

Syntheses and Characterization of Stable Pseudo-octahedral Tris-phenolato Complexes of Vanadium-(III), -(IV), and -(V)

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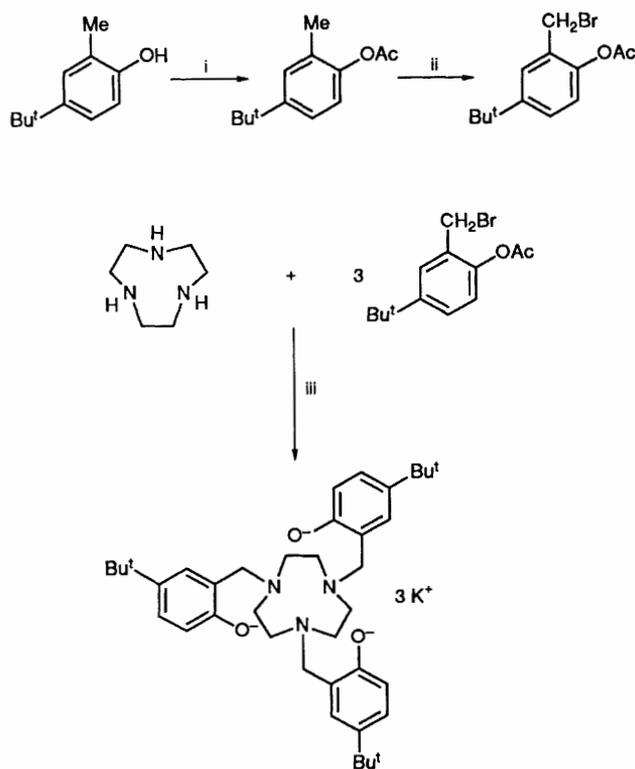
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Reaction of the anionic form of the hexadentate ligand 1,4,7-tris(5-*t*-butyl-2-hydroxybenzyl)-1,4,7-triazacyclononane (H_3L) with VCl_3 in MeCN affords LV^{III} which is oxidized chemically and electrochemically to $[LV^{IV}]^+$ and $[LV^V]^{2+}$; electrochemical, magnetic, and electronic spectroscopic properties of these complexes and the X-ray structure of $[LV][BPh_4]$ are reported.

Vanadium-phenolate binding is attracting the attention of inorganic chemists because of its role in bioinorganic chemistry; *e.g.* vanadium ions are bound to tyrosinate residues in vanadium-modified transferrin.¹ In contrast to the well known aqueous chemistry of V^{IV} and V^V where octahedral complexes containing VO^{2+} , VO^{3+} , or VO_2^+ groups prevail, these structural motifs do not appear abundant in vanadium-containing metalloproteins. Amavadin has been shown to contain an eight-co-ordinate V^{5+} ion without oxo-ligands,² and this structure has recently been modelled successfully.³ Carrano *et al.*⁴ synthesized vanadium(IV)/(V)-phenolate complexes but these contain VO^{2+} or VO^{3+} units. Cooper *et al.*⁵ have reported tris-catecholato V^{IV} complexes without VO groups

which can be oxidized to highly coloured V^V species. So-called 'bare,' *i.e.* without oxo-ligands, octahedral V^V complexes are exceedingly rare whereas a few V^{IV} complexes of this kind have been structurally characterized.⁶ We have started to investigate the co-ordination chemistry of a new series of hexadentate ligands derived from 1,4,7-tris(2-hydroxybenzyl)-1,4,7-triazacyclononane which contains the macrocyclic 1,4,7-triazacyclononane backbone and three phenolate-type pendant arms.⁷ Here we report three vanadium complexes with this type of ligand.

The potassium salt K_3L of 1,4,7-tris(5-*t*-butyl-2-hydroxybenzyl)-1,4,7-triazacyclononane (H_3L) was prepared in good yields according to the route depicted in Scheme 1.



Scheme 1. Synthesis of the ligand K_3L . Reagents: i, acetic anhydride; ii, CCl_4 -*N*-bromosuccinimide, azoisobutyronitrile; iii, 1,4,7-triazacyclononane, toluene, KOH.

