Ab Initio Self-consistent Field Molecular-orbital Calculation of the Ground State of Tetranitratotitanium(IV); Comments on the Reactivity of Anhydrous Metal Nitrates

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The electronic ground state of $[Ti(NO_3)_4]$ has been calculated using an *ab initio* SCF molecular-orbital (m.o.) procedure. A correlation is presented of the m.o.s of the complex with those of $[NO_3]^-$ calculated in the same basis set and it is seen that the overlaps between the metal $3d$ and ligand $2p_\sigma$ orbitals provide the major contributions to the metal–ligand bonding. The titanium configuration is calculated as $3d^{1.6}$ $4s^{0.2}$ $4p^{0.2}$ with the major loss of electron density from each nitrato-group being experienced by the terminal oxygen atom (*ca.* 0.3 e). The marked reactivity exhibited by anhydrous metal nitrates is discussed with reference to these results.

ANHYDROUS metal nitrates have attracted considerable interest [1-3] over the past two decades largely because of their volatility, vibrational spectroscopic properties, interesting structures, and remarkable chemical reactivity. At present the understanding of this last feature is particularly unsatisfactory and, for example, there is a real lack of definitive information concerning the mechanism of reactions such as the rapid nitration of hydrocarbons by $[Ti(NO_3)_4]$ [4] at room temperature.[5-8] Such

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[1] C. C. Addison and N. Logan, *Adv. Inorg. Chem. Radiochem.*, 1962, **1**, 848 and refs. therein.

[2] C. C. Addison and D. Sutton, *Progr. Inorg. Chem.*, 1967, **8**, 195 and refs. therein.

[3] C. C. Addison, N. Logan, S. C. Wallwork, and C. D. Garner, *Quart. Rev.*, 1971, **25**, 289 and refs. therein.

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reactivity appears clearly as a consequence of nitrate co-ordination and it is not manifest by ionic nitrates. We have calculated the electronic ground state of [Ti(NO$_3$)$_4$] by an *ab initio* SCF m.o. procedure, first because no such detailed assessment of the electronic structure of an anhydrous metal nitrate appears to have been made and secondly to see if there is any feature inherent in the electronic structure of this molecule which could provide an improved understanding of the reactivity shown by this and other anhydrous metal nitrates.

COMPUTATION AND RESULTS

The calculation of the electronic ground state of [Ti(NO$_3$)$_4$] was made, assuming D_{2d} symmetry, the molecular parameters [9] being shown in Figure 1. A basis of Gaussian-type functions (GTF) were employed. The titanium atomic orbitals (except the $4p$ and $3d$) and the nitrogen and oxygen $1s$ and $2s$ orbitals were each represented by three GTFs fitted to Slater-type orbitals (STO), the latter having the best-atom components of Clementi and Raimondi.[10] The titanium $4p$ orbitals were STOs of exponent unity fitted by three GTFs, and the $3d$ orbitals were expanded to five GTFs.[11] The oxygen and nitrogen $2p$ orbitals were each represented by four GTFs fitted to Hartree–Fock orbitals.[12]

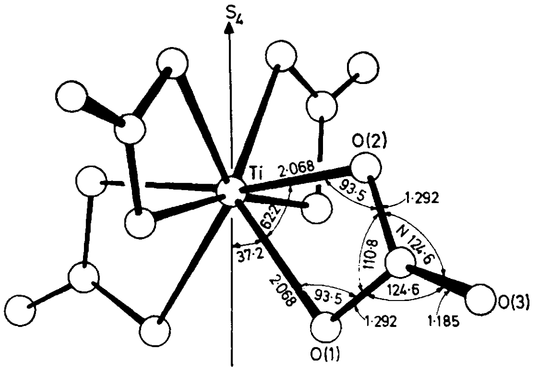

FIGURE 1 Molecular structure of [Ti(NO$_3$)$_4$]

Table 1 lists the calculated valence molecular orbitals (m.o.s) of [Ti(NO$_3$)$_4$]. As the titanium-atom configuration is formally d^0, the major components of these m.o.s arise from the nitrate ligands and therefore a correlation with the m.o.s of the nitrate ion is possible. The results of a calculation for $[NO_3]^-$ in D_{3h} symmetry, with [13] N–O 1.243 Å, using the same nitrogen and oxygen basis orbitals as used for [Ti(NO$_3$)$_4$], are shown in Table 2 and the following conclusions can be made.

