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Composition Space of the (CdO, $0.5Nb_2O_5$)/$(HF)_x$·Pyridine/H_2O System. Structure and Synthesis of $CdNb(py)_4OF_5$

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Introduction

Hydrothermal synthesis provides a low-temperature synthetic pathway to interesting solid state compounds. In this work, hydrogen fluoride is used to dissolve metal oxides in a pyridinium poly(hydrogen fluoride)/H_2O/pyridine solution under mild hydrothermal conditions (150 °C, autogenous pressure). Single crystals of new mixed metal compounds are recovered after slow cooling of the solutions. Previously, the (CuO, Nb_2O_5)/$(HF)_x$·pyridine/H_2O system[1] was studied as part of an investigation of factors governing the formation of centrosymmetric versus noncentrosymmetric structures,[2] and a three-component composition space diagram was constructed to relate the mole fractions of the reactants to the composition of the crystalline product. Phase stability and crystallization fields can be understood on the basis of the initial reactant concentrations.

Substitution of Cu^{2+} with Cd^{2+} in this system has been achieved, resulting in two new compounds. The first is a trimetallic cluster complex, $[pyH]_2[Cd(py)_4(NbOF_5)_2]$,[3] which is isostructural with its Cu analogue. The second, $CdNb(py)_4OF_5$, is an infinite chain compound closely related to $CuNb(py)_4OF_5$. In this paper conditions for selective crystallization from the (CdO, $0.5Nb_2O_5$)/pyridinium poly(hydrogen fluoride)/H_2O system in solvent pyridine are discussed, and the structure, synthesis, and infrared spectrum of a new cadmium niobium oxyfluoride, $CdNb(py)_4OF_5$, are reported.

Experimental Section

Caution. Pyridinium poly(hydrogen fluoride) is toxic and corrosive!

Materials. CdO (99%, Aldrich), Nb_2O_5 (99.9%, Aldrich), pyridine (99.8%, anhydrous, Aldrich), and pyridinium poly(hydrogen fluoride) [$(HF)_x$·py] (70% HF by weight, Aldrich) were used as received. Reagent amounts of deionized H_2O were used in the synthesis.

Synthesis. $CdNb(py)_4OF_5$ was synthesized by adding 9.63×10^{-2} g (7.5×10^{-4} mol) of CdO and 9.95×10^{-2} g (3.75×10^{-4} mol) of Nb_2O_5 to an FEP Teflon pouch[4] containing 9.88×10^{-2} g (3.75×10^{-4} mol) $(HF)_x$·py, 7.9×10^{-1} g (1×10^{-2} mol) pyridine, and 1.01×10^{-1} g (5.62×10^{-3} mol) of H_2O. The Teflon pouch was sealed and placed with 600 mL of deionized water in a 2000 mL autoclave (Parr) and heated to 150 °C for 24 h. The autoclave was then cooled to room temperature over an additional 24 h. The pouches were removed and opened in air, and the colorless crystals were recovered by filtration in about 40% yield based on cadmium oxide.

Table 1. Crystal Data for $CdNb(py)_4OF_5$

empirical formula $C_{20}H_{20}CdF_5N_4NbO$	fw 632.71
$a = 12.993(1)$ Å	space group $C2/c$ (No. 15)
$b = 10.733(1)$ Å	$T = 153(1)$K
$c = 16.878(3)$ Å	$D_{calc} = 1.799$ g cm^{-3}
$\beta = 97.11(1)°$	$D_{obs}{}^{a} = 1.78(2)$ g cm^{-3}
$V = 2335.6(4)$ Å^3	$\mu = 14.6$ cm^{-1}
$Z = 4$	$R^b(F) = 0.026$
	$R_w{}^c(F) = 0.031$

[a] Density measured by flotation pycnometry at 24 °C. [b] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [c] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$.

X-ray Crystallographic Analysis. The systematic absenses are consistant with either the acentric space group *Cc* (No. 9) or the centrosymetric $C2/c$ (No. 15). Four octants of data, $h\ k\ l$, $-h\ -k\ -l$, $h\ k\ -l$, and $-h\ -k\ l$, were collected (instead of the minimum two required for a monoclinic setting) to compare Friedel opposites. On the basis of the successful solution and refinement, the space group was determined to be the centrosymetric $C2/c$ (No. 15). All calculations were done using the TEXSAN[5] crystallographic software package from Molecular Structure Corporation. The Cd^{2+} and Nb^{5+} positions were found by direct methods,[6] while the remaining non-hydrogen atoms were determined from subsequent difference Fourier maps.[7] The O(1) and F(1) atoms were disordered over the same site, and the hydrogen atoms were placed in idealized positions. The largest remaining peak in the electron density map, 1.18 e Å^{-3}, is near the Cd site. Relevant crystallographic data are given in Table 1.

