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Crystal Structure of the Organic Metal $(DMET)_2BF_4$ with Two Columns along Two Crystallographic Axes

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(Received June 19, 1990)

The crystal structure of $(DMET)_2BF_4$: 5,6-dihydro-2-(4,5-dimethyl-1,3-diselenol-2-ylidene)dithiolo[4,5-*b*][1,4]dithiinium tetrafluoroborate (2:1), $(C_{10}H_{10}S_4Se_2)_2BF_4$, is determined. Crystal data: M_r=919.49, triclinic, $P\bar{1}$, a=7.032(2), b=7.812(3), c=27.502(11) Å, α=90.87(2), β=90.28(2), γ=106.22(2)°, V=1450.5(15) Å^3, Z=2, D_x=2.11 Mg m^{-3}, λ(Mo $K\alpha$)=0.71068 Å, μ=5.60 mm^{-1}, $F(000)$=890, T=297 K, R=0.077 for 4600 reflections. Two crystallographically independent DMET molecules separately form columns along nearly perpendicular directions, and ordered BF_4 anions are located between the DMET columns.

In recent years, radical salts of DMET, which is a hybrid donor between TMTSF and BEDT–TTF, with some monovalent anions have been studied.[1–5] In the course of the study, seven superconductors have been discovered. The DMET salts, in addition to superconductivity, exhibit a variety of electronic properties; metal, semiconductor, and spin density wave (SDW) transition.[3,5] The DMET salts were classified into five Groups on the basis of temperature dependence of conductivity and the shape of counter anions. The salts of Group 2, which is with tetrahedral anions, show metallic behavior at room temperature under the normal pressure. A metal-insulator transition occurs at low temperature.

Besides these attractive electronic properties, crystal structures of DMET salts are interesting from the point of view of the asymmetry of donor molecule. The crystal structure has been determined for PF_6,[6] ReO_4,[7] $Au(CN)_2$,[8] AuI_2,[9] $AuBr_2$,[10] $AuCl_2$,[11] IBr_2,[12] and I_3[13] salts. In these salts, except for the $AuBr_2$ salt of Group 5, DMET molecules are stacked with an alternate molecular orientation and form one-dimensional columns. Within the columns some short intermolecular contacts exist and some salts additionally have intermolecular contacts between the columns. These intra- and intercolumnar contacts highten the dimensionality of the salt.

The title compound show the room temperature conductivity of about 130 S cm^{-1}.[6] On cooling, the metallic character continues down to about 40 K, where the temperature dependence of the conductivity changes to that of insulator. These behaviors are characteristic to the salts of Group 2.[1] The EPR study revealed that an SDW transition occurred at 20 K. Although the transition temperature is a little lower than the temperature of the conductivity maximum, the metal-insulator transition is probably due to the formation of SDW.

The shape of $(DMET)_2BF_4$ crystals is not needle-like as seen in other DMET salts, but rhombus-like. It is suggested that $(DMET)_2BF_4$ has two-dimensionality. This conjecture was supported by the fact that the anisotropy of steady[14] and optical[15] conductivity of $(DMET)_2BF_4$ crystal was about 1 to 4, and was confirmed through the crystal structure determination reported preliminarily.[4] In this paper, the molecular structure and crystal structure of $(DMET)_2BF_4$ are reported in detail.

Experimental

Crystals of $(DMET)_2BF_4$ were prepared by electrochemical oxidation of DMET in 1,1,2-trichloroethane solution in the presence of $(n\text{-}Bu_4N)\cdot BF_4$ at a constant current (1 μA). D_m was not determined. The crystal used for the data collection was black and rhombus-like: 0.35×0.25×0.13 mm^3. The data collection was performed with the Rigaku AFC-M automated four-circle diffractometer with graphite monochromated Mo $K\alpha$ radiation (λ=0.71068 Å). Unit-cell dimensions were determined from 38 selected reflections (16°<2θ<28°). The intensity data were collected using the ω-scan technique (2θ<30°) and the ω–2θ scan technique (2θ>30°) with a scan rate 3.75° min^{-1} ($\Delta\omega$=1.55°+0.50°·tan θ) in ω to $(\sin\theta)/\lambda$= 0.65 Å^{-1} ($0\leq h\leq 8$, $-9\leq k\leq 9$, $-35\leq l\leq 35$). Two standard reflections (measured at an interval of 100 reflections) showed small (<0.6%) random variations. The data were corrected for absorption effect using a Gaussian integration procedure; T_{min}=0.26, T_{max}=0.50. 6516 independent reflections were collected and 4600 reflections ($|F_o|>3\sigma(|F_o|)$) were used in the structure refinement. Intensity statistics indicated space group $P\bar{1}$ rather than $P1$ and this choice was later confirmed by the successful structure solution and least-squares refinement. The Se and S atoms were located by the Patterson method and the structure was solved by successive Fourier synthesis and refined by the block-diagonal least-squares method. The atomic and anomalous scattering factors were taken from International Tables for X-ray Crystallography.[16] All computations were carried out using UNICS III program.[17] No hydrogen atoms were located. $\sum w\cdot(|F_o|-|F_c|)^2$ was minimized, where $w=\sigma^{-2}(|F_o|)$, with $\sigma(|F_o|)$ based on counting statistics. The maximum value of Δ/σ was 0.01 for B_{23} of C(8A) in the final least-squares cycle.

