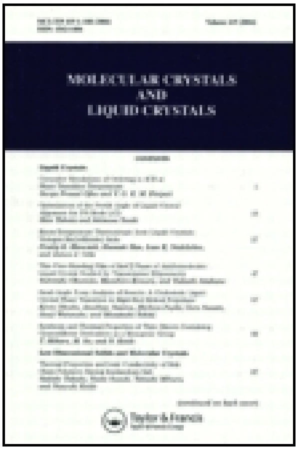

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# Effect of Anion Volume on Dimensionality of Radical Cation Salts

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# EFFECT OF ANION VOLUME ON DIMENSIONALITY OF RADICAL CATION SALTS

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Abstract New charge transfer salts with large anions : (TMTCF)$FeCl_4$, (C = S, Se) and $(TMTTF)_2Mo_6Cl_{14}$, are compared to the Bechgaard salts. An estimation of the anion volumes based on the unit-cell volumes is proposed. It is shown that increasing the anion size affects the dimensionality of the compounds.

## INTRODUCTION

A variety of inorganic anions fits the cavity between the correlated chains in the Bechgaard salts $(TMTSF)_2X$ or the isostructural $(TMTTF)_2X$ series. The influence of their symmetry and size has recently been investigated in detail[1] in relation to anion ordering and other structural and physical properties.

We recently prepared[2,3] TMTTF and TMTSF salts with two markedly different classes of inorganic anions : the magnetic transition metal tetrachlorides[2] $FeCl_4^-$ (S = 3/2), $MnCl_4^{2-}$ (S = 5/2) (and the non-magnetic $ZnCl_4^{2-}$), and the Mo(II) halide cluster anion[3] $Mo_6Cl_{14}^{2-}$. The latter is a discrete all-inorganic

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molecule with six outer chloride ligands surrounding the $Mo_6Cl_8^{4+}$ cluster core[4] isoelectronic with $Mo_6Se_8^{4-}$, the fundamental structural and electronic unit[5a] of the high-temperature and very high-field superconductors known as the "Chevrel phases".[5b] All of these anions are considerably larger in size than the commonly employed anions $Br^-$, $PF_6^-$, $BF_4^-$, $ClO_4^-$, etc... (by approximately a factor of 3 up to about 8).

An increased ratio of anion volume/cation volume is an important factor in changing the structure. In this paper we show that the Bechgaard phase is not stable with much larger anions and present a brief description of the crystal chemistry of $TMTCF^+FeCl_4^-$ (C = S, Se) and $(TMTTF)_2^{2+}Mo_6Cl_{14}^{2-}$. Furthermore we discuss the effect of successive increases of the anion volume on the dimensionality of those new solid state organic/inorganic materials.

## CRYSTAL CHEMISTRY

Since these anions are readily prepared as ammonium salts soluble in the common polar organic solvents, all new materials were obtained[2,3] by the usual electrocrystallization procedure. Complete structure determinations have been made for the three fully charge transfered (and therefore insulating) TMTCF salts discussed in this paper. Their crystallographic parameters are given in Table 1.

### $TMTTF^+FeCl_4^-$.

In this 1:1 insulating salt, the $TMTTF^+$ forms a stack with regular spacings between the ions (Figure 1b). The mode of overlapping along the stack however is different from the classical zig-zag type found in the 2:1 series. A criss-cross overlap of the molecules is observed (Figure 1a). Such a criss-cross mode of overlapping is reminiscent of the disordered

