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Crystal Structure of $F_2NO^+AsF_6^-$ and Method for Extracting Meaningful Geometries from Oxygen/Fluorine Disordered Crystal Structures

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Because of their similar space requirements and electronic configurations, oxygen and fluorine ligands in oxofluorides are frequently disordered, particularly when the central atom lies on an intramolecular rotation axis. Depending on the specific occupancy factors, the apparent X−O and X−F bond lengths and bond angles that are obtained from single-crystal X-ray diffraction studies can significantly deviate from the "true" bond lengths and angles. If the degree of disorder is relatively small, these disorder-induced deviations may go unnoticed. If, however, the degree of disorder is significant, the deviations from predicted and, in particular, from the theoretically calculated geometries become so large that they can no longer be ignored. A typical example of such an extreme case of F/O disorder is the SO_2F^- anion for which the observed S−O and S−F bond lengths vary from salt to salt, and all of them deviate from the theoretical predictions.[1]

When encountering and realizing the presence of a significant O/F disorder, crystallographers generally refrain from solving "flawed" data sets. This approach, however, is too conservative. As will be demonstrated in this communication for $F_2NO^+AsF_6^-$, there are many cases where meaningful structures can be derived from disordered data sets.

Our general approach to solving certain disordered structures is outlined for a linear $C_{\infty v}$ triatomic species FXO and a planar C_{2v} tetraatomic species F_2XO. Let us first consider the most simple case, the linear FXO species, whose geometry is fully determined by the two bond lengths R_{O-X} and R_{X-F}. If there is zero disorder, i.e., F occupancies of 100% and 0% for the F and O positions, respectively, R_{O-X} and R_{X-F} have their "true" values (Figure 1a). If there is complete disorder, i.e., 50% occupancy factors, the observed bond lengths become identical and equal to $(^1/_2)(R_{O-X} + R_{X-F})$. Hence, we have an approximately linear relationship between apparent bond lengths and occupancy factors. Although the assumption of a linear relationship might not be strictly valid because oxygen and fluorine differ by one electron, a simulation using weighting factors of 8 and 9, respectively, resulted in corrections of less than 0.5 pm for the extrapolated bond lengths. The midpoint of the plot in Figure 1a can always be obtained for any occupancy factor by dividing the sum of R_1 and R_2 by 2. To obtain the slope of the line, we must know at least one extra bond length and its occupancy factor to be able to extrapolate for 0% and 100% occupancy factors and to obtain the "true" bond distances for R_1 and R_2. This analysis shows that for any disordered triatomic $C_{\infty v}$ species the "true" bond distances R_1 and R_2 can be derived from a disordered data set if the occupancy factors are not 50% and if the actual occupancy can be calculated from the experimental data. Since for the actual occupancy factors the fit between the observed and calculated intensity data must be a maximum, these factors can be obtained by refining the R value as a function of the occupancy factors. The only constraints required for such a refinement are that the sums of the partial O/F occupancies for each position must equal 1.0 and that the total O and the total F occupancies each must also equal 1.0.

