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Vanadium-Induced Nucleophilic IPSO Substitutions in a Coordinated Tetrachlorosemiquinone Ring: Formation of the Chloranilate Anion as a Bridging Ligand

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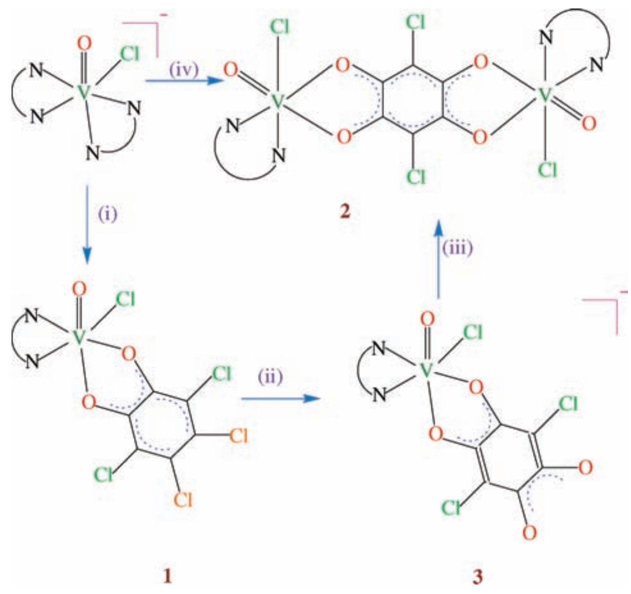
In basic media, the coordinated semiquinone radical in the spin-coupled [(bipy)ClV^{IV}O(TCSQ)] **1** (HTCSQ = tetrachlorosemiquinone) undergoes nucleophilic ipso substitution (OH$^-$ for Cl$^-$) to generate the chloranilate anion (CA^{2-}) that bridges the vanadium(IV) centers, forming a binuclear compound [(bipy)ClV^{IV}O(CA)OV^{IV}Cl(bipy)] **2**.

The coordination chemistry of vanadium with dioxolene-type ligands is an area of contemporary research interest.[1a−i] Much of these interests stem from the structural identification of a biological chromogen, called tunichrome.[1j−m] The later species with several pyrogallol moieties in it is believed to play a pivotal role in the sequestration of vanadium from seawater in to the blood cell of *Ascidians*, a group of marine protochordates.[1n,o] This proposal however has been contested recently by Michibata et al.[1p]

As a part of our ongoing program on oxovanadium(IV/V) chemistry,[2] we recently have synthesized (Scheme 1) a mixed-ligand compound [(bipy)ClV^{IV}O(TCSQ)] **1**,[3a] isolated as a dark purple solid in moderate yield (57%) when the precursor compound *cis*-[VO(bipy)$_2$Cl]Cl·2H$_2$O[3b] was allowed to react with H$_2$TCC[3a] in a dichloromethane/acetonitrile (1:1 v/v) solvent combination. The IR spectrum of this compound contains a strong band at 1444 cm^{-1} corresponding to the C−O stretching mode of a semiquinone moiety.[4] Thus, **1** has a rare distinction of being a vanadium(IV) compound bound to a semiquinone radical, also confirmed by single-crystal X-ray diffraction analysis.[5]

Scheme 1. Synthetic Protocol for the Preparation of the Complexes **1** and **2**[a]



[a] Conditions: (i) H$_2$TCC, DCM/CH$_3$CN; (ii) Bu$_4$NOH, O$_2$, CH$_3$CN, stirred; (iii) *cis*-[VO(bipy)$_2$Cl]Cl·2H$_2$O, CH$_3$CN, stirred; (iv) H$_2$TCC, CH$_3$CN, Bu$_4$NOH, O$_2$, stirred.

A molecular view of **1** is displayed in Figure 1. The coordination environment around vanadium is distorted octahedral in which the N(1), N(2), O(1), and Cl(1) atoms define the basal plane. The C−O bond lengths of the coordinated *o*-dioxolene often provide interesting clues as to the oxidation state of this redox-noninnocent ligand.[1i,4,6] These ligands in the quinone or semiquinone state generally have shorter C−O distances (ca. 1.28 Å)[4a,6,7] compared to the fully reduced catecholate ligand (ca. 1.34 Å).[1g,h,5] In compound **1**, the average C−O distance is 1.285 Å, and the C(2)−C(3) (1.371(9) Å) and C(4)−C(5) (1.367(9) Å) distances are much shorter than the remaining C−C distances

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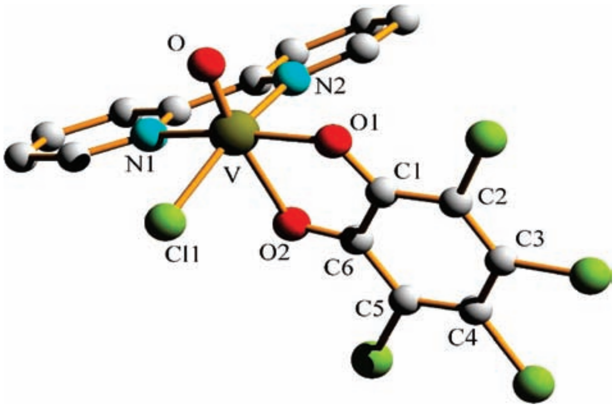

Figure 1. Perspective view and atom-numbering scheme for the neutral complex **1**. The hydrogen atoms have been omitted for clarity.

