

On the Structure and Reactivity of Peroxotransition-Metal Complexes

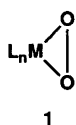
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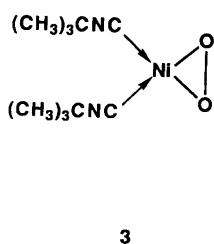
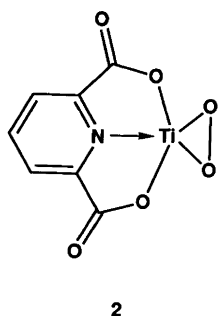
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The electronic structures of an early and a late η^2 -peroxotransition-metal complex have been investigated in an attempt to account for the similarities in the M–O and O–O bond lengths and the differences in reactivity in spite of the structural similarities around the metal peroxo group. Peroxotitanium(IV) 2,6-pyridinedicarboxylate is used as a model for an early η^2 -peroxotransition-metal complex while the late η^2 -peroxotransition-metal complex is modelled by peroxonickel(II) bis(*t*-butylisocyanate). The η^2 -peroxotitanium complex is most stable in the 1A_1 state and the η^2 -peroxonickel complex in the 3B_2 state. The bonding between the metal atom and the peroxo fragments is analyzed both in terms of the frontier orbitals and orbital population analysis. The reactivity of the two complexes with organic substrates is briefly discussed.

η^2 -Peroxotransition-metal complexes, **1**, play an important role in many different areas of chemistry, and much attention has been paid to their structures and reactivity.¹

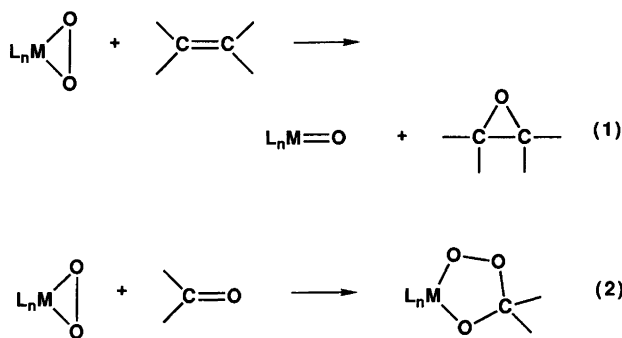


A variety of η^2 -peroxotransition-metal complexes, **1**, containing different transition metals, e.g., Ti, Nb, Ta, Mo, W, Co, Rh, Ir, Ni, Pd and Pt and a variety of organic ligands are known and have been characterized by X-ray diffraction.^{1b} Although the transition metal and ligand is varied in **1**, the M–O and O–O bonds lengths are, in many of the complexes, surprisingly constant; e.g., the peroxotitanium(IV) 2,6-pyridinedicarboxylate, **2**, has Ti–O and O–O bond lengths of 1.82 and 1.46 Å, respectively,² and the peroxonickel(II) bis(*t*-butylisocyanate), **3**, has Ni–O and O–O bond lengths of 1.81 and 1.45 Å, respectively.³



The reaction pattern of the η^2 -peroxotransition-metal complexes with organic substrates is different when passing from the early transition-metal complexes to the late transition-metal complexes. Many early peroxotransition-metal complexes are able to transfer an oxygen atom to an alkene to give an epoxide as the major product^{1c,4} [reaction (1)]. It is generally observed that alkenes with electron-donating substituents are more reactive than alkenes with electron-withdrawing substituents attached to the double bond, indicating that the peroxygen which is transferred to the alkene is electrophilic in nature.^{1c,f,4,5} Late η^2 -peroxotransition-metal complexes probably react in a different way: the peroxonickel oxidation of organic substrates is assumed to proceed along a free-radical pathway.^{1d} Furthermore, five-membered peroxometallacyclic adducts are isolated from the reaction of $(\text{Ph}_3\text{P})_2\text{MO}_2$ (M = Pd, Pt) with aldehydes and ketones⁶ [reaction (2)], hexafluoroacetone⁷ and electrophilic cyanoalkenes.⁸