Experimental details are similar to those reported in ref. 7. When a solution of VCl_3 in MeCN was refluxed under an argon atmosphere and an equimolar amount of K_3L was added to the hot solution, a pale green precipitate of LV^{III} (1) formed. Solid (1) is stable in air for days. Treatment of a suspension of (1) in MeOH with a few drops of conc. $HClO_4$ in the presence of air afforded a clear purple solution. Addition of $NaBPh_4$ initiated the precipitation of purple $[LV][BPh_4]$ (2).[†] Single crystals suitable for X-ray crystallography were obtained by slow evaporation of a MeCN solution of (2). $[LV][ClO_4]$ was obtained using $NaClO_4$ instead of $NaBPh_4$. When a solution of $[LV][ClO_4]$ in dry $MeNO_2$, to which $[NH_4]_2S_2O_8$ had been added, was stirred at 50 °C a deep blue solution was obtained from which, after addition of solid $[Bu^t_4N]ClO_4$, blue-black microcrystals of $[LV^V][ClO_4]_2$ (3) precipitated.[‡]

[†] Crystal data for (2): $[C_{39}H_{54}N_3O_3V][B(C_6H_5)_4]$, $M = 983$; orthorhombic, $P2_12_12_1$ (D_2^4 ; No. 19), $a = 10.839(4)$, $b = 19.39(1)$, $c = 26.42(2)$ Å, $U = 5552(5)$ Å³, $Z = 4$; $D_c = 1.18$ g cm⁻³. Crystal dimensions, $0.40 \times 0.41 \times 0.52$ mm³, Mo- K_α (0.7107 Å); $T = 298$ K, Syntex R3 four-circle diffractometer. Data were reduced using the SHELXTL PLUS program package and the structure was solved using this program. Hydrogen atoms were included at calculated positions with fixed U values (isotropic thermal parameters) of 0.08 Å²; $\mu = 0.22$ mm⁻¹; $3.0 < 2\theta < 50.0^\circ$; 5475 unique reflections; 4606 reflections with $I > 2.5\sigma(I)$; 473 least-squares parameters; $R = 0.063$ ($R_w = 0.051$). Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

[‡] All new compounds gave satisfactory elemental analyses (C, H, N).

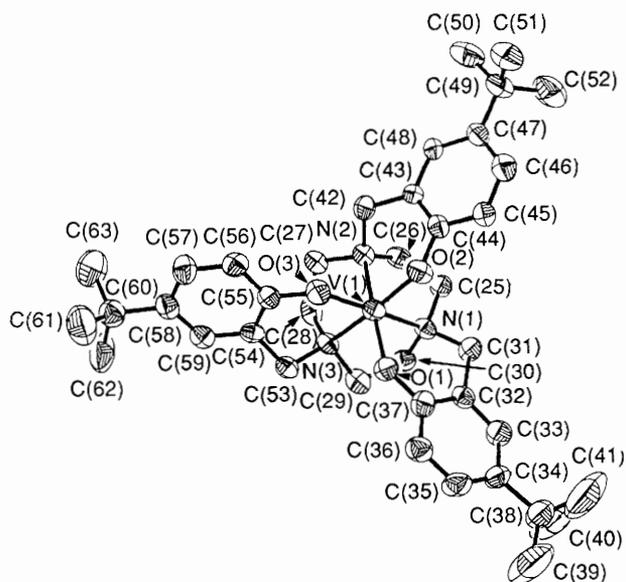


Figure 1. Structure of cation in crystals of (2). Important bond lengths (Å) and angles (°): V-N(1) 2.166(6), V-N(2) 2.169(5), V-N(3) 2.168(5), V-O(1) 1.831(4), V-O(2) 1.809(5), V-O(3) 1.834(5); N(1)-V-N(2) 79.6(2), N(1)-V-N(3) 80.3(2), N(1)-V-O(1) 87.1(2), N(1)-V-O(2) 90.1(2), N(1)-V-O(3) 167.2(2), N(2)-V-N(3) 79.4(2), N(2)-V-O(1) 164.0(2), N(2)-V-O(2) 88.0(2), N(2)-V-O(3) 92.3(2), N(3)-V-O(1) 89.6(2), N(3)-V-O(2) 165.4(2), N(3)-V-O(3) 88.3(2), O(1)-V-O(2) 101.0(2), O(1)-V-O(3) 99.1(2), O(2)-V-O(3) 99.8(2).

Complexes (1) and (2) have temperature-independent magnetic moments of 2.8 μ_B and 1.6 μ_B (90–298 K, Faraday method), respectively, which may be compared with the spin-only values of 2.83 μ_B for V^{III} (d^2) and of 1.73 μ_B (d^1); (3) is diamagnetic (V^V d^0).

