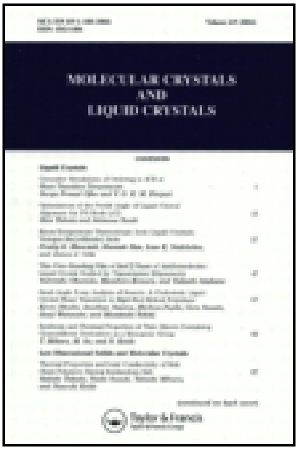

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Anion Symmetry and the Separability of Structural Parameters for Tetramethyltetraselenafulvalenium Salts, $(TMTSF)_2X$

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Anion Symmetry and the Separability of Structural Parameters for Tetramethyltetraselenafulvalenium Salts, $(TMTSF)_2X$

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Empirical correlations of various structural parameters for a series of $(TMTSF)_2X$ salts have been explored utilizing a van der Waals-like estimate for the radius of the counterion X. Included amongst the parameters studied are: (a) the lengths of the transverse cell constants **c** and **b**; (b) the interdonor Se . . Se contact distances; (c) the alternate separation between molecular centers of mass along the columnar stack of donors (**a**); and (d) the symmetry and strength of the anion coupling to its donor-dominated structural cavity. The notable result is that independent correlations are found for salts containing centrosymmetric and non-centrosymmetric anions.

Keywords: $(TMTSF)_2X$, symmetry, separability, structure

I. INTRODUCTION

The novel family of organic superconductors, $(TMTSF)_2X$, based on the electron donor tetramethyltetraselenafulvalene, TMTSF, and a host of complex inorganic anions, X, remains a source of much speculation, both as to the basic physics underlying the properties of these materials and as to the means by which the range of organic materials exhibiting superconductivity can be extended.

It was recognized early[1] that the structural motif universally adopted by the $(TMTSF)_2X$ salts plays a seminal role in determining not only their structural properties but their attendant physical properties. The basic features of the crystal structure shown by this family of salts, see Figure 1, can be succinctly summarized as follows: (a) zigzag columns of fractionally-charged (+ 0.5e) TMTSF cations extend along the *a* axis of the triclinic (space group P$\bar{1}$) unit cell; (b) intercolumnar interactions in the *ab* crystal plane are dominated by interdonor Se . . Se contacts which are commonly shorter than twice the van der Waals radius (2.0Å) of Se;[2] and (c) alternate sheets of donor columns are coupled along **c** *via* planes of anions which exhibit various types and degrees of disorder. The anions are required to lie on special positions

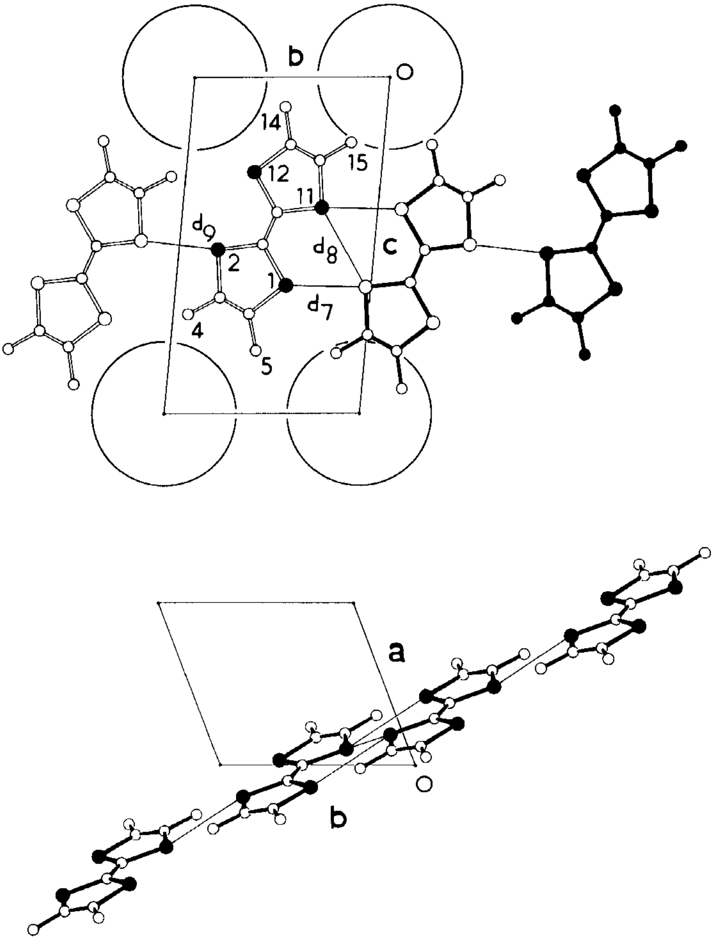

FIGURE 1 Elements of the crystal structure universally adopted by the $(TMTSF)_2X$ salts. Large open circles indicate the average positions (point symmetry C_i) of the counterion X, while thin lines denote short interdonor Se . . Se contacts.

which demand C_i site symmetry in space groups $P\bar{1}$. For O_h symmetry anions (PF_6^-, AsF_6^-, SbF_6^- and TaF_6^-), this does not require any positional disorder and the observed disorder appears to be mainly librational in character; for anions with T_d(BF_4^-, ClO_4^-, BrO_4^-, TcO_4^- and ReO_4^-), C_{2v}($PO_2F_2^-$) or C_{3v}(FSO_3^-) symmetry, positional disorder is demanded and librational disorder is superimposed.

It was also immediately obvious[1] that the length of **c** was highly dependent on the size of the anionic counterion. Previous empirical correlations[3] between anion size and the structural properties of the $(TMTSF)_2X$ salts have focused on the volume of the anion X and have treated centrosymmetric (O_h) and non-centrosymmetric (T_d, C_{2v} and C_{3v}) anions as members of the same statistical ensemble. The present effort was stimulated by the following considerations: (1) the disorder in these systems at high temperature must allow "on the average" for any nominal orientation of the anion relative to the more firmly fixed cation sheets; and (2) given the relatively weak (at room temperature) forces between anions and cations, a van der Waals-like estimate for anion size may well be more physically relevant than size estimates based on ionic or crystal radii[3,4] or *ab initio* quantum-chemical charge distributions.[5] Finally, attention is focused here on correlations based on anion radius rather than anion volume, and the analysis is limited, for the present, to data obtained at room temperature.[6]

II. METHOD

The estimated complex radii, R_I^{vdW}, employed in this study were very simply computed as follows. The crystallographic literature[7] was searched in order to find examples (limited in many cases) of crystal structures containing well-ordered anions from the set. From this search, a mean interatomic bond length (esd of the mean ~0.01Å) was calculated. To this mean bond length was added the appropriate van der Waals radius[2] for the terminal atom of the complex ion to yield a measure of the "van der Waals-like" anion radius (R_I^{vdW}). Two general examples will be given in detail for clarity: (1) PF_6^- (see Figure 2); mean P—F bond length, 1.60Å; Pauling's van der Waals radius for F, 1.35Å; ion radius (R_I^{vdW}) for PF_6^-, 2.95Å; (2) ClO_4^- (see Figure 2); mean Cl—O bond length, 1.44Å; Pauling's van der Waals radius for O, 1.40Å; ion radius (R_I^{vdW}) for ClO_4^-, 2.84Å. Following this prescription, column 3 of Table I was completed, with the exception of the dipolar fluorosulphate (FSO_3^-) and difluorophosphate

