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II. REACTION MECHANISMS; KINETICS

THE RELATION BETWEEN CHEMICAL REACTIVITY OF LIGANDS AND THE NATURE OF THE METAL–LIGAND BOND: NITRATO-COMPLEXES

C. C. ADDISON

Department of Chemistry, University of Nottingham (England)

It is now well known that in many anhydrous metal nitrates the bond between the metal and the nitrate group is covalent, so that these compounds are to be regarded as coordination complexes. Examples are now known which involve bivalent metals, *e.g.* $Mn(NO_3)_2$, $Ni(NO_3)_2$, $Cu(NO_3)_2$, $Zn(NO_3)_2$, trivalent metals, *e.g.* $Cr(NO_3)_3$ and tetravalent metals, *e.g.* $Ti(NO_3)_4$, $Sn(NO_3)_4$. These covalent nitrates form addition compounds with other ligands, *e.g.* $Sn(NO_3)_4 \cdot 2py$ and $Cu(NO_3)_2 \cdot 2MeCN$ so that a wide range of coordination complexes now exists in which the chemical reactivity of the nitrate group can be studied.

Some simple ligands show varying degrees of chemical reactivity depending on whether or not they are coordinated to a metal. Thus, the NH_3 group reacts readily with mineral acids, but it is more difficult to bring about this reaction when the NH_3 group is coordinated to a metal, *e.g.* in $[Co(NH_3)_6]^{3+}$. In general, however, coordination of a ligand reduces rather than enhances the chemical reactivity.

The nitrato-group is almost unique in that its chemical reactivity varies widely with the multiplicity of the metal–nitrate bond; also, the more multiple the bond becomes, the more reactive is the nitrate group. A very wide range of reactivity is involved; thus, the anhydrous nitrates of titanium(IV) and tin(IV) are so reactive that they will attack simple aliphatic hydrocarbons. The reaction may be followed by infrared spectroscopy, when it is seen that oxidation of the hydrocarbon occurs to give carboxylic acids, alkyl nitrates and nitroparaffins. With aromatic hydrocarbons, nitro-derivatives are rapidly formed at room temperature. With compounds such as ether or aniline, the oxidising properties of the nitrate group are so strong that the mixtures will either explode or burst into flames. This is in marked contrast with the inert character of the nitrate ion. The general position is summarised in Table I.

The only feature which differs in these compounds is the metal–nitrate bond, and recent work at Nottingham has attempted to explain the wide variation in chemical reactivity of nitrates on this basis.

Three types of covalent bond are possible, and these are shown in diagrammatic form in Fig. 1.

TABLE I

REACTIVITY OF METAL NITRATES

Nitrates	*Reaction with ethers, aniline, aliphatic hydrocarbons, etc.*
Ionic nitrates *e.g.* $Na^+NO_3^-$	no reaction
Covalent nitrates	
$Mn(NO_3)_2$, $Ni(NO_3)_2$, $Zn(NO_3)_2$	no reaction
$Ti(NO_3)_4$, $Sn(NO_3)_4$, $Cu(NO_3)_2$	violent reaction (explosion)

Decisions regarding the type of bond present in any particular complex have had to be based in the past on infrared spectra, and have been somewhat tentative, particularly in so far as bidentate bonding is concerned. The X-ray crystallography which we have now carried out on titanium(IV) nitrate gives stronger support to the interpretation of spectra than has been possible previously. The relevant absorption bands for a number of nitrates and nitrato-complexes are given in Table II.

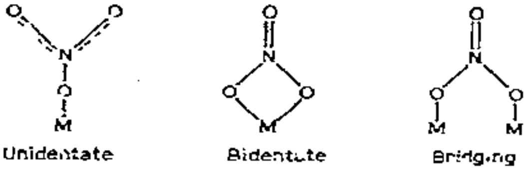


Fig. 1. Types of metal-nitrate bonding.

Nitratopentacarbonyl manganese is an excellent example of unidentate nitrate bonding; the nitrate groups are shielded from interaction with one another or with other metal atoms, and the coordination number of the metal also makes it almost certain that the nitrate is unidentate. Similar considerations apply to the other examples given under this heading (Table II) and it will be seen that the

TABLE II

INFRARED SPECTRA (cm^{-1})