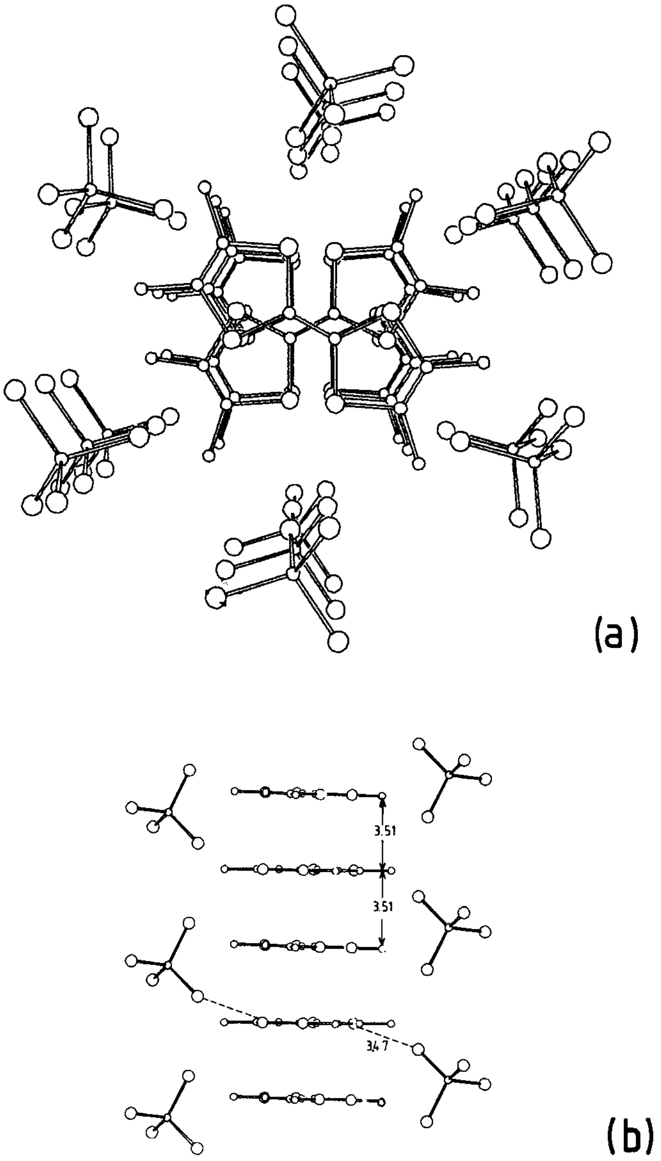

FIGURE I. Views of TMTTF $FeCl_4$ : (a) perspective down the stacking axis and (b) projection normal to the stack.

criss-cross sequence of the DBTTF's in the hexachlorostannate salts described by Shibaeva[6]. Although only the central C=C bond and two sulfur atoms of each individual ions are involved, this criss-cross mode of overlap still favors electron delocalization along the stack. There is no interchain interaction in TMTTF $FeCl_4$. Rather, the organic stacks are far apart in the rigid inorganic lattice. This material is best characterized then by its isolated organic stacks. This peculiarity may be the most important feature of this structure when compared to the Bechgaard salts in which an extended three-dimensional network of Se...Se interchains contacts develops because the organic stacks are next to each other.[7]

$TMTSF^+FeCl_4^-$

This salts acheives the same stoichiometry as its sulfur analog.

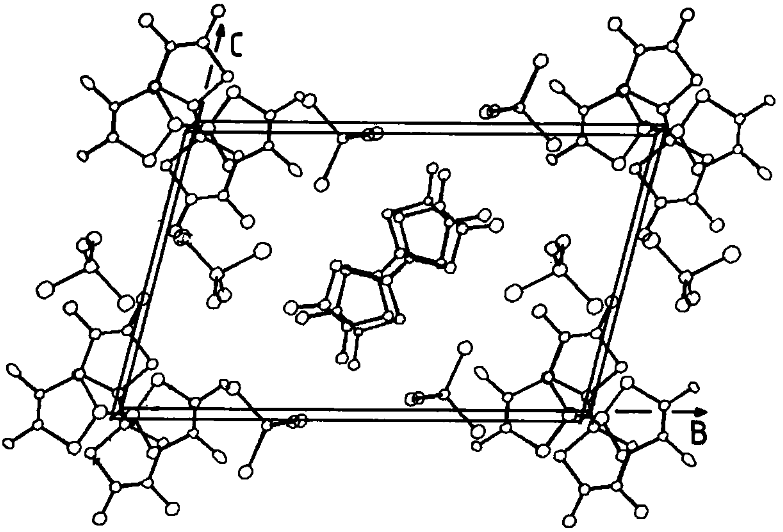

FIGURE 2 View normal to the (b, c) plane for TMTSF $FeCl_4$.

