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New Chemistry of the Triply Bonded Divanadium (V_2^{4+}) Unit and Reduction to an Unprecedented V_2^{3+} Core

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We report here the synthesis and characterization of seven new divanadium compounds with the paddlewheel geometry bridged by nitrogen-donating ligands. Five of these contain the diamagnetic V_2^{4+} core with short V–V distances of less than 2.0 Å, consistent with a formal triple bond. The V–V distances vary with the basicity of the bridging ligands; more basic ligands such as those of the guanidinate type have the shorter metal–metal separations, and those with the less basic formamidinate groups have longer separations. One compound, $V_2(DPhF)_4$ (DPhF = the anion of *N*,*N*′-diphenylformamidine), has been reduced by one electron, and two structures, $[K(THF)_3]V_2(DPhF)_4$ and $[K(18\text{-crown-}6)(THF)_2]V_2(DPhF)_4$, have been obtained. These have an unprecedented V_2^{3+} core where the formal oxidation state of each vanadium atom is +1.5. The decrease in V–V bond distance and the multiline EPR spectrum in the reduced species provide evidence that these two molecules contain a bond of order 3.5.

Introduction

Although it was in 1964 that the quadruply bonded Re_2^{6+} unit (in $Re_2Cl_8^{2-}$) was recognized[1] and in 1965 that the existence of Tc_2^{5+} (in $Tc_2Cl_8^{3-}$) and Mo_2^{4+} (in $Mo_2(O_2CCH_3)_4$) was established,[2,3] it was not until 1992 that the first compound of the triply bonded V_2^{4+} core, $V_2(DTolF)_4$ (DTolF = the anion of *N*,*N*′-di-*p*-tolylformamidine, which is shown in Figure 1a), was reported.[4] In the meantime thousands of compounds containing metal−metal bonds have been synthesized and characterized, and have found applications in catalysis,[5] medicine,[6] and supramolecular chemistry.[7] These molecules are, for the most part, composed of second- and third-row transition metals[8] as first-row metals are less prone to support metal−metal bonds. The exception is chromium, and its uniqueness in this regard may be explained by the ability of two Cr(II) atoms to come together to form a high-multiplicity, quadruple metal−metal bond. In much the same way, triply bonded divanadium compounds might be expected to be thermodynamically stable. Of course, this would also be true for the heavier group 5 metals, niobium and tantalum. However, the +2 ions of these metals have been shown to cleave C−N bonds in formamidinato ligands,[9]

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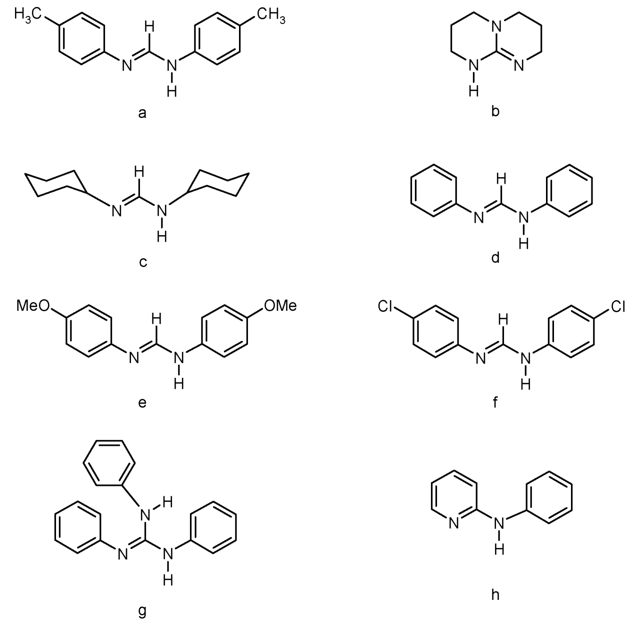

Figure 1. Precursors of the ligands that have been used to make divanadium compounds: (a) *N*,*N*′-di-*p*-tolylformamidine, HDTolF; (b) 1,3,4,6,7,8-hexahydro-2*H*-pyrimido[1,2-*a*]pyrimidine, Hhpp; (c) *N*,*N*′-dicyclohexylformamidine, HDCyF; (d) *N*,*N*′-diphenylformamidine, HDPhF; (e) *N*,*N*′-di-*p*-anisylformamidine, HDAniF; (f) *N*,*N*′-di-*p*-chloroformamidine, $HD^{Cl}PhF$; (g) 1,2,3-triphenylguanidine, HTPG; (h) anilinopyridine, Hap.

and compounds with a metal−metal bond have only been obtained in the case of ligands with fused-ring systems such as hpp[10,11] (the anion of 1,3,4,6,7,8-hexahydro-2*H*-pyrimido-[1,2-*a*]pyrimidine, which is shown in Figure 1b) and 7-azaindole[11,12] which resist cleavage. The +2 oxidation state is more accessible for vanadium than for the heavier congeners niobium or tantalum and, therefore, might be expected to yield more compounds containing triple metal−metal bonds. Indeed, theoretical calculations as early as 1985 suggested that V_2(carboxylato)$_4$ compounds should be stable,[13] but thus far these molecules have eluded all synthethic efforts, and only compounds containing the oxo-centered V_3O(carboxylate)$_6^{n+}$ species, $n = 0$, 1, are known.[14]

Nonetheless, in the 10 years since the report of $V_2(DTolF)_4$, the chemistry of the V_2^{4+} core has languished. Only two other compounds of V_2^{4+} have been described, $V_2(DCyF)_4$[15] (DCyF = *N*,*N*′-dicyclohexylformamidinate, which is shown in Figure 1c) and $V_2(hpp)_4$.[16] Both of these compounds are similar to the first one, but very little has been learned about the properties of these compounds (e.g., spectra, electrochemistry), and thus the general impression has arisen that the chemistry of multiply bonded divanadium compounds is quite limited. Presented here is a report of work which shows that this impression is incorrect. We have found that many other V_2^{4+}-containing compounds can be made, and include in this report the characterization of $V_2(DPhF)_4$, **1**, $V_2(DAniF)_4$, **2**, $V_2(D^{Cl}PhF)_4$, **3**, $V_2(TPG)_4$, **4**, and $V_2(ap)_4$, **5**, the ligands of which are depicted in Figure 1.

