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Synthesis, Bonding, and Reactivity of Oxide-Fluoride Vanadium(IV) Compounds with Neutral Chelate Ligands of the General Formula *cis*-[V^{IV}(=O)(F)(L$_{N-N}$)$_2$]$^+$

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Supporting Information Placeholder

ABSTRACT: Reaction of the oxidovanadium(IV)-L$_{N-N}$ species (L$_{N-N}$ is bipy = 2,2'-bipyridine or bipy-like molecules) with either BF$_4^-$ or HF, and or KF results in the formation of compounds of the general formula *cis*-[V^{IV}(=O)(F)(L$_{N-N}$)$_2$]$^+$. Structural and spectroscopic (EPR) characterization shows that these compounds are in the tetravalent oxidation state containing a terminal fluoride ligand. DFT calculations reveal that the V^{IV}-F bond is mainly ionic, which is reinforced by reactivity studies that demonstrate the nucleophilicity of the fluoride ligand.

The coordination chemistry with neutral ligands in both the *d*- and *p*-blocks is dominated by complexes of chlorides, bromides and iodides.[1] In marked contrast, their fluoride analogues were neglected for many years. Very recently a few research groups reported fluorides of the *s*-, *p*-, *d*- and *f*-blocks with various co-ligands.[2] Some of the reasons which render the study of coordination complexes of inorganic fluorides or oxide fluorides important and intrinsically interesting include: i) the very different properties of the metal center imposed by the fluoride ligands, which are a reflection of the strong M-F bonding, can lead to complexes which exhibit significantly different catalytic behaviour;[3] ii) some fluoride complexes are potent and specific fluorinating agents;[4] and iii) transition metal oxide-fluoride materials have very important optical, magnetic, luminescent, catalytic, *etc*. properties.[5]

A literature survey revealed that there are only a few examples of mononuclear vanadium(III)-fluoride[6] and oxide-fluoride vanadium(IV)[7] [OFV^{IV}], and vanadium(V)[8] complexes structurally characterized. The mononuclear OFV^{IV} compounds have the general formula [V^{IV}(=O)(F)$_x$(H$_2$O)$_y$L$_z$]$^{-/0}$ (x = 1/2/4; y = 0/1/2; z = 0/1 and L = bidentate chelate ligand).[7] Taking all these observations into account and drawing inspiration from an excellent review article reported by Reid and co-workers,[9] we sought to further extend the chemistry of oxide-fluoride vanadium(IV). In this report, we describe the synthesis and physicochemical characterization of the first series of discrete oxide-fluoride cationic complexes of the general formula *cis*-[V^{IV}(=O)(F)(L$_{N-N}$)$_2$]X. Moreover, we demonstrate the potential of this family of compounds as efficient fluorinating agents.

Treatment of one equivalent of V^{IV}OSO$_4$·5H$_2$O with two equivalents of 2,2'-bipyridine (bipy) in either aqueous HBF$_4$ or HF and/or KF at room temperature in the presence of the appropriate counterion in the cases of HF/KF, resulted in the formation of the compound *cis*-[V^{IV}(=O)(F)(bipy)$_2$]X (**1X**), [X = BF$_4^-$, ClO$_4^-$, SbF$_6^-$] (see Scheme 1, and SI). If 4,4'-dimethyl-2,2'-bipyridine (4,4'-dmbipy), 4,4'-di-tert-butyl-2,2'-bipyridine (4,4'-dtbipy) and 1,10-phenanthroline (phen) were used instead of bipy, the compounds *cis*-[V^{IV}(=O)(F)(4,4'-dmbipy)$_2$]BF$_4$·5H$_2$O (**2·5H$_2$O**), *cis*-[V^{IV}(=O)(F)(4,4'-dtbipy)$_2$]X (**3X**), [X = BF$_4^-$, ClO$_4^-$] and *cis*-[V^{IV}(=O)(F)(phen)$_2$]BF$_4$·H$_2$O (**4·H$_2$O**) were isolated respectively. Compounds **1-4** were characterized by X-ray diffraction analysis (**1SbF$_6$·H$_2$O** and **3BF$_4$**), high-resolution MS, IR, and EPR spectroscopies and magnetic susceptibility measurements (see the Supporting Information for full experimental details).
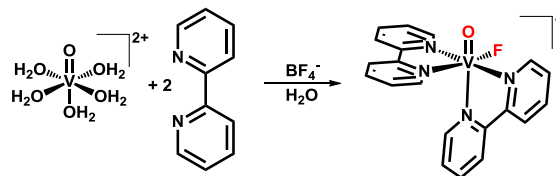
Scheme 1. The synthesis of the compound *cis*-[V^{IV}(=O)(F)(bipy)$_2$]BF$_4$