The two structures have in common the existence of isolated criss-cross TMTSF stacks which again are not dimerized since the molecules are located on centers of symmetry along $\vec{a}$.

An additional crystallographically independant TMTSF molecule is found however in the asymmetric unit giving another kind of stack which develops parallel to $\vec{a}$ in the center of the cell (Figure 2). This is a diadic colomn with the usual intradimer slipped overlap and some significant offset across the central C=C bond between the dimers. Note that this stack is also isolated, i.e. with no interchain Se...Se contacts, in a channel of $FeCl_4^-$ similar to that around the criss-cross stack. Finally we point out that the structure of TMTSF $FeCl_4$ is almost exactly although not isostructural to, that of $(TMTSF)(ReO_4)(C_2H_3Cl_3)_{0.25}$, the only other structurally characterized 1:1 salt, recently reported by Kobayashi et al.[8]

### $(TMTTF)_2^{2+}Mo_6Cl_{14}^{2-}$

This 2:1 fully charge transfered salt is formed by the composition of isolated organic and inorganic ions (Figure 3).

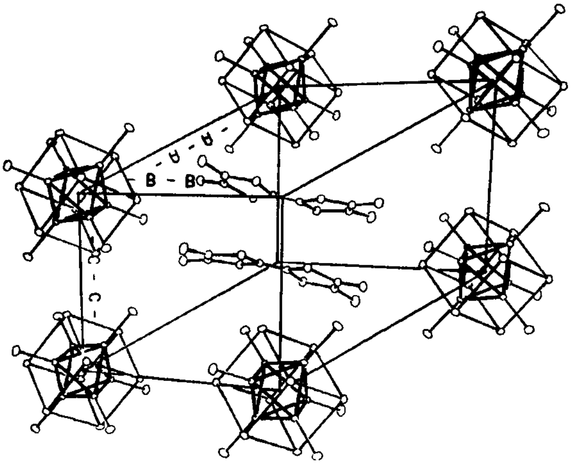

Figure 3 View of $(TMTTF)_2^{2+}Mo_6Cl_{14}^{2-}$. Two cluster anions are ommitted for clarity on this figure.

Indeed, the organic radical cations are dimerized and the dimer then form a large organic cation with a net charge of 2. Each individual ion is surrounded by eight nearest neighbours of opposite charge in a distorted cubic geometrical coordination.

This arrangement is typical of the CsCl structural type,[9] suggesting that the TMTTF dimers and the Mo(II) halide clusters are of comparable size. Thus, what we have in fact synthetized here is a giant CsCl isomorph.

## ESTIMATION AND COMPARISON OF ANION VOLUMES.

In order to discuss the effect of increasing the anion size in this series of TMTCF salts, we first need to estimate and compare the anion volumes. It is in general very difficult to calculate a volume for a polyatomic anion[10] yet effective ionic radii of the individual elements have been well characterized.[11] This is the case for $Br^-$ ($r_{Br}$ = 1,96 Å) and $I^-$ ($r_I$ = 2.20 Å). We plot in Figure 4 the unit-cell volume of $(TMTTF)_2X$, (X = Br, I) versus that of the monoatomic anion.

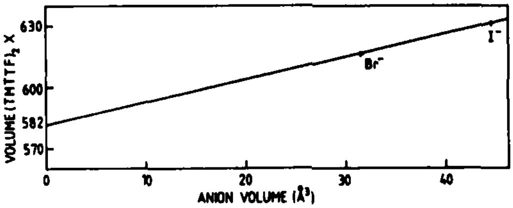

FIGURE 4 V(unit-cell) vs. V(anion).