We have investigated the electrochemistry of these molecules and have been rewarded with the observation of reversible (or at least quasi-reversible) reduction waves in all cases. This has led to the isolation of the first stable tetragonal paddlewheel complex with a rare M_2^{3+} core in $[K(THF)_3]V_2(DPhF)_4$, **6**, in which the potassium ions lie between the formamidinate anions as reported in our preliminary communication.[17] Here we also report the structure of a more stable analogue in which the K^+ ions are trapped by a crown ether, namely, $[K(18\text{-crown-}6)(THF)_2]V_2(DPhF)_4$, **7**. Oxidation states for isolated M_2^{n+} units had been previously restricted to only three values, namely $n =$ 4, 5, and 6, although the oxidation number 7 was recently discovered for M = Os[18] and Re[19] in complexes of the type $[M_2(hpp)_4Cl_2]PF_6$. While very high oxidation numbers are not uncommon in transition metal chemistry, it has been thought that these would not favor metal−metal bond formation due to the known contraction experienced by the d orbitals as the positive charge increases. On the other hand, oxidation numbers of less than 2 are uncommon for transition metals in general, except in the case of the coinage metals or when noninnocent ligands, i.e., those with π-acceptors, are present.[20] Therefore the average oxidation state of +1.5 in these unique V_2^{3+} cores is highly unusual.

Experimental Section

General Considerations. All syntheses and sample manipulations were carried out under an atmosphere of dry and deoxygenated argon with standard Schlenk and drybox techniques. Solvents were distilled under nitrogen from Na/K-benzophenone. $VCl_3 \cdot 3THF$ was prepared according to the literature method[21] and stored at −35 °C prior to use to prevent loss of THF. Di-*p*-anisylformamidine and di-*p*-chlorophenylformamidine were prepared by a reported method.[22] Methyllithium (1.6 M in diethyl ether) was purchased from Acros Organics. Sodium triethylborohydride (1 M in THF), diphenylformamidine, triethyl orthoformate, *p*-anisidine, *p*-chloroaniline, 2-anilinopyridine, and 18-crown-6 were purchased from Aldrich Chemical Co.; 1,2,3-triphenylguanidine was purchased from TCI America. Potassium graphite was prepared by combining an 8:1 molar ratio of graphite and K, and stirring under argon at 130 °C until the solid turned bronze in color. Then it was stored at −35 °C in a drybox until it was used.

Physical Measurements. Elemental analyses were performed by Canadian Microanalytical Service, Ltd., Delta, British Columbia,

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Canada. ^{1}H NMR spectra were recorded on a Mercury 300 NMR spectrometer. The cyclic voltammograms were recorded on a BAS 100 electrochemical analyzer in THF solutions containing 0.1 M $Bu^n{}_4NPF_6$ with Pt working and auxiliary electrodes and a Ag/AgCl reference electrode; scan rates were 100 mV s^{-1} in all cases. The EPR spectra were recorded on a Bruker ESP300 9.458 GHz spectrometer. UV/vis spectra were recorded on a Shimadzu 2501-PC spectrophotometer.

Abbreviations Used. DTolF = the anion of *N*,*N*′-di-*p*-tolylformamidine; DCyF = the anion of *N*,*N*′-dicyclohexylformamidine; hpp = the anion of 1,3,4,6,7,8-hexahydro-2*H*-pyrimido[1,2-*a*]pyrimidine; DPhF = the anion of *N*,*N*′-diphenylformamidine; DAniF = the anion of *N*,*N*′-di-*p*-anisylformamidine; $D^{Cl}PhF$ = the anion of *N*,*N*′-di-*p*-chloroformamidine; TPG = the anion of 1,2,3-triphenylguanidine; ap = the anion of anilinopyridine. The word "hexanes" describes a mixture of C_6H_{14} isomers.

Preparation of $V_2(NXN)_4$ Compounds. Compounds **1**−**5** were prepared as previously reported.[4] In a typical reaction, 0.40 g (1.07 mmol) of $VCl_3{\cdot}3THF$ was dissolved in 10 mL of THF and reduced by dropwise addition of 1 equiv of $NaEt_3BH$ at −78 °C. In a separate flask, 2 equiv of the corresponding ligand were deprotonated with MeLi at −78 °C. Each solution was brought to room temperature, and then cooled again to −78 °C. The ligand solution was then transferred by cannula into the V(II) solution. After stirring for 15−30 min at room temperature, the THF was removed by vacuum evaporation and the residue was extracted with ca. 40 mL of warm toluene (benzene in the case of **4** and **5**) and filtered through Celite. X-ray quality crystals were grown by the slow diffusion of hexanes into the corresponding toluene or benzene solution. Crystalline yields of compounds **1**−**5** were approximately 40%.

Preparation of 6. In a typical reaction, a solution of 60 mg (0.068 mmol) of $V_2(DPhF)_4$ in 15 mL of THF was added by cannula to a suspension of 25 mg (0.19 mmol) of KC_8 in 10 mL of THF at −78 °C. The mixture was stirred at −78 °C for 1 h, after which time the color of the solution turned from red to green. The mixture was filtered through Celite, and a mixture of hexanes (10 mL) was added. The solution was placed in a freezer at −10 °C. Very dark green blocklike crystals of **6** were obtained after 3 days, with a yield of approximately 10%.

Preparation of 7. The same procedure was followed for the synthesis of **6**, except, after reduction, the green filtrate was layered with an ether solution of 1.5 equiv of 18-crown-6. Slow diffusion yielded very dark green crystals after 3 weeks. Yields for this reaction were quantitative.

NMR Spectroscopy. ^{1}H NMR for **1** (C_6D_6, ppm): 5.953 (d, 16 H), 6.700−6.790 (m, 24 H), 10.007 (s, 4H). For **2** ($CDCl_3$, ppm): 3.607 (s, 24 H), 5.803 (d, 16 H), 6.341 (d, 16 H), 10.017 (s, 4 H). For **3** (C_6D_6, ppm): 5.517 (d, 16 H), 6.667 (d, 16 H), 9.680 (s, 4 H). For **4** ($CDCl_3$, ppm): 6.322 (s, 2H), 6.624−6.706 (m, 6H), 6.839 (t, 4H), 6.943 (d, 4H). For **5** (C_6D_6, ppm): complex signals ranging from 5.792 to 6.983 ppm.[23]

