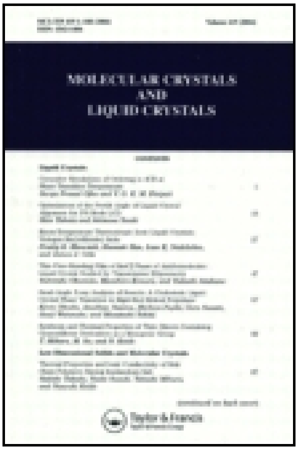

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Structure of Di-Tetramethyltetraselen-afulvalenium Perchlorate $(TMTSF)_2\ C\ell O_4$ in its Low Temperature (T ~ 10 K) Ordered Phase

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Structure of Di-Tetramethyltetraselenafulvalenium Perchlorate $(TMTSF)_2C\ell O_4$ in its Low Temperature (T ~ 10 K) Ordered Phase

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At T ~ 24K, the quasi one dimensional organic superconductor $(TMTSF)_2C\ell O_4$ shows a structural transition leading to a doubling (a × 2b × c) of the unit cell. The neutron average structure (i.e. superlattice reflections not included) at T = 7K has already been published. In the present paper, we report the results of a rigid body refinement of the low temperature (T ~ 10K) structure from both the earlier set of neutron main reflection intensities and an extra set of X-ray superlattice intensities.

This improved structural description clearly shows that the anion orientations alternate in the *b* direction only and that there is no significant TMTSF displacement from the average position.

We compare these results with recent structural data obtained on $(TMTSF)_2ReO_4$ which exhibits below T ~ 180 K an insulating ground state instead of the metallic one for the perchlorate salt.

1. INTRODUCTION

$(TMTSF)_2C\ell O_4$ belongs to the isomorphous series of tetramethyltetraselenafulvalene salts $(TMTSF)_2X$ where X stands for anions such as PF_6^-, AsF_6^-, ReO_4^-, $C\ell O_4^-$, NO_3^-, SCN^- . . . These compounds are being studied extensively because of their unusual physical properties.[1] Several of them become superconductors at low temperature (around 1–2 K) and under pressure. For instance, $(TMTSF)_2ReO_4$ exhibits superconductivity above 11.5 Kbar[2] (whereas the low pressure ground state is insulating due to a metal-insulator transition occuring at high temperature T ~ 180K and ambient pressure[3]). However $(TMTSF)_2C\ell O_4$ presents a different behaviour since it may be superconducting below 1.2K at ambient pressure.[4] Moreover its low temperature ground state is determined by the rate of cooling below about 40K. Slowly cooled samples (< 0.1 K/mn) exhibit superconductivity while fast cooling (> 40 K/mn) generates a magnetic insulating state.[5]

In $(TMTSF)_2X$ salts containing non centrosymmetric anions, these various behaviours are largely conditioned by structural phase transitions involving orientational ordering of the anions. At room temperature, these compounds are isostructural[6,7,8] and crystallize in the $P\bar{1}$ triclinic symmetry. TMTSF molecules are stacked along the *a* direction with a zig zag configuration. This leaves cavities in which anions are located at inversion centers of the unit cell. In the case of non centrosymmetric anions (such as $C\ell O_4^-$, ReO_4^-), it has been found that they present several orientations which are related by inversion and randomly distributed so that the inversion symmetry is an average effect. At low temperature, the anions order through a structural transition thus producing a superstructure. Various types of ordering can occur depending on the anion (symmetry, size. . .) and they are conveniently distinguished by the reduced wave vectors of the superstructure reflections.[9]

In $(TMTSF)_2ReO_4$, below 177 K, one observes a superstructure with a wave vector $\vec{q}_1$ = (1/2, 1/2, 1/2)[10] corresponding to the alternation of the two ReO_4^- orientations along the three unit cell axes a, b and c. This was deduced from an analysis of the superstructure reflection intensities[11] and confirmed recently by a full structure determination at 120 K.[12] Ordering of the anions also leads to an insulating state[3] (note that the a* component of the wave vector is equal to twice the Fermi wave vector and a large gap opens at the Fermi level).