The crystal structures of the cations of compounds *cis*-[V^{IV}(=O)(F)(bipy)$_2$]SbF$_6$·H$_2$O and *cis*-[V^{IV}=O(F)(4,4'-dtbipy)$_2$]BF$_4$ are shown in Figure 1. The geometry of the complex cation **1** is best described as a severely distorted octahedron with the vanadium center being displaced above the mean equatorial plane defined by three bipy nitrogen atoms and the fluorine atom by 0.27Å towards the oxido ligand. The notable structural feature of the cations is the presence of a fluorine atom in a position *cis* to the oxido ligand. The V^{IV}(=O) bond length of 1.630(2) Å in *cis*-[V^{IV}(=O)(F)(bipy)$_2$]$^+$ lies in the upper limit of the range observed for oxidovanadium complexes (≈ 1.56 - 1.63 Å).[10] The V^{IV}-F bond length of 1.855(2) Å is the shortest observed thus far for such compounds.[7] To the best of our knowledge, compounds **1SbF$_6$·H$_2$O** and **3BF$_4$** are the first examples of cationic

mononuclear oxidovanadium(IV) species containing the structural unit cis-[V^{IV}(=O)(F)]$^+$ which have been structurally characterized. The IR spectra of all the vanadium compounds display a very strong band in the range 960-970 cm^{-1} which was assigned to v(V^{IV}=O) (see SI). The IR spectrum of compound cis-[V^{IV}(=O)(F)(4,4'-dtbipy)$_2$]ClO$_4$ shows a strong band at 564 cm^{-1} which was absent from its chloro analogue, cis-[V^{IV}(=O)(Cl)(4,4'-dtbipy)$_2$]ClO$_4$, and this band was assigned to v(V^{IV}-F) (see SI).
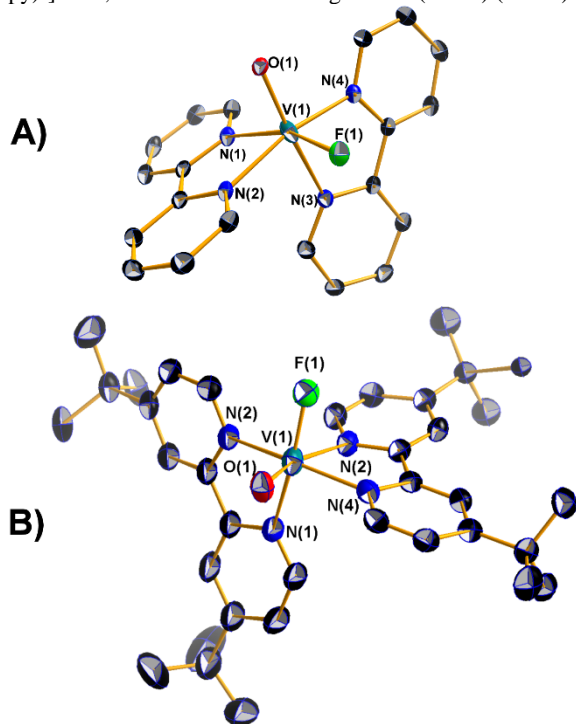

Figure 1. ORTEP diagrams of the cations cis-[V^{IV}(=O)(F)(bipy)$_2$]$^+$ (A) and cis-[V^{IV}(=O)(F)(4,4'-dtbipy)$_2$]$^+$ (B) with atomic numbering scheme and thermal ellipsoids at 50% probability level.
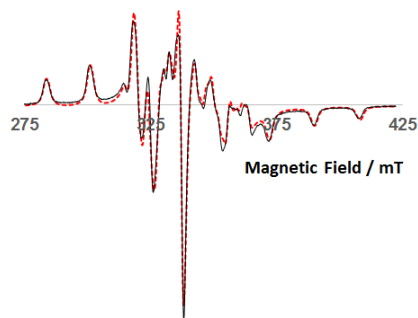

Figure 2. X-band cw EPR spectrum of a frozen solution of compound cis-[V^{IV}=O(F)(4,4'-dtbipy)$_2$]BF$_4$ in CH$_2$Cl$_2$ (1.00 mM) at 120 K (black line) and its simulated spectrum (red dashed line).

