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THE CRYSTAL AND ELECTRONIC STRUCTURES OF A NEW MOLECULAR CONDUCTOR, $(HMTTeF)_2[Pt(dmit)_2]$

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The crystal structure of $(HMTTeF)_2[Pt(dmit)_2]$ was determined. The unit cell contains four HMTTeF molecules. They are stacked to make a tetradic column. Tetradic columns link together, making a two-dimensional network by Te...Te short contacts. The $Pt(dmit)_2$ anions are located in the space between two-dimensional HMTTeF tetrad with their molecular plane almost perpendicular to the HMTTeF molecules.

The recent discoveries of organic superconductors have aroused a large interest in the field of molecular metals. The intermolecular interaction between multi-chalcogen π-donor and π-acceptor molecules is essential to enhance the dimensionality of the metals, which is useful for the suppression of the characteristic instabilities of molecular metals. We have been interested in the crystal structure and electrical properties of tellurium analogues of TTF(tetrathiafulvalene) and its derivatives, since a strong Te···Te interaction or interchain coupling and the large band width will be expected.

Recently HMTTeF(hexamethylenetetratellurafulvalene) was synthesized by Wudl and Ahron-Shalom.1) We report here the result of the crystal structure determination of $(HMTTeF)_2[Pt(dmit)_2]$ (dmit:isotrithionedithiolate). Two-dimensional intermolecular Te···Te network was observed in the srtucture of $(HMTTeF)_2$-$[Pt(dmit)_2]$ and its effect on the electronic structure is discussed.

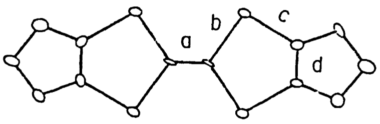
Black plates of $(HMTTeF)_2[Pt(dmit)_2]$ were obtained by the electrochemical oxidation (at a constant current of ca. 1μA) of a solution of HMTTeF and $(n\text{-}Bu)_4N[Pt(dmit)_2]$. The crystal data are: triclinic, $P\bar{1}$, a=15.466(4), b=13.525(4), c=10.586(3) Å, α=92.85(3), β=102.50(2), γ=75.91(2)°, V=2096.8 Å^3, Z=2. The structure was solved by the Patterson method and refined by the block-diagonal least-squares method. Independent 5514 reflections were used in the calculations. The final R value was 0.066.

Although suitable conducting paint was not available, preliminary measurements of conductivity were performed. The conductivity of the crystal was 20 S cm^{-1} at room temperature and the temperature dependence seems to be semiconducting.

The mean bond lengths of HMTTeF molecules are shown in Table 1 and the crystal structure is shown in Fig. 1. There are two crystallographically

Table 1. Comparison of the mean bond lengths(Å) of HMTTeF molecules. The bond lengths are averaged by assuming D_{2h} symmetry.

	HMTTeF(1)	HMTTeF(2)
a	1.23(3)	1.26(3)
b	2.13(1)	2.12(1)
c	2.08(1)	2.08(1)
d	1.34(3)	1.37(3)



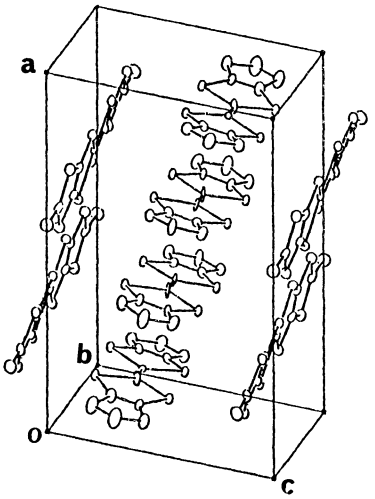


Fig. 1. The three-dimensional crystal structure of $(HMTTeF)_2$-$[Pt(dmit)_2]$.

independent HMTTeF molecules. The unit cell contains four HMTTeF molecules and they are stacked to make a tetradic column. Interplanar distances between HMTTeF molecules are 3.70 and 3.62 Å. HMTTeF molecules are nearly planar, but one of the heterocyclic rings of HMTTeF(1) is bent at the two tellurium atoms by about 9° from the plane of the tetratelluro-substituted ethylene moiety. The tetradic columns link together, making a two-dimensional network with Te···Te short contacts. The Te···Te distances within the HMTTeF tetrad are smaller in comparison with the van der Waals distance 4.12 Å and intermolecular contacts of chalcogen atoms shorter than the sum of the van der Waals radii are shown in Fig. 2.

