INORGANIC NITRATES AND NITRATO-COMPOUNDS

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1. Introduction

Many simple compounds containing the nitrate group have recently been made for the first time and some exhibit interesting and unexpected properties, for example, volatility and high reactivity. Nitrates are generally dealt with only briefly in textbooks; these often erroneously state that nitrates of some elements are unknown, and fail to refer to important older work. This Review outlines the methods of preparation and the important properties of compounds containing the nitrate group, but does not deal in general with the large number of co-ordination complexes of metal nitrates.

Recent research has indicated that compounds of elements (M) and the nitrate group can be divided into two classes according to whether the $M–NO_3$ bond is predominantly ionic or covalent. The main differences upon which this classification is based are summarised in Table 1 and emphasised where appropriate in the text. We propose to apply systematically the term *nitrate* to a compound in which the $M–NO_3$ bond is ionic, that is, a compound containing the nitrate ion, and to use the term *nitrato-compound*, or the prefix *nitrato* to the element, when the NO_3 group is covalently bonded through one or more of its oxygen atoms.

2. Preparative Methods

The four principal reagents which have been employed in the synthesis of inorganic nitrates and nitrato-compounds are aqueous nitric acid (HNO_3), dinitrogen tetroxide (N_2O_4), dinitrogen pentoxide (N_2O_5), and "chlorine nitrate" ($ClNO_3$). Which reagent is used and how it is applied in the preparation and isolation of a particular nitrate or nitrato-compound varies according to the physical properties and chemical reactivity of the product. Many hydrated metal nitrates can be isolated from aqueous nitric acid solution when hydrolytic or other reactions do not interfere, but the preparation of anhydrous nitrates or nitrato-compounds, with very few exceptions, such as those of the alkali metals, silver, and barium, require anhydrous conditions. The three principal non-aqueous reagents are not of equal applicability or convenience; for example, many anhydrous nitrates and nitrato-compounds can be prepared with liquid dinitrogen pentoxide[1,2] or a solution of dinitrogen tetroxide in an ionising organic solvent[3,4,5] but $Sn(NO_3)_4$ and $Al(NO_3)_3$ have been isolated only

¹ M. Schmeisser, *Angew. Chem.*, 1955, **67**, 493.
² B. O. Field and C. J. Hardy, *J.*, 1964, 4428.
³ C. C. Addison and B. J. Hathaway, *Proc. Chem. Soc.*, 1957, 19.
⁴ C. C. Addison, B. J. Hathaway, and N. Logan, *Proc. Chem. Soc.*, 1958, 51.
⁵ C. C. Addison and B. M. Gatehouse, *J.*, 1960, 613.

TABLE 1. *Main differences between nitrates and nitrato-compounds.*

	Nitrates, $M^+.NO_3^-$	Nitrato-compounds, $M-ONO_2$
Examples of M in	Anhydrous compounds: alkali metals; alkaline earth metals (except Be); some heavy metals (Ag, Cd, Co, Pb, Tl).	Anhydrous compounds: Be, Al; majority of heavy metals; halogens.
	Hydrated compounds: majority of metals	Hydrated compounds: some heavy metals (Zr, Th, U).
Conditions of preparation (Section 2)	Generally by aqueous methods.	Non-aqueous methods essential except for the few hydrated compounds.
Volatility (Section 3.2)	Low or involatile. Alkali-metal nitrates can be distilled at 300-500°/0·005. Majority of hydrated nitrates decompose on heating.	Many sublime at low temperature, *e.g.*, $Ti(NO_3)_4$ at 25°/0·005.
Infrared absorption (6—15μ region) (Section 5)	Three fundamental bands.	Six fundamental bands.
Reactions (Section 4)		
(*a*) With organic compounds, for example ethers, hydrocarbons.	Generally do not react at room temperature.	Rapid nitration and oxidation at room temperature.
(*b*) With liquid dinitrogen tetroxide.	Do not form addition compounds.	Form addition compounds, *e.g.*, $Cu(NO_3)_2.N_2O_4$.

from reactions involving $ClNO_3$.[6] This is an inconvenient reagent to use because it is an explosive gas at room temperature and the reaction has to be performed at low temperatures. There is also a limitation to the use of a solution of dinitrogen tetroxide in an electron donor solvent because the solvent may co-ordinate so strongly with the metal that its removal disrupts the entire molecule; $Zr(NO_3)_4$, for instance, cannot be obtained with the help of this reagent,[7] but can be prepared[8] with liquid N_2O_5.

The anhydrous inorganic nitrates and nitrato-compounds isolated up to early 1964 and their methods of preparation have been summarised in Table 2 based on a periodic classification.

[6] M. Schmeisser and K. Brandle, *Angew. Chem.*, 1961, **73**, 388.
[7] B. O. Field and C. J. Hardy, unpublished work 1962, and C. C. Addison, personal communication.
[8] B. O. Field and C. J. Hardy, *Proc. Chem. Soc.*, 1962, 76.

2.1. Nitric Acid.—Aqueous nitric acid reacts with many metals and their compounds. The rate of reaction and the nature of the products varies according to the metal or compound, the strength of acid, and the temperature. The presence of nitrous acid has an important influence on the reaction rate of metals, such as Bi, Cu, Ag, Hg and Fe, which have a negative oxidation–reduction potential relative to that of the standard hydrogen electrode.[9]

Metal carbonates and hydroxides dissolve rapidly in nitric acid, as also do most oxides although some of these become recalcitrant when they have been heated to a high temperature. Evaporation of the solution produced, to the point of crystallisation, usually gives a nitrate hydrate [e.g., $Cu(NO_3)_2,5H_2O$], an oxide- or hydroxide-nitrate, which is a salt intermediate in composition between normal nitrate and oxide or hydroxide [e.g., $ZrO(NO_3)_2,2H_2O$] or a hydrogen salt $\{e.g., H[Au(NO_3)_4],3H_2O\}$. Unusual products are obtained from (a) a solution of tin(II) oxide in nitric acid; this, on concentration, gives an explosive hydroxide-nitrate, $Sn_3(OH)_4(NO_3)_2$,[10] and (b) black silver oxide, which is oxidised by nitric acid to the black complex salt, $Ag_7O_8NO_3$.

Most non-metals and their anhydrous chlorides are oxidised by nitric acid to the corresponding acid, essentially the hydrated oxide; thus sulphur, phosphorus, and arsenic give sulphuric acid, phosphoric acid, and arsenic acid respectively. The explosive gas "fluorine nitrate", FNO_3, is formed when fluorine is bubbled through concentrated HNO_3,[9] and iodine reacts with concentrated HNO_3 to yield first a yellow powder, claimed[11] to be iodyl nitrate $IO(NO_3)$, which is further oxidised to iodic acid.

2.2. Dinitrogen tetroxide, N_2O_4.—Liquid N_2O_4 by itself reacts at low temperatures with only a few metals, e.g., Na, K, Ag, and Pb to form nitrates, with Zn to form the addition compound $Zn(NO_3)_2,2N_2O_4$,[12] and with Hg to form dinitratomercury(II). The uranium oxides UO_3 and U_3O_8 both produce $UO_2(NO_3)_2,N_2O_4$ from which the anhydrous compound $UO_2(NO_3)_2$ can be obtained by heating the addition complex in vacuum at 165° for two hours.[13] Alkali-metal salts react with liquid N_2O_4 to produce nitrates, $KCl \rightarrow KNO_3 + NOCl$ and $NaClO_3 \rightarrow NaNO_3 + NO_2 + ClO_2$. Provided there is a trace of water to initiate the reaction, liquid N_2O_4 reacts with lithium carbonate, and the carbonate, chloride, chlorate, oxide, and hydroxide of magnesium to form the respective metal nitrates.[14]

Liquid N_2O_4 is non-polar and so displays very poor solvent properties for metal salts and its reaction with many metals, for instance Cu, is

[9] P. J. Durrant and B. Durrant, "Introduction to Advanced Inorganic Chemistry", Longmans, London, 1962, p. 682.
[10] J. D. Donaldson and W. Moser, *J.*, 1961, 1996.
[11] T. Kikindai, *Compt. rend*, 1954, **238**, 1229.
[12] P. Gray and A. D. Yoffe, *Quart. Rev.*, 1955, **9**, 379.
[13] B. Jesowska-Trzebiatowska and B. Kedzia, *Bull. Acad. Polon. Sci. Sér. Sci. chim.*, 1962, **10**, No. 5, 213.
[14] J. D. Archambault, H. H. Sisler, and G. E. Ryschkewitsch, *J. Inorg. Nuclear Chem.*, 1961, **17**, 130.

TABLE 2. *Anhydrous nitrates and nitrato-compounds isolated up to 1964 and their methods of preparation.*

General methods—

a. Aqueous nitric acid on metal or hydroxide (also on fluorine and iodine).
b. Liquid N_2O_4 or N_2O_5 in ethyl acetate, on metal, chloride, or carbonyl.
c. Liquid N_2O_5 on metal, anhydrous chloride, hydrated nitrate, etc.
d. Chlorine nitrate on anhydrous chloride.
e. Gaseous NO_2–N_2O_4 at elevated temperature and pressure.

Special methods—

f. Dehydration of hydrate followed by vacuum distillation or sublimation.
g. Vacuum dehydration of hydrate at 100° (Sc).
h. Ozone on $BrNO_3$.
i. I_2 on $I(NO_3)_3$.
j. NO_2–N_2O_4 on carbonyl in gas phase [$FeO(NO_3)$].

Notes.

(i) Roman type is used for nitrates, Italic type for nitrato-compounds, and Bold type for compounds for which there is insufficient information to allow classification.
(ii) The absence of a formula indicates that the anhydrous compound is unknown.
(iii) Anhydrous double salts, e.g., $CsUO_2(NO_3)_3$, or addition complexes with N_2O_4 and N_2O_5, are not included unless simple nitrates are unknown (e.g., for Hf and Po).