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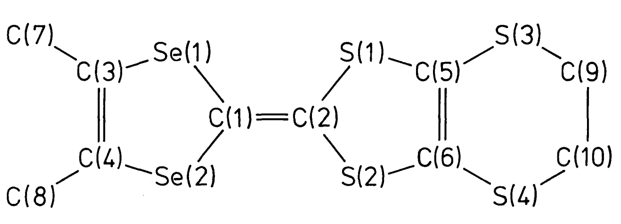

It resulted in the agreement factors R=0.077, wR=0.047 and S=8.32. No correction was made for the secondary extinction. A difference synthesis based on the structure factors derived from the final parameter values showed some peaks of density (−1.4 to 1.3 $e\cdot Å^{-3}$). The temperature factor of the ethylene group in one DMET molecule was anomalously large. Although a difference synthesis using all parameters showed no significant peak around the C(10A) atom, the difference synthesis using the final parameters except those for C(10A) showed double peaks (3.7 and 2.0 $e\cdot Å^{-3}$). The parameters reported for the C(10A) atom are, therefore, averaged ones in some way. ORTEP II[18] was used to produce crystal structure illustrations.

Results and Discussion

The final positional and thermal parameters are tabulated in Table 1.[19] The bond lengths and angles are given in Tables 2 and 3, respectively. The geometry of the DMET molecule A, which consists in the column along the a axis, is in reasonable agreement with those observed in other DMET salts[7-9,11,12] except ethylenedithio moiety ($-S-CH_2-CH_2-S-$). The apparent bond length of C(9A)–C(10A), given in the table, is shorter than those in other salts (ca. 1.51 Å) owing to the positional disorder of C(10A).

Table 1. Fractional Atomic Coordinates and the Equivalent Isotropic Temperature Factors of $(DMET)_2BF_4$

