

## Sigma Bond Cleavage in Coordinated Dioxygen: the Case of the $\mu$ -Peroxo Complex, $[(\text{THF})_3\text{Cl}_2\text{V}^{\text{III}}-(\text{O}_2^{2-})-\text{V}^{\text{III}}\text{Cl}_2(\text{THF})_3]$ and Vanadyl Formation in Solution

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### Abstract

The results of orbital interaction calculations of a comparative nature, using the extended Hückel approach, are presented for several low-valence vanadium complexes with side-on bonded dioxygen; these are believed to be produced upon reaction of low valence vanadium species with molecular oxygen. In the mononuclear complex  $[\text{Cl}_5\text{V}^{\text{IV}}(\eta^2\text{-O}_2^{2-})]^{3-}$  and the *trans*-bent  $\mu$ -peroxo dinuclear complex,  $[\text{Cl}_5\text{-V}^{\text{III}}(\text{O}_2^{2-})\text{V}^{\text{III}}\text{Cl}_5]^{6-}$ , cleavage of the O–O bond is not indicated. However, in the dihapto  $\mu$ -peroxo dinuclear complexes  $[\text{Cl}_5\text{V}^{\text{III}}-(\eta^2\text{-O}_2^{2-})-\text{V}^{\text{III}}\text{Cl}_5]^{6-}$  and  $[(\text{H}_2\text{O})_3\text{Cl}_2\text{V}^{\text{III}}-(\eta^2\text{-O}_2^{2-})-\text{V}^{\text{III}}\text{Cl}_2(\text{H}_2\text{O})_3]$ , with the latter being used as an approximation for  $[(\text{THF})_3\text{Cl}_2\text{V}^{\text{III}}(\eta^2\text{-O}_2^{2-})\text{V}^{\text{III}}\text{Cl}_2(\text{THF})_3]$ , effective metal d  $\rightarrow$  ligand  $\sigma^*$  backdonation results in O–O bond cleavage. The results of the calculations indicate that an intermediate for which the last-named complex could serve as a model could possibly be responsible for O–O bond cleavage in coordinated dioxygen and subsequent generation of vanadyl species in solution. Potential implications for processes of  $\text{O}_2$ -activation and O-atom insertion by transition metal centers are discussed.

### Introduction

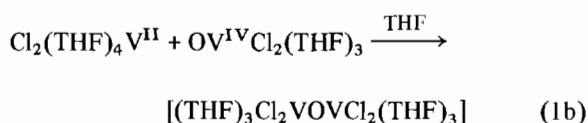
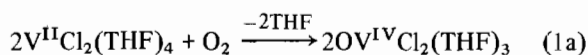
The reactions of molecular oxygen with transition metal centers have been the subject of intense interest recently [1], primarily because of their importance in yielding insights into biological  $\text{O}_2$ -activation processes [1a, 2]. In the oxidation of low-valence transition metals by molecular oxygen, dinuclear  $\mu$ -oxo dimers have been well established [3, 4] as isolable intermediates, in both aqueous

and organic [5] media. These intermediates have been observed for Cr(III) [4c–e, 6a] ( $[\text{Cr}-\text{O}-\text{Cr}]^{4+}$ ), V(III) [4b, 6b, c] ( $[\text{V}-\text{O}-\text{V}]^{4+}$ ), Fe(III) [5, 7, 8a, b] ( $[\text{Fe}-\text{O}-\text{Fe}]^{4+}$ ), Co(III) [9a] ( $[\text{Co}-\text{O}-\text{Co}]^{4+}$ ) Mn(III) [9b] copper and other metals [9c, 10]. A common mode of production of the dinuclear  $\mu$ -oxo intermediate in all the above-cited cases has been shown to proceed [4b, 6b, c] through a reaction pathway involving initial production of a metalloxo, 'yl' species (e.g. vanadyl,  $\text{VO}^{2+}$ ) by reaction of the metal (usually initially divalent) with molecular oxygen; this process involves O–O bond breaking and is thought to be poorly understood [4, 6]. This species then reacts further with the divalent metal to yield the isolable  $\mu$ -oxo dimer (e.g.  $\text{VO}^{2+} + \text{V}^{2+} \rightarrow [\text{V}-\text{O}-\text{V}]^{4+}$ ). For the production of the initial metalloxo species from reaction of the transition metal with molecular oxygen, there has been strong indirect evidence for the existence of dinuclear  $\mu$ -peroxo complexes as precursors [8a–c, 11, 12]. For instance, in oxidation of  $\text{FeCl}_2$  by  $\text{O}_2$  yielding  $\text{FeOCl}_2$ , evidence [5] for  $[\text{Cl}_2\text{Fe(III)}-(\text{O}_2^{2-})-\text{Fe(III)Cl}_2]$ ; in oxidation, by  $\text{O}_2$  in toluene at low temperature, of Co(II) protoporphyrin IX dimethyl ester [13] and *meso* tetra *m*-tolyl porphyrin Fe(II) [12a], evidence for intermediates  $[(\text{P})\text{Co(III)}-(\text{O}_2^{2-})-\text{Co(III)(P)}]$  and  $[(\text{P})\text{Fe(III)}-(\text{O}_2^{2-})-\text{Fe(III)(P)}]$  (P = porphyrinato) respectively. The general mode of reactivity with  $\text{O}_2$  thus appears to be similar for all metals cited. In the case of synthetic catalytic oxidations by  $\text{O}_2$  [8e, 14, 15], there is some evidence [17d] that dinuclear  $\mu$ -peroxo active species are involved. The ubiquitous synthetic olefin epoxidations [2d, 16, 17] are of course other examples of biomimetic  $\text{O}_2$ -activation where the active oxygenators are still little understood. Although in cytochrome P-450 oxygenations [2a], 'oxenoid' [18] active species have been preferred to the alternative dinuclear  $\mu$ -peroxo species, the generation of the active oxygenator through O–O bond scission