Group IA	IIA	IIIA	IVA	VA	VIA	VIIA	VIII		
HNO_3									
$LiNO_3$ [b,f]	$Be(NO_3)_2$ [b,e] $Be_4O(NO_3)_6$ [b,e]	—							
$NaNO_3$ [a]	$Mg(NO_2)_2$ [b]	—							
KNO_3 [a]	$Ca(NO_3)_2$ [b]	$Sc(NO_3)_3$ [g]	$Ti(NO_3)_3$ [c,d] $TiO(NO_3)_2$ [b]	$VO(NO_3)_3$ [e] $VO_2(NO_3)$ [b]	$Cr(NO_3)_3$ [c] $CrO_2(NO_3)_2$ [c]	$Mn(NO_3)_2$ [c,b]	$Fe(NO_3)_3$ [b] $FeNO(NO_3)_3$ [b,e] $FeO(NO_3)$ [j]	$Co(NO_3)_2$ [b]	$Ni(NO_3)_2$ [b]
$RbNO_3$ [a]	$Sr(NO_3)_2$ [a]	$Y(NO_3)_3$ [e]	$Zr(NO_3)_4$ [c] $ZrO(NO_3)_2$ [b]	$NbO(NO_3)_3$ [c]	$MoO_2(NO_3)_2$ [c]	Tc	$RuNO(NO_3)_3, N_2O_4$ [c]	Rh	$Pd(NO_3)_2$ [c]
$CsNO_3$ [a]	$Ba(NO_3)_2$ [a]	$La(NO_3)_3$ [e,**]	$Hf(NO_3)_4, N_2O_5$ [c]	$TaO(NO_3)_3$ [c]	$WO_2(NO_3)_2$ [c]	Re	Os	Ir	Pt
Fr	$Ra(NO_3)_2$ [a]	Ac†							

TABLE 2.—*continued*

I_B	II_B	III_B	IV_B	V_B	VI_B	VII_B	O
							He
						$FNO_3{}^a$	Ne
		$Al(NO_3)_3{}^d$	Si	P	S	$ClNO_3{}^e$	Ar
$Cu(NO_3)_2{}^{b,c,f}$	$Zn(NO_3)_2{}^{b,c,e}$	Ga	Ge	As	Se	$BrNO_3{}^d$ $Br(NO_3)_3{}^c$ $BrO_2(NO_3)^h$	Kr
$AgNO_3{}^a$	$Cd(NO_3)_2{}^b$	$In(NO_3)_3{}^c$	$Sn(NO_3)_4{}^d$	$SbO(NO_3)_3{}^c$	Te	$INO_3{}^f$ $I(NO_3)_3{}^d$ $IO(NO_3)_3{}^a$	Xe
$Au(NO_3)_3{}^c$	$Hg(NO_3)_2{}^{b,c}$	$TlNO_3{}^a$	$Pb(NO_3)_2{}^a$	$Bi(NO_3)_3{}^b$	$Po(NO_2)_4,N_2O_4{}^b$	At	Rn

* Lanthanide series		Generally $M(NO_3)_3$•			
†Actinide series	$Th(NO_2)_4{}^{b,e}$	Pa	$UO_2(NO_2)_2{}^{b,c}$		Simple anhydrous nitrates not reported for higher members.

exceedingly slow. However, when N_2O_4 is dissolved in an organic electron-donor solvent such as ethyl acetate or acetonitrile, the ionisation of N_2O_4 is enhanced and since the metal nitrato-compound produced is usually soluble in the organic solvent, the rate of reaction is very much increased. Addison and his co-workers have studied the behaviour of this reagent in detail and have used it, generally dissolved in dry ethyl acetate, for the preparation of the following anhydrous compounds from the starting material indicated:

Metal: $Cu(NO_3)_2$[3]; $Cd(NO_3)_2$, $Co(NO_3)_2$, $Hg(NO_3)_2$, $Mn(NO_3)_2$[5]; $Ca(NO_3)_2$, $Mg(NO_3)_2$[15]; $Zn(NO_3)_2$[16]; $UO_2(NO_3)_2$[17]; also $Bi(NO_3)_3$ by Straub and his co-workers.[18]

Anhydrous chloride: $Be(NO_3)_2$, $Be_4O(NO_3)_6$[19]; $Ni(NO_3)_2$[20]; $Fe(NO_3)_3$, $FeNO(NO_3)_4$[4].

Carbonyl (in liquid N_2O_4): $Fe(NO_3)_3$, $FeNO(NO_3)_4$[4]; $Co(NO_3)_2$, $Ni(NO_3)_2$[20].

Carbonyl (in the gas phase): $FeO(NO_3)$ [the carbonyls of Co and Ni give nitrites].[20]

Some metal oxides react at high temperatures and pressures with N_2O_4 to produce an N_2O_4 addition compound of the metal nitrate or nitrato-compound, e.g. MgO, ZnO and CuO at 87° and 14·5 atmospheres' pressure. Other metal oxides require much lower temperatures and pressures; HgO, Hg_2O, and $Ca(OH)_2$ react at 25° and 1·1 atm.[21] The lanthanide nitrates can be prepared by heating the sesquioxides (M_2O_3) with N_2O_4 at 150°c for 24 hours in a sealed tube.[22]

2.3.   Dinitrogen Pentoxide, N_2O_5.—Dinitrogen pentoxide dissolved in concentrated nitric acid was used by Guntz and Martin in 1909 to dehydrate the hydrated nitrates of Mn, Cu, Ni, and Co and to isolate the anhydrous compounds $M(NO_3)_2$ for the first time.[23]

Schmeisser and his co-workers allowed liquid N_2O_5 to react with metal oxides and anhydrous chlorides and obtained N_2O_5 addition compounds. They prepared the anhydrous nitrato-compounds: $CrO_2(NO_3)_2$, $VO(NO_3)_3$, $MoO_2(NO_3)_2$, $WO_2(NO_3)_2$, $SbO(NO_3)_3$, and $Ti(NO_3)_4$ by heating the addition compounds in a vacuum.[1] The Reviewers[2] extended the method to isolate $Zr(NO_3)_4$, $Ti(NO_3)_4$, $Hf(NO_3)_4,N_2O_5$, $NbO(NO_3)_3$, $Au(NO_3)_3$, $In(NO_3)_3$, $Pd(NO_3)_2$, $Zn(NO_3)_2$, $Cu(NO_3)_2$, $FeNO(NO_3)_4$, $Hg(NO_3)_2$,

[15] C. C. Addison and A. Walker, *J.*, 1963, 1220.

[16] C. C. Addison, J. Lewis, and R. Thompson, *J.*, 1951, 2829.

[17] C. C. Addison, H. A. J. Champ, N. Hodge, and A. H. Norbury, *J.*, 1964, 2354.

[18] D. K. Straub, H. H. Sisler, and G. E. Ryschkewitsch, *J. Inorg. Nuclear Chem.*, 1962, 24, 919.

[19] C. C. Addison and A. Walker, *Proc. Chem. Soc.*, 1961, 242.

[20] C. C. Addison, "Advances in Chemistry Series", Amer Chem. Soc., Special Publ. No. 14, 1962, 131.

[21] J. R. Ferraro and G. Gibson, *J. Amer. Chem. Soc.*, 1953, **75**, 5747.

[22] T. Moeller, V. D. Aftandilian, and G. W. Cullen, "Inorganic Syntheses", McGraw Hill, V, 1957, 37 ff.

[23] A. Guntz and F. Martin, *Bull. Soc. chim. France*, 1909, **5**, 1004.

$Be_4O(NO_3)_6$, and $RuNO(NO_3)_5(N_2O_4)_{0\cdot75}$ from the metal, hydrated nitrate, or anhydrous chloride. The nitrato-compound $TaO(NO_3)_3$ has also been prepared[24] by this method from the pentachloride and from vacuum-dried hydroxide.

Liquid N_2O_5 has advantages over N_2O_4 in the preparative field because its reactions do not require the presence of an electron-donor solvent. It is, however, sometimes desirable to dissolve N_2O_5 in an inert solvent such as carbon tetrachloride or trichlorofluoromethane in order to carry out the reaction at a low temperature or to moderate its rate. Trinitrato-chromium(III) has been prepared[25] by adding N_2O_5 to a suspension of chromium cabonyl in CCl_4 at $20°$; and $Br(NO_3)_3$ has been prepared[26] from BrF_3 and N_2O_5 in trichlorofluoromethane at -30 to $-50°$. Under the latter conditions ClO_2 and N_2O_5 give NO_3Cl.

Most non-metal halides react with liquid N_2O_5 to form an oxyhalide or an oxide; $SiCl_4$, BCl_3, and PCl_5 give SiO_2, B_2O_3, and $POCl_3$ respectively,[1]

2.4. Chlorine Nitrate, $ClNO_3$.—This is one of the most powerful nitrating agents known; at room temperature it reacts explosively with most metals, metal chlorides, and organic compounds, but at between $-40°$ and $-70°$ the reaction can be controlled. Schmeisser and his co-workers have used it to prepare[6] the nitrato-compounds $Sn(NO_3)_4$, $Ti(NO_3)_4$, and $I(NO_3)_3$ from the respective anhydrous chlorides; they also prepared $Al(NO_3)_3$ from aluminium tribromide and $ClNO_3$ in liquid bromine. Most non-metal chlorides react with $ClNO_3$, and the formation of compounds such as $B(NO_3)_3$ and $S(NO_3)_2$ have been postulated[6] as the initial product, but oxidation–reduction reactions then take place and the final products are usually highly polymeric and of indefinite composition.

3. Structures and Physical Properties

3.1. Structures.—(a) *Nitrates*. Metal nitrates are quite different structurally from salts of the type $M_m(XO_3)_n$ formed by other elements of Group V. The NO_3^- ion is geometrically similar to the planar BO_3^{3-} and CO_3^{2-} ions and differs from the pyramidal PO_3^{3-}, SO_3^{2-}, and ClO_3^- ions of the elements of the second Short Period. The N–O bond length is generally close to $1\cdot22$ Å[27] and the structure of the ion can be explained in terms of valence bond theory as a resonance hybrid of three canonical forms (I), (II), and (III), or of molecular orbital theory by assuming that nitrogen

(I)   (II)   (III)
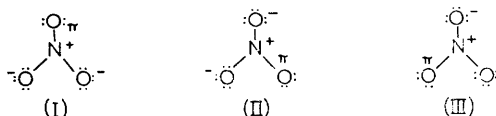
[24] K. W. Bagnall, D. Brown, and P. J. Jones, *J.*, 1964, 2396.
[25] C. C. Addison and D. J. Chapman, *J.*, 1964, 539.
[26] M. Schmeisser and L. Taglinger, *Angew. Chem.*, 1959, **71**, 523: *Chem. Ber.*, 1961, **94**, 1533.
[27] A. F. Wells, "Structural Inorganic Chemistry", 3rd Edition, Oxford Univ. Press, 1962; R. L. Sass *et al.*, *Acta Cryst.*, 1957, **10**, 567.

forms three σ bonds using sp^2 hybrid orbitals for the purpose, and that the p_z orbitals of the nitrogen and the three oxygen atoms combine to form a π molecular orbital containing two electrons. The length of the N–O bond is the same as that in nitric acid and not much greater than that of a double bond (1·19 Å) in N_2O and NO_2. Its explanation poses a similar problem to that of the short S–O bonds in a number of molecules. There is, however, a notable exception in the higher value (1·267 Å) found in a neutron diffraction study of lead nitrate.[28]

A number of different crystalline forms are displayed by many metal nitrates and these depend upon the temperature and treatment to which they have been subjected. There is, however, considerable lack of agreement on the details as the work on the alkali-metal nitrates, discussed in detail in the Supplements[29] to Mellor's Comprehensive Treatise on Inorganic and Theoretical chemistry, shows.

