Inorganic Chemistry

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

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Supporting Information

ABSTRACT: Reaction of the oxidovanadium(IV) $-L_{N-N}$ species $(L_{N-N} \text{ is bipy} = 2,2'-\text{bipyridine or bipy-like})$ molecules) with either BF₄⁻ 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 (electron paramagnetic resonance) characterization shows that these compounds are in the tetravalent oxidation state containing a terminal fluorido ligand. Density functional theory calculations reveal that the V^{IV}-F bond is mainly electrostatic, which is reinforced by reactivity studies that demonstrate the nucleophilicity of the fluoride ligand in a halogen exchange reaction and in fluorination of various organic substrates.

oordination 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 coligands.² Some of the reasons that render the study of coordination complexes of inorganic fluorides or oxido fluorides important and intrinsically interesting include the following: (i) The very different properties of the metal center imposed by the fluorido ligands, which are a reflection of the strong M-F bonding, can lead to some complexes that exhibit significantly different catalytic behavior.³ (ii) Some fluorido complexes are potent and specific fluorinating agents.⁴ (iii) Transition-metal oxido-fluorido materials have very important optical, magnetic, catalytic, etc., properties.⁵

A literature survey revealed that there are only a few examples of mononuclear vanadium(III) fluorido⁶ and vanadium(IV) oxido-fluorido⁷ [OFV^{IV}] and vanadium(V)⁸ complexes that have been structurally characterized. The mononuclear OFV^{IV} compounds have the general formula $[V^{IV}(=O)]$ - $(F)_x(H_2O)_yL_z]^{-/0}$ (x = 1/2/4, y = 0/1/2, and z = 0/1; L = bidentate chelate ligand).⁷ Taking all of these observations into account and drawing inspiration from an excellent review article of Reid and co-workers,⁹ we sought to further extend the

chemistry of vanadium(IV) oxido-fluorido compounds. In this report, we describe the synthesis and physicochemical characterization of the first series of discrete oxido-fluorido cationic complexes of the general formula $cis [V^{IV}(=O)(F)(L_{N-N})_2]A$. Moreover, we demonstrate the potential of this family of compounds as efficient as fluorinating agents.

The treatment of 1 equiv of V^{IV}OSO₄·5H₂O with 2 equiv of 2,2'-bipyridine (bipy) in either aqueous HBF₄ or HF and/or KF (1 equiv) at room temperature in the presence of the appropriate counterion in the cases of HF/KF resulted in formation of the compound cis- $[V^{IV}(=O)(F)(bipy)_2]A$ (1A; A = BF₄⁻, ClO₄⁻, SbF_6^{-}) (see Scheme 1 and the Supporting Information, SI). If

Scheme 1. Synthesis of the Compound cis-[V^{IV}(= $O(F)(bipy)_2]BF_4$



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 $cis-[V^{IV}(=O)(F) (4,4'-\text{dmbipy})_2]BF_4\cdot 5H_2O$ (2.5H₂O), cis-[V^{IV}(=O)(F)(4,4' $dtbipy)_2]A'(3A); A = BF_4', ClO_4'), and cis-[V^{IV}(=O)(F) (phen)_2$]BF₄·H₂O (4·H₂O) were isolated, respectively. Compounds 1-4 were characterized by X-ray diffraction analysis $(1SbF_6 \cdot H_2O \text{ and } 3BF_4)$, high-resolution mass spectrometry (MS), IR and electron paramagnetic resonance (EPR) spectroscopies, and magnetic susceptibility measurements (see the SI for full experimental details).

The crystal structures of the cations of compounds cis-[V^{IV}(= $O(F)(bipy)_2$]SbF₆·H₂O and *cis*-[V^{IV}=O(F)(4,4'-dtbipy)_2]BF₄ are shown in Figure 1. The geometry of the complex cation 1 is

Received: December 15, 2015



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 the 50% probability level.

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 0.27 Å toward 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 ($\approx 1.56-1.63$ 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 1SbF₆·H₂O and 3 are the first examples of cationic mononuclear oxidovanadium(IV) species containing the structural unit *cis*- $[V^{IV}(=O)(F)]^+$ that have been structurally characterized.

The IR spectra of all of the vanadium compounds display a very strong band in the range 960–970 cm⁻¹, which was assigned to $\nu(V^{IV}=O)$ (see the SI). The IR spectrum of the compound *cis*- $[V^{IV}(=O)(F)(4,4'-dtbipy)_2] \cdot ClO_4$ (3 · ClO₄) shows a strong band at 564 cm⁻¹, which was absent from its chlorido analogue, *cis*- $[V^{IV}(=O)(Cl)(4,4'-dtbipy)_2]ClO_4$, and this band was assigned to $\nu(V^{IV}-F)$ (see the SI).

