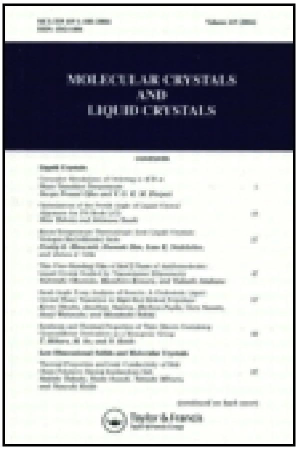

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Preparation of Superconducting $(TMTSF)_2NbF_6$ by Electrooxidation of TMTSF Using Ionic Liquid as Electrolyte

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High-quality single crystals of an organic superconductor $(TMTSF)_2NbF_6$ *(TMTSF: tetramethyltetraselenafulvalene) were prepared using room-temperature ionic liquid 1-ethyl-3-methylimidazolium·*NbF_6 *as electrolyte. The crystal is isostructural to the other members of the TMTSF superconducting family,* $(TMTSF)_2X$ *with octahedral anions X. The crystal and band structures and temperature dependence of electrical resistivity were reported. The salt exhibited a metal–insulator transition at 12 K due to the spin density wave formation at ambient pressure and became superconducting with* $T_c = 1.26\,K$ *(on-set) at* $P_c = 1.2\,GPa$.

Keywords: crystal and band structures; electrocrystallization; ionic liquid; $(TMTSF)_2NbF_6$; TMTSF superconductor

INTRODUCTION

The investigation of room-temperature (RT) ionic liquids has largely focused on systems of 1,3-dialkylimidazolium cation and inorganic anion(s) [1]. Although chlorometallate systems have many fascinating

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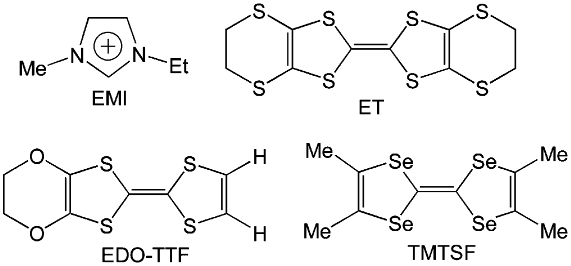
properties such as negligible vapor pressure, wide electrochemical window, thermal stability, low viscosity, and high ionic conductivity, they are sensitive to moisture. Following a report on air-stable 1-ethyl-3-methylimidazolium (EMI, Scheme 1)–based RT ionic liquids containing tetrafluoroborate and acetate anions in 1992 by Wilkes and Zaworotko [2], a wide range of new ionic liquids have been developed incorporating many different anions [3–5]. Among them, several EMI-based ionic liquids have been reported to be more conductive than 0.1 M potassium chloride solution (1.3×10^{-2} S cm^{-1} at 25°C) [5–11].

Because ionic liquids are commonly composed of organic cation and inorganic anions, they might be used as an electrolyte for electrocrystallization of cation radical salts. No other solvents are needed when the donor species are soluble in the ionic liquid. Even a nonpolar solvent such as benzene, which usually affords a less-conductive solution of electrolyte and hence is unfavorable for the electrocrystallization, can be used without any trouble. This might give a chance of preparing new organic (super)conductors that include solvent molecules such as κ-$(ET)_2X(solv)$ ($X = M(CF_3)_4$, M = Au, Ag, Cu) [12], β''-$(ET)_4X(solv)$ ($X = M(oxalate)_3$, M = Fe, Cr, Ga) [13,14], and so on.

In most cases, the obtained salts are identical to those prepared using conventional electrolytes such as tetrabutylammonium (TBA)X. In some cases, however, the ionic liquid provides new or high-quality salts that have not been harvested using conventional electrolyte. For example, $(EMI)F(HF)_{2.3}$, in which anions are a mixture of $H_2F_3^-$ and $H_3F_4^-$, gives single crystals of a new Mott insulator α'-$(ET)_2H_2F_3$ [15]. The electrooxidation of EDO-TTF in the presence of ionic liquid $(EMI)SbF_6$ produces single crystals of $(EDO\text{-}TTF)_2SbF_6$ that show the peculiar metal–insulator (MI) transition comprising the simultaneous occurrence of charge-ordering, anion-ordering, Peierls-like superlattice formation and partial molecular deformation (MI transition temperature (T_{MI}) = ca. 240 K) as observed in $(EDO\text{-}TTF)_2PF_6$ [16].