(b) *Nitrato-compounds.* When the NO_3 group is covalently bonded through one of the oxygen atoms to another atom (X) the N–O bond lengths lie between 1·36 and 1·41 Å for the N–O(X) bond, and between 1·22 and 1·29 Å for the other N–O bonds, for instance in nitric acid(IV),[30] fluorine nitrate(V),[31] and methyl nitrate(VI),[31,32] (all in the vapour phase):
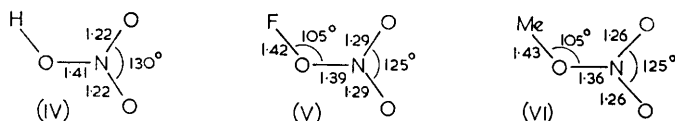
The structure of the anhydrous volatile compound dinitratocopper(II) has been determined[33] by electron diffraction in the vapour phase (in which its vapour density corresponds to the monomer[34]), and it is of considerable interest in that the nitrato-groups are bidentate, *i.e.*, bonded through two of the oxygen atoms as in (VII), and not as first reported.[35] The bonding of the

$$NO_{av} = 1·30 \pm 0·04 \text{ Å}$$
$$Cu\text{–}O = 2·00 \pm 0·02 \text{ Å}$$
$$Cu\text{–}N = 2·30 \pm 0·03 \text{ Å}$$
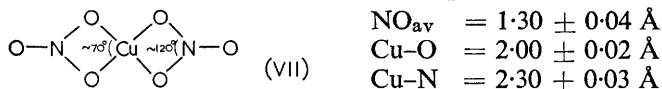
NO_3 groups is different in the crystalline state, and X-ray diffraction data have been interpreted[36] in terms of two different types of NO_3 group. Eight oxygen atoms are linked to each copper atom, two by bonds of length 1·9 Å, and six by weaker bonds of length about 2·5 Å. The long bonds are regarded as being largely ionic and the short bonds as covalent, and

[28] W. C. Hamilton, *Acta Cryst.*, 1957, **10**, 103.
[29] "Mellor's Comprehensive Treatise on Inorganic and Theoretical Chemistry", Vol. II, Suppl. II, Parts 1 and 2, The Alkali Metals, Longmans, London, 1961.
[30] L. R. Maxwell and V. M. Mosley, *J. Chem. Phys.*, 1940, **8**, 738.
[31] L. Pauling and L. O. Brockway, *J. Amer. Chem. Soc.*, 1937, **59**, 13.
[32] J. C. D. Brand and T. M. Cawthon, *J. Amer. Chem. Soc.*, 1955, **77**, 319.
[33] R. E. LaVilla and S. H. Bauer, *J. Amer. Chem. Soc.*, 1963, **85**, 3597.
[34] C. C. Addison and B. J. Hathaway, *J.*, 1958, 3099.
[35] H. Bauer and C. C. Addison, *Proc. Chem. Soc.*, 1960, 251.
[36] S. C. Wallwork, *Proc. Chem. Soc.*, 1959, 311.

the structure has been formulated as $[Cu(NO_3)]_n{}^{n+},n(NO_3)^-$; replacement of the nitrate ions by perchlorate ions could account for the existence of the compound $Cu(NO_3)(ClO_4)$.[37] However, this structure does not provide an immediate explanation of the volatility, and the infrared spectrum[38] contains no bands which can definitely be assigned to the nitrate ion*. A further refinement of the structural analyses has indicated[39] a more normal, distorted $(4 + 2)$ co-ordination for each copper atom instead of the $(6 + 2)$ co-ordination suggested above.

The occurrence of nitrato-groups bidentate to one metal atom in the solid state has been suggested on the evidence of X-ray diffraction measurements on the crystalline nitrato-complexes $UO_2(NO_3)_2,6H_2O$[40] and $RbUO_2(NO_3)_3$[41] containing the uranyl group. The structure $[UO_2(NO_3)_2-(H_2O)_2]$, $4H_2O$ proposed[40] for the hexahydrate accords better with recent infrared data[42] than the structure $[UO_2(H_2O)_6](NO_3)_2$, suggested previously;[43] the two planar nitrato-groups appear to be disposed asymmetrically about the uranyl group (VIII) (the uranyl oxygens, which are not shown
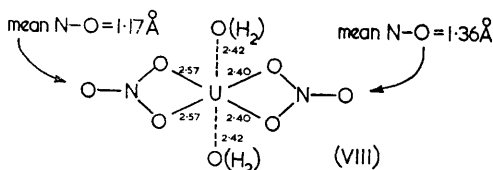
above, are approximately at right angles to the plane of the paper and the $\angle$ O–U–O $= 173°$). The very different mean N–O distances in the two NO_3 groups are difficult to understand.

3.2. Melting Points, Boiling Points, and Volatility.—Although most anhydrous metal nitrates are stable at the melting point there are frequently large discrepancies between published values of this property, and the melting point cannot generally be taken as an accurate indication of purity. Melting points for some of these nitrates are given in Table 3 mainly to show that a clear trend is not apparent in the series of nitrates of the alkali and alkaline earth metals.

* [*Note added in proof:* Logan, Simpson, and Wallwork (*Proc. Chem. Soc.*, 1964, 341) have shown that two forms of $Cu(NO_3)_2$ exist, and that these differ in their X-ray powder photographs and infrared spectra. The published crystal structure[36] is said to relate to the α-form, whereas the published infrared spectra[5] relate to the β-form.]

[37] B. J. Hathaway, *Proc. Chem. Soc.*, 1958, 344.

[38] C. C. Addison and B. J. Hathaway, *J.*, 1960, 1468.

[39] S. C. Wallwork, Internat. Congress of Internat. Union of Crystallog., Rome, Sept. 1963.

[40] J. E. Fleming and H. Lynton, *Chem. and Ind.*, 1960, 1416.

[41] J. L. Hoard and J. D. Stroupe, quoted in "Spectroscopic Properties of Uranium Compounds", by G. H. Dieke and A. B. F. Duncan, McGraw Hill, New York, 1949, p. 13.

[42] J. G. Allpress and A. N. Hambly, *Austral. J. Chem.*, 1959, **12**, 569.

[43] V. N. Volovenko, E. V. Stroganov, A. P. Sokolov, and V. N. Zandin, *Radiokhimiya*, 1960, **2**, 24.

The relatively low melting points of the alkali-metal nitrates have been explained[44] as being due to the formation of association complexes which contribute a term to the overall entropy of melting without greatly increasing the heat of fusion. Differential thermal analysis (see section 4.4) is particularly useful in the determination of melting points and the temperatures of phase transitions. A number of commonly available anhydrous and hydrated nitrates have been examined in this way.[45,46]

TABLE 3. *Melting points of anhydrous metal nitrates.*

M in MNO_3	Li	Na	K	Rb	Cs	Ag	Tl
M. p.[41]	255°	307°	333°	310°	414°	212°	206°
M in $M(NO_3)_2$	Mg	Ca	Sr	Ba			
M. p.[44]	*	561°	605°	595°			

* Anhydrous $Mg(NO_3)_2$ decomposes almost immediately on melting.[47]

Melting points, and particularly the so-called "boiling-points", are even less reproducible and meaningful for *hydrated* metal nitrates than for anhydrous ones because these compounds tend to dissolve in the water of crystallisation, and also to decompose by the loss of water and nitrate groups simultaneously or consecutively according to the experimental conditions (see also section 4.4 on thermal decomposition). On the other hand, stable nitrato- and nitrato-oxide compounds, which sublime or distil in a vacuum, have been isolated for a number of metals and non-metals (Table 4). However, m.p.s have been given for only a few of these, partly because of the experimental difficulties of handling them under anhydrous conditions. The vapour of dinitratocopper(II)[48] and the solid compounds of several other metals[2] have been shown, by infrared spectroscopy, to contain covalent nitrato-groups. These nitrato-compounds exhibit high volatility compared with the low volatility[49] of the alkali-metal nitrates (Table 4). The latter are ionic in the solid state and are probably similar in the vapour state to the slightly volatile ionic alkali-metal chlorides which, from measurement of electron diffraction, dipole moments, and photodissociation,[9] have been postulated to exist as ion pairs in the vapour state. A qualitative comparison of the volatility of the nitrato-compounds with that of the covalent chlorides of the respective metals can be made, but a quantitative comparison is not possible with the exception of dinitratocopper(II), because boiling points or sublimation temperatures have not been measured under identical conditions, or as a function of the pressure.

[44] W. J. Davis, S. E. Rogers, and A. R. Ubbelohde, *Proc. Roy. Soc.*, 1953, *A*, **220**, 14.
[45] S. Gordon and C. Campbell, *Analyt. Chem.*, 1955, 27, 1102.
[46] M. M. Karavaev and I. P. Kirillov, *Izvest. V.U.Z., M.V.O. S.S.S.R. Khim., i khim. Technol.*, 1959, 2, 231.
[47] C. C. Addison and J. M. Coldrey, *J.*, 1961, 468.
[48] B. M. Gatehouse, Ph.D. Thesis, London, 1958.
[49] C. J. Hardy and B. O. Field, *J.*, 1963, 5130.

3.3. **Solubility.**—Metal nitrates are soluble in water, but there is considerable variation in the molar solubility, and the temperature coefficient of solubility, through a series of metal nitrates of similar formula, *e.g.*, for alkali-metal nitrates:

Metal		Na	K	Rb	Cs
Solubility (moles/kg. H_2O）	0°	8·6	1·32	2·36 (20°)	0·47
	100°	22·0	25·3	31·8	10·5

No simple correlation is apparent between the solubility of a metal nitrate and the ionic or hydrated radius of the cation. Concentrated aqueous solutions of metal nitrates can be visualised as consisting of small unhydrated nitrate ions packed between large hydrated cations. The occurrence of nitrato-complexes is thought[50] to be the exception, for instance, the strong association of NO_3 groups with the ions of Th^{4+} and In^{3+} in aqueous solution as indicated by Raman spectra.