(1.432(8)−1.401(8) Å) of the *o*-dioxolene ring, indicating the semiquinone state of the ligand.[4,6,7] The crystallographic data thus suggest compound **1** to be an oxovanadium(IV) compound connected to a semiquinone radical.

Magnetic susceptibility measurements for the polycrystalline sample of **1** reveal that the compound is diamagnetic in the temperature range 1.8−300 K. This diamagnetism is certainly due to a strong antiferromagnetic interaction between the two $S = 1/2$ spins, carried by the vanadium(IV) and a coordinated semiquinone radical.

When the reaction between *cis*-[VO(bipy)$_2$Cl]Cl·2H$_2$O and H$_2$TCC has been repeated in the presence of an added base (tetrabutylammonium hydroxide or Et$_3$N) with subsequent exposure to atmospheric oxygen (method A, Supporting Information), the product obtained is a binuclear compound [(bipy)ClV^{IV}O(CA)OV^{IV}Cl(bipy)] **2** in ca. 40% yield. Interestingly, this reaction involves an ipso replacement of two chloro groups in the coordinated TCC^{2-} ligand by the incoming hydroxo groups from the added base to form the chloranilate anion [CA^{2-}] as a bridge between the metal centers. The IR spectrum of **2** contains two strong bands at 1554 and 1377 cm^{-1} which are diagnostic of the dianionic bis-bidentate bridging mode of the coordinated CA^{2-} ligand.[8]

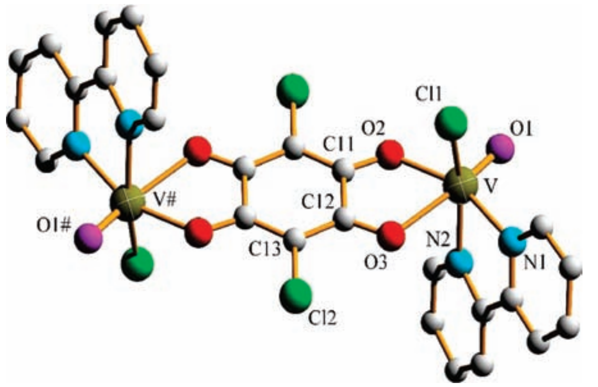

Figure 2. Ball-and-stick view of the centrosymmetric binuclear complex **2** showing the numbering scheme. The H atoms are omitted for clarity, and the symmetry-related atoms are shown with a # symbol.

The perspective view of the X-ray crystal structure of **2** is shown in Figure 2, confirming its proposed composition. The coordination geometry around each vanadium center is best described as a distorted octahedron with an equatorial plane, defined by the chlorido ligand Cl(1), two nitrogen atoms (N(1) and N(2)) from bipy, and the O(2) from the bridging dioxolene moiety, while the terminal oxido group O(1) and the second oxygen atom O(3) of the chloranilate dianion occupy the axial sites. The C(12)−C(11) and the

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(5) Crystal data for **1**: C$_{16}$H$_8$Cl$_5$N$_2$O$_3$V, $M = 504.43$, triclinic, space group $P\bar{1}$, $a = 8.1177(19)$ Å, $b = 9.394(2)$ Å, $c = 13.531(3)$ Å, $\alpha = 96.038(4)°$, $\beta = 92.073(4)°$, $\gamma = 115.399(4)°$, $V = 923.1(4)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.815$ g cm^{-3}, $F(000) = 500$, μ(Mo Kα) $= 1.282$ mm^{-1}, $T = 293(2)$ K, 4565 unique reflections [R(int) = 0.0453], R (on F) = 0.0915, R_w (on F^2) = 0.2149 (based on all data). Crystal data for **2**: C$_{26}$H$_{16}$Cl$_4$N$_4$O$_6$V$_2$, $M = 504.43$, triclinic, space group $P\bar{1}$, $a = 6.873(2)$ Å, $b = 8.512(3)$ Å, $c = 13.076(4)$ Å, $\alpha = 98.602(6)°$, $\beta = 95.049(6)°$, $\gamma = 105.828(6)°$, $V = 720.9(4)$ Å^3, $Z = 1$, $\rho_{calcd} = 1.668$ g cm^{-3}, $F(000) = 362$, μ(Mo Kα) $= 1.067$ mm^{-1}, $T = 233(2)$, 3620 unique reflections [R(int) = 0.04], R (on F) = 0.0775, R_w (on F^2) = 0.1278 (based on all data).

