

## A Tetranuclear Polyfunctional Sodium–Vanadium(III) Complex containing a Vanadium(III)–Vanadium(III) Double Bond

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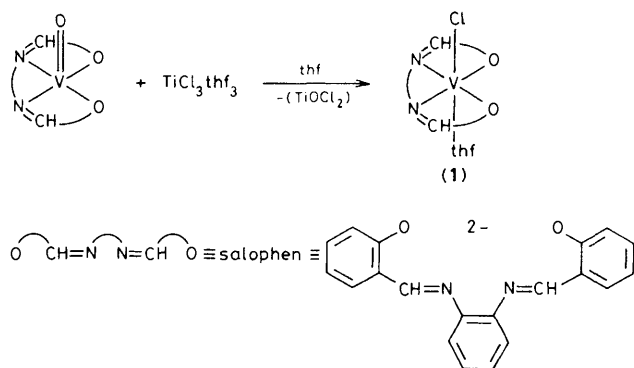
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Reduction of *N,N'*-*o*-phenylenebis(salicylideneiminato)chlorovanadium(III), [(thf)V(salophen)Cl] (thf = tetrahydrofuran), with sodium metal caused the dimerization of two metallic moieties through two C–C bonds leading to a tetranucleating ligand binding two sodium cations and two vanadium(III) joined by a double bond [2.406(3) Å].

A major goal in co-ordination chemistry is to design complexes which can act as electron reservoirs and contain different reactive sites in their structure. These are two important prerequisites for complexes used for promoting the activation of small organic molecules. Tetradentate Schiff bases are appropriate ligands for building up such complexes.<sup>1–3</sup> In this context, we are currently studying the

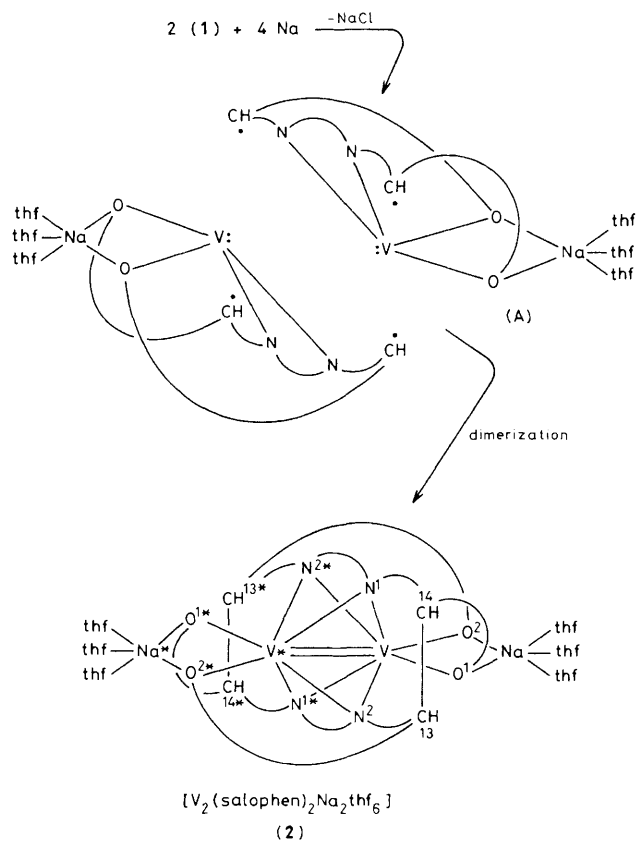
reduction of vanadium(IV)<sup>4</sup> and vanadium(III) Schiff base complexes. Moreover, it must be emphasized that the knowledge of the co-ordination chemistry of vanadium in a low oxidation state is surprisingly poor,<sup>5</sup> in spite of its role in N<sub>2</sub><sup>6</sup> and O<sub>2</sub><sup>7</sup> reduction, and in the chemistry of some naturally occurring systems.<sup>8</sup>

The present report concerns the chemical reduction of



complex (1), [V(Cl)(salophen)(thf)] [thf = tetrahydrofuran; salophen = *N,N'*-*o*-phenylenebis(salicylideneiminato) dianion] obtained from the reduction of [VO(salophen)] or [V(salophen)Cl<sub>2</sub>]. The synthesis of the related complexes [V(salophen)(X)py<sub>*n*</sub>] [X = Cl, Br; py = pyridine; *n* = 1, 2] has been reported,<sup>9</sup> but they cannot be utilized owing to the presence of pyridine. A thf suspension of [VO(salophen)] was treated with an equimolar thf solution of [TiCl<sub>3</sub>thf<sub>3</sub>]. From the resulting solution complex (1) crystallized out in a few minutes (*ca.* 89%),<sup>†</sup> while an unidentified oxotitanium species remained in solution (Scheme 1). The structure proposed for (1) is based on a preliminary X-ray analysis.<sup>10</sup>

