# Synthesis and Crystal Structure of $[Zn^{II}(LH_3)(L)V^{IV}][PF_6]_3$ [$LH_3$ = *N,N′,N″*-Tris(*2S*)-2-hydroxypropyl-1,4,7-triazacyclononane]: A Chiral Mixed-Metal Pendant-Arm Macrocyclic Dimer Containing Non-Vanadyl Vanadium(IV)

**Ian Fallis, Louis J. Farrugia, Norman M. Macdonald, and Robert D. Peacock***

Department of Chemistry, University of Glasgow, Glasgow G12 8QQ, U.K.

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Vanadium coordination chemistry is currently undergoing a renaissance, largely due to the realization that the metal is present in many biological systems.[1] Despite the fact that bioinorganic vanadium is frequently non-vanadyl, the vast majority of characterized $V^{IV}$ and $V^{V}$ complexes are of the oxocations, $[VO]^{2+}$ or $[VO_2]^+$. Non-vanadyl, "bare", vanadium(IV) or vanadium(V) complexes are still rather unusual. Apart from the notable case of the vanadium(IV) sepulchrate complex,[2] which has all N donors, most non-vanadyl vanadium(IV) complexes have mixed N,O donor sets. Recent examples of such complexes have carboxylate,[3] phenolate,[4,5] and catecholate[6] oxygen donors respectively.

We are exploring the chemistry of the ligand *N,N′,N″*-tris(*2S*)-2-hydroxypropyl-1,4,7-triazacyclononane [$LH_3$] which has three tertiary amine and three **alcohol** or **alkoxy** donors and have reported the structures of hydrogen-bridged dimers of $Co^{III}$,[7] $[Co(LH_3)(L)Co]^{3+}$ and of mixed-valence $Mn^{II}$,$Mn^{IV}$ [8] $[Mn(LH_3)(L)Mn]^{3+}$ as well as the monomeric complexes[8b,9] $[Ni(LH_3)]^{2+}$ and $[Mn(LH_3)]^{2+}$. We report in this communication the preparation and structure of the first **mixed-metal** hydrogen-bridged dimer of $LH_3$, $[Zn^{II}(LH_3)(L)V^{IV}][PF_6]_3$ (**1**), which contains trigonal prismatic zinc(II) and pseudooctahedral (non-vanadyl) vanadium (IV).

**1** was prepared by addition of $LH_3$ to a solution of $VOCl_2$ which had been reduced to the V(III) state by zinc amalgam, followed by subsequent reflux of the solution in air. The resulting greyish solution was treated with $[NH_4][PF_6]$ and the precipitate washed with acetone. The acetone dissolved out a yellow diamagnetic species (which we believe to be the corresponding $V^{V}$ complex) and left behind **1** as a lilac powder which was recrystallized from MeCN under nitrogen to give lilac prisms of crystallographic quality[10] (**1** is slowly oxidized in solution by molecular oxygen to give the $V^{V}$ species).

**1** crystallizes in the same space group (*R*3) as the $Mn^{II}$, $Mn^{IV}$ mixed-valence hydrogen bridged dimer, $[Mn(LH_3)(L)Mn]^{3+}$.[8] The $Zn^{II}$ complex, $[Zn(LH_3)]^{2+}$, has trigonal prismatic geometry (twist angle, $\phi$[11] = 55.5°) and the $V^{IV}$ complex, $[V(L)]^+$, has pseudooctahedral geometry with $\phi = 20.6°$. The larger twist toward trigonal prismatic symmetry shown by $[VL]^+$ compared to that of $[MnL]^+$ ($\phi = 10.9°$)[8] or [CoL] ($\phi = 10.2°$)[7] is expected since the $d^1$ configuration shows little preference for octahedral vs trigonal prismatic geometry.[12]