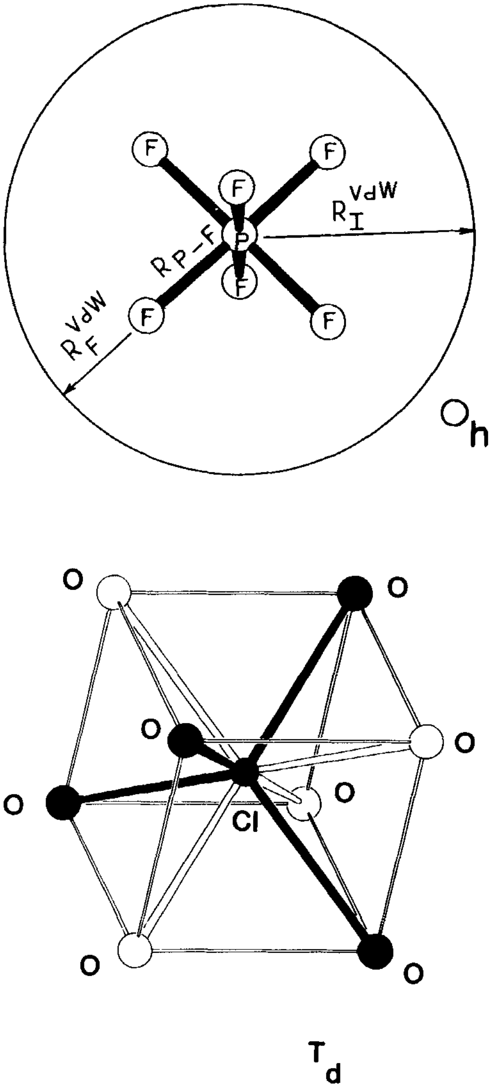

FIGURE 2 *Top:* The octahedral (O_h) hexafluorophosphate ion (PF_6^-) and the trace of its van der Waals sphere of radius R_I^{vdw} ($= R_{P—F} + R_F^{vdw}$). *Bottom:* Two orientations of the tetrahedral (T_d) perchlorate ion (ClO_4^-) within the cube defined by its statistically disordered oxygen atoms.

($PO_2F_2^-$) anions, Figure 3. For these cases, two radii are given in Table I, one for each of the heteroatomic bonds. As it will be assumed that all anions are statistically disordered at room temperature, the maximal radii, 2.89Å for FSO_3^- and 2.92Å for $PO_2F_2^-$, will be employed in the following empirical correlations.

TABLE I

Various estimates of complex ion radii (Å)

Ion	$R_I^{ionic,a}$	$R_I^{vdW,b}$	$R_I^{theor.,c}$
BF_4^-	2.54	2.72	2.54
ClO_4^-	2.64	2.84	2.76
FSO_3^-	2.68 (S—O) 2.55 (S—F)	2.82 (S—O) 2.89 (S—F)	2.77
$PO_2F_2^-$	2.73 (P—O) 2.60 (P—F)	2.87 (P—O) 2.92 (P—F)	
PF_6^-	2.81	2.95	2.80
BrO_4^-	2.81	3.01	
AsF_6^-	2.89	3.05	2.94
TcO_4^-	2.93	3.10	
ReO_4^-	2.94	3.12	
SbF_6^-	3.03	3.19	3.08
TaF_6	3.07	3.29	

[a] Based on the tabulated crystal radii of R. D. Shannon (*Acta Crystallogr.*, **A32**, 751 (1976)).

[b] Based on accepted bond lengths and Pauling's van der Waals radii (O, 1.40Å; F, 1.35Å).

[c] Based on *ab initio* quantum-chemical charge distributions (H. Teramae, K. Tanaka and T. Yamabe, *Solid State Commun.*, **44**, 431 (1982); H. Teramae, K. Tanaka, K. Shiotani and T. Yamabe, *ibid*, **46**, 633 (1983)).

Also contained in Table I are estimates of R_I based on tabulated[4] crystal radii for the elements, column 2 of Table I, where $R_I^{ionic} = r_i + 2r_o$ with r_i equal to the crystal radius of the inner element of the complex ion—the P atom in PF_6^-, and r_o equal to the crystal radius of the outer element in the complex ion—the F atoms in PF_6^-, and ion radii ($R_I^{theor.}$) derived from charge distributions based on *ab initio* quantum-chemical computations.[5] In general, R_I^{vdW} and R_I^{ionic} are comparable (within a scale factor), and the essentially equivalent ion radii for the sets (ClO_4^-, FSO_3^-, and $PO_2F_2^-$) and (TcO_4^- and ReO_4^-) are shown by both methods. There are, however, differences (for example, PF_6^- and BrO_4^- have equivalent R_I^{ionic}, while their R_I^{vdW} are significantly different, Table I), and these differences would be amplified if correlations employing ion volume were utilized.

III. RESULTS AND DISCUSSION

In this section, descriptions of results obtained from empirical correlations based on R_I^{vdW} for various crystallographic parameters are presented. In all cases, the statistical set is small (4–7 data points),

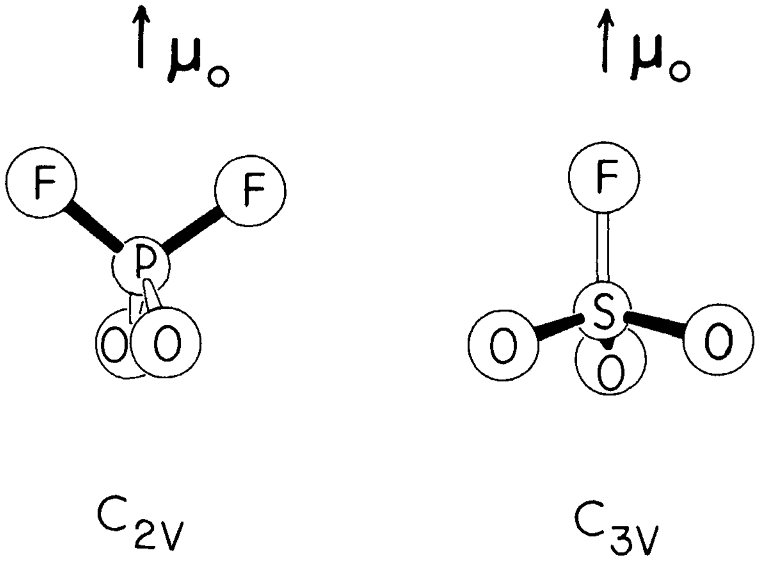

FIGURE 3 The dipolar difluorophosphate ($PO_2F_2^-$; point symmetry C_{2v}) and fluorosulphate (FSO_3^- ; point symmetry C_{3v}) anions.

but the results will be taken to imply general agreement over a larger basis set, if and when available.