Complex (1) undergoes a rather complex transformation with sodium metal. A thf suspension of (1) (1 mol) was treated with sodium sand (2 mol) for 1 h at room temperature, and the resulting deep-orange solution refluxed for 1 h. Sodium chloride was filtered off and on addition of Et<sub>2</sub>O complex (2) crystallized out (*ca.* 55%).<sup>‡</sup> Scheme 2 depicts the formation of complex (2), which can be considered as resulting from the dimerization of fragment (A), formed by a two electron reduction of (1). The reaction shown in Scheme 2 does not cause any change in the oxidation state of vanadium, but leads to the reduction of the salophen ligand *via* the formation of a formal biradical on the imino carbon atoms. These carbon radicals couple joining two (A) fragments. The vanadium–vanadium double bond can be formally seen as resulting from the coupling of d<sup>2</sup> carbenes. A view of the structure of (2)<sup>‡</sup> is



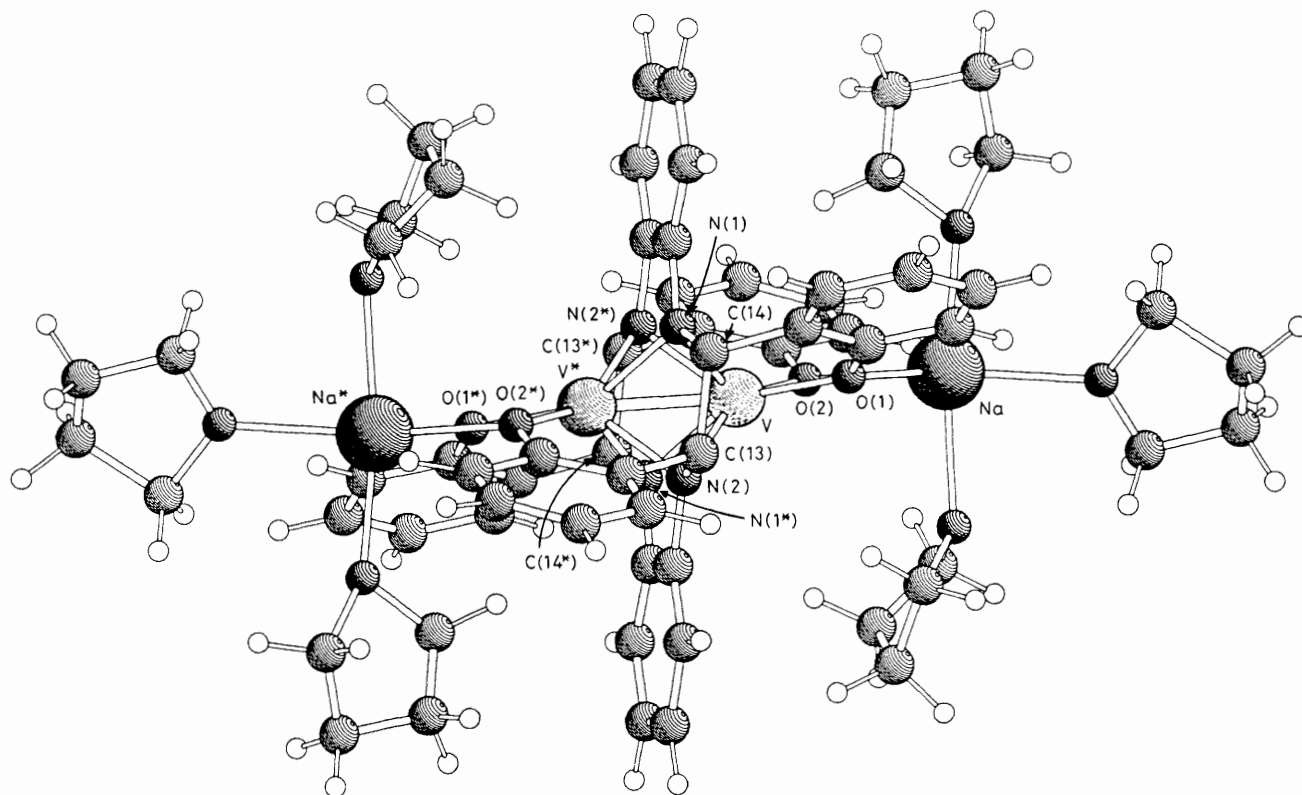
shown in Figure 1 and, in a simplified form, in Scheme 2, both having the same numbering scheme. The most relevant bond distances are reported in the caption to Figure 1. Complex (2) has *C*<sub>2</sub>(1) symmetry. The four metal atoms Na\*, V\*, V, and Na are nearly co-linear and they are bound closely together by a polynucleating ligand derived from the reductive coupling of two salophen units. The original salophen moiety lost its stereochemical rigidity and planarity because of the cleavage of the C–N double bonds to single bonds [C(13)–N(2), 1.480(9); C(14)–N(1), 1.487(9) Å]. The sodium cation is five-co-ordinate and vanadium(III) seven-co-ordinate. The V–N bond distances are very similar to those found in similar complexes,<sup>4,10</sup> while the V–O bond distances are significantly longer. The V–V bond distance [2.406(3) Å] is as expected for a double bond,<sup>11</sup> and complex (2) is diamagnetic.