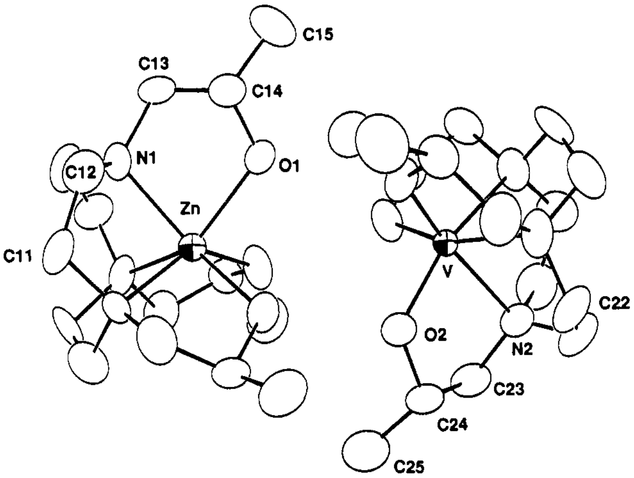

**Figure 1.** Molecular structure and atomic labeling scheme for $[Zn(LH_3)(L)V][PF_6]_3$ (**1**), with thermal parameters shown at the 20% probability level. Important bond lengths (Å) and bond angles (deg) are as follows: Zn–N(1) = 2.146(10), Zn–O(1) = 2.110(9), V–N(2) = 2.177(13), V–O(2) = 1.872(9); N(1)–Zn–N(1) = 81.6(4), O(1)–Zn–O(1) = 86.9(4), N(1)–Zn–O(1) = 78.5(4), N(2)–V–N(2) = 81.5(5), O(2)–V–O(2) = 97.5(5), N(2)–V–O(2) = 79.6(5).

A particularly interesting structural feature is the dramatic difference between the relative lengths of the M–N and M–O bonds in the two parts of the dimer. Whereas the Zn–N and

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(10) X-ray parameters for **1**: $C_{30}H_{63}F_{18}N_6O_6P_3VZn$, $M_r$ = 1155.1, rhombohedral, *R*3; $a$ = 10.430(1) Å, $c$ = 36.852(2) Å; $V$ = 3471.8(5) Å$^3$; $Z$ = 3; $\rho_{calc}$ = 1.66 g/cm$^3$; $F(000)$ = 1779; λ(Mo Kα) = 0.71069 Å); μ(Mo Kα) = 9.44 cm$^{-1}$; $T$ = 25 °C. A total of 2197 unique data (θ range 2–25°; $h$, −12 → +12; $k$, 0 → +12; $l$, 0 → +43) were measured from a crystal measuring 0.07 × 0.1 × 0.5 mm on a Enraf-Nonius CAD4-F diffractometer with graphite monochromated Mo Kα X-radiation using θ/2θ scans and corrected for Lorentz polarization and absorption/extinction (DIFABS[13]; max/min corrections 1.19 and 0.74, respectively). The structure was solved by heavy atom methods and subsequent electron density difference synthesis and was refined by full-matrix least-squares methods using 1392 observed data [$F_o > 3\sigma F_o$]. Refinement was by full-matrix least-squares methods, minimizing the function $\sum w(|F_o| - |F_c|)^2$ with the weighting function $w = [\sigma^2(F_o) + 0.002F_o]^{-1}$. The final $R$ ($R_w$) values were 0.074 (0.075) for 197 parameters. Hydrogen atoms, except the OH atoms, were incorporated at fixed positions with C–H = 1.08 Å. The O–H hydrogens were not observed in the difference map and were not included in the calculations. Their presence may be inferred from the short O(1)···O(2) contact of 2.68(1) Å. The known *S* conformation of the chiral C atoms was assumed. Neutral atom scattering factors were taken from ref 14 with corrections applied for anomalous scattering. All calculations were carried out on a MicroVAX computer using either the Glasgow GX suite of programs[15] or SHELX76 for full-matrix refinement.

(11) The angle $\phi$ is defined as the angle of twist away from an exactly staggered arrangement of ligators as viewed down the $C_3$ axis. Thus $\phi$ is 0° for octahedral geometry and 60° for trigonal prismatic geometry.

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**Figure 2.** $^{13}C$ DEPT NMR spectra of **1** in DMF solution: (a) proton-decoupled $^{13}C$ spectrum; (b) 90° pulse for CH; (c) 135° pulse for $CH_3$ (positive) and $CH_2$ (negative).

Zn–O bond lengths are very similar, the V–O bond length is shorter than the V–N one by about 30 pm. This effect is found in other structurally characterized complexes of $LH_3$ and can be correlated with $p^{\pi}$ donation from the filled p orbitals on the oxygen to the $t_{2g}$ orbitals on the metal, as the population of the latter is altered. Thus in the complexes with filled $t_{2g}$ orbitals ($Zn^{II}$, $Co^{III}$,[7] $Ni^{II}$ [9]), where no $p^{\pi}$ donation is possible, the M–N and M–O distances are essentialy equal. However, when the $t_{2g}$ set is half-full, the M–O distance is shorter than the Mn–N one by 11 pm ($Mn^{II}$,[8] alcohol ligators) or 19 pm ($Mn^{IV}$,[8] alkoxide ligators), and when the $t_{2g}$ set is singly occupied (as in the $V^{IV}$ ion in **1**), this difference increases to 30 pm.