(i) Magnitudes of the transverse cell constants c and b

As noted above, it was almost immediately recognized[1] that the length of the **c** axis (the direction along which planes of cations and anions alternate, see Figure 1) was rather dramatically dependent on anion size. In Figure 4, plots of $|\mathbf{c}|$ versus R_I^{vdW} are presented. It is immediately obvious that strong, but independent correlations between $|\mathbf{c}|$ and R_I^{vdW} for salts with centrosymmetric and non-centrosymmetric anions are demanded. Quantitatively, the linear dependence of $|\mathbf{c}|$ on R_I^{vdW} for salts with centrosymmetric and non-centrosymmetric anions are given in eqns. (1) and (2), respectively:

$$|\mathbf{c}| = 1.300\,R_I^{vdW} + 9.696\,(r^2 = 0.959)\,(\text{centrosymmetric}); \qquad (1)$$

$$|\mathbf{c}| = 0.692\,R_I^{vdW} + 11.325\,(r^2 = 0.987)\,(\text{non-centrosymmetric}). \qquad (2)$$

The projected crossover of the line for salts with centrosymmetric anions with that for salts with non-centrosymmetric anions occurs at 2.68Å—a value near R_I^{vdW} for BF_4^-, 2.72Å.

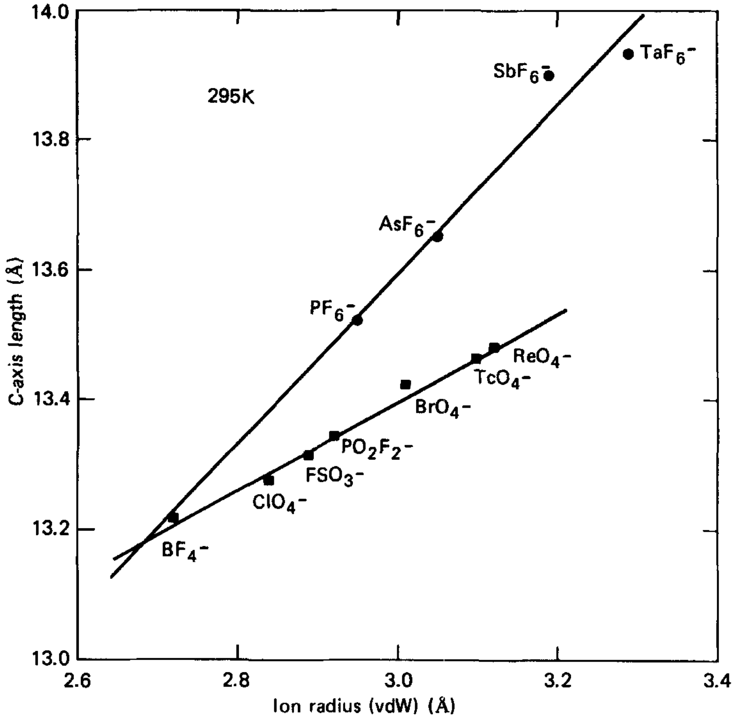

FIGURE 4 Plot of c-axis length (T = 295K) versus ion radius (R_I^{vdW}). Separate correlations for salts with centrosymmetric (●) and non-centrosymmetric (■) anions are clearly indicated. The superimposed lines are least-squares fits to the data.

It has been stated many times in the literature[1] that only the c-axis length correlates with anion size. From Figure 5, however, it is immediately evident that the b-axis (the direction along which donor columns interact, see Figure 1) length for the limited number of salts with centrosymmetric anions is essentially invariant (range 0.02Å), while the variation over the more extended set of salts with non-centrosymmetric anions is notable (0.19Å). Moreover, there is a linear variation of $|\mathbf{b}|$ with R_I^{vdW} for salts with non-centrosymmetric anions as expression by eqn. (3):

$$|\mathbf{b}| = 0.279\,R_I^{vdW} + 6.880\,(r^2 = 0.959)\,(\text{non-centrosymmetric}). \qquad (3)$$

In this instance, the crossover of the essentially invariant b-axis magnitude for salts with centrosymmetric anions and the linear variation for salts with non-centrosymmetric anions occurs near R_I^{vdW} for the BrO_4^- anion.

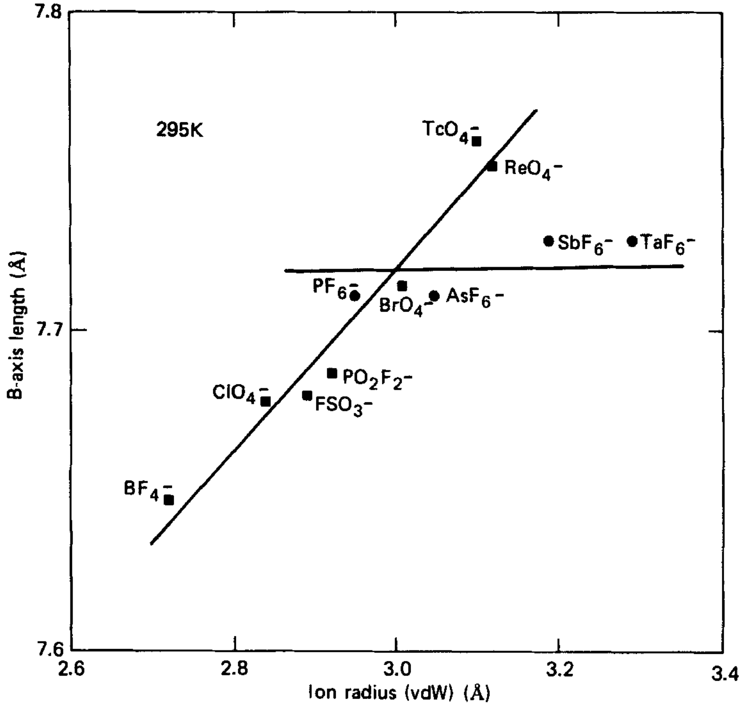

FIGURE 5 Plot of *b*-axis length (T = 295K) versus ion radius (R_I^{vdW}). The superimposed line for salts with non-centrosymmetric anions (■) is a least-squares fit to the data; the superimposed line for salts with centrosymmetric anions (●) is a "guide-to-the-eye".