If we assume that the unit-cell volume is determined by the sum of two contributions : the molecular and the anion volumes, extrapolating at $V_{anion}$ = 0 gives a $(TMTTF)_2$ volume of 582 Å$^3$. The volume of the TMTTF ion is assumed to be half this volume. Substracting these contributions from the actual unit-cell volumes leaves the anion volumes given in

TABLE I Crystallographic parameters for TMTCF$_x$Y salts.

| C, Anion | x | Space Group | Z$^a$ | a | b | c | α | β | γ | Volume | a$^b$ |
|---|---|---|---|---|---|---|---|---|---|---|---|
| S, $FeCl_4^-$ | 1 | $P2_1/n$ | 4 | 7.024 | 21.348 | 12.386 | | 97.11 | | 1843.0 | 1.65 |
| Se, $FeCl_4^-$ | 1 | $P\bar{1}$ | 4 | 7.528 | 20.116 | 12.661 | 75.58 | 94.22 | 93.49 | 1850.0 | 2.32 |
| S, $Mo_6Cl_{14}^{2-}$ | 2 | $P\bar{1}$ | 1 | 11.677 | 12.412 | 9.453 | 101.37 | 109.90 | 59.77 | 1112.5 | 2.38 |

a Z is the number of (TMTCF$_x$Y) units in the unit cell.

b d is the calculated density.

TABLE II Anion volume (Å$^3$) in (TMTCF)$_x$Y, C = S, Se.

| C | $BF_4^-$ | $ClO_4^-$ | $BrO_4^-$ | $ReO_4^-$ | $PF_6^-$ | $AsF_6^-$ | $TaF_6^-$ | $SbF_6^-$ | $FeCl_4^-$ | $Mo_6Cl_{14}^{2-}$ |
|---|---|---|---|---|---|---|---|---|---|---|
| S | 66.55 | 74 | | 94.4 | 95 | | | 116 | 169.7 | 530.5 |
| Se | 67 | 74.4 | 87.2 | 90.5 | 94.3 | 100 | 115.6 | 117 | 151.5 | |
| $V_{anion}V_{BF_4}$ | 1 | 1.1 | 1.3 | 1.4 | 1.4 | 1.5 | 1.7 | 1.7 | 2.4 | 7.9 |

Table 2. We plot in Figure 5 the difference in the unit-cell volumes of the S and Se salts versus the volume of $(TMTSF)_2X$ for the same anion. If this difference is due solely to the difference in volume of the molecules we expect a constant as indicated in Figure 5.

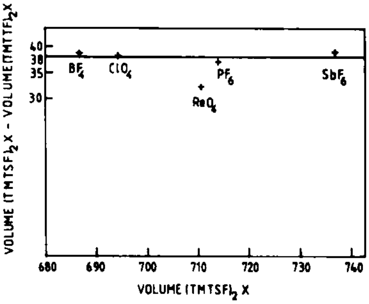

FIGURE 5 Plot of the difference in the unit-cell volume of $(TMTCF)_2X$ versus the volume of $(TMTSF)_2X$. A line at $V=38$ $\mathring{A}^3$ is shown.

Hence, the volume of $(TMTSF)_2$ is estimated to be 38 Å larger than $(TMTTF)_2$, which gives 630 $\mathring{A}^3$. Finally, the anion volumes used below are scaled for comparison to that of $BF_4^-$, the smallest polyatomic anion used in these series.

## DISCUSSION

What have we learned by making materials with increasingly larger inorganic anions ? First of all this prompted us to realize that the magic $(TMTCF)_2X$ salts, with correlated organic stacks, only have small anions, i.e. those in the range 1 to 1.7 in volume. Indeed, $TaF_6^-$ and $SbF_6^-$, the largest anions preserving the 2:1 stoichiometry, are only 70 % larger that $BF_4^-$. $ClO_4^-$, for example, is 10 % larger.

Then, by using $FeCl_4^-$, 2.5 times larger than $BF_4^-$, one isolates the organic stacks from each other. That the same result is found in $(TMTSF)(ReO_4)(C_2H_3Cl_3)_{0.25}$ with an anion smaller than $FeCl_4^-$ by a factor of 2 is, at first, somewhat surprising. We estimate however the effective volume of $ReO_4^-$ and the solvent molecule to be 151.5 $\mathring{A}^3$ in this structure, 2.2 times that of $BF_4^-$ and somewhat larger than $SbF_6^-$. We suggest the steric effect of the solvent molecule simply reinforce the size effect of the anion.