η^2 -Peroxotransition-metal complexes are prepared in different ways depending on the transition metal; for the early transition-metal complexes the oxygen source is usually



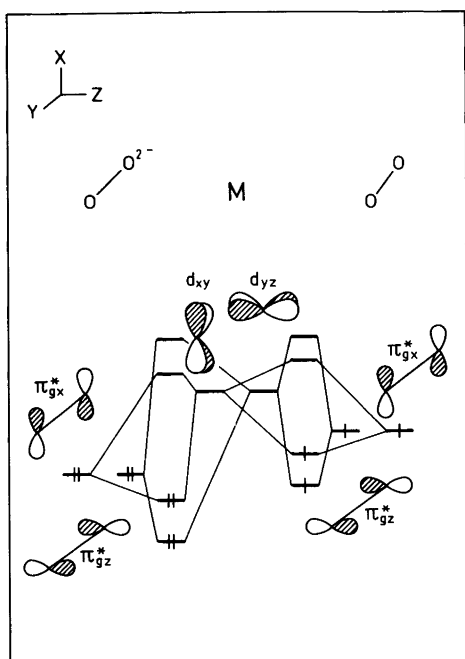
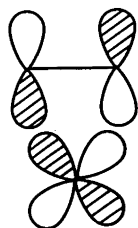


Fig. 1. A schematic interaction diagram of a peroxide anion (left-hand side) and molecular oxygen (right-hand side) with proper transition-metal d-orbitals in the middle (no occupancy of the d-orbitals is taken into account).

hydrogen peroxide while it is usually molecular oxygen for the late transition-metal complexes.^{1c}

The bonding of the peroxide/molecular oxygen moiety to transition metals has also received considerable interest.⁹ With the frontier orbitals of the peroxide anion shown to the left in Fig. 1 and the triplet ground state of molecular oxygen shown to the right, an interaction involving the π_g^* orbitals of the peroxide/molecular oxygen fragment and the proper transition-metal d-orbitals has been suggested to account for the bonding in the η^2 -peroxotransition-metal complexes.^{1b,f,5,10}

For peroxotitanium(IV) porphyrin, in addition to the interaction shown in 4, a weak δ -interaction has also been observed.¹¹ The singlet state of peroxonickel(II) bis(*t*-butylisocyanate) has been investigated using the INDO method and it was found that the peroxygen-nickel bonding is accomplished mainly through mixing of the molecular oxygen π_u and σ_g with nickel $3d_{z^2}$ and $3d_{x^2-y^2}$ and of the peroxygen π_g^* orbital with nickel $3d_{yz}$.¹²



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In terms of the frontier orbitals, the interaction of e.g. a d^0 -titanium(IV) complex with the π_g^* orbitals of the peroxide anion shown on the left in Fig. 1 should imply donation of electron density from the anion peroxide to titanium, mainly through an interaction similar to that outlined in 4. However, the formation of, e.g., the peroxo complexes at the end of the transition-metal series takes place by an interaction of molecular oxygen with, e.g., a d^{10} transition metal, in principle leading to donation of electron density from the metal into the π_g^* orbitals of molecular oxygen shown on the right in Fig. 1; in other words the opposite process of that operative in the early transition metals.

Below we focus our attention on the η^2 -peroxotitanium(IV) and the η^2 -peroxonickel(II) complexes, 2 and 3, respectively, in an attempt to explain the electronic structure of these two different types of complex. We will analyze the bonding patterns in terms of the molecular orbitals of the two extreme η^2 -peroxo-transition-metal complexes, 2 and 3, and, on basis of their electronic structure, we will discuss briefly their reaction pattern. To this end we have used *ab initio* calculations.