The MeCN solution electronic spectra consist of the following transitions at λ_{max}/nm (ϵ/l mol⁻¹ cm⁻¹): (1): 540 (3700), 360 (4550), and 273 (1.74×10^4); (2): 553 (9500), 430 (7200), 310sh, and 266 (1.33×10^4); (3): 719 (3.74×10^4), 327 (1.31×10^4), and 260 sh. The very intense low-energy transition in each spectrum is assigned to a phenolate-to-metal charge transfer (CT) transition which shifts to longer wavelengths on increasing the formal oxidation number of the vanadium ion in (1), (2), and (3). Concomitantly, the molar extinction coefficient of this transition increases. Complex (3) exhibits the most intense phenolate-to-vanadium(v) CT transition reported to date for phenolato or catecholato vanadium(v) complexes.

Figure 1 shows the structure of the cation in crystals of (2).[†] The vanadium(IV) ion is in a pseudo-octahedral environment consisting of three amine nitrogens of the macrocyclic 1,4,7-triazacyclononane backbone and three phenolate oxygen atoms (*fac*- N_3O_3 donor set). The average V-O bond length of 1.827 Å is significantly shorter than in the catecholato vanadium(IV) complex $[Et_3NH][V(cat)_3] \cdot MeCN [1.930(3)$ Å].⁵

Figure 2 displays the cyclic voltammogram (CV) of $[LV]$ in MeCN solution $\{[complex] \approx 10^{-3} M; 0.10 M [Bu^t_4N]PF_6\}$ at a glassy carbon working electrode in the potential range -2.10 to +1.3 V vs. $Ag/AgCl$ (EtOH, saturated LiCl); ferrocene (Fc) was added as internal standard. At scan rates of 20–200 mV/s three reversible one-electron waves were detected at $E_{1/2}^{3-}$ values of +0.38, -0.50, and -2.41 V vs. Fc^+/Fc . Coulometric measurements on LV and $[LV][ClO_4]$ at 0.00 V

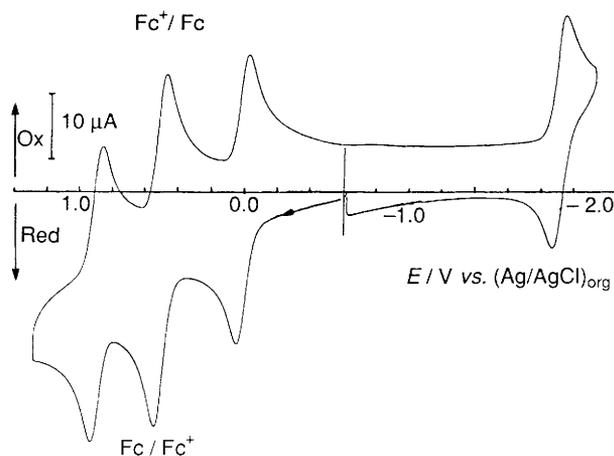
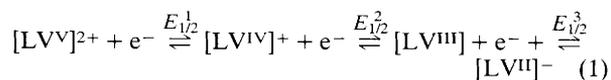


Figure 2. Cyclic voltammogram of [LV] in MeCN (0.1 M [Bu₄N]PF₆ supporting electrolyte, glassy carbon working electrode, ferrocene internal standard, scan rate 200 mV s⁻¹).

and +0.60 V vs. Fc⁺/Fc, respectively, indicated that each species is oxidized by 1.0 ± 0.1 electrons per vanadium centre as was judged by the absorption spectra of the fully oxidized solutions. Similar experiments with [LV][ClO₄]₂ showed that at potentials >0.7 V vs. Fc⁺/Fc no electrochemical process occurred but at 0.00 V vs. Fc⁺/Fc a one-electron reduction to [LV]⁺ was observed. These experiments prove the assignment of CV waves as in equation (1).



The CVs of [LV][ClO₄] and (3) are identical under the same conditions. Thus the oxidation states V^{II} to V^V are accessible without changing the co-ordination sphere at the vanadium centre. It has not as yet been possible to isolate the [LV^{II}]⁻ species which on the time scale of a coulometric measurement appears to be unstable in MeCN solution.

In summary, we have shown that it is possible to stabilize 'bare' V^V, V^{IV}, and V^{III} ions in solution and in the solid state by using a macrocyclic ligand which contains three phenolate pendant arms.

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