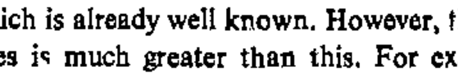
	ν_4		ν_1	ν_2
Unidentate				
$(CO)_5MnNO_3$	—	1486	1284	1010
$(dipy)Pd(NO_3)_2$	—	1517	1274	979
Me_3SnNO_3	—	1488	1268	1031
$Me_2Sn(NO_3)_2$	—	1550	1270	1000 (all split)
Bidentate				
$Sn(NO_3)_4$	1630	—	1255	983
$Ti(NO_3)_4$	1628	—	1225	988
$Zr(NO_3)_4$	1631	—	1284	1015
Uni- and Bidentate				
$Cr(NO_3)_3$	1631	1544	1283	990

highest frequency observed is normally in the region of 1500 cm^{-1}, which is the NO_2 asymmetric stretch; only occasionally do unidentate nitrates exceed this value. On the other hand, those nitrates which we believe to contain bidentate nitrate groups show an upper absorption band around 1630 cm^{-1}, and we associate this with the N═O stretch (see Fig. 1) which is characteristic of the terminal N–O bond in a bidentate nitrate. Some nitrates, *e.g.* $Cr(NO_3)_3$, and nitrato-complexes can contain both uni- and bidentate nitrate groups.

We have found that those compounds which contain unidentate nitrate groups (according to the infrared spectrum) are not reactive, whereas those which contain bidentate nitrate groups (again according to the infrared spectrum) possess strong oxidising powers towards many organic substances. It is therefore logical to deduce that the high chemical reactivity is possessed by nitrate groups bonded to a metal atom in bidentate fashion. If, however, the same species is produced when the nitrate group break away, irrespective of its bonding to the metal, then all nitrates should possess the same chemical reactivity. We believe, however, that this is not the case, and that the species produced in the course of reaction is determined by the way in which the nitrate group is bonded to the metal. The position is summarised in Table III.

TABLE III

RELATION BETWEEN BONDING AND REACTIVITY

Bonding		*Reactivity*
Ionic	$M^{n+}(NO_3^-)_n \longrightarrow M^{n+} + nNO_3^-$	unreactive
Unidentate	$M^{n+}{-}O{-}NO_2 \nearrow M^{n+} + NO_3^-$	unreactive
	$M^{n+}{-}O{-}NO_2 \searrow M^{n+}{-}O^{\cdot} + NO_2^{\cdot}$	slight reactivity due to NO_2.
Bidentate	 $M^{n+}(O_2)N{=}O \longrightarrow M^{(n-1)+} + NO_3^{\cdot}$	highly reactive

Depending on the strength of the sigma bond by which one oxygen atom is bonded to the metal in a unidentate nitrate, either a nitrate ion is produced, or the NO_2 radical. (To date, the latter has been found to occur only with anhydrous beryllium nitrate.) The reactivity to be expected in this second case is that of the NO_2 radical, which is already well known. However, the chemical reactivity of the bidentate nitrates is much greater than this. For example, dinitrogen tetroxide gives stable solutions in ethers at room temperature, whereas tin(IV) nitrate will ignite in contact with diethyl ether.

We therefore postulate that the species which is responsible for oxidation of organic compounds by anhydrous metal nitrates is the NO_3 radical, which is known to be highly reactive and that this is produced by dissociation of bidentate nitrate groups. If this hypothesis is to be supported there are a number of consequences which must also hold true:

1. Metals should have a lower valency state available.
2. Reactivity should occur only with bidentate nitrates.
3. Change from bidentate to unidentate bonding in a complex should result in loss of chemical reactivity.
4. Bidentate nitrates should not pass through a unidentate intermediate state.

The first of these requirements is found to be true. Copper(II) nitrate is bidentate in the gas phase and probably in solution in solvents of low polarity also. Reduction to the copper(I) state would explain why copper(II) nitrate reacts vigorously with ethers. In contrast, nitrates of Co^{II}, Ni^{II} and Zn^{II} are not reactive. Reduction of Ti^{IV} to Ti^{III} is not difficult; titanium(IV) nitrate oxidises aliphatic hydrocarbons, and the first stage in this reaction may well be

$$Ti(NO_3)_4 \rightarrow Ti(NO_3)_3 + NO_3$$

Reduction of Zr^{IV} to Zr^{III} is more difficult, and zirconium(IV) nitrate is much less reactive than the titanium compound. Tin(IV) nitrate reacts with hydrocarbons more readily than does titanium(IV) nitrate, and this may be attributed to initial production of two NO_3 radicals:

$$Sn(NO_3)_4 \rightarrow Sn(NO_3)_2 + 2NO_3 .$$

The second requirement has already been referred to. Experimental evidence at present available also meets the third requirement. Tin(IV) nitrate crystallises from pyridine in the form of small, transparent crystals of the bis-pyridine adduct $Sn(NO_3)_4 \cdot 2py$. In this compound the infrared spectrum (Table IV) is characteristic of a 6-coordinate complex of tin with four unidentate nitrate groups. The bis-pyridine adduct does not react with diethyl ether, whereas the parent nitrate reacts violently. There are many other examples in which a change from bidentate to unidentate bonding is accompanied by loss of chemical reactivity. For example, copper(II) nitrate is reactive in solutions of solvents having weak ligand powers (*e.g.* nitrobenzene) in which its bidentate nitrate groups are retained, but loses this reactivity in solutions (*e.g.* in methyl cyanide) in which coordination of the solvent brings about conversion of bidentate to unidentate nitrate bonding.

