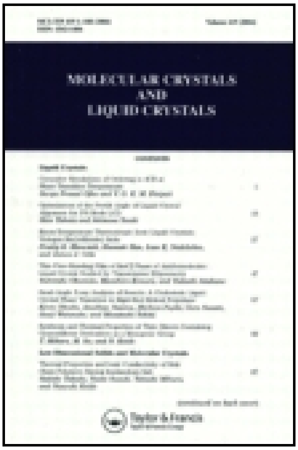

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Low Temperature (4K) and High Pressure (6.5 Kbars) Crystal Structures of $(TMTSF)_2PF_6$

Bernard Galiois [a] , Jacques Gaultier [a] , Christian Hauw [a] , Daniel Chasseau [a] , Alain Meresse [a] , Alain Filhol [b] & Klaus Bechgaard [c]

[a] Laboratoire de Cristallographie, Université de Bordeaux I, 351, Cours de la Libération, 33405, TALENCE CEDEX, France

[b] Institut Laüe Langevin, XI56, 38042, GRENOBLE CEDEX, France

[c] Department of General and Organic Chemistry, H.C. ORSTED Institute, DK2100, Copenhagen, Denmark

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LOW TEMPERATURE (4K) AND HIGH PRESSURE (6.5 Kbars) CRYSTAL STRUCTURES OF $(TMTSF)_2PF_6$.

Bernard GALIOIS, Jacques GAULTIER, Christian HAUW, Daniel CHASSEAU, Alain MERESSE, Alain FILHOL* and Klaus BECHGAARD $^\Delta$
Laboratoire de Cristallographie, Université de Bordeaux I,
351, Cours de la Libération, 33405 TALENCE CEDEX (France)
*Institut Laüe Langevin, X156, 38042 GRENOBLE CEDEX (France)
$^\Delta$Department of General and Organic Chemistry, H.C. ORSTED Institute, DK2100 COPENHAGEN, Denmark.

Abstract We have performed structural investigation of the $(TMTSF)_2PF_6$ salt at low temperature (neutron diffraction) and under pressure (X.Ray diffraction). Evolutions of the main structural parameters are described. Their descriptions allow the first structural approach of pressure effects on the Bechgaard salts and give comparative informations for a same compound.

INTRODUCTION

It is now well known that the Bechgaard salts exhibit a metallic behaviour at high temperatures and undergo different transitions to low temperature and (or) under pressure. For several salts, such as $(TMTSF)_2PF_6$ or $(TMTSF)_2A_sF_6$, the phase diagram is well determined {1}, so that the nature of the ground state for a given (P,T) value is known to be either insulating or superconducting. The mechanisms of these various instabilities are presently understood through theoretical models {2,3} in which the main parameters are given by the room temperature structure. In fact, all these compounds are isostructural. They crystallize in a (P $\bar{1}$) triclinic space group. Their structure have been extensively described {4,5} and may be well characterized by short intra and interchain Se – Se contacts, the magnitude of which may smoothly differ with anion {6}.

Up to now, the temperature and pressure dependence of these structural parameters are almost unknown and predictable changes are only proposed by existing theories {3}. To check these models, (300K, 1bar) structural determinations of $(TMTSF)_2X$ salts are not necessary sufficient while the structural investigations under temperature and pressure conditions will be a better basis in the understanding of the relationships between crystal structure and physical properties.

Thus, in this paper, we describe the low temperature (4K,1bar) and the high pressure (300K, 6.5 Kbars) structures of $(TMTSF)_2PF_6$.

EXPERIMENTAL PART

The low temperature investigation was carried out by neutron diffraction on the 4 circle diffractometer "D10" at the high flux reactor of the Institut Laüe Langevin at Grenoble.(λ=1.500 Å).The sample was a hydrogenated twinned crystal of 0.3×0.5×2.9 mm^3. The geometry of the twinning is such as only 0kℓ reflections of the reciprocal space are superimposed so that recorded intensities of the 0kℓ plane have been corrected to take into account the contribution of the considered sublattice. A set of 1248 reflections were recorded in the $0 < \frac{\sin\theta}{\lambda} < 0.471$ Å^{-1} range.

Pressure measurements were performed by X ray diffraction with a gasketed diamond anvil cell set on a 2 circle Stoe Diffractometer. Water was used as the pressure transmitting medium. Accuracy in the pressure determination is estimated to ∿ 0.5 kbar. Crystal sizes are 0.10×0.10×0.15 mm^3. At P = 6.5 Kbars, 1822 intensities have been recorded by ω scans, with a molybdene wavelength ($0 < \frac{\sin\theta}{\lambda} < 0.594$ Å^{-1}).