(ii) Interstack Se . . Se contact distances

The presence of several short interstack Se . . Se contacts (denoted d_7, d_8 and d_9 in Figure 1) has been considered[3,8] to be an important contributor to both the sizeable transverse (**b**) bandwidth[9-11] and the achievement of bulk superconductivity in the $(TMTSF)_2X$ salts.[1] It has been previously indicated[3] that a linear relationship exists between anion volume and the weighted (by occurrence) average of d_7 and d_9 $[(2d_7 + d_9)/3]$. While d_7, d_8 and d_9 are essentially invariant with R_I^{vdW} for salts with centrosymmetric anions, it is evident from Figure 6 that a plot of these interaction parameters versus R_I^{vdW} for salts with non-centrosymmetric anions shows distinct non-linearity. In detail, d_7 and d_9 show parallel decreases as R_I^{vdW} decreases, while d_8 increases as R_I^{vdW} decreases. Most interesting are the divergent dependences of d_7 and d_8 on R_I^{vdW}. As can be seen in Figure 1, d_7 and d_8 form the parts of a bifurcated interdonor Se . . Se interaction

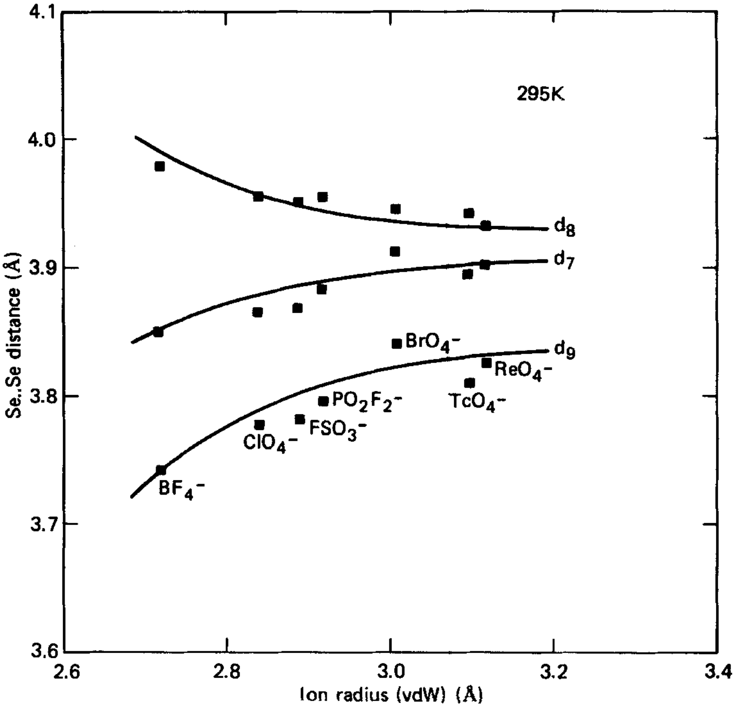

FIGURE 6 Plot of the interdonor Se . . Se contact distances d_7, d_8 and d_9 versus ion radius (R_I^{vdW}) for several salts with non-centrosymmetric anions. The superimposed curves are "guides-to-the-eye".

system. At large R_I^{vdW}, these contact distances are nominally equivalent (differing by 0.03Å for the perrhennate salt) and apparently converging asymtotically to a value near 3.92Å (close to that, ~3.94Å, uniformly displayed by salts with centrosymmetric anions). As R_I^{vdW} decreases, an asymmetry in this bifurcated interaction system is introduced, with the difference (d_8 − d_7) reaching 0.13Å for the tetrafluoroborate salt. It is also to be noted that directionally d_7 and d_9 nominally parallel **b**, while d_8 nearly parallels [011], see Figure 1. In this context, then, the apparent linear variation of |**b**| with R_I^{vdW} for salts with non-centrosymmetric anions can be seen to be simply a composite result of the non-linear trends for d_7, d_8 and d_9.

(iii) Intracolumnar effects

Recently,[3,12–14] the effect of anion size and symmetry on the structural parameters of the zig-zag column of partially oxidized donor molecules (Figure 7) has come under scrutiny. In the crystalline motif

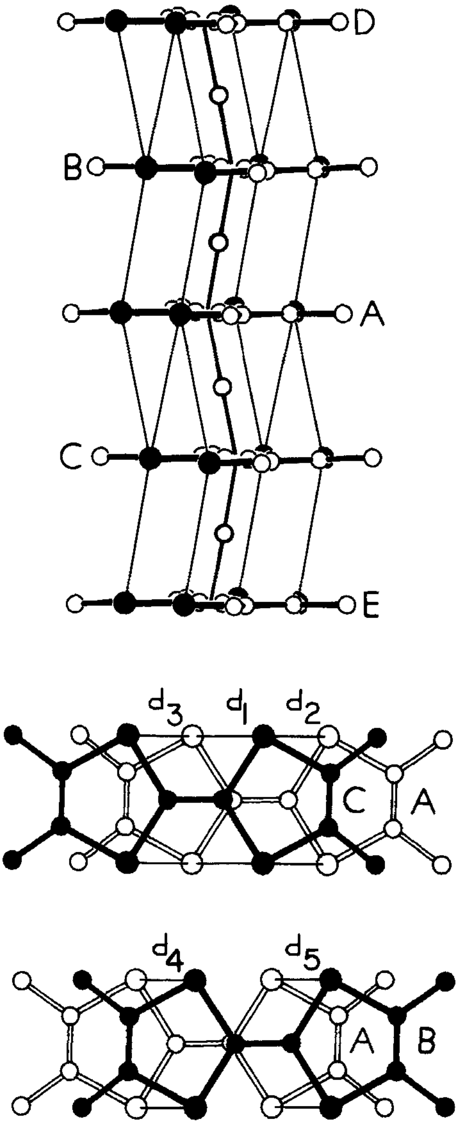

FIGURE 7 *Top:* An isolated columnar array of interacting donors. Thin lines denote intracolumnar Se . . Se interactions; thicker lines (interrupted by open circles) trace the zig-zag pattern of the molecular centers of mass (and inversion symmetry elements). The labeled donors are of the following coordinate types: A (x,y,z); B $(-x, 1 - y, 1 - z)$; C $(1 - x, 1 - y, 1 - z)$; D $(-1 + x,y,z)$; E $(1 + x,y,z)$. *Bottom:* Molecular overlap patterns for donor pairs of the types (A,C) and (A,B).

adopted by the $(TMTSF)_2X$ salts, all donor molecules have identical environments, lie in parallel planes by inversion symmetry, but only alternate spacings between parallel planes are required to be equivalent by translational symmetry. Previous empirical efforts[3,13] have focused on the mean separation between molecular planes, with the most reliable derivation of the interplanar distances based on the well-determined Se atom coordinates. As has been noted earlier,[3] the difference in mean separation between alternate pairs of donors is small (*ca.* 0.01–0.03Å), and correlation with anion size is hampered by the fact that this difference is on the same order of magnitude as the deviation of individual Se atoms from the mean plane.