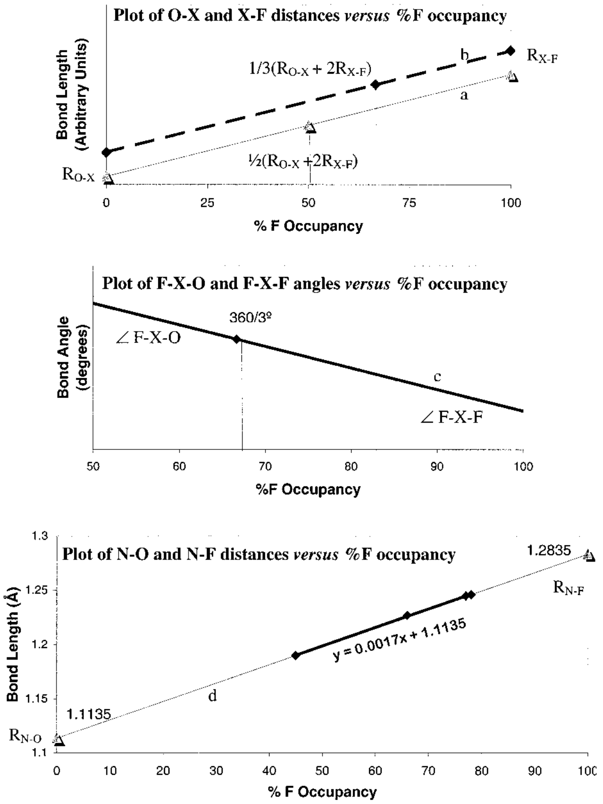

Figure 1. (a) Fluorine occupancy factors (FOF) vs O−X and X−F bond lengths for a linear $C_{\infty v}$ FXO species. (b) FOF vs O−X and X−F bond lengths for a planar C_{2v} F_2XO species. (c) FOF vs F−X−O and F−X−F bond angles for a planar C_{2v} F_2XO species. (d) FOF vs the N−O and N−F bond lengths in F_2NO^+. The data points are "apparent" N−O and N−F bond lengths and the averaged bond length. The "true" N−O and N−F bond lengths of F_2NO^+ are intersections with the 0% and 100% F occupancy lines. (e) FOF vs the F−N−O and F−N−F bond angles in F_2NO^+. The intersections of the line with the fluorine occupancy lines of 50% and 100% gives the true F−N−O and F−N−F bond angles.

The same principal can be applied to the tetraatomic C_{2v} species F_2XO. Here, however, we must determine, in addition to the two bond lengths R_1 and R_2, also one bond angle. Furthermore, the average bond length for equal occupancies is not at the 50/50 position but at the $^2/_3$ F occupancy position because we have two fluorine atoms and only one oxygen atom. The equilibrium bond length becomes $(^1/_3)(2R_{X-F} + R_{O-X})$, as shown in Figure 1b, which becomes the swivel point through which all possible lines must pass. Again, if the observed apparent bond distances are not identical for all three bonds, one can obtain the corresponding occupancy factors by refining the observed diffraction data for a

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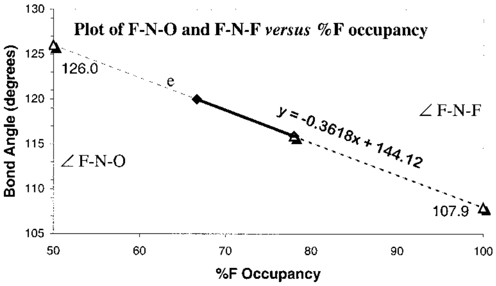

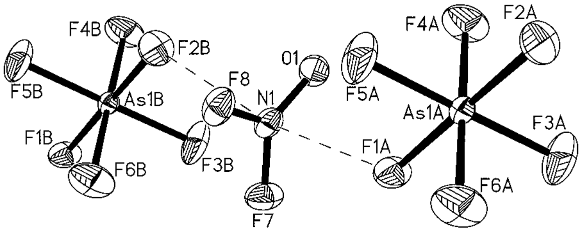

F1A = -1/2 + x, 3/2 –y, -1/2 + z; F2B = 1/2 + x, 3/2 –y, -1/2 + z
N1-F1A = 2.460(5) Å; N1-F2B = 2.584(5) Å

Figure 2. A 30% ORTEP plot of $F_2NO^+AsF_6^-$ showing the fluorine bridging between F_2NO^+ cations and the trans fluorine ligands of AsF_6^-, resulting in an infinite chain structure.

minimum R value using the following constraints. The total F occupancies must be 2.0, the total O occupancy must be 1.0, and the total O/F occupancy at each position must be 1.0. The "true" values of R_{O-X} and R_{X-F} are again obtained by extrapolation of the resulting line to F occupancy factors of 0% and 100%, respectively.

The "true" bond angle in C_{2v} F_2XO is obtained in an analogous manner by plotting the F−X−F and F−X−O bond angles versus the F occupancy factors (Figure 1c). For equal occupancies (F occupancy of $^2/_3$), all three bond angles must be equal and be 120°. Again, a plot of the observed bond angles against the occupancy factors, obtained as described above by refinement of the observed data for a minimum R value, and extrapolation for 100% F and 50% F occupancies yield the "true" F−X−F and F−X−O bond angles, respectively. The F−X−O and F−X−F bond angles are connected by the relationship $\angle F-X-O = (^1/_2)(360 - \angle F-X-F)$.

