



Targeting Oxide Concentration in Tantalum Oxide-Fluoride Anions

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ABSTRACT

The design of both molecular and non-molecular solid materials with specific properties fundamentally relies on the controlled synthesis of crystals with desired functional groups, bonding motifs, polarity, chirality, and more. To this end, fluoride and oxide-fluoride anions have been utilized as basic building units (BBUs) in the synthesis of noncentrosymmetric racemic materials for their ability to create polar axes that facilitate the breaking of an inversion center as demonstrated in a series of compounds with $[\text{MF}_6]^{2-}$ anions ($\text{M} = \text{Ti}, \text{Zr}, \text{Hf}$). Targeting an analog with a $[\text{TaOF}_5]^{2-}$ anion, the phase space of $(\text{CuO}, \text{Ta}_2\text{O}_5)/\text{bpy}/\text{HF}_{(\text{aq})}/\text{H}_2\text{O}$ ($\text{bpy} = 2,2'$ -bipyridine) was investigated and three new compounds with Cu-bpy cations and Ta-fluoride or Ta-oxyfluoride anions were synthesized: $[\text{Cu}(\text{bpy})_2][\text{TaF}_6]$, $[\text{Cu}(\text{bpy})_2][\text{Ta}_2\text{OF}_{10}]$, and $[\text{Cu}(\text{bpy})\text{F}(\text{H}_2\text{O})_2][\text{TaF}_7] \cdot \text{H}_2\text{O}$ with the anions $[\text{TaF}_6]^{-}$, $[\text{Ta}_2\text{OF}_{10}]^{2-}$, and $[\text{TaF}_7]^{2-}$, respectively. The formation of these anions was found to be a product of both the concentration of hydrofluoric acid in solution and the ratio of metal-oxide starting materials to ligand. This work contributes to the understanding of mixed anion formation in the solid state.

1. Introduction

Many properties require certain symmetry elements to be present or absent, such as nonlinear optical activity and circular dichroism require the absence of an inversion center [1–4], while other properties require specific electronic [5,6], polarity, or geometric considerations [7]; examples include the electron counting rules in band theory to determine if the material is an insulator or conductor [8], a net polar moment for pyroelectricity [9,10], and triangular motifs to promote magnetic frustration in some magnetic materials, respectively [11,12]. It is therefore a foundation to designing molecular and non-molecular solid materials with specific properties to know what synthetic conditions yield desired structural functional groups, building units, bonding motifs and the like. To this end, using basic building units (BBUs) with mixed anions to assemble materials is a promising route to materials design [13]. Further, combining different BBUs with different symmetry or polarity elements allows for an additive approach to materials design: such has been seen through the combination of chiral and polar BBUs in the synthesis of noncentrosymmetric racemate compounds [1,14,15].

Tantalum anions host a wide variety of sizes, geometries, and polarities, making them candidate BBUs for a wide variety of materials with physical properties [16–19]. Further, the solubility of tantalum oxide (Ta_2O_5) in hydrofluoric acid solutions allows for extensive study of Ta-fluoride and Ta-oxide/fluoride anions [2,13,18–20]. Ta-fluoride anions $[\text{TaF}_x]^{5-x}$ range from octahedral ($x = 6$) to the distorted capped-cube of ($x = 9$) and the octahedral dimer $[\text{Ta}_2\text{F}_{11}]^{-}$ [21–25].

Ta-oxyfluoride anions exhibit an even broader range of sizes and geometries, from octahedral $[\text{TaOF}_5]^{2-}$ to its dimer $[\text{Ta}_2\text{OF}_{10}]^{2-}$ [26], and tetramer $[\text{Ta}_4\text{O}_4\text{F}_{16}]^{4-}$ [19], adamantane-like cage $[\text{Ta}_4\text{O}_6\text{F}_{12}]^{4-}$ [27], the hexanuclear cage-like cluster $[\text{Ta}_6\text{O}_9\text{F}_{18}]^{3-}$ [19], and one dimensional chains of $[\text{TaOF}_4]^{-}$ and more [19,28–30]. Further, the formation of many of these fluoride and oxyfluoride anions is understood through the relationship of the amount of dissociation of aqueous hydrofluoric acid and organic bases needing protonation, therefore, controlling the amount of fluoride ions in solution [18,19].

