ANHYDROUS METAL NITRATES

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I. Introduction

Until recent years, the field of metal nitrate chemistry was largely concerned with compounds containing the nitrate ion. There are two obvious reasons for this. Firstly, most of the known anhydrous metal nitrates were ionic compounds; secondly, solution properties were normally studied in aqueous media. Covalent bonds between metal atoms and nitrate groups cannot normally withstand the combined effects of high dielectric constant and solvation by water molecules, so that the effects observed in aqueous solution are properties of the free ions. Survey of the literature (Section VIII) reveals that nitrates of many metals are known in hydrated form, but that until recently very few anhydrous nitrates had been prepared. This applies particularly to the transition metals, where attempts to remove the molecules of water from the hydrate usually lead to hydrolytic decomposition through hydroxide nitrates to the hydroxide or the oxide, with evolution of nitric acid.

The presence of water, therefore, imposes severe limitations on the chemical behavior of the nitrate group; in this environment it cannot display its full versatility, and the present literature on this subject gives an entirely false impression of the range of behavior of which the nitrate group is capable. Anhydrous metal nitrates which are strongly covalent in character can be prepared in nonaqueous media (Section II). Some of these compounds are found to be volatile and monomeric in nonaqueous solution, and are strong oxidizing agents. Again, covalent bonding can involve one or two (or perhaps even three) of the oxygen atoms in the nitrate group, and the chemical reactivity of the covalent nitrate group seems to vary markedly with the number of oxygen atoms involved in bonding.

This versatility in nitrate chemistry forms the main theme of this article. It is not yet possible to present a completely systematic picture, since the anhydrous nitrates of some metals have still to be prepared and many aspects of the bonding and reactivity of metal nitrates have not yet been explored. Attention will therefore be focused on individual compounds which are representative of particular structures or properties. The article includes a brief summary of properties characteristic of free nitrate ions and ionic nitrates, so that comparison can be made with the covalent nitrates and their derivatives. Section VIII gives a systematic review of the metal nitrates now known, surveyed on the basis of the Periodic Table. Coordination complexes containing nitrate groups as ligands are not included unless they have some direct bearing on the properties of the simple nitrate. Again, we have regarded a general treatment of the molecular addition compounds of metal nitrates as being beyond the scope of this article, but some discussion of them is inevitable. For example, metal nitrates often crystallize from liquid dinitrogen tetroxide as addition compounds with the tetroxide, and some simple nitrates (e.g., iron) are at present known only in this form.

II. Preparative Methods

Methods are subdivided below according to the reagent or reaction medium employed. Examples illustrating each method are given here, and further examples will be found in Section VIII.

A. CRYSTALLIZATION FROM AQUEOUS SOLUTION

This simple method is available for the nitrates of sodium, potassium, rubidium, caesium, thallium(I), barium, lead, and silver, each of which will crystallize from aqueous solution at room temperature. Solutions of the nitrates, free from other anions, are obtained by the usual methods e.g., reaction of nitric acid with the metal or its carbonate or oxide. These nitrates may also be prepared, of course, by the more complicated techniques described below, but the use of such techniques is unnecessary in these cases.

In crystallizing in anhydrous form from water, the nitrates of the alkali metals (sodium to caesium) resemble the chlorates, but differ from the salts of many di- and tribasic oxy-acids, e.g., sulfates, phosphates, and carbonates, which are usually heavily hydrated. The same difference can be observed in the oxy-acid salts of some complex ions; tetramminecopper(II) sulfate crystallizes as the monohydrate $[Cu(NH_3)_4]SO_4 \cdot H_2O$, whereas the nitrate $[Cu(NH_3)_4](NO_3)_2$ crystallizes in anhydrous form.

B. DEHYDRATION OF HYDRATES

A limited number of anhydrous nitrates may be obtained in this way. Lithium nitrate crystallizes from aqueous solution as the hydrate $LiNO_3 \cdot 3H_2O$, from which anhydrous $LiNO_3$ is obtained on heating. The nitrates of the alkaline earth metals show an interesting gradation. Barium, strontium, and calcium nitrates crystallize from aqueous solution at 20° as $Ba(NO_3)_2$, $Sr(NO_3)_2 \cdot 2H_2O$, and $Ca(NO_3)_2 \cdot 4H_2O$, respectively, and anhydrous strontium and calcium nitrates are readily obtained on heating the hydrates. However, when the hydrates $Mg(NO_3)_2 \cdot 6H_2O$ and $Be(NO_3)_2 \cdot 4H_2O$ are heated, hydrolysis occurs and nitric acid is evolved.

Efforts to obtain the anhydrous compound from the nitrate hydrate are more successful if the temperature at which dehydration is carried out is reduced. The anhydrous nitrates of lanthanum, praseodymium, and neodymium are obtained by heating the hexahydrates, whereas cerium(III) nitrate was not obtained in this way (*1*). However, Walden and Birr (*2*) claimed to have prepared anhydrous $Ce(NO_3)_3$ by dehydration of its hydrate over phosphoric oxide in a desiccator at 140°. Anhydrous manganese(II) nitrate has also been obtained by dehydration of the solid hydrate over phosphoric oxide in a vacuum desiccator at room temperature (*3*), but similar treatment of zinc nitrate hydrate gave an insoluble basic salt.

A number of claims are made in early work which cannot be accepted without some reserve, since it was not always established by analysis that the product was in fact the anhydrous nitrate, and physical techniques for confirming the presence of the nitrate group (and the absence of water) in the product were often not available. Hydrated scandium nitrate, $Sc(NO_3)_3{\cdot}4H_2O$, is said to give anhydrous $Sc(NO_3)_3$ under vacuum at 100° (*4*), and the pentahydrate $Dy(NO_3)_3{\cdot}5H_2O$ loses its water of crystallization in a dry atmosphere (*5*). These observations are not consistent with the results of thermogravimetric analysis of these compounds (*6*), but the temperature ranges involved in the two cases are quite different. Cadmium nitrate can be prepared by heating its hydrate (*7*); this is feasible in view of the ionic character of the anhydrous salt. When gallium metal is dissolved in concentrated nitric acid, and the product freed from water and excess nitric acid by powdering in a vacuum or in a stream of dry air, the product is said to be anhydrous $Ga(NO_3)_3$ (*8*). The process of dehydration over phosphoric oxide in a vacuum desiccator can be a lengthy operation. A product believed to be anhydrous bismuth nitrate was prepared by desiccation of the hydrate $Bi(NO_3)_3{\cdot}5H_2O$ for a period of one year (*9*); the monohydrate may also be heated gently in an atmosphere of dry carbon dioxide (*10*).

C. Metathesis or Displacement in Nonaqueous Solvents

There are two main reasons why this method has been little used. Firstly, it usually involves reaction of the metal halide with silver nitrate, and the limited solubility of these compounds in organic solvents raises immediate problems. Secondly, anhydrous metal nitrates formed in this way tend to crystallize from solution as addition compounds with organic solvents, and the final removal of combined solvent is often as difficult as is the removal of water. The formation of a bismuth nitrate in acetone solution by reaction of bismuth trichloride with silver nitrate has been described (*11*), and analogous reactions leading to the formation of the corresponding nitrates in acetone were carried out with solutions of $SbCl_3$, $FeCl_3$, $CoCl_2$, $ZnCl_2$, $CdBr_2$, $HgCl_2$, and $SnCl_2$. In none of these reactions, however, was the solid anhydrous nitrate isolated. Guntz and Martin (*12*) attempted the preparation of anhydrous nitrates by using displacement reactions between metals and silver nitrate solutions. Manganese and copper metals were added to solutions of silver nitrate in acetone and in phenyl cyanide, and the metals manganese, copper, nickel, and cobalt were added to solutions of silver nitrate in liquid ammonia. In all cases displacement occurred, and solvated nitrates were obtained as products. Displacement of silver from a solution of silver nitrate in methyl cyanide by copper gives the cuprous salt, and evaporation of the resulting solution yields the addition compound $CuNO_3{\cdot}4CH_3CN$. Efforts to remove the solvent resulted in decomposition of the nitrate (*13*, *14*). The same complex has been prepared by reaction of copper powder with a solution of cupric nitrate in methyl cyanide (*14*).

An attempt has been made to prepare uranium tetranitrate by addition of the stoichiometric amount of silver nitrate in methyl cyanide to a solution of uranium tetrachloride in acetone. After removal of silver chloride, the green solution of uranium tetranitrate was evaporated under vacuum at room temperature, but as the product separated it decomposed spontaneously to uranyl nitrate (*15*). In this instance the difficulty encountered in the preparation lies not so much in the technique employed as in the inherent instability of uranium(IV) nitrate.

D. REACTIONS IN ANHYDROUS NITRIC ACID

Surprisingly, this method has met with little success. It might have been supposed that reaction of anhydrous metal halides with pure nitric acid would yield the anhydrous nitrate with evolution of hydrogen chloride, but this is not the case. The reaction of anhydrous nitric acid with $CrCl_2$, $CrCl_3$, $MnCl_2$, $FeCl_2$, $FeCl_3$, $CoCl_2$, $NiCl_2$, and $CuCl_2$ has been studied; in all cases hydrated nitrates were produced (*16*). It is concluded that nitric acid reacts with anhydrous metal chlorides as though it were an equilibrium mixture of the free acid, acid anhydride, and water:

$$2HNO_3 \rightleftharpoons N_2O_5 + H_2O.$$

The transition metal ions have a strong affinity for water, which is removed by precipitation of the hydrated salt. Solvolysis to give nitrates is no doubt the first step in the reaction of the chlorides $SiCl_4$, $TiCl_4$, $SnCl_4$, and $SbCl_5$ with pure nitric acid, but the products obtained were the metal oxides combined with some water or nitric acid (*17*).

The behavior of picrates and acetates has also been studied. Potassium and thallium(I) picrates reacted with nitric acid and on evaporation at 40°, under reduced pressure, crystalline mixtures of the nitrates with picric acid were obtained. Zinc, copper, and nickel picrates did not give pure nitrates, but on reaction of lead picrate with nitric acid, pure lead nitrate precipitated at room temperature (*17*). The replacement of the acetate by the nitrate group has some unusual features. It has been observed in the authors' laboratory that the stability of a metal acetate-nitrate often exceeds that of the simple acetate or nitrate; this is no doubt connected with the close similarity in shape and dimensions of the two groups. In consequence, we have found that in reactions of anhydrous metal acetates with nitrate ions, partial replacement frequently occurs. Jander and Wendt (*17*) studied the reaction between zinc acetate and nitric acid; the product contained nitrate and acetate groups in equivalent amounts. Cadmium acetate, however, reacted to give pure cadmium nitrate and acetic acid.

E. Use of Dinitrogen Pentoxide in Nitric Acid

The main disadvantage in the use of nitric acid alone arises from the water which may be produced either by dissociation or in the course of reaction. One method of obviating this is to use solutions of dinitrogen pentoxide in nitric acid, so that any water produced in the system is immediately converted into nitric acid. Furthermore, the pentoxide undergoes ionic dissociation, $N_2O_5 \rightleftharpoons NO_2^+ + NO_3^-$, in solution in nitric acid (*18*), so that this medium has obvious promise for the production of nitrates. The fact that it has been little used is no reflection on its potentialities; many metal nitrates have not yet been prepared, and more recent experiments using dinitrogen pentoxide have tended to concentrate on the application of the pentoxide alone or dissolved in aprotic solvents.

Anhydrous nitrates of copper(II), manganese(II), nickel(II), and cobalt(II) were prepared by condensation of dinitrogen pentoxide onto solutions of the nitrate hydrates in nitric acid (*19*). Kolb (*20*) and Misciatelli (*21*) reported the preparation of anhydrous thorium tetranitrate by this method, and the reaction has been studied in more detail by Ferraro and associates (*22*). The hydrate $Th(NO_3)_4 \cdot 4H_2O$ was treated with a solution of dinitrogen pentoxide in 100% nitric acid at 25°. Under these conditions, the first product isolated was the addition compound $Th(NO_3)_4 \cdot 2N_2O_5$; the combined pentoxide was removed by heating at 150–160° for 4 hours under vacuum, to leave the anhydrous nitrate. Späth (*23*) used a modification of this technique to prepare what was probably the first authentic sample of anhydrous uranyl nitrate. The dihydrate was dissolved in fuming nitric acid, and the solution treated with dinitrogen pentoxide and dinitrogen tetroxide. A light yellow product precipitated which contained combined oxides of nitrogen; the latter were removed by vacuum treatment at 163°. There is some doubt about the purity of products thought by Marketos (*24*) and Ditte (*25*) to be anhydrous uranyl nitrate.

F. Use of Dinitrogen Pentoxide Alone

This oxide has not been used in the past to the same extent for the preparation of anhydrous nitrates as has dinitrogen tetroxide, but recent work (*26*) indicates that its reaction with hydrated nitrates may be a fairly general method for the preparation of anhydrous nitrates. In many cases the same products are obtained as with dinitrogen tetroxide, but there are some instances in which it offers definite advantages. It is more reactive, and is of particular value in the preparation of nitrates of the early transition metals where oxide-nitrates are usually formed. In practice, its manipulation is more difficult since at any temperature above 0° it begins to decompose into the tetroxide and oxygen, and the range of solvents in which it can be dissolved without reaction is not so extensive as for dinitrogen tetroxide. It is known to dissolve in carbon tetrachloride, chloroform, and sulfuryl chloride (*27*), but there is little other information on its solubility in, or reactions with, organic solvents. In consequence, it has often been used undiluted in reactions with solids [e.g., CrO_3, $KCrO_3Cl$ (*27*), UO_3 (*28*)] or liquids [e.g., CrO_2Cl_2 (*27*)]. Pure dinitrogen pentoxide melts at 41°, but as usually prepared from nitric acid and phosphoric oxide it contains some nitric acid and dinitrogen tetroxide, and the impure material can be handled in the form of a liquid at 30° (*29*). In the liquid state it is virtually a nonconductor, and is presumed to have the structure $O_2N{\cdot}O{\cdot}NO_2$ found for the vapor; any self-ionization in the liquid will no doubt give the NO_2^+ and NO_3^- ions characteristic of the solid state. In reaction with halides, metal nitrates are produced and nitryl chloride is evolved. Dinitrogen pentoxide has also been found to react directly with some metals [e.g., Na, K, Mg, Fe, Cu, Zn, Cd, Hg (*30*, *31*)].