Elemental Analyses. Anal. Calcd (found) for **1**: C, 70.74 (70.92); H, 5.02 (5.18); N, 12.69 (12.64). For **2**, $C_{60}H_{60}V_2N_8O_8$: C, 64.17 (63.84); H, 5.39 (5.76); N, 9.98 (8.99). For **3**, $C_{52}H_{36}V_2N_8Cl_8$: C, 53.92 (54.05); H, 3.13 (3.10); N, 9.67 (9.59). For **4**, $C_{79}H_{67}V_2N_{12}$: C, 73.76 (73.23); H, 5.25 (5.27); N, 13.07 (12.20). For **5**, $C_{47}H_{39}V_2N_8$: C, 69.03 (68.49); H, 4.81 (4.91); N, 13.70 (13.79). The instability of compound **6** precluded satisfactory analysis.[24]

Electronic Spectroscopy. λ_{max} (nm) (ϵ/M^{-1} cm^{-1}) in THF for **1**: 464 (90, sh), 398 (1700). For **2**: 488 (300), 414 (540). For **3**: 455 (50, sh), 405 (1600). For **4**: 588 (730). For **5**: 533 (950), 411 (2500). For the formamidinato compounds there was also a very weak shoulder around 560 nm, which was not discernible in the spectrum of $V_2(ap)_4$ or $V_2(TPG)_4$.

Crystallographic Studies. Single crystals of **1**−**7** were obtained as described above. Each crystal was mounted on a glass fiber with silicone grease and transferred to a goniometer. The crystals were cooled to −60 °C under a stream of nitrogen, except for **2**, which was cooled to −80 °C. Geometric and intensity data were collected on a Bruker SMART 1000 CCD area detector system using 0.3° ω-scans at 0°, 90°, and 180° in ϕ, with Mo Kα radiation (λ = 0.71073 Å). Cell parameters for **1**−**6** were determined using the program SMART.[25] Data reduction and integration were performed with the software package SAINTPLUS.[26] Absorption corrections were applied using the program SADABS.[27] Crystal and space group symmetries for all compounds were determined using the XPREP program.[28] For all compounds, the positions of some or all of the non-hydrogen atoms were found by direct methods or the Patterson method using the program SHELXS.[29] The positions of the remaining non-hydrogen atoms were located by use of a combination of least-squares refinement and difference Fourier maps in the SHELXL-97[30] program. Non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were included in the structure factor calculations at idealized positions. Crystal data and refinement results for all compounds are listed in Table 1. Selected bond distances and angles are listed in Table 2.

Crystals of **7** exhibited nonmerohedral twinning. The twin indexing program GEMINI[31] gave two similar, but statistically different unit cells. The cell parameters were further optimized with the nonlinear least squares lattice parameter routine of SMART. Two sets of integrated intensities were generated with each of the two contributing orientation matrixes. The intensity data set from the major component (a = 12.479(2) Å, b = 12.592(2) Å, c = 13.363(2) Å, α = 65.337(2)°, β = 65.078(2)°, γ = 88.078(2)°, V = 1704.6(4) Å^3) was used successfully for structure solution and refinement (Table 1).

The potassium cation in **7** was found on a crystallographic inversion center and was coordinated by one 18-crown-6 and two THF solvent molecules. The 18-crown-6 moiety was disordered in two positions with occupancies of 0.546(3) and 0.454(3), respectively. The THF molecules were also disordered and were refined with restraints on the distances.

Results and Discussion

The five new V_2^{4+} compounds **1**−**5**, along with the three previously known, are listed in Table 3, where some additional information about each one is also presented. It will be noted that these are all similar in three respects. (1) Each one is a neutral paddlewheel molecule with four NXN^- bridging ligands. (2) All compounds have been accurately

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Table 1. Crystal Data and Structure Refinement for **1**−**7**

compound	**1**	**2**	**3**	**4**·4benzene	**5**·2benzene	**6**	**7**
empirical formula	$C_{52}H_{44}N_8V_2$	$C_{60}H_{60}N_8O_8V_2$	$C_{52}H_{36}Cl_8N_8V_2$	$C_{100}H_{88}N_{12}V_2$	$C_{56}H_{48}N_8V_2$	$C_{64}H_{68}KN_8O_3V_2$	$C_{72}H_{84}KN_8O_8V_2$
fw	882.83	1123.04	1158.37	1559.70	934.90	1138.24	1330.45
space group	$P2/n$	$P\bar{1}$	$Fddd$	$P\bar{1}$	$P\bar{1}$	$Pna2_1$	$P\bar{1}$
a (Å)	17.874(1)	10.2646(6)	26.596(2)	14.405(1)	9.908(1)	20.249(1)	12.479(2)
b (Å)	10.3011(8)	10.3332(6)	27.238(2)	15.082(1)	10.163(1)	12.4492(6)	12.592(2)
c (Å)	24.416(2)	13.9625(9)	29.798(2)	21.210(2)	12.761(1)	22.957(1)	13.363(2)
α (deg)	90	80.265(1)	90	72.170(2)	97.989(2)	90	65.337(2)
β (deg)	102.156(2)	75.071(1)	90	79.445(2)	109.990(2)	90	65.078(2)
γ (deg)	90	81.160(1)	90	69.961(2)	101.325(2)	90	88.078(2)
vol (Å^3)	4394.7(6)	1400.9(2)	21586(2)	4105.3(6)	1154.1(2)	5786.9(5)	1704.6(4)
Z	4	1	16	2	1	4	1
d (calc, g/cm^3)	1.334	1.331	1.426	1.262	1.345	1.306	1.296
μ (mm^{-1})	0.472	0.396	0.786	0.285	0.453	0.448	0.396
final R indices $[I > 2\sigma(I)]$[a,b]	R1 = 0.057, wR2 = 0.136	R1 = 0.040, wR2 = 0.104	R1 = 0.037, wR2 = 0.086	R1 = 0.055, wR2 = 0.106	R1 = 0.030, wR2 = 0.085	R1 = 0.046, wR2 = 0.081	R1 = 0.089, wR2 = 0.186
R indices (all data)	R1 = 0.089, wR2 = 0.153	R1 = 0.048, wR2 = 0.110	R1 = 0.060, wR2 = 0.100	R1 = 0.111, wR2 = 0.128	R1 = 0.032, wR2 = 0.087	R1 = 0.081, wR2 = 0.095	R1 = 0.108, wR2 = 0.199

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR2 = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$, $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, where $P = [\max(F_o^2 \text{ or } 0) + 2(F_c^2)]/3$.

