

BRIEF COMMUNICATION

Reinvestigation of $\text{CuNbOF}_5 \cdot 4\text{H}_2\text{O}$

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The infrared spectrum of $\text{CuNb}(\text{OH}, \text{F})_7 \cdot 3\text{H}_2\text{O}$ confirms the presence of the NbOF_5^{2-} anion. Disorder in the crystal structure of $\text{CuNbOF}_5 \cdot 4\text{H}_2\text{O}$ caused misleading bond valence results and led to the assignment of the incorrect formula. © 1997 Academic Press

INTRODUCTION

Bond valence sums can be very useful tools for the analysis of crystallographic models (1, 2). Many examples may be cited where incorrect crystal structures were corrected by the use of this simple yet powerful technique (3, 4). However, if there is unrecognized disorder in a crystal structure, its effects on the observed bond lengths can make the application of bond valence sums difficult and lead to incorrect conclusions about the structure.

A recent example of this problem is found in the compound $\text{CuNbOF}_5 \cdot 4\text{H}_2\text{O}$. Its structure was originally reported by Fischer *et al.* (5, 6) to consist of chains of alternating corner sharing $[\text{NbF}_4(\text{F}/\text{O})_{2/2}]^{0.5-}$ and $[\text{Cu}(\text{H}_2\text{O})_4(\text{F}/\text{O})_{2/2}]^{0.5+}$ octahedra (the $X_{n/2}$ notation indicates a bridging ligand), isostructural with $\text{CuTiF}_6 \cdot 4\text{H}_2\text{O}$. Recently, the compound was reinvestigated by Fourquet and co-workers (7). Their careful crystallographic analysis confirmed the $\text{CuTiF}_6 \cdot 4\text{H}_2\text{O}$ structure type. However, since oxygen and fluorine are essentially equivalent in X-ray diffraction and protons are difficult to locate, the assignment of O^{2-} , OH^- , H_2O , or F^- on any of the ligand sites in the structure is equally valid in terms of the refinement. To overcome this problem, Fourquet attempted to use bond valence calculations to identify which of the possible ligands occupied each position. Their calculations appeared to rule out the presence of O^{2-} and it was proposed that the octahedra were actually $[\text{Nb}(\text{OH}/\text{F})_4\text{F}_{2/2}]^0$ and $[\text{Cu}(\text{H}_2\text{O})_3(\text{OH}/\text{F})_1\text{F}_{2/2}]^0$ corresponding to an overall formula of $\text{CuNb}(\text{OH})_x\text{F}_{7-x} \cdot 3\text{H}_2\text{O}$ ($x \approx 3$).

However, we believe that while the atomic positions and connectivity of the crystal structure determined by Fourquet are correct, disorder between O^{2-} and F^- in the structure was overlooked, resulting in an incorrect interpretation of bond valence calculations and, ultimately, the incorrect formula. Our own investigation with infrared spectroscopy confirms the original formula $\text{CuNbOF}_5 \cdot 4\text{H}_2\text{O}$. The potential pitfall in the use of bond valence when disorder is present is discussed.

EXPERIMENTAL

$\text{CuNbOF}_5 \cdot 4\text{H}_2\text{O}$ was synthesized based on the method of Fourquet (7) with minor modifications. 0.40g (5.0×10^{-3} mol) CuO (99.99 + %, Aldrich) and 0.66g (2.5×10^{-3} mol) Nb_2O_5 (99.9%, Aldrich) were dissolved in 40 mL of aqueous HF (5 N) in a polypropylene beaker. The solution was then heated to 80°C and evaporated to dryness. This dissolution and evaporation was then repeated twice. The product was a light blue powder obtained in 95.5% yield based on copper and assuming the formula $\text{CuNbOF}_5 \cdot 4\text{H}_2\text{O}$.

X-ray powder diffraction (XRD) patterns were obtained on a Rigaku powder diffractometer using $\text{CuK}\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$) and a nickel filter. Mid-IR spectra were obtained on a Biorad FTS-60 FTIR spectrometer at 2 cm^{-1} resolution. The samples were run as KBr pellets and the sample chamber was thoroughly purged with N_2 gas.

RESULTS

The XRD pattern of the synthesized powder is shown in Fig. 1, along with the calculated pattern (8) based on the crystal structure reported in Ref. (7). The close match and nearly identical synthesis conditions indicate that the polycrystalline sample produced by our experiments is the same material as the crystals produced by Fourquet.