Whether or not the presence of dinitrogen tetroxide in the pentoxide is a disadvantage appears to depend on the type of metal compound used in the reaction. In the preparation of zirconium and hafnium tetranitrates from the tetrachlorides (*32*), and titanium tetranitrate from the hydrate (*26*), Field and Hardy employed the impure pentoxide. However, Gibson *et al.* found that the reaction of uranium trioxide with dinitrogen pentoxide was erratic so long as dinitrogen tetroxide was present, but proceeded smoothly with the pure pentoxide (*28*). The reaction follows the same pattern when the pentoxide is used in solution in carbon tetrachloride. The adduct $UO_2(NO_3)_2{\cdot}N_2O_5$ is obtained as the initial product, and its thermal stability is lower than that of the corresponding adduct $UO_2(NO_3)_2{\cdot}N_2O_4$ obtained in reactions with dinitrogen tetroxide. The addition compound $UO_2(NO_3)_2{\cdot}N_2O_5$ was also obtained in an interesting solid-solid reaction involving UO_3 and the pure pentoxide. Uranium trioxide (325-mesh) was stirred with pure dinitrogen pentoxide in powder form at 0–10°, when a light orange mixture was originally formed. Within 10 minutes the powder conglomerated into beads; at this stage, the mixture suddenly turned bright yellow in color without any evident heat of reaction, giving a finely divided powder of the compound $UO_2(NO_3)_2{\cdot}N_2O_5$ (*28*). It seems likely that reaction of UO_3 actually occurs with N_2O_5 vapor, but the use of mixed powders is a convenient method of maintaining a high concentration of pentoxide vapor at the surface of the metal oxide.

G. Reactions Involving Halogen Nitrates

Since dinitrogen pentoxide is solid at room temperature, it is difficult to find a generally applicable technique by which the pure compound can be used at low temperatures. Some metal nitrates are only stable at low temperatures, and there are obvious disadvantages in the use of the pentoxide alone in these cases. The difficulty can be overcome by the use of the halogen nitrates, which are low melting. Chlorine nitrate is prepared by condensing together chlorine monoxide and dinitrogen pentoxide in a liquid-air bath. The mixture is then held for some hours at −80°, when the following reaction occurs:

$$Cl_2O + N_2O_5 \rightarrow 2ClNO_3.$$

The liquid may then be allowed to warm to room temperature (*33*). The compound may also be prepared by reaction of chlorine monoxide with dinitrogen tetroxide at −30° (*34*):

$$2Cl_2O + N_2O_4 \rightarrow 2ClNO_3 + Cl_2.$$

Chlorine nitrate melts at −107°, to a yellow liquid. The heat of vaporization is 7.3 kcal/mole, and the Trouton constant 25.1; by extrapolation, the boiling point is 18° (*35*). The infrared spectrum indicates that the structure is $Cl{\cdot}O{\cdot}NO_2$ (*36*). The chlorine atom is believed to carry a partial positive charge, $Cl^{\delta+}\text{-}ONO_2^{\delta-}$, so that in reaction the compound is a ready source of nitrate ions (*37*).

Because of its low melting point, reactions with liquid chlorine nitrate can be carried out conveniently at the temperature of solid carbon dioxide (−80°). For example (*37*),

$$TiCl_4 + 4ClNO_3 \rightarrow 4Cl_2 + Ti(NO_3)_4.$$

Chlorine, and excess of unreacted chlorine nitrate, can be readily removed in vacuum at −80°. Similarly, the nitrates $B(NO_3)_3$ (−78°), $Al(NO_3)_3$ (−7°), and $Sn(NO_3)_4$ (−60°) are said to be prepared by this method at the temperatures shown. Reactions of chromyl and vanadyl chlorides with chlorine nitrate yield the oxide-nitrates $CrO_2(NO_3)_2$ and $VO(NO_3)_3$.

Some relevant reactions have also been carried out with bromine trinitrate, prepared by the reactions:

$$BrF_3 + 3N_2O_5 \rightarrow Br(NO_3)_3 + 3NO_2F$$

or

$$BrF_3 + 3HNO_3 \rightarrow Br(NO_3)_3 + 3HF.$$

However, the compound melts with decomposition at 48°, so that it does not have the physical advantages of chlorine nitrate. It reacts with tin tetrabromide at −40° according to the equation:

$$3SnBr_4 + 4Br(NO_3)_3 \rightarrow 3Sn(NO_3)_4 + 8Br_2$$

and the colorless tin tetranitrate formed sublimes in vacuum at 40° (*37*).

This preparative technique has considerable potential value, and it is unfortunate that these interesting reactions have been published without analytical or physical evidence to support the identity of the products.

H. REACTIONS WITH ACETYL NITRATE

Dinitrogen pentoxide may also be used indirectly in the liquid state at 0° by dissolving it in acetic anhydride, when it is converted to acetyl nitrate. Crude acetyl nitrate prepared in this way has been purified by distillation under a pressure of 70 mm, the fraction boiling at 20–25° being used for the preparation of metal nitrates (*38*). To date, the only reactions studied appear to be those with copper, lead, and magnesium oxides which are converted to the corresponding anhydrous nitrates in 3 hours at 0°. Acetyl nitrate decomposes above 60°, and explodes on rapid heating. It is probably desirable to dilute the compound with such liquids as carbon tetrachloride, and the method obviously merits further study. Benzoyl and benzyl nitrates did not give satisfactory results (*39*).

I. REACTIONS IN DINITROGEN TETROXIDE

This compound provides an excellent medium for the preparation of many anhydrous nitrates. It is liquid at room temperature (m.p. −11.2°, b.p. 21.15°) and is commercially available in some countries. A product of high purity may be prepared conveniently in the laboratory by heating dried lead nitrate (*40*, *41*). The N_2O_4 molecule is represented by a single structure, $O_2N{\cdot}NO_2$, in the solid (*42*) and gaseous states (*43*). In the liquid state this structure predominates, but other structures are present also; the polarization properties of the liquid have been interpreted on the basis of a small content of $NO^+{\cdot}NO_3^-$ ion pairs (*44*). Chemical evidence is entirely consistent with the formation of NO^+ and NO_3^- ions, so that the equilibrium

$$N_2O_4 \rightleftharpoons NO^+ + NO_3^-$$

represents the typical self-dissociation of the liquid. This has been confirmed by several elegant methods (*45*, *46*). The ionization will be extremely small in the pure liquid, but is enhanced when the tetroxide (dielectric constant 2.42) is diluted with liquids of high dielectric constant; Raman spectra of solutions of the tetroxide in pure nitric acid indicate complete dissociation into NO^+ and NO_3^- ions (*47*).

1. Solvolysis

It follows from the above that solvolysis of metal salts in this medium will result in the formation of anhydrous metal nitrates. Some metal chlorides undergo solvolysis, but the exact influence which the particular metal, its valency, and the ionic or covalent character of the chloride have on the extent to which solvolysis occurs is not yet fully understood. The anhydrous chlorides AgCl, NaCl, KCl, $BeCl_2$ (*48*), $FeCl_3$ (*49*), $SnCl_4$ (*50*), and $CrCl_3$ (*51*) do not react with liquid dinitrogen tetroxide. Traces of moisture, however, can promote reaction, and the reaction between moist potassium chloride and dinitrogen tetroxide is a standard method for the preparation of nitrosyl chloride (*52*). With some chlorides an equilibrium occurs; for example, when pure zinc chloride is treated with dinitrogen tetroxide at 20°, the liquid is immediately colored red:

$$ZnCl_2 + N_2O_4 \rightleftharpoons Zn(NO_3)_2 + 2NOCl$$

but six successive treatments with the liquid tetroxide were necessary for complete conversion of chloride to nitrate (*53*). In contrast, the reverse reaction is completed in a single stage. Some chlorides, e.g., $TiCl_4$ (*54*), UCl_4, and UCl_5 (*55*), undergo ready solvolysis. The solvolysis of bromides and iodides has not been studied to any extent. On very little evidence, it would appear that solvolysis occurs with increasing readiness in the order $Cl^- < Br^- < I^-$.

The reaction of liquid dinitrogen tetroxide with oxides to yield anhydrous nitrates was probably first noted by Oswald (*56*), who obtained sodium nitrate in this fashion. Subsequent studies have shown this method to be a general one. However, at room temperature and pressure the reactions are frequently slow. For example, after 40-hour contact at 20°, conversion of calcium oxide to nitrate:

$$CaO + 2N_2O_4 \rightarrow Ca(NO_3)_2 + N_2O_3$$

is only 50% complete (*57*). Zinc oxide reacts more rapidly:

$$ZnO + 4N_2O_4 \rightarrow Zn(NO_3)_2 \cdot 2N_2O_4 + N_2O_3$$

and the tetroxide addition compound has no cohesive character, so that the reaction is 95% complete after 20 hours at 20° (*57*). Sodium peroxide reacts slowly:

$$Na_2O_2 + N_2O_4 \rightarrow 2NaNO_3$$

and the extent of reaction is only 20% after 48 hours at 20° (*57*). The reactions often proceed more readily in closed containers at elevated temperatures and the resultant high pressures (*58*, *59*); this is a useful modification of the method in the case of anhydrous nitrates with high thermal stability. The oxides which have been studied are listed in Table I. Where an N_2O_4 adduct is first formed, the tetroxide can be removed by heating under vacuum.

TABLE I

REACTION OF METAL OXIDES WITH LIQUID DINITROGEN TETROXIDE

Oxide	Product	Reference
Na_2O_2	$NaNO_3$	*57*
MgO	$Mg(NO_3)_2 \cdot N_2O_4$	*58*, *60*
CaO	$Ca(NO_3)_2$	*56–58*, *61–63*
SrO	$Sr(NO_3)_2$	*58*
BaO, BaO_2	$Ba(NO_3)_2$	*58*, *64*
L_2O_3 (L = Y, La, Pr, Nd, Sm, Gd)	$L(NO_3)_3$	*65*, *66*
UO_3, U_3O_8, $UO_{2.2}$	$UO_2(NO_3)_2 \cdot N_2O_4$	*59*
CuO, Cu_2O	$Cu(NO_3)_2 \cdot N_2O_4$	*58*
Ag_2O, AgO	$AgNO_3$	*58*, *63*, *67*
ZnO	$Zn(NO_3)_2 \cdot 2N_2O_4$	*57*, *58*, *68*, *69*
Hg_2O, HgO	$Hg(NO_3)_2 \cdot N_2O_4$	*58*, *70*
PbO, Pb_3O_4, PbO_2	$Pb(NO_3)_2$	*58*

Solvolysis has also been studied to a limited extent using metal hydroxides and metal carbonates. Sodium hydroxide, when carefully dried, reacts vigorously with liquid dinitrogen tetroxide, and the product shows 94% conversion to nitrate (*71*). Magnesium hydroxide also reacts, but conversion to nitrate is not complete (*60*). Dry lithium carbonate (*60*) and sodium carbonate (*71*) also react:

$$M_2CO_3 + 2N_2O_4 \rightarrow 2MNO_3 + CO_2 + N_2O_3$$

and the same reaction has been reported for magnesium carbonate (*60*), calcium carbonate (*62*), and zinc carbonate (*72*). As these are again solid-liquid reactions, they also require very long contact for complete reaction; reaction rates are increased in the presence of traces of water but nitrite is then introduced into the product. These reactions would not normally be used as preparative methods for the metal nitrates referred to, but they may be of use in other instances.

Some salts, which are not attacked by liquid dinitrogen tetroxide alone, do undergo rapid solvolysis when the tetroxide is diluted by electron-donor solvents. This aspect is discussed below.

2. Reaction with Metals

Dinitrogen tetroxide resembles water in that it attacks only a limited number of metals at room temperature. The reaction, represented by the equation

$$M + N_2O_4 \rightarrow MNO_3 + NO$$

has been observed for the alkali metals (*73, 74*), zinc (*68*), and mercury (*70*), but most other metals [including barium, strontium, and calcium (*48*)] do not react in the massive state. Reactivity does sometimes vary with physical state; metallic silver deposited as a mirror from ammoniacal silver nitrate solution is readily attacked by the liquid tetroxide. Where reaction with metals does occur, some of the nitric oxide formed remains in the liquid as dinitrogen trioxide; this enhances the dielectric constant of the medium in the neighborhood of the metal surface, and increases reaction rate. The trioxide appears to take no part in the reaction, since products from reaction mixtures containing up to 70% of dinitrogen trioxide consist entirely of the metal nitrate (*68*).

3. Reaction with Metal Carbonyls

This method has been found to be an excellent one for the preparation of anhydrous nitrates of some transition metals. The carbonyl groups are not oxidized in the course of the reaction, e.g.,

$$Ni(CO)_4 + 2N_2O_4 \rightarrow Ni(NO_3)_2 + 2NO + 4CO.$$

No interfering anions are therefore involved, since carbon monoxide escapes from the system. The reactions can be conducted using the metal carbonyl and dinitrogen tetroxide alone, but are more readily controlled in the presence of an organic solvent. The rate of reaction depends greatly on the physical state of the metal carbonyl. Liquid carbonyls (nickel tetracarbonyl and iron pentacarbonyl) react violently; solid carbonyls react much more slowly, and reaction rate is a function of surface area. All reactions are strongly dependent on temperature; dimanganese decacarbonyl and dicobalt octacarbonyl react quite readily with dinitrogen tetroxide at room temperature, but reaction stops almost completely at 0°. The reactions with nickel tetracarbonyl and iron pentacarbonyl, which proceed with explosive violence at 0°, can be moderated somewhat at lower temperatures. By this method the anhydrous nitrates of manganese (*75*), cobalt (*76*), and nickel (*77, 78*) have been prepared. They are first isolated as the adducts $Mn(NO_3)_2{\cdot}N_2O_4$, $Co(NO_3)_2{\cdot}2N_2O_4$, and $Ni(NO_3)_2{\cdot}N_2O_4$, from which the dinitrogen tetroxide can be removed by heating under vacuum. With iron and chromium carbonyls the products are the adducts $Fe(NO_3)_3 \cdot N_2O_4$ (*49*) and $Cr(NO_3)_3 \cdot 2N_2O_4$ (*51*), which cannot be so decomposed.