TABLE IV

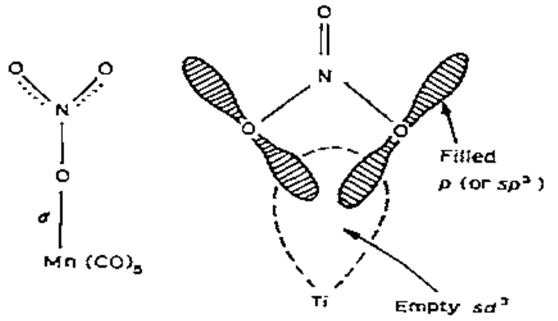
CHANGE IN SPECTRUM AND REACTIVITY ON COMPLEXING*

	ν_4		ν_1	ν_2
$Sn(NO_3)_4$ reacts with hydrocarbons inflames with aniline	1630	—	1255	983
$Sn(NO_3)_4 \cdot 2py$ inert	—	1552	1304	1008

* Similarly for $Ti(NO_3)_4$, $Cu(NO_3)_2$, $Cr(NO_3)_3$. Reactivity of solutions depends on solvent.

Mechanism of NO_3 release

If a bidentate nitrate group is bonded by two sigma-type bonds from the metal to two oxygen atoms, it would be expected that these bonds would break in stepwise fashion. This, however, would mean that a unidentate nitrate would be produced by the breaking of one of the M–O bonds. Since this is unreactive, and since both bonds can not be regarded as breaking simultaneously, we believe that the traditional picture of bonding by two sigma bonds can not be a true one. We consider that some form of three-centre bond, as shown in Fig. 2 accounts more satisfactorily for the behaviour of a bidentate nitrate. For $Ti(NO_3)_4$, for example, we may consider the bond as being formed when four NO_3^- ions are brought into contact with a Ti^{4+} ion. In the extreme form of electron distribution in the nitrate ion, the single *s* and three *p* orbitals (or the four sp^3 hybrids) are filled, leaving a vacant *p* orbital on the nitrogen atom at right angles to the plane of the group. Under conditions in which two oxygen atoms are equidistant from the Ti^{4+} ion, overlap of filled oxygen orbitals with empty orbitals of the Ti ion can occur, as shown in Fig. 2. When the NO_3 unit leaves the complex, the breaking of only a single three-centre bond is involved. The metal orbital will retain an electron, so that the NO_3 unit can dissociate from the complex as an NO_3 free radical.



Unidentate Bidentate

Fig. 2. Bonding in unidentate and in bidentate nitrates.

The actual molecular orbital involved in bidentate bonding may, in fact, be

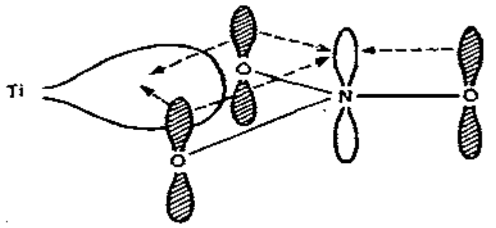


Fig. 3. Back-donation of oxygen electrons.

more complicated than this. The multiplicity in the N–O bonds of the nitrate ion is produced by back-donation of electrons from filled oxygen orbitals to the vacant orbital on the nitrogen atom, as illustrated in Fig. 3. When a vacant metal orbital is introduced between two oxygen atoms, the oxygen electrons are donated to this orbital also, so that in this sense the nitrogen atom is also involved in bidentate bonding. On this picture it is also clear that the electron deficiency on nitrogen which results from the proximity of the vacant metal orbital will be restored by additional back donation from the terminal oxygen, thus increasing this N–O stretching frequency.

The structure of titanium(IV) nitrate

The arguments advanced in this paper are based on the assumption that those reactive nitrates to which bidentate bonding is attributed do, indeed, possess this structure. S. C. Wallwork, W. B. Simpson and C. D. Garner, in the Nottingham laboratories, have recently established this for the titanium compound by X-ray crystallography. The crystal consists of separate $Ti(NO_3)_4$ molecules, and no nitrate groups are sufficiently near to metal atoms in adjacent molecules to act as bridge groups. There are four molecules per unit cell. In each molecule there are four bidentate nitrate groups, as shown in Fig. 4. The nitrate groups are disposed round the metal atom to form a flattened tetrahedron in which two opposite angles are