The $Pt(dmit)_2$ anions are located in the space between two-dimensional HMTTeF tetrad with their molecular plane almost perpendicular to the HMTTeF molecules. $(HMTTeF)_4(PF_6)_2$ is the first charge-transfer salt of HMTTeF, whose crystal structure was determined by the X-ray methods.$^{2)}$ In this salt, HMTTeF molecules are stacked to make a trimeric molecular column of HMTTeF and the remaining neutral one is located in the space between HMTTeF columns with their plane almost parallel to the direction of the columns. In the recently found monoclinic form of β-$(HMTTeF)_2PF_6$, a similar molecular arrangement was observed.$^{3)}$ This molecular arrangement seems to be a characteristic feature of the salts with considerably large two-dimensionality.$^{4)}$ Pairs of $Pt(dmit)_2$ molecules are arranged along the direction approximately parallel to the long axis of the $Pt(dmit)_2$ molecules (Fig. 3).

Figure 4 shows intermolecular overlap integrals(S) of the HOMO(highest occupied molecular orbital) of the HMTTeF molecule and the LUMO(lowest unoccupied molecular orbital) of $Pt(dmit)_2$. The overlap integrals between HMTTeF molecules within the tetrads of HMTTeF molecules are very large compared with other chalcogen fulvalene compounds: the overlap integral of TTFs in TTF.TCNQ is 5×10^{-3} $^{5)}$ and that of TMTSFs in $(TMTSF)[Ni(dmit)_2]$ is 40×10^{-3}.$^{6)}$ The overlap integrals of inter-tetrads of HMTTeF columns ($C \approx D$) are one-third of those of

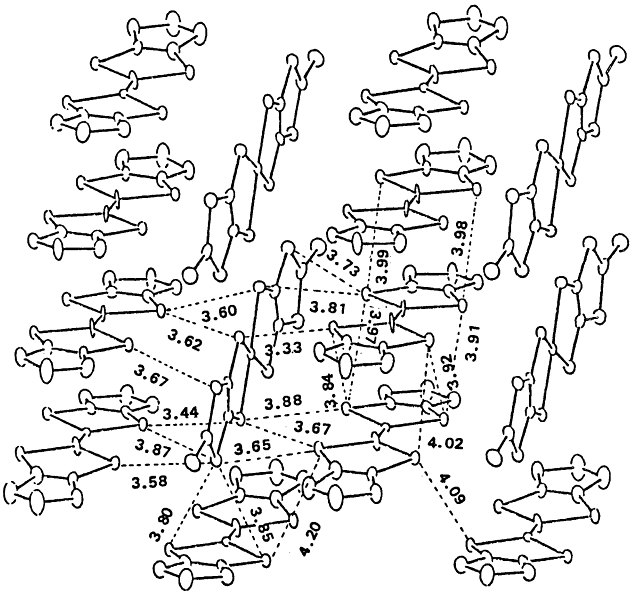


Fig. 2. Intermolecular short contacts of chalcogen atoms in $(HMTTeF)_2[Pt(dmit)_2]$.

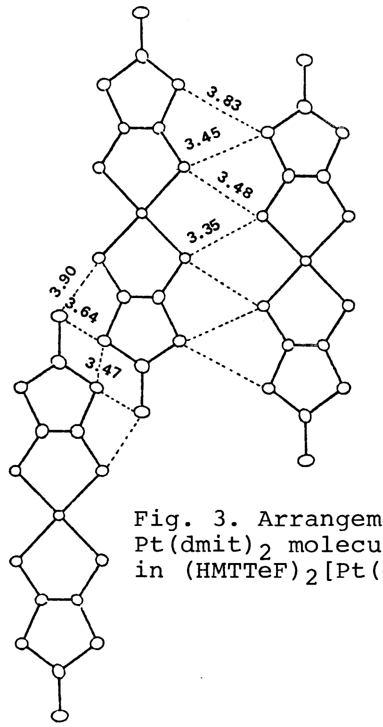
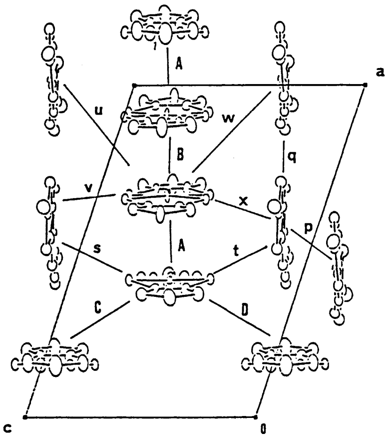


Fig. 3. Arrangement of $Pt(dmit)_2$ molecules in $(HMTTeF)_2[Pt(dmit)_2]$.



A	-63.58	s	-2.622
B	60.28	t	5.805
C	21.07	u	-1.393
D	21.56	v	-3.179
p	1.683	w	1.540
q	-1.608	x	5.065

Fig. 4. Overlap integrals ($\times 10^{3}$) of the HOMO(HMTTeF) and LUMO($Pt(dmit)_2$).