The two main conditions for the formation of simple anhydrous nitrates are that the dinitrogen tetroxide should be in the liquid state, and in large excess. Reaction between metal carbonyl and nitrogen dioxide vapors gives rise to nitrites as initial products [e.g., $Ni(NO_2)_2$ (*78*)]. In the liquid state, the isolation of intermediate products (the metal carbonyl nitrates) is seldom possible, but the compound $Mn(CO)_5NO_3$ has been obtained from the reaction of dimanganese decacarbonyl with controlled amounts of dinitrogen tetroxide (*79*).

4. Use of Dinitrogen Tetroxide-Solvent Mixtures

Dinitrogen tetroxide is almost unique among nonaqueous solvents in that its reactivity can be modified, often to a remarkable extent, by dilution with organic solvents. Those solvents which behave in this way are of two types, the inert solvents and the electron-donor solvents. The inert solvents stimulate tetroxide reactivity by increasing the dielectric constant of the medium, and hence the self-ionization of dinitrogen tetroxide to NO^+ and NO_3^- ions. The presence of organic solvents also enables reaction products such as nitrates to dissolve in the medium; because of the small dielectric constant (2.42) of liquid dinitrogen tetroxide, no simple inorganic salts dissolve in the pure liquid. Nitromethane is a typical inert diluent; it is miscible in all proportions with dinitrogen tetroxide (*80*) and has a dielectric constant of 37. Although copper metal does not react with nitromethane or dinitrogen tetroxide alone, reaction is vigorous with a solution containing 75–90 mole % of nitromethane, and the electrical conductivity of the mixture is also at its maximum at this composition. The solution becomes green, and the compound $Cu(NO_3)_2 \cdot N_2O_4$ separates on evaporation. The product of reaction of the mixture with zinc metal, $Zn(NO_3)_2 \cdot 2N_2O_4$, is the same compound as is produced in dinitrogen tetroxide alone. Indium metal dissolves in a nitromethane-dinitrogen tetroxide mixture (though not in the tetroxide alone) and the nitrate $In(NO_3)_3$ separates as a tetroxide adduct (*81*). Uranium metal dissolves more slowly, and the maximum rate of reaction occurs at 30 mole % nitromethane (*82*). The liquid turns green, due partly to the presence of a U(IV) species in solution; when all the metal is dissolved the green color disappears, since the U(IV) oxidized by the tetroxide to U(VI) in solution is no longer replaced by more U(IV) from the metal. The compound $UO_2(NO_3)_2 \cdot N_2O_4$ separates from the solution in a form which depends upon the composition of the medium. It can be thrown out of solution in an equimolar N_2O_4-CH_3NO_2 mixture as a light yellow powder by addition of excess dinitrogen tetroxide; alternatively, it can be obtained in the form of beautiful large yellow crystals (up to 1 cm in length) by allowing dinitrogen tetroxide vapor to dissolve slowly in a concentrated solution of the yellow powder in nitromethane (*83*). It is probable that the nitrates of many other metals can be prepared in this way, but nitromethane solutions have not been much used because the same products are often prepared more rapidly by using mixtures of the tetroxide with electron-donor solvents.

The dinitrogen tetroxide molecule is electron-deficient, and this leads to the formation of addition compounds with many organic solvents which possess an atom capable of donating electrons to the tetroxide. The composition and some properties of these compounds in the solid state have been studied in the case of carboxylic acids (*84*), esters (*84*, *85*), anhydrides (*85*), ketones (*84*, *85*), ethers (*86–92*), nitriles (*84*, *85*), nitrosamines (*84*, *93*), sulfoxides (*94*), and amines (*95*, *96*). The liquid state is rather more complicated; the NO^+ ion as well as the N_2O_4 molecule is electron-deficient, and each species is associated with solvent molecules. The liquid mixtures are best represented by the equilibrium

$$[(\mathrm{Don})_n\cdot\mathrm{NO}]^+ + \mathrm{NO_3}^- \rightleftharpoons n(\mathrm{Don}) + \mathrm{N_2O_4} \rightleftharpoons (\mathrm{Don})_n\cdot\mathrm{N_2O_4}.$$

The ultraviolet spectra of these mixtures indicate that discrete molecules of addition complex are not formed, but that partial electron transfer to the N_2O_4 and NO^+ species occurs (*97*). By the use of such physical properties as the vapor pressure (*98*), viscosity (*99*), volume of mixing (*100*), and heat of mixing (*81*), it is possible to arrange donor solvents in order of the degree to which they associate with dinitrogen tetroxide; this is also the order in which they stimulate the self-ionization, and thus the chemical reactivity, of dinitrogen tetroxide.

One of the major advantages in the use of these mixtures in preparative work arises from the fact that metal halides, which do not undergo solvolysis in the tetroxide alone, will often react vigorously with donor solvent mixtures. Ethyl acetate and methyl cyanide have found widest use in this connection. The anhydrous chlorides $BeCl_2$ (*48*) and $FeCl_3$ (*49*) are unreactive in the pure liquid tetroxide, but nitrosyl chloride is evolved copiously on addition of ethyl acetate. Reactivity of the tetroxide with metals is also stimulated by addition of donor solvents; manganese, cobalt, copper, cadmium, indium, and uranium are examples of metals which react with ethyl acetate–dinitrogen tetroxide mixtures, but not with the tetroxide alone. Dimethyl sulfoxide has been recently shown to be an excellent diluent for reactions with metals. It has the high dielectric constant of 46 (*101*), excellent donor properties towards dinitrogen tetroxide (*94*), and is a good solvent for metal salts. Its mixtures with dinitrogen tetroxide react with vanadium, molybdenum, antimony, silver, bismuth, and lead (*102*), but aluminium, titanium, iron, chromium, nickel, and tin show little or no tendency to react even in this medium.

A variety of products may be obtained on crystallization from these solutions. The product varies with the metal concerned, and also with the solvent and its concentration; they may be classified as follows:

(a) pure metal nitrate;
(b) metal nitrate-N_2O_4 addition compound;
(c) metal nitrate-solvent addition compound;
(d) metal nitrate-N_2O_4-solvent addition compound.

Examples of each type of product are given in Table II; where addition compounds are obtained, the anhydrous nitrate may sometimes be isolated by heating the adduct under vacuum. However, this is not invariably the case, and each adduct is an individual problem in this respect.

TABLE II
PRODUCTS OF REACTION OF METALS WITH DINITROGEN TETROXIDE–ELECTRON DONOR SOLVENT MIXTURES

Metal	Reaction medium: N_2O_4 mixed with	Product	Reference
Cadmium	Ethyl acetate	$Cd(NO_3)_2$	*67*
Manganese	Ethyl acetate	$Mn(NO_3)_2 \cdot N_2O_4$	*75*
Cobalt	Ethyl acetate	$Co(NO_3)_2 \cdot 2N_2O_4$	*103*
Uranium	Ethyl acetate	$UO_2(NO_3)_2 \cdot 2CH_3COOC_2H_5$	*70*
Indium	<20% Methyl cyanide	$In(NO_3)_3 \cdot 2N_2O_4$	*81*
	>20% Methyl cyanide	$In(NO_3)_3 \cdot 2CH_3CN$	*81*
Copper	5–30% Phenyl cyanide	$Cu(NO_3)_2 \cdot 2C_6H_5CN \cdot 4N_2O_4$	*104*
Bismuth	Dimethyl sulfoxide	$Bi(NO_3)_3 \cdot 3(CH_3)_2SO$	*102*

J. USE OF MOLTEN SALTS

In all methods so far discussed in this section, both the reagents and the reaction medium have been readily volatile, and where the product is soluble they may be removed from this product by vaporization. The main problem in the use of molten salts as reaction media lies in the difficulty of isolating a soluble product, and the method has been little used for the preparation of anhydrous nitrates. Anhydrous mercury(II) nitrate has been prepared by dissolving the dihydrate in molten mercuric bromide (*105*); water of crystallization evaporated at the temperatures corresponding to the liquid range of mercury(II) bromide (238–320°). Anhydrous lanthanum nitrate has been prepared by reaction of lanthanum oxide, La_2O_3, with molten ammonium nitrate at 170°. When the solution became clear, the temperature was raised slowly and excess ammonium nitrate removed by volatilization (*106*). Clearly this method is of use only in the case of nitrates having high thermal stability.

III. The Nitrate Ion

A. DIMENSIONS

The nitrate ion has a symmetrical planar structure, and is geometrically similar to the ions BO_3^{3-} and CO_3^{2-}, with which it is isoelectronic. The N—O bond distance is near 1.22 Å (*107, 108*). A value of 2.19 Å for the ionic radius of the nitrate ion was calculated from the lattice parameters of cubic modifications of rubidium and thallium nitrates (*109*); this is to be compared with the "thermochemical" radius (1.89 Å) based on the lattice energies of the alkali nitrates (*110*). In a study of the physical properties of melts of the alkali metal nitrates, Janz and James (*111*) have proposed a disk-like model for the nitrate ion, formed by rotating the planar ion about its C_3 axis. When the N—O distance is corrected to allow for the Van der Waals radius of the oxygen atoms, a disk is obtained having diameter 4.62 Å and thickness 2.2 Å. The corresponding volume of the nitrate ion, 24.8 $Å^3$, is then the same as that of the spherical chloride ion.

B. ELECTRONIC STRUCTURE

The nitrogen atom may be considered to form three planar sp^2 hybrid orbitals, leaving one p orbital perpendicular to this plane. The sp^2 hybrid orbitals overlap with oxygen orbitals, but it is not yet certain whether the oxygen bonding orbitals are sp hybrids or pure p orbitals. The molecular orbitals for a molecule of type AB_3 have been drawn up by Walsh (*112*), using pure p orbitals on atom B, and applied to the nitrate ion. Friend and Lyons (*113*) prefer to consider sp hybridization for each oxygen atom. If three bonds are thus formed between the sp hybrid orbitals of the three oxygen atoms, and the three sp^2 hybrids of the nitrogen atom, the p orbitals perpendicular to the plane of the NO_3 group will form π molecular orbitals. For each oxygen atom there remains an sp orbital (n_{sp}) and a pure p orbital (n_p), each of which is nonbonding. The increasing orbital energy sequence (*113*) is then

$$3\sigma,\ 3n_{sp},\ \pi_1,\ 2n_p,\ \pi_2,\ \pi_3,\ n_p,\ \pi_4^*,\ 3\sigma^*.$$

The π_1 orbital is bonding, the π_2 and π_3 orbitals are nonbonding and degenerate, and the π_4^* orbital is antibonding. As there are 24 electrons to be arranged in the molecular orbitals, it follows that the π_4^* orbital and the three antibonding σ^* orbitals will be left vacant. Using more detailed calculations, McEwen (*114*) has refined this energy sequence.

In each approach, three π orbitals are filled (only one of which is a bonding orbital) and this accounts satisfactorily for the observation that the N—O bond length (1.22 Å) approaches the classical N=O double bond length of 1.19 Å.

C. ELECTRONIC ABSORPTION SPECTRUM

The absorption spectrum of the nitrate ion has been the subject of several investigations. There are two absorption bands. A high intensity band occurs near 200 mμ, and a value of 10,000 has been reported for the extinction coefficient (*115*, *116*). The low intensity band occurs at 302.5 mμ, with an extinction coefficient of 7.06 per ion (*117*). These values were determined for aqueous solutions of metal nitrates. The spectrum for an aqueous solution of sodium nitrate is given in Fig. 1 (*116*). The precise values for λ_{max} and ϵ are influenced by the presence of other electrolytes in the solution.

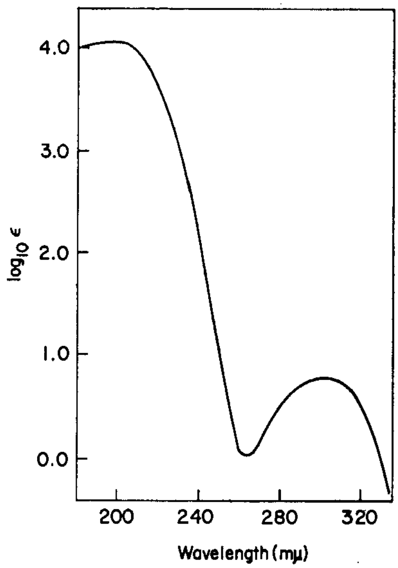


FIG. 1. Ultraviolet absorption spectrum of an aqueous solution of sodium nitrate.

There has been much discussion as to the origin of these two absorption bands. One school of thought (*118*, *119*) attributes the high intensity band to a charge-transfer process from the nitrate ion to surrounding solvent. Another view (*113*, *114*, *116*) is that the absorption is due to excitation of an electron from either of the filled π_2 or π_3 orbitals to the vacant antibonding π orbital, π_4^* (a $\pi \rightarrow \pi^*$ type of transition which is symmetry-allowed). There is more general agreement on the low intensity band. This can be attributed to a symmetry-forbidden internal transition in the nitrate ion, and the intensity and polarization data (*113*) are consistent with this being an $n \rightarrow \pi^*$ transition. There is an additional possibility, however, that it may be a weakly allowed $n \rightarrow \sigma^*$ transition (*114*).