Herein, the variation in the distance between molecular centers of mass (designated ΔM_a) along the stacking axis **a** is considered.[12] It is to be noted that the center-of-mass coordinates are probably as well determined as any derived structural parameter, in that various random (and possibly systematic) errors in the individual Se atom coordinates may well be averaged out. Results of these computations for several $(TMTSF)_2X$ salts are presented in Figure 8. It is readily seen that ΔM_a for the pair of donors (A,B) is virtually independent of anion size or symmetry, with a range of only 0.007Å. The mean value for ΔM_a(A,B) is 3.584Å, with an estimated standard deviation of the mean of ±0.004Å. Thus, ΔM_a(A,B) is only very slightly dependent on or independent of anion size and symmetry.

In contrast, ΔM_a(A,C) is dependent, albeit weakly, on anion size, showing a range of 0.04Å over the four salts with non-centrosymmetric anions of Figure 8. Moreover, there is some indication (as for the Se . . Se contact distances of Figure 6) that this variation is nonlinear in R_I^{vdW}. As espoused earlier,[12] the antecedent of the differing behaviors of ΔM_a(A,B) and ΔM_a(A,C) seems to be directly related to the different manner in which these alternate pairs interact with the anion subsystem. The donor pair (A,B) lies within the same set of anion spheres in the **bc*** plane, while the donor pair (A,C) lies between alternate planes of anions along **a**. The details of donor-anion coupling in the $(TMTSF)_2X$ salts leading to this differentiation in the behavior of ΔM_a(A,B) and ΔM_a(A,C) lie mainly in Se(donor) . . anion contacts and methyl group (donor) . . . anion interactions, which are considered extensively in the following section.

(iv) Anion-donor coupling: strength and symmetry considerations

It has been noted by several groups[3,6] that the structural cavity in which the anion resides in the $(TMTSF)_2X$ salts is principally determined by the terminal methyl groups of the TMTSF donor, see

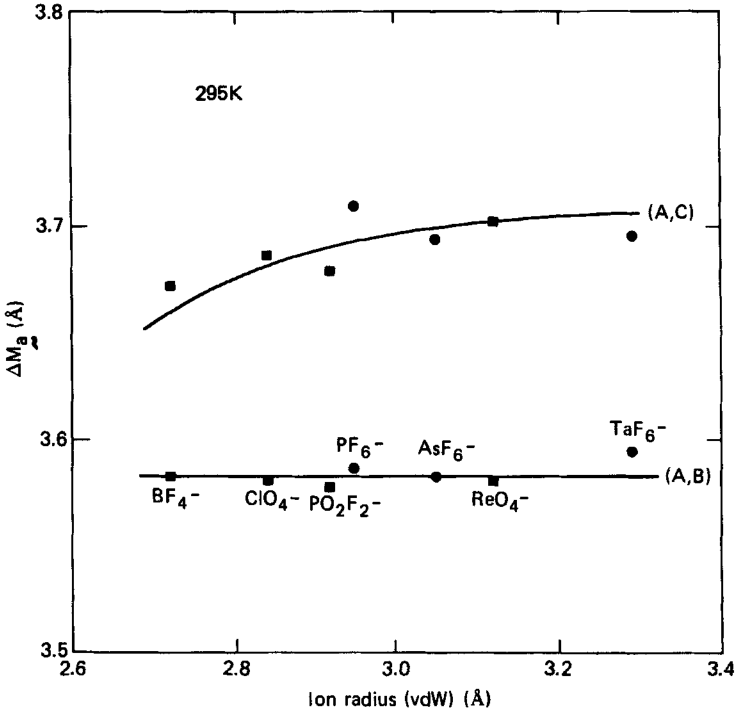

FIGURE 8 Plot of ΔM_a (T = 295K) versus ion radius (R_I^{vdW}) for donor pairs of the types (A,C) and (A,B) for salts with centrosymmetric (●) and non-centrosymmetric (■) anions.

Figure 9. In addition, there is a significant donor-anion interaction involving a Se atom of one of the donor molecules (labeled B in Figure 9) defining the structural cavity and one of the terminal atoms of the anion.[1] Both the terminal methyl group-anion and Se-anion interactions have been invoked as principal factors in the anion-ordering transition for salts with non-centrosymmetric anions.[3,6,15] It has also become evident[16] that anion ordering is a prerequisite for the achievement of a superconducting ground state.

The distribution of the interacting methyl groups (and their inversion symmetry mates) about the average position of the anion X is depicted in Figure 10. While the array of methyl groups is required only to be centrosymmetric, the actual distribution is that of a skewed, trigonal antiprism (point symmetry D_{3d}), but close to octahedral symmetry (O_h).[17–18] The Se atoms nearest the anion, Se(12) and Se(12′), cap the trigonal faces of the methyl group-based antiprism, Figure 10. Of particular importance has been the recognition[15,17–19] that while

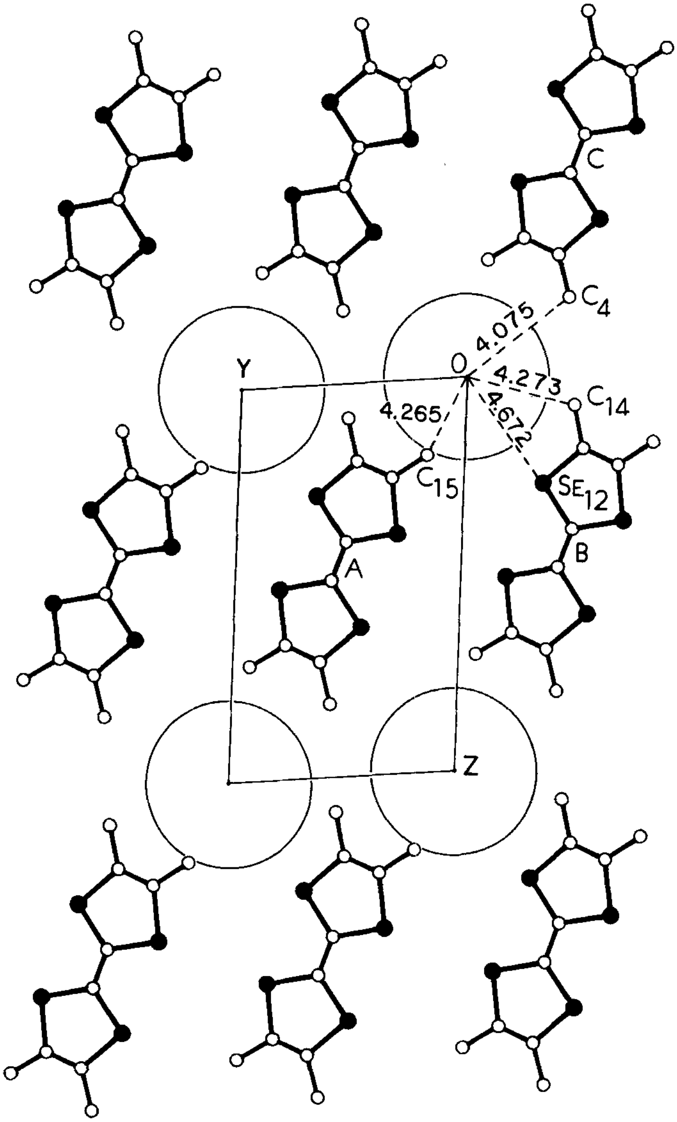

FIGURE 9 The (100) projection of the crystal structure of $(TMTSF)_2ClO_4$. The perchlorate anions are represented by spheres of radius R_I^{vdW}. The labeled donors have the following coordinate transformations: A (x,y,z); B $(x, -1 + y, z)$; C $(x, -1 + y, -1 + z)$. Dashed lines denote the interaction vectors R_4, R_{14}, R_{15} and R_{Se}.