SCHEME 1 Chemicals in text.

On the other hand, TBA·SbF_6 provides $(EDO\text{-}TTF)_4(Sb_2F_{11})_{0.85}(H_2O)_4$, which is not isostructural to $(EDO\text{-}TTF)_2PF_6$ [17].

Here we report the preparation of high-quality single crystals of $(TMTSF)_2NbF_6$ by use of a RT ionic liquid, $(EMI)NbF_6$ [18]. Previously, the TMTSF salt was obtained by Bechgaard using TBA·NbF_6 [19], but no detailed data were reported concerning the crystal structure at ambient pressure and superconductivity up to 1.2 GPa, owing to the poor quality of the single crystal [19]. The disappearance of the high-field EPR intensity and the broadening of the signal below 14 K at ambient pressure strongly suggest the long-range magnetic ordering as observed for the other TMTSF salts with octahedral anions [20].

EXPERIMENTAL

Crystal Growth

Electrooxidation of TMTSF (15 mg) dissolved in a mixture of $(EMI)NbF_6$ (100 mg) and distilled CH_2Cl_2 (18 ml) under a constant current of 0.2–0.5 μA for a period of 2 weeks provides needle-shaped single crystals of $10 \times 0.5 \times 0.3\,mm^3$ of $(TMTSF)_2NbF_6$. Use of tetrahydrofuran instead of CH_2Cl_2 afforded tiny and thin single crystals.

Crystal Structure

The intensity data for the structural analysis were collected in an automatic four-circle diffractometer or an oscillator-type imaging plate with a monochromated MoKα radiation at RT. The structures were solved by a direct method using a SHELXS-97 or SIR 92 program [21]. The refinements of the structures were performed by full matrix least squares method (SHELXL-97 or CRYSTAN 6.3) [21]. The parameters were refined by adopting anisotropic temperature factors for nonhydrogen atoms. The positions of hydrogen atoms were calculated by assuming a C−H bond length of 0.96 Å and sp^3 conformation of the carbon atoms. The temperature factors of hydrogen atoms were fixed at 1.2 times U_{eq} of the carbon atom. The atomic coordinates, equivalent isotropic thermal parameters, bond lengths, and angles are provided as a CIF file in the supplementary information. (Cambridge Crystallographic Data Centre; deposition number CCDC 271391).

Transport Measurements

Transport measurements were performed by a four-probe method using the evaporated gold film as the electrodes, and annealed gold wires (10 μmϕ) were attached by gold paste (Tokuriki 8560-1A) at ambient pressure as well as under pressure with Be/Cu clump cell from RT to 0.6 K.

Band Structure Calculations

Band structure was calculated based on the crystal structure by extended Hückel tight-binding method with single-ζ parameters including d-orbitals of selenium atoms.

RESULTS AND DISCUSSION

The crystal belongs to triclinic system, $P\bar{1}$, $a = 7.290(4)$, $b = 7.726(2)$, $c = 13.900(5)$ Å; $\alpha = 82.86(2)$, $\beta = 85.50(3)$, $\gamma = 71.57(3)°$; $V = 735.26$ Å^3; $Z = 1$; $R = 0.0682$; GooF $= 0.714$. The disordered anion NbF_6 resides at an inversion center and was refined by assuming two orientations. Figure 1 shows the crystal structure of $(TMTSF)_2NbF_6$, which is

