.600(2) Å. The chlorine atoms of the anion apart from the TMTSF dimers are omitted for clarity.

form dimers. In the dimers, short intermolecular contacts between selenium atoms are observed, namely 3.598(1) (Se(1)-Se(4')) and 3.582(1) Å (Se(2)-Se(3')). These distances are shorter than the sum of van der Waals radii of two selenium atoms, 4.0 Å. The average bond distances and angles of the ligands are listed in Table 1 together with those of other chromium-dioxolene complexes. The oxidation state of dioxolene ligands has been estimated from C-O and C-C bond distances, and O-Cr-O bite angles[7]. The typical C-O distances of semiquinonate and catecholate are 1.29 and 1.35 Å, respectively. These values are observed in chromium-dioxolene complexes, which was reported previously. The difference in the O-Cr-O angles is also found for the complexes of semiquinonate (81.6°) and catecholate (83.6°). One electror reduction of $Cr(Cl_4SQ)_3$ is expected to afford a mono-anionic specie: $[Cr(Cl_4SQ)_2(Cl_4Cat)]^{-}$[7], formally containing a catecholate and twc

TABLE 1. Intramolecular Bond Distances (Å) and Angles (°) for Members of the Chromium Dioxolene Complexes.

| Compound | Ligand | Cr-O (Å) | O-C (Å) | C-C (Å) | O-Cr-O |
|---|---|---|---|---|---|
| $Cr(Cl_4SQ)_3 \cdot CS_2 \cdot 1/2C_6H_6$ [a] | | 1.949(5) | 1.28(1) | 1.40(1) | 81.8(2) |
| $Cr(3,5\text{-}DTBSQ)_3$ [b, c] | | 1.932(5) | 1.289(8) | 1.40(1) | 81.4(2) |
| $Cr(Cat)_3^{3-}$ [d] | | 1.986(3) | 1.349(3) | 1.41(1) | 83.6(1) |
| $1 \cdot 0.5CH_2Cl_2$ | I | 1.926(6) | 1.315(9) | 1.40(1) | 84.1(2) |
| | II | 1.951(5) | 1.298(9) | 1.41(1) | 82.2(2) |
| | III | 1.964(5) | 1.288(9) | 1.40(1) | 81.7(2) |
| | ave. | 1.947(6) | 1.300(9) | 1.40(1) | 82.7(2) |

[a] ref [4]. [b] 3,5-DTBSQ = 3,5-di-*tert*-butylsemiquinonate. [c] ref [5]. [d] ref [6].

semiquinonates. In the complex **1**·$0.5CH_2Cl_2$, as can be seen in Table 1, there are some differences in the values of the distances and angles between ligand **I** and the other two ligands (**II** and **III**). The average Cr-O distance (1.926(6) Å) of ligand **I** is shorter than those of ligand **II** and **III** (1.951(5) and 1.964(5) Å), and the average C-O distance of **I** is 1.315(9) Å, longer by 0.03 Å than the values observed for the ligand **II** and **III**. Additionally, the bite angle is larger by 2 degree than those in the other ligands. These structural parameters of the ligand **I** are characteristics of catecholate. The semiquinonate form shows an asymmetric IR band at 1460 $cm^{-1}$, while the catecholate form has two characteristic bands at near 1260 and 1480 $cm^{-1}$. The complex **1** exhibits a band at 1250 $cm^{-1}$ in addition to a band at 1450 $cm^{-1}$, showing the formation of catecholate. Figure 2 shows an arrangement of the TMTSF dimers and $[Cr(Cl_4SQ)_2(Cl_4Cat)]^-$ anions. Each TMTSF dimer is associated with six

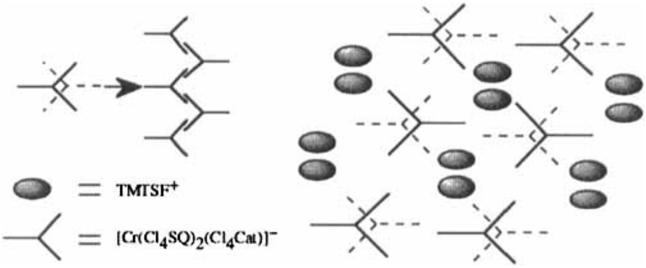

FIGURE 3. Schematic drawing of the crystal packing structure of **1**·$0.5CH_2Cl_2$. Block and dashed lines denote that the anions sit on the upper and lower sites, respectively.