Little quantitative information is available on solubilities of nitrates in organic solvents, *e.g.*, alcohols, ethers, ketones, and organo-nitrogen compounds, although some of these have been used in the separation of metals and in analytical chemistry. The solubilities of silver nitrate, and the dinitrato-compounds of copper(II) and zinc(II) are compared in Table 5 for four different solvents.[51]

TABLE 5. *Solubilities of silver nitrate and dinitrato-compounds of copper and zinc in various solvents at 20° (except where otherwise stated).*

Solvent	Solubility (moles per mole of solvent)		
	$Cu(NO_3)_2$	$Zn(NO_3)_2$	$AgNO_3$
H_2O	0·144 (25°)	0·122 (25°)	0·242
Ethyl acetate	0·71 (25°)	>0·6	0·014
Nitromethane	0·016	0·0015	negligible
Acetonitrile	0·074	0·15	0·27

The high solubility in ethyl acetate of the covalent copper and zinc compounds (5 times higher than in water on a molar basis), and the low solubility of the ionic silver nitrate, led to the inference that high solubility in this kind of solvent was mainly a consequence of the covalent bonding between the metal and the nitrato-group. However, anhydrous cadmium nitrate is ionic in the solid state and is also very soluble in ethyl acetate, hence the bond character is only one of a number of contributory factors.

The solubilities of many metal nitrates have been determined in tri-n-butyl phosphate (TBP) largely because the solvent is used in the separation of uranium and plutonium from fission products. A summary of the results obtained up to 1958 has been given by McKay and Healy[52] who

[50] C. K. Jorgenson, "Inorganic Complexes", Academic Press, London, 1963, p. 82.
[51] C. C. Addison, B. J. Hathaway, N. Logan, and A. Walker, *J.*, 1960, 4308.
[52] H. A. C. McKay and T. V. Healy, Progress in Nuclear Energy, Series III, Process Chemistry, Pergamon Press, London, 1958, Vol. 2, pp. 549.

TABLE 4. *Physical properties of volatile nitrates and nitrato-compounds.*

Class	Compound	Ref.	M.p.	Ref.	Volatility (°C/mm.Hg.)	Ref.	B.p. of chloride
	$Au(NO_3)_3$	a			Subl. 80/0·004	a	$AuCl_3$, subl. 265°
	$Cu(NO_3)_2$	b	255—256°	b	V.p. 150/0·25 to 214/3·0; ht. of sublimation 15 kcal/mole		$CuCl_2$ decomp. to $CuCl$, 993°
	$FeNO(NO_3)_4$	c			Subl. 120/vac. 120/0·001	b	$FeCl_3$, 315°
Nitrato-compounds	$Hf(NO_3)_4 \cdot N_2O_5$	a			Subl. 100/0·01	c	$HfCl_4$, subl. 417°
	$Hg(NO_3)_2$?	c			Subl. in vac. 240/0·07	a	$HgCl_2$, 302°
	$In(NO_3)_3$	a			Subl. 130/0·001	a	$InCl_3$, subl. <400°
	$Pd(NO_3)_2$	a			Subl. 80/0·003	a	$PdCl_2$, m.p. 500° (decomp.)
	$Sn(NO_3)_4$	d	58	e, a	Subl. 40/vac.	d	$SnCl_4$, 114°
	$Ti(NO_3)_4$	e			Subl in vac. 20/0·02	e	$TiCl_4$, 136°

TABLE 4.—continued

Class	Compound	Ref.	M.p.	Ref.	Volatility (°C/mm.Hg.)	Ref	B.p. of chloride
	$Zn(NO_3)_2$	a			Subl. 275/0·03	a	$ZnCl_2$, 732°
	$Zr(NO_3)_4$	f			Subl. 100/0·01	f	$ZrCl_4$, subl. 331°
	FNO_3	g	−175	h	B.p. −42	h	FCl, −101°
	$ClNO_3$	i	−107	j	B.p. −18	j	Cl_2, −34°
Nitrato-oxide compounds	$Be_4O(NO_3)_6$	k			Subl. 125/0·05	a	$BeCl_2$, 520°
	$CrO_2(NO_3)_2$	l	−70	l	B.p. 28/0·001	l	CrO_2Cl_2, 117°
			−35	m	B.p. 45/2	m	
	$VO(NO_3)_3$	l	2	e	B.p. 68—70/vac.	e	$VOCl_3$, 127°
Ionic nitrates	MNO_3 (where M=Li, Na, K, Rb, Cs).		253 (Li) to 414 (Cs)		Distil at 350—500/0·005		E.g., NaCl, 1413°
	NH_4NO_3	o	169		Subl. 75/0·001	n	Subl, 335°

[a] B. O. Field and C. J. Hardy, *J.*, 1964, 4428. [b] C. C. Addison and B. J. Hathaway, *Proc. Chem. Soc.*, 1957, 19; *J.*, 1958, 3099. [c] C. C. Addison, B. J. Hathaway, and N. Logan, *Proc. Chem. Soc.*, 1958, 51. [d] M. Schmeisser and K. Brandle, *Angew Chem.*, 1957, **69**, 781. [e] M. Schmeisser, *Angew. Chem.*, 1955, **67**, 493. [f] B. O. Field and C. J. Hardy, *Proc. Chem. Soc.*, 1961, 76. [g] G. H. Cady, *J. Amer. Chem. Soc.*, 1934, **56**, 2635. [h] P. J. Durrant and B. Durrant, "Introduction to Advanced Inorganic Chemistry," Longmans, London, 1962, p. 94. [i] H. Martin and Th. Jacobsen, *Angew. Chem.*, 1955, **67**, 524. [j] H. Martin, *Angew. Chem.*, 1958, **70**, 97. [k] C. C. Addison and A. Walker, *Proc. Chem. Soc.*, 1961, 242. [l] M. Schmeisser and D. Lutzow, *Angew. Chem.*, 1954, **66**, 230. [m] W. H. Hartford and M. Darrin, *Chem. Reviews*, 1958, 58, 1-61; these authors claim m.p. in ref (l) too low owing to supercooling. [n] C. J. Hardy and B. O. Field, *J.*, 1963, 5130. [o] Ray and Jana, *J.*, 1913, **103**, 1565.

showed that for highly soluble salts the composition of the saturated solutions corresponds to the formation of definite solvates; for instance, $UO_2(NO_3)_2(TBP)_2$, which has a sharp m.p. of $-6°$. Solubilities of a few anhydrous and hydrated metal nitrates and of $UO_2(NO_3)_2,6H_2O$ in TBP are given in Table 6. In general, anhydrous ionic metal nitrates have low solubilities in TBP whereas hydrated ionic metal nitrates show appreciable solubility and water is also dissolved with them.

TABLE 6.   *Solubilities of metal salts in TBP at 25°.*

Solid phase	Solubility of salt (moles/l.)	Solubility of water (moles/l.)
$LiNO_3,H_2O$	1·32	3·14
$NaNO_3$	0·054	—
KNO_3	0·0025	—
$Ca(NO_3)_2,4H_2O$	0·99	1·84
$Sr(NO_3)_2,4H_2O$	0·19	3·19
$Sr(NO_3)_2$	0·016	—
$Ba(NO_3)_2$	0·00075	—
$Cu(NO_3)_2,6H_2O$	1·14	2·28
$Co(NO_3)_2,6H_2O$	0·83	3·20
$UO_2(NO_3)_2,6H_2O$	1·6	0·33

3.4.   Other Physical Properties.—Molten salts, particularly nitrates and chlorides, are being studied extensively for use as high-temperature solvents and reaction media, and an increasing amount of information on their viscosity, electrical conductivity, and surface tension is becoming available.

Viscosities of the nitrates of Li, Na, K, NH_4, Tl, and Ag, and electrical conductances of the nitrates of Li, Na, K, Rb, Cs, Tl, and Ag, expressed as a function of temperature, have been tabulated by Ubbelohde and his co-workers,[53] and association into complexes has been postulated to explain the lower melting points of these salts than of the ionic halides of the corresponding metals.

The surface tensions of the anhydrous nitrates of the alkali metals and Tl, Ag, Ca, Sr, and Ba have been measured over wide temperature ranges by Addison and Coldrey.[47] They consider that a degree of covalency is evident in the nitrates of metals in Groups I and II in the liquid state.

The densities and some other physical properties of solid metal nitrates and their aqueous solutions are generally given in compilations of physical properties of inorganic substances, but these are usually derived from single measurements and few detailed studies have been made. A notable exception is found in the determination of data on aqueous and organic solutions relevant to solvent extraction recovery systems for nuclear fuel.[54]

[53] J. P. Frame, E. Rhodes, and A. R. Ubbelohde, *Trans. Faraday Soc.*, 1959, **55**, 2039.
[54] C. M. Slansky, Progress In Nuclear Energy, Series III, Process Chemistry, Pergamon Press, London, 1958, Vol. 2, p. 535.

4. Reactions

The more important reactions of inorganic nitrates and nitrato-compounds are summarised for convenience under the headings of oxidation, nitration, hydrolysis, thermal decomposition, radiolytic decomposition, and addition compounds with N_2O_4 and N_2O_5. Some of the reactions, for instance the reduction of nitrate to ammonia and to nitric acid, which are used in the analytical determination of the nitrate group are discussed at the end of this Section.

4.1. Oxidation Reactions.—The explosive oxidation of sulphur and carbon by solid potassium nitrate mixed in the form of gunpowder has been known in Europe since the thirteenth century and has had a profound effect on the development of the modern World. All solid nitrates and nitrato-compounds are oxidising agents to a greater or less extent and will react with organic matter to form carbon monoxide, carbon dioxide, and oxides of nitrogen. Intimate mixtures of nitrates with certain metals can explode violently; the mixture of zirconium powder and $UO_2(NO_3)_2$, $6H_2O$ formed during the selective dissolution of uranium from a zirconium–uranium alloy by concentrated nitric acid is extremely sensitive to percussion.[55] Solid nitrates, and liquid nitric acid, have been used as a source of oxygen in rocket propellants.

