A Highly Reduced V_2^{3+} Unit with a Metal−Metal Bond Order of 3.5

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Since the discovery of the first dimetal species containing a quadruple bond, $Re_2Cl_8^{2-}$, nearly 40 years ago, the chemistry of metal−metal bonded species has grown at a rapid pace so that there are now thousands of such compounds that have been studied and characterized.[1] This field has been considered mature, and there is generally good understanding of the bonding and electronic structures.[2] Furthermore, there are many important applications of such compounds: catalysis,[3] medicinal chemistry,[4] and some are potent reducing agents that can be used in synthesis.[5]

The most important structural motif thus far is the "paddlewheel" complex where two metal atoms are embraced by four bridging ligands, such as carboxylates, amidates, amidinates, and others. Many transition elements form compounds with this structural motif, and bond orders can vary from $^1/_2$ to 4. However, oxidation states for isolated M_2^{n+} units have been restricted to only three values, n = 4, 5, and 6. Although higher 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 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, that is, those with π-acceptors, are present.[6]

By judicious ligand selection, we have recently prepared the first dinuclear complexes where the total charge of the M_2 unit is 7+. This was accomplished for M = Os[7] and Re[8] in complexes of the type $[M_2(hpp)_4Cl_2]PF_6$, where hpp is the anion of 1,3,4,6,7,8-hexahydro-2H-pyrimido[1,2a]pyrimidine.

We now report the isolation and structural characterization of the first four-bladed paddlewheel complex having an M_2^{3+} unit in $K(THF)_3[V_2(DPhF)_4]$, **1**, Figure 1, where DPhF is the anion of N,N'-diphenylformamidine.[9] This dark green compound was obtained by reduction of the reddish-brown, triply bonded $V_2(DPhF)_4$ precursor,[10] **2**, using potassium graphite in THF as shown in eq 1.

$$V_2(DPhF)_4 + KC_8 \rightarrow K(THF)_3[V_2(DPhF)_4] + 8C \quad (1)$$

Compound **1** is extremely air-sensitive. The reaction was carried out under Ar, and solvents were rigorously dried by fresh distillation over Na/K alloy. Rapid crystallization was carried out by filtering the THF reaction mixture and adding just enough hexanes to evolve a precipitate. The solution was then placed in the freezer at −10 °C, and crystals appeared after 48 h. Rapid crystallization at low temperature is very important, as slower crystallization by diffusion of hexanes into the THF solution yielded only the red **2** over several days. Some of **2** is present even when short crystallization times are used.[11]

The precursor **2** is in itself interesting. It represents just the fourth diamagnetic divanadium(II,II) compound that has been structurally characterized. It has the typical paddlewheel geometry and possesses a V−V $\sigma^2\pi^4$ triple bond with a length of 1.979(1) Å, which is similar to those found in $V_2(DTolF)_4$[12] (1.978(2) Å) and $V_2(DCyF)_4$[13]
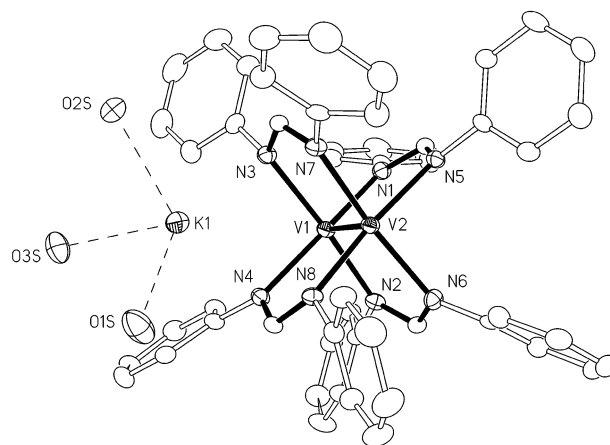

Figure 1. Thermal ellipsoid plot of $K(THF)_3[V_2(DPhF)_4]$, **1**. Thermal ellipsoids are shown at the 30% probability level, and hydrogen atoms have been omitted for clarity. Selected distances (in Å): V1−V2 1.9295(8), V1−N 2.137[3], V2−N 2.146[3], V1- - -K1 3.904(1).

(1.968(2) Å). It should be noted that the V−V bonds are the only metal−metal bonds, other than the so-called supershort Cr−Cr quadruple bonds, that are shorter than 2.00 Å.

In **1**, the paddlewheel structure is conserved, but the V−V bond contracts significantly to a distance of 1.9295(8) Å, a difference of about 0.05 Å when compared to the neutral species. The shortening of this bond is consistent with the addition of one electron 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 and that the dimetal core has a $\sigma^2\pi^4\delta$ configuration. This situation may be compared to that 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.[14] 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.[15] Finally, the decrease in the torsion angle from about 2.4° in the neutral species to about 1.6° in the reduced species points toward improved δ overlap.