Calculations

The calculations were performed for two complexes: peroxotitanium(IV) 2,6-pyridinedicarboxylate, 2, based on the experimental crystal geometry² and peroxonickel bis(*t*-butylisocyanate), 3, (the *t*-butyl group was replaced by a methyl group in the calculations) also based on the experimental crystal geometry.³ All the calculations were carried out with the GAUSSIAN 88 program.^{13a} The basis sets were taken from Poirier *et al.*^{13b} For Ti and Ni we used 8s4p2d basis sets with the contraction scheme [62111111/5112/32(1)] while for C, N and O we used 4s2p basis sets with contraction schemes [5211/41]; hydrogen was represented by a 2s [31] basis.^{13b} Since this work deals mainly with comparison of the valence shells of 2 and 3 these basis sets, which are of the split valence type, were considered appropriate. No geometry optimization was performed. Hartree-Fock type wavefunctions were calculated for both singlet and triplet state of 2 and 3. The calculations were spin-restricted because they are easier to interpret than the spin-unrestricted calculations.

Results and discussion

Table 1 gives some electronic data of interest to the present study.

The ground state of 2 is 1A_1 with a total energy of -1618.634 a.u. It is more stable than the lowest triplet state by several hundred kcal mol⁻¹. Owing to the large energy separation between the lowest singlet and triplet states of 2 we have confined our attention to the 1A_1 state of the system. In contrast with this, the most stable electronic state of 3 is a triplet state (3B_2) which is 341 kcal mol⁻¹ more stable than the lowest singlet state.

Table 1. Some electronic parameters for **2** and **3**.

	2	3
Electronic state	1A_1	3B_2
Total HF energy (a.u.)	-1618.634	-1919.686
Atomic charge		
Metal	2.24	1.22
Peroxygen	-0.42	-0.31
Bond order		
Metal–peroxygen	0.11	0.07
Peroxygen–peroxygen	-0.05	0.06
Gross orbital population		
Metal		
4s	0.17	0.37
3d _{z²}	0.33	1.99
3d _{xz}	0.15	2.00
3d _{yz}	0.71	0.47
3d _{x²-y²}	0.15	1.98
3d _{xy}	0.19	1.98
Peroxygen		
2s	1.98	1.97
2p _x	1.88	1.50
2p _y	1.00	1.04
2p _z	1.48	1.84

The orbital analysis of the valence orbitals of **2** and **3** is presented in Fig. 2. In the titanium complex, **2**, [Fig. 2(a)] the bonding of the peroxy fragment to the titanium atom is the result of two principal interactions: (i) a σ -type $\pi_{gz}^*(O_2) - 3d_{yz}(Ti)$ with a bond order of 0.072 per Ti–O bond and (ii) a δ -type $\pi_{gx}^*(O_2) - 3d_{xy}(Ti)$ with a bond order of 0.016 per Ti–O bond. The bond order between the two peroxygens is negative (-0.052) at this geometry, indicating an inherent instability of the peroxy group.

The net atomic charge on each peroxygen in **2** is -0.42 which means that the original O_2^{2-} peroxide anion has transferred about 1.2 electrons to the titanium region. This is consistent with an electron count of about 16.6 at the peroxy fragment. We can hence identify the peroxy fragment as an O_2^- -like group attached to titanium, which in turn acts as an acceptor of surplus charge.

In the nickel complex, **3**, the bonding of the peroxy fragment is mainly the result of just one interaction; electron donation from $3d_{yz}(Ni)$ to $\pi_{gz}^*(O_2)$ with a bond order of 0.034 per Ni–O bond. The bond order between the two peroxygens in **3** is positive ($+0.061$). The net atomic charge on each peroxygen in **3** is -0.31 meaning that the original O_2 molecule has accepted about 0.6 electrons from the nickel domain. We can hence also here identify the peroxy fragment as an O_2^- -like group attached to nickel, which acts as an electron donor. The gross orbital populations of **2** and **3** given in Table 1 reflect the similarities and the differences at the peroxygen and the metal in the complexes.