The mid-infrared spectrum is in good agreement with the previously reported spectra of $\text{CuNbOF}_5 \cdot 4\text{H}_2\text{O}$ (9) and

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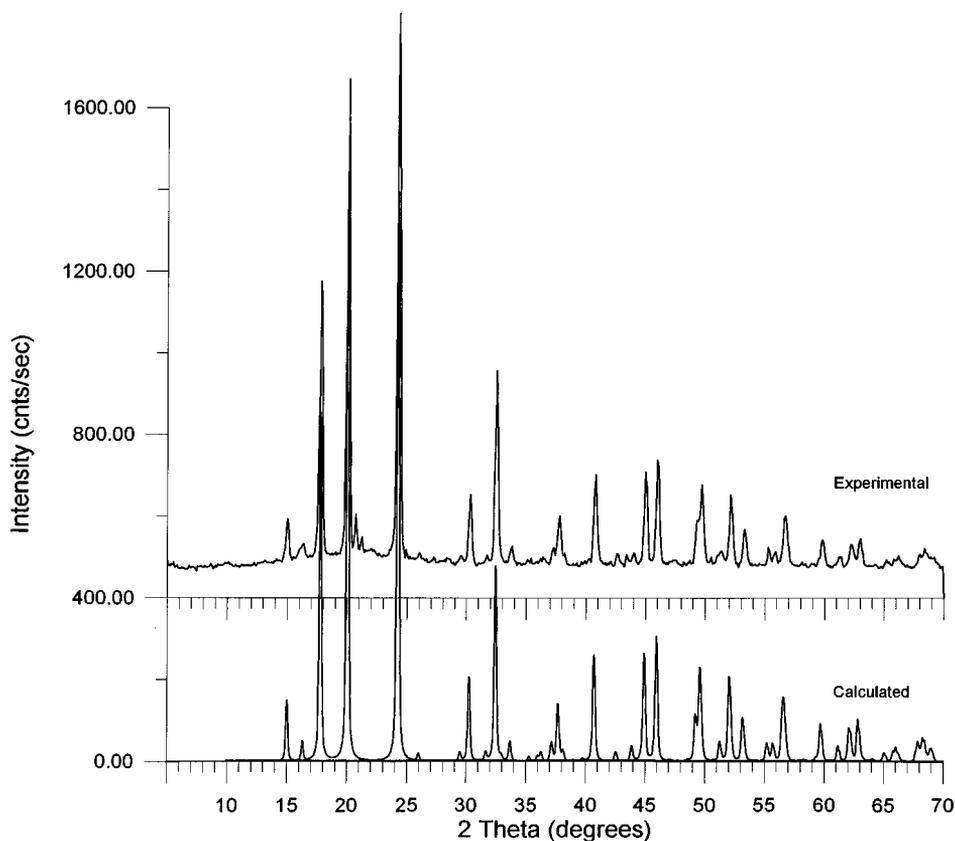


FIG. 1. Experimental XRD pattern of $\text{CuNbOF}_5 \cdot 4\text{H}_2\text{O}$ (top) and calculated pattern (bottom) from crystal data in Ref. (7).

other $[\text{NbOF}_5]^{2-}$ compounds (10, 11). Peaks are assigned as follows (s = strong, m = medium, b = broad): $\nu(\text{Nb}=\text{O}) = 972 \text{ cm}^{-1}$ (s), $\nu_s(\text{NbF}_4) = 614 \text{ cm}^{-1}$ (m), $\nu_{as}(\text{NbF}_4) = 570 \text{ cm}^{-1}$ (s), $\nu(\text{Nb}-\text{F}') = 462 \text{ cm}^{-1}$ (m), $\nu(\text{H}_2\text{O}) = 3444 \text{ cm}^{-1}$ (sb), $\delta(\text{H}_2\text{O}) = 1616 \text{ cm}^{-1}$ (mb).

