[Contribution from the Baker Laboratory of Chemistry, Cornell University]

# Structures of Complex Fluorides.[1,2] The Structure of Sodium Octafluotantalate, $Na_3TaF_8$

By J. L. Hoard, W. J. Martin, M. E. Smith and J. F. Whitney

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Sodium fluotantalate crystallizes in a four-molecule monoclinic unit having $a = 11.52$, $b = 5.38$, $c = 11.21$ Å., $\beta = 120°55'$, and the space group $C^6_{2h}$–C2/c. Scattering by tantalum dominates the diffraction intensities and greatly facilitates the determination of structure while severely limiting the accuracy with which fluorine and sodium positions can be fixed. The structure is a salt-like aggregate of sodium and complex $TaF_8^{-3}$ ions. Within the estimated accuracy of the determination the $TaF_8^{-3}$ ion in the crystal could have exactly the configuration of the square Archimedean antiprism of symmetry $D_{4d}$–$\bar{8}2m$. However, the most probable configuration for the anion shows some departure from the ideal shape, presumably in consequence of somewhat less than ideal packing relations in the crystals.

## Introduction

The more plausible configurations accessible to a molecule or complex ion of formula $AB_8$ seem to be four in number.[3,4] These are the cube, the square or Archimedean antiprism of point group $D_{4d}$-$\bar{8}2m$, the dodecahedral arrangement ($D_{2d}$-$\bar{4}2m$) established[3] for $Mo(CN)_8^{-4}$, and an undecahedron of comparatively low symmetry ($C_{2v}$-mm2) derived from the trigonal prism by adding atoms along the normals to two of the three rectangular faces. It may seem surprising that only the $Mo(CN)_8^{-4}$ type of configuration has thus far been established for a discrete group $AB_8$. The steric properties of the cube, however, are relatively poor.[3] The necessity for using f-orbitals of the central atom in forming cubic bond functions also has been cited as unfavorable.[4a] According to Kimball[4a] the three other configurations are given by appropriate linear combinations of spd orbitals, but Higman,[4b] in work just published, concludes that one f-orbital is required for the $Mo(CN)_8^{-4}$ configuration. The steric properties of the undecahedron have not been fully investigated since the low symmetry precludes an obvious choice of the precise shape which would minimize the repulsive energy associated with interpenetration of coördinated atoms. The superior steric properties of the square (Archimedean) antiprism have long been recognized; in this respect the antiprism is much more favorable than the cube and is slightly more favorable than the dodecahedral $Mo(CN)_8^{-4}$ configuration.

In this paper we present evidence that the $TaF_8^{\equiv}$ ion, as it exists in crystalline $Na_3TaF_8$, assumes nearly the configuration of the square antiprism. The full symmetry of the antiprism cannot be required in space group theory; in $Na_3TaF_8$ only a twofold symmetry axis is required for the complex anion. It is unfortunate that the corresponding niobate, $Na_3NbF_8$, cannot be prepared[1e] since it should present a much more favorable case for accurate evaluation of the positions of fluorine atoms.

## Experimental

Following the procedure of Balke[5] $Na_3TaF_8$ was prepared in slightly acidic (HF) solution made up with NaF and $TaF_5$ in the mole ratio 4:1. Crystals were obtained both by isothermal evaporation and by slow cooling of the solutions. The habit of growth described by Balke[5] was found to be more characteristic of the crystals obtained by the cooling technique.

Oscillation and Weissenberg photographs were taken with single crystal specimens ground to cylindrical form along appropriate rational directions. Characteristic Cu K$\alpha$ radiation was used for the most part but one important zone of reflections was recorded with Mo K$\alpha$. Intensities on zero layer Weissenberg photographs were estimated quantitatively by visual comparison with a carefully calibrated intensity scale. Both the multiple film technique and controlled variations in exposure time were used at different stages to cover adequately the intensity range. The intensities were corrected by the usual Lorentz and Thomson factors and for absorption in the specimen as a function of scattering angle. Finally, after Fourier syntheses had established the principal details of the structure, experimental amplitudes were put upon an approximately absolute basis.