(*i*) The nine highest-filled m.o.s of [Ti(NO$_3$)$_4$] are closely spaced in energy (−14.9 to −16.6 eV),[*] are essentially non-bonding, and correlate with the $1e''$ (π) and $1a_2'$ (σ) oxygen lone-pair m.o.s of the ligands. (*ii*) The group of six m.o.s (−16.8 to −18.9 eV) correlate with the $4e'$ nitrate orbitals which are mainly oxygen $2p_\sigma$ orbitals. Four of these six m.o.s, the $13b_2$, $15e$, $15a_1$, and $14e$, have significant titanium $3d$ character and provide the major contributions to the metal–ligand bonds. The net metal–ligand bonding interactions are described in Table 3 in terms of Mulliken bond-overlap populations and it is seen that the major interactions do involve the titanium $3d$ and oxygen $2p$ atomic orbitals. The $14a_1$ m.o. (−18.9 eV) has a small titanium $4s$ component and contributes to the metal ($4s$)–oxygen ($2p$) bond-overlap population (Table 3). (*iii*)

TABLE 1

Calculated energy and composition of molecular orbitals of [Ti(NO$_3$)$_4$]

Valence molecular orbitals		Atomic-orbital character (%)								
		Ti			N		O(1,2)		O(3)	
Orbital	Energy (eV)	$3d$	$4s$	$4p$	$2s$	$2p$	$2s$	$2p$	$2s$	$2p$
$3a_2$	−14.9					1		53		47
$18e$	−15.4			1		1		56		43
$3b_1$	−15.5							87		12
$15b_2$	−16.0					1	3	94		1
$17e$	−16.0	1						90		9
$16e$	−16.2	1				4	5	66		25
$16a_1$	−16.4	3				3	5	74		16
$2a_2$	−16.4							100		
$2b_1$	−16.6	6				4		55		35
$15a_1$	−16.8	7						32		61
$14b_2$	−16.9			1		1		19		78
$15e$	−17.0	6						49		44
$14e$	−17.5	4		1		1		79	1	13
$13b_2$	−18.7	16				2	1	67	2	13
$14a_1$	−18.9		3				3	80	2	13
$13e$	−22.7					19	15	26	15	24
$13a_1$	−22.9		1			19	11	23	18	28
$12b_2$	−23.0					18	13	25	18	25
$12e$	−23.5	4				28	14	30	3	22
$12a_1$	−23.9	5				25	14	33	3	19
$1a_2$	−24.2					58		24		18
$11b_2$	−24.3	2		4		27	14	37		16
$11e$	−24.5	1		−1		54	1	28	1	17
$1b_1$	−24.8	1				54		31		14
$10e$	−26.2			3	18	1	29	18	19	11
$10b_2$	−26.4	2		1	18	1	31	20	19	10
$11a_1$	−27.2		7		18	1	27	24	16	6
$9e$	−39.9	1				25	71	3		
$10a_1$	−39.9	1				25	72	2		
$9b_2$	−40.0					24	72	2		
$8e$	−42.2					33	28	4	32	3
$8b_2$	−42.3	1				32	28	4	32	3
$9a_1$	−42.5		−1			33	28	3	33	3
$7b_2$	−48.5			−1	47		21	6	20	6
$7e$	−48.5			−3	48		21	6	21	6
$8a_1$	−48.6		−2		47		24	6	19	6
Inner molecular orbitals										
$6b_2$	−57.8	Ti $3p$								
$6e$	−58.1									
$7a_1$	−86.7	Ti $3s$								
$5b_2$	−433.2				N $1s$					
$6a_1$	−433.2									
$5e$	−433.2									
$4b_2$	−490.5	Ti $2p$								
$4e$	−490.5									
$3b_2$	−553.9						O(1,2) $1s$			
$5a_1$	−533.9									
$3e$	−553.9									
$2e$	−553.9									
$2b_2$	−553.9									
$4a_1$	−553.9									
$1b_2$	−557.3								O(3) $1s$	
$3a_1$	−557.3									
$1e$	−557.3									
$2a_1$	−584.7	Ti $2s$								
$1a_1$	−4 937.4	Ti $1s$								

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[*] 1 eV $\approx 1.60 \times 10^{-19}$ J.

[9] C. D. Garner and S. C. Wallwork, *J. Chem. Soc.* (*A*), 1966, 1496.

[10] E. Clementi and D. L. Raimondi, *J. Chem. Phys.*, 1963, **38**, 2696.

[11] H. Basch, C. J. Hornback, and J. W. Moskowitz, *J. Chem. Phys.*, 1969, **51**, 1311.

[12] R. F. Stewart, *J. Chem. Phys.*, 1969, **50**, 2485.

[13] L. E. Harris, *J. Chem. Phys.*, 1973, **58**, 5615.