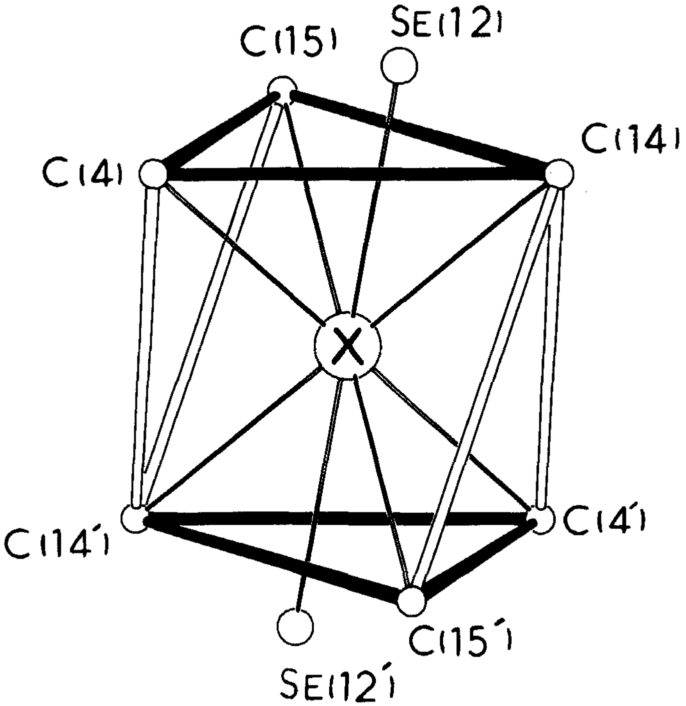

FIGURE 10 Distribution of the interaction vectors R_4, R_{14}, R_{15}, R_{Se} and their inversion mates about the anion X.

the cavity geometry is largely invariant across the series of $(TMTSF)_2X$ salts, anions of different symmetries adopt different orientations within the structural cavity.

Given the pervasive structural regularity of the structural cavity,[15,18] it is interesting to consider the match-up between the geometrical features of the anion cavity and the symmetry axes for various types of anions. In Figure 11, the AsF_6^- anion is oriented in its structural cavity based on published atomic coordinates.[6b] It is immediately obvious that each of the three methyl group interaction vectors lies qualitatively parallel to one of the three-fold axes of the AsF_6^- octahedron. Quantitatively, the angular deviation between the methyl group interaction vector and the normal to the appropriate triangular face of the AsF_6^- octahedron is only 3° for C(4) . . . C(4'), 6° for C(14) . . . C(14'), and 11° for C(15) . . . C(15'); a trend which inversely parallels the strength of the methyl group interactions as judged by their distance from the center of mass of the anion, Figure 11. To complete the analysis, the Se(12) . . . Se(12') interaction vector

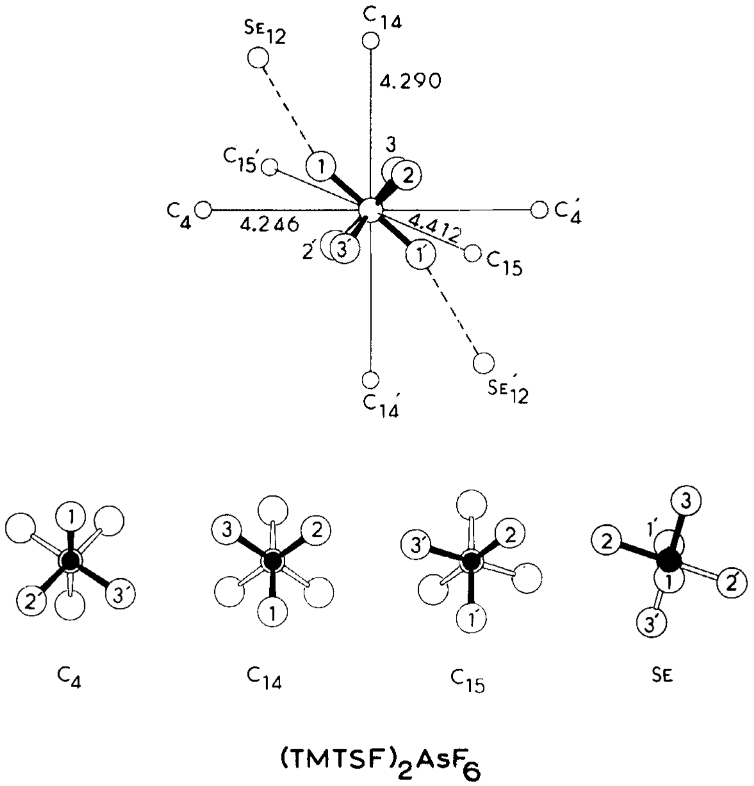

FIGURE 11 *Top:* Disposition of the six closest methyl groups and two Se atoms about the AsF$_6^-$ anion in the structure of (TMTSF)$_2$AsF$_6$ (T = 295K). *Bottom:* Projection views down the R$_4$, R$_{14}$, R$_{15}$ and R$_{Se}$ interaction vectors.

lies only 14° from one [F(1)-As-F(1')] of the four-fold axes of the AsF$_6^-$ octahedron. On the whole then, the structural cavity in the (TMTSF)$_2$X salts seems remarkably well-suited to the accommodation of an anion of O$_h$ symmetry. A fact which, in addition to the intrinsic centrosymmetry of the cavity, likely accounts for the absence of significant positional disorder[6a–d] for salts with octahedral anions.