In this article, we report three new Ta-fluoride and Ta-oxyfluoride compounds. Chiral, metal-centered BBUs were combined with Ta-fluoride/oxyfluoride anions targeting a noncentrosymmetric, polar, racemate with the anion $[\text{TaOF}_5]^{2-}$, a Group V, oxyfluoride analog to the Group IV series of compounds of the formula Δ , Λ - $[\text{Cu}(\text{bpy})_2 \cdot \text{H}_2\text{O}][\text{MF}_6]_2 \cdot \text{H}_2\text{O}$ ($\text{bpy} = 2,2'$ -bipyridine, $\text{M} = \text{Ti}, \text{Zr}$, or Hf) [14,15]. Exploratory synthesis towards this target yielded the compounds $[\text{Cu}(\text{bpy})_2][\text{TaF}_6]$ (1), $[\text{Cu}(\text{bpy})_2][\text{Ta}_2\text{OF}_{10}]$ (2), and $[\text{Cu}(\text{bpy})\text{F}(\text{H}_2\text{O})_2][\text{TaF}_7] \cdot \text{H}_2\text{O}$ (3) with the anions $[\text{TaF}_6]^{-}$, $[\text{Ta}_2\text{OF}_{10}]^{2-}$, and $[\text{TaF}_7]^{2-}$, respectively. These newly synthesized compounds are structurally characterized and the formation of the anions in the presence of metal chelated cations builds on the works by Lu [18] and Wu [19] which described the basicity of organic bases and anion formation, as well as the role of acid concentration in conjunction with the basic ligands.

Abbreviations: BBU, basic building unit; bpy, 2,2'-bipyridine; ETM, early transition metal.

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2. Methods

Hydrofluoric acid (HF) is toxic and corrosive! HF must be handled with extreme caution and with the appropriate protective gear [31–33].

2.1. Materials

Ta₂O₅ (Aldrich, 99 % trace metals basis), CuO (Sigma-Aldrich, ≥99.0 %), 2,2'-bipyridine (bpy, Sigma-Aldrich, ≥99 %), HF_(aq) (Sigma-Aldrich, 48 % wt. in H₂O, ≥99.99+ % trace metals basis) were used as received. Reagent amounts of deionized water were used.

2.2. Hydrothermal Synthesis

The compounds reported in this article were synthesized via the hydrothermal pouch method [15]. In each reaction, heat sealed Teflon pouches were charged with reagents and loaded into a 125 mL Parr autoclave in sets of six with 40 mL deionized water added as backfill. Autoclaves were heated at a rate of 5 °C/min to 200 °C (compound 1) or 150 °C (compounds 2 and 3) and held for 24 h before slow cooling at a rate of 0.1 °C/min to room temperature. Solid products were recovered by vacuum filtration.

Compound 1, [Cu(bpy)₂][TaF₆] was synthesized in a pouch containing 0.1707 mmol CuO, 0.0854 mmol Ta₂O₅, 0.2538 mmol bpy, 0.4 mL HF_(aq) (11.04 mmol), and 0.7 mL deionized water. Orange block crystals were recovered by vacuum filtration along with the phase [Cu(bpy)₃][TaF₆]₂ [34].

Compound 2, [Cu(bpy)₂][Ta₂OF₁₀] was synthesized in a pouch containing 0.0415 mmol CuO, 0.0829 mmol Ta₂O₅, 0.2070 mmol bpy, 0.4 mL HF_(aq) (11.04 mmol), and 0.15 mL deionized water. Blue plate crystals were recovered by vacuum filtration along with other unidentified phases.

Compound 3, [Cu(bpy)F(H₂O)₂]₂[TaF₇]•H₂O was synthesized in a pouch containing 0.1707 mmol CuO, 0.0854 mmol Ta₂O₅, 0.2538 mmol bpy, 0.1 mL HF_(aq) (2.76 mmol), and 1 mL deionized water. Blue block crystals were recovered by vacuum filtration along with other unidentified phases.