In the case of $(TMTSF)_2C\ell O_4$ a structural transition occurs at T ~ 24 K in slowly cooled samples. The superstructure reflections are characterized by the reduced wave vector $\vec{q}_2$ = (0, 1/2, 0).[13] This transition is revealed for example by anomalies in the specific heat[14] or in the conductivity[15] behaviour as a function of temperature ($d\rho/dT$ only increases in the vicinity of 24 K) and is considered as previously mentioned in the perchlorate salt to be driven by an ordering of the anion orientations. Since the superstructure involves only a doubling of the periodicity along the *b* direction this implies that the $C\ell O_4^-$ tetrahedra order with the same orientation in the *a c* planes while the orientation alternates from plane to plane in the *b* direction.

In order to confirm the superstructure ordering of $(TMTSF)_2C\ell O_4$ and to compare its low temperature structure with that of $(TMTSF)_2ReO_4$ (the only one in the series to have been studied in detail) we have performed a low temperature structure analysis of the perchlorate salt using new X ray data together with the earlier neutron collected set of intensities.

2. PRELIMINARY RESULTS

Neutron data were obtained at T = 7 K from a twinned single crystal ($3 \times 0.4 \times 0.3$ mm^3) mounted on the four circle diffractometer D 10 at the Institut Laue Langevin–Grenoble. The corresponding results, already published elsewhere[16] are only summarized below.

Thermal expansion of the unit cell was measured (7 K to 300 K) and does not show any abrupt change at the transition temperature in contrast to the 0.5° change in the lattice parameter γ observed for the ReO_4 salt by Guy et al.[17]

$(TMTSF)_2C\ell O_4$ Lattice parameters:

T = 300 K[8] a = 7.266 Å b = 7.678 Å c = 13.275 Å V = 694.4 Å^3

$\alpha = 84.58°$ $\beta = 86.73°$ $\gamma = 70.43°$

T = 7 K[16] a = 7.068 Å b = 7.638 Å c = 13.123 Å

$\alpha = 84.50°$ $\beta = 88.00°$ $\gamma = 68.92°$ V = 658.2 Å^3

As the available neutron flux and the crystal sizes did not allow to collect superlattice reflections, only a set of 970 main reflection intensities ($0 < \sin\theta/\lambda < 0.513$ Å^{-1}) were collected at T ~ 7 K. The corresponding structures (space group $P\bar{1}$) was refined in the $a \times b \times c$ unit cell to R = 0.09. Since no superlattice intensities were included in the refinement, the structure is only an average one giving however valuable information on the organic TMTSF sublattice.

Intrastack interactions show a weak dimerization (d_1 = 3.56 Å, d_2 = 3.52 Å) not observed at room temperature (d_1 = 3.64 Å;

d_2 = 3.63 Å)[8] and an improvement of the transverse overlap components between neighbouring TMTSF molecules within a given stack (Δt_1 = 0.07 Å, $\Delta t'_1$ = 0.03 Å).[16]

Nevertheless, the largest modifications are found in the transverse interactions as shown in table 1. Interstack Se-Se contacts undergo an important shortening at low temperature which is even more pronounced for the A-B molecular contacts than for the A-C ones (A, B and C molecules are labelled in Figure 1).

TABLE I

Comparison of intermolecular distances (Å) within a stack and of shortest interstack distances at 300 K and 7 K. (7 K values are from the average structure calculations. As the $C\ell O_4^-$ ordering was not described, the shortest Se-O distance is not mentioned).