The ultraviolet spectra of ionic metal nitrates in the solid state are essentially the same as in aqueous solution, though change of cation introduces some variation in both absorption and λ_{max} (*120*). For solid sodium nitrate, Friend and Lyons (*113*) showed that the low intensity band moves from the value of 302.5 mμ found for aqueous solutions to about 284 mμ; more recently, Cleaver and associates (*121*) have compared the ultraviolet spectra of crystalline nitrates of sodium, potassium, rubidium, and caesium. On heating the solids, abrupt shifts in absorption maxima occur at solid phase transition points and at the melting points. The electronic spectra for molten ionic nitrates are again similar to those observed for the solids and aqueous solutions; the electronic transitions are influenced by interactions between the nitrate ion and surrounding cations in the melt, so that the characteristics of the spectrum vary with the cation used. Detailed measurements have been carried out on the pure alkali metal nitrates (*121*) and on molten mixtures (*121, 122*). Systematic changes in the cation composition of a binary melt produce systematic shifts in the energy of the $n \rightarrow \pi^*$ transition. For example, λ_{max} for molten potassium nitrate at 352°C is 306 mμ; addition of anhydrous calcium nitrate rapidly increases the intensity of this absorption band, and when the electrical equivalent fraction of Ca^{2+} ions is 0.558, λ_{max} is reduced to 290 mμ (*122*).

D. VIBRATIONAL SPECTRUM

In the study of the structure of anhydrous metal nitrates, the infrared spectrum has proved, to date, to be the most important physical property. Thus, when a nitrate ion becomes bonded covalently to a metal atom, the molecular symmetry alters and in consequence the number of vibrational frequencies and their selection rules also vary. The free nitrate ion will be discussed here, and the relation between spectra and type of covalent bonding will be treated in Section V.

The nitrate ion belongs to the symmetry point group D_{3h}. It can be shown (*123*) that the free ion possesses four fundamental vibration frequencies; two of these are each doubly degenerate, and the other two are nondegenerate. One of the latter (the totally symmetrical N—O stretch) is not infrared active but appears in the Raman spectrum. The modes of vibration for the nitrate ion (*123*) are given in Fig. 2. The four frequencies are numbered ν_1, ν_2, ν_3, and ν_4, in the order in which the irreducible representations to which they belong, occur. The symmetry species are also shown

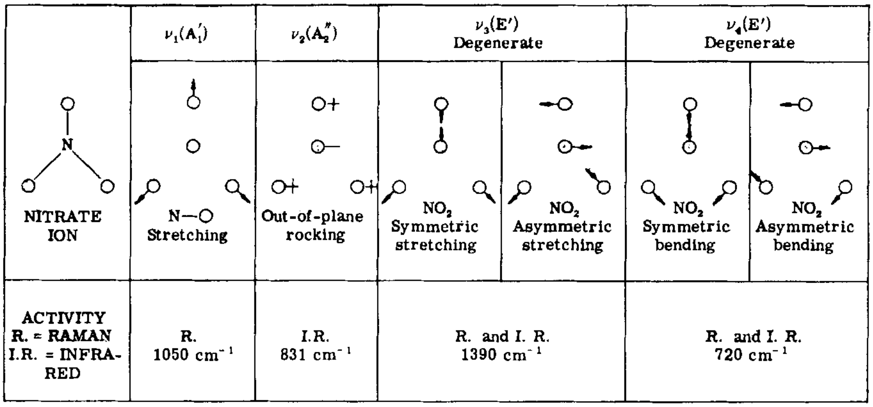


FIG. 2. Modes of vibration for the nitrate ion.

in Fig. 2. The frequencies calculated for the nitrate ion by Herzberg (*123*) are:

$$\nu_1 = 1050 \text{ cm}^{-1};\ \nu_2 = 831 \text{ cm}^{-1};\ \nu_3 = 1390 \text{ cm}^{-1};\ \nu_4 = 720 \text{ cm}^{-1}.$$

The alkali metal nitrates, and certain of the alkaline earth metal nitrates, give infrared spectra which resemble closely the predicted spectrum. This is illustrated in Table III where the frequencies are also classified under D_{3h} symmetry.

TABLE III

INFRARED SPECTRA OF SOME ALKALI METAL NITRATES (CM^{-1})

Compound	ν_1	ν_2	ν_3	ν_4
$LiNO_3$	—	840	1374	736
$NaNO_3$	—	837	1381	725
KNO_3	1052 (w)	826	1383	715

The values quoted are those determined by Buijs and Schutte (*124*); very similar results have been obtained by Ferraro (*125*), Vratny (*126*), and Miller and Wilkins (*127*). It is clear that with metal nitrates of this type, any interaction with the metal ion is insufficient to restrict the normal vibrations of the nitrate ion, and ionic metal nitrates are normally defined as those which give this type of infrared spectrum.

IV. Ionic Metal Nitrates

As explained above, an ionic nitrate is readily recognized by reference to its infrared spectrum. While ionic nitrates are certainly formed by the most electropositive metals, there is no rigid correlation between the type of metal-to-nitrate bonding and the electropositive character of the metal concerned, particularly so far as the less electropositive metals are concerned. Thus barium nitrate and lead nitrate are both ionic solids; silver nitrate is ionic but cupric nitrate is strongly covalent, and among the anhydrous nitrates of other transition metals no simple pattern has yet emerged from which one might predict the ionic or covalent character. Several factors are no doubt involved, of which the most important is probably the complexing power of the metal towards ligands in which oxygen is the donor atom. Some reference to ionic nitrates has already been made; this section will deal with some of the general properties of simple salts containing the free nitrate ion, using the alkali metal nitrates as typical examples. We shall discuss these nitrates by reference to the vapor, liquid, and solid states.

A. The Vapor State

The vapors of the alkali metal nitrates do not appear to have been studied, and this aspect of their chemistry has novelty and much potential interest. Until recent years, the concept that anhydrous metal nitrates might be stable as vapors was not generally accepted, and was, indeed, almost a contradiction in terms. The observation (to be discussed in later sections) that some metal nitrates, e.g., copper nitrate, could be stable in the vapor state has perhaps resulted in volatility being related too closely with covalency. The alkali metal nitrates represent the opposite extreme. The ionic solids melt to give stable liquids, which must presumably have finite vapor pressures; if so, it must be possible to distill them. Hardy and Field (*255*) have recently confirmed this. Nitrates of lithium, sodium, potassium, rubidium, and caesium were each heated at reduced pressure (5×10^{-3} mm Hg) in a silica tube placed in a furnace at 450–500°. A cold finger at 20° was inserted in the tube at such a position that metal nitrate could only reach it via the vapor phase. Distillation began as soon as the nitrate melted, and gram quantities of pure nitrate were collected on the cold finger; the process was most efficient in the case of caesium nitrate. One of the many questions of great interest which arise from these observations is the structure of the vapor species. The fact that the solids are ionic lattices need not necessarily have any bearing on the structure in the vapor, and to regard the vapor as being composed of ion pairs at these relatively low temperatures is to underestimate the potentialities of the nitrate group.

B. The Liquid State

Many ionic nitrates give stable melts. Some relevant temperatures for the alkali metal nitrates are given in Table IV.

TABLE IV
STABILITY OF MOLTEN ALKALI METAL NITRATES

Compound	M.P. (°C) (*128*)	T_1[a]	T_2[b] (*132*)
$LiNO_3$	255	410 (*129*)	474
$NaNO_3$	308	380 (*130*)	529
KNO_3	334	400 (*131*)	533
$RbNO_3$	306	—	549
$CsNO_3$	414	600 (*129*)	584

[a] T_1 = temperature (°C) at which decomposition of the melt is first detected.

[b] T_2 = temperature (°C) at which the dissociation pressure of oxygen reaches 1 atmosphere.

The initial decomposition of the melt is difficult to detect, so that the temperature T_1 is only an approximate value. Nevertheless, it is clear that melts are stable over a temperature range of at least 70°. Each nitrate decomposes to give nitrite and oxygen in the first instance; since dissociation pressures can be measured with accuracy, the temperature T_2 (Table IV) is a more reliable guide to stability than is T_1. It is interesting to note that in spite of the wide range of size and polarizing power of the alkali metal ions, the variation in decomposition temperatures is not large, so that the nitrate ions in the melt are behaving essentially as kinetically free species. This is supported by recent measurements of the Raman (*111*) and infrared (*133, 134*) spectra of the melts, which show that the nitrate ion does not depart greatly from the D_{3h} symmetry of the free ion. From the Raman spectra, there is a regular variation in stretching force constant with polarizing power of the cation, but this amounts to only 8% on going from caesium nitrate to lithium nitrate.

The most direct evidence for the ionic nature of the melts is furnished by their electrical conductivity (Table V). Specific conductivities (column 2) were determined at the temperatures quoted, which were selected to enable direct comparison to be made for melts near 400°C. The molar conductivities (column 3) were determined at temperatures 10% (°K) above the individual melting points. The high values of conductivity indicate that ionic conduction occurs in the molten salts.

The relatively low melting points of the alkali metal nitrates is a surprising feature; the values given in Table IV are 300–500° lower than those of the corresponding chlorides. From consideration of the lattice energies of the solids (*138*) it is not immediately obvious why this should be the case. The nonspherical shape of the nitrate ions may be partly responsible; Janz and James (*111*) have calculated that there is more unoccupied space in the solid nitrates than in the chlorides, which would allow the nitrates

TABLE V
ELECTRICAL CONDUCTIVITY OF THE MOLTEN ALKALI METAL NITRATES

Compound	Specific conductivity[a] (ohm^{-1} cm^{-1})	Molar conductivity[a] (ohm^{-1} cm^2)	Activation energy[b] (kcal/mole)
$LiNO_3$	1.61 (402°)	44	3.37
$NaNO_3$	1.29 (387°)	55	2.97
KNO_3	0.83 (405°)	45	3.65
$RbNO_3$	0.64 (409°)	33	3.48
$CsNO_3$	0.59 (447°)	46	2.97

[a] References *135, 136*.
[b] References *135–137*.

to become liquid at lower temperatures than salts such as the chlorides in which spherical ions allow close packing. Many physical properties of the melts are dependent to a lesser degree on anion shape, and there is an extensive analogy between the thermodynamic properties of liquid nitrates or their mixtures, and those of the corresponding halides (*109*). Surface properties are also similar. Figure 3 compares the surface tensions of the molten nitrates and chlorides of the metals of Groups I and II. The variation in

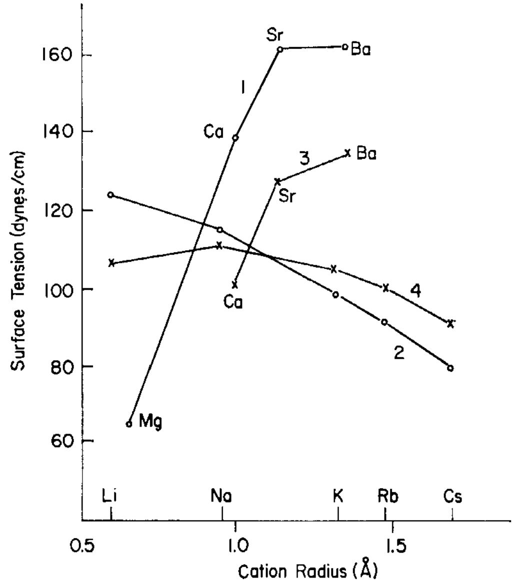


FIG. 3. Surface tensions of molten Group I and Group II metal chlorides and nitrates. 1: Group II chlorides at 1000°. 2: Group I chlorides at 800°. 3: Group II nitrates at 595° (Ba), 615° (Sr), or 560° (Ca). 4: Group I nitrates at 425°.

tension with cation size follows the same trend with each anion, and with the alkali metal salts the actual values of surface tension are also similar (*128*).

The low melting points of the alkali metal nitrates has led to their widespread use as reaction media. The liquids can be handled readily in Pyrex glass apparatus, which is not corroded. The available liquid range can be extended by the use of mixtures, usually of eutectic composition. The low temperatures available by this means are illustrated in Table VI.

TABLE VI
MELTING POINTS OF EUTECTIC MIXTURES OF ALKALI METAL NITRATES (*139*)

Components	M.P. (°C)
$LiNO_3$—$NaNO_3$	206
$LiNO_3$—KNO_3	125
$LiNO_3$—$CsNO_3$	174
$LiNO_3$—$NaNO_3$—KNO_3	120
$NaNO_3$—KNO_3	223
$NaNO_3$—$RbNO_3$	178
KNO_3—$RbNO_3$	291
KNO_3—$CsNO_3$	~200

Although there are many analogies in the physical properties of the molten alkali metal nitrates and chlorides, there are marked contrasts in the type of reaction which can be carried out in the two media. A full discussion on the use of molten nitrates as nonaqueous solvents is outside the scope of this review, but brief reference should be made to the influence which the oxidizing and complexing powers of the nitrate group exert on the type of reaction which is possible. Thus, Gruen (*140*) has shown that uranium tetrafluoride dissolves in LiCl—KCl eutectic to give stable green solutions. However, if a uranium tetrahalide is added to $LiNO_3$—KNO_3 at 175°, the reaction

$$U^{4+} + 2NO_3^- \rightarrow UO_2^{2+} + 2NO_2$$

occurs rapidly. Experiments of this type have led to the general conclusions that the U(III), U(IV), and U(VI) states are each stable in solution in molten halides, but that only the U(VI) valency state is stable in molten nitrates. Reduction by metals is possible in molten halides, but not in molten nitrates. Dissolution of neptunium tetrachloride in molten $LiNO_3$—KNO_3 gives a green solution whose ultraviolet absorption spectrum is almost identical with that of Np(V) in aqueous solution, so that lower oxidation states of neptunium are oxidized to Np(V) in nitrate melts, in contrast to the U(VI) state for uranium. Americium trichloride in $LiNO_3$—KNO_3 gives a pink solution which is characteristic of Am(III); the fact that oxidation in the nitrate melt does not occur is consistent with the increasing stability of the lower oxidation states of the transuranium elements as the series is ascended (*141*). The competition between nitrate and chloride ions as ligands to metal ions can also be observed in molten nitrate media. Cobalt chloride undergoes the simple ionization, $CoCl_2 \rightarrow Co^{2+} + 2Cl^-$, in molten $LiNO_3$—KNO_3; the Co^{2+} ion is associated with six NO_3^- ions, perhaps as the complex $[Co(NO_3)_6]^{4-}$. On addition of potassium chloride to the melt, the absorption spectrum indicates a change to the complex $[CoCl_4]^{2-}$ (*142*). Similar reactions have been studied for solutions of nickel chloride (*143*), and chromatographic separations of many cations, using molten $LiNO_3$—KNO_3 as the liquid medium, can be interpreted satisfactorily on the basis of the relative stability of the complex ions formed (*141*).