Described as orthorhombic but with a marked monoclinic aspect,[5] the crystals prove to be monoclinic. The unit cell has $a = 11.52$, $b = 5.38$, $c = 11.21$ Å. (Cu K$\alpha$, $\lambda = 1.5418$ Å.), $\beta = 120°55'$, with an accuracy of 0.3%. All observed spectra meet the requirements of the space groups $C^6_{2h}$-C2/c and $C^4_s$-Cc. A negative test for pyroelectricity supports C2/c as more probable and the subsequent structure determination is satisfactorily described in terms of this group. The monoclinic unit contains four stoichiometric molecules of $Na_3TaF_8$ giving a calculated density of 4.33 g./cc.

As suggested by Balke's description[5] the crystals are pseudo-orthorhombic. A face-centered pseudo-orthorhombic unit containing eight molecules with axes defined in terms of the monoclinic set by

$$\vec{A} = \vec{a},\ \vec{B} = \vec{b},\ \vec{C} = \vec{a} + 2\vec{c}$$

is especially convenient for calculation since the angle between $\vec{A}$ and $\vec{C}$ is 90° ± 4'. No difference in spacing between corresponding pairs of planes assigned orthorhombic indices ($H0L$) and ($H0\bar{L}$) could be detected for any such pair. The orthorhombic cell has $A = 11.52$, $B = 5.38$, $C = 19.24$ Å. with $B$, of course, as the only axis of twofold symmetry. Balke's[5] axes have $B$ and $C$ interchanged from our description. In point of fact the dimensions of the monoclinic unit are also pseudohexagonal, and twinning on the monoclinic (010) of a type expected for trigonal symmetry is rather commonly observed.

## Determination of Structure

A cursory analysis of Patterson syntheses of $h0l$ and $hk0$ $|F|^2$ data suffices to place tantalum atoms on twofold axes of the monoclinic unit in the special positions[6] 4(e): $0y\,{}^1/_4$; $0\bar{y}\,{}^3/_5$; etc., of C2/c, with

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[1] For earlier papers in this series see This Journal, (a) **57**, 1985 (1935); (b) **61**, 1252 (1939); (c) **61**, 2849 (1939); (d) **62**, 3126 (1940); (e) **63**, 11 (1941); (f) **64**, 633 (1942); (g) **64**, 1139 (1942); (h) **64**, 1233 (1942).

[2] Presented in part at the Sixth Annual Symposium of the Division of Physical and Inorganic Chemistry of the American Chemical Society, Columbus, Ohio, December, 1941. This paper is based on material contained in the Cornell doctoral theses of W. J. Martin (1941), and J. F. Whitney (1945).

[3] J. L. Hoard and H. H. Nordsieck, This Journal, **61**, 2853 (1939).

[4] (a) G. E. Kimball, *J. Chem. Phys.*, **8**, 188 (1940); (b) B. Higman, *ibid.*, **21**, 2224 (1953).

[5] C. W. Balke, This Journal, **27**, 1146 (1905).

[6] "International Tables for X-Ray Crystallography," Vol. 1, Kynoch Press, Birmingham, England, 1952, p. 101.

$y = 0.56$. For all *hOl* reflections tantalum atoms scatter exactly in phase and may be presumed to determine the phase of most (actually all) such reflections. The *hOl* amplitude data[7] required for a Fourier synthesis of electron density projected on (010) were obtained from a crystal ground to cylindrical form along *b* to a diameter of 0.10 mm. Photographs obtained with CuK$\alpha$ were exceptionally satisfactory for reading intensities, and reflections corresponding to every theoretically observable $\{hOl\}$, 73 forms in all, were recorded.

Two Fourier projections of electron density on (010) were computed: (1) a standard synthesis with experimental amplitudes as Fourier coefficients, and (2) a modified synthesis with the calculated contribution of tantalum subtracted from each experimental amplitude to give the corresponding Fourier coefficient. Experimental amplitudes at the CuK$\alpha$ limit are still substantial with dominant contributions from tantalum; as all tantalum contributions are absent from the difference synthesis the largest source of error arising from finite termination of the Fourier series is eliminated.[8] We were quite unprepared to find that the two syntheses give only small differences ($\lesssim 0.004$) in the parameters of fluorine and sodium atoms, especially since a study[9] of uranium hexafluoride completed a few months earlier had shown that elimination of uranium contributions from the experimental amplitudes (Cu K$\alpha$) was essential for satisfactory definition of fluorine positions on Fourier projections. A separate synthesis of tantalum contributions shows, however, that while tantalum peaks are surrounded by pronounced diffraction ripples, positions of the light atoms do not fall where this false electron density is changing rapidly.