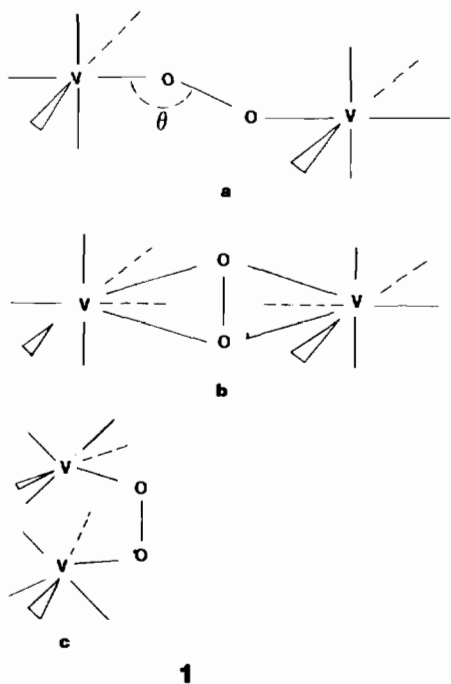
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is still little understood [19]. In the cytochrome *c*-oxidases, responsible for reduction of  $O_2$  transported from the respiratory interface, bimetallic  $\mu$ -peroxo  $-\text{Fe(III)}-(O_2^{2-})-\text{Cu(II)}-$  species have been strongly implicated as active oxygenating intermediates, and  $\mu$ -oxo dimers, e.g.  $-\text{Fe(II)}-\text{O}-\text{Cu(II)}-$  have been observed in many cases [20]. In this brief communication studying a case of divanadium  $\mu$ -oxo dimer formation, we report theoretical evidence, for the first time to our knowledge, that O–O bond breaking can occur in a coordinated dioxygen, with a  $d-\sigma^*$  interaction intimately involved.

Our attention was directed to recent work in which a dinuclear  $\mu$ -oxo V(III) intermediate species,  $[(\text{THF})_3\text{Cl}_2\text{VOVCl}_2(\text{THF})_3]$ , containing the  $\text{V}^{\text{III}}-\text{O}-\text{V}^{\text{III}}$  moiety delineated earlier, was isolated from THF solution at low temperature by Chandrasekhar and Bird [21] and its crystal structure determined. In this work, following the proposed initial production of V(II) through reduction of  $\text{V}^{\text{III}}\text{Cl}_3$  by  $\text{AlEt}_3$ , the following reaction scheme could be formulated:



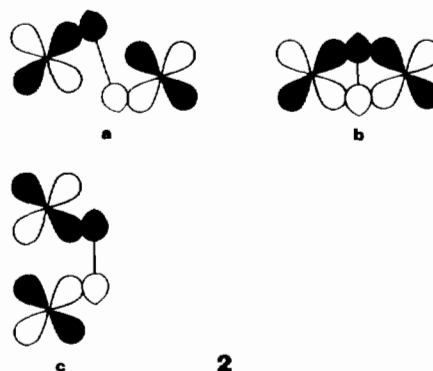
Scheme 1.



We wished to probe this system, specifically as regards presumed O–O bond cleavage in step 1a and eventual formation of the  $\mu$ -oxo dimer.

### Geometry of Dinuclear $\mu$ - $O_2$ Intermediates

As was sought to be demonstrated in the introductory section above, there has been strong experimental evidence for dinuclear  $\mu$ -peroxo intermediates as precursors to the isolable dinuclear  $\mu$ -oxo dimers for virtually all transition metal ions considered. Besides the possible *trans*-bent (**1a**) and dihapto (**1b**) structures for dinuclear  $\mu$ - $(O_2)^*$  intermediates, an additional structure is a *cis*-bent structure of the skeletal form **1c**; this was considered, for instance, by Hoffmann *et al.* [22] in theoretical treatment of porphyrinato transition metal complexes with bridging dioxo ligands. There is substantial electron density resident in each of the  $d_\pi$  orbitals in the case of V(II), and the expected  $d-\sigma^*$  interactions



corresponding to the structures **1** are shown in schematic in **2**. We considered the structures **1a**, **1b** as well as a  $\eta^2$ -mononuclear structure in our study of O–O bond weakening. Our original contention was that only in the case of the  $\eta^2$ -dinuclear structure (**1b**) would O–O  $\sigma^*$  orbital population from  $d-\sigma^*$  interaction be significant to cause O–O bond rupture; the  $\eta^2$ -mononuclear and the *trans*-bent dinuclear structures would yield more stable complexes. The *cis*-bent structure (**1c**) was not considered at this point. Extended Hückel methodology [23] with a fragment approach [24] for the metal-centered orbitals was adopted in this work. The case where all ligands coordinated to the V, taken to be in the  $d^3$  V(II) state, were chloro ligand was considered first, since this high symmetry state would highlight any bonding trends observed. The results of a total of four performed calculations are reported in this brief communica-

\* $O_2$  here is generic for  $O_2$ ,  $O_2^-$  and  $O_2^{2-}$ .