2.3. Single Crystal X-ray Diffraction

Suitable single crystals were mounted on a MitiGen mount with paratone oil. The crystals were analyzed on a XtaLAB Synergy diffractometer equipped with a micro-focus sealed X-ray tube PhotonJet (MoKα, λ = 0.71073 Å) source and a Hybrid Pixel Array (HyPix) detector at 100 K. Temperature was controlled by with an Oxford Cryostystems low-temperature device. Run list generation, data integration and finalization were performed with the CrysAlisPro software; [35] a numerical absorption correction was applied. The structure was solved using Intrinsic Phase matching as implemented in ShelXT [36] within the Olex2 program [37]. The crystallographic models were refined with ShelXT using a least squares minimization.

2.4. Diffuse Reflectance UV–Visible Spectrometry

The UV-VIS-NIR spectrum in diffuse reflectance mode was collected on lightly grounded powder using a Cary 5000 UV–Vis–NIR double beam spectrophotometer with a monochromator. BaSO₄ powder was used for the baseline collection, whereas a mixture of sample powder with BaSO₄ was used for the data collection at room temperature. Absorbance data was converted from reflectance data in-software using the Kubelka-Munk equation $\alpha/S = (1-R)^2/2R$, where α and S are the absorption and scattering coefficients respectively, and R is the reflectance.

3. Results and Discussion

3.1. Structural Descriptions

The formation conditions of different Ta-fluoride and Ta-oxyfluoride building units were investigated through their combination with Cu-bpy chiral units. Exploration of the CuO/Ta₂O₅/bpy/HF_(aq) system (bpy = 2,2'-bipyridine) yielded three new centrosymmetric compounds with three different Ta-oxyfluoride anions: TaF₆[−] (compound 1), Ta₂OF₁₀^{2−} (compound 2), and TaF₇^{2−} (compound 3). An overview of the crystal structures of these compounds is given in Table 1.

Compound 1 has the formula [Cu(bpy)₂][TaF₆] and crystallizes in the triclinic space group *P* $\bar{1}$. The asymmetric unit is composed of one [Cu(bpy)₂]⁺ cation and one [TaF₆][−] anion. The cation displays *C*₁ symmetry and has both handedness (Δ and Λ), with the enantiomers being related by an inversion center. The Cu²⁺ compound [Cu(bpy)₃][TaF₆]₂ was also found in all samples containing compound 1, the tri-bpy complex has been characterized by Nisbet et al. [34]

To further investigate the geometry of the cations, the τ_4 parameter ($\tau_4 = \frac{360-(\alpha+\beta)}{360-2\theta}$, $\theta = \cos^{-1}(\frac{1}{3}) \approx 109.5^\circ$) [38] was used, where α and β are the two largest angles of the coordination center. The τ_4 parameter is an indicator of molecular geometry, with a value of 0 indicating a square planar geometry and a value of 1 corresponds to a tetrahedral geometry. In compound 1, the τ_4 value is 0.665 suggesting a distorted geometry that is neither square planar or tetrahedral.

Heterochiral π - π stacking interactions between cation enantiomers of different handedness run along both the **c** (Fig. 1a) and **b** (Fig. 1b) axes. Torsion angles *T*₁ and *T*₂ were used to describe these interactions further, with the *T*₁ angle representing the relative direction of the interacting ligands and the *T*₂ angle defining the stacking interactions of the ligands (additional information on these angles can be found in the Supporting Information) [39,40]. For the heterochiral overlap along the **b** axis, *T*₁ is equal to 122.812° indicating the cations are arranged in a head-to-tail orientation; the *T*₂ angle is equal to 86.887° signifying a nonparallel stacking interaction with one of the two C₅N rings overlapping. The same types of overlap are observed in heterochiral π - π stacking interactions along the **c** axis, where head-to-tail interactions with one overlapping C₅N ring overlap were observed (*T*₁ = 113.733°, *T*₂ = 48.827°) (see Figure 1).

The [TaF₆][−] anion features six Ta–F bonds with lengths ranging from 1.8874 to 1.9005 Å: the variance in Ta–F bond lengths hints at a small out of center distortion creating a polar axis within the anion. The inversion center relating the two anions leads to a net cancellation of the anions' polar moments.

Compound 2 has the formula [Cu(bpy)₂][Ta₂OF₁₀] and crystallizes in the space group *P* $\bar{1}$ and its asymmetric unit contains one cation and one anion. The full structure contains two of each, with cation and anion

Table 1
Basic crystallographic information for compounds 1, 2, and 3. Complete crystallographic information is available in the Supporting Information.