HMTTeF molecules within tetrads ($A \approx B$). As first approximation, we neglect the other overlap integrals, because they are negligibly small.7) The energy band was calculated based on the simple tight-binding methods in the case of t=A/C=3. We could not experimentally estimate the exact charge transfer value of this salt, because there is no standard sample of various valence state of HMTTeF salts. If we assume the formal charge of $Pt(dmit)_2$ is -1.0, as the starting material $(n\text{-}Bu)_4N[Pt(dmit)_2]$, the energy band is 3/4 filled. Figure 5 shows the energy band of $(HMTTeF)_2[Pt(dmit)_2]$, and there remains no Fermi surface. Thus, this compound seems to be non-metallic. It will be worthwhile to point out that the periodicity of the molecular array is closely correlated to the nature of the band structure. For example, if the energy band is calculated by assuming more simple diadic structure of $(HMTTeF)_2[Pt(dmit)_2]$ as shown in Fig. 6, instead of the tetradic structure shown in Fig. 5, there appears two-dimensional Fermi surface similar to that of well-known organic superconductor β-$(BEDT\text{-}TTF)_2I_3$.8) In this case much wider metallic band than those ever obtained in molecular conductors will be expected. This indicates a possibility of the design of new molecular superconductors based on HMTTeF.

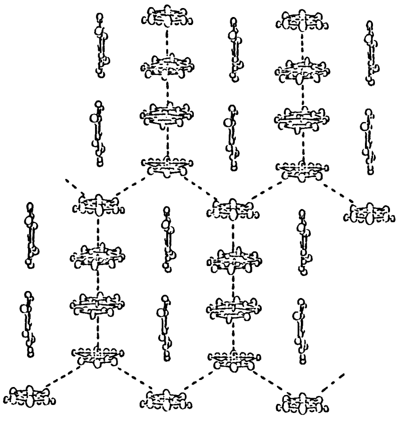


Fig. 5a.

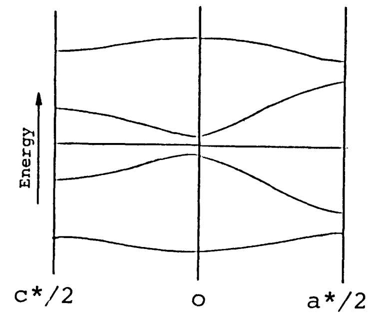


Fig. 5b.

Fig. 5. a) The tetradic structure of HMTTeF molecules in (HMTTeF)$_2$-[Pt(dmit)$_2$]. b) The energy band of (HMTTeF)$_2$[Pt(dmit)$_2$].

Fig. 6. a) Proposed diadic structure of (HMTTeF)$_2$-[Pt(dmit)$_2$]. b) The energy band of the diadic structure. c) The closed Fermi surface of the diadic structure.

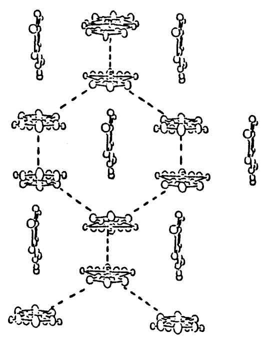


Fig. 6a.

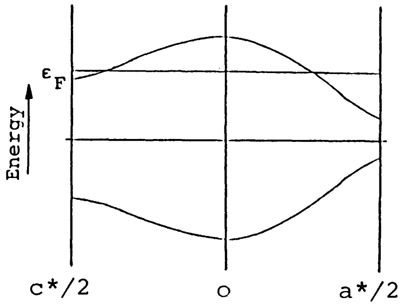


Fig. 6b.

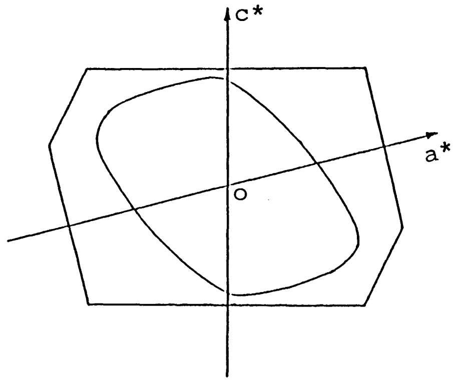


Fig. 6c.

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3) The lattice constants of the monoclinic form are a=17.355(3), b=13.777(4), c=28.105(6) Å, β=99.18(2)°. The details of the crystal structure will be reported elsewhere.

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7) Owing to the large intermolecular overlap integrals between HMTTeF molecules, there may be some possibility that the energy levels other than HOMO will be mixed. Then the energy band width will become much larger compared with that expected in this calculation.

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