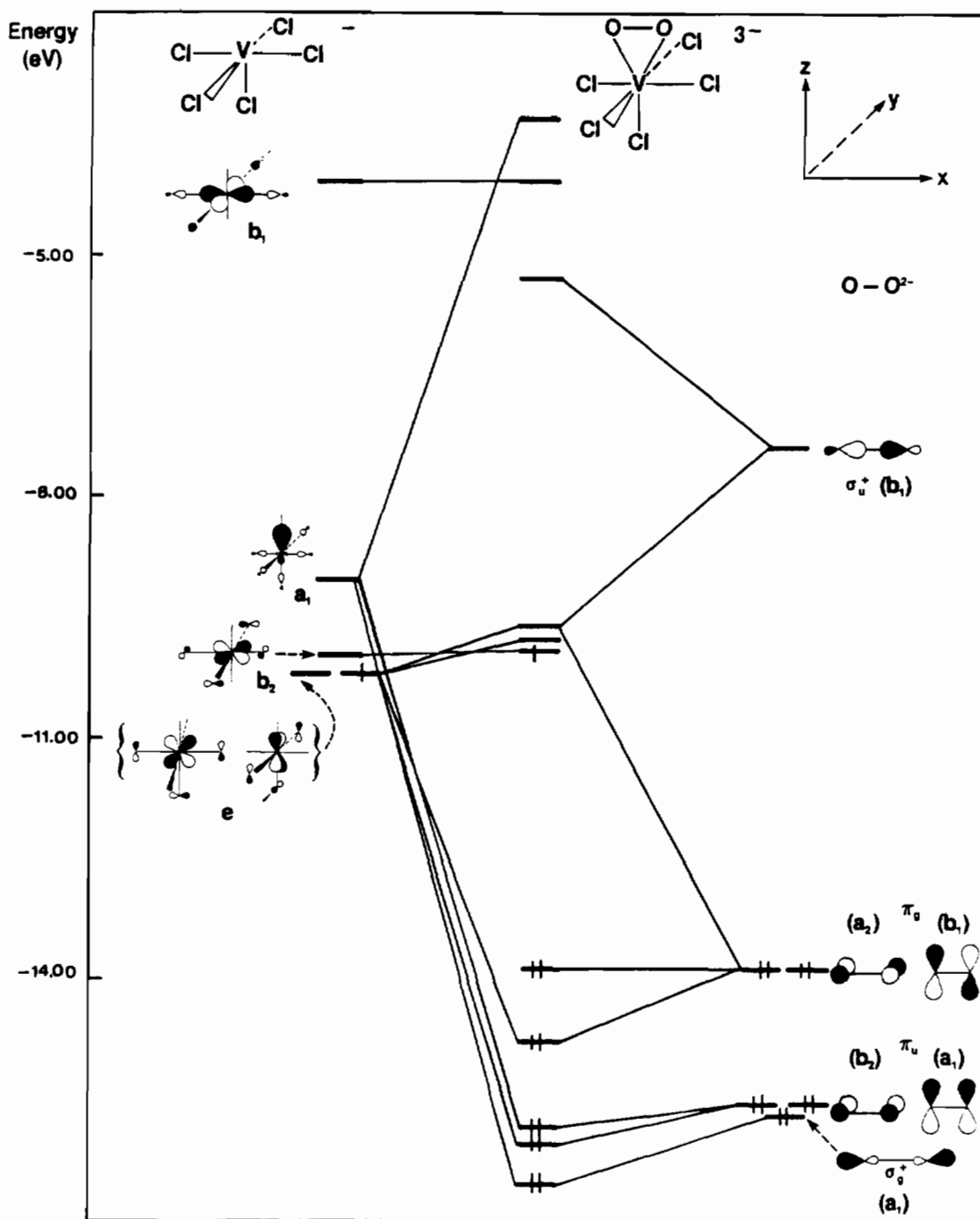


Fig. 1. Orbital interaction diagram of  $O_2^{2-}$  (with the O—O distance taken as 1.46 Å) with the metal fragment  $[Cl_5V(II)]^-$ , to produce  $[Cl_5V(O_2)]^{3-}$ . Orbital symmetry labels are  $C_{4v}$  for  $[VCl_5]^-$  and  $D_{\infty h}$  ( $C_{2v}$ ) for  $O_2^{2-}$ . Note that the dioxygen  $\sigma_u^+$  orbital has been significantly lowered due to stretching of the O—O bond.

tion: for  $[Cl_5V(\eta^2-O_2)]^{3-}$  with O—O = 1.21 Å and 1.46 Å; for  $[Cl_5V(\eta^2-O_2^{2-})VCl_5]^{6-}$ ; for  $[(H_2O)_3Cl_2V(\eta^2-O_2^{2-})VCl_2(H_2O)_3]$  with  $H_2O$  taken as an approximation for THF; and for  $[Cl_5V(trans-bent-O_2^{2-})VCl_5]$  with O—O distance 1.46 Å, V—O distance 1.81 Å and  $\theta(V-O-V)$  (*cf.* 1a) = 145°, approximating reported distances and angles [25].