The X-band cw EPR spectrum of a frozen (120 K) solution of cis-[V^{IV}=O(F)(4,4'-dtbipy)$_2$]BF$_4$ (CH$_2$Cl$_2$) shows well-resolved sixteen peaks originating from the hyperfine coupling with the vanadium atom ($I = 7/2$) and the fluorine ($I = 1/2$) superhyperfine coupling (Figure 2, solid line). The fit of these EPR spectra considering a rhombic symmetry yields the spin Hamiltonian parameters, $g_x = 1.969$, $g_y = 1.984$ $g_z = 1.944$ $A_{x(51V)} = -55.4 \times 10^{-4}$, $A_{y(51V)} = -54.3 \times 10^{-4}$, $A_{z(51V)} = -161 \times 10^{-4}$, $A_{x(19F)} = 41.1 \times 10^{-4}$ cm^{-1}, $A_{y(19F)}$

$= 40.1 \times 10^{-4}$ cm^{-1} and $A_{z(19F)} = 10.7 \times 10^{-4}$ cm^{-1}. Application of the additivity relationship[11] gives a value of $A_z = -40.1 \times 10^{-4}$ cm^{-1} for the fluorine atom which is in the middle compared to the chlorine atom [44.1 x 10^{-4} cm^{-1}] and the hydroxide group [38.7 x 10^{-4} cm^{-1}] as expected.

DFT calculations, employing the PBE0/Def2-TZVP∪6-31+G(d)(E) computational protocol, reveal that the V^{IV}-F bond is mainly ionic with a dissociation energy of 46.8 kcal/mol.[12] The optimized geometry along with selected structural parameters are given in SI (Figure S1). According to Natural Bond Orbital (NBO) population analysis[13] the estimated Wiberg Bond Order (WBO) for the V-F bond is 0.718 which is less than that of a typical single covalent bond. On the other hand, the natural atomic charges Q_V and Q_F on the V and F atoms are 0.781 and -0.528 |e| respectively, are indicative of a significant electrostatic character of the V-F bond. Taking into account the composite nature of the V-F interaction we employed also the Atoms In Molecules (AIM) and Electron Localization Function (ELF) methods as implemented in Multiwfn 3.3.7 software.[14] The contour plots of the Laplacian of the Electron Density, $\nabla^2\rho$ and of the ELF on the plane defined by the V, F and O nuclei are depicted in Figure 3.
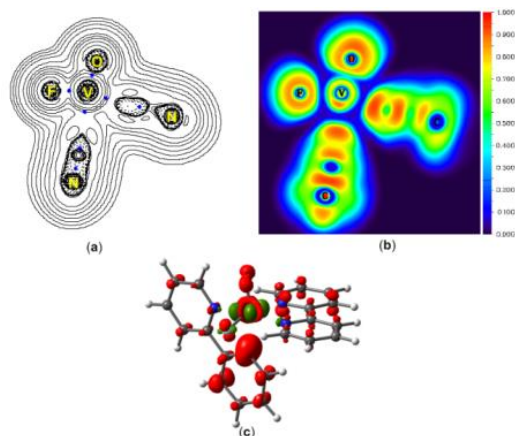

Figure 3. Contour line maps of $\nabla^2\rho$ (a), ELF (b) and 3D plot of the Fukui function, f^- (red color represents electrophilic attack sites) for the [VOF(bipy)$_2$]$^+$cation (c).

Bond critical points (BCPs) were used in order to investigate the nature of the V-F bond. The first and second derivatives at the critical points validate the assumption of the V-F ionic bonding. The low electron density [$\rho(\mathbf{r}) = 0.114$] at the critical points and the positive Laplacian ($\nabla^2\rho_{BCP} = 0.704$) are clear evidence that the bond is more ionic than covalent. The $|V_{BCP}|/G_{BCP}< 1$, and $\nabla^2\rho_{BCP}> 0$ characterize an ionic bond. The AIM parameters calculated through the BCP between V and F, point out that electrostatic interactions dominate the V-F bond with covalent and dispersion forces having only a minor role.