For oxidation-reduction reactions in molten nitrates, a sequence of redox potentials will apply which may differ appreciably from that which is accepted for aqueous solutions. Thus, dichromates dissolve in molten $NaNO_3$—KNO_3 eutectic mixtures, but the reaction

$$Cr_2O_7^{2-} + NO_3^- \rightarrow 2CrO_4^{2-} + NO_2^+$$

proceeds at a measurable rate at 250° (*144*). When no other ions are present, the reaction

$$NO_2^+ + NO_3^- \rightarrow N_2O_5$$

follows, but if other ions, e.g., bromide, are present oxidation can occur (*145*):

$$NO_2^+ + Br^- \rightarrow NO_2Br \rightarrow NO_2 + \tfrac{1}{2}Br_2.$$

Further work of this kind will define new scales of reactivity which may prove to be important in synthetic inorganic chemistry.

C. The Solid State

Calculated values for lattice energies are given in Table VII.

TABLE VII

LATTICE ENERGIES (KCAL/MOLE) OF THE ALKALI METAL NITRATES

Reference	$LiNO_3$	$NaNO_3$	KNO_3	$RbNO_3$	$CsNO_3$
Yatsimirskii (*110*)	187	176	160	153	148
Waddington (*138*)	195	176	159	155	145

The values calculated by Yatsimirskii, using the Kapustinskii formula, are seen to be in good agreement with those obtained by Waddington from the values of the hydration heats of the ion pairs.

Crystals of the alkali metal nitrates have interesting optical properties.

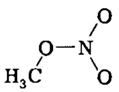
In sodium nitrate, for example, the nitrate ions lie in parallel planes perpendicular to the threefold axis of the rhombohedral crystals. In this respect the NO_3^- ions resemble the CO_3^{2-} ions in calcite, and their polarizability is greater when the electric vector of the incident light wave lies in the plane of the groups than it is when the vector is perpendicular to the groups. This leads to birefringence in sodium nitrate which is even more pronounced than the well-known effect in calcite (*146*).

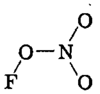
The chemical properties of ionic metal nitrates are best referred to in comparison with covalent nitrates, and will be treated in this way. For example, solid alkali metal nitrates behave as oxidizing agents when heated, hence the use of potassium nitrate as a constituent of gunpowder. However, oxidizing power increases with the covalency of the metal-nitrate bond, and some covalent nitrates can act as oxidizing agents at room temperature.

V. Covalent Bonding of the Nitrate Group

A. Types of Bonding

One of the most useful comparisons which can be made in this connection is that between the ion NO_3^- and the oxide NO_3. The two units differ by one electron only, yet the loss of this electron converts a stable ion into a highly unstable oxide. The high stability of the free nitrate ion indicates that the electron distribution in the ion (Section III) is also a stable one. In contrast, the oxide NO_3 has not even been properly characterized; there is some spectroscopic evidence for its formation in the reaction of ozone with dinitrogen pentoxide, or fluorine with nitric acid, and it may be produced as a transient intermediate in some gas phase reactions of nitrogen dioxide. In view of this, it might be argued that any influence, such as covalent bonding, which tends to restrict the distribution of electrons among appropriate molecular orbitals in the nitrate ion must inevitably lead to instability. This point of view is supported by the chemistry of nonmetal nitrates, such as methyl and fluorine nitrates which have the following structures





The C—O or F—O bond modifies the electron distribution in the NO_3 group, so that alkyl nitrates are explosive and fluorine nitrate is highly reactive. Until recent years it was therefore reasonable to deduce that covalent bonding between metal atoms and nitrate groups would lead to instability, and this was also in accord with the chemistry of metal nitrates as indicated by published literature. Thus, the known simple metal nitrates were almost all ionic salts; anhydrous nitrates were unknown for most of the transition metals, where covalency might have been expected; nitrates were known for some transition metals in the form of hydrates, but here the water molecules coordinate to the metal atom and the nitrate is ionic. Again, the nitrate group was found to occur only rarely in coordination complexes, and even then the substitution of more than one nitrate group into a complex was unusual. In the spectrochemical series, which places ligands in order of their crystal field effects, the nitrate group is often not mentioned (*147*). This is understandable since the spectra involved are usually measured in aqueous solution, but when ligands are arranged in order of nucleophilic power, as determined by rates of substitution in cobalt complexes in solution in methyl alcohol, the nitrate group again occupies a humble position at the bottom of the list (*148*).

Recent research work has changed this general picture completely and has shown that nitrate chemistry, as we know it in aqueous medium, is only a small part of the behavior of which the nitrate group is capable. When zinc metal reacts with solutions of ethylammonium nitrate in liquid dinitrogen tetroxide, a crystalline product is obtained of composition $(EtNH_3)_2[Zn(NO_3)_4]$. Conductivity, transport, and other physical measurements show that the $[Zn(NO_3)_4]^{2-}$ ion is a stable unit in solution in nitromethane and other nonaqueous solvents, and is therefore a coordination complex in which all ligands are nitrate groups (*149*). Such complexes will not be discussed in detail in this review, but it is relevant that similar tetranitrato-metal complexes are now known also for manganese (*150*), iron (*151*), cobalt (*150, 152*), nickel (*150*), and copper (*150*). The heavy metals give stable hexanitrato complex ions, e.g., $[Ce(NO_3)_6]^{2-}$, $[Th(NO_3)_6]^{2-}$, and $[U(NO_3)_6]^{2-}$ (*15, 153*). Simple anhydrous nitrates of many metals have now been prepared by reactions carried out in nonaqueous solvents. Some of their properties (e.g., volatility) are quite unexpected, and leave no doubt that in the appropriate environment the nitrate group can be a strong ligand to a metal atom. Recognizing this, Straub *et al.* (*150*) have calculated the parameter *Dq* for solutions containing the $[Ni(NO_3)_4]^{2-}$ ion in nitromethane, and compared the value with those for some other corresponding Ni(II) complexes (Table VIII). It is of considerable interest that NO_3^- is found to occupy a position slightly lower than water, but greater than dimethyl sulfoxide or the chloride ion.

TABLE VIII
SPECTROCHEMICAL SERIES FOR Ni(II) COMPLEXES

Ligand:	H_2O	NO_3^-	$(CH_3)_2SO$	Cl^-
Dq (cm^{-1}):	860	801	773	720

It is therefore quite clear that covalent metal nitrates and their derivatives are much more stable than the nonmetal nitrates; and it is possible that some form of back-donation of electrons from a metal atom to the empty orbitals of the nitrate group may make a contribution to this stability. The number, and the nature, of the bonds involved provide the main theme underlying most of the current investigations, and we may now consider the various ways in which such bonding can occur. These are illustrated in Fig. 4.

Unidentate bonding

Bidentate bonding

Terdentate bonding

Bonding as a bridge group

FIG. 4. Types of covalent bonding of the nitrate group.

All four types of bonding are theoretically possible, and we shall now consider each one individually.

B. UNIDENTATE BONDING

Covalent bonding of the nitrate group is readily recognized from its infrared spectrum. In compounds where the nitrato group is bonded through one oxygen atom, the symmetry of the group is lowered from the point group D_{3h} for the free ion to C_{2v}. This results in a loss of degeneracy in the vibrations designated ν_3 and ν_4 for the nitrate ion. There are therefore six vibrations for the covalent nitrate group, and all the vibrations are both Raman and infrared active. They are designated ν_1, ν_2, ν_3, ν_4, ν_5, and ν_6 according to the irreducible representations of the point group, C_{2v}. The form of these vibrations (*123*) is given in Fig. 5, which also shows the symmetry species involved. The original assignment of the vibrational spectrum was assisted by the fact that the highly polarized lines in the Raman spectrum are caused by vibrations of the type A_1, and further differentiation can sometimes be made by the use of isotopes. By these means the

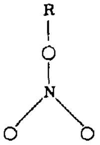
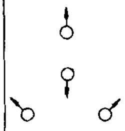
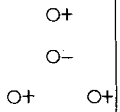
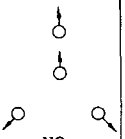
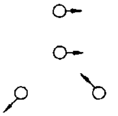
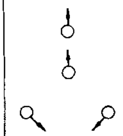
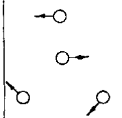
	$\nu_2(A_1)$	$\nu_6(B_2)$	$\nu_1(A_1)$	$\nu_4(B_1)$	$\nu_3(A_1)$	$\nu_5(B_1)$
 NITRATO GROUP	 N—O Stretching	 Out-of-plane rocking	 NO_2 Symmetric stretching	 NO_2 Asymmetric stretching	 NO_2 Symmetric bending	 NO_2 Asymmetric bending
ACTIVITY R. = RAMAN I. R. = INFRA-RED	R. and I. R.	R. and I. R.	R. and I. R.	R. and I. R.	R. and I. R.	R. and I. R.

FIG. 5. Modes of vibration for the unidentate nitrato group.

bands for nitric acid (*154*) and methyl nitrate (*155*) were assigned (Table IX) and the results used as a basis for the assignment of nitrato complexes of the type M—ONO_2 (*156*).

Comparison of Figs. 2 and 5 shows that several important changes have occurred:

(a) ν_1 for the ion becomes ν_2 in the covalently bonded group. Because of lowering of symmetry, this vibration now becomes active in the infrared, and the appearance of a ν_2 band in the spectrum is therefore a useful indication of the presence of a covalent nitrate group. The different values for ν_2 give some idea of the strength of the covalent bond, and Gatehouse *et al.* (*156*) have used the variation in this frequency to place a number of nitrato complexes in order of metal-nitrate bond strength.

(b) ν_2 for the ion becomes ν_6 in the covalent nitrate. Values for ν_6 are almost invariably at lower frequencies than ν_2 for the ion, so that the out-of-plane vibration requires less energy when the nitrate group is bonded to another atom.

(c) The degenerate vibration ν_3 for the ion is split into ν_1 and ν_4 in the nitrato group. Ferraro (*125*) has suggested that the extent of this splitting ($\nu_4 - \nu_1$) is a criterion of the strength of the covalent bond, and the values given in Table IX below show that $\nu_4 - \nu_1$ gives the same sequence for covalency as does the variation in ν_2 for the nitrato group. Increase in the strength of the bond to the oxygen atom concerned (Fig. 5) has the effect of fixing this atom in space, and is equivalent to an increase in weight at this position. The influence of such an increase will be more pronounced on the asymmetric than on the symmetric NO_2 stretching frequency, so that as the metal and the degree of covalency change, ν_4 varies more than does ν_1. From a detailed study of the infrared spectra of many metal nitrates dissolved in tributyl phosphate, Katzin (*253*) concludes that a $\nu_4 - \nu_1$ splitting of less than about 100 cm^{-1} can be attributed to electrical asymmetry rather than covalent bonding.

(d) ν_4 is also a degenerate vibration in the ion, and gives rise to ν_3 and ν_5 in the nitrato group. These vibrations are often very weak and are sometimes not observed in covalent nitrates. Symmetry considerations (Fig. 5) suggest that ν_5 will be affected more than will ν_3 by change in the atom to which the nitrato group is attached.

The actual frequencies for the nitrato group cannot be predicted as for the free nitrate ion, since the absorption frequency will vary according to the strength of the metal-oxygen bond. Since this is generally unknown, the force constants for the nitrogen-oxygen bonds are also unknown. In some nitrates, the nitrato groups may be bonded as bidentate groups; again, in the solid state there are pronounced lattice forces which often give rise to additional spurious absorption bands, so that the infrared spectrum of a simple nitrate in the solid state is not an ideal basis on which to define the typical frequencies for a truly unidentate nitrato group. It is therefore preferable to select a compound in which the nitrato groups are shielded from interaction with one another or with other metal atoms, and where the coordination number of the metal makes it almost certain that the nitrato group is indeed unidentate. Nitratopentacarbonylmanganese is excellent in this respect, and its infrared spectrum is given in Table IX; ν_3 and ν_5 were not observed in this spectrum, but the more important bands ν_1, ν_2, ν_4, and ν_6 are regarded as quite characteristic of a unidentate nitrato group bonded to a manganese atom. With most of the heavy metals, the variation in these bands is relatively small from one metal to another. Nitratotrimethyltin is also a suitable compound from this point of view, and the infrared bands given by the nitrato group agree closely with those

TABLE IX

INFRARED SPECTRUM OF THE UNIDENTATE NITRATO GROUP (CM^{-1})

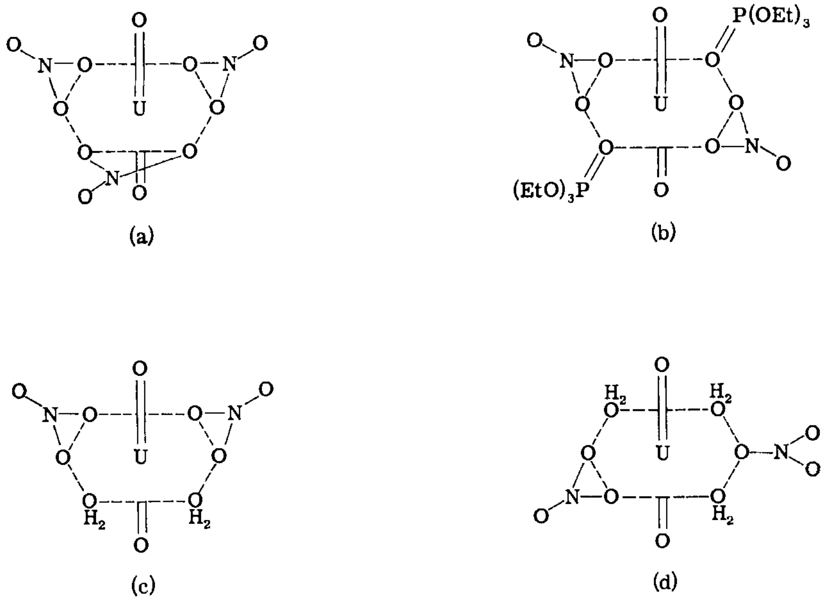
Compound	ν_2	ν_6	ν_1	ν_4	ν_3	ν_5	Ref.
$(CO)_5MnNO_3$	1010	805	1284	1486	—	—	*79*
Me_3SnNO_3	1031	780	1268	1488	727	—	*158*
$(dipy)Pd(NO_3)_2$	979	801	1274	1517	—	—	*156*
CH_3NO_3 (vapor)	854	759	1287	1672	657	578	*155*
HNO_3 (vapor)	886	765	1320	1710	—	583	*154*
DNO_3 (vapor)	888	764	1313	1685	—	543	*154*

for the manganese compound (Table IX). The palladium compound listed is perhaps less ideal since two nitrato groups are present, but again agreement is generally good.