Atom	$10^4\cdot x$	$10^4\cdot y$	$10^4\cdot z$	B_{eq}[a)]/Å^2	Atom	$10^4\cdot x$	$10^4\cdot y$	$10^4\cdot z$	B_{eq}/Å^2
Molecule A					Molecule B				
Se(1)	2034(2)	−1303(2)	−576.5(4)	2.79(4)	Se(1)	−2727(2)	2599(2)	4586.3(4)	2.69(4)
Se(2)	3195(2)	2466(2)	−45.6(4)	2.67(4)	Se(2)	1877(2)	3737(2)	4381.2(4)	2.73(4)
S(1)	1645(4)	−3175(4)	496 (1)	2.7 (1)	S(1)	−1694(4)	1218(4)	5669 (1)	2.7 (1)
S(2)	2785(4)	279(4)	1008 (1)	2.6 (1)	S(2)	2575(4)	2256(4)	5471 (1)	3.1 (1)
S(3)	1122(5)	−5345(4)	1371 (1)	4.1 (1)	S(3)	−1357(5)	81(4)	6672 (1)	3.3 (1)
S(4)	2447(5)	−1231(4)	1993 (1)	3.7 (1)	S(4)	3778(4)	1298(5)	6437 (1)	3.7 (1)
C(1)	2516(15)	−27(14)	12 (4)	2.3 (3)	C(1)	−135(14)	2734(14)	4800 (4)	2.5 (3)
C(2)	2329(15)	−849(13)	440 (3)	2.1 (3)	C(2)	184(14)	2136(14)	5259 (3)	2.1 (3)
C(3)	2579(14)	783(14)	−964 (3)	2.3 (3)	C(3)	−1824(15)	3589(13)	3970 (4)	2.9 (4)
C(4)	3061(14)	2413(15)	−741 (4)	2.9 (4)	C(4)	138(15)	4099(14)	3873 (4)	2.8 (4)
C(5)	1703(14)	−3223(14)	1125 (4)	2.8 (4)	C(5)	−108(14)	999(13)	6147 (4)	2.3 (3)
C(6)	2248(14)	−1616(14)	1353 (4)	2.6 (4)	C(6)	1806(15)	1449(15)	6050 (4)	2.8 (4)
C(7)	2390(15)	440(16)	−1517 (4)	3.6 (4)	C(7)	−3487(16)	3757(16)	3640 (4)	3.2 (4)
C(8)	3537(16)	4220(15)	−976 (5)	4.1 (4)	C(8)	1154(16)	4917(14)	3413 (4)	3.0 (4)
C(9)	1150(23)	−4918(18)	2024 (4)	6.8 (6)	C)9)	620(16)	−406(16)	7040 (4)	4.0 (4)
C(10)	2010(35)	−3407(20)	2213 (5)	14.9 (11)	C(10)	2551(17)	1094(16)	7027 (4)	3.8 (4)
BF_4									
B(1)	5581(21)	3362(19)	2314 (5)	3.6 (5)					
F(1)	6417(11)	5124(10)	2369 (3)	7.4 (3)					
F(2)	6878(12)	2428(11)	2449 (3)	7.6 (4)					
F(3)	3933(11)	2829(11)	2591 (3)	6.9 (3)					
F(4)	5102(11)	2975(10)	1834 (2)	6.2 (3)					

a) $B_{eq}=(4/3)\cdot(B_{11}\boldsymbol{a}\cdot\boldsymbol{a}+B_{12}\boldsymbol{a}\cdot\boldsymbol{b}+B_{13}\boldsymbol{a}\cdot\boldsymbol{c}+\cdots)$.

Table 2. Bond Lengths (l)

Bond	l/Å	l/Å	Bond	l/Å	l/Å
DMET	Molecule A	Molecule B		Molecule A	Molecule B
Se(1)–C(1)	1.868(10)	1.886(10)	S(3)–C(9)	1.822(13)	1.842(13)
Se(1)–C(3)	1.909(11)	1.909(11)	S(4)–C(6)	1.778(11)	1.775(11)
Se(2)–C(1)	1.881(11)	1.834(10)	S(4)–C(10)	1.758(16)	1.830(12)
Se(2)–C(4)	1.913(10)	1.929(11)	C(1)–C(2)	1.339(14)	1.391(14)
S(1)–C(2)	1.755(10)	1.745(10)	C(3)–C(4)	1.359(15)	1.354(15)
S(1)–C(5)	1.730(11)	1.759(11)	C(3)–C(7)	1.539(14)	1.513(16)
S(2)–C(2)	1.764(10)	1.754(11)	C(4)–C(8)	1.513(17)	1.515(14)
S(2)–C(6)	1.723(11)	1.752(11)	C(5)–C(6)	1.350(15)	1.322(14)
S(3)–C(5)	1.741(11)	1.751(10)	C(9)–C(10)	1.268(19)	1.527(15)
BF_4					
B(1)–F(1)	1.343(16)		B(1)–F(3)	1.358(15)	
B(1)–F(2)	1.370(19)		B(1)–F(4)	1.370(15)	

Table 3. Bond Angles (θ)