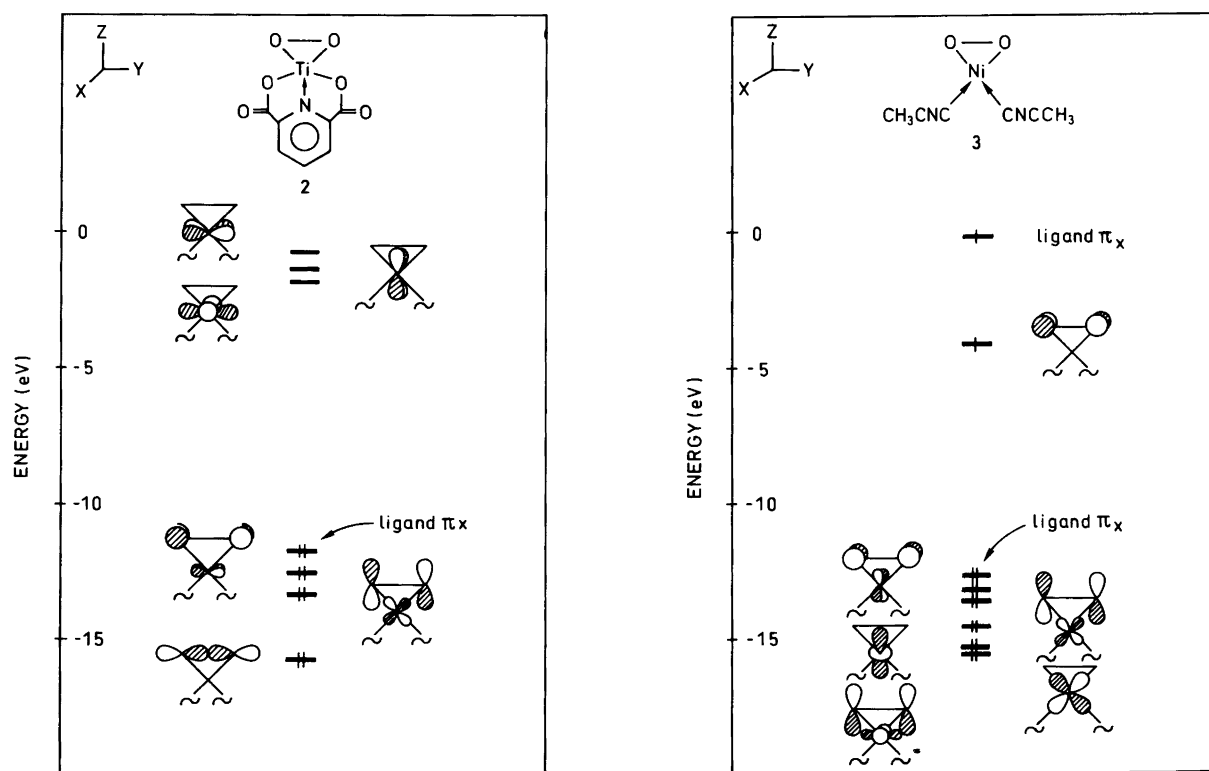


Fig. 2. (a) The frontier orbitals of peroxotitanium(IV) 2,6-pyridinedicarboxylate, **2** (only the peroxotitanium part is shown). (b) The frontier orbitals of peroxonickel(II) bis(methylisocyanate), **3** (only the peroxy part is shown).

We can thus, to a certain extent, identify the peroxo fragment of the two complexes **2** and **3** as an O_2^- species attached to the transition metal; this fact may account for the structural similarities between the peroxo groups of the two compounds. With the relatively low bond order between the peroxyoxygen and the metal fragments in **2** and **3** one might perhaps consider the interaction to be electrostatic. Note also the close match in gross orbital populations for the peroxygens in **2** and **3**.