LATTICE PARAMETERS EVOLUTION

Lattice parameters at respectively (4K, 1bar), (300K, 1.5Kbar) and (300K, 6.5 Kbars) are listed in table 1, comparatively to their (300 K, 3 Kbars){ 7 } values already determined.

	a (Å)	b (Å)	c (Å)	α(°)	β(°)	γ(°)	V (Å³)
300K, 1bar {4}	7.297	7.711	13.522	83.39	86.27	71.01	714
4 K, 1bar	7.076	7.632	13.322	84.14	88.05	70.13	673
300K,1.5Kbar	7.279	7.699	13.490	83.50	86.37	70.78	709
300K,3Kbars{7}	7.196	7.693	13.518	83.76	86.08	70.64	702
300K,6.5Kbars	7.135	7.598	13.325	83.64	87.03	70.50	677

TABLE 1. Lattice parameters of $(TMTSF)_2PF_6$

*Effects induced either by temperature or pressure show the same evolution for a given parameter : increase of α and β ; decrease of a,b,c and γ.

*The most significant variation $\Delta x/x_{RT,1bar}$ where Δx is defined as $X-X_{RT,1bar}$, is found in the a direction which thus appears to be more dependent to applied contraints.

*Results obtained by Morosin et al {7} show a good agreement with our values under pressure except for the c parameter which seems to be surevaluated when the curve c = f(P) is plotted.

*PARKIN et al {8} showed that the critical pressure P_c, above which a superconducting state is formed, may be correlated with the c lattice parameter at ∿300K,1bar . According to the P_c value of PF_6 {9} and the c = 13.123 Å lattice parameter of the ClO_4 compound at 7K {10} a similar calculation at low temperature gives a c variation ∿0.23% Kb^{-1}. Under pressure, the exprimental c variation is ∿ 0.22% Kb^{-1}. Pressure effects added to temperature effects lead to a smaller c variation ∿0.15% Kb^{-1} with (300K,1bar) and 1.7K, 7Kbars) data (to be published).

*Detailed lattice parameters evolution as a function of temperature is given figure 1. No important anomaly is observed at the metal to insulator transition T ∿ 12 K. More sensitive results {11} obtained by capacitance measurements confirm this latter point.

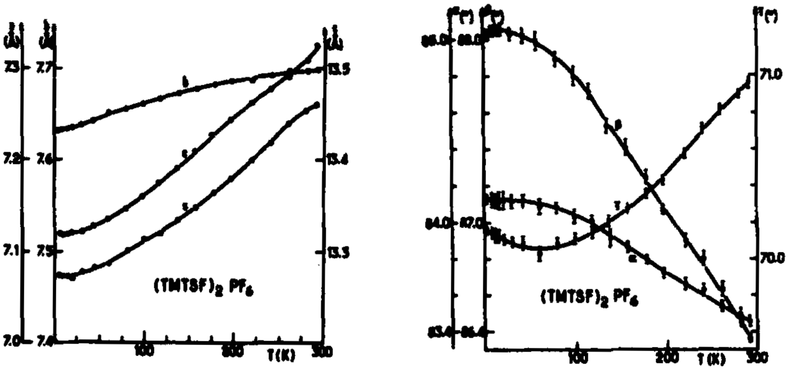

FIGURE 1 Lattice parameters evolution as a function of temperature

STRUCTURAL RESULTS

Crystal structure determinations were carried out with the same least square refinement method based on Fo.Final reliability factors are R = 0.078 at T = 4 K and R = 0.048 at P = 6.5 Kb. As no evidence in the loss of inversion center has been observed, the two structures were thus determined in the $P\bar{1}$ space group. For an easier comparison with room temperature structural data, the same notation will be used in the below description. Atomic coordinates, bond lengths and angles will be published in detail elsewhere.

*TMTSF packing

At room temperature, the stacking along the a axis is slightly dimerized (d_1 = 3.63 Å; d_2 = 3.66 Å). The corresponding interplanar distances, at T = 4 K and P = 6.5 Kbars are reported in table 2. Under pressure, d_1 and d_2 distances are equal. Looking to the low temperature distances, the question naturally arises whether only pressure effects suppress dimerization. In fact at T = 4 K, the observed difference is on the edge of significance. Therefore, it is quite difficult to speak of dimers under constraint.