Angle	$\theta/°$	$\theta/°$	Angle	$\theta/°$	$\theta/°$
DMET	Molecule A	Molecule B		Molecule A	Molecule B
C(1)-Se(1)-C(3)	94.2(4)	92.5(5)	Se(1)-C(3)-C(7)	115.4(8)	113.1(7)
C(1)-Se(2)-C(4)	94.7(5)	94.5(4)	C(4)-C(3)-C(7)	125.4(10)	126.8(10)
C(2)-S(1)-C(5)	97.2(5)	95.8(5)	Se(2)-C(4)-C(3)	117.0(8)	116.2(8)
C(2)-S(2)-C(6)	95.8(5)	94.9(5)	Se(2)-C(4)-C(8)	115.2(8)	115.4(7)
C(5)-S(3)-C(9)	103.6(6)	102.8(5)	C(3)-C(4)-C(8)	127.8(10)	128.4(10)
C(6)-S(4)-C(10)	101.9(6)	100.3(5)	S(1)-C(5)-S(3)	115.0(6)	113.7(5)
Se(1)-C(1)-Se(2)	114.9(5)	116.6(6)	S(1)-C(5)-C(6)	115.6(8)	116.3(8)
Se(1)-C(1)-C(2)	121.8(8)	120.3(7)	S(3)-C(5)-C(6)	129.3(9)	129.9(9)
Se(2)-C(1)-C(2)	123.3(8)	123.2(7)	S(2)-C(6)-S(4)	115.1(6)	113.7(6)
S(1)-C(2)-S(2)	112.6(5)	114.3(6)	S(2)-C(6)-C(5)	118.8(8)	118.5(8)
S(1)-C(2)-C(1)	123.4(8)	124.2(8)	S(4)-C(6)-C(5)	126.2(9)	127.8(8)
S(2)-C(2)-C(1)	124.0(8)	121.5(7)	S(3)-C(9)-C(10)	122.3(11)	112.4(9)
Se(1)-C(3)-C(4)	119.2(7)	120.1(8)	S(4)-C(10)-C(9)	131.9(14)	113.5(8)
BF_4					
F(1)-B(1)-F(2)	110.7(10)		F(2)-B(1)-F(3)	108.6(11)	
F(1)-B(1)-F(3)	110.6(12)		F(2)-B(1)-F(4)	107.8(12)	
F(1)-B(1)-F(4)	109.0(11)		F(3)-B(1)-F(4)	110.0(10)	

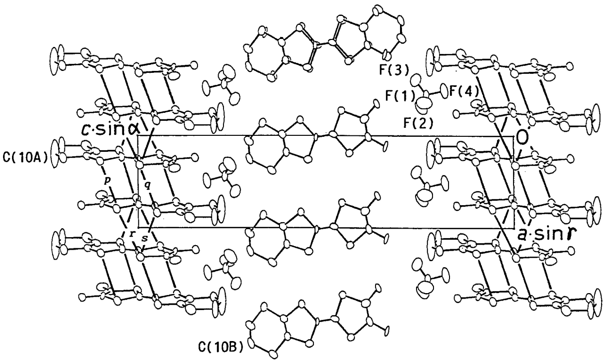

Fig. 1. Crystal structure of $(\mathrm{DMET})_2\mathrm{BF}_4$ viewed along the b axis. Thermal ellipsoids indicate the region of 50% probability. Thin solid lines show the shorter intermolecular contacts than the sum of van der Waals radii. Their distances; p=3.771(3) Å, q=3.735(3) Å, r=3.939(2) Å and s=3.803(3) Å.

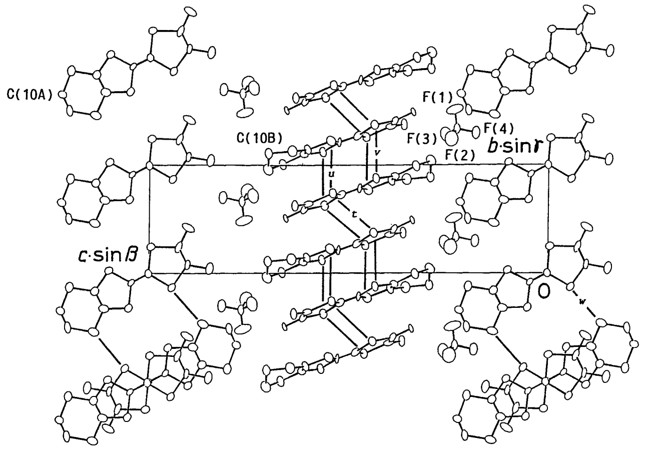

Fig. 2. Crystal structure of $(\mathrm{DMET})_2\mathrm{BF}_4$ viewed along the a axis. Thermal ellipsoids indicate the region of 50% probability. Thin solid lines show the shorter intermolecular contacts than the sum of van der Waals radii. Their distances; t=3.924(2) Å, u=3.825(4) Å, v=3.837(4) Å and w=3.618(4) Å.

The DMET molecule A is almost planar except for the "averaged" C(10A) atom. The other atoms are within about 0.07 Å from the molecular plane determined by the Se(1A), Se(2A), S(1A), S(2A), C(1A), and C(2A) atoms.