Spectroscopic Measurements. The Mid-IR (400−4000 cm^{-1}) spectrum was collected using a Bomem MB-100 Fourier transform infrared spectrometer equipped with a DTGS detector operating at a resolution of 2 cm^{-1}.

Nonlinear Optical Measurements. Second-order nonlinear optical measurements were performed on sifted (35−250 mm) $CdNb(py)_4OF_5$ powder, using the standard Kurtz technique.[8,9] The powder was sifted to investigate coherence length phase matching of any second-order nonlinear optical effects. A tunable light source was provided by optical parametric amplification based instrumentation.[10] No second harmonic generation (SHG) was observed in any of the samples.

Results

Three regions exist in the composition space of the (CdO, $0.5Nb_2O_5$)/$(HF)_x$·py/H_2O system shown in Figure 1. In region **A** only a clear colorless solution is observed in the reaction pouches as all species remain in solution. In regions **B** and **C**, $[pyH]_2[Cd(py)_4(NbOF_5)_2]$ and $CdNb(py)_4OF_5$ crystals are formed, respectively.

$CdNb(py)_4OF_5$ contains non-intersecting chains of corner-shared $[Cd(py)_4(O/F)_{2/2}]^{0.5+}$ and $[NbF_4(O/F)_{2/2}]^{0.5-}$ octahedra. The Cd^{2+} is coordinated by two axial (O, F) at 2.290(2) Å and

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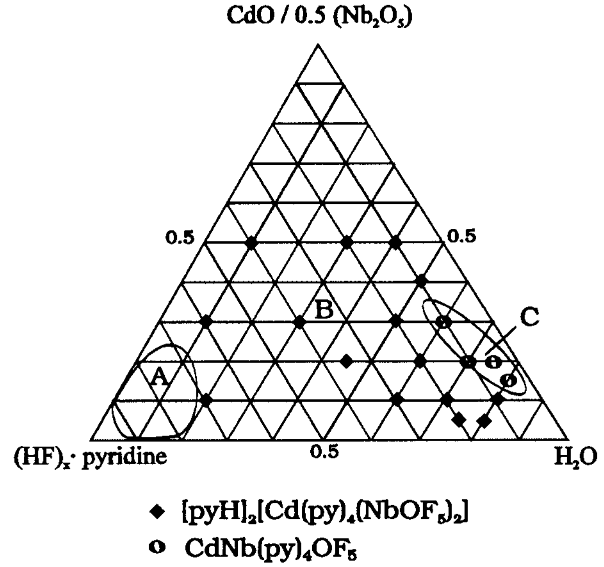

Figure 1. Composition space of the (CdO, $0.5Nb_2O_5$)/$(HF)_x$. pyridine/H_2O) system in excess pyidine, with A−C representing three general synthetic regimes.

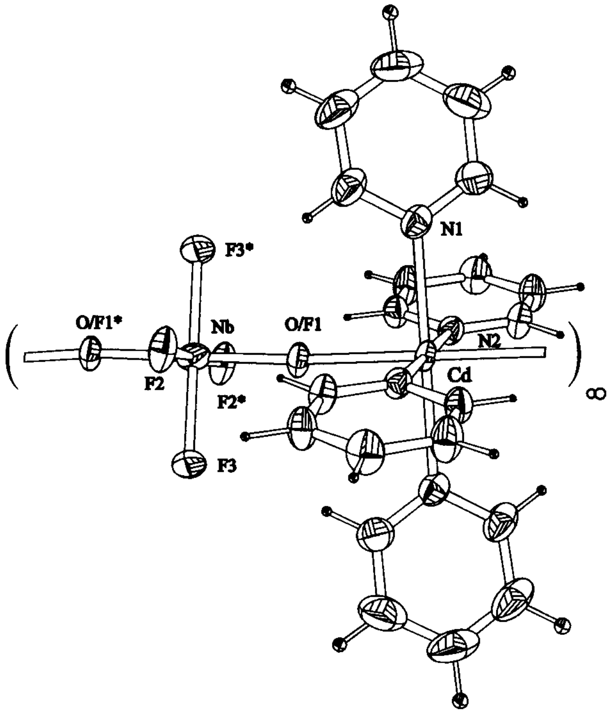

Figure 2. Thermal ellipsoid plot (50% probability) of $CdNb(py)_4OF_5$.

four equatorial pyridines at an average Cd−N bond length of 2.344(4) Å. The Nb^{5+} is coordinated equatorially by four fluorides at an average Nb−F bond length of 1.916(2) Å and axially by statistically disorderd oxide and fluoride ligands with an average Nb−O/F bond length of 1.925(2) Å.