TABLE 2

Electronic structure of the nitrate ion

Molecular orbitals		Atomic-orbital character (%)					
		N			O		
Symmetry	Energy (eV)	$2s$	$2p_\sigma$	$2p_\pi$	$2s$	$2p_\sigma$	$2p_\pi$
$2a_2''$	10.30			41			59
$1e''$	-4.7						100
$1a_2'$	-5.0					100	
$4e'$	-6.1		1		1	97	
$3e'$	-12.4		22		26	52	
$1a_2''$	-14.3			59			41
$4a_1'$	-15.3	16			54	30	
$2e'$	-30.0		32		64	4	
$3a_1'$	-37.6	50			39	11	

	Atomic-orbital population	
	N	O
$2s$	1.318	1.856
$2p_\sigma$	2.179	2.982
$2p_\pi$	1.179	1.607
Charge/e	+0.33	−0.44

TABLE 3

Electronic structure of $[Ti(NO_3)_4]$

(*a*) Orbital population

Ti				Nitrate		
$3d$	1.569	b_1	0.163	N	$2s$	1.343
		b_2	0.432		$2p$	3.310
		a_1	0.314	Charge/e		+0.35
		e	0.660	O(1)	$2s$	1.859
$4s$	0.157				$2p$	4.500
$4p$	0.187	e	0.068	Charge/e		−0.36
		b_2	0.120	O(2)	$2s$	1.851
					$2p$	4.535
Charge/e	+2.10			Charge/e		−0.38
				O(3)	$2s$	1.850
					$2p$	4.287
				Charge/e		−0.14

(*b*) Bond-overlap population

Ti	O	O(1)–Ti	O(2)–Ti	O(3)–Ti
$3d$	$2s$	0.025	0.020	0.000
$3d$	$2p$	0.126	0.120	0.002
$4s$	$2s$	0.028	0.041	0.001
$4s$	$2p$	0.013	0.023	0.006
$4p$	$2s$	0.064	0.076	0.009
$4p$	$2p$	0.013	0.029	−0.001
	Total	0.224	0.261	0.017
N	O	O(1)–N	O(2)–N	O(3)–N
$2s$	$2s$	−0.149	−0.145	−0.180
$2s$	$2p$	0.285	0.281	0.283
$2p$	$2s$	−0.113	−0.102	−0.111
$2p$	$2p$	0.442	0.427	0.695
	Total	0.455	0.450	0.668

Six ($13e$, $13a_1$, $12b_2$, $12e$, $12a_1$, and $11b_2$) of the seven m.o.s between −22.7 and −24.3 eV correlate with the 3e′ (N–O σ-antibonding) m.o.s of the ligands. The $12e$ and $12a_1$ m.o.s have small titanium $3d$ components and provide small contributions to the metal ($3d$)–oxygen ($2p$) overlap population, whilst the $11b_2$ m.o. has a significant metal ($4p$)–oxygen ($2s$) bonding component. (*iv*) The N–O π-bonding orbitals of the $[NO_3]^-$ groups ($1a_2''$) correlate with the $1a_2$, $11e$, and $1b_1$ m.o.s of $[Ti(NO_3)_4]$ at −24.2, −24.5, and −24.8 eV, respectively. The latter two m.o.s have small contributions from the metal orbitals. (*v*) The $10e$, $10b_2$, and $11a_1$ m.o.s of $[Ti(NO_3)_4]$ at −26.2, −26.4, and −27.2 eV correlate with the $4a_1'$ (N–O σ-antibonding) ligand orbitals. The first of these m.o.s has 3% titanium $4p$ character, and the last has 7% titanium $4s$ character, and they provide significant contributions to the metal ($4p$)–oxygen ($2s$) and metal ($4s$)–oxygen ($2s$ and $2p$) overlap populations respectively. (*vi*) The remaining valence m.o.s of $[Ti(NO_3)_4]$ are considerably more tightly bound and those between −40 and −49 eV are essentially nitrate in character. Of these the $9e$, $10a_1$, $9b_2$, $8e$, $8b_2$, and $9a_1$ m.o.s correlate with the $2e'$ (N–O σ-bonding) orbitals of the nitrate groups, whilst the $7b_2$, $7e$, and $8a_1$ m.o.s of the complex correlate with the $3a_1$ (N–O σ-bonding) orbitals of the ligands. (*vii*) The lowest-energy levels are the 'core' orbitals with relative energies calculated as Ti $3p >$ Ti $3s \gg$ N $1s >$ Ti $2p >$ O(co-ordinated) $1s \sim$ O(terminal) 1s $>$ Ti $2s \gg$ Ti $1s$.