	300 K[8]	7 K[16] (a × b × c)
Intrastack distances		
d_1	3.64	3.56
d_2	3.63	3.52
Intrastack shortest Se-Se distances		
d_9	3.778	3.57
d_{10}	3.865	3.72
d_{11}	3.955	3.78
Shortest Se-O distance		
d_{12}	3.34	—

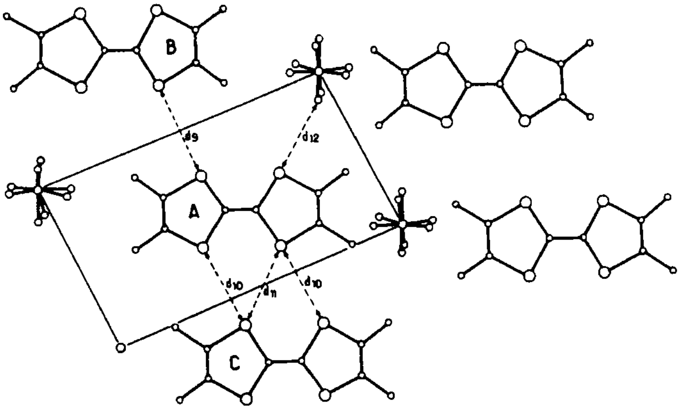

FIGURE 1 $(TMTSF)_2C\ell O_4$: projection along *a* of the (a × b × c) unit cell relative to the average structure description at T = 7 K. The shortest interstack contacts (Se-Se and Se-O) are labelled with the numbering corresponding to table 1. Symmetry operations are : A (x, y, z), B(− x, 2 − y, 1 − z), C(1 − x, − y, 1 − z)

This analysis can be considered only as a first step in the determination of the low temperature structure since the problems of centrosymmetry (the P$\bar{1}$ space group was assumed) and especially anion ordering could not be investigated.

3. DETAILED SUPERSTRUCTURE AT 11 K

a) Experimental

To determine the structural changes associated with the 24 K transition, we have measured 234 superlattice reflections at 11 K using X ray diffraction. The crystal was mounted in a Displex cryocooler placed on a modified Huber goniometer in the normal beam lifting counter geometry. CuKα radiation was selected using a doubly-bent graphite monochromator. Reflections from the (2kℓ), (± 1kℓ) and (0kℓ) reciprocal planes were measured. Intensities were collected as the maximum height of the peak and were thus not corrected for background. This was considered to be an acceptable approximation (a similar procedure has given good results in the case of $(TMTSF)_2ReO_4$[11]) and was also motivated by the rapid decrease of the superlattice reflection intensities with irradiation time[18] so that a fast measurement procedure was prefered. Actually these intensities were reduced by a factor of 2 after about 16 hours of irradiation and the crystal had to be translated with respect to the X-ray beam when the irradiation was too strong.

Collected intensities were corrected for polarization and were normalized to take account of irradiation effects. X-ray absorption was neglected.

b) Superstructure refinement method

The refinement was performed in the low temperature a × 2b × c unit cell. The geometry of the organic TMTSF molecules being already known from the average structure a rigid body refinement method† was used to limit the number of variable parameters. The program has been modified to accept both neutron and X ray scattering factors so that the two sets of collected intensities (720 main reflections with $I_{obs} > 2.56\ \sigma\ (I_{obs})$; 234 superstructure reflections) were introduced in the refinement, each of them characterized by an independent scale factor.

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†ORION program (André, Renaud, Fourme, 1971).

Starting atomic coordinates and thermal parameters are based on our previously determined average structure.[16] The doubling of the b parameter leads to consider two $C\ell O_4^-$ tetrahedra. Since final results obtained either with a P1 or P$\bar{1}$ space group do not show significant differences, the P$\bar{1}$ centrosymmetric description was prefered. Positions of the atoms of the two $C\ell O_4^-$ anions, in the b direction are thus related by the inversion center which is located at the origin of the unit cell, midway between two Cℓ atoms (see Figure 2).

Atoms are distributed between three groups (two independant TMTSF and one $C\ell O_4^-$) each of them corresponding to 7 parameters to be refined (3 rotations, 3 translations and one isotropic thermal parameter). In the last stage of the refinement, the Cℓ and O atomic positions were then independently refined. Final atomic coordinates are listed in table 2.