Overlapping displacements deduced from the position of the center of gravity of neighbouring molecules, in the stack are nearly equivalent. The variation of the angle of the normal to the molecular plane with the a axis is less than 0.2° so that TMTSF molecular stacking is thus unchanged under pressure or temperature conditions.

Interchain distances (figure 2) show that the irregular contacts already observed at room temperature between nearest interstack molecules still exist at 4 K or under pressure. Se-Se distances are mentionned in table 2. Their relative difference are nearly unchanged either under pressure or at 4 K.

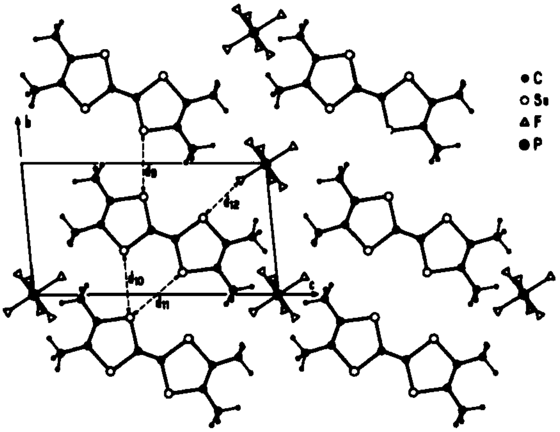

FIGURE 2 : View along a showing Se-Se and Se-F interstack distances

An interesting point lies in the evolution of the ϕ angle between the TMTSF molecular plane and the shortest interstack Se-Se contacts. ϕ decreases under constraint ($\phi_{300\ K} = 18.4°$, $\phi_{6.5\ Kb} = 17.7°$; $\phi_{4K} = 15.9°$). As the angle of TMTSF molecular plane with the a axis is unchanged, such an observed variation may be explained by shifts of the TMTSF molecule corresponding to the shortest Se-Se contacts. Transverse components of such a displacement (in the TMTSF plane) are found to be ∿ 0.1 Å while longitudinal component (parallel to the stacking direction) may differ under low temperature or pressure conditions (∿0.2 Å at T = 4 K; ∿ 0.1 Å under 6.5Kb).

	300K,1bar	4K,1bar	300K,6.5Kb
interstack distances			
d_1	3.63	3.52	3.56
d_2	3.66	3.55	3.56
interstack distances			
d_9	3.88	3.71	3.73
d_{10}	3.93	3.74	3.78
d_{11}	3.96	3.86	3.85
shortest Se-F distance			
	3.23	3.06	3.12

TABLE 2 : Shortest distances in $(TMTSF)_2PF_6$

*Anion disorder

Another important result of these comparative structures is given by thermal isotropic parameters (B_{eq}) of the fluorine atoms. At room temperature {4 }, F atoms have rather large thermal parameters suggesting a disorder of the anion. At P = 6.5 Kbars (table 3) these values decrease and their difference to an average selenium B_{eq} are reduced. The PF_6 disorder is minimized under pressure. According to the diffraction method used in the low temperature determination, thermal parameters have in fact a nuclear origin, therefore their magnitudes may not be directly compared with the two first set of data outcoming from X ray diffraction calculations. Nevertheless, at T = 4K, Se and F atoms have quite identical values, even if the F_3 motion is still slightly larger. The PF_6 disorder is thus nearly suppressed. No distinct maxima positions of F atoms observed in nuclear density maps after refinement confirm this latter point.

B_{eq}	300K,1bar	300 K,6.5Kbars	4K,1bar
F_1	9.36 (Å^2)	6.03	0.57
F_2	8.75	4.64	0.50
F_3	11.12	7.20	0.71
Se	2.8	2.05	0.52

TABLE 3 : Comparison of isotropic thermal parameters (B_{eq}) of fluorine atoms to the average B_{eq} value of Se atoms.

As the Se-F and $C_{(methyl)}$-F shortest distances (table 2) decrease under applied constraint, interactions between organic stacks and anions are more significant. At low temperature, H-F distances (for F atoms close to the bc plane) ∿ 2.46 Å are found to be shorter than the 2.52 Å Van der Waals contacts. Such H-F interactions have been already observed at T ∿ 125K in $(TMTSF)_2AsF_6$ {12}.

In conclusion, this work is the first one which shows temperature and pressure structural effects on a $(TMTSF)_2X$ compound. In $(TMTSF)_2PF_6$, changes induced under pressure or at low temperature are very similar. Nevertheless intra and interchain Se-Se distances, anion disorder are more perturbed at 4K than under a 6.5 Kbars pressure. Further investigations at upper pressures are in progress as well as a (1.7 K, 7 Kb) structural determination.

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