Table 2. Selected Bond Lengths and Angles[a]

	1	**2**	**3**	**4**	**5**	**6**	**7**
V−V (Å)	1.979(1) 1.978(1)	1.9876(5)	1.974(1) 1.982(1)	1.9521(7)	1.9425(4)	1.9295(8)	1.924(2)
V−N (Å)	2.101[3] 2.102[3]	2.106[2]	2.093[2] 2.113[2]	2.094[3]	2.149[1] (*py*) 2.046[1] (*im*)	2.142[3]	2.155[4]
V−V−N (deg)	94.46[7] 94.47[7]	94.33[4]	94.21[6] 94.42[6]	93.82[7]	94.49[3]	95.03[9]	95.0[1]
cis-N−V−N (deg)	89.7[1] 89.7[1]	89.68[6]	89.72[9] 89.66[9]	89.8[1]	89.66[5]	89.6[1]	89.6[2]
trans-N−V−N (deg)	171.0[1] 171.0[1]	171.12[6]	171.6[1] 171.2[1]	172.3[1]	168.37(4)	169.7[1]	170.0[2]

[a] Values in square brackets represent errors in average measurements.

Table 3. Compounds Containing the V_2^{4+} Core

ligand	V−V bond distance (Å)	torsion angles (deg)	reduction potential, V	ref
DTolF	1.978(2)	5.4(2)[a] 9.6(6)[b]	*c*	4, 32
DCyF	1.968(2)	*c*	*c*	15
hpp	1.932(1)	0	*c*	16
DPhF[d]	1.979(1) 1.978(1)	2.1 2.8	−1.46	this work
DAniF	1.9876(5)	0	−1.77	this work
D^{Cl}PhF[d]	1.974(1) 1.982(1)	1.0 7.7	−1.23	this work
TPG	1.9521(7)	14.0	−1.99	this work
ap	1.9425(4)	0	−1.82	this work

[a] Tetragonal polymorph. [b] Orthorhombic polymorph. [c] Not reported. [d] Two crystallographically independent molecules in the unit cell.

characterized as to structure by single-crystal X-ray crystallography, and the V−V distances are all within the relatively narrow range 1.93−1.99 Å, while torsion angles are close to 0°. (3) Each of the compounds dissolved in THF displays a (quasi)reversible reduction wave.

Syntheses. The paddlewheel compounds **1**−**5** were synthesized by the following metathesis reaction, where NXN represents the anion of the bidentate ligand:

$$2VCl_2\cdot nTHF + 4Li(NXN) \xrightarrow{THF,\ rt} V_2(NXN)_4 + 4LiCl$$

It should be noted that special attention must be given to the careful preparation and purification of the starting materials and to control of stoichiometry to ensure success of the reaction. Purple solutions of VCl_2 in THF are made by reducing $VCl_3(THF)_3$ with an equivalent of $NaEt_3BH$. Since $VCl_3(THF)_3$ loses coordinated solvent, it is necessary to use freshly prepared crystalline material or crystals that have been stored at low temperature in a drybox. Whenever excess of V(III) is present, it is not unusual to find tris-chelating compounds such as V(formamidinate)$_3$ as contaminants.[32] Alternatively, an excess of ligand can generate species such as [V(formamidinate)$_3$]$^-$. All compounds are air-sensitive; therefore all reactions are carried out under Ar, and solvents must be rigorously dried by fresh distillation over K/Na alloy. Contact with oxygen has been shown to produce compounds such as the dinuclear dioxo-bridged $V_2(\mu\text{-}O)_2(\mu$-formamidinate$)_2(\eta^2$-formamidinate$)_2$ compounds or the mononuclear VO(formamidinate)$_2$ species.[32] Even when precautions are taken to avoid contaminants, it is often found that, upon removal of the reaction solvent (THF) in the preparation of compounds such as **1**−**5**, oily red residues are obtained generally commingled with some red solid. We found that, in the case of $V_2(D^{Cl}PhF)_4$, limiting the reaction time to 15 min at room temperature decreased the oiliness of the crude residue. Generally, the source of

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(32) Cotton, F. A.; Daniels, L. M.; Murillo, C. A. *Inorg. Chem.* **1993**, *32*, 2881.

the oiliness can be removed by washing with small amounts of benzene or toluene, leaving the products as red solids. After removal of THF, the crude residues are best allowed to remain under reduced pressure for only a short time, from about 15 min to $^1/_2$ h. If, for any reason, there is accidental exposure of the solid to a small amount of atmospheric oxygen, darkening of the surface occurs. Should this happen, the discolored surface layer can be removed by washing the solid with small amounts of toluene or THF, although it is best to avoid having to wash the residue at all, because the compounds are moderately soluble in these solvents. The products can then be separated from the side product, LiCl, by extraction with warm toluene or benzene, filtration through Celite, and diffusion of hexanes to produce X-ray quality crystals. Interestingly, although the reaction mixtures and benzene (or toluene) extracts are always dark red in color, crystals of $V_2(TPG)_4$ are green. This feature, the oiliness of the residue in all cases, and the fact that the crystallization solutions remain highly colored even after complete diffusion suggest that a dark red uncharacterized and highly soluble side product is uniformly obtained. It should be noted that reactions with less basic ligands such as *N*,*N′*-di(3,5-dichlorophenyl)formamidinate do not produce dinuclear compounds and only the corresponding tris-chelated mononuclear complex Li(THF)$_4$[V(formamidinate)$_3$] can be isolated.[33] Attempts to allow the reaction to proceed at higher temperatures lead to cleavage of the formamidinate groups as indicated by crystallographic studies of the vanadium products. Cleavage of formamidinate groups has been documented for reactions with the heavier congeners.[9] Reaction of VCl_2 solutions with *N*,*N′*-di-*p*-trifluoromethylphenylformamidinate does not produce isolable dinuclear complexes either.

The reduction of **1** is accomplished by treatment of the precursor with KC_8 yielding a brilliant green solution (within which graphite is suspended) after stirring a few minutes at −78 °C. Rapid crystallization of **6** must be carried out by filtering the THF reaction mixture and adding just enough hexanes to evolve a precipitate. By placing the solution in a freezer at −10 °C, crystals form within 48 h. Rapid crystallization at low temperature is very important as slower crystallization rates by diffusion of hexanes into the THF solution yields only red **1**. Some of compound **1** is generally present even when short crystallization times are used. On the other hand, when crown ether is introduced, the compound becomes insoluble in THF and **7** is quite stable in the solid form, resisting decomposition at room temperature under an inert atmosphere indefinitely.