#### Fragment Orbitals for Mononuclear and Dinuclear Species

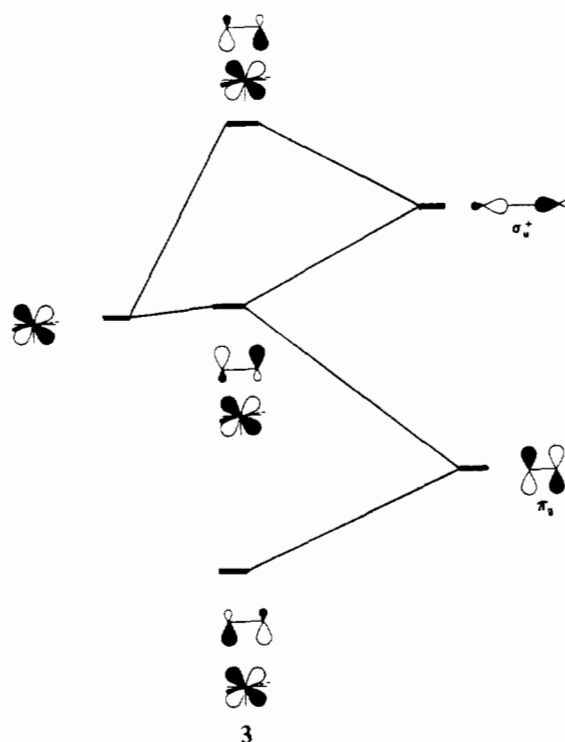
Figure 1 shows an interaction diagram for the formation of  $[Cl_5V(O_2)]^{3-}$  from  $VCl_5^-$  and  $O_2^{2-}$  fragments. Since the calculation for  $[Cl_5V(O_2)]^{3-}$  with an O—O bond length of 1.21 Å (more closely approximating that in free molecular  $O_2$ ) indicates

substantial reduction of the O<sub>2</sub> ligand, an O–O distance of 1.46 Å, typical for a η<sup>2</sup>-peroxo ligand [26] was taken in Fig. 1 and subsequent calculations. The well-known frontier orbitals of O<sub>2</sub> appear on the right side of Fig. 1 with both C<sub>2v</sub> and D<sub>∞h</sub> labels. The lowest orbital is the σ-symmetry a<sub>1</sub>, having lone-pair character, followed at slightly higher energy by the bonding π<sub>u</sub> pair. The degenerate HOMOs are the antibonding π<sub>g</sub> set. σ<sub>u</sub><sup>+</sup> is strongly σ-antibonding, but has dropped in energy relative to free (neutral) O<sub>2</sub> due to O–O bond stretching. On the left side of the figure are the d orbitals of VCl<sub>5</sub><sup>−</sup>. The two highest (b<sub>1</sub>, a<sub>1</sub>) energy orbitals are metal–ligand σ-antibonding. The b<sub>1</sub> orbital (metal x<sup>2</sup> – y<sup>2</sup>) is destabilized by interaction with four basal chlorides, whereas the a<sub>1</sub> (z<sup>2</sup>) orbital interacts primarily with the apical chloride and is less destabilized. p–d mixing hybridizes the metal orbital away from the apical chloride, toward the open coordination site and further reduces the antibonding interaction. The remaining three metal d orbitals (b<sub>2</sub> and the e pair) have V–Cl π\* character. xy (b<sub>2</sub>) appears at higher energy than the e pair, xz and yz, because xy interacts with *four* chloride ligands in a π-antibonding way.

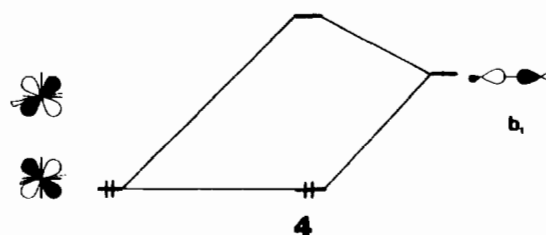
Interacting the two fragments allows the metal z<sup>2</sup> orbital to interact with σ<sub>g</sub><sup>+</sup> and one member of the π<sub>u</sub> set. The z<sup>2</sup> becomes a V–O σ\* orbital and the two filled oxygen levels mix with z<sup>2</sup> to give its σ bonding counterpart. The second member of the oxygen π<sub>u</sub> pair is stabilized by a π interaction with the vanadium yz orbital. One of the π<sub>g</sub> orbitals (a<sub>2</sub>) has a poor δ type overlap with metal xy and remains at the same energy. The other π<sub>g</sub> (b<sub>1</sub>) orbital can mix with metal xz and oxygen σ<sub>u</sub><sup>+</sup> to give a three orbital, two-electron interaction shown in a simplified way in 3.