4.2. Nitration Reactions.—Hydrated metal nitrates react with aliphatic hydrocarbons in sealed tubes at 100—150° to produce, in general, a mixture of nitro-alkanes and oxidation products.[56,57] Aromatic hydrocarbons are not nitrated when heated with the anhydrous nitrates of K, Na, NH_4, Ba, Pb, or Ag, but in the presence of aluminium trichloride they are nitrated at 30—40°.[56] These salts are probably not effective as nitrating agents alone because they are ionic nitrates and are unable to produce the necessary reactive species such as $NO_3\cdot$ or $NO_2\cdot$ radicals or the nitronium ion, NO_2^+.

Metal nitrato-compounds with the covalent structure $M-O-NO_2$ are generally highly reactive owing to dissociations occurring at the M–O or O–N bond (or both) to give $NO_2\cdot$ radicals. This behaviour is similar to the dissociation of alkyl nitrates, $R-O-NO_2$ to give $NO_2\cdot$ radicals, which is an important step in the reactions (and pyrolysis) of alkyl nitrates,[58] and is in contrast to the nitration of aromatic compounds by alkyl nitrates in the presence of sulphuric acid[59] when the nitronium ion, NO_2^+, is the active species. The stronger the covalent bond between the metal or non-metal and the nitrato-group the more reactive is the nitrato complex and the more likely is the complex to be volatile; the highly volatile titanium

[55] F. S. Martin and B. O. Field, A.E.R.E. Report C/R 2692 (1958).
[56] A. V. Topchiev, "Nitration of Hydrocarbons and Other Organic Compounds", Pergamon Press, London, 1959.
[57] F. Asinger, G. Geiseler, and W. D. Wirth, *Chem, Ber.*, 1957, **90**, 1987.
[58] P. Gray and A. D. Yoffe, *Chem. Rev.*, 1955, **55**, 1069.
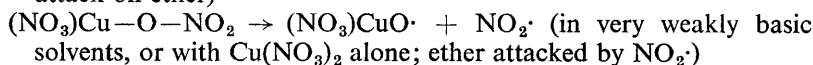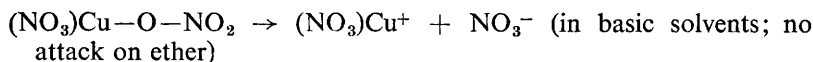[59] R. Boschan, R. T. Merrow, and R. W. van Dolah, *Chem. Rev.*, 1955, **55**, 485.

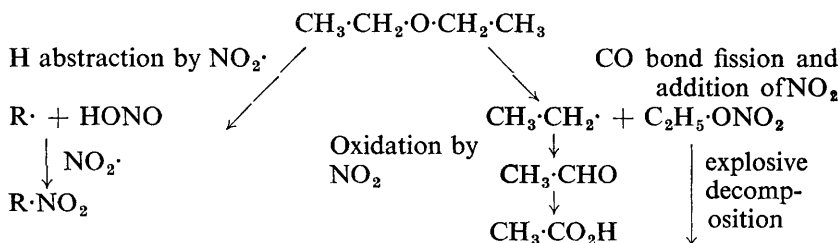compound $Ti(NO_3)_4$ readily nitrates and oxidises paraffinic hydrocarbons at 25°.[60]

The reactions of the anhydrous volatile copper compound $Cu(NO_3)_2$ with diethyl ether, dimethyl ether, and nitromethane have been studied in detail by Addison and his co-workers.[20] When $(CuNO_3)_2$ is dissolved in a basic solvent (L) a complex such as (IX) is formed, and the strength of the $Cu-ONO_2$ bonds varies with the nature of L. When ether vapour is

$$O_2NO-\underset{\underset{L}{|}}{\overset{\overset{L}{\diagup}}{Cu}}-ONO_2 \quad \text{(IX)}$$
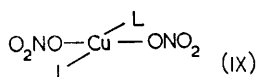
passed into a solution of $Cu(NO_3)_2$ in nitrobenzene, NO_2 and acetaldehyde are evolved and a green solid is precipitated. When ether is added to a solution of $Cu(NO_3)_2$ in ethyl acetate or methyl cyanide it does not react because these solvents co-ordinate so strongly to the copper atom that the $Cu-ONO_2$ bond is so weakened that dissociation to $NO_2\cdot$ radicals does not occur:

$(NO_3)Cu-O-NO_2 \rightarrow (NO_3)Cu^+ + NO_3^-$ (in basic solvents; no attack on ether)

$(NO_3)Cu-O-NO_2 \rightarrow (NO_3)CuO\cdot + NO_2\cdot$ (in very weakly basic solvents, or with $Cu(NO_3)_2$ alone; ether attacked by $NO_2\cdot$)

Thus the anhydrous nitrato-copper compound can be regarded as a low-temperature source of NO_2 radicals and the reaction with ether can be formulated as

$$CH_3\cdot CH_2\cdot O\cdot CH_2\cdot CH_3$$

H abstraction by $NO_2\cdot$ ╱ ╲ CO bond fission and
                                                     addition of NO_2
R· + HONO ╱ $CH_3\cdot CH_2\cdot + C_2H_5\cdot ONO_2$

│ $NO_2\cdot$ Oxidation by   ↓
↓ NO_2 $CH_3\cdot CHO$ │ explosive
R·NO_2 ↓   │ decomp-
                            $CH_3\cdot CO_2H$ ↓ osition

In addition, nitrate ions and hydroxyl ions may result from the $NO_3,CuO\cdot$ radical formed initially.

Nitromethane is a good solvent for $Cu(NO_3)_2$ on account of its high dielectric constant, and the solution is stable at room temperature, but NO_2 is evolved when the solution is boiled and a green salt containing copper is precipitated. This reaction probably proceeds by a free-radical mechanism in the same way as that with ether and the gas-phase reaction of NO_2 with nitromethane at 400°.

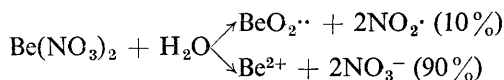[60] B. O. Field and C. J. Hardy, J., 1963, 5278.

Chlorine nitrate and fluorine nitrate react explosively in contact with many inorganic and organic compounds, but under controlled conditions, *i.e.*, at low temperature in a suitable organic solvent, $ClNO_3$ will both nitrate and chlorinate organic compounds. The many reactions of halogen nitrates have been reviewed recently.[6]

4.3. Hydrolysis.—Anhydrous and hydrated metal nitrates and nitrato-compounds in general dissolve in water to give nitrate ions and metal ions, or hydrolysis products of the metal ion, *e.g.*,

$$x\mathrm{Fe}^{3+} + y\mathrm{H_2O} \rightleftharpoons \mathrm{Fe}_x(\mathrm{OH})_y^{3x-y+} + y\mathrm{H}^+$$
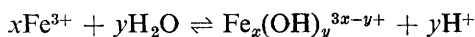
Hydrolytic reactions of this kind have been reviewed by Sillén;[61] they depend primarily on the nature of the metal and occur with compounds containing many other anionic groups, for example chloride, perchlorate, and sulphate, and will not be discussed further.

Dinitratoberyllium(II) evolves brown fumes on dissolving in water, and produces nitrate and nitrite ions in sodium hydroxide solution, in contrast to the anhydrous ionic nitrates of Ca, Sr, and Ba.[15,20] It has been suggested that the dissociation of the covalently bonded $-\mathrm{Be-O-NO_2}$ group by the breaking of the O–N bond can explain the small amount of nitrite formed:

$$\mathrm{Be(NO_3)_2} + \mathrm{H_2O} \diagdown \begin{array}{l} \nearrow \mathrm{BeO_2}^{\cdot\cdot} + 2\mathrm{NO_2}^{\cdot} \ (10\%) \\ \searrow \mathrm{Be}^{2+} + 2\mathrm{NO_3}^- \ (90\%) \end{array}$$

The NO_2 produced gives equal quantities of nitrite and nitrate ions. In non-aqueous media, such as ethyl acetate, the anhydrous beryllium compound dissolves to a pale yellow solution which has an absorption spectrum corresponding to that of NO_2.[20]

The volatile nitrato-oxide compound of beryllium, $Be_4O(NO_3)_6$, hydrolyses slowly in water, to give only nitrate ions. This compound is thought to have the same structure as the volatile acetato-oxide compound, $Be_4O(Ac)_6$; each nitrato-group is part of a six-membered ring with two of the oxygen atoms bonded to beryllium atoms. It is therefore suggested[15,20] that the $-NO_2$ group cannot break away as in dinitratoberyllium(II).

No other conclusive example has yet been found of a covalent nitrato-compound of a metal which gives nitrite ions on hydrolysis; highly covalent nitrato-compounds of titanium[60] and zirconium,[8] which might be expected to react in this way, only give nitrate ions on hydrolysis. The unusual binuclear nitratonitrosylruthenium complex[62,63] $Ru_2N_6O_{15}$ (for which infrared spectroscopy shows nitrite ions and nitrito- and nitro-groups to be absent) gives nitrite on hydrolysis. However, this cannot unequivocally be said to arise from the co-ordinated nitrato-groups because the nitrosyl

[61] L. G. Sillén, *Quart. Rev.*, 1959, **13**, No. 2, 146.
[62] F. S. Martin, J. M. Fletcher, P. G. M. Brown, and B. M. Gatehouse, *J.*, 1959, 76.
[63] D. Scargill and J. M. Fletcher, *Proc. Chem. Soc.*, 1961, 251.

groups may be more reactive than in the more usual series of complexes of the general formula, $RuNO(NO_3)_x(H_2O)_{5-x}$, which do not give nitrite on hydrolysis.