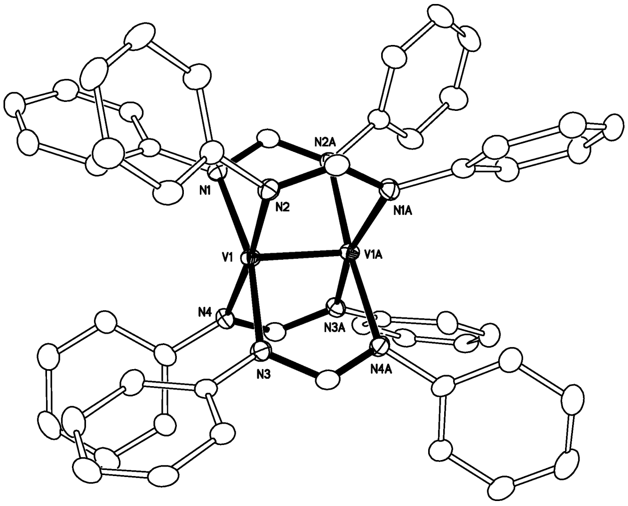

Figure 2. Thermal ellipsoid plot of $V_2(DPhF)_4$, **1**. Thermal ellipsoids are shown at the 30% probability level; hydrogen atoms have been omitted for clarity. Only one of the two independent molecules in the asymmetric unit is shown.

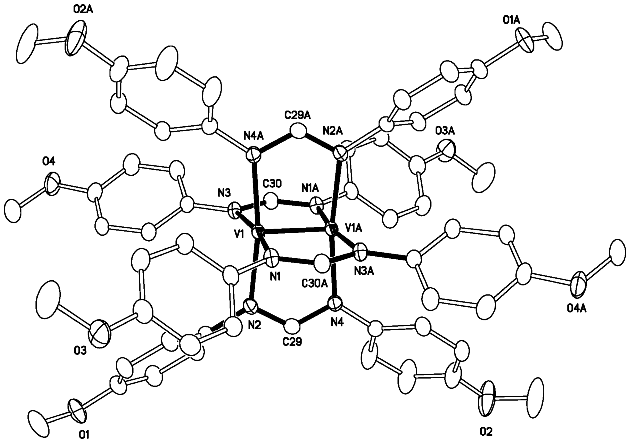

Figure 3. Thermal ellipsoid plot of $V_2(DAniF)_4$, **2**. Thermal ellipsoids are shown at the 30% probability level; hydrogen atoms have been omitted for clarity.

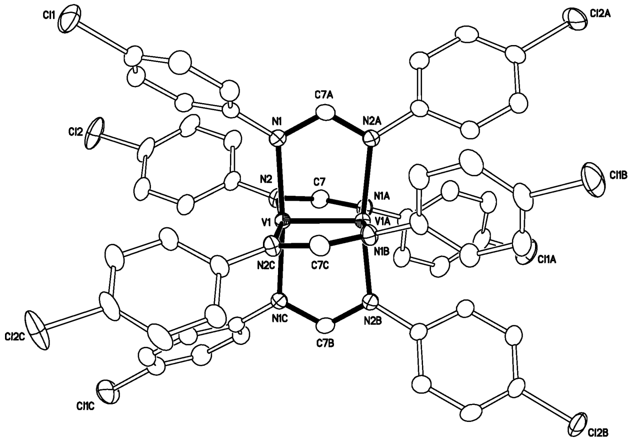

Figure 4. Thermal ellipsoid plot of one of the two crystallographically independent molecules in $V_2(D^{Cl}PhF)_4$, **3**. Thermal ellipsoids are shown at the 30% probability level; hydrogen atoms have been omitted for clarity.

Structural Considerations. The thermal ellipsoid plots of the five new V_2^{4+} molecules listed in Table 3 are shown in Figures 2−6. Each compound has the typical paddlewheel geometry with V−V bond distances ranging from 1.943 Å

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(33) Preparation and crystal data for Li(THF)$_4$[V(formamidinate)$_3$]: This compound was made by following the same procedure as for compounds **1**−**5**. When the toluene filtrate was layered with hexanes, only a red oil was obtained. The oil was redissolved by heating the hexanes/toluene supernatant, and the flask was stored at 10 °C. After 2 weeks, copious oil and a few red crystals were obtained. Empirical formula: $C_{55}H_{53}Cl_{12}LiN_6O_4V$, $P\bar{1}$, $a = 11.0014(7)$ Å, $b = 15.975(1)$ Å, $c = 18.905(1)$ Å, $\alpha = 98.468(1)°$, $\beta = 96.081(1)°$, $\gamma = 105.737(1)°$, $V = 3125.7(3)$ Å^3, $Z = 2$, $T = 213(2)$ K.; cell parameters were refined with 4405 reflections within a 2θ range of 4.408−44.578°. A total of 8151 unique reflections ($2\theta \leq 45.04°$) were measured. Full-matrix least-squares refinement of F^2 (712 parameters) converged to R1 = 0.090 and wR2 = 0.153 for all data.

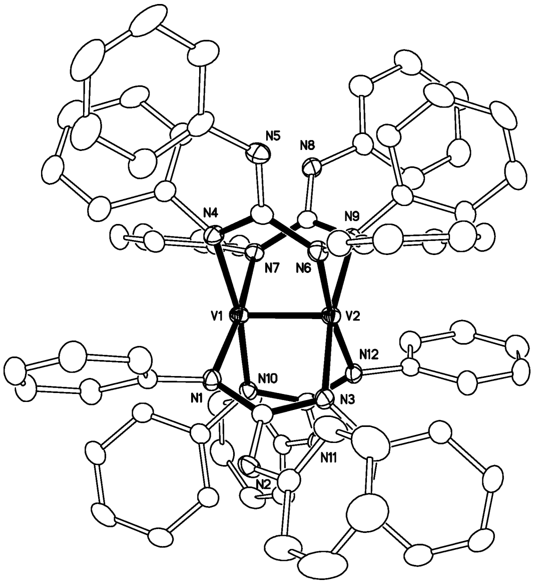

Figure 5. Thermal ellipsoid plot of $V_2(TPG)_4$, in **4**·4benzene. Thermal ellipsoids are shown at the 30% probability level; hydrogen atoms and interstitial benzene molecules have been omitted for clarity.