The geometry of the molecule B, which consists in the column along the b axis, is slightly different from those observed in other salts. In the molecule B the bond length of C(1B)-C(2B) is longer and that of C(5B)-C(6B) is shorter than the corresponding lengths in other DMET salts. The molecule B is almost planar except for the C(10B) atom. It is about 0.8 Å apart from the molecular plane determined as molecule A; the other atoms are within about 0.2 Å from the plane. Such magnitude of the deviation from the planality has been reported for other DMET salts.

As seen in Fig. 1, there exist two types of DMET columns along the a and the b axes. A similar structure was reported for $(\mathrm{DIMET})_2\mathrm{ClO}_4$;[20] DIMET ($\mathrm{C_{10}H_{10}S_6}$) is a 2-(4,5-dimethyl-1,3-dithiol-2-yliden) analog of DMET. In both types of columns A and B, DMET molecules stack with an alternate orientation related by an inversion center. The $\mathrm{BF_4}$ anion is located in between two types of columns (a crystallographic general point), and no orientational disorder is detected.

In the column A, the molecular plane determined with two Se, two inner S and two central C atoms is almost normal to the a axis (87.4°). The angle between the normal to the plane and the stacking axis (2.6°) is very small as compared with those in other $(\mathrm{DMET})_2\mathrm{X}$ (typically ca. 20°).[7–9,11,12] Although two interplanar distances are almost equal (3.51 and 3.52 Å) to each other, two intermolecular contact patterns between the neighboring molecules in the columns are different.

One type of overlap has four Se–S contacts (refered as *p* and *q* in the Figure) shorter than the sum of the van der Waals radii, the other has two Se–Se (*r*) and two Se–S (*s*) ones. It is noted that the ethylenedithio moiety is not responsible for shorter contacts. There also exist short intermolecular contacts between the adjacent two columns A as seen in Fig. 2, where the interatomic (two Se–S) contacts (*w*) indicated are shorter than the sum of the van der Waals radii. These contacts lie between the molecules related by an inversion. The pattern of the intermolecular contacts within and between columns A has not been seen in other DMET salts and is different from that of the column B of this salt. This stacking mode, however, resemble that of TMTSF salts.[21]

In the column B, the normal to the molecular plane is tilted by 23.7° from the *b* axis. The DMET molecules are stacked with an alternate molecular orientation related by an inversion center as in the column A. Two interplanar distances are not equal (3.56 and 3.59 Å) to each other. One type of overlap has four shorter Se–S contacts (*u* and *v*), and the other has two shorter Se–Se contacts (*t*) and four slightly longer Se–S ones. This stacking mode has widely been observed in other DMET salts.[6–13] As shown in Fig. 1, there is no short intermolecular contact between the columns B. It is noted that the ethylenedithio moiety is not responsible for shorter contacts in both types of overlap of DMET molecules within the columns A and B.

Between the column A and the column B there is no short intermolecular contact. The BF_4 anions exist between the columns A and B, and are ordered. They are surrounded by four DMET molecules, and each BF_4 anion contacts with four methyl groups and two ethylene groups.

The little dimerization of DMET molecules within the one-dimensional columns seems responsible for metallic behavior at room temperature under the normal pressure. The same conjecture will apply to $(DMET)_2BF_4$. Comparing the structure of the column with those in other DMET salts, the structure of the column B resembles those of $(DMET)_2[Au(CN)_2]$[8] and $(DMET)_2[AuCl_2]$.[11] Interatomic distances of $(DMET)_2BF_4$ within the column are, however, slightly longer than those of the $Au(CN)_2$ and the $AuCl_2$ salts. Accordingly, the interaction within the column is weak in the BF_4 salt. The lower conductivity at room temperature than $Au(CN)_2$ and $AuCl_2$ salts is probably due to these differences in the interatomic distances and interaction.

Although ReO_4 is the same in shape, i.e., tetrahedral, the crystal structure of $(DMET)_2[ReO_4]$ is very different from that of $(DMET)_2BF_4$ probably because of the larger anion size.[7] In this respect, crystal structures of other tetrahedral anions are interesting, and the result will be published shortly.[12,22]

This work was supported in part by Grant-in-Aid for Specially Promoted Research No. 63060004 from the Ministry of Education, Science and Culture.

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