4.4. Decomposition.—(a) *Thermal.* The long-established view of the thermal decomposition of metal nitrates is that the first step is probably the loss of oxygen with the formation of metal nitrite. If this is stable at the temperature of the experiment the reaction stops, *e.g.*, the alkali-metal nitrates at temperature less than about 750°:

$$2MNO_3 \rightleftharpoons 2MNO_2 + O_2$$
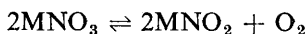
The equilibrium pressure of oxygen is 1 atmosphere at the following temperatures: Li, 474°; Na, 525°; K, 533°; Rb, 548°; Cs, 584°.[64] If the nitrite is unstable at the given temperature, further decomposition into metal oxide and oxides of nitrogen occurs, and the amount of nitrite at any given time depends on the relative rates of decomposition of the nitrate and nitrite; thus for $Ba(NO_3)_2$ at 600°:

$$Ba(NO_3)_2 \rightarrow Ba(NO_2)_2 + O_2$$
$$Ba(NO_2)_2 \rightarrow BaO + NO + NO_2$$
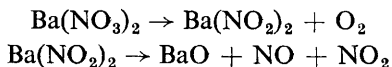
If the nitrite is very unstable, the only product is the oxide, provided it is stable at the given temperature:

$$Pb(NO_3)_2 \rightarrow PbO + 2NO_2 + \tfrac{1}{2}O_2$$
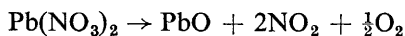
Finally, if the oxide is thermally unstable at the temperature at which the nitrate and nitrite decompose, the metal is produced:

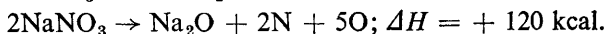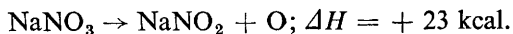$$AgNO_3 \rightarrow Ag + NO_2 + \tfrac{1}{2}O_2$$
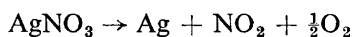
The above treatment is over-simplified; other reactions are known to proceed simultaneously for many nitrates, and the nature and amounts of the products frequently depend upon the rate of heating and the size of the sample. In addition, a hydrated nitrate can behave differently from the anhydrous nitrate or nitrato-complex of the same metal. Much of the early work in this field consisted of qualitative observations on materials of unknown purity and it is not surprising that some of the results are apparently contradictory and that there is little detailed knowledge of the basic reactions.

The decomposition of the alkali-metal nitrates illustrates some of the simultaneous and consecutive reactions which can occur even for these "simple" ionic salts. Sodium nitrate decomposes rapidly above 800°c to give a substantial amount of oxide,[65] as well as nitrite, and as the tempera-

[64] M. C. Sneed and R. C. Bransted, "Comprehensive Inorganic Chemistry", Van Nostrand, New York, 1957, p. 125.
[65] K. Leschewski and G. Zulla, *Ber. Ges. Freunden tech. Hochschule, Berlin*, 1942, **1**, 168.

ture is increased sodium peroxide is also formed.[66] It seems likely that alkali-metal ions, nitrate ions, and nitrite ions (all probably as ion-pairs) exist in the vapour phase at these temperatures, because these metal nitrates and nitrites can be distilled without decomposition at temperatures in the range 450—550°/10^{-3}mm.[49] The two main reactions for alkali-metal nitrates are endothermic:[66]

$$NaNO_3 \rightarrow NaNO_2 + O; \; \Delta H = + 23 \text{ kcal.}$$
$$2NaNO_3 \rightarrow Na_2O + 2N + 5O; \; \Delta H = + 120 \text{ kcal.}$$

But when the nitrate is heated in the presence of a metal with a high heat of combustion, it is possible for an exothermic chain reaction to be initiated which may lead to an explosion:

$$3KNO_3 + 5Al \rightarrow 3KAlO_2 + Al_2O_3 + 3/2N_2$$

When molten mixtures of sodium nitrate and potassium nitrate are used for the heat treatment of metals and alloys it is therefore necessary not to exceed certain maximum temperatures to avoid serious accidents.[67]

The thermal decomposition of hydrated heavy-metal nitrates and nitrato-compounds is more complicated than that of the alkali-metal nitrates, because hydrolysis can occur and complexes (probably polymeric) containing hydroxo- and oxo-groups in addition to nitrato- and nitrito-groups, and nitrate and nitrite ions, can be formed as intermediates. An empirical formula for such an intermediate with a definite X-ray pattern is $Ni(NO_3)$-$(OH),\frac{1}{2}H_2O$.[68] Thermogravimetric analysis (T.G.A.), in which loss of weight is measured as a function of temperature, and differential thermal analysis (D.T.A.), in which the thermal capacity is measured relative to that of a standard substance, have been used in recent years to study these reactions. The results must, however, be interpreted with caution unless chemical analysis and/or infrared spectra are also available at intermediate stages. T.G.A. of rare-earth nitrates has been claimed[69] to show the formation of intermediate oxide-nitrates mixed with the oxides, but an infrared study of praseodymium nitrate shows that it decomposes *via* an intermediate nitrite.[70] T.G.A. is particularly useful for determining the temperature at which the final stable product is obtained, and results for forty-five metal nitrates have been collected by Duval[71] who has discussed their application in quantitative analysis. The thermal decomposition of ten anhydrous[45] and several hydrated nitrates[45,46] has been studied with the D.T.A. method. A further complication which adds to the difficulty of

[66] K. Leschewski and W. Degenhard, *Ber.*, 1939, **72**, 1763.
[67] H. Remy, "Treatise on Inorganic Chemistry", Vol. 1, Elsevier, London, 1956, p. 601.
[68] E. M. Vander Wall, U.S.A.E.C. Report IDO-14597 (1962).
[69] W. W. Wendlandt and J. L. Bear, *J. Inorg. Nuclear Chem.*, 1960, **12**, 276.
[70] F. Vratny, *et al.*, *Trans. Faraday Soc.*, 1960, **56**, 1051; *J. Inorg. Nuclear Chem.*, 1961, **17**, 281.
[71] C. Duval, "Thermogravimetric Analysis of Inorganic Compounds", Elsevier, London, 1963.

understanding the reactions is the occurrence of allotropic forms of the final product. There is X-ray diffraction and other evidence[72,73] that the thermal decomposition of the dihydrate of dinitratouranyl(II) (obtained from the more common hexahydrate) at temperatures up to about 450° can give uranium trioxide with at least three different crystallographic forms (β, γ, and amorphous), and that the major product can be any of these, according to the experimental conditions.

(b)   *Radiolytic.*   The overall effect of irradiating solutions of metal nitrates with X-rays,[74] fast neutrons, or gamma-rays,[75] is to reduce nitrate ion to nitrite ion and to liberate oxygen and hydrogen. A little nitrogen is also produced from concentrated solutions of nitrates.[75] The large reduction in the hydrogen yield as the nitrate concentration is increased can be qualitatively explained by the reaction of nitrate ions with diffusing hydrogen atoms:

$$NO_3^- + H \rightarrow NO_2 + OH^-$$
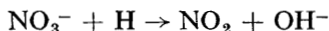
Irradiation of these solutions with fission recoil fragments does not produce nitrite, but greatly increases the yield of nitrogen, and the stoicheiometry of the gaseous products from solutions of calcium nitrate[75] corresponds to the overall equations:

$$Ca(NO_3)_2,H_2O \rightarrow Ca(OH)_2 + N_2 + \tfrac{5}{2}O_2$$

$$H_2O \rightarrow H_2 + \tfrac{1}{2}O_2$$
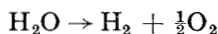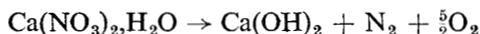
Nitrogen is thought to be produced by the direct action of highly energised ions or electrons on the nitrate ion, and the nature of the cation has little effect on the nitrogen yield.

The irradiation of crystalline metal nitrates in a nuclear reactor generally gives equivalent amounts of oxygen gas and nitrite ions mainly by electronic ionisation and excitation rather than by elastic collisions with particles.[76,77] The photolysis of solid nitrates of the alkali metals and some heavy metals with light from a high-pressure mercury arc produces nitrite and oxygen with a quantum yield varying from 0·002 to 0·19;[78] water of hydration increases the sensitivity to radiation.

4.5.   Addition Compounds of Metal Nitrates and Nitrato-compounds with N_2O_4 and with N_2O_5.—These are important intermediates in the isolation of many metal nitrates and nitrato-compounds from reactions involving N_2O_4 or N_2O_5; they are generally thermally unstable and dis-

[72] R. S. Ondrecjin, U.S.A.E.C. document, TID 17733 (1963).
[73] R. S. Ondrecjin and T. P. Garrett, *J. Phys. Chem.*, 1961, **65**, 470.
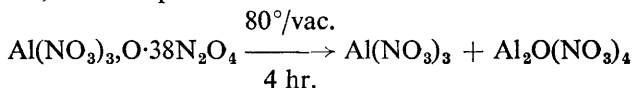[74] N. A. Bakh, Conf. Acad. Sci., U.S.S.R., Peaceful Uses of Atomic Energy, 1955 (referred to in ref. 75).
[75] R. G. Sowden, *Trans. Faraday Soc.*, 1959, **55**, 2084.
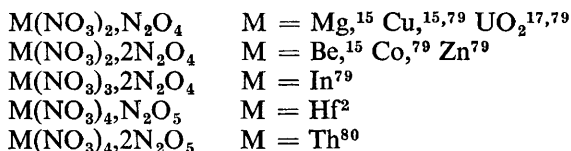[76] G. Hening, R. Lees, and M. S. Matheson, *J. Chem. Phys.*, 1953, **21**, 664.
[77] D. Hall and G. N. Walton, *J. Inorg. Nuclear Chem.*, 1959, **10**, 215.
[78] D. Doigan and T. W. Davis, *J. Phys. Chem.*, 1952, **56**, 764.

sociate when heated in a vacuum to produce the simple nitrate or nitrato-compound and oxides of nitrogen. The conditions of thermal dissociation must be carefully controlled, particularly if the required product is itself thermally unstable, because then complex mixtures of oxide-nitrates can easily be formed; for example[14]

$$Al(NO_3)_3,O\cdot38N_2O_4 \xrightarrow[\text{4 hr.}]{\text{80°/vac.}} Al(NO_3)_3 + Al_2O(NO_3)_4$$

Among the more definitely characterised addition compounds are

|	
$M(NO_3)_2,N_2O_4$	$M = Mg,^{15} Cu,^{15,79} UO_2^{17,79}$
$M(NO_3)_2,2N_2O_4$	$M = Be,^{15} Co,^{79} Zn^{79}$
$M(NO_3)_3,2N_2O_4$	$M = In^{79}$
$M(NO_3)_4,N_2O_5$	$M = Hf^2$
$M(NO_3)_4,2N_2O_5$	$M = Th^{80}$

These addition compounds give the simple anhydrous compound on heating in a vacuum for times and at temperatures which vary with their stability; for instance, 5 hr. at $160°/10^{-5}$ mm. for the thorium addition compound and 52—$54°/10$—160 mm. for the magnesium compound.