The frontier orbitals of [Cl<sub>5</sub>V(O<sub>2</sub>)VCl<sub>5</sub>]<sup>6−</sup> are derived from the orbitals of O<sub>2</sub><sup>2−</sup> and VCl<sub>5</sub><sup>2−</sup> in Fig. 2; the parenthetical labels for O<sub>2</sub><sup>2−</sup> are again in C<sub>2v</sub>. The left side of the figure shows the relevant orbitals of [VCl<sub>5</sub><sup>2−</sup>]<sub>2</sub>. The lowest orbitals for this are the π(e<sub>u</sub>) and the π\*(e<sub>g</sub>) combinations of vanadium xz and yz, followed by δ and δ\* orbitals (b<sub>1u</sub>, b<sub>2g</sub>) of metal xy character. Immediately above are the bonding and antibonding z<sup>2</sup> combinations (a<sub>1g</sub>, a<sub>2u</sub>).

Inserting the O<sub>2</sub><sup>2−</sup> fragment between the two Cl<sub>5</sub>V<sup>2−</sup> units gives a bonding description similar to the mononuclear case but with additional symmetry restrictions now mediating some of the orbital interactions. For the lower three O<sub>2</sub><sup>2−</sup> orbitals, the interactions are similar to those in Cl<sub>5</sub>V(O<sub>2</sub>)<sup>3−</sup>. σ<sub>g</sub><sup>+</sup> interacts with the bonding combination of metal z<sup>2</sup>, and one of the π<sub>u</sub> orbitals (a<sub>1</sub>) interacts with the out-of-phase z<sup>2</sup> (a<sub>2u</sub>) combination to form σ-bonding and antibonding pairs. Likewise, the second metal π<sub>u</sub> orbital (b<sub>2</sub>) forms a π-bonding level by interacting with the bonding combination of vanadium



yz. The π<sub>g</sub> orbitals are split since a<sub>2</sub> interacts only weakly with one of the metal xy orbitals (b<sub>2g</sub>) and remains approximately non-bonding, whereas b<sub>1</sub> is pushed down by a strong bonding interaction with one of the vanadium xz. Finally, the σ<sub>u</sub><sup>+</sup> interacts with the lower-energy vanadium xz (left member of the e<sub>u</sub> pair) as shown schematically in 4. The situation in 4, where the lower, bonding mixture of metal orbitals and σ<sub>u</sub><sup>+</sup> is filled, can be contrasted with the situation in Cl<sub>5</sub>V(O<sub>2</sub>)<sup>3−</sup> (3) in which it is empty. In 3, one of the oxygen π<sub>g</sub> orbitals mixes in and pushes this orbital high enough in energy to remain empty. In [Cl<sub>5</sub>V(O<sub>2</sub>)VCl<sub>5</sub>]<sup>6−</sup>, symmetry restrictions require the corresponding oxygen orbital to mix with the out-of-phase metal xz combination, as mentioned above, rather than the in-phase combination (as in 4). The result is a low energy, occupied orbital with substantial O–O σ\* character. The additional calculation we carried out on the similar dinuclear complex, [(H<sub>2</sub>O)<sub>3</sub>Cl<sub>2</sub>V-η<sup>2</sup>-(O<sub>2</sub><sup>2−</sup>)-VCl<sub>2</sub>-(H<sub>2</sub>O)<sub>3</sub>] used as a model for [(THF)<sub>3</sub>Cl<sub>2</sub>V-(O<sub>2</sub><sup>2−</sup>)-