The overall reliability factor $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ is ~ 0.164 (R ~ 0.189 for superstructure reflections only and R ~ 0.144 for main reflections). This latter value is larger than the previous one (R = 0.09) obtained in the unconstrained refinement of the average structure. Several limitations may explain such relatively high R values:

—the refinement method limits the number of degrees of freedom (rigid body constraint)

—X-ray peak intensities instead of integrated ones introduce errors which are estimated to be in the range 5–10%

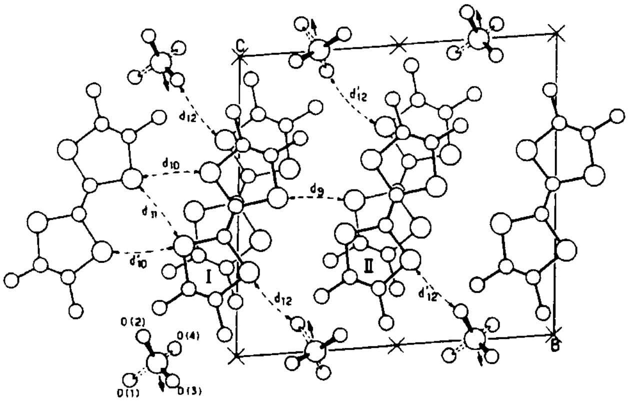

FIGURE 2 Projection along *a* of the (a × 2b × c) low temperature primitive unit cell. The direction of the Cℓ displacements are given by arrows, the inversion centers of the unit cell are marked by crosses. Heavy lines define the (x, y, z) TMTSF molecules of each independent (I & II) stacks and the numbering of the shortest Se-Se interactions corresponds to the notation of table 4.

—The joint use of X ray and neutron data leads to atomic thermal parameters mixing both electronic and nuclear contributions.

—The small difference between neutron and X-ray data also influence the overall R value.

We are nevertheless confident that our results provide a reliable description of the main structural changes which are involved in the low temperature ground state.

c) Structural results

Organic sublattice

Figure 2 shows the projection of the structure in the *b c* plane. Heavy lines represent the two TMTSF groups (labelled I and II) independently refined. The remaining molecules are obtained by symmetry. Bond lengths and angles in both types of TMTSF species derived from the average structure determination were constrained in the refinement.

The angles between the chain direction (*a* axis) and the normal to the TMTSF(I) and TMTSF(II) molecular planes are 1.82° and 1.40° respectively while the angle between the two normals is 1.30°.

The low temperature organic lattice is built from two independent segregated stacks of TMTSF(I) and TMTSF(II) (Figure 3a). The interplanar distances (table 3) are close to those of the average structure and thus confirm the increase of the diadic character ($\Delta = d_1 - d_2 = 0.04$ Å) of the stacks at low temperature. Such an organization thus contrasts with that of $(TMTSF)_2ReO_4$ in which stacks are homologous and built by alternance of pairs of TMTSF(I) and TMTSF(II) molecules (Figure 3b). A strong tetramerization is therefore clearly observed as shown by the noticeable difference ($\Delta \sim 0.10$ Å) existing between the largest and the smallest interplanar distances.

Moreover, rigid body translational shifts of the TMTSF molecules from their average position are less than 0.02 Å, so that the organic lattice is only weakly distorted below the transition. This is in agreement with the suggestions of POUGET et al[13] and differs from the relatively large translations of the TMTSF groups (0.022 Å, − 0.002 Å, 0.062 Å along *a*, *b*, *c* respectively) observed in the perrhenate salt.[12]

Therefore, the shortest intermolecular Se-Se distances (table 4) do not differ much from the results mentioned in the average structure description. The shortest one ($d_9 = 3.57$ Å) appears clearly smaller than the corresponding distance (3.68 Å) in the perrhenate salt.[12] This is also true for all interchain distances and may be correlated to

TABLE II

Atomic coordinates in the (a, 2b, c) low temperature unit cell.