	1	2	3
Formula	[Cu(bpy) ₂][TaF ₆]	[Cu(bpy) ₂][Ta ₂ OF ₁₀]	[Cu(bpy)F(H ₂ O) ₂] ₂ [TaF ₇]•H ₂ O
Anion	TaF ₆ [−]	Ta ₂ OF ₁₀ ^{2−}	TaF ₇ ^{2−}
Space Group	<i>P</i> $\bar{1}$ (2)	<i>P</i> $\bar{1}$ (2)	<i>P</i> 2 ₁ /c (14)
a (Å)	8.6142(2)	9.9747(2)	21.5414(2)
b (Å)	9.4665(2)	10.1496(2)	7.44480(10)
c (Å)	14.3714(2)	13.4325(3)	33.4908(2)
α (°)	107.742(2)	73.894(2)	90
β (°)	92.637(2)	74.678(2)	99.3450(10)
γ (°)	107.465(2)	70.793(2)	90
V (Å ³)	1052.48(4)	1211.16(5)	5299.69(9)
Z	2	2	8
CCDC	2293940	2293941	2293943

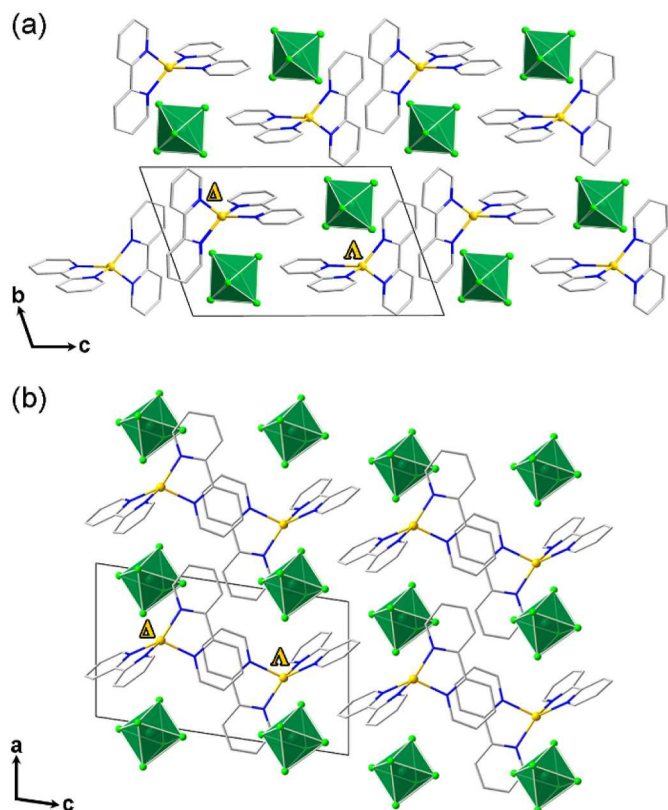


Fig. 1. Structure of Compound 1 as viewed down the (a) *a* axis, and the (b) *b* axis. Dark green, yellow, light green, blue, and gray spheres represent Ta, Cu, F, N, and C respectively, green polyhedra represent Ta-centered anions. Hydrogen atoms on the ligands have been omitted for clarity.

pairs related by an inversion center. The cation, $\text{Cu}(\text{bpy})_2^{2+}$ has C_1 symmetry and displays both Δ and Λ enantiomers stacking along the *c* axis. With a τ_4 parameter value of 0.326, the geometry is between square planar and a tetrahedra. Torsion angles of 127.383° and 88.638° for T_1 and T_2 respectively, indicate a head-to-tail orientation of the heterochiral cations with nonparallel stacking and overlap of only one C_5N ring between (Figure 2).

The anion $\text{Ta}_2\text{OF}_{10}^{2-}$ is a dimer of TaOF_5^{2-} anions corner sharing through the O atom. The dimer is not entirely linear with a Ta1-O-Ta2 angle of 168.564° ; further, out of center distortions occur within the Ta-centered octahedra as the Ta–O bonds range from 1.9026 (Ta1–O) to 1.9111 Å (Ta2–O) and the Ta–F bonds range from 1.8962 to 1.9268 Å. It should be noted that the dimer anion observed differs from previous literature reports for its non-linear connection of the dimer as well as its longer Ta–O/F bond lengths [26,41,42].