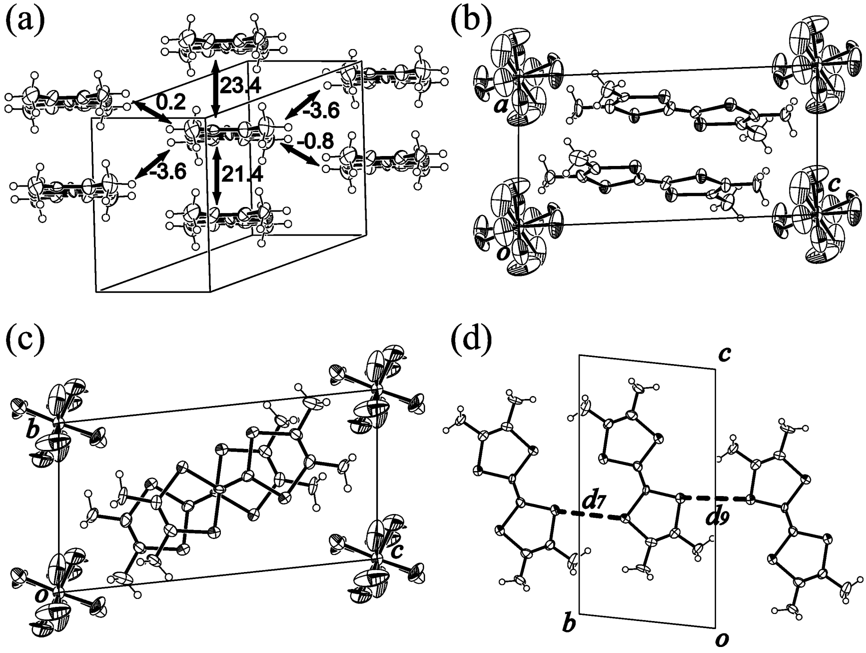


FIGURE 1 Crystal structure of $(TMTSF)_2NbF_6$ (a) viewed along the molecular long axis (the numbers indicate the overlap integrals in 10^{-3} units), (b) view along the b^*-axis, (c) viewed along the a^*-axis, and (d) Se··Se atomic contacts along the side-by-side direction.

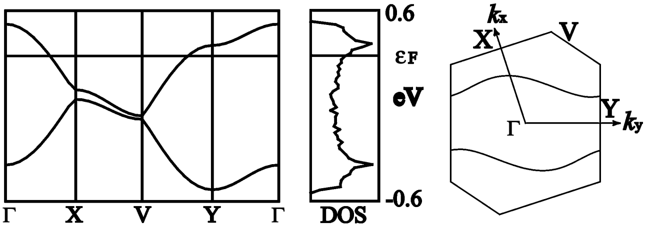


FIGURE 2 Calculated energy dispersion, density of states (DOS), and Fermi surface of (TMTSF)$_2$NbF$_6$ by a tight-binding model based on the extended Hückel method.

isostructural to other members of (TMTSF)$_2$X family (X = PF$_6$, AsF$_6$, SbF$_6$, TaF$_6$, ClO$_4$, and ReO$_4$) [19,22]. TMTSF molecules form a segregated column along the face-to-face direction ($\|a$-axis, Fig. 1a), and two TMTSF molecules form a zigzag dimer within a column as a unit (Fig. 1b,c). There are no inter- and intracolumn Se··Se atomic contacts shorter than the sum of the van der Waals radii (3.80 Å) [23] as usual for the family with octahedral anions (Fig. 1d, $d_7 = 3.97$ Å, $d_9 = 3.96$ Å).

Figure 2 depicts the calculated energy dispersion, density of states (DOS), and Fermi surface. Because of the lack of enough side-by-side transfer interactions, the Fermi surface is not closed but open along the k_y-direction with fair warping along the k_x-direction as those of other (TMTSF)$_2$X [22d,f,24].