The sites of electrophilic attack on the [VOF(bipy)$_2$]$^+$cation were examined by the Fukui electrophilic attack function. The $f^-(\mathbf{r})$ was calculated as $f^-(\mathbf{r}) = \rho_N(\mathbf{r}) - \rho_{N+1}(\mathbf{r})$, whereas $\rho_N(\mathbf{r})$ and $\rho_{N+1}(\mathbf{r})$ are the electron densities of the [VOF(bipy)$_2$]$^+$cation and [VOF(bipy)$_2$]$^{2+}$dication respectively on the optimized geometry of the [VOF(bipy)$_2$]$^+$cation. Inspection of the respective 3-D plot of the electrophilic attack Fukui function, $f^-(\mathbf{r})$ reveals that the F and O ligands are susceptible to electrophilic attack (red color) (Figure 3c) or in other words they are expected to act as nucleophiles. Surprisingly, one out of the two N donor atoms of each of the two bipy ligands is also susceptible to electrophilic attack.

The implication of the ionic nature of the $V^{IV}-F$ bonding interaction in *cis*-[V^{IV}(=O)(F)(4,4'-dtbipy)$_2$]ClO$_4$ (**3ClO$_4$**) was explored in reactivity studies. The reaction of **3ClO$_4$** with Me$_3$Si−Cl[15] showed 100% conversion to Me$_3$Si−F over a few minutes, with its chloro analogue as the V^{IV}-containing product. In order to confirm unambiguously the complex's fluorinating efficiency, we investigated the reaction of **3ClO$_4$** with the substrates 4-methylbenzene-1-sulfonyl chloride, tert-butyl bromoacetate and trityl-4-methylbenzenesulfonate which gave us the fluoro derivatives of the substrates (see SI, Figures S3-S5). These reactions show attack by fluoride at the electrophilic component of the substrates, demonstrating that the $V^{IV}-F$ bond in this compound is nucleophilic and reactive.

In conclusion, the mononuclear oxide-fluoride vanadium(IV) compounds, with chelate neutral donor ligands, of the general formula *cis*-[V^{IV}(=O)(F)(L$_{N-N}$)$_2$]$^+$ were isolated by simply interacting the species [V^{IV}(=O)(L$_{N-N}$)$_2$]$^{2+}$ with either HBF$_4$, or HF, and or KF in aqueous solution. These compounds were characterized by X-ray diffraction, spectroscopy and density functional theory. Our results support the expected ionicity of the V^{IV}-F bond. On the basis of its ionic bonding, the terminal fluoride was determined to be nucleophilic in a halogen exchange reaction and in fluorination of various organic substrates. Efforts to explore the potential for these compounds to act as nucleophilic fluorinating agents for other organic substrates are currently in progress.

ASSOCIATED CONTENT

Supporting Information

X-ray crystallographic data (CIFs), full experimental details, IR and EPR data, and DFT results. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes
The authors declare no competing financial interests.

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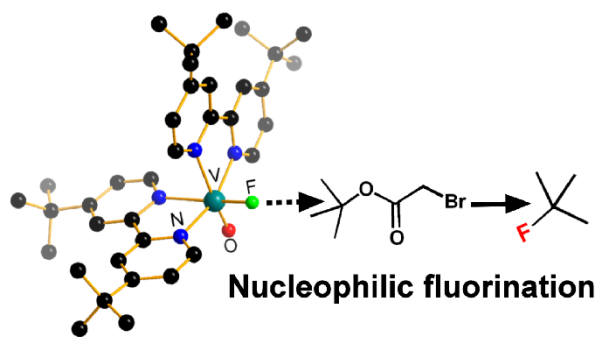
Nucleophilic fluorination

Reaction of the oxidovanadium(IV)-L_{N-N} species (L_{N-N} is bipy = 2,2'-bipyridine or bipy-like molecules) with a fluoride source (BF_4^-, HF, MF) afforded the compounds *cis*-$[V^{IV}(=O)(F)(L_{N-N})_2]X$ ($X = BF_4^-$, ClO_4^-, SbF_6^-). Structural and spectroscopic characterization and density functional theory have been used to characterize these compounds and their ability to act as efficient fluorinating agents was demonstrated.