In this same vein, trends in the interaction distances R$_4$, R$_{14}$, R$_{15}$, and R$_{Se}$ with R_I^{vdW} for salts with octahedral anions are presented in Figure 12. Over the limited number of salts, all interaction distances appear to vary linearly with R_I^{vdW} according to eqns. (4) through (7):

$$R_4 = 0.600\,R_I^{vdW} + 2.412\,(r^2 = 0.998)\,(\text{centrosymmetric}); \quad (4)$$

$$R_{14} = 0.171\,R_I^{vdW} + 3.771\,(r^2 = 0.992)\,(\text{centrosymmetric}); \quad (5)$$

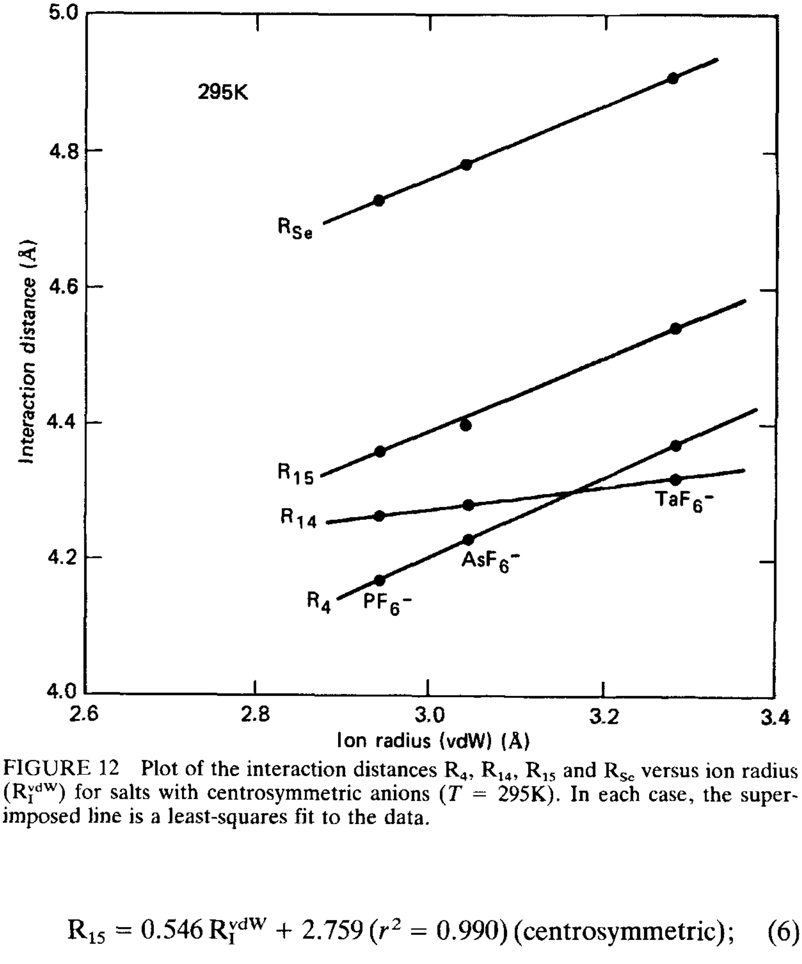

FIGURE 12 Plot of the interaction distances R_4, R_{14}, R_{15} and R_{Se} versus ion radius (R_I^{vdW}) for salts with centrosymmetric anions (T = 295K). In each case, the superimposed line is a least-squares fit to the data.

$$R_{15} = 0.546\,R_I^{vdW} + 2.759\,(r^2 = 0.990)\,(\text{centrosymmetric}); \qquad (6)$$

and,

$$R_{Se} = 0.543\,R_I^{vdW} + 3.139\,(r^2 = 0.999)\,(\text{centrosymmetric}). \qquad (7)$$

It is interesting to note that R_4, R_{15} and R_{Se} show essentially parallel trends, while the increase of R_{14} with R_I^{vdW} is much less pronounced in spite of the fact that C(14) and Se(12) are situated within the same donor (see Figure 9). Finally, the contact distance Se(12) . . F(1) [$d_{Se\,..\,F}$, see Figure 11], which is fairly well determined in these salts which exhibit minimal anion disorder, also appears to be a linear function of R_I^{vdW}:

$$d_{Se\,..\,F} = -0.415\,R_I^{vdW} + 4.459\,(r^2 = 0.999)\,(\text{centrosymmetric}), \qquad (8)$$

with the negative slope reflecting the decrease in $d_{Se\,...\,F}$ with increasing R_I^{vdW} and implying a rather dramatic increase in interaction strength.

Given that the cavity symmetry is nearly invariant to anion type,[15,18] it is likely that four-coordinate anions with T_d, C_{2v} or C_{3v} symmetry (see Figures 2 and 3) would find the symmetry potential of the structural cavity somewhat less well-suited. As noted earlier,[6,18] idealized AX_4^-, $AX_2Y_2^-$, AX_3Y^- and AXY_3^- anions are non-centrosymmetric. Thus at a fundamental level, there is a symmetry mismatch between a non-centrosymmetric anion and the centrosymmetric geometry of its structural cavity. An immediate consequence of this symmetry mismatch is a positional disorder of the terminal atoms of the anion for these salts (Figure 2).

This concept is extended in Figure 13, where views of the anion-methyl group interactions for $(TMTSF)_2ClO_4$[6f] are presented. From Figure 13 it is particularly clear that the interaction vectors C(4) . . . C(4′) and C(14) . . . C(14′) lie nearly parallel (the angular deviation is about 7° in each case) to a two-fold symmetry axis of the perchlorate anion, irrespective of the anion orientation. Equivalently, these interaction vectors closely follow four-fold symmetry axes of the "cube" defined by the eight half-weighted, oxygen atom positions. In fact, the near orthogonality[18] of the interaction vectors C(4) . . . C(4′) and C(14) . . . C(14′) ideally matches the interaxial angles of the two-fold axes of the tetrahedra or the four-fold axes of the "cube". The striking feature of Figure 13 is the absence of near colinearity of the C(15) . . . C(15′) and Se(12) . . . Se(12′) interaction vectors and any of the symmetry axes of the individual anion tetrahedra or their composite cube.

Two implications of this symmetry differentiation of the interaction vectors of the structural cavity for salts with four-coordinate, nominally tetrahedral, anions seem to be important. Firstly, the C(4) . . . C(4′) and C(14) . . . C(14′) interaction vectors are incapable of inducing anion ordering, as they do not differentiate between the two oppositely oriented tetrahedra. In contrast, the interaction vectors C(15) . . . C(15′) and Se(12) . . . Se(12′) are likely principal