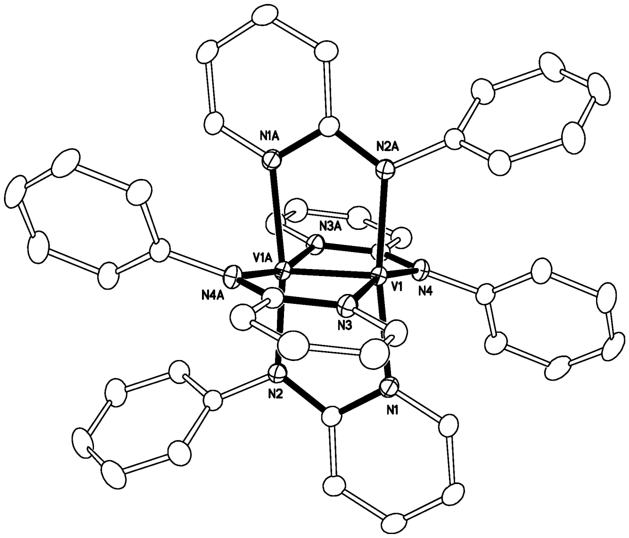

Figure 6. Thermal ellipsoid plot of $V_2(ap)_4$, **5**·2benzene. Thermal ellipsoids are shown at the 30% probability level; hydrogen atoms have been omitted for clarity.

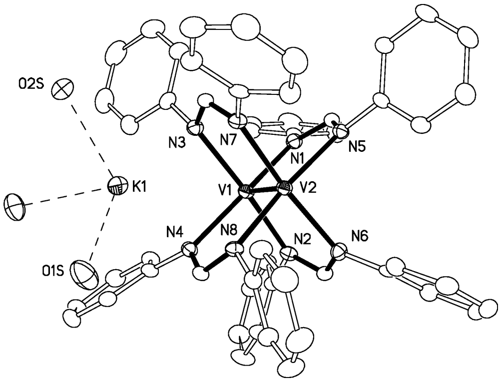

Figure 7. Thermal ellipsoid plot of $[K(THF)_3]V_2(DPhF)_4$, **6**. Thermal ellipsoids are shown at the 30% probability level; hydrogen atoms and THF carbon atoms have been omitted for clarity.

in **5** to 1.988 Å in **2**. The longer bond distances correspond to the formamidinates, while the shorter ones belong to compounds with the more basic guanidinate and aminopyridinate ligands. The diamagnetism exhibited by **1**−**5** and the short V−V bond distances are consistent with the assignment of a $\sigma^2\pi^4$ triple bond to each. It is notable that the V−V bonds are the only known metal−metal bonds, other than the fully developed Cr−Cr quadruple bonds, that are shorter than 2.00 Å. The V−V bond is so short, in fact, that it is shorter than the natural bite of the formamidinate ligands. This is manifested in the distortion of the ligand bridge shown by the V−V−N angles, which are all greater than 90°, and in the trans N−V−N angles, which are all less than 180°. For comparison, the "formal shortness ratio" (FSR),[8] a measure of bond shortness normalized to atomic size, of the V−V bond in these molecules ranges from 0.794 in **5** to 0.812 in **2**. For $Cr_2(DTolF)_4$, the FSR is 0.814,[4] while the shortest Cr−Cr bond in $Cr_2(2\text{-MeO-5-MeC}_6H_3)_4$ has a FSR of 0.770.[8]

The crystal structure of $[K(THF)_3]V_2(DPhF)_4$, **6**, is shown in Figure 7. The anion has a paddlewheel structure, somewhat similar to that of **1**, but there is a decrease in the V−V distance from 1.979(1) to 1.9295(8) Å and a small increase in the average V−N distance. The shortening of the V−V bond of 0.05 Å is consistent with the addition of one electron into a V−V bonding orbital and the increase in the formal bond order from 3 to 3.5. The magnitude of this change suggests that the additional electron resides in the δ-orbital, generating a $\sigma^2\pi^4\delta$ configuration in the reduced species. The influence of a δ electron on the bond length may be compared to the case of the dimolybdenum carboxylates, whose electronic structure is well understood. The difference in bond length between $Mo_2(TiPB)_4^{n+}$ (where TiPB is the anion of 2,4,6-triisopropylbenzoic acid and $n = 0$ and 1) with a $\sigma^2\pi^4\delta^2$ quadruple bond and the $\sigma^2\pi^4\delta$ oxidized species is +0.06 Å.[34] This is similar to the change in bond length of −0.05 Å when going from a $\sigma^2\pi^4$ to a $\sigma^2\pi^4\delta$ configuration in the divanadium compounds. The change in V−N distances is also indicative of the lowering of the overall charge on the dimetal core; the average distance increases from 2.101[3] to 2.142[3] Å upon reduction. Similar variations are observed in the series of compounds $M_2(hpp)_4^{n+}$ ($n = 0, 1, 2$), for M = Mo[35] and W.[36] Finally, the decrease in the average torsion angle from about 2.4° in the neutral species to about 1.6° in the reduced species points toward improved δ orbital overlap.

There is an additional feature in the structure of **6**, namely, the presence of the K^+ ion, coordinated by only three THF molecules and associated also with the DPhF ligands. As shown in Figure 7, the K^+ cation is found in the cleft created by two of the formamidinate groups. This type of association of an alkali metal cation with some of the ligands of an

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(34) Cotton, F. A.; Daniels, L. M.; Hillard, E. A.; Murillo, C. A. *Inorg. Chem.* **2002**, *41*, 1639.

(35) (a) Cotton, F. A.; Daniels, L. M.; Murillo, C. A.; Timmons, D. J.; Wilkinson, C. C. *J. Am. Chem. Soc.* **2002**, *124*, 9249. (b) Cotton, F. A.; Gruhn, N. E.; Gu, J.; Huang, P.; Lichtenberger, D. L.; Murillo, C. A.; Van Dorn, L. O.; Wilkinson, C. C. *Science* **2002**, *298*, 1971.

(36) (a) Cotton, F. A.; Huang, P.; Murillo, C. A. *Inorg. Chem. Commun.* **2003**, *6*, 121. (b) Cotton, F. A.; Huang, P.; Murillo, C. A.; Wang, X. *Inorg. Chem. Commun.* **2003**, *6*, 121.