Redox reactions of transition metal chelate complexes lead either to a change in the oxidation state of the metal or the generation of free radical, electrophilic, and nucleophilic sites on the ligand.<sup>12</sup> The reductive coupling of imino groups from the salophen ligand was also observed in the one-electron reduction of Ni<sup>II</sup> complexes with alkali metals.<sup>13</sup> The C–C bond distances are similar in both cases. A two electron reduction of [Ni(salophen)] led to a polymeric material, rather than to a dimeric complex like (2).<sup>13</sup> A feature of the nickel complexes is that the C–C bond can be cleaved under mild conditions, providing two electrons for redox processes.<sup>13</sup> Two characteristics of complex (2), which is very reactive with many substrates, have to be considered when noting the curiosities of the structure. (i) The polyfunctionality, provided by the presence of very different reactive sites in the structure: the sodium cation is the acidic site, while vanadium in a low

<sup>†</sup> Satisfactory analytical data have been obtained.

<sup>‡</sup> *Crystal data:* C<sub>64</sub>H<sub>76</sub>N<sub>4</sub>Na<sub>2</sub>O<sub>10</sub>V<sub>2</sub>, *M* = 1209.20, monoclinic, *P*2<sub>1</sub>/*n*, *a* = 10.651(5), *b* = 21.268(8), *c* = 13.581(6) Å, β = 92.51(5)°, *U* = 3073.5(4) Å<sup>3</sup>, *D*<sub>c</sub> = 1.307 g cm<sup>-3</sup>, *Z* = 2, *F*(000) = 1272. Intensity data were collected with Mo-*K*<sub>α</sub> to θ = 27° using the θ–2θ scan mode. Unit cell parameters were obtained from accurate centring of 25 strong reflections. Intensities of 3094 independent reflexions were measured with an Enraf–Nonius CAD-4 diffractometer equipped with a graphite monochromator. No correction for absorbance was applied. The positional parameters of the vanadium ion were determined by a three dimensional sharpened Patterson map. The remaining atoms were localized by direct methods, temporarily eliminating the large structure factors of the vanadium ion, and by weighted difference Fourier maps followed by least-squares refinements and further Fourier maps. 2206 Reflexions [*F*<sub>o</sub> > 2σ(*F*<sub>o</sub>)] were used in the anisotropic refinement with unit weights; the final *R*-index was 0.0675.

The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.



**Figure 1.** A view of complex (2). Bond distances (Å): V–V\*, 2.406(3); V–O(1), 2.003(6); V–O(2), 1.994(5); V–N(1), 2.050(5); V–N(2), 2.087(6); V–N(1\*), 2.082(5); V–N(2\*), 2.050(6); Na–O(1), 2.280(6); and Na–O(2), 2.334(7). \* = -x, -y, -z.

oxidation state is the electron rich, nucleophilic site. A similar arrangement of acidic–basic sites was observed in bifunctional cobalt(1)–sodium complexes active in carbon dioxide fixation.<sup>3</sup> (ii) The electron rich nature, since complex (2) can be considered as a potential 'six electron reservoir' consisting of the two C–C bonds joining the salophen units and the possible VIII–V<sup>IV</sup> oxidation process.

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