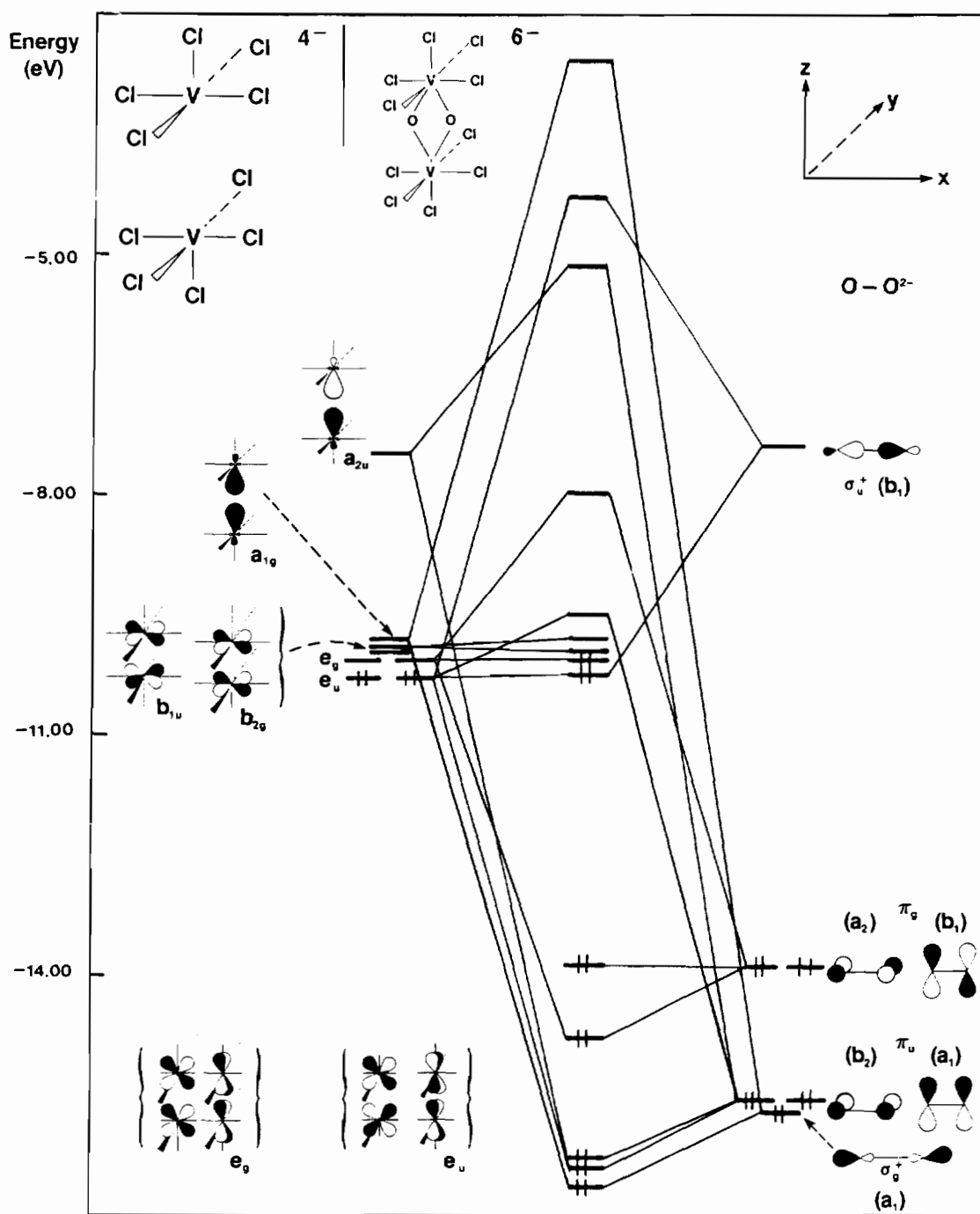


Fig. 2. Orbital interaction of the dinuclear fragment  $[\text{Cl}_5\text{V}^{\text{II}}-\text{V}^{\text{I}}\text{Cl}_5]^{6-}$  with dioxygen, in which the O-O distance is 1.46 Å, approximating a peroxo ligand, to yield  $[\text{Cl}_5\text{V}^{\text{II}}-(\eta^2-\text{O}_2)-\text{V}^{\text{I}}\text{Cl}_5]^{6-}$ .

$\text{VCl}_2(\text{THF})_3$ ] again indicated substantial population of the  $\sigma^*$  orbital. These calculations are summarized in a comparative manner in Table I, which gives O-O overlap populations (where available) and oxygen fragment orbital occupations for  $\text{O}_2^{2-}$  and the complexes. Overlap populations appear to indicate that

in the case of the  $\mu-\eta^2-(\text{O}_2^{2-})$  dinuclear complexes only the O-O bond is broken, with population of the O-O  $\sigma^*$  orbital being determinative. A caveat concerning our calculations on the dinuclear species, especially as applicable to other transition metals, should be mentioned. Our analysis assumes a low-spin

TABLE I. O–O Overlap Populations and O<sub>2</sub><sup>2-</sup> Fragment Orbital Occupations for the Species shown. In Each Case, the O–O Distance was 1.46 Å

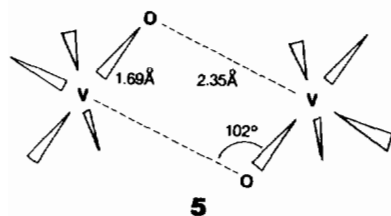
Compound	O–O overlap population	Orbital occupations			
		$\sigma_u^+$	$\pi_g$	$\pi_u$	$\sigma_g^+$
O <sub>2</sub> <sup>2-</sup>	0.346	0.00	2.00 2.00	2.00 2.00	2.00
[Cl <sub>5</sub> V(O <sub>2</sub> )] <sup>3-</sup>	0.375	0.02	a <sub>2</sub> : 1.91 b <sub>1</sub> : 1.81	b <sub>2</sub> : 1.92 a <sub>1</sub> : 1.94	1.99
[Cl <sub>5</sub> V(O <sub>2</sub> )VCl <sub>5</sub> ] <sup>6-</sup>	-0.025	1.11	a <sub>2</sub> : 1.67 b <sub>1</sub> : 1.82	a <sub>1</sub> : 1.77 b <sub>2</sub> : 1.84	2.00
[(H <sub>2</sub> O) <sub>3</sub> Cl <sub>2</sub> V(O <sub>2</sub> )VCl <sub>2</sub> (H <sub>2</sub> O) <sub>3</sub> ]	0.015	1.02	a <sub>2</sub> : 1.65 b <sub>1</sub> : 1.80	a <sub>1</sub> : 1.77 b <sub>2</sub> : 1.84	1.99
[Cl <sub>5</sub> V–O–O–VCl <sub>5</sub> ] <sup>6-</sup>	0.225	0.11			1.98

electronic configuration, but the closely-spaced group of five d-orbitals in Fig. 2 suggests that a high-spin complex should also be considered possible.