	x/a	y/b	z/c
CL	−0.00335	−0.24556	−0.00377
O(1)	−0.03736	−0.32736	−0.04247
O(2)	0.12857	−0.28420	0.08763
O(3)	0.06716	−0.19246	−0.07749
O(4)	−0.20781	−0.18714	0.03694
SE(1)	0.31054	−0.07934	0.61939
SE(2)	0.15278	0.12871	0.51067
SE(3)	0.38290	−0.16560	0.38592
SE(4)	0.21930	0.04060	0.27691
C(1)	0.23135	0.02154	0.70013
C(2)	0.16211	0.11120	0.65591
C(3)	0.25171	−0.00160	0.49426
C(4)	0.08604	0.20193	0.70350
C(5)	0.24591	−0.00633	0.81347
C(11)	0.37689	−0.15031	0.24140
C(12)	0.30731	−0.06281	0.19547
C(13)	0.27916	−0.03698	0.40056
C(14)	0.28875	−0.03796	0.07934
C(15)	0.46267	−0.23977	0.18724
H(101)	0.11300	0.18724	0.79149
H(102)	0.16121	0.24602	0.67252
H(103)	−0.08458	0.23682	0.69251
H(111)	0.18988	0.05731	0.85796
H(112)	0.39947	−0.04663	0.83358
H(113)	0.16214	−0.05204	0.83925
H(121)	0.23491	0.03733	0.06030
H(122)	0.19568	−0.06544	0.04679
H(123)	0.43904	−0.07020	0.04294
H(131)	0.41319	−0.22414	0.10043
H(132)	0.39717	−0.28649	0.21552
H(133)	0.61703	−0.26765	0.18519
SE(21)	0.30663	0.41913	0.61887
SE(22)	0.15768	0.62795	0.51227
SE(23)	0.37991	0.33511	0.38422
SE(24)	0.22502	0.54215	0.27726
C(21)	0.22952	0.51914	0.70078
C(22)	0.16403	0.60913	0.65747
C(23)	0.25247	0.49795	0.49443
C(24)	0.09021	0.69936	0.70605
C(25)	0.24126	0.49030	0.81391
C(31)	0.37680	0.35170	0.23974
C(32)	0.31092	0.43956	0.19468
C(33)	0.28025	0.46350	0.40023
C(34)	0.29509	0.46547	0.07868
C(35)	0.46055	0.26270	0.18468
H(201)	0.11534	0.68372	0.79411
H(202)	0.16806	0.74271	0.67634
H(203)	−0.06980	−0.26582	0.73418
H(211)	0.18660	0.55352	0.85909
H(212)	0.39389	0.44875	0.83454

TABLE II (continued)

Atomic coordinates in the (a, 2b, c) low temperature unit cell.

	x/a	y/b	z/c
H(213)	0.15478	0.44547	0.83832
H(221)	0.24412	0.54081	0.06046
H(222)	0.20091	0.43936	0.04492
H(223)	0.44567	0.43248	0.04284
H(231)	0.41277	0.27947	0.09764
H(232)	0.39238	0.21668	0.21172
H(233)	0.61483	0.23367	0.18334