In order to determine which infrared bands are most sensitive to change in the degree of covalency, we may compare the spectra for the nitrato-metal complexes with those given by methyl nitrate, nitric acid, and deuterium nitrate (Table IX), in which the nitrato group is bonded to light atoms and the degree of covalency is near 100%. ν_2 is diminished by about 100 cm^{-1}, but the most spectacular change occurs in ν_4, where the increase in frequency is as much as 200 cm^{-1}. A similar effect is observed with certain metal nitrates, such as the beryllium compounds discussed below, where covalency is believed to be particularly strong.

C. Bidentate Bonding

Although there is no doubt that the nitrate group can bond in this way, there are very few authentic examples in which bidentate bonding occurs. This is all the more surprising since the isoelectronic carbonate group is well known as a bidentate ligand, and complexes such as $[Co(NH_3)_4CO_3]^+$ have long been used as starting materials in synthetic work. This apparent difference in behavior cannot be attributed wholly to the double charge on the carbonate ion since the acetate ion, which is similar in shape and dimensions and carries a single charge, also behaves readily as a bidentate ligand. The earliest examples were provided by the nitrato-uranyl complexes. A series of compounds $M[UO_2(NO_3)_3]$ (where M = NH_4, K, Rb, Cs) *(159)* is known and an X-ray study of the rubidium salt leaves no doubt that the complex anion exists as a separate entity *(160)*. Each uranyl group is surrounded by an equatorial ring of six oxygen atoms (at a distance of 2.72 Å from the uranium atom), which are provided by three bidentate nitrato groups. The structure is shown in Fig. 6a, the six oxygen atoms concerned being joined by dotted lines for clarity. All the physical properties of solutions of alkylammonium uranyl nitrates in nitromethane can be interpreted satisfactorily in terms of the trinitrato-uranyl ion, so that this ion is stable also in solutions in nonaqueous solvents *(161)*. There is X-ray evidence for a similar structure (Fig. 6b) for the addition compound uranyl nitrate-bis(triethylphosphate) in which each nitrato group is bidentate *(162)*. Gatehouse and Comyns *(157)* and Allpress and Hambly *(251)* have interpreted the infrared spectra of uranyl nitrate dihydrate (Fig. 6c) and trihydrate (Fig. 6d) on the same model, and this is supported by X-ray data *(252)*. It should be noted that for the trihydrate both a unidentate and a bidentate nitrato group are involved. These two structures account better for the splitting of the planar modes which occur in the infrared spectrum than do other obvious isomeric forms.



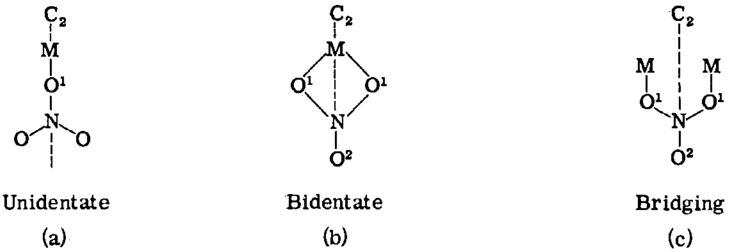
(a) (b) (c) (d)

FIG. 6. Bidentate bonding of nitrato groups in uranyl complexes.

The impression given by existing literature, that bidentate bonding by the nitrate group is rare, may well prove to be quite erroneous. We believe that many nitrato complexes and even simple nitrates, in which the nitrate group is at present classed as unidentate, may prove on closer examination to involve bidentate groups. This position arises because no clear distinction can be made at present on the basis of infrared spectra alone (see below) and few studies involving other techniques have been made on these compounds. Three examples will illustrate this point of view. The cupric nitrate molecule in the vapor state, for which both unidentate and terdentate bonding had been proposed, is now found to contain bidentate nitrato groups. Half of the nitrate groups in solid copper nitrate also display some bidentate character. Since this compound has held a key position in this field of study, its structure is discussed individually below. Cobalt nitrate forms a complex $[Co(Me_3PO)_2(NO_3)_2]$ with trimethylphosphine oxide, which might well have been regarded as a 4-coordinate complex. However, on full X-ray analysis of its structure, Cotton and Soderberg (*163*) found that the cobalt atom is surrounded by six oxygen atoms in irregular 6-coordination, so that the nitrate groups are actually bidentate. Again, the reflectance spectra and the electronic absorption spectra of nitromethane solutions of a series of methyltriphenylarsonium salts of the anion $[M(NO_3)_4]^{2-}$ (where M = Mn, Co, Ni, or Cu) have been studied

(150). These measurements indicate that the manganese and cobalt complexes are 4-coordinate, but that in the case of nickel and copper the metal atom may be 6-coordinate in the complex. Ultimately it may be found to be generally true that bidentate nitrato groups occur wherever a metal atom has an apparently low coordination number (on the basis of unidentate nitrate bonding) in an environment where a higher coordination number would have been expected.

It has been mentioned that a clear distinction cannot be drawn between unidentate and bidentate nitrato groups on the grounds of infrared spectra alone. This applies to a bridging nitrate group also, and the reason for this is illustrated in Fig. 7.



Unidentate (a)

Bidentate (b)

Bridging (c)

FIG. 7. Symmetry of unidentate, bidentate, and bridging nitrato groups.

Provided that the metal, nitrogen, and oxygen atoms are coplanar, a C_2 axis passing along one N—O bond exists for each structure, and each of the molecules possesses C_{2v} symmetry irrespective of the type of bonding. Each structure would then possess the same elements of symmetry, and give rise to the same six infrared active vibrations. Where the M—O^1 bond order in the unidentate nitrate case approaches unity, the metal will no longer be coplanar with the NO_3 group; the symmetry is reduced to C_s, but six infrared active vibrations will still be observed. When the unidentate group is compared with the bidentate or bridging group, shifts in certain of the frequencies can be predicted, and in this respect infrared studies have proved useful in determining structure. However, the general arguments applied to bidentate and bridging groups are so similar that infrared spectra are unlikely to be of much value in distinguishing between these two modes of bonding. Since these arguments are discussed below in connection with bridge bonding, they need not be referred to at this stage.

D. THE BRIDGING NITRATE GROUP

The first definite evidence that the nitrate group can bond in this way was provided by the crystal structure of anhydrous cupric nitrate *(164)*, shown in Fig. 8. The main feature of the structure is the presence of infinite chains parallel to the *a* axis, formed by alternate copper atoms and nitrate groups. Three such chains are shown in Fig. 8, and four more are represented, for clarity, by vertical full lines. The lengths of the bonds joining the copper atoms to oxygen atoms of these bridging nitrate groups are 1.95 and 1.99 Å, which are typical of the shorter Cu—O bonds in previously determined structures in which oxygen is coordinated to copper (*165*).

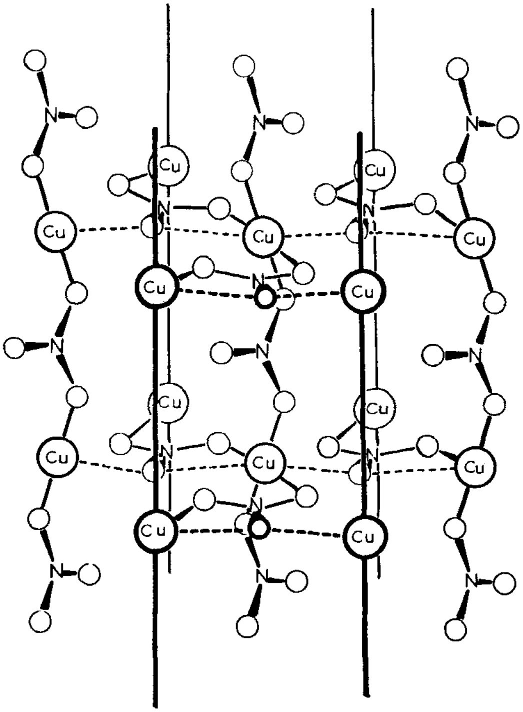


FIG. 8. Structure of solid copper(II) nitrate.

The chains are arranged parallel to each other in a pseudohexagonal manner, and are linked sideways by nitrate groups which lie approximately in planes perpendicular to the chains. In these planes, each nitrate group again bridges two copper atoms, with Cu—O distances of 1.97 and 2.04 Å. The third oxygen atom forms weaker bonds of lengths 2.43 and 2.64 Å to two copper atoms. Since the 2.04—Å and 2.64—Å bonds involve the same copper atom, this nitrate group is displaying some bidentate behavior. Viewing the structure as a whole, the bonding of the nitrate groups is such as to surround each copper atom with a distorted octahedron of oxygen atoms. When copper nitrate reacts with nitrosyl perchlorate, one of the nitrate groups is replaced to give a product $Cu(NO_3)(ClO_4)$ (*166*); since two types of nitrate bonding are involved in the structure of copper nitrate, the replacement of half of the nitrate groups in this structure by perchlorate groups may account for the formation of this product.

Although the solid copper nitrate structure indicated the ability of the nitrate group to bridge two metal atoms, the group is nevertheless part of an infinite lattice, and it was obviously desirable to continue to search for a compound in which the nitrate group would act as a bridge group within a single molecule. An excellent example has now been found in basic beryllium nitrate, in which the nitrate group displays bridge bonding to a remarkable extent (*167*). Beryllium chloride undergoes solvolysis in mixtures of liquid dinitrogen tetroxide and ethyl acetate to give pale straw-colored crystals of the addition compound $Be(NO_3)_2 \cdot 2N_2O_4$. When heated in a vacuum, this decomposes in two stages. Dinitrogen tetroxide is evolved rapidly at 50°, leaving anhydrous beryllium nitrate, $Be(NO_3)_2$, as a white powder which has no detectable volatility. This is stable to about 125°, when sudden decomposition occurs to give brown fumes of nitrogen dioxide and a volatile beryllium compound which separates from the gas phase as colorless crystals. This has the formula $Be_4O(NO_3)_6$ and is believed (*168*) to possess the structure shown in Fig. 9. All six nitrate groups bridge beryllium atoms, and it is clear that in the future this property must be regarded as characteristic of nitrate chemistry. There is an obvious analogy with basic beryllium acetate. The outer sphere of oxygen atoms will carry a larger charge than will the methyl groups which occupy these positions in the basic acetate, and in consequence the basic acetate is soluble, but the basic nitrate is insoluble, in nonpolar solvents such as chloroform, benzene, and carbon tetrachloride.

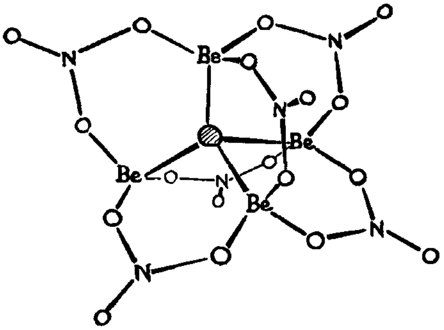


FIG. 9. Basic beryllium nitrate.

The infrared spectrum of basic beryllium nitrate consists of the following bands (cm^{-1}): 1630 (*vs.b*) 1550 (*sh.*on 1630 band) 1280 (*vs.b*) 1226 (*s.sp*) 1147 (*w*) 1065 (*s.b*) 863 (*s*) 805 (*s*) 767 (*s*) 715 (*w*). These bands have not all been assigned, especially in the lower frequency range, since Be—O stretching frequencies and ring deformation frequencies occur here also. However, the band which has probably the greatest significance in the present context is the high frequency nitrate vibration at 1630 cm^{-1}. In the particular case of basic beryllium nitrate we have the advantage of having some information about its structure, but it is of interest to examine the kind of conclusions which might be drawn from this high frequency vibration in a case where structure is not known. If the nitrate group is strongly bonded in unidentate fashion, ν_2, the NO stretching vibration (represented by the stretching of the bond $N—O^1$, Fig. 7a) decreases towards the limiting value of about 850 cm^{-1}. The vibration ν_4 increases to 1600–1700 cm^{-1} (Table IX); this vibration is antisymmetrical and therefore would not be polarized in the Raman spectrum. In the case of a bridging nitrate (Fig. 7c) which is strongly coordinated, the bond order of the $M—O^1$ bonds approaches unity. The bonds $N—O^1$ are therefore also near to single bonds, which means that the bond $N—O^2$ acquires double bond character. In the bridging nitrate, the vibration ν_2 refers to the stretching of this $N—O^2$ bond. The N=O stretching frequency lies in the range 1600–1700 cm^{-1} (absorption at 1696 cm^{-1} has been assigned (*169*) to the N=O stretch in the vapor of nitrous acid), so that absorption in this range may also be assigned to ν_2 for a bridging nitrate. However, this vibration is a totally symmetrical one, and would thus be a strongly polarized band in the Raman spectrum. Again, the restriction imposed on the NO_2 asymmetrical stretch ν_4 by bridge bonding will decrease the frequency ν_4 to the region of 1200–1300 cm^{-1}. Nakamoto and co-workers (*170*) have recently reassigned the infrared spectra of a series of unidentate, bidentate, and bridging carbonato complexes on the basis of the arguments discussed above.

It will be seen therefore that the infrared spectrum, taken in conjunction with the Raman spectrum, can be of definite value in determining the mode in which covalent nitrate groups are bonded. Infrared absorption in the 1600–1700 cm^{-1} region is characteristic only of strong covalent bonding, but if this band can be assigned to either ν_2 or ν_4 with the aid of the Raman spectrum, then the type of bonding can be deduced with some confidence.