It is interesting to speculate whether the smaller $FeF_4^-$ would both preserve the Bechgaard phase and induce the desired localized spins.[12] Unfortunately however, it appears difficult to stabilize Fe(III) in tetrahedral coordination by fluorine.[13] Rather, coordination by six fluoride ions preferred, as in $KFeF_4$[14] in which corner-sharing octahedra are observed.

Finally, the formation of a mixed organic/inorganic solid with a cluster anion 8 times larger than $BF_4^-$ (an additional three-fold increase compared to $FeCl_4^-$), clearly is at the expense of the organic chain formation, since isolated dimers are stabilized in the lattice.

## CONCLUSION

An estimation of the effective anion volumes based on the actual unit-cell volumes in a series of radical cations salts has been presented. It has then been found that, within the TMTCF family of donors, a moderate increase of the anion volume results in a decoupling of the organic stacks. A large increase of the anion volume now, as in $(TMTTF)_2^{2+}Mo_6Cl_{14}^{2-}$, prevents the one-dimensional chain formation and results in the stabilisation of a giant isomorph of a simple inorganic structure with isolated organic and inorganic ions. We feel this is a general approach to the control of the dimensionality of charge transfer complexes. For example, isolated TCNQ stacks have previously been observed in a complex with large ditoluenechromium cations.[15] We beleive that the systematic modification of the coupling between the organic donors, simply by a careful choice of the anion volume, opens up new routes for tailoring organic solids.

## ACKNOWLEDGMENT

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## REFERENCES

1. J.P. Pouget, R. Moret, R. Comes, K. Bechgaard, J.M. Fabre and L. Giral, Mol. Cryst. Liq. Cryst. 79, 129 (1982).
2. P. Batail, J.B. Torrance, L. Ouahab, M. Pylman and S.S.P. Parkin, to be published.
3. L. Ouahab, P. Batail A. Souizi, A. Robert and C. Perrin, to be published.
4. See, for example, F.A. Cotton and G. Wilkinson, Advanced Inorganic Chemistry, (1980), (Wiley & Sons, New York), 4th Ed. p. 881.
5. a) T. Hughbanks and R. Hoffmann, J. Amer. Chem. Soc., (1983), 105, 1150. b) R. Chevrel and M. Sergent, Topics in Current Physics : Superconductivity in Ternary Compounds, O. Fischer and B. Maple Ed., (Springer Verlag, Berlin), (1982).
6. R.P. Shibaeva et al., Kristallografija (russ. ed.), 25 (1980), 507.
7. P.M. Grant, J. de Phys. (1983), C3, 44, 847.
8. H. Kobayashi, A. Kobayashi, Y. Sasaki, G. Saito and H. Inokuchi, Bull. Chem. Soc. Jpn., 56, 2894 (1983).
9. See, for example, ref. 4, p. 16.
10. S.S.P. Parkin, in Physics and Chemistry of Electrons and Ions in Condensed Matter, edited by J.B. Acrivos, (Reidel, New York), p. 655 (1984).
11. R.D. Shannon and C.T. Prewitt, Acta Cryst. (1976), A32, 751.
12. As suggested by F. Wudl, personnal communication.
13. G. Ferey, personal communication. The only tetrahedral transition metal tetrafluoride stabilized as a discrete anion is the diamagnetic $ZnF_4^{2-}$ in $CaZnF_4$ : H.G. von Scnering, D. Vu, K. Peters, Zeit. fur Cryst. (1983), 165, 305.
14. G. Heger, R. Geller and D. Babel, Solid St. Commun. (1971), 9, 335.
15. R.P. Shibaeva, L.O. Atovmyan and L.P. Rozenberg, J. Chem. Soc. Chem. Commun. (1969), 649.