All atoms of the cell are resolved (Fig. 1) on a (010) projection. The eight fluorine atoms forming a ring about tantalum are classified into four structurally equivalent pairs, and the 32 fluorine atoms of the monoclinic unit are placed[6] in 8(f) of C2/c, *xyz;* etc., with four distinct sets of parameters. Of the twelve sodium ions, eight are placed in 8(f), four in 4(a): 000; 00 $^1/_2$; etc. The parameter data of Table I are averaged values from the two synthesis.

TABLE I

FINAL PARAMETERS OF THE STRUCTURE

| | | Atomic coördinates | | | | | |
|---|---|---|---|---|---|---|---|
| | | Pseudo-orthorhombic | | | Monoclinic | | |
| Atom | Position | $X$ | $Y$ | $Z$ | $x$ | $y$ | $z$ |
| Ta | 4(e) | $-^1/_8$ | 0.560 | $^1/_8$ | 0 | 0.560 | $^1/_4$ |
| $Na_I$ | 4(a) | 0 | 0 | 0 | 0 | 0 | 0 |
| $Na_{II}$ | 8(f) | 0.165 | 0.505 | 0.052 | 0.217 | 0.505 | 0.104 |
| $F_I$ | 8(f) | − .212 | .365 | .197 | − .015 | .365 | .394 |
| $F_{II}$ | 8(f) | − .099 | .750 | .209 | .110 | .750 | .418 |
| $F_{III}$ | 8(f) | − .009 | .375 | .180 | .171 | .375 | .360 |
| $F_{IV}$ | 8(f) | .023 | .750 | .106 | .129 | .750 | .212 |

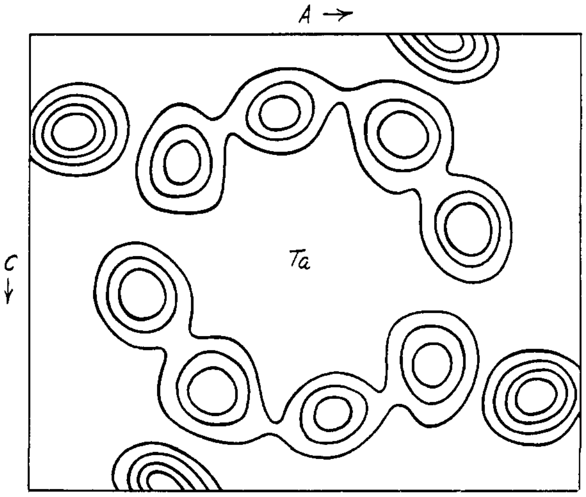

Fig. 1.—One-eight of the difference synthesis of *HOL* amplitudes projected onto the pseudo-orthorhombic (010) face.

Some special aspects of the procedure for placing amplitude data on an absolute basis are to be noted. Since the K and L absorption edges for tantalum correspond to shorter wave lengths than the 1.54 Å. of Cu K$\alpha$, we have subtracted ten from the listed Thomas–Fermi *f*-values for all $\sin \theta/\lambda$ to get an effective form factor. We obtain thereby an approximate model for the scattering of a neutral atom rather than for tantalum in the complex ion. We note also that there is a dominant contribution $|f_{Ta} \pm f_{Na}|$ to every *hOl* amplitude, a relation which facilitates the determination of separate thermal parameters for tantalum as distinct from sodium and fluoride atoms.

An effective Thomas–Fermi form factor with thermal parameter, $B$, of $0.8 \times 10^{-16}$ cm.$^2$ for tantalum and Hartree form factors with $B = 1.6 \times 10^{-16}$ cm.$^2$ for sodium and fluorine gives a fairly good fit between calculated and appropriately scaled observed *hOl* reflection amplitudes. In absolute value the 73 distinct observed amplitudes for the four-molecule monoclinic unit lie in the range 34–238, and the reliability index, $R = \Sigma||F_0| - |F_c||/\Sigma|F_0|$, is 0.084. An empirically derived form factor for tantalum, showing slightly less curvature than the Thomas–Fermi function in the range $0.15 < \sin \theta/\lambda < 0.40$ and requiring a somewhat larger scale factor for observed amplitudes ($38 \lesssim |F_0| \lesssim 255$), leads to an $R$ of 0.067. This latter choice tends to avoid large discrepancies between calculated and observed amplitudes throughout the range of $\sin \theta/\lambda$; it is used in computing the difference synthesis. We cannot say whether the empirical form factor actually gives a better account than the Thomas–Fermi model of the tantalum scattering or merely takes account of a systematic trend with $\sin \theta/\lambda$ in the errors of estimating observed intensities.