E. Terdentate Bonding

No compound has yet been found which displays this type of bonding. There seems to be no theoretical reason why this "face-on" or "sandwich" type of bonding should not occur; it would involve overlap of metal *d* orbitals with π orbitals of the nitrate group of suitable symmetry. This type of bonding was first postulated (*171*) for the cupric nitrate molecule in the vapor phase, it being considered that a bond capable of maintaining a heavy metal nitrate as a stable vapor must involve the maximum possible covalency, in which the whole NO_3 group might be expected to participate. This suggestion has since proved to be incorrect (see below).

Any consideration of the infrared spectrum to be expected from a terdentate nitrate is not profitable until it has been possible to examine a compound in which this type of bonding is known to occur. It will be clear from the above discussion that insufficient is known about covalent metal-nitrate bonding to permit forecasts of the circumstances under which any particular structure will occur. Progress in the immediate future therefore depends to a large extent on the discovery of compounds which can be proved to contain new types of bonding. This in turn places renewed emphasis on the need for continued effort in preparative inorganic chemistry.

F. Structure of Copper(II) Nitrate in the Vapor Phase

This compound will be discussed individually since it illustrates the problems involved and there were no obvious analogies (in contrast to basic beryllium nitrate) on the basis of which the structure could be deduced. The vapor was shown to be monomeric from its vapor pressure (*171*) and mass spectrum (*172*). Assuming that each nitrate ion is bonded to the copper ion in the same manner, there are three possible structures for the molecule involving unidentate, bidentate, and terdentate bonding of the nitrate group. It was first suggested that the thermal properties of cupric nitrate were best explained on the basis of a "sandwich" structure. From the vapor pressure-temperature relation (*171*), the thermodynamic functions for the vaporization process have been calculated, and are given for three temperatures in Table X.

TABLE X
Thermodynamic Functions for the Vaporization of Anhydrous Copper(II) Nitrate

T (°K)	ΔH (cal/mole)	ΔG (cal/mole)	ΔS (cal/mole/°)
453	15,600	6200	20.8
473	15,600	5730	20.9
493	15,600	5330	20.8

The heat of vaporization ΔH is surprisingly low; it is of the same order as values for the carbonyls of metals of the chromium group, and some cyclopentadienyl compounds (e.g., ferrocene). However, solid copper nitrate does not possess a molecular structure (Fig. 8), so that vaporization is a more complicated process than it is for the metal carbonyls. A study of the structure in the vapor state by electron diffraction was undertaken by

S. H. Bauer at Cornell University. Measurements were made on the vapor from a sample of copper nitrate at 180°; in a preliminary examination of the data (*173*) visually estimated intensities were used for the computation of a radial distribution curve, and this indicated an unsymmetrical structure in which the copper was bonded to one unidentate and one terdentate nitrate group. The electron diffraction data have now been fully analyzed, and this structure shown to be incorrect. Of the many models tested, the model with approximately V_d symmetry containing two bidentate nitrate groups is the one which correlates best with the experimental radial distribution curve (*174*). This structure is shown in Fig. 10. The copper atom has the four nearest oxygen atoms at 2.00 Å; the O—Cu—O angle is 70°, and the Cu—N distance is 2.30 Å. In the nitrate groups the average N—O distance is 1.30 ± 0.04 Å, and the ONO angle is 120°.

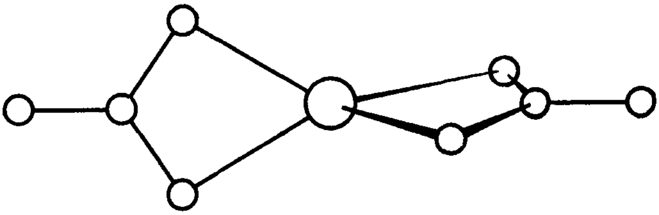


FIG. 10. Structure of copper(II) nitrate in the vapor phase.

VI. Influence of Covalency on the Properties of Metal Nitrates

If the study of covalent bonding was of interest from the structural aspect only, it would have limited significance. However, the degree of covalency determines the chemical reactivity as well as the physical properties. In general, the stronger the covalent bond the more reactive does the compound become. The more important properties introduced by covalency will be outlined here, and further examples will be found in the systematic treatment given later.

A. VOLATILITY

Ability to exist in the gas phase is generally indicative of covalency in nitrates. Covalent nitrates are not usually stable in the liquid state, but can often be sublimed; it is this ability to pass directly from the solid state to the stable vapor which can be attributed to covalency. It should be remembered, however, that the alkali metal nitrates can be distilled. The sublimation of cupric nitrate and basic beryllium nitrate has already been referred to. The anhydrous nitrates of zinc (*30*), mercury (*70*), zirconium (*32*), and hafnium (*30*) also sublime as do some addition compounds, such as $Fe(NO_3)_3 \cdot N_2O_4$ (*49*) and $Al(NO_3)_3 \cdot 2CH_3CN$ (*175*). The term "volatile metal nitrate" has been applied by the present authors to those nitrates which sublime readily at pressures of 10^{-1}–10^{-2} cm Hg and at low temperatures (100–200°). It now seems likely that the covalent nitrates of other metals (e.g., nickel and manganese) classified as nonvolatile may in fact show some slight tendency to sublime on heating under sufficiently high vacuum. On the other hand, heavy metal nitrates [e.g., $Cd(NO_3)_2$] which show an infrared spectrum typical of an ionic structure, and which do not give stable melts, are not likely to sublime whatever the experimental conditions.

The only vapor pressure measurements which have been carried out are those on cupric nitrate (Table XI). The stability of the vapor is greater than that of the solid; in the absence of other gases there is no evidence for the decomposition of the vapor below 226°, whereas decomposition of the solid is measurable even below 190° (*171*).

TABLE XI

VAPOR PRESSURE OF ANHYDROUS COPPER NITRATE

Temperature: (°C)	157.0	172.8	186.4	189.5	202.0	215.2	222.6
Vapor pressure: (mm Hg)	0.32	0.59	0.99	1.15	1.87	2.84	3.59

B. SOLUBILITY IN ORGANIC SOLVENTS

Covalent bonding enhances solubility in polar organic solvents. This is to be expected, since covalent nitrates usually dissolve as monomers in which there is the minimum of residual electrical field. The actual solubility values also depend upon the readiness with which the metal is solvated. The solubilities of two covalent nitrates [$Cu(NO_3)_2$ and $Zn(NO_3)_2$] are compared with those for the ionic silver nitrate in Table XII (*176*).

TABLE XII

SOLUBILITY OF ANHYDROUS NITRATES

	Solubility[a] (gm/100 gm solvent)		
Solvent	$Cu(NO_3)_2$	$Zn(NO_3)_2$	$AgNO_3$
Water	150 (25°)	128 (25°)	228
Ethyl acetate	151 (25°)	>136	2.7
Nitromethane	5.1	0.45	(negligible)
Methyl cyanide	33.7	71	112

[a] At 20° except where otherwise stated.

The high solubility of all three compounds in methyl cyanide is primarily the result of the high complexing power of methyl cyanide towards each of the metal atoms; each compound crystallizes from solution as an addition compound with methyl cyanide. The complexing power of nitromethane is very weak; all three solubilities are considerably reduced, but the influence of covalent bonding can now be seen. The most striking feature is the very high solubility of copper and zinc nitrates in ethyl acetate, compared with the value for silver nitrate. This is not due entirely to differences in nitrate bonding, however, since cadmium nitrate, which is ionic, is very soluble in ethyl acetate. It is relevant that copper and zinc form many stable complexes in which oxygen is the donor atom, whereas silver coordinates more readily with the nitrogen atom. It is also interesting to note that anhydrous copper nitrate is much more soluble in ethyl acetate than in water; 1 mole dissolves in 7.0 moles of water, but in only 1.41 moles of ethyl acetate. The heats of solution of the anhydrous salt in a large excess of water or ethyl acetate are 17.2 ± 0.1 and 15.9 ± 0.3 kcal/mole, respectively (*247*).

No simple anhydrous nitrate has been found which is soluble without decomposition in nonpolar solvents such as the aromatic or aliphatic hydrocarbons.

C. Decomposition in Water

When anhydrous metal nitrates are added to water, dissociation usually takes place to give the hydrated metal cation and nitrate anions. Beryllium nitrate, in which there is strong covalent bonding, behaves differently (*48*). When added to water, brown fumes are evolved; when hydrolyzed in sodium hydroxide solution, both nitrate and nitrite ions are produced. The amount of nitrite produced is about 5% of the nitrate added, and is largely independent of the concentration of the sodium hydroxide solution, within the range 0.05–2 *N*. The anhydrous (ionic) nitrates of barium, strontium, calcium, and magnesium dissolve in water to give metal and nitrate ions only, and the unusual behavior of beryllium nitrate is attributed to the strength of the metal-oxygen bond. Thus with the alkyl nitrates the dissociation into radicals is known to be an important step in their pyrolysis (*177*):

$$R - O - NO_2 \rightarrow R - O^{\cdot} + NO_2^{\cdot}.$$

This dissociation may also occur in a nitrate group covalently bonded to a metal:

$$M\overset{a}{—}O\overset{b}{—}NO_2 \rightarrow M - O^{\cdot} + NO_2^{\cdot}.$$

The dissociation occurs at bond *a* or bond *b*, or at both bonds, depending on their relative strengths. The size and polarizing power of the beryllium atom is presumably sufficient to raise the bond strength of *a* to the same order as that of *b*. In addition to the usual form of ionization, the dissociation

$$Be(NO_3)_2 \rightarrow (NO_3)Be - O^{\cdot} + NO_2^{\cdot}$$

is therefore considered also to occur to a small extent. The $NO_2^{\cdot}$ radicals are responsible for the brown fumes on addition to water in an open vessel; when beryllium nitrate is hydrolyzed in a closed vessel in sodium hydroxide solutions, hydrolysis will occur to give equal quantities of nitrate and nitrite, so that about 10% of the original nitrate dissociates in this way.

It is of interest to compare the behavior of basic beryllium nitrate. In this compound each nitrate group is part of a 6-membered ring (Fig. 9). The $NO_2^{\cdot}$ radical can no longer break away as in the simple nitrate, since two oxygen atoms are now bonded to beryllium atoms. This compound hydrolyzes slowly in alkaline solution to give nitrate ions only.

In nonaqueous media, such as ethyl acetate, anhydrous beryllium nitrate dissolves and gives a pale yellow color to the solution; the absorption spectrum shows that the color is due to nitrogen dioxide (*48*). It is likely that as further nitrates are prepared, other examples of such behavior will be found. Certain ruthenium nitrates are also believed to give nitrite on hydrolysis (*178*).

D. Reaction with Aliphatic Compounds

Ionic metal nitrates do not react with organic solvents at room temperature, but the behavior of certain covalent metal nitrates is in sharp contrast to this. The reaction of anhydrous copper nitrate with ethers has been examined in some detail (*179*, *184*). If a small amount of diethyl ether is added to an excess of copper nitrate, reaction is vigorous and nitrogen dioxide and acetaldehyde are evolved. On one occasion, ether was slowly evaporated from a solution of copper nitrate in ether at 50°. When the solution became viscous, brown fumes were suddenly evolved and this was followed by a violent explosion. The reaction occurs only under conditions in which the strong covalent bonds between copper and the nitrate groups are maintained. Whether or not the copper nitrate-ether reaction occurs can therefore be determined by the solvent in which the reaction is carried out. Thus when ether vapor is passed into a solution of copper nitrate in nitrobenzene (in which the copper nitrate is present as a monomer), a reaction occurs, since coordination or solvation of the copper atom by nitrobenzene is insufficient to weaken the $Cu—NO_3$ bond. When ethyl acetate or methyl cyanide is used as solvent, no reaction occurs, even though copper nitrate is still a monomer in these solvents. These solvents presumably solvate the copper atom more strongly, and in consequence weaken the Cu—NO_3 bond to such a degree that reaction with ether is no longer possible.

Since reaction is a function of covalency, it is suggested that it involves the type of dissociation already proposed for beryllium nitrate. The position is summarized as follows:

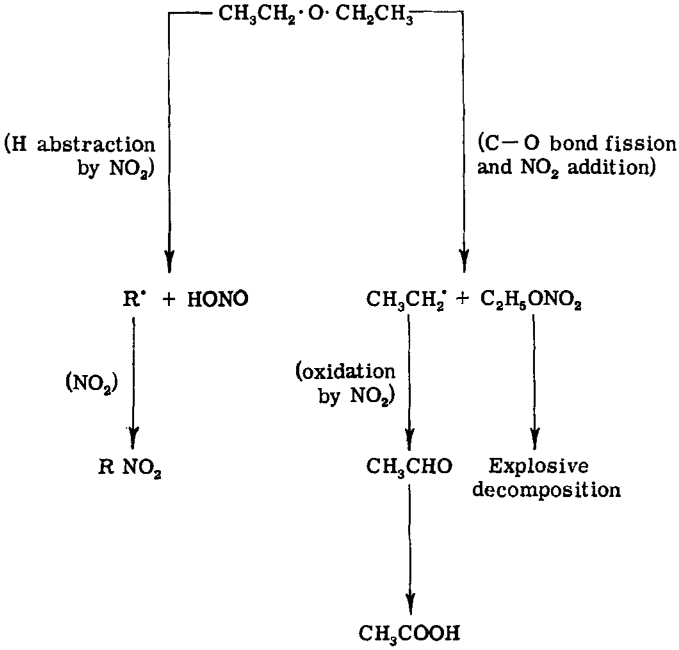
$$(NO_3)Cu—O—NO_2 \rightarrow (NO_3)Cu^+ + NO_3^-$$

(in basic solvents; no reaction with ether)

$$(NO_3)Cu—O—NO_2 \rightarrow (NO_3)CuO^{\cdot} + NO_2^{\cdot}$$

(the nitrate alone in contact with ether, or in solution in weakly basic solvents; ether attacked by $NO_2^{\cdot}$).