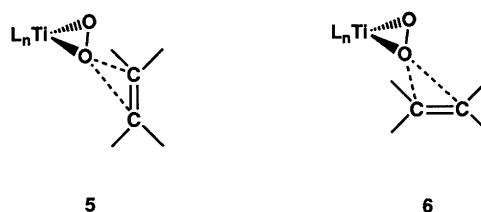
Let us now turn to a discussion of the frontier orbitals of the peroxotitanium complex, **2**, and the peroxonickel complex, **3**. The frontier orbitals of **2** are depicted in Fig. 2(a). The highest occupied molecular orbital (HOMO) of **2** is found at -11.75 eV; it is of ligand π_x character. Directly below the HOMO, at -12.54 eV, is an orbital which is of peroxyoxygen π_{gx}^* and titanium $3d_{xy}$ character. 0.77 eV lower in energy is the orbital which is a combination of π_{gz}^* at the peroxygens and $3d_{yz}$ at titanium, and at -15.73 eV the $\sigma(O-O)$ is located. The lowest unoccupied molecular orbital (LUMO) at -1.76 eV is located at the titanium atom as a combination of $4s$ and $3d_{x^2-y^2}$, and above this are the titanium $3d_{xz}$ and $3d_{xy}$ orbitals located. The $\sigma(O-O)^*$, which is of interest in relation to the reactions of **2**, is found in the positive region of the energy scale and is not shown in Fig. 2(a).

The frontier orbitals of **3** are shown in Fig. 2(b). The two singly occupied orbitals (SOMOs) are found at about 0 eV and at -4.05 eV. The first one is mainly of ligand π_x character, while the second is confined to the peroxyoxygen fragment and of π_{gx}^* character. The highest doubly occupied MO is of ligand π_x character and is not directly involved in the bonding of the peroxo group to the Ni atom. The next doubly occupied MOs are, in the order of appearance, (i) a bonding combination of peroxy π_{uz} and Ni $3d_{xz}$ (ii) a bonding combination of peroxy π_{gx}^* with Ni $3d_{yz}$ (iii) an almost pure Ni $3d_{z^2}$ (iv) an almost pure Ni $3d_{yz}$ (v) a bonding combination of peroxy π_{uz} with $3d_{x^2-y^2}$. The LUMOs of **3** are mainly (i) of Ni s character and (ii) of $\sigma(O-O)^*$ character.

Comparison of the frontier orbitals of the two systems in Fig. 2 reveals that the two SOMOs of **3** are located several eVs higher in energy than is the HOMO of **2**. The higher energy of the SOMOs in **3** might, to a certain extent, be analogous to the situation described by Fig. 1: the interaction of the nickel atom with triplet molecular oxygen (to the right in Fig. 1) mainly involves occupied metal orbitals interacting with the SOMOs of molecular oxygen thus pushing up the orbitals as indicated in Fig. 1 (note that the metal d-orbitals are unoccupied in the center of Fig. 1) giving one electron located on the isocyanate ligands and one electron on the peroxygens. For the titanium complex the metal orbitals are unoccupied and this leads to occupation of the lower part of the interacting orbitals only, as in the left part in Fig. 1.

In the following we briefly discuss the reactivity of the η^2 -peroxotitanium(IV) and the η^2 -peroxonickel(II) com-