The surprisingly close agreement of peak positions given by the standard and modified Fourier syntheses cannot be taken to indicate a highly accurate determination of parameters. Both syntheses bear the full weight of errors in estimating intensities dominated by tantalum contributions, and neither has been corrected for finite termina-

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(7) HOL and HKO Amplitude data for $Na_3TaF_8$ have been deposited as Document number 4228 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington 25, D. C. A copy may be secured by citing the Document number and by remitting $1.25 for photoprints, or $1.25 for 35 mm. microfilm in advance by check or money order payable to: Chief, Photoduplication Service, Library of Congress.

(8) W. Cochran, *Acta Cryst.*, 4, 408 (1951).

(9) J. L. Hoard and J. D. Stroupe, Atomic Energy Commission Document MDDC 427 (1944; declassified Oct. 7, 1946).

tion of sodium and fluorine contributions to the series. This latter may not be insignificant in view of the fact that sodium and fluorine peaks on the projections are less sharply resolved from one another than they are from tantalum. Such corrections could be estimated from a synthesis of calculated amplitudes but the corrected parameters would still carry the full effect of errors in intensity estimations. We believe that quantitative measurements of intensities and of the scattering curve for tantalum are prerequisite to a fully detailed analysis that could claim high accuracy. We consider that the parameter data of Table I probably give the projected positions of fluorine and sodium atoms to within about 0.05 Å. Nor shall we be able to do better than this in the determination of $y$ parameters.

The octagonal array of eight fluorine atoms around tantalum in the projection strongly suggests a discrete $TaF_8^{-3}$ group having nearly the configuration of the square antiprism. If, for the anion centered at 0, 0.56, $^1/_4$, we put four fluorine atoms in the plane $y \approx 0.37$ and four others in $y \approx 0.75$, we get an antiprismatic configuration of average bond distance 2.0 Å. Further, if sodium in 8(f) be assigned $y \approx {}^1/_2$, satisfactory packing relations for sodium and fluorine (considered as ions) result for the cell as a whole. The subsequent analysis supports this interpretation with some refinement of the approximate parameters.

Inspection of the approximate structure makes it apparent that a Fourier synthesis of $hk0$ amplitudes will give projected electron densities of particularly poor resolution. The direction parallel to (010) giving optimum though far from complete resolution is along the normal to (001), *i.e.*, the direction of the pseudo-orthorhombic $C$ axis as defined under Experimental. Accordingly specimens were cut from relatively large crystals and ground to cylindrical form along $C$. Zero layer Weissenberg photographs with rotation about $C$ provide the required $HK0$ intensities. ($A$, $B$, $C$ and $HKL$ refer to the face-centered pseudo-orthorhombic unit containing eight molecules.) At most 22 forms $\{HK0\}$, all for $K \lesssim 6$, can be recorded with Cu K$\alpha$ radiation. Although reflections H80, H/4 integral, are dominated by tantalum scattering, sodium and fluorine make substantial contributions. The remarkably favorable phase relations (especially for 080) obtaining among the light atoms is, in part, a consequence of the layering of the structure along $B$; this layering requires trivial contributions from the light atoms and from tantalum for H80, H/4, half-integral. By using Mo K$\alpha$ radiation we have recorded 62 of a total of 76 forms $\{HK0\}$ in the range covered, including five with $K = 12$ and six {H80}, H/4 integral. Our most satisfactory photographs were obtained with a relatively thick rod of 0.47 mm. diameter, requiring large corrections for variation of absorption with angle. Since also the background was heavy, we feel that the accuracy attained in estimating intensities is a good deal less than for the $hk0$ data.

The binding energy of only the K electrons in tantalum corresponds to a greater frequency than that of a quantum of Mo K$\alpha$ radiation. A Thomas-Fermi form factor for tantalum and Hartree form factors for fluorine and sodium with values of the thermal parameter $B$ as determined for the $h0l$ data prove to be satisfactory for calculating $HK0$ amplitudes. The phases of all important $HK0$ amplitudes, as determined from the approximate structure already described, agree in sign with the calculated contributions of tantalum.