Compound 3 has the formula $[\text{Cu}(\text{bpy})\text{F}(\text{H}_2\text{O})_2]_2[\text{TaF}_7] \cdot \text{H}_2\text{O}$ and crystallizes in the monoclinic space group $P2_1/c$. The asymmetric unit contains four $\text{Cu}(\text{bpy})\text{F}(\text{H}_2\text{O})_2^{2+}$ cations, two TaF_7^{2-} anions, and two unbound water molecules (Figure 3). Unlike the cations in compounds 1 and 2, compound 3 is five coordinate and there are two of each Δ and Λ enantiomer in the asymmetric unit. There are two sets of heterochiral π - π stacking interactions: located at $\sim \frac{1}{2}c$ and $\sim \frac{1}{4}c$ and running along the *b* axis (Figure 3b). The resulting π - π stacking interactions are of a head-to-tail orientation ($T_1 = 131.904^\circ$) with both C_5N rings overlapping ($T_2 = 97.766^\circ$) for interactions at $\sim \frac{1}{2}c$, while interactions at $\sim \frac{1}{4}c$ are also head-to-tail oriented ($T_1 = 100.111^\circ$) but with only one C_5N ring overlapping ($T_2 = 51.043^\circ$). Further characterization of the cation included an evaluation with the τ_5 parameter. This parameter is a measure of the molecular geometry of a 5-coordinate metal center with the formula $\tau_5 = \frac{\beta - \alpha}{60}$, where β and α are the two largest valence angles

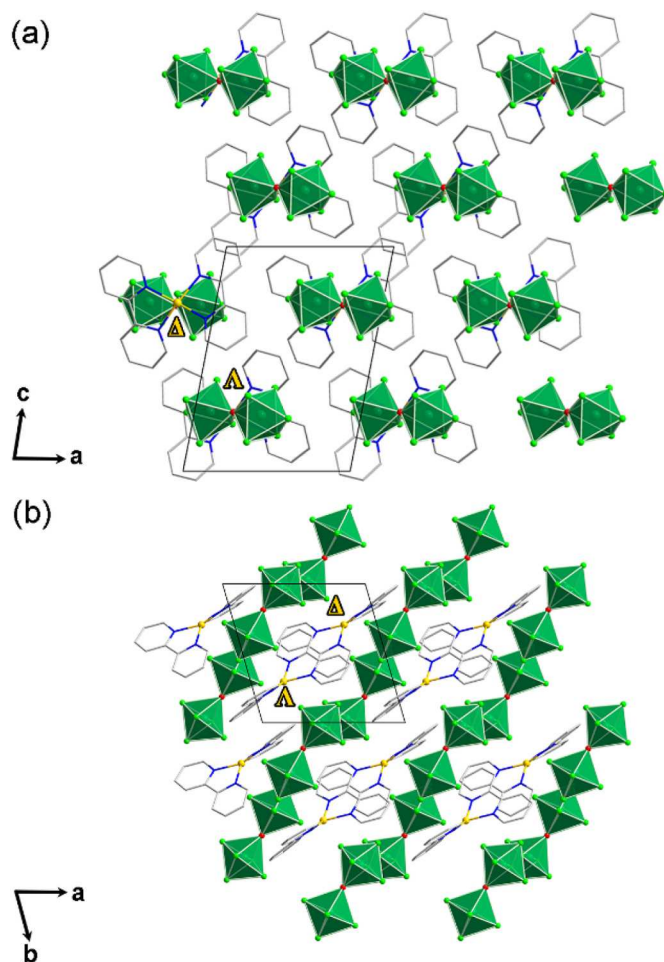


Fig. 2. Structure of Compound 2 as viewed down the (a) *b* axis, and the (b) *c* axis. Dark green, yellow, light green, red, blue, and gray spheres represent Ta, Cu, F, O, N, and C respectively, green polyhedra represent Ta-centered anions. Hydrogen atoms on the ligands have been omitted for clarity.

