Synthesis and X-Ray Structures of Bis(3,5-di-*tert*-butylcatecholato)(phenanthroline)vanadium(IV) and its Vanadium(V) Analogue [V(dtbc)$_2$(phen)][SbF$_6$]

Themistoklis A. Kabanos,[a] Andrew J. P. White,[b] David J. Williams[b] and J. Derek Woollins*[b]

[a] *Department of Chemistry, Section of Inorganic and Analytical Chemistry, University of Ioannina, 45110 Ioannina, Greece*

[b] *Department of Chemistry, Imperial College, South Kensington, London SW7 2AY, UK*

Bis(3,5-di-*tert*-butylcatecholato)(phenanthroline)vanadium(IV) **1** is prepared, and oxidised with silver hexafluoroantimonate to give its vanadium(V) analogue **2**; both complexes are characterised by X-ray crystallography revealing significant differences in their coordination geometry.

There is a well developed chemistry for V^{IV}/V^{V} 'oxo' species ($VO^{2/3+}$, VO_2^+) but very few simple non-oxo vanadium complexes with chelating ligands have been prepared and fully characterised.[1–5] The biological importance of these systems is the subject of increasing interest and has recently been highlighted.[3] Only two X-ray structures of non-oxo V^V complexes have been reported,[1,4] the anionic $[V(dtbc)_3]^-$ (dtbc = 3,5-di-*tert*-butylcatecholate) and the neutral $[V(N_3S_2)(dtbc)(phen)]$ (phen = phenanthroline). It has been reported[6] that on going from V^{IV} to V^V in $[V^{IV/V}O(salen)]^{0/+}$ [salen = *N*,*N*′-ethylenebis(salicylideneaminato)] there are significant changes in the V–O (salen) bond lengths. Here, we report on the preparation and X-ray crystal structures of V^{IV} and V^V complexes $[V(dtbc)_2(phen)]$ **1** and $[V(dtbc)_2(phen)][SbF_6]$ **2**, which enables comparison of the coordination geometries about vanadium for these two different oxidation states.

Compound **1** was prepared[7] by sequentially adding phenanthroline (2.0 mmol) and H_2dtbc (4.0 mmol) to bis(pentane-2,4-dionato)oxovanadium(IV) (2.0 mmol) in CH_2Cl_2 [eqn. (1)]. The resulting black precipitate was washed with CH_2Cl_2 and dried *in vacuo* (yield 95%) Compound **2** was obtained in 94% yield by addition of silver hexafluoroantimonate to a suspension of **1** in CH_2Cl_2 [eqn. (2)]. After removal of the Ag, the filtrate was treated with pentane to precipitate **2**.† Crystals of **1** and **2** suitable for X-ray analysis‡ were obtained by diffusion of pentane into dichloromethane solutions.

$$[VO(acac)_2] + phen + 2H_2dtbc \rightarrow [V(dtbc)_2(phen)] + 2Hacac + H_2O \quad (1)$$

$$[V(dtbc)_2(phen)] + AgSbF_6 \rightarrow [V(dtbc)_2(phen)][SbF_6] + Ag \quad (2)$$

Both compounds are air stable solids but decompose in solution (especially **2**) on exposure to air. The ^{51}V NMR

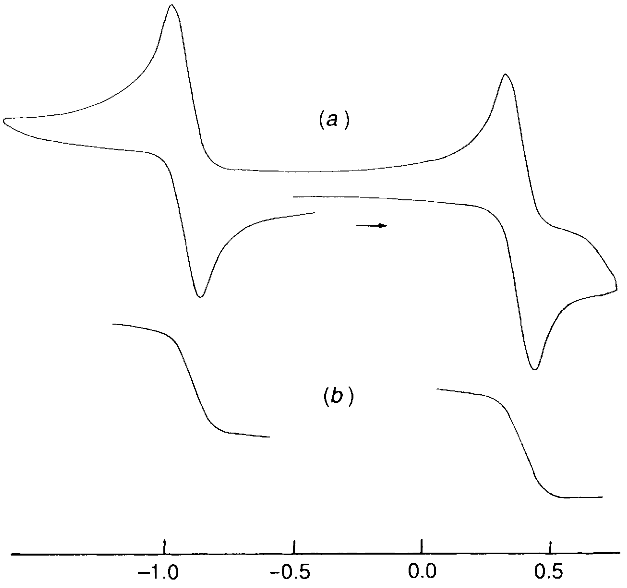

Fig. 1 (*a*) DC cyclic voltammogram for the oxidation and reduction of **1** in CH_2Cl_2 (10^{-3} mol dm^{-3}) with $[Bu_4N][BF_4]$ (0.1 mol dm^{-3}) at the platinum electrode with a scan rate of 100 mV s^{-1}. (*b*) DC polarogram of the same solution as in (*a*) at a dropping mercury electrode.