The X-band continuous-wave (cw) EPR spectrum of a frozen (120 K) solution of *cis*-[V^{IV}=O(F)(4,4'-dtbipy)₂]BF₄ (in CH₂Cl₂) shows well-resolved 16 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 $g_x = 1.969$, $g_y = 1.984$, $g_z = 1.944$, $A_x(^{51}V) = -55.4 \times 10^{-4}$, $A_y(^{51}V) = -54.3 \times 10^{-4}$, $A_z(^{51}V) = -161 \times 10^{-4}$, $A_x(^{19}F) = 41.1 \times 10^{-4}$ cm⁻¹, $A_y(^{19}F) = 40.1 \times 10^{-4}$ cm⁻¹, and $A_z(^{19}F) = 10.7 \times 10^{-4}$ cm⁻¹. Application of the additivity relationship¹¹ 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



Figure 2. X-band cw EPR spectrum of a frozen solution of the compound *cis*- $[V^{IV}=O(F)(4,4'-dtbipy)_2]BF_4$ in CH₂Cl₂ (1.00 mM) at 120 K (black line) and its simulated spectrum (red dashed line).

chlorine atom $[44.1 \times 10^{-4} \text{ cm}^{-1}]$ and the hydroxide group $[38.7 \times 10^{-4} \text{ cm}^{-1}]$ as expected.

Density functional theory (DFT) calculations, employing the PBE0/Def2-TZVPU6-31+G(d)(E) computational protocol, reveal that the V^{IV}-F bond is mainly electrostatic with a dissociation energy of 46.8 kcal/mol.¹² The optimized geometry along with selected structural parameters is given in the SI (Figure S1). According to natural bond orbital population analysis,¹³ the estimated Wiberg bond order 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 vanadium and fluorine atoms of 0.781 and -0.528 e, respectively, are indicative of the significant electrostatic character of the V-F bond. The contour plots of the Laplacian of the electron density, $\nabla^2 \rho$, and of the ELF on the plane defined by the vanadium, fluorine, and oxygen nuclei are depicted in Figure 3.¹⁴



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

The low electron density $[\rho(r) = 0.114]$ at the critical points and the positive Laplacian ($\nabla^2 \rho_{BCP} = 0.704$) are clear evidence that the bond is more electrostatic than covalent.

Inspection of the respective 3D plot of the electrophilic attack Fukui function, $f^{-}(r)$, reveals that the fluorine and oxygen 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 nitrogen donor atoms of each of the two bipy ligands is also susceptible to electrophilic attack.

The implication of the electrostatic nature of the V^{IV} -F bonding interaction in $3 \cdot ClO_4$ was explored in reactivity studies. The reaction of $3 \cdot ClO_4$ with Me₃Si-Cl¹⁵ showed 100% conversion to Me₃Si-F over a few minutes, with its chlorido analogue as the V^{IV}-containing product. In order to confirm unambiguously the complex's fluorinating efficiency, we investigated the reaction of $3 \cdot ClO_4$ with the substrates 4methylbenzene-1-sulfonyl chloride, *tert*-butyl bromoacetate, and trityl 4-methylbenzenesulfonate, which gave us the fluorido derivatives of the substrates in yields of 100% based on the vanadium compound (see the SI, Figures S2–S4). 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 vanadium(IV) oxido– fluorido 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 HBF₄ or HF and/or KF in aqueous solution. These compounds were characterized by X-ray diffraction, spectroscopy, and DFT. Our results support the expected electrostatic character of the V^{IV}-F bond. On the basis of its electrostatic bonding, the terminal fluorido ligand 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

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorg-chem.5b02895.

Full experimental details, IR and EPR data, and DFT results (PDF)

X-ray crystallographic data in CIF format (CIF)

X-ray crystallographic data in CIF format (CIF)

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

The authors gratefully acknowledge for the support the Greek Community Support FrameworkIII (MIS91629), the Research Promotional Foundation of Cyprus and the European Structural Funds (ANABA Θ MI Σ H/ Π A Γ IO/0308/32, Y Γ EIA/BIO Σ /0308(BIE)/13), the Unit ORBITRAP-LC-MS as well as Prof. Dr. Ioannis K. Gallos and Professor Leroy (Lee) Cronin.

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