At ambient pressure the RT conductivity (σ_{RT}) is 120 S cm^{-1}, which is the least conductive one among the superconducting (TMTSF)$_2$X, as shown in Table 1 [19,23,25], and may suggest that our sample of the NbF$_6$ salt still includes some imperfections. Figure 3 shows the temperature dependence of resistivity. The metallic behavior following $\rho_{\|a} \propto T^2$ in the 300–85 K range was observed down to 12 K, at which an abrupt transition to insulating state occurred. The insulating phase is most plausibly assignable to the spin density wave state because of the close similarities of T_{MI}, crystal, and band structures with other (TMTSF)$_2$X with octahedral anions in this work and observation of long-range magnetic ordering below T_{MI} from the high-field EPR measurement in Ref. [20]. The insulating state was suppressed to lower temperatures as the applied hydrostatic pressure increased (T_{MI} = ca. 10 K at 0.5 GPa, ca. 4 K at 1.0 GPa). At 1.2 GPa, a superconducting transition with on-set temperature of 1.26 K (midpoint $T_c = 1.12$ K) was observed. The superconducting T_c was suppressed by a rate of $dT_c/dP = -0.8$ K GPa^{-1} above 1.2 GPa, and the rate is in good

TABLE 1 Symmetry of X, RT Conductivity (σ_{RT}), Unit Cell Volume (V), Ion Radius of Anion (r), Critical Pressure (P_c), Critical Temperature (T_c), and Origin of the MI Transition of Organic Superconductors $(TMTSF)_2X$

X	Symmetry	σ_{RT} (S cm^{-1})	V (Å^3)	r^a (Å)	$P_c{}^b$ (GPa)	T_c (K)	Origin of MI transition^c	Ref.
PF_6	Octahedral	540	714.3	2.95	0.65	1.1	SDW (12 K)	20
AsF_6	Octahedral	430	719.9	3.05	0.95	1.1	SDW (12 K)	20
SbF_6	Octahedral	500	737.0	3.19	1.05	0.38	SDW (17 K)	20
NbF_6	Octahedral	120	735.3	3.20	1.2	1.12	SDW (12 K)	—
TaF_6	Octahedral	300	735.6	3.29	1.1	1.35	SDW (11 K)	20
ClO_4	Tetrahedral	700	694.4	2.84	0	1.4	SDW (6.5 K by rapid cool)	20
ReO_4	Tetrahedral	300	710.5	3.12	0.95	1.2	OD (177 K)	20
FSO_3	Pseudo-tetrahedral	1600	695.3	2.89	0.5	ca.3	OD (88 K)	22c

[a] Ref. 28a.

[b] P_c: critical pressure for superconductivity.

[c] Origin of MI transition with T_{MI} in parentheses. SDW: spin density wave, OD: order–disorder transition of anion molecules.

accordance with those observed for other $(TMTSF)_2X$ salts: –1.0 for X = ClO_4 [25], −0.9 for X = PF_6 [26] under hydrostatic pressure.

Table 1 compares the unit cell volume, critical pressure P_c, T_c, T_{MI}, and the origin of the MI transition for all members of superconducting $(TMTSF)_2X$. The fairly good linear relations have been reported

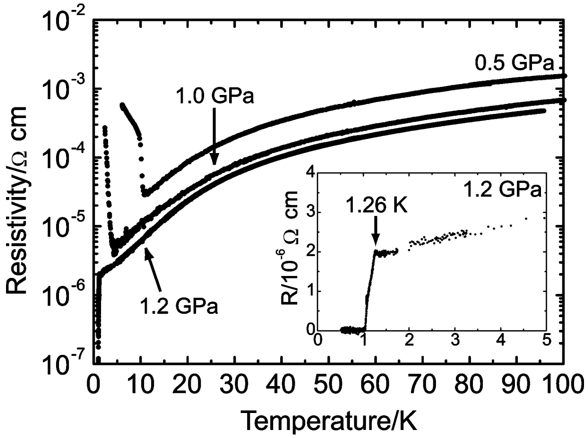


FIGURE 3 Temperature dependence of resistivity of $(TMTSF)_2NbF_6$ along the a-axis. Inset shows a superconducting transition with on-set of 1.26 K at 1.2 GPa.