[43]. For compound 3, τ_5 ranges from 0.206 to 0.371, which are intermediate between a square pyramidal geometry ($\tau_5 = 0$) and a trigonal bipyramidal geometry ($\tau_5 = 1$).

Two TaF_7^{2-} anions are present in each asymmetric unit, both with pentagonal bipyramidal geometry. Neither pentagonal ring is planar and between the anions, the 14 Ta–F bond lengths vary from 1.900 to 2.010 Å, with the longest bond in each anion present in the pentagonal ring.

Compound 3 exhibits a hydrogen bonding network that interconnects the cations, anions, and free water molecules (Fig. 3c). On each anion, four of the five equatorial F atoms hydrogen bond with water molecules bound to the cation; one F interacts with both bound water molecules on a neighboring cation, two F interact with free water molecules.

3.2. Reduction of Cu in Compound 1

The crystals of compound 1 were observed as an orange/amber color, suggesting the reduction of the Cu^{2+} starting reagent to Cu^+ in the products. This reduction was further confirmed by structural solution of compound 1, as the cation co-crystallizes with a known 1^- anion (TaF_6^-), necessitating a cation charge of $1+$ for charge balance.

While the precise mechanism of the reduction of Cu^{2+} to Cu^+ cannot be elucidated with certainty, and the reducing agent unidentified, the authors speculate that the increased reaction temperature—and therefore pressure—from which compound 1 crystallized from contributed to an increased susceptibility of Cu^{2+} reduction [44]. Reduction of Cu^{2+}

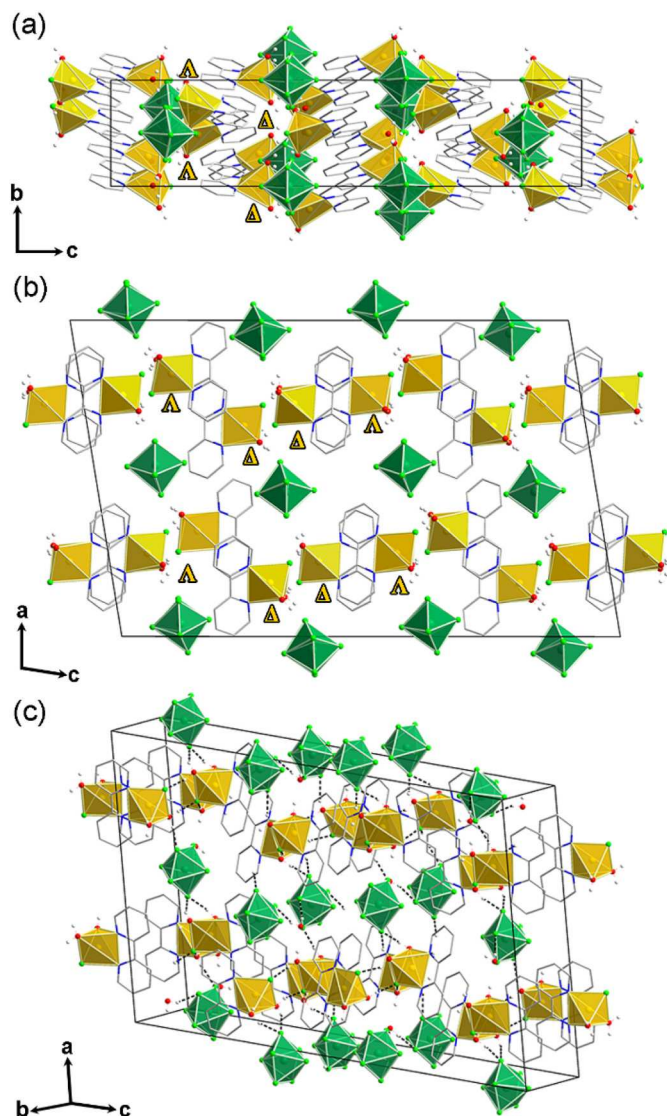


Fig. 3. Structure of Compound 3 as viewed down the (a) *a* axis, and the (b) *b* axis. Hydrogen bonding network between coordination water hydrogen and anions is shown in (c), H-bonds are depicted with dashed black lines. Dark green, yellow, light green, red, blue, and gray spheres represent Ta, Cu, F, O, N, and C, respectively, green polyhedra represent Ta-centered anions and yellow polyhedra represent Cu-centered cations. Non-coordinating water and hydrogen atoms on the ligands have been omitted for clarity.

was only observed at the elevated temperature of 200 °C and observed in all reactions conducted at this temperature, implying that the increase in temperature is a major driving force for the formation of Cu^+ ions. Further, the Cu^+ ions are stabilized in solution at 200 °C owing to the considerably decreased dielectric constant of water at this temperature, allowing the suppression of the Cu^+ disproportionation reaction [45].