DISCUSSION

Nb^{5+} in aqueous HF solution is only known to exist as $[\text{NbOF}_5]^{2-}$ and $[\text{NbF}_6]^-$, with $[\text{NbOF}_5]^{2-}$ accounting for 100% of the Nb^{5+} in solutions of 22 wt% HF or less (12). Cu^{2+} in acidic aqueous solution exists as $[\text{Cu}(\text{H}_2\text{O})_4(\text{H}_2\text{O})_2]^{2+}$ (four tightly bound equatorial ligands and two weakly Jahn–Teller bonded axial ligands). It coordinates only very weakly to F^- and precipitates as $\text{Cu}(\text{OH})_2$ upon coordination by OH^- (13). Therefore, we can conclude that $[\text{Cu}(\text{H}_2\text{O})_4(\text{H}_2\text{O})_2]^{2+}$ and $[\text{NbOF}_5]^{2-}$ are the major, if not the only species in solution under the acidic, HF rich reaction conditions. A 1:1 combination of $[\text{Cu}(\text{H}_2\text{O})_4]^{2+}$ and $[\text{NbOF}_5]^{2-}$ could easily crystallize from such a solution, forming $\text{CuNbOF}_5 \cdot 4 \text{H}_2\text{O}$. By contrast, it would be impossible for a compound containing a large number of hydroxide anions coordinated to Nb^{5+} or

Cu^{2+} , such as the one proposed by Fourquet, to crystallize from this strongly acidic solution.

The infrared spectrum of this material supports this conclusion, clearly indicating the presence of $[\text{NbOF}_5]^{2-}$. The strong $\nu(\text{Nb}=\text{O})$ peak at 972 cm^{-1} proves that O^{2-} is present in the structure, eliminating $\text{CuNb}(\text{OH})_x\text{F}_{7-x} \cdot 3\text{H}_2\text{O}$ ($x \approx 3$) as a possible formula. In addition, the relatively high energy $\nu(\text{Nb}=\text{O})$ peak along with the low energy $\nu(\text{Nb}-\text{F}')$ peak indicate a short, strong $\text{Nb}=\text{O}$ bond trans to a long, weak $\text{Nb}-\text{F}'$ bond, and the symmetric and asymmetric $\nu(\text{NbF}_4)$ peaks are consistent with C_{4v} symmetry. These features are observed in crystallographic determinations of the $[\text{NbOF}_5]^{2-}$ anion in ordered structures. For example, ordered $[\text{NbOF}_5]^{2-}$ is found in $[\text{pyH}^+]_2[\text{CuNb}_2(\text{py})_4\text{O}_2\text{F}_{10}^{2-}]$ (11) (Fig. 2). Niobium is displaced from the center of the octahedron with a short $\text{Nb}=\text{O}$ bond ($1.728(8) \text{ \AA}$) and a long trans $\text{Nb}-\text{F}'$ bond ($2.099(8) \text{ \AA}$) and the anion displays the predicted C_{4v} symmetry.

Fourquet found bond valence sums for O^{2-} on the three niobium ligand sites ranging from 0.93 to 1.18 ($R_0(\text{Nb}-\text{O}) = 1.911$), nowhere near the expected value of 2.00, and concluded that no O^{2-} existed in the structure. However,

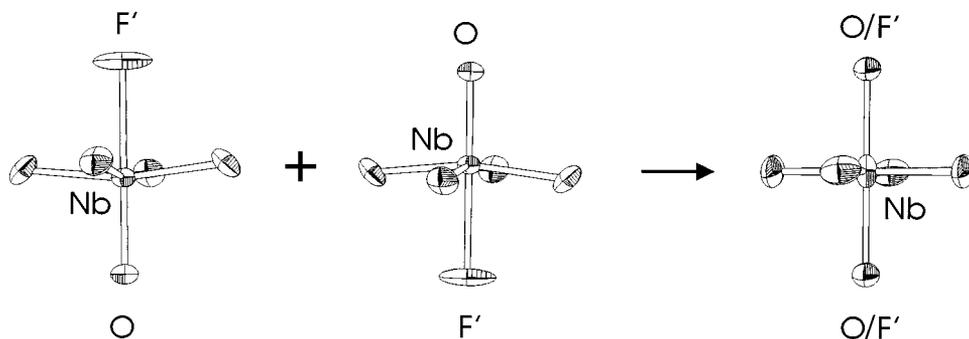


FIG. 2. Possible disorder mechanism in $\text{CuNbOF}_5 \cdot 4\text{H}_2\text{O}$ and $\text{CuNbOF}_5 \cdot 4(\text{py})$. The average of the two oppositely oriented acentric $[\text{NbOF}_5]^{2-}$ octahedra appears centrosymmetric. The niobium thermal ellipsoid is elongated along the bridging axis in the centrosymmetric octahedron, reflecting the distortions from the center of the octahedra in the acentric anions. (from $[\text{pyH}^+]_2[\text{CuNb}_2(\text{py})_4\text{O}_2\text{F}_{10}^{2-}]$ (acentric) and $\text{CuNbOF}_5 \cdot 4(\text{py})$ (centrosymmetric) (11).