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average C−O chloranilate bond distances are 1.524(4) and 1.260(3) Å, respectively, and are characteristic of the CA^{2-} bridging moiety.[8]

Mechanistically, the synthesis of **2** from the reaction sequence followed in method A appears quite interesting and probably involves the formation of **1** as a precursor which subsequently is converted to the $[(bipy)ClV^{IV}O(CA)]^-$ anion, **3**, as an intermediate (Scheme 1). This necessitates the replacement of two chloro groups in the coordinated $TCSQ^-$ ligand in **1** by the hydroxo groups from the added base. This is a metal-induced reaction, as revealed from control experiments. The attached $[(bipy)ClV^{IV}O]$ moiety facilitates the drainage of electron density from the coordinated TCSQ ring that favors the aromatic nucleophilic ipso substitution of the chloro groups,[9] leading to the formation of the chloranilate anion. In fact, the reaction of **1** with Bu_4NOH in acetonitrile did produce **3**, which unlike its diamagnetic precursor is expected to be EPR-active and shows an axial spectrum ($g_{\|} = 1.965$, $g_{\perp} = 1.988$, $A_{\|} = 163 \times 10^{-4}$ cm^{-1}, $A_{\perp} = 48 \times 10^{-4}$ cm^{-1}) at 77 K with two sets of eight-line patterns (Figure S1, Supporting Information), typical of mononuclear vanadium(IV) (^{51}V, $I = 7/2$). The OH^- for Cl^- substitution in the TCSQ ring in **1**, followed by aerial oxidation generates the CA^{2-} anion that makes the vanadium(IV) unpaired electron in **3** available for the display of the characteristic EPR. The chloranilate dianion thus formed has an exceptional chelating ability[8] that enables it to act as a bridge between the two adjacent vanadium centers, thus forming **2**. In fact, we have been successful in isolating **2** in moderate yield (25%) by combining **1** with *cis*-$[VO(bipy)_2Cl]Cl\cdot 2H_2O$ in acetonitrile in the presence of an added base (method B, Supporting Information).

For complex **2**, the χT versus T and χ versus T plots are displayed in Figure 3. At 300 K, the χT value is 0.71 cm^3 K mol^{-1}, which decreases monotonically with decreasing temperature to reach a value of 0.01 cm^3 K mol^{-1} below 5 K. This behavior is characteristic of antiferromagnetic coupling between the magnetic centers within this molecule. On the basis of its molecular structure, and the diamagnetic nature of the bridging chloranilate dianion, the complex can be viewed magnetically as a dinuclear complex composed of two octahedral vanadium(IV) centers ($S = 1/2$). Therefore, the magnetic properties have been analyzed using a Heisenberg $S = 1/2$ dimer model and the following Hamiltonian: $H = -2J(S_V\cdot S_{V\#})$, where S_V and $S_{V\#}$ are the spin operators for both V and V(#). The experimental data have been very well reproduced using the Bleaney−Bowers expression of the magnetic susceptibility deduced from the above Hamiltonian.[10] The best set of parameters obtained using this model is $J/k_B = -31(1)$ K ($-22(1)$ cm^{-1}) and $g = 1.97(2)$. It is worth mentioning that the CA^{2-} ligand is magnetically efficient enough to bridge antiferromagnetically two widely separated V(IV) centers (V···V# separations, 8.153 Å). The sign of the magnetic interaction implies that these vanadium(IV) units possess an $S_T = 0$ spin ground state.

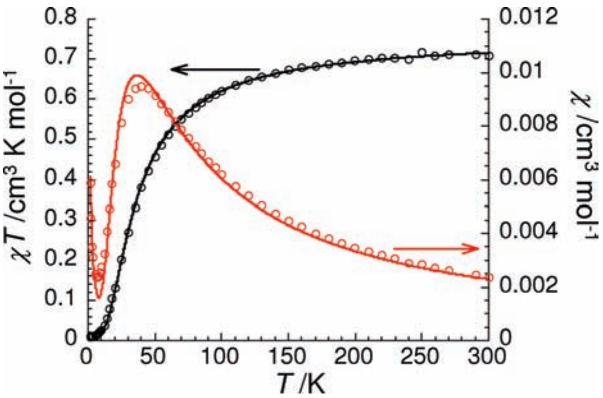

Figure 3. χT vs T (in black) and χ vs T (in red) plots for **2** (with $\chi = M/H$) under 1 kOe. The solid lines represent the best simulations obtained with the models described in the text.

In summary, nucleophilic substitution in a coordinated tetrachlorosemiquinonato ring has been reported for the first time. Only the chloro groups which are in para positions with respect to the semiquinonato oxygen atoms in the TCSQ ring have been replaced. The electron-accepting vanadium(IV) center, attached to these donor oxygen atoms in **1**, takes out the excess electronic charge and activates the ring for such ipso substitution.[9] Recently, Bruijnincx et al.[11] have reported such unusual conversion of tetrachlorocatechol to chloranilic acid by a copper(II)-mediated oxidative double dehalogenation reaction.

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Supporting Information Available: X-ray crystallographic files in CIF format and detailed syntheses and characterization data for **1** and **2** and an EPR spectrum (77 K) of **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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