3.3. Formation of Different Ta-Oxyfluoride Anions

Since the 1970s, the formation of different oxyfluoride anions has been studied in relation to the organic bases in solution—beginning with Olah's reagent as a nucleophilic fluorinating agent [18,19,46–50]. Within the realm of Ta-oxyfluoride anion formation in the presence of hydrofluoric acid, the pK_a of the organic bases allows for control over which anion species form: for instance, a high pK_a base such as quinuclidine ($\text{pK}_a = 10.87$) grants a higher concentration of fluoride anions, while a smaller pK_a base—like 2,2'-bipyridine ($\text{pK}_a = 4.23$)—yields

lower fluoride concentrations [18,19]. Ligands with high pK_a value are more readily protonated by hydrofluoric acid in solution, leading to a higher dissociation of the acid into H^+ and F^- ions. The opposite is also true, ligands with low pK_a values are protonated less and therefore do not lead to much HF dissociation. It was also observed that formation of oxyfluoride anions does not occur with organic ligands with pK_a values lower than that of the weak hydrofluoric acid ($\text{pK}_a = 3.17$) [18].

In this study, only one organic base, 2,2'-bipyridine (bpy), was used across a large phase space with differing ratios of base to metal-oxides (Fig. 4, *x* axis) as well as through a range of pH values (Fig. 4, *y* axis) with the aim of creating compounds formed of discrete Ta-oxyfluoride anions and Cu-bpy cations. The case of making metal-ligand cations differs from the aforementioned studies in that the protonation of the ligand does not occur appreciably, and therefore the equilibrium established between ligand basicity and HF dissociation is less pronounced.

Without organic bases to protonate, what is the relationship between the concentration of the organic base in solution and the fluoride ion concentration and subsequently, the Ta-oxyfluoride anion formed? When the ratio of ligand to metal-oxide starting reagents (CuO and Ta_2O_5 , which are held at a constant ratio of 1 mol Cu:1 mol Ta) is low, only Ta-fluoride anions form and as the ratio increases beyond 2:1, Ta-oxyfluoride anions appear at low acid concentrations. The preference for formation of fluoride ions over oxyfluoride ions appears to be an issue of solubility; at low acid and base concentrations (low ratio, 1:1 and high pH), the tantalum oxide starting reagent is not completely soluble, consistent with previous findings [51–53]. Incomplete dissociation of Ta_2O_5 creates a relatively higher $[\text{F}^-]:[\text{Ta}^{5+}]$ ratio, leading to the formation of fluoride-rich anions. As the base:metal-oxide ratio increases, a trend can be perceived by moving from left to right in Fig. 4, Ta_2O_5 becomes more soluble, leading to the anion formation rules previously established by Lu and Wu [18,19]. At low base:metal-oxide starting ratios, the pK_a of the solution can be thought of as being lower—closer to that of hydrofluoric acid—but instead of decreasing the dissociation of HF, there is limited Ta_2O_5 . It has been noted that early transition metal(ETM)-oxyfluoride anions have not been observed with ratios of base:ETM less than 1.5, hinting that this is an upper limit for ETM-oxide reaction and a lower limit for base-HF dissociation relationships.