Two Fourier projections of electron density on (001) were computed, a standard synthesis and a difference synthesis from which tantalum contributions were insofar as possible eliminated. The first of these fixes the $y$ parameter of tantalum at $0.560 \pm 0.002$, corresponding to a determination of the equilibrium position of a tantalum atom within 0.01 Å. The difference synthesis then gives a projection from which the positions of the lighter atoms are more easily read. However, the results obtained from the two projections are in fair agreement, and we give them equal weight since the elimination of tantalum contributions from the modified projection is not a highly reliable procedure. At best no atom on the (001) projection attains the degree of resolution characteristic of the (010) synthesis. This incompleteness of resolution is more pronounced along $A$ so that generally we have used freely $x$ parameters given by the $h0l$ analysis to help unscramble the incompletely resolved peaks of the (001) projections. No apparent contradictions arise from this procedure.

Parameter values along $b$ rounded off to the nearest 0.005 are given for sodium and fluorine atoms in Table I. Except possibly for $F_{IV}$, which shows superior resolution, the values given have an estimated uncertainty of ±0.01 in the fractional coördinate or of about 0.05 Å. in the absolute coördinate. A small difference in parameter for $F_I$ and $F_{III}$ is indicated by both syntheses. Since, by virtue of the very small $b$ translation, the accuracy in the determination of absolute atomic coördinates along $b$ seems comparable with that along $a$ and $c$ we have not applied the least squares technique[10] to the $HK0$ data as a possible means of improving the accuracy of the determination. It would doubtless be worthwhile were both the experimental amplitudes and the tantalum scattering curve established from really quantitative measurements.

Based upon the four molecule monoclinic unit to facilitate comparison with $h0l$ data the 62 $\{HK0\}$ amplitudes recorded with Mo K$\alpha$ lie in the absolute range, $11 \lesssim |F_0| \lesssim 205$. The value of the reliability index for these reflections is 0.118, a result which is not unsatisfactory as compared with the lower value 0.084 or even 0.067 quoted for the $h0l$ data. The dominant tantalum contribution to $HK0$ amplitudes depends on a variable parameter, thus lowering materially the amplitude scale (*i.e.*, yielding a lower root-mean-square unitary structure factor) as compared with the $h0l$ data. Further, the use of Mo K$\alpha$ results in the inclusion of a large proportion of relatively weak reflections with complex indices and a consequent further lowering of the average amplitude. Under these conditions the percentage accuracy in determining both the experi-

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[10] E. W. Hughes, This Journal, **63**, 1737 (1941).