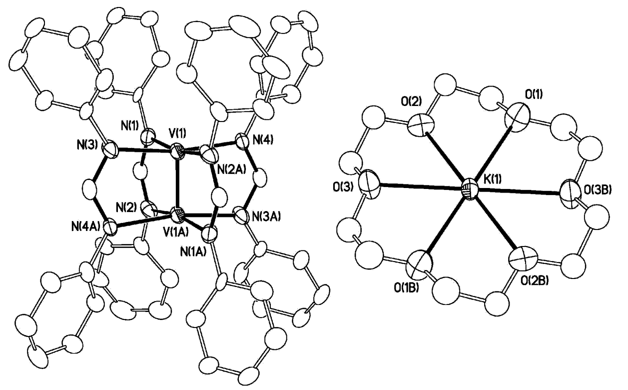

Figure 8. Thermal ellipsoid plot of [K(18-crown-6)(THF)$_2$]$V_2(DPhF)_4$, **7**. Thermal ellipsoids are shown at the 30% probability level. Only one orientation of the disordered phenyl rings and crown ether is shown. THF molecules coordinated apically to the K^+ cation and hydrogen atoms have been omitted for clarity.

M_2 paddlewheel molecule is not without precedent and has been observed in $Nb_2(hpp)_4$[11] and $W_2(hpp)_4$.[36] Although these compounds were first isolated in crystals of $M_2(hpp)_4 \cdot 2NaEt_3BH$,[11,37] having Na^+ ions occupying pockets between the paddles, the metal−metal bond distances were essentially identical whether with or without the associated alkali cations. In **6**, there are long K···N separations averaging 3.124[3] Å and three THF molecules at a relatively long average K···O distance of 2.729[4] Å, similar to those found in other K(THF) containing compounds.[38] Even though the M−M distances were unaffected by the presence or absence of the alkali metal in such dinuclear Nb and W complexes, this is not a trend that is necessarily general especially when small changes in distances, such as the difference of 0.05 Å between V−V bond distances in **1** and **6**, are being considered.

In order to establish that the K^+ cation does not seriously perturb the paddlewheel geometry and that there is not a significant effect in the metal−metal separation, the potassium cation in **6** was sequestered by reaction with 18-crown-6. The result is **7**, the structure of which is shown in Figure 8, where the K^+ cation is not associated with the divanadium species in any way. The V−V bond distance of 1.924(2) Å is the same, within 3σ, as that found in **6** (1.9295(8) Å). This is also true for the V−N distances, which are only slightly longer, averaging 2.155[4] Å as compared to 2.142[3] Å in **6**. However, small changes are observed in the cis N−V−N bond angles which are more square and uniform in the absence of the associated K^+ cation, 88.9(2)°, 89.5(2)°, 89.8(2)°, and 90.1(2)°, while the presence of the cation in **6** gives rise to a slight opening of the angle between the two blades embracing the cation to 93.7[1]° as compared to 90.5[1]° on the other side of the molecule. The average torsion angle in **7** is 0°, as required by crystallographic symmetry.

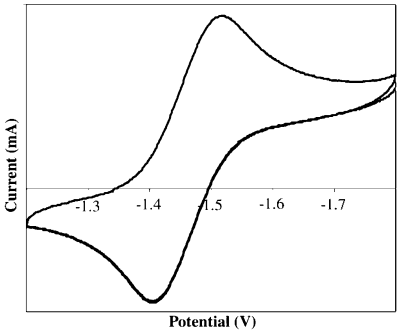

Figure 9. Cyclic voltammogram of $V_2(DPhF)_4$, **1**, in THF with 0.1 M Bu_4NPF_6 supporting electrolyte. $E_{1/2} = -1.46$ vs Ag/AgCl. Scan rate = 0.1 V/s.

Electrochemistry. Because of our recent interest in the oxidation of M_2^{4+} complexes to M_2^{5+}, M_2^{6+}, and even M_2^{7+}, we investigated the electrochemistry of V_2^{4+} compounds, and this has led to the important advance in the chemistry of metal−metal bonds discussed above, namely, the preparation and structural characterization of the first tetragonal paddlewheel complex having an M_2^{3+} core.[39] While no reversible oxidation occurs, there is a reversible reduction. In all the thousands of tetragonal paddlewheel compounds having metal−metal bonded dinuclear units, reduction to an M_2^{3+} core is a very unusual observation.[39,40] The reduction wave in the cyclic voltammogram for **1** is shown in Figure 9. The reduction product can be formally considered to provide an example of the rare oxidation state V^+ known only in relatively exotic species such as [V(mesitylene)$_2$]$^+$.[41] However, we consider it more likely that the additional electron is located in the δ bonding orbital, where it is delocalized in a V_2^{3+} core which would be expected to have an overall electron configuration of $\sigma^2\pi^4\delta$ and a metal−metal bond order of 3.5, consistent with the shortening of the V−V in going from **1** to **6** and **7**.

Each of the compounds, **1**−**5**, exhibits a similar reduction wave, the potentials of which are listed in Table 3. There is a notable trend in reduction potential: as the bridging ligand becomes more basic, the reduction potentials become more negative; it becomes more difficult to add an additional electron to the valence, presumably δ-type, orbital. A similar, but opposite, correlation between oxidation potentials and the ligand basicity of various formamidinate ligands has been shown in dinickel,[42] diruthenium,[43] and dimolybdenum[44]

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(37) Cotton, F. A.; Huang, P.; Murillo, C. A.; Timmons, D. J. *Inorg. Chem. Commun.* **2002**, *5*, 501.

(38) For comparison see Evans et al. (Evans, W. J.; Brady, J. C.; Ziller, J. W. *Inorg. Chem.* **2002**, *41*, 3340), Karsch et al. (Karsch, H. H.; Volker, G. W.; Reisky, M. *Chem. Commun.* **1999**, 1695), and Yélamos et al. (Yélamos, C.; Heeg, M. J.; Winter, C. H. *Inorg. Chem.* **1998**, *37*, 3892), where the K−O distances are 2.638(2) Å in [K(DMI)(THF]$_n$ (DMI = 2,3-dimethylindolide), 2.708 Å in [(THF)K($C_5H_4CH_3CH_2$-PPh_2)]$_n$, and 2.716(5) Å in [($Ph_2C_3HN_2$)K(THF)]$_6$, respectively.

(39) A report of the possible existence of a tetragonal paddlewheel complex having a Co_2^{3+} core has appeared, but structural characterization is lacking: He, L.-P.; Yao, C.-L.; Naris, M.; Lee, J. C.; Korp, J. D.; Bear, J. L. *Inorg. Chem.* **1992**, *31*, 620.