When the organic base concentration in solution remains the same and the concentration hydrofluoric acid is added, the concentration of fluoride ions increases and the more fluoride rich anions form [28]. This trend can be viewed by taking any of the ligand:metal-oxide ratios found

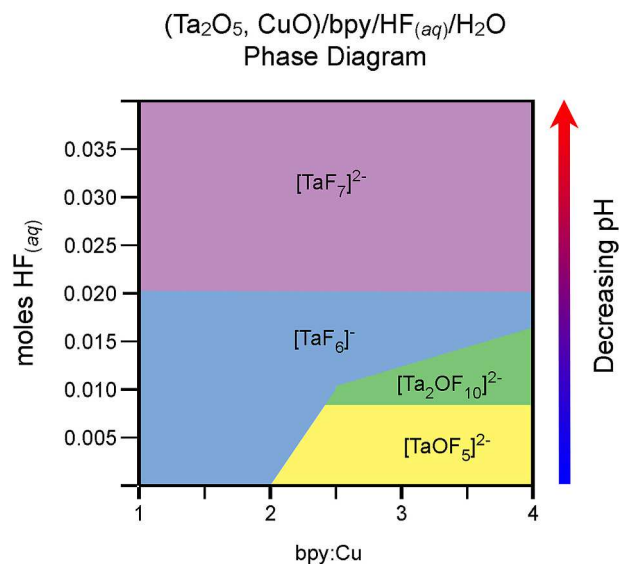


Fig. 4. Estimations of where different Ta-O/F anions can be found within the $(\text{Ta}_2\text{O}_5, \text{CuO})/\text{bpy}/\text{HF}_{(\text{aq})}/\text{H}_2\text{O}$ phase diagram at 150 °C.

on the x-axis and moving upward. As the concentration of hydrofluoric acid is increased, the fluoride ion concentration increases to a level that eventually yields the fluoride only anions. A previous study showed that successively, the anions $[\text{TaOF}_5]^{2-}$, $[\text{TaF}_6]^-$, $[\text{TaF}_7]^{2-}$, $[\text{TaF}_8]^{3-}$ and $[\text{TaF}_9]^{4-}$ form as concentration of acid is increased [28], additionally, the present work found that the intermediate anion $[\text{Ta}_2\text{OF}_{10}]^{2-}$ forms between the anions $[\text{TaOF}_5]^{2-}$ and $[\text{TaF}_6]^{2-}$, in what appears to be a narrow range. The fluoride rich anions $[\text{TaF}_8]^{3-}$ and $[\text{TaF}_9]^{4-}$ were not observed within the limits of acid concentrations used in this study.

Further, under the conditions tested in this study, the larger chain, prismatic, and tetrameric anions $\text{TaO}_4\text{F}_4^{2-}$, $\text{Ta}_6\text{O}_9\text{F}_{18}^{6-}$, and $\text{Ta}_4\text{O}_4\text{F}_{16}^{4-}$, respectively, were not observed, owing to the low pK_a of the bpy ligand and the limited range of acid concentrations used. It must also be noted that the boundaries depicted in Fig. 4 are largely estimated on the areas of phase space explored in this work and do not represent an exhaustive investigation of the phase space nor have they been rigidly defined experimentally.

4. Conclusions

Three new compounds were synthesized featuring three distinct Ta-fluoride or Ta-oxyfluoride anions. The phase space of $(\text{CuO}, \text{Ta}_2\text{O}_5)/\text{bpy}/\text{HF}_{(\text{aq})}/\text{H}_2\text{O}$ was investigated with differing ratios of ligand:metal-oxide starting reagents as well as range of acid concentrations. It was found that fluoride-rich anions form in regions of high acid concentration and where metal-oxide starting reagents have limited reactivity; oxyfluoride anions form after a 1:1.5 threshold ratio of ligand:metal-oxide and at low acid concentrations owing to limited dissociation of hydrofluoric acid. At any ligand:metal-oxide ratio, an increase in added acid concentration increases the amount of fluoride observed in the anion. These studies contribute to understanding new facets of mixed anion formation and allows for a targeted approach to designing materials with specific basic building units that can contribute to the emergence of physical properties.

Associated content

Additional X-ray crystallographic data for compounds 1–3 (CCDC 2293940, 2293941, 2293943); additional structural characterization data for compound 1–3.

CCRediT authorship contribution statement

Kendall R. Kamp: Conceptualization, Investigation, Formal analysis, Writing – original draft, Writing – review & editing, Visualization. **Yiran Wang:** Conceptualization, Methodology, Writing – original draft. **Kenneth R. Poeppelmeier:** Supervision, Project administration, Funding acquisition.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.solidstatesciences.2023.107369>.

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