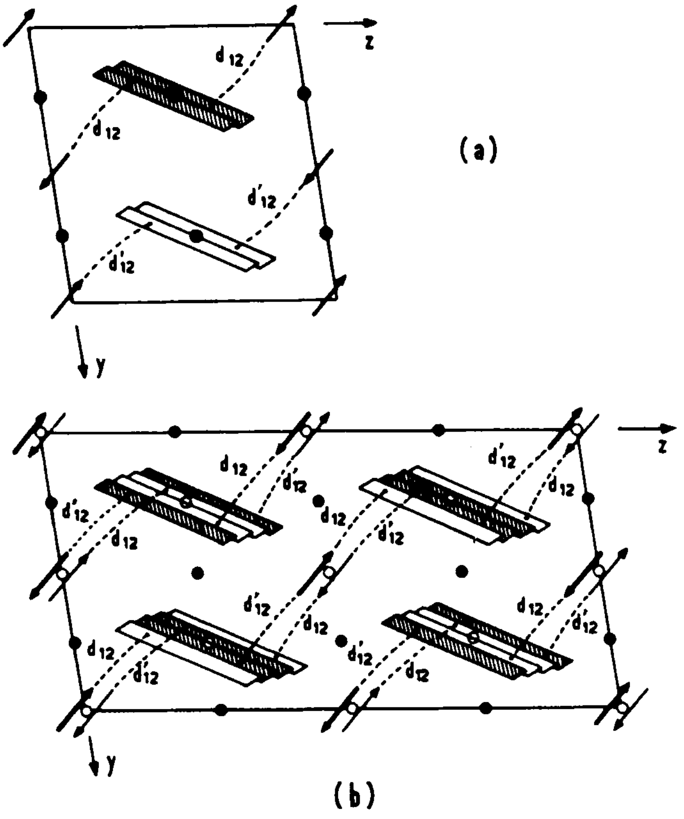

FIGURE 3 Schematic projection along a showing for each organic stack, the repeat unit of TMTSF molecules included in the low temperature unit cell a) $(TMTSF)_2C\ell O_4$ b) $(TMTSF)_2ReO_4$ The shortest Se-O distance relative to each TMTSF (either d_{12} or d'_{12}) is mentioned. Hatched and white rectangles represent independent TMTSF(I) and TMTSF(II) molecules respectively. Arrows represent the anions. Solid circles: inversion centers at $x = \pm 1/4$ Open circles: Inversion centers at $x = 0$.

TABLE III

Interplanar distances (Å) between TMTSF molecules in a given stack (TMTSF molecular planes are defined by Se atoms only). Symmetry operations: x, y, z; −x, −y, 1 − z and x, y, z; 1 − x, −y, 1 − z for d_{I1} and d_{I2} calculations respectively. x, y, z; −x, 1 − y, 1 − z and x, y, z; 1 − x, 1 − y, 1 − z of d_{II1} and d_{II2} calculations.

7 K (a × b × c)	10 K (a × 2b × c)
$d_1 = 3.56$	$d_{I1} = 3.560$ $d_{II1} = 3.565$
$d_2 = 3.52$	$d_{I2} = 3.522$ $d_{II2} = 3.518$

the difference in temperature. In fact, at 125 K, the shortest Se-Se distance in $C\ell O_4$ is found to be 3.65 Å[19] i.e. very similar to the ReO_4 case.

Modifications in transverse interactions between neighbouring stacks may be described by the variations of the Se-Se contacts and of the ϕ angle between the molecular TMTSF plane and the shortest d_9 Se-Se distance. From 300 K down to 7 K, the decrease of the Se-Se interchain distances is associated with a variation $\Delta\phi \sim 3.20°$ ($\phi_{300K} = -17.10°$; $\phi_{7K} = -13.90°$) (Figure 4). At any temperature, this angle is always smaller in the $C\ell O_4$ salt than in the other compounds such as in the PF_6 salt (PF_6 : $\phi_{300K} = -18.44°$, $\phi_{4K} = -15.10°$).[20]

In a given stack (Figure 2), each TMTSF molecule shows an identical environement with an equal shortest Se-O contact ($d_{12} = 3.49$ Å for stacks I, $d'_{12} = 3.35$ Å for stacks II) close to the sum of the Van der Walls radii ($d_{VdW} = 3.51$ Å).