The more covalent the bond between a metal and the NO_3 group the more likely is the molecule to form an adduct with N_2O_4 or N_2O_5; thus the ionic nitrates of the alkali metals and of Ca, Sr, Ba, and Cd do not form these adducts. Magnesium nitrate is the only ionic nitrate known to form such an addition compound and the bonding of N_2O_4 in this adduct is different from that in the addition compounds formed with nitrato-compounds, for example in $Cu(NO_3)_2,N_2O_4$. This difference in bonding is clearly seen in differences in behaviour on thermal dissociation. The shapes of the vapour pressure–temperature curves for the dissociation of $Mg(NO_3)_2,N_2O_4$ and $Cu(NO_3)_2,N_2O_4$ are not the same; the magnesium compound shows a sudden pressure increase at 52—$54°$ when an irreversible reaction occurs

$$Mg(NO_3)_2,N_2O_4 \rightarrow Mg(NO_3)_2 + N_2O_4$$
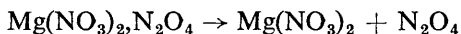
but a smooth curve is obtained for the reversible reaction:

$$Cu(NO_3)_2,N_2O_4 \rightleftharpoons Cu(NO_3)_2 + N_2O_4$$
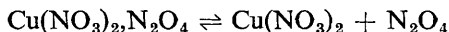
The structure of these addition compounds is open to some doubt; neither $Zn(NO_3)_2$ nor N_2O_4 reacts appreciably with dry ether but the addition compound $Zn(NO_3)_2,2N_2O_4$ reacts vigorously. Formulation as nitrosonium salts, for example $(NO^+)_2[Zn(NO_3)_4]^{2-}$, is particularly attractive as the solid compounds exhibit a sharp absorption band at 2260—2300 cm.$^{-1}$, characteristic of the NO^+ group.[15,79] The complexes $Fe(NO_3)_3$,

[79] C. C. Addison and B. J. Hathaway, Chem Soc. Special Publication, No. 10, 1957, 33.

[80] J. R. Ferraro, L. I. Katzin, and G. Gibson, *J. Amer. Chem. Soc.*, 1955, **77**, 327.

N_2O_4, formulated[4] as $(NO^+)[Fe(NO_3)_4]^-$, and $Hf(NO_3)_4,N_2O_5$,[2] are stable and can be sublimed as such in a vacuum. In general the co-ordinated oxides of addition can be replaced by other compounds, such as pyridine (py) in $UO_2(NO_3)_2,N_2O_4$ which gives $UO_2(NO_3)_2$,2py.

4.6.   Reactions of Importance in Chemical Analysis.—The reduction of the nitrate ion to ammonia has long been used for the determination of nitrate, and is usually carried out in strongly alkaline solution in the presence of aluminium, zinc, or Devarda's alloy (50 Cu, 45 Al, 5 Zn):

$$3NO_3^- + 8Al + 2H_2O + 5OH^- \rightarrow 8\ AlO_2^- + 3NH_3$$
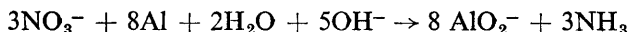
The ammonia is distilled into a standard solution of an acid and the excess of acid is titrated with a standard solution of alkali. The nitrate ion can also be reduced to ammonia in neutral solution by the use of Arndt's alloy (60 Mg, 40 Cu).

The reduction of nitric acid to nitric oxide occurs when a solution of the acid or a nitrate in concentrated sulphuric acid is shaken with mercury:

$$2HNO_3 + 6Hg + 3H_2SO_4 \rightarrow 2NO + 3Hg_2SO_4 + 4H_2O$$
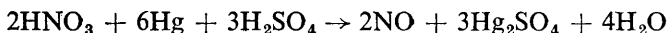
This reaction is used for the estimation of nitrates, or nitrites, or oxides of nitrogen, in commercial sulphuric acid, in the Lunge nitrometer. Ferrous salts reduce nitric acid to nitric oxide which in the cold dissolves in the excess of ferrous salt to give a dark brown solution, the "brown ring" in the qualitative test for nitrate. The solution evolves nitric oxide on heating:

$$6FeSO_4 + 2HNO_3 + 3H_2SO_4 \rightarrow 3Fe_2(SO_4)_3 + 2NO + 4H_2O$$
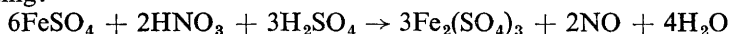
Various other reactions involving the reduction of the nitrate ion, both catalytically and by strong reducing agents, have been discussed by Szabo and Bartha.[81]
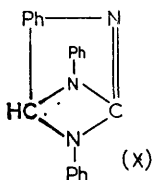
Other tests for nitric acid and nitrates are (i) the red colour with a solution of brucine in concentrated sulphuric acid, (ii) the deep blue colour with a solution of diphenylamine in concentrated sulphuric acid, (iii) the evolution of red-brown oxides of nitrogen on heating with concentrated sulphuric acid and copper turnings, and (iv) the white crystalline precipitate which develops on adding a solution of the nitron reagent (1 % w/v in 5 % acetic acid) to a solution of the nitrate acidified with acetic or sulphuric

[81] Z. G. Szabo and L. G. Bartha, "Recent Aspects of the Inorganic Chemistry of Nitrogen", Chemical Society Special Publication, No. 10, 1957, p. 131.

acids. The nitron reagent is now widely used for the gravimetric determination of nitrate in the presence of many other ions. Nitron (X) is a strong organic base, 4,5-dihydro-1,4-diphenyl-3,5-phenylimino-1,1,4-triazole (to which a sterically improbable structure is commonly ascribed), and gives a 1:1 complex with the formula $C_{20}H_{16}N_4,HNO_3$.

5. Spectra

The infrared and Raman spectra of simple metal nitrates in the solid state and in aqueous solution have been known for many years, as exemplified by the work of Menzies.[82] The publishing of many data since about 1957 on the vibrational spectra of ionic nitrates and covalent nitrato-compounds has been stimulated in part by the preparation and study of anhydrous and volatile nitrato-compounds, and also by the widespread interest in the separation of metals by solvent extraction of their nitrates. In most of the recent work the infrared absorption technique has been applied to solid compounds over the easily accessible wavelength range 2—15μ and this field will mainly be discussed in this Section. The application of the Raman and infrared techniques to the study of molten metal nitrates has been reviewed recently[83] and will only be mentioned briefly, as will the well-known ultraviolet spectrum of the nitrate ion.

5.1. Infrared Spectra of Solid Metal Nitrates and Nitrato-compounds.— The nitrate ion belongs to the group of planar XY_3 molecules and has D_{3h} symmetry, which gives rise to four fundamental vibrations, one of which is infrared forbidden. In compounds in which the NO_3 group is covalently bonded through one of the oxygen atoms the symmetry of the group is lowered to C_{2v} and six fundamental vibrations are expected. Arising out of the different symmetries of the nitrate ion and the nitrato-group two different conventions are used[84] in numbering the vibrations and these are given in Table 7 to avoid confusion in subsequent discussion. The frequencies given for the vibrations of the nitrato-group are those found experimentally in the early work[84] on nitrato-co-ordination complexes of various metals, and are included for comparison with those of the nitrate ion.[85]

Although the spectra in the 2—15μ region can often be used[5,15] to distinguish clearly between the nitrate ion and the covalent nitrato-group, it should be noted that the symmetry of the nitrate ion can be lowered if it is subject to the field of a crystal lattice and that in ionic crystals the cohesive energy can be of the same order of magnitude as the bond energies of covalent compounds. A detailed study by Buijs and Schutte[86] of the

[82] A. C. Menzies, *Nature*, 1929, **124**, 511.
[83] S. C. Wait and G. J. Janz, *Quart. Rev.*, 1963, **17**, 225.
[84] B. M. Gatehouse, S. E. Livingstone, and R. S. Nyholm, *J.*, 1957, 4222.
[85] G. Herzberg, "Infrared and Raman Spectra of Polyatomic Molecules", Van Nostrand, New York, 1945, p. 178.
[86] K. Buijs and C. J. H. Schutte, *Spectrochim. Acta.*, 1962, **18**, 307.

infrared spectra of the anhydrous nitrates of Li, Na, K, Ca, Sr, and Ba has shown that the assumption[87] of partially covalent bonding is not necessary to explain the observed differences from ideal D_{3h} symmetry in these compounds. Unfortunately, these authors[86] use a different notation from other workers in the field and this can lead to confusion; they refer to the very strong ν_3 band for the nitrate ion (Table 7) as ν_4 and *vice versa*.

TABLE 7.   *Description of the vibrations of the nitrate ion and nitrato-group.*

		Nitrate ion, NO_3^-		
Type	$\nu_1 (A'_1)$	$\nu_2 (A''_2)$	$\nu_3 (E')$	$\nu_4 (E')$
Assignment	NO stretch	out-of-plane bend	NO_2 asymm. stretch	NO_2 bend (planar rock)
Active in infrared (I) or Raman (R)	R	I	I,R	I,R
Frequency (cm.$^{-1}$)	1050	831	1390	720

			Nitrato-group, $O \cdot NO_2$			
Type	$\nu_2 (A_1)$	$\nu_6 (B_2)$	$\nu_1 (A_1)$	$\nu_4 (B_1)$	$\nu_3 (A_1)$	$\nu_5 (B_1)$
Assignment	NO stretch	out-of-plane rock	NO_2 symm. stretch	NO_2 asymm. stretch	NO_2 bend symm.	NO_2 bend asymm. (out-of-plane rock
Active in infrared (I) or Raman (R)	I,R	I,R	I,R	I,R	I,R	I,R
Frequency (cm.$^{-1}$)	1034—970	800—781	1290—1253	1531—1481	$\sim$739	$\sim$713

The infrared spectra measured by various workers are generally consistent with: (i) the nitrate ion being present in (*a*) the anhydrous nitrates of the metals Li, Na, K, Rb, Cs, Mg, Ca, Sr, Ba, Cd, Co, Pb, Ag; (*b*) the hydrated nitrates of the metals Cd, Co, Cu, Fe^{III}, Ni, Zn; (ii) the coordinated nitrato-group being present in (*a*) the anhydrous compounds (many of which are volatile, see Table 4) of the metals Be, Cu, Hg^{II}, In, Mn, Pd, Ti^{IV}, Zn, Zr and groups Be$_4$O(VI), FeNO(III), NbO(III) and in $(NH_4)_2[Ce(NO_3)_6]$; (*b*) the hydrated compounds. $Th(NO_3)_4,4H_2O$, $ZrO(NO_3)_2,2H_2O$, $RuNO(NO_3)_3,2H_2O$, and $6 \cdot 3 \ UO_2(NO_3)_2,2H_2O$.