We believe that the dimer remains intact in non-aqueous solvents (as do the $Co^{III}$,$Co^{III}$ and $Mn^{II}$,$Mn^{IV}$ dimers). Evidence comes from the fact that the solid-state absorption and CD spectra are identical to those obtained in MeCN or DMF solutions. Acidification with trifluoroacetic acid (which protonates the $[VL]^+$ half) results in the solution turning yellow, suggesting oxidation to a $V^V$ species. A singlet at 22 ppm in the $^1H$ NMR spectrum (vide infra) may be caused by the bridging protons.

Despite the paramagnetism of the complex we have obtained reasonably well resolved $^{13}C$ and $^1H$ NMR spectra. The $^{13}C$ DEPT sequence (Figure 2) shows sharp signals due to the diamagnetic $[Zn(LH_3)]^{2+}$ part of the dimer and weaker, broader signals due to the paramagnetic $[V(L)]^+$ part. Assignments are as follows: methyls, 21.60 ppm (Zn) and 20.82 ppm (V); methylenes (ring), 50.58 (Zn) and 50.06 ppm (V); methylenes (arm), 64.04 (Zn) and 65.35 ppm (V); methines 63.92 (Zn) and 64.94 ppm (V). The $^1H$ NMR spectrum shows both "normal" ($[Zn(LH_3)]^{2+}$) and shifted ($[V(L)]^+$) resonances. Assignment of the methylene resonances is difficult, but the methyl signals are clearly seen at 1.28 ppm ($[Zn(LH_3)]^{2+}$) and 1.39 ppm ($[V(L)]^+$) and the methine resonances at 4.22 ppm (Zn) and 4.35 ppm (V). A broadened singlet at 22 ppm may be due to the bridging protons (14.6 ppm in $[Co(LH_3)(L)Co]^{3+}$).[7]

Unlike the complexes with phenolate[4,5] or catecholate[6] ligands which are black or dark purple due to extensive charge-transfer absorption in the visible region, **1** is pale lilac. The color is caused by a single absorption band (of $V^{IV}$) at 550 nm ($\epsilon = 60$ mol$^{-1}$ dm$^3$ cm$^{-1}$) partially overlapped by the tail of a charge-transfer transition ($\lambda_{MAX} = 330$ nm, $\epsilon = 1560$ mol$^{-1}$ dm$^3$ cm$^{-1}$). The circular dichroism spectrum of the visible transition is of a single sign and has a dissymmetry factor of $8 \times 10^{-3}$ confirming that the transition is magnetic dipole allowed and must be assigned to the $^2A$ or $^2E$ ($^2T_{2g}$) $\rightarrow$ $^2E(^2E_g)$ transition expected for a $d^1$ ion in $C_3$ symmetry. There is no sign of a second transition at low energy corresponding to the intra-configurational $^2A(^2T_{2g}) \leftrightarrow {}^2E(^2T_{2g})$ transition. This is presumably hidden under the vibrational spectrum and suggests that the $^2A$–$^2E$ ($^2T_{2g}$) trigonal splitting must be rather small.

The CV of **1** shows a reversible wave at +0.105 V vs $Fc/Fc^+$ due to the $V^{IV}/V^V$ couple. This is compatable with the complex being oxidized to $V^V$ by molecular oxygen. The $V^{IV}$ state in **1** is considerably less stable to oxidation to $V^V$ than in the analogous complexes with phenolate (+0.38 V) or catecholate (+0.18 V) ligands. We believe that the reason why the $V^{IV}$ species is easily isolated is because of the hydrogen bridge to the $Zn^{II}$ species. Indeed we have not been able to isolate a $V^{IV}$ species unless zinc is used in the reduction. Furthermore protonation of the dimer appears to result in oxidation to a $V^V$ species. The reduction to $V^{III}$ (at approximately –1 V vs $Fc/Fc^+$) appears to be irreversible. The negative potential of this reduction compared to the phenolate complex (–0.5 V) corresponds to the higher energy of the charge-transfer transition in **1**.

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**Supplementary Material Available:** For **1**, Tables A–E, listing anisotropic thermal parameters, complete bond lengths and bond angles, calculated hydrogen positional parameters, fractional co-ordinates for non-hydrogen atoms, and details of the crystallographic data collection and refinement (10 pages). Ordering information is given on any current masthead page.