$[pyH]_2[Cd(py)_4(NbOF_5)_2]$ contains clusters of one $[Cd(py)_4O_{2/2}]^0$ octahedron corner-shared with two $[NbF_5O_{1/2}]^-$ octahedra. Lattice pyridinium (pyH^+) cations between clusters balance the charge. $CdNb(py)_4OF_5$ contains only coordinated pyridine with no pyridinium cations. Infrared spectroscopy (IR) can distinguish between coordinated pyridine and pyridinium[11] and was used to confirm this observation. Characteristic IR bands for coordinated pyridine at 1600 and 627 cm^{-1} are present in $CdNb(py)_4OF_5$, while the pyridinium stretches observed in $[pyH]_2[Cd(py)_4(NbOF_5)_2]$ at 1630, 1531, 1337, and 1259 cm^{-1} are absent. The Nb═O stretch is observed at 901 cm^{-1} and two Nb−F stretches are observed at 591 and 550 cm^{-1}.

Discussion

Composition space diagrams (see Figure 1) illustrate the dependence of crystallization of one species over another on the mole fractions of the reaction components. Regions of selective crystal growth can be clearly observed and related to the starting concentration of each reactant. In region **A**, high concentrations of $(HF)_x$·py cause all species to remain in solution. In regions **B** and **C**, the $(HF)_x$·py concentration appears to be the controlling factor in the crystal growth of $[pyH]_2[Cd(py)_4(NbOF_5)_2]$ versus $CdNb(py)_4OF_5$. At high HF concentrations the solvent pyridine is protonated, supplying the pyridinium cations needed to crystallize $[pyH]_2[Cd(py)_4(NbOF_5)_2]$. As more water is added, less pyridine is protonated (k_b(water) > k_b(pyridine)). With less pyridinium available, $CdNb(py)_4OF_5$ dominates. This is similar to the (CuO, $0.5Nb_2O_5$)/$(HF)_x$·py/H_2O system reported earlier.[1] However, CdF_2 forms readily in the CdO/Nb_2O_5 system, as observed by X-ray powder diffraction, lowering the effective Cd^{2+} concentration and leading to a larger area of $[pyH]_2[Cd(py)_4(NbOF_5)_2]$ crystallization.

In the (CuO, $0.5Nb_2O_5$)/$(HF)_x$·py/H_2O system similar species are observed, an isostructural cluster complex, $[pyH]_2[Cu(py)_4(NbOF_5)_2]$, and a similar linear chain compound, $CuNb(py)_4OF_5$. Upon replacement of the Jahn−Teller distorted Cu^{2+} metal ion with the non-Jahn−Teller Cd^{2+}, the packing changes slightly in the linear chain species. Specifically, the angle between the chains shifts to pack the larger $Cd(py)_4{}^{2+}$ cations more efficiently, resulting in expansion of the *a* axis and contraction of the *b* axis compared with the Cu compound.

The use of bond valence[12] provides some insight into the structural differences between $CdNb(py)_4OF_5$ and $CuNb(py)_4OF_5$. In $CuNb(py)_4OF_5$, the charge of the Cu^{2+} is mainly distributed on the pyridine rings, +0.3 for each group, with the Jahn−Teller bonds to oxygen and fluorine accounting for only +0.16 and +0.13, respectively. The Cd^{2+} valence, in $CdNb(py)_4OF_5$, is much more evenly distributed between the ligands, owing to the absence of an electronic distortion. For $CdNb(py)_4OF_5$, the Cd^{2+} charge is distributed +0.35, for each pyridine ring, +0.35 and +0.27 for oxygen and fluorine, respectively.

The systematic absences in the single-crystal X-ray diffraction data of $CdNb(py)_4OF_5$ are consistent with either the centric space group *C*2/*c* (No. 15) or the acentric *Cc* (No. 9); however, the null response from the SHG tests favors the disordered centric (*C*2/*c*) model. In the centric model three possible disorder mechanisms exist: an interchain, an intrachain, and a random cancellation of the acentric intraoctahedral distortions of the $NbOF_5{}^{2-}$ groups. All three models would result in disorder in the asymmetric unit between O^{2-} and F^-, allowing the acentric $[NbOF_5]^{2-}$ to occupy a center of inversion in the crystal structure.[13]

Conclusion

In the search for new mixed-metal oxyfluorides, $CdNb(py)_4OF_5$ and $[pyH]_2[Cd(py)_4(NbOF_5)_2]$ were discovered in the (CdO, $0.5Nb_2O_5$)/$(HF)_x$·py/H_2O composition space. The $(HF)_x$·

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py concentration is the controlling factor in the formation of $CdNb(py)_4OF_5$ or $[pyH]_2[Cd(py)_4(NbOF_5)_2]$.

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Supporting Information Available: Packing diagram for $CdNb(py)_4OF_5$ (1 page). An X-ray crystallographic file, in CIF format, is available. Access and/or ordering information is given on any current masthead page.

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