### Vanadyl Formation in Solution

The analyses presented in Figs. 1 and 2 appear to indicate that a vanadyl species, if produced in solution, could emanate from the interaction of two metal centers with dioxygen, through the intermediacy of a  $\mu\text{-}\eta^2$ -(peroxo) complex. It is to be noted that while *trans*-bent dinuclear  $\mu$ -peroxo structures have been isolated in the case of a number of transition metals, e.g. Co [25], a  $\mu\text{-}\eta^2$ -(peroxo) dinuclear structure has been isolated only in the case of U in [Cl<sub>3</sub>O<sub>2</sub>U–(O<sub>2</sub>)–UO<sub>2</sub>Cl<sub>3</sub>]<sup>4-</sup>, where the role of f orbitals in stabilization of the complex is not yet fully known [27].

A possible intermediate between a  $\mu\text{-}\eta^2$ -(O<sub>2</sub><sup>2-</sup>) structure and two vanadyl species in solution is a structure in which one of the V–O bonds is slightly elongated for each vanadium; this type of structure is observed in a series of complexes of which [V<sub>2</sub>O<sub>4</sub>–



F<sub>2</sub>(bpy)<sub>4</sub>], which was isolated in crystalline form by Guerchais and coworkers [28], is representative. In this complex then, the distance (see 5) corresponding to the bonding, V–O(proximal) interaction is 1.69 Å, whilst the V–O(distal) distance is 2.35 Å. The Bragg–Slater atomic radii for V and O [29] sum to 1.95 Å, although it may be observed

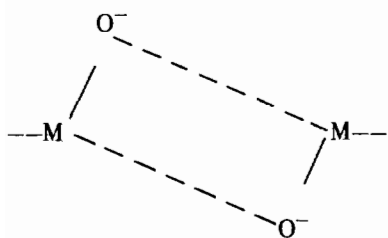
that in [(THF)<sub>3</sub>Cl<sub>2</sub>VOVCl<sub>2</sub>(THF)<sub>3</sub>] the V–O(main-axial THF) and the V–O(*trans*-axial THF) distances are 2.17 and 2.26 Å respectively [21]. Thus the 2.35 Å V–O distance in the bipy-complex could, conceivably, be considered to be within the limits of a bonding interaction. A plausible mode for the production of vanadyl species from the interaction of V(II) and molecular oxygen in THF medium, which emerges from the results of the present analysis, could then be as formulated in Scheme 2.

The present authors wish to point out that Scheme 2, and particularly the intermediate labeled (G) in Step 2, are important in several respects: (i) A generalized form of the scheme, *viz.* L<sub>n</sub>M(II) + O<sub>2</sub> + L'<sub>n</sub>M'(II) →  $\mu\text{-}\eta^2$ -(O<sub>2</sub><sup>2-</sup>) intermediate → L<sub>(n-1)</sub>M(IV)O + OM'(IV)L'<sub>(n-1)</sub>; L<sub>n</sub>M(II) + OM'(IV)L'<sub>(n-1)</sub> → L<sub>(n-1)</sub>M(III)–O–M'(III)L'<sub>(n-1)</sub> etc. (the transition metal typically, but not necessarily\* initially divalent) may represent a general mode of reactivity for molecular oxygen, as the work on other metal ions summarized in the introduction strongly indicates. More conclusive evidence for this would of course depend upon a similar theoretical examination of other metal ions yielding similar results. (ii) Theoretical analysis of dinuclear transition metal intermediates containing doubly bridged species by Burdett [30] has shown that the asymmetric bond breaking scheme depicted in Step 2 is more favorable than a symmetric one. (iii) The general mode of reactivity in (i) above, if indeed correct, could account for the production of the  $\mu$ -oxo Fe(III) porphyrin dimers inevitably produced [2a, 8, 12] upon oxidation by O<sub>2</sub> of free (*i.e.* unattached to a protein substrate) ferrous porphyrins\* in the following way (P = porphyrinato):