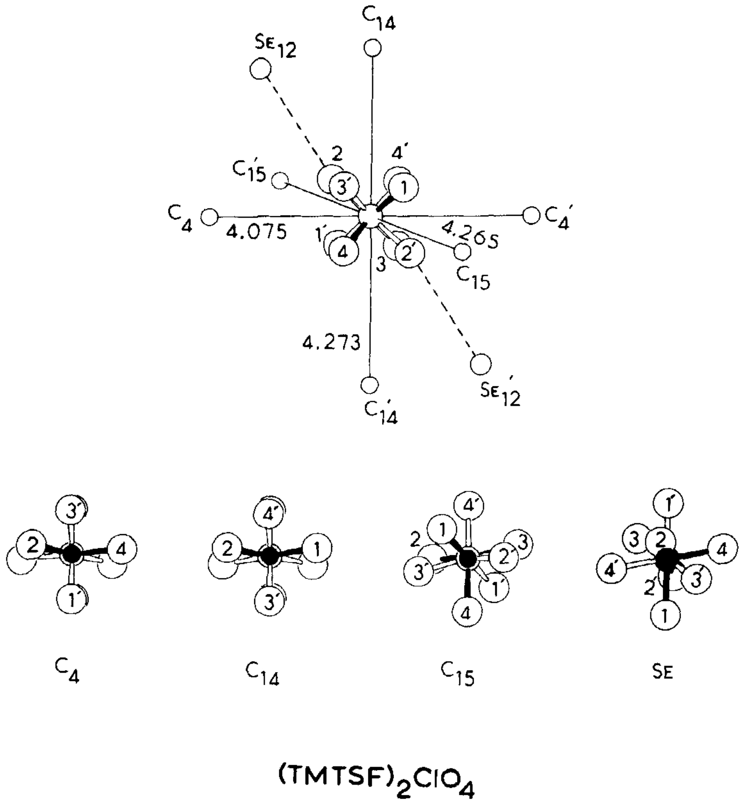

FIGURE 13 *Top:* Disposition of the six closest methyl groups and two Se atoms about the disordered ClO_4^- anion in the structure of $(TMTSF)_2ClO_4$ (T = 295K). *Bottom:* Projection views down the R_4, R_{14}, R_{15} and R_{Se} interaction vectors.

structural components leading to anion ordering. Secondly, it is interesting to consider salts where the four-coordinate anion possesses a permanent dipole moment, μ_0. Two salts with dipolar anions, $(TMTSF)_2FSO_3$[6g,20–21] and $(TMTSF)_2PO_2F_2$,[6h] have been extensively studied. For an $AX_2Y_2^-$ anion [e.g., $PO_2F_2^-$, C_{2v}], μ_0 is constrained to lie along its unique molecular two-fold axis. If there is a tendency for μ_0 to parallel or become parallel with the symmetry direction defined by the interaction vector C(4) . . . C(4′) or C(14) . . . C(14′), then it seems possible that a cooperative, ferroelectric state could become competitive with the superconducting ground state at low temperature. Such an eventuality could offer an explanation as to the absence of superconductivity in $(TMTSF)_2PO_2F_2$,[6h] even under relatively high external pressure. In contrast, for an AX_3Y^- or

AXY_3^- anion [e.g., FSO_3^-, C_{3v}], μ_0 is constrained to lie along its unique three-fold axis. For this case, it seems unlikely that μ_0 will parallel any symmetry axis of the structural cavity, making a ferroelectric ground state less probable. In fact, $(TMTSF)_2FSO_3$ does show evidence of weak superconductivity and superconducting diamagnetic screening[20–21] at low temperature under an applied pressure of about 6 kbar.

Similarly, trends in the interaction distances R_4, R_{14}, R_{15} and R_{Se} with R_I^{vdW} for salts with tetrahedral anions (Figure 14) are quite different than those exhibited (Figure 12) by salts with octahedral anions. While all the interaction distances show a linear variation with ion size for salts with octahedral anions, only R_4 and R_{15} appear to vary linearly with R_I^{vdW} for salts with tetrahedral anions according

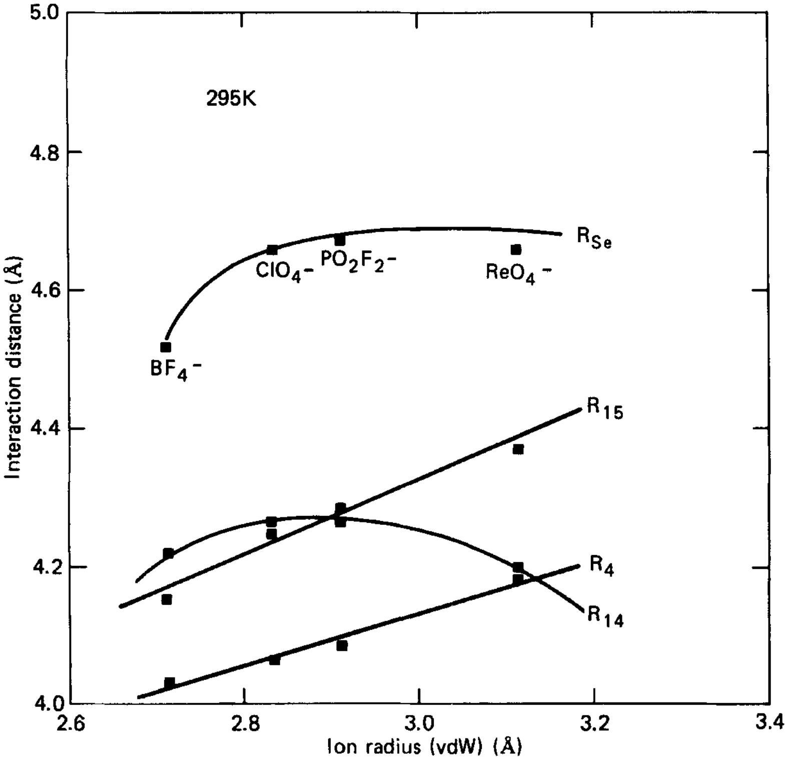

FIGURE 14 Plot of the interaction distances R_4, R_{14}, R_{15} and R_{Se} versus ion radius (R_I^{vdW}) for salts with non-centrosymmetric anions (T = 295K). For the interaction distances R_4 and R_{15}, the superimposed line is a least-squares fit to the data. For the interaction distances R_{14} and R_{Se}, the superimposed line is a "guide-to-the-eye".

to eqns. (9) and (10):

$$R_4 = 0.399 R_I^{vdW} + 2.946 (r^2 = 0.973) (\text{non-centrosymmetric}); \quad (9)$$

$$R_{15} = 0.510 R_I^{vdW} + 2.796 (r^2 = 0.965) (\text{non-centrosymmetric}). \quad (10)$$

In contrast, R_{14} and R_{Se} are distinctly non-linear parameters, Figure 14, with R_{14} appearing to exhibit a broad maximum and R_{Se} appearing to saturate and become invariant near R_I^{vdW} = 2.8 Å, a value close to that for the ClO_4^- anion. Unfortunately, systematic errors in the contact distances Se . . O ($d_{Se\,..\,O}$) and Se . . F ($d_{Se\,..\,F}$), owing to disorder of the tetrahedral anion, preclude an analysis of their variation with anion size.

IV. SUMMARY

A "van der Waals-like" estimate for the radius of the counterion X in $(TMTSF)_2X$ salts has been utilized to study the dependence of various structural parameters on anion size. Empirical results for the magnitude of the transverse cell constants **c** and **b**, the alternate separation between molecular centers of mass along the longitudinal **a** axis, the magnitude of the interdonor Se . . Se interactions, and the strength of the coupling of the anion to its donor-dominated structural cavity clearly indicate that independent correlations are demanded for salts with centrosymmetric (O_h) and non-centrosymmetric (T_d) anions. In addition, a thorough study of the correspondence between molecular symmetry of an anion and the geometrical features of its structural cavity accounts for the absence of significant disorder for salts with octahedral anions and leads to a proposal for the likely structural components involved in the disorder/order transition in salts with tetrahedral anions.

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