The nature of the bonding in the nitrato-compounds of the above metals merits closer examination. The strong band usually assigned to the asymmetric stretching frequency (ν_4) of the nitrato-group in some of these compounds occurs[2] at as high a value as 1620—1646 cm.$^{-1}$, and the difference between this band and that usually assigned to the symmetric stretching frequency (ν_1) is greater than 400 cm.$^{-1}$. These values are the highest reported for nitrato-compounds of metals and we have related them[2] to the

[87] J. R. Ferraro, *J. Mol. Spectroscopy*, 1960, **4**, 99.

presence of *bridging* nitrato-groups from a comparison of the spectra with those of a number of compounds in which it is believed that the nitrato-group must be (*a*) *unidentate* to satisfy the known co-ordination number of the metal, *e.g.*, nitrato-complexes of Co^{III} amines, hexanitrato-complexes of U^{VI} and Ce^{IV}; (*b*) *bidentate* according to *X*-ray evidence, *e.g.*, $Rb[UO_2(NO_3)_3]$, $UO_2(NO_3)_2,6H_2O$; and (*c*) *bridging* two metal atoms according to *X*-ray evidence, *e.g.*, $Cu(NO_3)_2$, or by analogy with similar compounds of known structure, *e.g.*, $Be_4O(NO_3)_6$, which is similar to $Be_4O(Ac)_6$.

All the compounds believed to contain the unidentate nitrato-group give two main bands (sometimes split) in the 1200—1600 cm.$^{-1}$ region which lie within the limits ν_4 1560—1454, ν_1 1346—1254, with a difference $(\nu_4-\nu_1)$ of between 100 and 300 cm.$^{-1}$. The uranyl compounds which contain the bidentate nitrato-group have two strong bands which lie within the above ranges for the unidentate nitrato-group. It would, however, be unwise to infer that a bidentate nitrato-group cannot be distinguished from a unidentate group on the basis of the bands in this region because the uranyl compounds containing the bidentate group are octaco-ordinated with respect to the metal, whereas the others are hexaco-ordinated, and the bond angles may be considerably different.

We think that it is significant that the anhydrous compounds Be_4O-$(NO_3)_6$, $NbO(NO_3)_3$, $In(NO_3)_3$, $Pd(NO_3)_2$, $Ti(NO_3)_4$, and $Zr(NO_3)_4$ have strong bands lying well outside the limits given above for ν_4 and ν_1 in unidentate nitrato-compounds. We therefore suggest that the occurrence of a strong band at a frequency greater than 1570 cm.$^{-1}$ together with a strong band at a frequency less than about 1280 cm.$^{-1}$ may indicate a *bridging* nitrato-group. An attempt to assign these bands is being made* because they are not identical to those named ν_4 and ν_1 for the unidentate nitrato-group. Information about the structures of these compounds from *X*-ray or neutron diffraction measurements will be required to substantiate the above suggestions, and the measurement of infrared spectra in the region in which the metal–oxygen bonds are expected to vibrate (300—500 cm.$^{-1}$) would be particularly useful in determining whether a compound contains unidentate or bidentate nitrato-groups, but little information about this region has been published. Great care is required to obtain meaningful spectra of these covalent nitrato-compounds owing to their high reactivity; for instance, the compound $Ti(NO_3)_4$ reacts rapidly[60] with the paraffinic hydrocarbons used to prepare mulls.

5.2 Infrared and Raman Spectra of Metal Nitrates in Solution and in the Molten State.—The infrared and Raman spectra of metal nitrates have been studied less in aqueous and organic solvents than in the solid state, but interest in this field is increasing, as it is also in regard to molten salts. Published data up to 1958 on the Raman spectra of metal nitrates in

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*Unpublished work by the Reviewers, 1964; also independent work by Professor C. C. Addison and his co-workers (personal communication).

solution were discussed by Gatehouse;[48] considerable deviations were found from the spectra expected for the D_{3h} symmetry of the nitrate ion. More recent work[88,89] has indicated strong association of the nitrate ion with Th^{IV} and In^{III} in aqueous solution. It is expected that further measurements by the Raman method, in conjunction with X-ray diffraction studies on the solutions, will considerably advance our knowledge of the structure and bonding in solutions of electrolytes.

Infrared spectra have been measured for solutions of metal nitrates in organic solvents, particularly in tri-n-butyl phosphate,[90,91] and solutions of tri-n-octylphosphine oxide in carbon tetrachloride and tri-n-octylamine in benzene.[92] In general, the ν_1 and ν_4 frequencies of the nitrato-group are independent of the solvent, but strongly dependent on the metal ion, and a separation of between 150 and 250 cm.$^{-1}$ between these two frequencies is found for many of the complexes; this separation corresponds to that for unidentate bonding in many solid nitrato-complexes.

The experimental techniques which have been developed recently for the study of vibrational spectra of molten salts, and the qualitative and quantitative interpretation of the spectra, have been the subject of many recent reviews[83] and monographs.[93] The molten nitrates of the alkali metals and silver have been extensively examined, partly because they are non-corrosive and low-melting and have a reasonable thermal stability. They are examples of highly ionic salts with simple cations and a highly polarisable anion; the latter acts as an ideal "detector" of changes in electrostatic forces as the composition of the melt is altered. The general conclusions deduced from the vibrational spectra of molten salts are that ionic and molecular species known to exist in aqueous solution and solid phases retain their identity in the molten state. Environmental perturbations and ionic and molecular interactions are clearly revealed and can be understood in terms of short-range ordering in the melt and strong cation–anion forces.

5.3. Ultraviolet Spectra of the Nitrate Ion.—Many non-metallic inorganic ions in solutions give intense absorption bands in the ultraviolet region, but only the absorption of the monatomic ions, such as halide, or quasi-monatomic ions, such as hydroxide, can be ascribed with certainty to anion–solvent charge-transfer transitions.[94] The intense absorption of the polyatomic ions is less sensitive to environmental effects and it is accompanied by weak absorption at longer wavelengths of the n → σ^* or n → π^* type. The latter bands indicate the presence of low energy σ^* and π^* orbitals which serve as the upper levels of the strongly absorbing

[88] R. E. Hester, *Diss. Abs.*, 1962, **23**, 1510.
[89] R. E. Hester and R. A. Plane, *Inorg. Chem.*, 1964, **3**, 769.
[90] J. R. Ferraro, *J. Inorg. Nuclear Chem.*, 1959, **10**, 319.
[91] L. I. Katzin, *J. Inorg. Nuclear Chem.*, 1962, **24**, 245.
[92] J. M. P. J. Verstegen, *J. Inorg. Nuclear Chem.*, 1964, **26**, 25.
[93] D. W. James, "Selected Topics in Molten Salt Chemistry," ed. M. Blander, Interscience Publishers, New York, 1963, ch. "Vibrational Spectra of Molten Salts".
[94] S. F. Mason, *Quart. Rev.*, 1961, **15**, No. 3, 355.

$\sigma \rightarrow \sigma^*$ and $\pi \rightarrow \pi^*$ transitions in the polyatomic ions. The absorption of the nitrate ion in aqueous solution may be compared (see Table 8) with

TABLE 8.   *Ultraviolet spectra of various ions.*

Ion	Solvent	$\lambda_{max.}$(Å)	$\epsilon_{max.}$	Ref.
Cl^-	H_2O	1810	$\sim 10^4$	94
Br^-	H_2O	1995; 1900	11,000; 12,000	94
OH^-	H_2O	1870	5,000	94
NO_2^-	H_2O	3570; 2980; 2110	23; 8; 6000	94
NO_3^-	H_2O	3025; 1936	7; 8800	94
NO_3^-	molten $LiClO_4$	2830; 1950	17·4; 8270	95

that in molten $LiClO_4$ at 140°, and with that of some other ions in aqueous solution. In molten $LiClO_4$ the intense band is considered[95] to be the electronically allowed $A_1' \rightarrow E_1'$ ($\pi \rightarrow \pi^*$) transition involving a shift of electronic charge-density from the oxygens towards the nitrogen; it is suggested[95] that experimental difficulties may have led to this band's being overlooked in other work on crystalline and molten alkali-metal nitrates.

6.   Conclusions

Anhydrous nitrates of several metals, such as silver and the alkali metals, have long been known, but Guntz and Martin isolated the first anhydrous compounds of the transition metals Co, Cu, Mn, and Ni with the nitrate group in 1909. The first *volatile* nitrato-compounds to be isolated were those of Cr and V by Schmeisser and his co-workers in 1954. Since then, many metals have been shown to form slightly volatile nitrates or highly volatile nitrato-compounds (Table 4) and volatility cannot now be regarded as an unusual property of these compounds, but rather as a consequence either of the intrinsic stability of the nitrate ion in an anhydrous compound such as sodium nitrate, or of the strong covalent bonding of the nitrato-groups to the central metal atom and their screening effect on the cationic charge. This covalent bonding of one or more oxygen atoms of the nitrato-group may be so strong that dissociation of the group in certain organic media occurs not at the metal–oxygen bond but at a nitrogen–oxygen bond to give an $NO_2\cdot$ radical with powerful nitrating properties.

Nitrates or nitrato-compounds of some of the rarer metals, *e.g.*, Nb, Ta, Hf, V, in addition to some of the more common ones, Al, Sn, Zr, are generally not considered, in current textbooks, to exist in an anhydrous stoicheiometric form, but work over the last ten years has shown that they can be so prepared. The more extensive application of the non-aqueous methods based on N_2O_4, N_2O_5, and $ClNO_3$ may lead to the preparation of anhydrous nitrates or nitrato-compounds of some of the elements for which no

[95] D. W. James, C. R. Boston, and G. P. Smith, *J. Chem. Phys.*, 1964, **40**, 609.

3*

such compounds are known at present, *e.g.*, Ge, Pa, Tc (Table 2). Detailed investigation of the infrared spectra and *X*-ray or neutron diffraction of the presently known anhydrous and hydrated compounds is expected to greatly increase our knowledge of the bonding of the nitrate group in them and their behaviour under many conditions.

The Reviewers consider that systematic use of the terms *nitrate* and *nitrato-compound* as has been attempted in this Review, will help the understanding by non-specialists of the various preparative methods used, and properties observed, in this field. Whilst it is possible and often convenient to divide these compounds into two general classes on account of the criteria summarised in Table 1, there are some properties and reactions, *e.g.*, solubility, m.p., and hydrolysis, which cannot at present be seen to reflect clearly the character of the metal–nitrate bond.   The application of the term nitrate or nitrato-compound to a particular compound at present must be carefully decided in the light of experimental evidence from measurement of infrared spectra, *X*-ray diffraction, volatility, and reactivity, and compounds for which insufficient evidence is available should be regarded as nitrates for the present.