(40) There are only two sets of structurally characterized compounds having M_2^{3+} units, M = Fe and Co, but these are neutral, highly paramagnetic molecules having the formula $M_2[RC(NPh)_2]_3$, R = H, C_6H_5, and only three formamidinate or benzamidinate bridging ligands instead of four ligands in **6** and **7**. See: (a) Cotton, F. A.; Daniels, L. M.; Falvello, L. R.; Matonic, J. H.; Murillo, C. A. *Inorg. Chim. Acta* **1997**, *256*, 269. (b) Cotton, F. A.; Daniels, L. M.; Maloney, D. J.; Matonic, J. H.; Murillo, C. A. *Inorg. Chim. Acta* **1997**, *256*, 283.

(41) See for example: (a) Calderazzo, F.; Ferri, I.; Pampaloni, G.; Englert, U. *Organometallics* **1999**, *18*, 2452. (b) Calderazzo, F.; Pampaloni. G.; Rocchi, L.; Marchetti, F. *J. Organomet. Chem.* **1991**, *417*, C16. (c) Reference 20, pp 733−735.

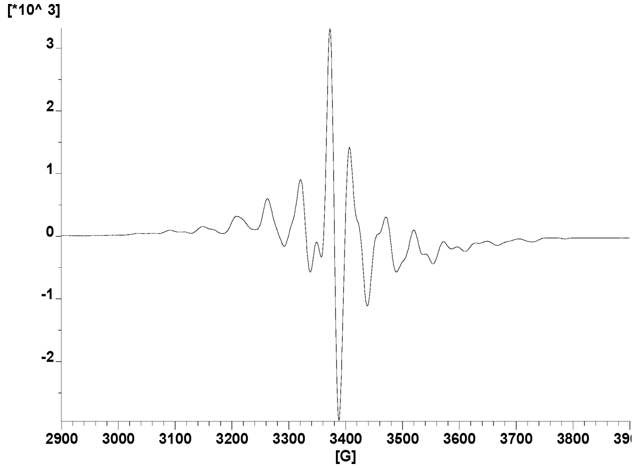

Figure 10. Electron paramagnetic resonance spectrum (9.5 GHz) of **6** in a THF glass at 6 K.

paddlewheel-type compounds. Furthermore, the V−V distances correlate fairly well with the reduction potentials. The more negative reduction potentials belong to the molecules with the shorter bonds, while the more accessible potentials correspond to those with the longer bonds.

Finally, the reduction potentials correlate with the low-energy electronic absorptions. Each of the V_2^{4+} molecules with formamidine ligands display two weak transitions, the first ranging from 455 to 488 nm for the D^{Cl}PhF and DAniF compounds, respectively, and the second one appearing as a very weak shoulder at around 560 nm. For $V_2(ap)_4$ the first transition is shifted to 533 nm. In the case of $V_2(TPG)_4$, only one transition is observed at 588 nm. Although these transitions cannot at present be assigned with certainty, it is clear that, as the transition becomes more energetic, the reduction potential becomes less negative. This trend allows the following interpretation: (1) the LUMO is destabilized as the ligands become more basic, blue-shifting the transitions and facilitating reduction, and (2) the low-energy transition has the same character in each compound. A similar correlation was found in the reduction of diruthenium formamidinates.[45] We are pursuing DFT and other types of calculations to learn more about the electronic structure of these molecules.

EPR Spectroscopy. For the reduced species in **6** and **7**, our view that the additional electron is introduced into the δ metal bonding orbital, where it is delocalized in a V_2^{3+} core, is further supported by EPR spectroscopy. A frozen THF glass of **6** at 6 K gave a multiline spectrum, shown in Figure 10, which indicates that the electron is coupling with each ^{51}V ($I = {}^7/_2$, ∼100%) atom equally. A simulation of the main feature gives a g value of 1.9999. Although this is close to the free-electron value, the complicated hyperfine splitting pattern indicates that much of the unpaired electron density is localized on the dimetal core. A similiar spectrum was obtained for **7** in an acetonitrile glass.

Concluding Remarks

With the preparation of a series of paddlewheel compounds having ligands of varied basicity, we have shown that vanadium offers a rich chemistry. A careful analysis of the synthetic methodology shows the importance of stoichiometric control, purity of the starting materials, and control of the reaction conditions for the successful preparation of tetragonal paddlewheel complexes with short vanadium−vanadium triple bonds of less than 2.0 Å. Our data indicate that the length of the V−V bond depends on the basicity of the bridging ligands, with those having the more basic guanidinate core being shorter than those having the less basic formamidinate groups. Furthermore, use of highly electron withdrawing substituents such in *N,N′*-di(3,5-dichlorophenyl)formamidinate favors the formation of tris-chelating mononuclear complexes or even cleavage of the formamidinate groups. An important effect is observed in the reduction potential also. More importantly, divanadium complexes with the less basic formamidinate ligands can be chemically reduced with KC_8 to generate the first tetragonal paddlewheel complexes with a V_2^{3+} core and a bond between vanadium atoms of order 3.5, with a $\sigma^2\pi^4\delta$ electronic configuration having one unpaired electron delocalized in the V_2 unit. The formal oxidation state of 1.5 for each vanadium atom in these V_2^{3+} units is unprecedented in coordination chemistry without π-donor ligands but more importantly has allowed extension of the attainable range of oxidation states in metal−metal bonded systems which a year ago was restricted to the range of +4 to +6 for n in M_2^{n+} units and that has now been extended to the range of n of +3 to +7.

Acknowledgment. We thank Mr. Chris Fewox and Dr. Murali Ayaluru for help with EPR spectroscopy, which was supported by NSF CHE-0092010. We are grateful to the National Science Foundation and Robert Welch Foundation for support, and E.A.H. thanks the NSF for a predoctoral fellowship.

Supporting Information Available: A displacement ellipsoid plot in pdf and CIF of $Li(THF)_3$[V(di(3,5-dichlorophenyl)formamidinate)$_3$] and additional crystallographic data in CIF format for **1**−**7**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(42) Lin, C.; Protasiewicz, J. D.; Ren, T. *Inorg. Chem.* **1996**, *35*, 7455.

(43) (a) Lin, C.; Ren, T.; Valente, E. J.; Zubkowski, J. D. *J. Organomet. Chem.* **1999**, *579*, 114. (b) Lin, C.; Ren, T.; Valente, E. J.; Zubkowski, J. D *J. Chem. Soc., Dalton Trans.* **1998**, 571.

(44) Lin, C.; Protasiewicz, J. D.; Smith, E. T.; Ren, T. *Inorg. Chem.* **1996**, *35*, 6422.

(45) Lin, C.; Ren, T.; Valente, E. J.; Zubkowski, J. D.; Smith, E. T. *Chem. Lett.* **1997**, 753.