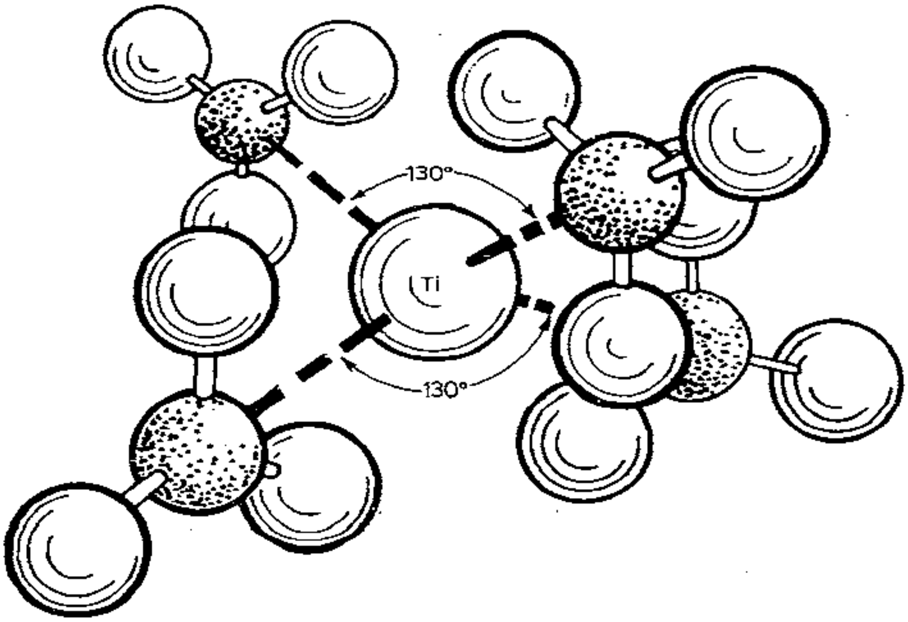


Fig. 4. The structure of titanium tetranitrate.

increased from the tetrahedral angle to 130°. The terminal N–O bonds are shorter, and the other two N–O bonds in each nitrate group longer, than the value 1.22 Å for the nitrate ion. The broken lines in Fig. 4 are included to indicate directions and do not imply direct Ti–N bonding. The nitrate groups lie in two planes at right angles to each other. It is convenient to consider the molecule as being constructed originally from the square-planar form shown in Fig. 5.

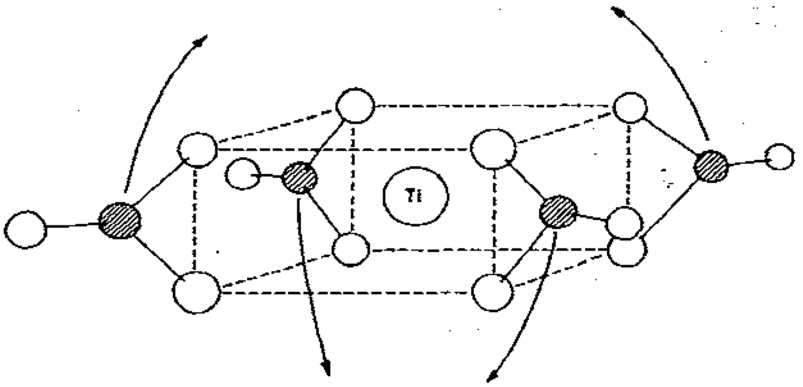


Fig. 5. The structure of tetranitratotitanium(IV).

In order to achieve closer packing of the eight oxygen atoms surrounding the titanium atom, two NO_3 groups are then moved upwards, and two downwards, as illustrated in Fig. 5.

Reactivity of bridging nitrate groups

The only example in which this type of bonding has been established is basic beryllium nitrate, the structure of which is shown in Fig. 6. As expected, the infrared spectrum of this compound shows the same N═O absorption band at 1630

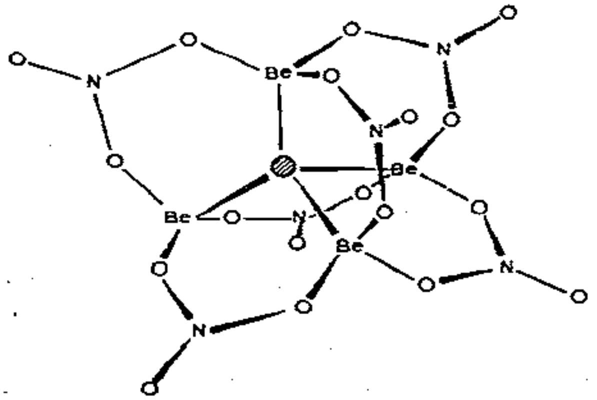


Fig. 6. The structure of basic beryllium nitrate.

cm^{-1} as is observed for the bidentate nitrates. However, the bonding between metal and oxygen atoms must now be largely *sigma* in character, and it becomes more difficult to envisage any mechanism by which a bridging nitrate group can dissociate from the molecule in a single step. Consistent with this, we find that basic beryllium nitrate does not display the same order of reactivity as is found for the bidentate nitrates.