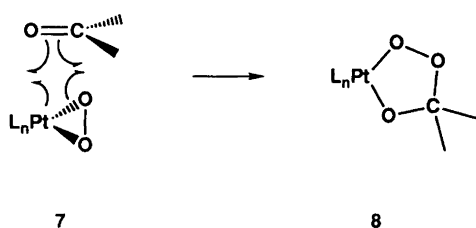
plexes, **2** and **3**, in terms of the electronic structure presented here. It is generally observed that peroxo and peroxide complexes of the early transition metals react with, e.g., alkenes to give epoxides as the major product [reaction (2)] and that alkenes with electron-donating groups attached to the double bond are more reactive than alkenes with electron-withdrawing groups attached to the double bond. This observation is in accordance with the character of the frontier orbitals of the η^2 -peroxotitanium(IV) complex, **2**; the two orbitals which originate mainly from the peroxyoxygen $\pi(O-O)^*$ orbitals located at -12.54 and -13.31 eV can interact with the alkene $\pi(C-C)^*$, either with the alkene oriented perpendicular or parallel to the peroxo-titanium plane. The alkene $\pi(C-C)$ orbital is, in these two orientations, set up for an interaction with the $\sigma(O-O)^*$ of the peroxo fragment, through which donation of electron density from the alkene leads to cleavage of the peroxyoxygen-titanium and the peroxyoxygen-peroxyoxygen bonds. This suggestion is also supported by the low gross orbital population value of the $2p_y$ orbital of the peroxyoxygen compared with the higher gross orbital population of the $2p_x$ and $2p_z$ orbitals (see Table 1). The two possible orientations relative to the titanium peroxo plane of the alkene interacting with one of the peroxygens in the η^2 -peroxotitanium(IV) complex are shown in **5** and **6**.



The two orientations, **5** and **6**, are similar to those suggested for the oxygen transfer reactions from, e.g., $MoO(O_2)_2$, and from the Sharpless titanium tartate peroxide complexes.^{4b,5a,b,14} The frontier orbitals of the η^2 -peroxotitanium(IV) complex, **2**, seem not to support a peroxometallacyclic intermediate in the oxygen-transfer reaction.¹⁵

The reactivity of η^2 -peroxonickel(II) complexes is very different from that of η^2 -peroxometal complexes of the early transition metals; the oxidation of organic compounds using nickel peroxide is assumed to proceed through a free-radical pathway, as indicated by isotope and EPR studies.¹⁶ The free radical pathway of η^2 -peroxonickel(II) complexes is in accordance with the electronic structure obtained in the present study. The most stable state of **3** is the 3B_2 state indicating that the complex is expected to react as a radical rather than as a closed-shell system. The reaction can, e.g., take place as a radical reaction via one of the peroxygens as one electron is located there as depicted in Fig. 2(b). This is in accordance with the reactivities of

η^2 -peroxonickel(II) complexes with systems containing X–H bonds (X = O, N) and active C–H bonds as these are found to proceed through hydrogen abstraction.^{1d} The frontier orbitals of **3** might also, to a certain extent, be used to explain one of the more interesting reactions of the late η^2 -peroxometal complexes, e.g., the formation of five-membered peroxometallic adducts. To account for the formation of these five-membered peroxometallic complexes it is suggested that the SOMO, or one of the occupied MOs, located at the metal interact with the π (C=O) orbital of the carbonyl at the axial site of the square planar complex, **7**, followed by a radical attack by one of the peroxygens on the carbonyl carbon leading to **8**.



These results are in agreement with the experimental observations for the reaction of ketones with $(\text{Ph}_3\text{P})_2\text{PtO}_2$.¹⁷ Interaction of the metal with the substrate followed by insertion into the peroxygen–metal bond is probably also operative for other types of substrates, e.g., electrophilic cyanoalkenes leading to five-membered peroxometallic adducts. As only electrophilic alkenes undergo this reaction^{8,18} interaction with an electron-rich center such as the metal atom might be the first step. The late η^2 -peroxometal complexes are electron rich at the metal, whereas the early η^2 -peroxo metal complexes, being electron poor at the metal, are unable to ‘activate’, e.g., electrophilic cyanoalkenes. Furthermore, the frontier orbitals of the two systems are also different; the early η^2 -peroxometal complexes have the LUMO energies located several eVs lower in energy than have the late η^2 -peroxometal complexes. The early η^2 -peroxometal complexes are thus able to interact more effectively with donor systems at the peroxygens than are the late η^2 -peroxometal complexes, owing to the low energy of the acceptor orbitals of the former complexes. We therefore suggest that early η^2 -peroxometal complexes transfer the oxygen to an alkene as outlined in **5** or **6**, whereas late η^2 -peroxometal complexes activate the alkene at the electron-rich metal followed by insertion into the peroxy–metal bond.

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