$[Cr(Cl_4SQ)_2(Cl_4Cat)]^-$ anions through the Se···Cl contacts, which are also connected through Cl···Cl contacts to form a one-dimensional column structure. The dimers are interposed among the adjacent 1-D anion columns as schematically shown in Figure 3.

Solid state absorption spectrum of **1** shows that the pattern in the visible region is similar to a solution spectrum of $[Cr(3,5\text{-}DTBSQ)_2(3,5\text{-}DTBCat)]^-$ [5], where 3,5-DTBSQ and -DTBCat is 3,5-di-*tert*-butyl-semiquinonate and -catecholate, respectively. In addition, the complex shows a characteristic absorption band at 2300 nm. The corresponding band is observed in a series of the valence tautomerism complexes of Mn, Fe and Co metal ions[8]. These bands are assigned to the intramolecular intervalence transition (IT) between catecholate and semiquinonate, and show the strong evidence for the existence of two different oxidation state ligands, semiquinonate and catecholate. A single Lorenzian EPR signal is observed in the complex at 77 K. The obtained isotropic *g* value is 1.973 which is similar to that of $[Cr(SQ)_2(Cat)]^-$ measured in solution[9]. This indicates that unpaired electrons come from the $[Cr(Cl_4SQ)_2(Cl_4Cat)]^-$ moiety. Though the additional EPR signal from the cationic part is also expected, the obtained one is a single signal, which is accounted for by the spin cancellation of the TMTSF radical cations in the dimer. The complex shows semiconducting behavior at room temperature with room temperature conductivity 2.2 × $10^{-5}$ S·cm$^{-1}$. Low-conductive behavior of the complex is consistent with the result that the complex does not have any conduction columns. Figure 4 shows the temperature dependence of $\chi_M T$ and $1/\chi_M$ of **1**. As mentioned above, the complex consists of the TMTSF$^+$ cations and [Cr(Cl$_4$SQ)$_2$(Cl$_4$Cat)]$^-$ anions, and each of them may have a $S$ = 1/2 spin. Then, if there is no magnetic interaction among them, the $\chi_M T$ value

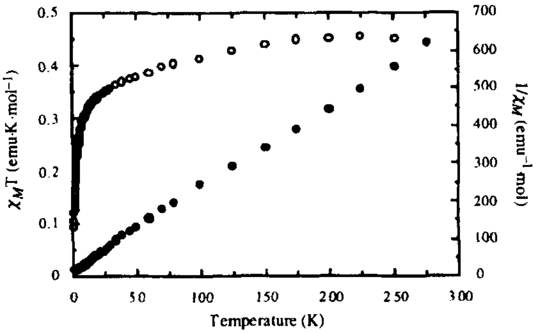

FIGURE 4. Temperature dependence of $\chi_M T$ and $1/\chi_M$ of **1**.

can be estimated to be 0.75 emu·K·mol$^{-1}$, assuming isotropic $g$ = 2.00. At room temperature, the observed $\chi_M T$ value is 0.42 emu·K·mol$^{-1}$ which is smaller than the theoretical value. The small $\chi_M T$ value indicates the spin cancellation in the TMTSF dimers, and is consistent with the result of the EPR measurement. Therefore, the apparent magnetic susceptibility is attributed to the [Cr(Cl$_4$SQ)$_2$(Cl$_4$Cat)]$^-$ anions. The $\chi_M T$ value is nearly independent on temperature in the range 150-300 K. To the contrary, the value gradually decreases with decreasing temperature below 150 K. The decrease of the $\chi_M T$ value is attributable to the intermolecular antiferromagnetic interaction among $[Cr(Cl_4SQ)_2(Cl_4Cat)]^-$ anions.

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