between the T_{MI} and unit cell volume, average intercolumn Se··Se distance $[(2d_7+d_9)/3]$, or anion volume [22e,27]. However, the order–disorder transition temperature (T_{MI}(OD)) does not exhibit a good relation with these structural parameters. The T_{MI} or P_c has also been known to relate with the ion size of the anion as pointed out by Kistenmacher [28a], Cowan [28b], and Saito and Yoshida [28c] (Fig. 4) with

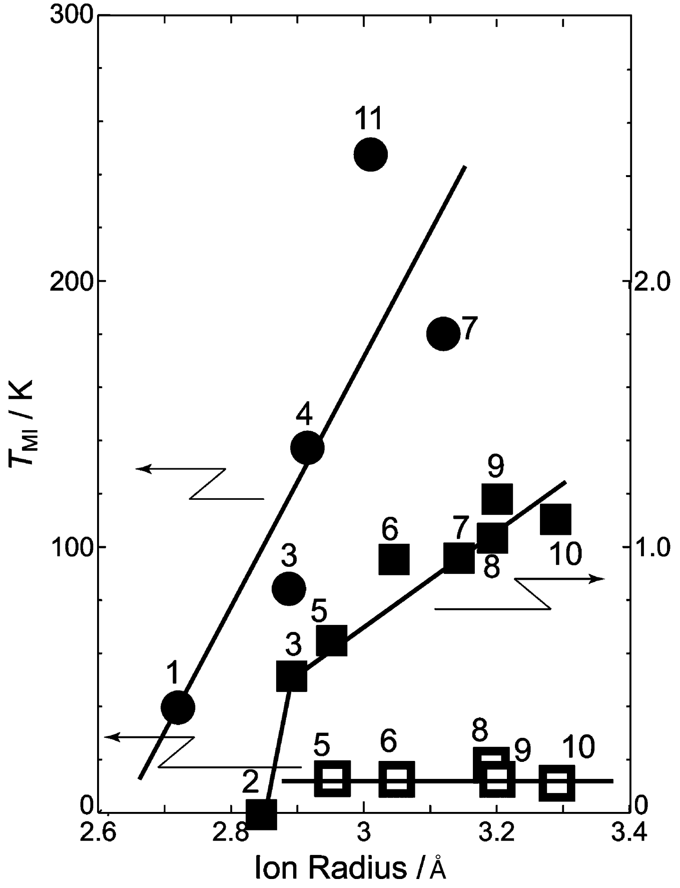


FIGURE 4 Metal–insulator transition (T_{MI}(OD): ● for tetrahedral anions, T_{MI}(SDW): □ for octahedral anions) and critical pressure (P_c: ■) of $(TMTSF)_2X$ as a function of the anion radius. 1: X = BF_4, 2: ClO_4, 3: FSO_3, 4: F_2PO_2, 5: PF_6, 6: AsF_6, 7: ReO_4, 8: SbF_6, 9: NbF_6, 10: TaF_6, and 11: BrO_4. For BF_4, F_2PO_2, and BrO_4 salts, the values of T_{MI}(OD) and anion radius are used as follows: BF_4 salt ($r = 2.72$ Å, T_{MI}(OD) = 40 K), F_2PO_2 salt ($r = 2.90$ Å, T_{MI}(OD) = 137 K), and BrO_4 salt ($r = 3.01$ Å, T_{MI}(OD) = 250 K).

less scattering compared with the aforementioned relations. The results (T_{MI}(SDW) and P_c) of the NbF_6 salt well fit into the relations in Fig. 4, indicating that the NbF_6 salt is a member of superconducting $(TMTSF)_2X$ family with octahedral anion and the critical parameters are mainly governed by the anion size.

CONCLUSION

In conclusion we demonstrated that the RT ionic liquid can be used as an electrolyte to afford high-quality single crystals of a new organic superconductor $(TMTSF)_2NbF_6$. The crystal and band structures and transport property of the NbF_6 salt indicate that the salt is a new member of the superconducting $(TMTSF)_2X$ family, exhibiting common structural and physical features among the salts with an octahedral anion.

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