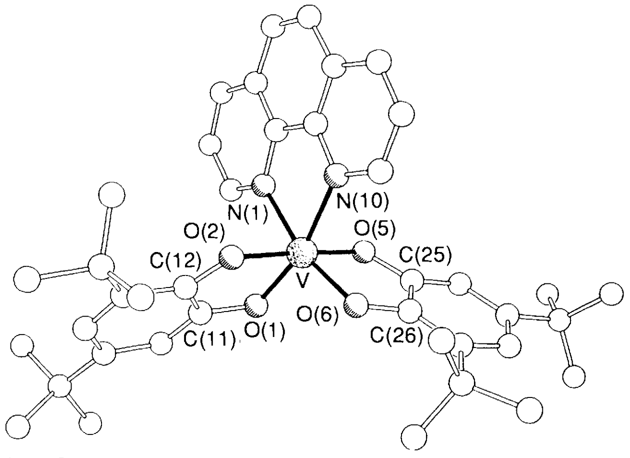

Fig. 2 The X-ray structure of the anion in **2**. **1** has a similar gross structure. Selected bond lengths (Å) and angles (°) for **1** and **2** (in square brackets): V–N(1) 2.122(12) [2.116(9)], V–N(10) 2.171(11) [2.115(8)], V–O(1) 1.926(9) [1.903(6)], V–O(2) 1.885(11) [1.892(7)], V–O(5) 1.897(11) [1.896(6)], V–O(6) 1.918(9) [1.875(7)], mean C–O 1.34 [1.32]. N(1)–V–N(10) 74.6(5) [78.1(3)], O(1)–V–O(2) 81.4(4) [80.2(3)], O(5)–V–O(6) 80.3(4) [81.0(3)], N(1)–V–O(1) 85.3(4) [88.7(3)], N(1)–V–O(2) 104.3(4) [91.1(3)], N(10)–V–O(1) 151.8(4) [165.1(3)], N(1)–V–O(2) 84.6(5) [92.9(3)], N(1)–V–O(5) 85.8(5) [88.0(3)], N(10)–V–O(5) 108.3(5) [91.7(3)], O(1)–V–O(5) 89.3(4) [94.8(3)], O(2)–V–O(5) 165.6(4) [175.0(3)], N(1)–V–O(6) 153.0(5) [165.7(3)], N(10)–V–O(6) 87.9(4) [92.9(3)], O(1)–V–O(6) 117.4(4) [101.3(3)], O(2)–V–O(6) 94.1(5) [100.6(3)].

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† Both compounds gave satisfactory microanalyses and the expected IR and UV–VIS spectra.

‡ *Crystal data* **1**, $C_{40}H_{48}N_2O_4V{\cdot}0.5CH_2Cl_2$, M = 714.2, monoclinic, a = 15.905(6) b = 16.698(6), c = 16.077(5) Å, β = 106.31(3)°, U = 4098 Å^3, space group $P2_1/a$, Z = 4, D_c = 1.156 g cm^{-1}, μ(Cu-Kα) = 29.3 cm^{-1}. Data were measured on a Nicolet R3m diffractometer with graphite monochromated Cu-Kα radiation using ω-scans. The structure was solved by direct methods and refined anisotropically to give R = 0.102, R_w = 0.092 for 2566 independent observed reflections [$|F_o| > 3\sigma(|F_o|)$, $2\theta \leqslant 100°$]. The high final R values are a consequence of the small crystal size (0.04 × 0.07 × 0.18 mm) and the presence of disordered CH_2Cl_2.

2, $C_{40}H_{48}N_2F_6O_4SbV{\cdot}2CH_2Cl_2$, M = 1077.3, monoclinic, a = 13.713(2), b = 17.425(3), c = 21.332(4) Å, β = 104.47(1)°, U = 4936 Å^3, space group $P2_1/n$, Z = 4, D_c = 1.450 g cm^{-3}, μ(Cu-Kα) = 84.5 cm^{-1}. Data were measured as above. The structure was solved by direct methods and refined anisotropically using absorption corrected data to give R = 0.077, R_w = 0.073 for 3951 independent observed reflections [$|F_o| > 3\sigma(|F_o|)$, $2\theta \leqslant 116°$].

Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

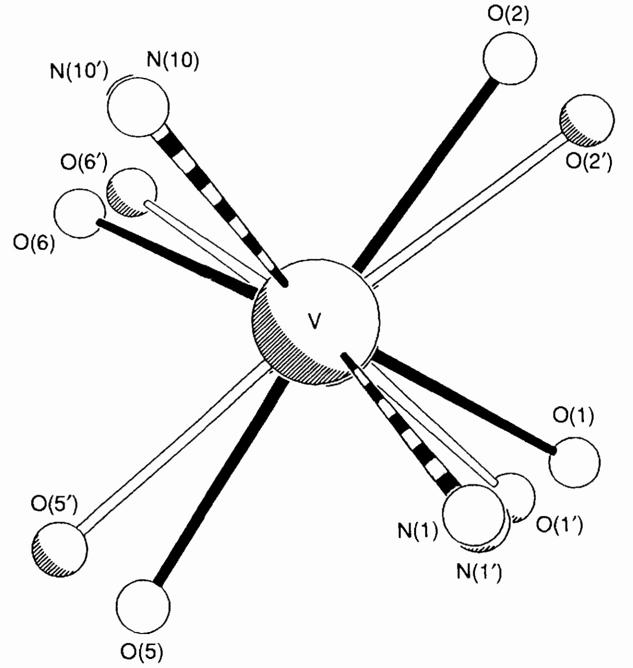

Fig. 3 Superimposition of the coordination spheres of **1** (solid bonds) and **2** (open bonds) viewed down the common N–V–N plane (broken bonds)

spectrum of **2** was not readily observable because of linewidth/sensitivity problems, however, the corresponding BF_4^- salt in $CDCl_3$ gave a signal at $\delta = -202$ (relative to $VOCl_3$) with $\nu_{1/2} = 950$ Hz.

The redox properties of **1** in CH_2Cl_2 have been studied by DC-cyclic voltammetry and polarographic techniques (Fig. 1). The complex displays two reversible one-electron redox processes [eqns. (3) and (4); $E_{1/2}$ *versus* normal hydrogen electrode].

$$[V(dtbc)_2(phen)]^+ + e^- = [V(dtbc)_2(phen)] \quad E_{1/2} = +0.42\ V \qquad (3)$$

$$[V(dtbc)_2(phen)] + e^- = [V(dtbc)_2(phen)]^- \quad E_{1/2} = -0.89\ V \qquad (4)$$

Fig. 2 shows a perspective view of the cation in **2** (**1** has a similar gross structure). Both **1** and **2** crystallise in centrosymmetric space groups thus both Δ and Λ forms are present. It is interesting to note that, of the three possible configurational isomers only the sterically most demanding is observed *i.e.* with the two 3-*tert*-butyl groups *syn*. The V–O bond lengths in **1** and **2** are all equivalent, being independent of the oxidation state of the vanadium atom and the nature of the *trans* atom (average V–O 1.907 and 1.892 Å for **1** and **2**, respectively). Similarly, there are no significant differences in the V–N bond lengths. The bite angles of the two ligands do not differ between the two structures. However, comparison of the coordination angles reveals a marked distortion in the octahedral geometry of **1** *cf.* **2**. If one defines the equatorial planes of the octahedra as comprising of the vanadium atoms and the two nitrogen atoms of the phenanthroline together with the *trans* oxygen atoms O(1)/O(1′) and O(6)/O(6′) then two principal differences between **1** and **2** are apparent (Fig. 3). Firstly, the axial O(2)–O(5) axis is noticeably twisted from an orthogonal relationship with the equatorial plane and secondly, there is a more pronounced out of plane twisting of the O(1)–V–O(6) plane w.r.t. the N–V–N plane within the equatorial plane in **1**. This is also reflected by a variation of up to 17° in the angles subtended at vanadium by the different substituent atoms on going from **1** to **2**. Thus, the significant difference on changing oxidation state is in the coordination angles and not in the bond lengths with V^{IV} being very much more distorted than V^V. The substantial difference in geometry between **1** and **2** is quite remarkable and may have important implications in understanding the role of vanadium in biological systems.

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References

1 M. E. Cass, N. R. Garolon and C. G. Pierpont, *Inorg. Chem.*, 1986, **25**, 3962.
2 T. W. Hambley, C. J. Hawkins and T. A. Kabanos, *Inorg. Chem.*, 1987, **26**, 3740.
3 M. Carrondo, M. Duarte, J. Pessoor, J. Silvod, J. F. Silva, M. Vaz and L. Vilas-Boas, *J. Chem. Soc., Chem. Commun.*, 1988, 1158.
4 T. A. Kabanos, A. M. Z. Slawin, D. J. Williams and J. D. Woollins, *J. Chem. Soc., Chem. Commun.*, 1990, 193.
5 U. Auerbach, B. Della Veolova, K. Wieghardt, B. Nuber and J. Weiss, *J. Chem. Soc., Chem. Commun.*, 1990, 1004.
6 J. A. Bonadies, W. M. Butler, V. L. Pecoraro and C. J. Carrano, *Inorg. Chem.*. 1987, **26**, 1218.
7 This complex was prepared by a modification of the reported procedure: B. Gallefi and M. Postel, *Nouv. J. Chim.*, 1984, **8**, 481.