In contrast, in the perrhenate salt, notable differences are observed. In a given stack, the Se-O distances are $d_{12} = 3.66$ Å and $d'_{12} = 2.99$

TABLE IV

Interstack Se-Se distances (Å) in $(TMTSF)_2C\ell O_4$ (distances numbering is given Figure 2)

	7 K (a × b × c)	10 K (a × 2b × c)
d_9	3.57	3.56
d_{10}	3.72	3.71
d'_{10}	3.72	3.73
d_{11}	3.78	3.79

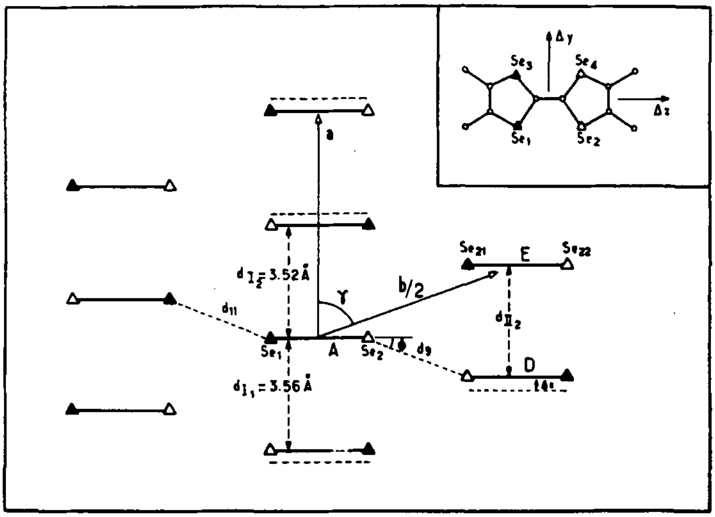

FIGURE 4 Schematic definition of the ϕ angle. Dashed and heavy lines represent respectively the 300 K and 10 K position of the molecular plane. Symmetry operations: A (x, y, z) of the (I) stacking D (− x, 1 − y, 1 − z) E (x, y, z) of the (II) stacking. The $\Delta\phi \sim 3.2°$ is due to a ($\Delta x \simeq 0.27$ Å, $\Delta y = -0.13$ Å, and $\Delta z \sim 0$) displacement of the D molecule. The inset figure gives definition of the y and z directions in the TMTSF molecular plane.

Å (Figure 3b). If the first one is larger than those of the CℓO$_4$ compound the second one (2.99 Å) is unusually shorter so that a weak chemical bond is formed in this latter case.

Anion sublattice

Table 5 gives bond lengths and angles of the CℓO$_4^-$ anions at low temperature. The Cℓ-O(3) distance is about 0.10 Å shorter than the three other ones; angles involving the O(3) atom appear larger than the other ones (~ 8°). The CℓO$_4$ tetrahedron is thus distorted. This contrasts with the case of (TMTSF)$_2$ReO$_4$ where the Re—O bond lengths are all close to 1.70 Å and the bond angles nearly equal to their ideal value.[12]

Our structure determination confirms the CℓO$_4$ anion ordering suggested by the $\vec{q}_2$ (0, 1/2, 0) reduced wave vector of the superstructure. As displayed on Figures 2 and 5, the two anion orientations alternate along the *b* direction and are related through inversion center (located halfway between the anions) of the P$\bar{1}$ space group. In the *a* and *c* directions, the anions keep the same orientation.

In addition the chlorine atoms are shifted from their average position by 0.023 Å, − 0.066 Å and 0.048 Å along *a*, *b* and *c* respectively.

TABLE V

Bond lengths (Å) and angles (°) in the $C\ell O_4^-$ anion

O(1)—CL	1.49(3)
O(2)—CL	1.48(3)
O(3)—CL	1.39(4)
O(4)—CL	1.51(3)
O(1)—CL—O(2)	1C6(1)
O(1)—CL—O(3)	114(1)
O(1)—CL—O(4)	104(1)
O(2)—CL—O(3)	114(2)
O(2)—CL—O(4)	105(1)
O(3)—CL—O(4)	112(1)
SE(24)—CL—O(2)	140(1)
SE(4)—CL—O(3)	125

The corresponding displacements are marked by arrows in Figure 2. Their magnitude is similar to that observed for the Re atoms.[12] However it is important to point out that the b-c displacements of the Re atoms are in opposite directions than for the Cℓ atoms.