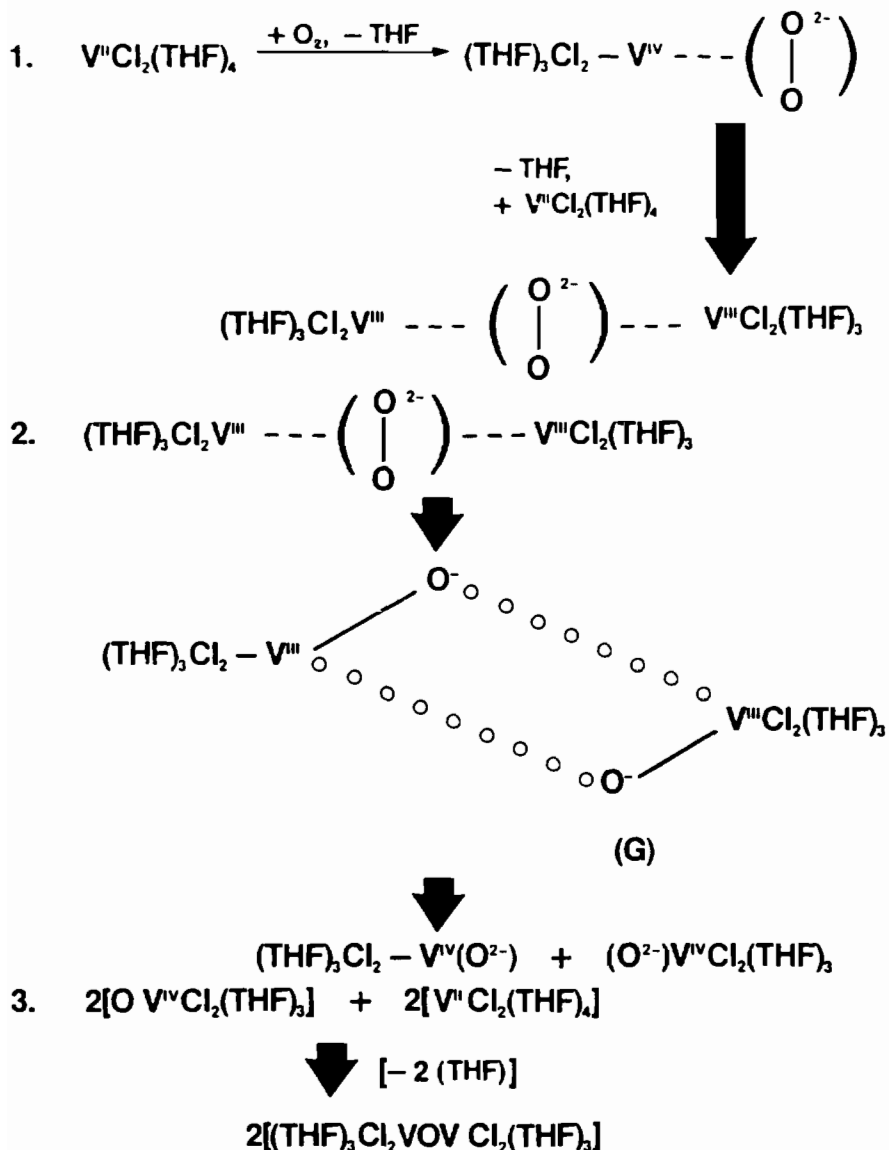
\*For Mn(III) → Mn(V) (metal initially trivalent) *cf.* ref.16a.

\*Strong evidence for the earlier-predicted porphyrinato 'ferryl' species, (P)Fe<sup>IV</sup>O, has been obtained e.g. by Balch *et al.* [31].

(a)  $(P)Fe(II) + O_2 \rightarrow (P)Fe(\eta^2-O_2^{2-})$ ; (b)  $(+P)Fe(II) \rightarrow [(P)Fe(III)-\eta^2-(O_2^{2-})-Fe(III)(P)] \rightarrow 2[(P)Fe(IV)-(O^{2-})]$ ; (c)  $(P)Fe(IV)(O^{2-}) + (P)Fe(II) \rightarrow [(P)Fe(III)-O-Fe(III)(P)]$ . (iv) a generalized form of the intermediate for V represented by (G) in step 2, *viz.*



could potentially serve as a vehicle for O-atom transfer to a ligand coordinated to either metal center, assuming applicability of (i) above. V and Mo peroxo complexes have been implicated in ligand hydroxylation and epoxidation in biomimetic studies by Mimoun and coworkers [32], with the form of the active O-transfer agent not definitively characterized but possibly dinuclear rather than 'oxenoid' [16b, 33]. The scheme in (i) above, it must be qualified, is only one of perhaps many possible pathways for O-O bond rupture and subsequent  $\mu$ -oxo dimer formation and by no means exclusive. The relative ease of O-O bond breaking apparent from the present work however indicates that it is a favorable



Scheme 2.

pathway. As one example of an alternative pathway, of course, electrophilic attack by a metal ion on the mononuclear  $\eta^2$ -peroxo complex of Fig. 1 may be considered.

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## Appendix

Calculations of the extended Hückel type [23] were performed using previously published parameters [34] listed in Table II.

TABLE II. Extended Hückel Parameters for V.  $\xi_1/c_1$  and  $\xi_2/c_2$  are Exponents and Coefficients in a Double Zeta Expansion

Atom	Orbital	$H_{ii}$ (ev)	$\xi_1$	$c_1$	$\xi_2$	$c_2$
V	4s	-8.81	1.30			
	4p	-5.52	1.30			
	3d	-11.00	4.75	0.4755	1.70	0.7052