The merits of our approach are examined for $F_2NO^+AsF_6^-$ (Figure 2). Although the existence of F_2NO^+ salts had been known since 1966 [2] and the cation had been characterized by vibrational[3,4] and NMR[2,4−6] spectroscopy and theoretical calculations,[7,8] the exact geometry of F_2NO^+ was still unknown. We have now prepared a sample of $F_2NO^+AsF_6^-$ according to the literature method[3] and grown single crystals from an anhydrous HF solution by slow cooling. The X-ray diffraction data were collected[9] and refined by standard methods.[10] Although the resulting R factor of 3.17% (wR2 = 7.33%) and reasonable thermal parameters indicated a well-determined structure, the apparent N−F (124.6(4) and 125.1(4) pm) and N−O (118.5(4) pm) bond lengths and F−N−F (115.5(3)°) and O−N−F (122.1(3)° and 122.4(3)°) bond angles deviated strongly from the theoretical predictions[7,8] and suggested oxygen/fluorine disorder. This was confirmed by refining the structure with variable occupancy factors as outlined above. A minimum R value of 3.03% (wR2 = 6.68%) was obtained for fluorine occupancy factors of 78% and 77% for the two F/O positions and of 45% for the one O/F position. A plot of the apparent N−F and N−O bond lengths as a function of the calculated occupancy factors, together with the equilibrium point $(^1/_3)(2R_{X-F} + R_{O-X})$, is shown in Figure 1d and results in a straight line. Extrapolation of this line to 0% and 100% fluorine occupancy results in the following "true" bond lengths: R_{NO} = 111.4 pm and R_{NF} = 128.4 pm. Application of the outlined method to the bond angles (Figure 1e) results in the following "true" angles ∠F−N−F = 107.9° and ∠O−N−F = 126°. The "true" values, determined in this manner, agree well with those predicted by the density functional B3LYP method[8] (Table 1), particularly if it is kept in mind that the B3LYP method tends to slightly overestimate the bond lengths. While it is easy to estimate the uncertainty in the apparent bond distances and angles, an estimate of the error caused by the occupancy factor analysis is more complex and depends on the shallowness of the minimum of the R versus occupancy factor plot and possible slight nonlinearity of the bond distgance−occupancy factor curves.

Table 1. Comparison of the "Apparent" and "True" Experimental Results and the Calculated Geometries of F_2NO^+

	experimental		calculated[a]
	"apparent"	"true"	B3LYP/6-311+G(2d)
R_{N-F} (pm)	124.5(4) 124.6(4)	128.4	131.2
R_{N-O} (pm)	119.0(4)	111.4	112.9
∠F−N−F (deg)	115.9(3)	107.9	108.4
∠F−N−O (deg)	122.0(3) 122.1(3)	126.0	125.4

[a] Data from ref 8.

In summary, the above analysis demonstrates that the geometry of F_2NO^+, extracted from an oxygen/fluorine disordered structure, is in very good agreement with the theoretical predictions particularly if the inherent differences between solid state and free gaseous species are kept in mind. It also suggests that the proposed approach might be applicable to other disordered structures. It also points out the merits of comparing experimental oxofluoride crystal structures with theoretical calculations. In this manner, the possible presence of O/F disorder may be detected. If the presence of O/F disorder is suspected, it can be substantiated by refinement of the structure with variable occupancy factors and checking for a decrease in the R value.

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Supporting Information Available: An X-ray crystallographic file in CIF format of the disordered $F_2NO^+AsF_6^-$ structure. This material is available free of charge via the Internet at http://pubs.acs.org.

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(9) X-ray data: $F_2NO^+AsF_6^-$, AsF8NO, fw = 256.93, monoclinic, $P2_1/n$, a = 751.3(2) pm, b = 808.3(2) pm, c = 1031.4(2) pm, β = 107.46(3)°, V = 0.5975(2) nm^3, Z = 4, d_{calcd} = 2.856 Mg/m^3, temperature = 193 K, 1367 independent reflections (R_{int} = 0.0372), R1 = 0.0303, wR2 = 0.0668, S = 1.028.

(10) The occupancies of F and O were refined using free variables. The oxygen/fluorine occupancies at the three positions refined to 55/45%, 23/77%, 22/78%, respectively. The structure was solved using direct methods and refined by least-squares method using SHELXTL 5.10 software suite (Bruker AXS, Madison, WI).