4. DISCUSSION

Owing to the difficulties mentioned in sections III a & b and especially the inaccurate intensity data, the present analysis yields a reliability factor (0.164) and standard deviations which are somewhat higher than for a conventional structure determination. However, we are confident about having determined the main structural features involved in the 24 K transition for slowly cooled samples namely an orientational ordering of the $C\ell O_4$ anions with a weak distortion of the organic stacks.

In $(TMTSF)_2ReO_4$, translations of TMTSF lead to a "2 k_F" distortion of the stacks. The periodicity along the *a* axis is thus characterized by a tetramerization ($d_1 = d_2 = 3.60$ Å, $d_3 = 3.50$ Å) and the overlap between neighbouring molecules in a given stack change in accordance with the observed translation.

The a* component of the perchlorate wave vector implies no change of the chain periodicity below the transition, even if the diadic character is increased at low temperature. The assumption of undistorted stack is confirmed by the non observation of rigid translation of the TMTSF molecules. The low temperature ground state still remains a conducting state.[14]

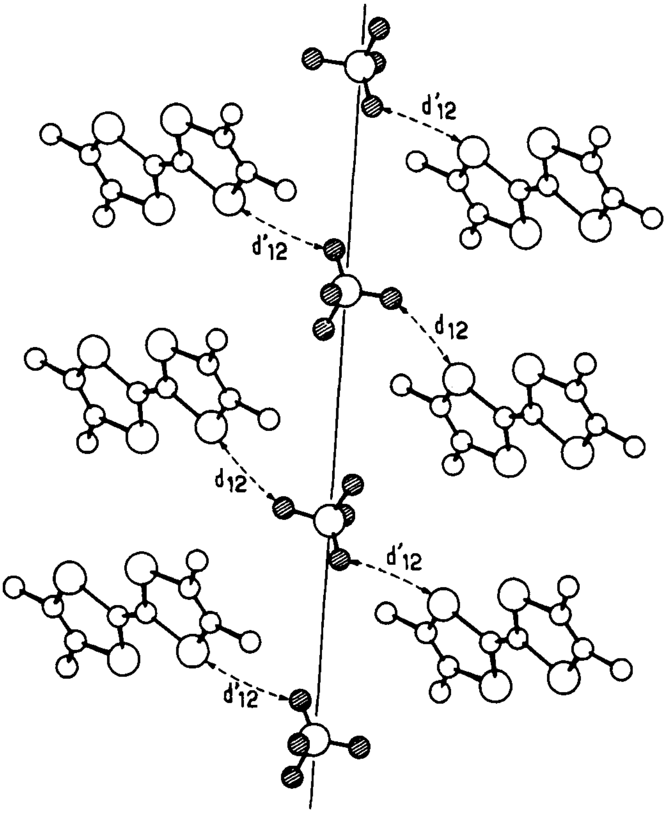

FIGURE 5 Orientational ordering of the $C\ell O_4^-$ anions in the b direction and shortest Se-O interactions between each anion and neighbouring TMTSF molecules.

Structural results can help us to understand why organic sublattices of these two salts are involved in a very different way. Comparison of interactions between organic stacks and anion allows to conclude in the importance of the anions size. These interactions become weaker (longer Se-O distances) as the size of the anion decreases. The short Se-O distance (2.99 Å) forming a weak chemical bond in the ReO_4 compound indicates that the anions strongly interact with their organic environment. The occurrence of a ReO_4^- ordering associated with a structural distortion of the TMTSF stack may be due to the large size of the anion. Larger Se-O distances in the $C\ell O_4^-$ salt indicates a less highly bound anion in its cavity and thus an easier orientational ordering without any distortion of the organic environment. Actually, the non observation of distorted stacking in the perchlorate salt confirms the special behaviour of this compound already pointed out by Kistenmacher[21] who mentioned that the size of the $C\ell O_4^-$ anion seems too small to induce structural changes leading to an insulating ground state at a temperature coincident with the anion ordering temperature.

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