Table 4 lists the lowest-energy virtual orbitals with their principal atomic-orbital contributions.

TABLE 4

Lowest-energy virtual orbitals of $[Ti(NO_3)_4]$

Orbital	Energy (eV)	Principal atomic-orbital character	
$4b_1$	−2.9	Ti $3d_{x^2-y^2}$	Ti $3d$ *
$19e$	−1.5	Ti $3d_{xz}$, $3d_{yz}$	
$17a_1$	−1.2	Ti $3d_{z^2}$	
$16b_2$	−0.8	Ti $3d_{xy}$	
$20e$	−0.4	Nitrate π * ($2a_2''$)	
$4a_2$	−0.2		
$5b_1$	0.1		
$18a_1$	6.4	Ti $4s$	Ti $4s$,* $4p$ *
$21e$	6.7	Ti $4p_x$, $4p_y$	
$17b_2$	6.9	Ti $4p_z$	

DISCUSSION

The metal configuration is calculated to be $3d^{1.6}$ $4s^{0.2}$ $4p^{0.2}$, leading to a formal charge on the titanium of +2.10 e. Thus there is a loss of electron density per nitrato-group of *ca.* 0.5 e. The calculated atomic charges (Tables 2 and 3) show that the electron density on the nitrogen atom remains essentially unchanged from $[NO_3]^-$ to $[Ti(NO_3)_4]$ and, although that on the oxygen atoms bonded to the metal is somewhat reduced, the major change in electron density occurs at the terminal oxygen atom where there is a net loss of *ca.* 0.3 e. Thus co-ordination results in a net drift of charge across the nitrato-group, from the terminal oxygen to the metal atom. Such electron migration affects the N–O bond-overlap populations of the nitrato-groups. The value of 0.52 in $[NO_3]^-$ increases to 0.67 for the terminal N–O bond but decreases to 0.45 for the two N–O bonds involving the co-ordinated oxygen atoms. Such changes are reflected in force constants estimated for bidentate nitrato-groups.[14] This electron drift is also reflected in the calculated oxygen 1*s* ionization potentials of $[Ti(NO_3)_4]$. The core ionization potential for the terminal oxygen atoms is calculated to be 3.4 eV greater than the value for the co-ordinated oxygen atoms, in line with the calculated charge distributions. Although such a splitting is probably not given accurately by the restricted basis calculations described here and such measurements have been attempted previously without success,[15] the value of photoelectron spectroscopic measurements for nitrato-complexes would appear to merit further study.

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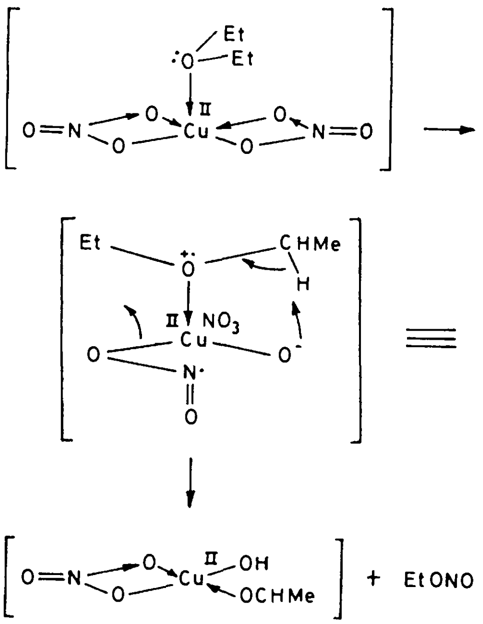
[14] R. E. Hester and W. E. L. Grossman, *Inorg. Chem.*, 1966, **5**, 1308.

[15] C. D. Garner and J. A. Connor, unpublished work.

It is of interest to note that the relative energies of the *d* orbitals of a metal ion in a ligand field such as that due to the co-ordinated oxygen atoms of $[Ti(NO_3)_4]$, assessed using a point-charge model,[16] compares very favourably with the $3d^*$-orbital sequence, $d_{x^2-y^2} < d_{xz}, d_{yz} < d_{z^2} < d_{xy}$, calculated here.

Addison and Sutton [17] established that the energy of the $n \longrightarrow \pi^*$ electronic transition of the nitrate group occurs at a higher energy when this group is co-ordinated to a metal atom than for ionic nitrates. Assuming that the coulombic repulsion terms are not significantly different in these two situations, the results obtained here are consistent with the sense of this spectral shift. Thus, the mean energy separation between the σ-lone-pair m.o.s and the π^* orbital of the nitrato-groups of $[Ti(NO_3)_4]$ (Tables 1 and 4) is *ca.* 16.1 eV, whereas the corresponding separation in the nitrate ion (Table 2) is *ca.* 15.2 eV.