the infrared spectrum shows that $[\text{NbOF}_5]^{2-}$ is indeed present. Since niobium lies on a center of inversion in the unit cell, placing an O^{2-} on any of the niobium ligand sites would automatically generate another O^{2-} in the position trans to it. Therefore, $[\text{NbOF}_5]^{2-}$ must be disordered with one site split between O^{2-} and F^- and the other two sites fully occupied by F^- to produce the needed one oxide and five fluorides. As a result of this disorder, the short $\text{Nb}=\text{O}$ bond and the long $\text{Nb}-\text{F}'$ bond are averaged. The true bond length information critical to the valence calculation is lost, resulting in the inability to identify O^{2-} through bond valence sums.

An identical situation exists in the analogous compound $\text{CuNbOF}_5 \cdot 4(\text{py})$ ($\text{py} = \text{pyridine}$) (11). It is composed of linear chains of alternating $[\text{NbF}_4(\text{F}/\text{O})_{2/2}]^{0.5-}$ and $[\text{Cu}(\text{py})_4(\text{F}/\text{O})_{2/2}]^{0.5+}$ octahedra. The infrared spectrum shows the characteristic peaks of the acentric $[\text{NbOF}_5]^{2-}$ anion (11), but niobium is again found on an inversion center (Fig. 2). The assignment of $[\text{NbOF}_5]^{2-}$ in this case is indisputable as it is necessary to balance the charge of $[\text{Cu}(\text{py})_4]^{2+}$. The O^{2-}/F^- disorder is located on the site bridging copper and niobium, based on the fact that copper and niobium are bridged by O^{2-} in $[\text{pyH}^+]_2[\text{CuNb}_2(\text{py})_4\text{O}_2\text{F}_{10}^{2-}]$.

Bond valence calculations on $\text{CuNbOF}_5 \cdot 4(\text{py})$ using $R_0(\text{M}-\text{X}) = [R_0(\text{M}-\text{O}) + R_0(\text{M}-\text{F})]/2$ for the bridging O/F site give a valence of 0.977 (compared to 1.056 for $\text{CuNbOF}_5 \cdot 4\text{H}_2\text{O}$). The nonbridging F(1) and F(2) give valences of 0.767 and 0.729 respectively (compared to 0.765 and 0.729 in $\text{CuNbOF}_5 \cdot 4\text{H}_2\text{O}$) (2). In both cases, disorder prevents bond valence calculations from identifying the O^{2-} in the structure. The similarity of the bond valence results, along with the infrared evidence, leads us to conclude that O^{2-} and F^- are disordered on the bridging site in both $\text{CuNbOF}_5 \cdot 4(\text{py})$ and $\text{CuNbOF}_5 \cdot 4\text{H}_2\text{O}$.

CONCLUSION

This case points out one of the limitations of the bond valence method, and of X-ray crystallographic analysis itself. Fourquet's crystallographic determination of the structure was careful and precise. Unfortunately, even the best X-ray analysis cannot differentiate between F^- and O^{2-} when disorder is present. As a result, over reliance on this one technique can lead to incorrect conclusions. In this case, fluorine elemental analysis ($\text{F} = 26.3 \pm 2.0\%$) (7) agrees more closely with the original formula of $\text{CuNbOF}_5 \cdot 4\text{H}_2\text{O}$ ($\text{F} = 28.0\%$) than with $\text{CuNb}(\text{OH})_x\text{F}_{7-x} \cdot 3\text{H}_2\text{O}$, $x \approx 3$ ($\text{F} = 22.5\%$ when $x = 3$). Infrared evidence and the known species in solution under the reaction conditions also strongly suggest that $\text{CuNbOF}_5 \cdot 4\text{H}_2\text{O}$ is the correct formula. However, the misleading bond valence results appeared to eliminate $\text{CuNbOF}_5 \cdot 4\text{H}_2\text{O}$, and led the authors to an incorrect alternative answer.

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(b) Valence sums calculated with the formula: $S_i = \exp[(R_0 - R_i)/B]$, where: S_i = bond valence of bond "i," R_0 = constant dependent on the bonded elements, R_i = bond length of bond "i," $B = 0.370$. $\sum S_i$ = bond valence sum for a certain site. $R_0(\text{Nb}-\text{O}) = 1.911$, $R_0(\text{Nb}-\text{F}) = 1.822$, $R_0(\text{Cu}-\text{O}) = 1.679$, $R_0(\text{Cu}-\text{F}) = 1.594$.
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