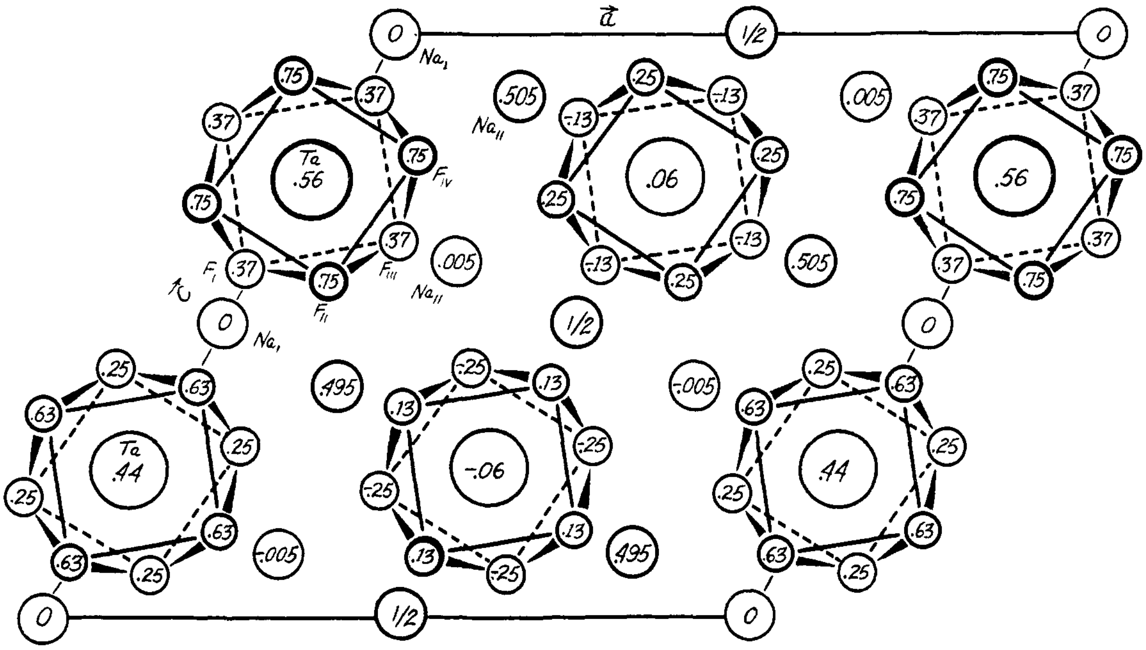

Fig. 2.—Projection of the structure onto (010) with $y$ coördinates of all atoms indicated. For F$_I$ and F$_{III}$ more precise $y$ parameters are 0.365 and 0.375, respectively.

mental and calculated amplitudes is bound to suffer and the value of $R$ thereupon increases.

According to our calculations none of the 14 unrecorded $\{HK0\}$ forms lying in the range of sin $\theta/\lambda$ covered should have given observable reflections; in fact, only three of these are near to the recordable lower limit. The one real though not serious qualitative discrepancy is for 840, which has experimental and calculated amplitudes of 53 and 14, where the observable minimum corresponds to about 30 (orthorhombic unit).

### Discussion of the Structure

The data of Table I yield Ta–F bond distances in the complex anion (Fig. 2) ranging from 1.93 to 2.01 Å. with an average of 1.98 Å. Since virtually identical dimensions have been observed for a number of isomorphous pairs of tantalum and niobium compounds, the following bond distances are suitable for comparison: in NbF$_7^=$ and TaF$_7^=$,[1b] 1.97 Å.; in NbOF$_5^=$[1e] 1.88 Å. Some trend with coördination number is indicated, but the accuracy attained in this and the earlier studies does not permit of very definite conclusions on a purely experimental basis.

The parameter data give a somewhat distorted antiprism as the most probable configuration for TaF$_8^{-3}$ in the crystal. Introduction of minor shifts within the estimated accuracy of the parameter determinations could give the ideal configuration of maximum symmetry $\bar{8}2m$. For the regular antiprism (all edges equal) a bond distance of 1.98 Å. requires an edge length of 2.41 Å. The configuration as determined has an average separation between adjacent pairs of fluorine atoms of 2.41 Å. with no deviation as large as 0.10 Å. The average value for the eight edges bounding "square" faces is 2.40 Å. and for the eight edges connecting square faces while separating triangular faces is 2.42 Å.

Each sodium ion lying in a symmetry center has six near fluorine neighbors in octahedral coördination. Na$_I$–F distances lie between 2.26 and 2.45 Å. with an average of 2.35 Å. The smallest of these, Na$_I$—F$_I$ = 2.26 Å., may be compared with the Na$^+$–F$^-$ separation of 2.31 Å. in sodium fluoride. It would be increased most efficiently by making the $y$ parameter of F$_I$ greater than 0.365 (Fig. 2). Each sodium ion in the general position has eight near fluorine neighbors at distances lying between 2.29 (Na$_{II}$–F$_{III}$) and 2.50 Å. with an average of 2.42 Å. The closest contacts between neighboring complex ions are achieved by pairs of F$_I$ atoms related by symmetry centers at 0, $^1/_2$, 0, etc. (not occupied by Na$^+$); the calculated separation, 2.65 Å., is 0.05 Å. less than the normal van der Waals diameter, estimated as the ionic diameter for a coördination number of six. Other F–F contacts between complex ions range upward from 2.77 Å.

We would characterize the rather complex packing relations as satisfactory but not ideal. It appears likely that a small difference in the $y$ parameters of F$_I$ and F$_{III}$ as indicated by the Fourier analysis is real. Starting from an average or "expected" value of $y$ = 0.370 a small increase for F$_{III}$ tends to ease the closest Na$_{II}$–F contact; $y$ = 0.375 yields Na$_{II}$–F$_{III}$ = 2.29 Å. A similar increase in $y$ for F$_I$ would ease the Na$_I$–F$_I$ contact but would simultaneously give too small a separation of two F$_I$ atoms. The value $y$ = 0.365 for F$_{II}$ seems to be a compromise (Fig. 2) which makes Na$_I$–F$_I$ = 2.26 Å., F$_I$–F$_I$ = 2.65 Å., both close to the respective acceptable minimum separations.

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