The comparable energies calculated for the $3d^*$ and nitrate π^* orbitals (Table 4) further support the idea [18] that nitrato-groups can function as effective π-acceptor ligands. The negative energies calculated for the lowest-lying virtual orbitals of this neutral molecule clearly indicate that $[Ti(NO_3)_4]$ should exhibit a considerable and positive electron affinity. We believe that such an electron affinity is probably the general feature responsible for the remarkable reactivity of the anhydrous metal nitrates $[Ti(NO_3)_4]$,[5-8] $[Sn(NO_3)_4]$,[19] $[Cu(NO_3)_2]$,[1,20] and $[Co(NO_3)_3]$ [21] which will oxidize and/or nitrate a wide variety of organic compounds at ambient temperatures.



SCHEME 1

There is little direct information presently available concerning the mechanism of these reactions. The most definitive experimental studies of this problem appear to be those of Amos *et al.*[8] and Coard and Powell.[20] The former showed that $[Ti(NO_3)_4]$ will nitrate aromatic hydrocarbons very efficiently at room temperature and, for monosubstituted benzene derivatives, the pattern of *ortho-*, *meta-*, and *para*-substitution closely resembled that obtained using a HNO_3–H_2SO_4 mixture as the nitrating agent, *e.g.* chlorobenzene experiences 32% *ortho* and 68% *para* nitration with $[Ti(NO_3)_4]$. Coard and Powell [20] showed that at temperatures below 5 °C diethyl ether reacts with $[Cu(NO_3)_2]$ to produce ethyl nitrite and complexed acetaldehyde. In view of the postulated electron affinity of the anhydrous metal nitrates, we suggest that the first step in the reaction between an anhydrous metal nitrate and a hydrocarbon species corresponds to the electron-transfer process (1). This process should be the more readily accomplished if the metal M has an oxidation

$$RH + [M(NO_3)_x] \longrightarrow [RH]^+[M(NO_3)_x]^- \qquad (1)$$

state $<x$ readily accessible, and a correlation of this feature of the metal with the reactivity of anhydrous metal nitrates has already been presented.[5] Subsequent to reaction (1), it is suggested that an internal redox reaction proceeds within the $[M(NO_3)_x]^-$ ion to form NO_2 and restore the metal to its original oxidation state. The NO_2 thus produced would be expected to react rapidly with the radical cation RH^+ to form either RH and $[NO_2]^+$ or $[RH(NO_2)]^+$. In the former of these instances the pattern of nitration of RH clearly would be expected to resemble closely that observed using HNO_3–H_2SO_4 mixtures. However, this similarity is also anticipated for the latter situation, the NO_2 radical attacking the radical cation preferentially at sites with the highest

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[16] C. D. Garner and F. E. Mabbs, *J. Chem. Soc.* (*A*), 1970, 1711.

[17] C. C. Addison and D. Sutton, *J. Chem. Soc.* (*A*), 1966, 1524.

[18] B. Harrison, N. Logan, and J. B. Raynor, *J.C.S. Chem. Comm.*, 1974, 202.

[19] C. C. Addison and W. B. Simpson, *J. Chem. Soc.*, 1965, 598.

[20] L. C. Coard and R. E. Powell, *J. Chem. Soc.* (*A*), 1967, 296.

[21] R. J. Fereday, N. Logan, and D. Sutton, *Chem.Comm.*, 1968, 271.

concentration of unpaired electron density. For example, this favours *o* and *p* nitration of toluene, as shown in Figure 2.

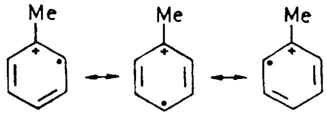

FIGURE 2 Preferred canonical forms for the toluene radical cation

The information presently available concerning the reactivity of anhydrous metal nitrates gives no real guidance as to whether or not the reactions between $[M(NO_3)_x]$ and RH species proceed *via* formation of a specific $[(RH)M(NO_3)_x]$ complex. Probably this aspect of the reactions varies with the nature of both reactants. Thus complex formation seems unlikely to occur between $[Ti(NO_3)_4]$ and benzene; however, it is an attractive possibility for $[Cu(NO_3)_2]$ and diethyl ether. Scheme 1 outlines how, after formation of $[Cu(NO_3)_2{\cdot}OEt_2]$, electron transfer from diethyl ether to the $Cu(NO_3)_2$ moiety could occur and thus lead to formation of ethyl nitrite and co-ordinated acetaldehyde.

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