As shown in Figure 1, the K^+ cation is found in one of the pockets between two of the formamidinate groups. This type of association of an alkali metal cation with some of the ligands of an M_2 paddlewheel molecule is not without precedent and has been observed in $Nb_2(hpp)_4$[16] and $W_2(hpp)_4$.[15] Although these compounds were first isolated in crystals of $M_2(hpp)_4 \cdot 2NaEt_3BH$,[17] 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 **1**, there are long K- - -N distances averaging 3.124[3] Å and three THF molecules at a relatively long average distance of 2.729[4] Å, similar to those found in other K(THF)-containing compounds.[18]

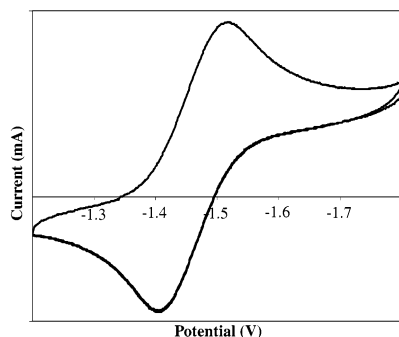**Figure 2.** Cyclic voltammogram of **2**, 2.0 mM in THF with 0.1 M Bu$_4$NPF$_6$ supporting electrolyte, a platinum disk working electrode, and a platinum wire auxiliary electrode. $E_{1/2} + -1.46$ V, $\Delta E_p = 0.11$ V versus Ag/AgCl.

It is noteworthy that the cyclic voltammogram of **2** (Figure 2) shows a reversible wave. As there is no potassium present in the system, it is clear that the reduced species does not require K$^+$ for electrochemical stability. This supports the view that the K cation is merely filling a void in the crystal packing network. Thus, we expect the structure of the paddlewheel we have found in **1** to be about the same as that which will be found in a crystal where no such association occurs, and we are currently trying to trap the cation with crown ethers. There are, however, some slight deviations from the ideal paddlewheel-type structure due to the presence of the K$^+$ cation. For example, the V−N distances adjacent to the cation are 2.148[3] Å, while those opposite of the cation are 2.135[3] Å. Furthermore, the presence of the cation 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.

Although the reduced species, **1**, can be formally considered to provide an example of the rare oxidation state V$^+$, our view that the additional electron is introduced into the δ bonding orbital, where it is delocalized in a V$_2{}^{3+}$ core, is further supported by EPR results. A frozen THF solution of **1** at 6 K gave a 15-line spectrum which indicates that the electron is coupling with each ^{51}V ($I = {}^7/_2$) 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 the unpaired electron is localized on the dimetal core.

In conclusion, the isolation of the first V$_2{}^{3+}$ compound is the harbinger of the chemistry of low-valent paddlewheel compounds,[19] thus expanding the available dimetal oxidation states beyond 4, 5, and 6. Additionally, this structure contains one of the very few examples of a vanadium atom with a formal oxidation state of less than 2 in the absence of π-acids.[20] We believe that the presence of a vanadium−vanadium bond plays an important role in delocalizing the extra electron density and thus stabilizing the highly reduced V$_2{}^{3+}$ unit.

Supporting Information Available: Crystallographic data for compounds **1** and **2** (CIF). Thermal ellipsoid plot of **2** and EPR spectrum of **1** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(9) Crystal data for **1**: *Pna*2$_1$, $a = 20.249(1)$ Å, $b = 12.4492(6)$, $c = 22.957(1)$, $V = 5786.9(5)$ Å^3, $Z = 4$, $T = 213(2)$ K, cell parameters were refined with 5019 reflections within a 2θ range of 5.186−43.113°. A total of 10 209 unique reflections ($2\theta \leq 50.00°$) were measured. Full-matrix least-squares refinement of F^2 (703 parameters) converged to $R = 0.0809$ and wR2 = 0.0948.

(10) V$_2$(DPhF)$_4$ was synthesized by a method similar to that of the *p*-tolyl analogue. See: Cotton, F. A.; Daniels, L. M.; Murillo, C. A. *Angew. Chem.* **1992**, *31*, 737. Anal. Calcd for C$_{52}$H$_{44}$V$_2$N$_8$: C, 70.74; H, 5.02; N, 12.69. Found: C, 70.92; H, 5.18; N, 12.64. ^{1}H NMR δ (ppm, in C$_6$D$_6$): 5.953 (d, 16H, aromatic), 6.736 (m, 24H, aromatic), 10.007 (s, 4H, methyne). UV/vis $\lambda(\epsilon)$, nm (M^{-1} cm^{-1}) in THF: 464(90), 398(1730). Crystal data for **2**: *P*2/*n*, $a = 17.874(1)$ Å, $b = 10.3011(8)$ Å, $c = 24.416(2)$ Å, $\beta = 102.156(2)°$, $V = 4394.7(6)$ Å^3, $Z = 4$, $T = 213(2)$ K, cell parameters were refined with 6688 reflections within a 2θ range of 4.52−50.04°. A total of 7761 unique reflections ($2\theta \leq 50.08°$) were measured. Full-matrix least-squares refinement of F^2 (575 parameters) converged to $R = 0.0892$ and wR2 = 0.1533.

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