The anhydrous nitrate is therefore regarded as a low temperature source of NO_2 radicals, which is consistent with the observation that the greater the nitrate:ether ratio, the more vigorous does the reaction become. The reaction between NO_2 and the ether is complex, but will include reactions of the type set out in the following scheme:



A green solid product remains, which has a remarkably consistent analysis corresponding to $Cu_2(OH)(CH_3COO)(NO_3)(NO_2)$, and nuclear magnetic resonance confirms that all carbon present is in the form of the acetate ion. The ions NO_3^- and OH^- may well result from the $NO_3{\cdot}Cu{\cdot}O^{\cdot}$ radical originally produced; nitrite is formed in the course of hydrogen abstraction, and acetate as a result of oxidation.

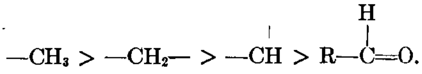
It follows from the above that diethyl ether is attacked at the C—O rather than the C—C bonds. Examination of a series of ethers, and other compounds containing the C—O bond, has shown that copper nitrate is a highly specific reagent. The results are summarized in Table XIII. There is a sharp contrast in the behavior of dimethyl and diethyl ethers. Dimethyl ether was condensed onto copper nitrate at −70°; on warming to −20°, ether evaporated to leave a pale blue solid which melted at −12° and was stable up to 50°.

TABLE XIII

BEHAVIOR OF COPPER NITRATE TOWARDS ORGANIC SOLVENTS

Compound	Behavior
Dimethyl ether	Addition compound $Cu(NO_3)_2 \cdot 1.5Me_2O$; very slow reaction with excess nitrate
Diethyl ether	Reaction under all conditions; explosive with excess nitrate
Di-*n*-propyl ether	Nitrate dissolves and reacts
Di-isopropyl ether	No solution or reaction
Di-*n*-butyl ether	Nitrate dissolves and reacts
Ethyl acetate	Solution but no reaction
Tetrahydrofuran	Reaction, with flashes of light, on contact; fairly stable solution
Dioxan	Solution but no reaction

Ether is evolved from the molecular compound $Cu(NO_3)_2 \cdot 1.5Me_2O$, on addition of water. The difference in reactivity might have been explained if dimethyl ether acted as a strong ligand to copper, thus preventing reaction by weakening the $Cu—NO_3$ bond, but there is no evidence that its coordinating powers differ so greatly from those of diethyl ether. However, if we interpret the reactions as involving attack by NO_2 on the ether, then there is an analogy with the high temperature nitration of paraffins and ether by nitrogen dioxide. With the paraffins, the lowest members are the least reactive of the series (*180, 181*), and the higher aliphatic ethers give higher yields of nitro compounds (*182*). There is also a striking difference in the behavior of copper nitrate with *n*-propyl and isopropyl ether, so that the hydrogen atoms in α position to the oxygen atom play an important role in the reaction. This is also in accord with the known hydrogen abstraction reactions of the NO_2 free radical. The ease with which hydrogen is abstracted from an organic molecule depends on the strength of the C—H bonds; for paraffins and aldehydes this is represented by the series



$$-CH_3 > -CH_2- > -\overset{|}{C}H > R-\overset{\overset{H}{|}}{C}=O.$$

From this mechanism it is understandable that the groups RCH_2—O— and R_2CH—O— should differ in reactivity.

The reaction of copper nitrate with nitromethane is perhaps the most surprising chemical property so far observed for a covalent metal nitrate, especially as nitromethane serves as a very satisfactory inert medium for reactions of dinitrogen tetroxide. Solutions of copper nitrate are stable indefinitely at room temperature, but reaction occurs if the solution is kept at the boiling point (101°) for some time (*176*). There is a delay period which is characteristic of free radical reactions, followed by sudden reaction. On boiling 0.135 *M* solution for 2 minutes, the solution suddenly evolves nitrogen dioxide copiously, and a green complex copper salt is deposited. More dilute solutions behave similarly, but longer delay times are involved. Copper nitrate dissolves readily as a monomer in nitromethane, but since the latter is a very weak ligand it will not decrease the strength of the Cu—NO_3 bond. Conditions are therefore ideal for the dissociation of the nitrate to the nitrogen dioxide radical. Its reaction with nitromethane at 100° is nevertheless surprising, and it is possible that nitromethane reacts in the enol form, CH_2=NO(OH).

Although a mechanism based on dissociation to give NO_2 radicals can therefore correlate these unusual properties of covalent nitrates, an alternative mechanism in which the molecule decomposes to give nitrogen trioxide is a possibility in cases where the metal concerned has an available lower valency. For example, with copper nitrate the dissociation

$$Cu(NO_3)_2 \rightarrow CuNO_3 + NO_3$$

would be involved. It has been shown (*183*) that nitrogen trioxide is the active species in certain gas phase reactions of nitrogen dioxide, but not enough is yet known of the properties of nitrogen trioxide to determine whether this mechanism is feasible.

Reaction mechanisms involving the release of NO_3 or NO_2 free radicals have been postulated also for the reaction of titanium tetranitrate with *n*-dodecane (*26*). With these reactants in 1:2 mole ratio, reaction at 20° for 30 minutes gave about 10% of an alkyl nitrate. Reaction for 16 hours in 1:1 mole ratio gave a carboxylic acid together with alkyl nitrate and a nitroalkane; no alkyl nitrite was found. The products resemble those obtained by Titov and Shchitov (*185*) from the reaction of paraffins with dinitrogen pentoxide, where the NO_3 radical is again considered to be the active species.

The reaction of metal nitrates with aliphatic hydrocarbons is influenced by the structure of the hydrocarbon. In the work of Topchiev (*186*) and Konovalov (*187*) (in which hydrated nitrates were used) branched-chain hydrocarbons were usually found to react rather more readily than the straight-chain hydrocarbons. This contrasts with the behavior of ethers discussed above (Table XIII).

E. Aromatic Nitration by Metal Nitrates

Aromatic hydrocarbons do not undergo nitration by ionic metal nitrates (*186*), since the free nitrate ion does not readily give rise to NO_2 or NO_3 radicals. Nitration is possible, however, by using covalent metal nitrates. In 1925 Menke (*188*) observed that iron, copper, nickel, cobalt, aluminium, cerium, and uranyl nitrates could function as strong nitrating agents towards aniline and phenol, whereas the nitrates of the alkali or alkaline earth metals either failed to react or were poor nitrating agents. Bacharach (*189*) confirmed this, and showed that lithium nitrate was more reactive than the nitrates of the other alkali metals. In these reactions the metal nitrates (hydrated when the anhydrous salt was not known) were dissolved in acetic anhydride, anhydrous acetic acid, or mixtures of the two liquids, and it was assumed that acetyl nitrate, or acetylorthonitric acid $(CH_3COO)_2N(OH)_3$, was the species responsible for nitration. The reactions gave rise to *o*-nitration, as does acetyl nitrate. This interpretation of the reactions is incomplete in that it does not explain the profound influence exerted by the metal concerned on both reaction rates and yields. It should be noted that the solution of a metal nitrate hydrate in acetic anhydride will tend to produce the anhydrous metal nitrate in solution. In view of the reactivity of copper nitrate discussed above, it seems possible that the anhydrous nitrates themselves (or derivatives containing at least one metal-nitrate bond, such as a covalent metal nitrate-acetate) may play an important part in the mechanism. There are at least two pieces of evidence in support of this. Firstly, anhydrous uranyl nitrate reacts rapidly with toluene to give a red solution from which nitrotoluenes can be sepa-

TABLE XIV

Nitration of Benzylidene Diacetate by Metal Nitrates in Acetic Acid

Nitrate used	Type of bond in anhydrous nitrate	% Yield of *p*-nitrobenzylidene diacetate
$Cu(NO_3)_2$ hydrate	strongly covalent	79
$Zn(NO_3)_2$ hydrate	covalent	23
$Fe(NO_3)_3$ hydrate	covalent	19
$Bi(NO_3)_3$ hydrate	covalent	19
$Ni(NO_3)_2$ hydrate	covalent	12
$Mg(NO_3)_2$ hydrate	ionic	8
$Co(NO_3)_2$ hydrate	ionic and covalent	4
$Ca(NO_3)_2$	ionic	0
$Pb(NO_3)_2$	ionic	0

rated (*83*); zirconium tetranitrate behaves similarly (*32*). Secondly, Davey and Gwilt (*190*) compared the efficiency of a series of metal nitrates in the nitration of benzylidene diacetate; 21 gm of this compound was dissolved in 100 ml acetic acid, the metal nitrate (25–50 gm) added, and the mixture refluxed for several hours. The yields of the *p*-nitro derivative obtained are given in Table XIV.

There is a direct correlation between the covalency of the metal nitrates and the efficiency of their solutions as nitrating agents; the efficiency of copper nitrate far exceeds that of the other nitrates tested, and further study of the species present in these solutions would seem to be desirable.

VII. Decomposition of Metal Nitrates

Apart from the decomposition of the nitrate group which inevitably occurs when metal nitrates act as oxidizing agents in mixtures with metals (e.g., aluminum) or nonmetals (e.g., carbon, sulfur), the main types of decomposition can be discussed under three headings: (1) decomposition by water or organic solvents; (2) decomposition by irradiation; (3) thermal decomposition. The first type of decomposition has already been discussed in Section VI; the general principles governing the second and third types will be considered at this stage.

A. DECOMPOSITION ON IRRADIATION

Irradiation experiments have been concerned almost entirely with ionic nitrates. These salts, usually in the solid state, have been irradiated by fast electrons (*191*, *192*), γ-rays (*191*, *193*), X-rays (*194*), or ultraviolet light (*191*, *195*). A Co^{60} source has usually been used as the source of γ-radiation, and ultraviolet radiation is provided by a high pressure mercury arc. Maddock and Mohanty (*191*) carried out electron irradiations using 2-Mev electrons accelerated by a Van der Graaff machine, and the samples were so distributed that their thickness in the direction of the beam was less than half the range of the electrons in the compound concerned.

Although the mode of decomposition is similar in each case, there still appears to be a little doubt as to whether the primary radiolytic fragments produced on breakdown of the NO_3^- group by irradiation are NO_2^- and O, or NO_2 and O^-. The production of nitrite ion is generally favored:

$$MNO_3 \rightarrow MNO_2 + O$$

and is supported by the infrared spectra (*194*), ultraviolet spectra (*196*), and X-ray diffraction data (*194*) for irradiated nitrate crystals. Magnetic susceptibility measurements on extensively radiolyzed potassium nitrate crystals indicate the presence of molecular oxygen in the crystals, together with nitrite ions (*197*). In this connection it is important to distinguish between the anhydrous and hydrated salts. When an aqueous solution of a metal nitrate is irradiated, it is generally accepted (*198*) that the first stage of the reduction of nitrate to nitrite involves the H atoms formed during the radiolysis of water:

$$H + NO_3^- \rightarrow NO_2 + OH^-$$

and that the formation of NO_2^- from NO_2 is a second stage in the process.

The paramagnetic absorption spectrum of crystals of lanthanum magnesium nitrate hydrate incorporating americium showed three kinds of magnetic centers, all of which could be attributed to NO_2 molecules (*199*). Measurements of the absorption spectrum of an extensively irradiated sample of lead nitrate failed to show any such absorptions (*191*), so that the radiolytic behavior of nitrate hydrates may well be quite different from that of the anhydrous nitrates. On solution in water, and in some cases fusion, irradiated anhydrous nitrates release gaseous oxygen, and nitrite can be determined spectrophotometrically in the solutions. The yields of NO_2^- and O_2, as determined by analysis of an irradiated sample of sodium nitrate, were found to be precisely in the ratio $NO_2^-:O_2 = 2:1$ (*193*).

The photochemical decomposition of a number of solid nitrates under the influence of light from a mercury arc (*195*) produces nitrite and oxygen. The approximate quantum yields vary from 0.002 for lithium nitrate to 0.19 for caesium nitrate, in the order $LiNO_3$, $Sr(NO_3)_2$, NH_4NO_3, $AgNO_3$, $Pb(NO_3)_2$, $La(NO_3)_3$, $Ba(NO_3)_2$, KNO_3, $La(NO_3)_3 \cdot 6H_2O$, and $CsNO_3$. Water of hydration increases the sensitivity to radiation, and the rate of decomposition of the anhydrous nitrates varies in roughly the same manner as the polarizing power of the cations. Decomposition of barium nitrate by fast electrons also yields nitrite and oxygen (*192*).

The mechanism for the radiation-induced decomposition of the nitrates is a complex one. Following initial rupture into NO_2^- and O fragments, the reactions

$$NO_3^- + O \rightarrow NO_2^- + O_2$$

and

$$NO_2^- + O \rightarrow NO_3^-$$

take place. Experimental results for sodium, potassium, caesium, barium, and lead nitrates are compatible with this scheme. Silver nitrate does not follow the same kinetics; the rate of production of nitrite falls off rapidly as dose is increased, and some silver oxide is found in the products (*200*). It is relevant that the G value (compare Table XV) for nitrite production in the radiolysis of aqueous silver nitrate solutions is negligible, the main product being metallic silver (*198, 201*). With the other nitrates (excluding silver) the complexity arises partly from the fact that lattice changes occur during irradiation, which affect the relative importance of these reactions. Using 240-curie Co^{60} as a source of γ-radiation, Johnson and Forten *(193)* have produced some interesting correlations in support of this. The variations in density, heat of solution, and nitrite yield for various nitrates were studied as irradiation proceeded. The change in nitrite yield coincided with changes in heat of solution and density, and the parameter which accounts best for the variations is the closeness of packing of the crystal structure. With potassium nitrate, for example, there is an abrupt decrease in the density at a dose of about 34×10^{20} ev/gm, and this coincides with a sharp break in the nitrite-yield curve. The results in Table XV compare the sensitivity of different metal nitrates to γ-radiation.

TABLE XV

DECOMPOSITION OF SOME METAL NITRATES UNDER γ-RADIATION

Compound	*G* value (molecules decomposed per 100 ev absorbed)			
$NaNO_3$	0.16 *(193)*	0.25 *(202)*	0.37 *(194)*	0.2 *(203)*
KNO_3	1.38 *(204)*	1.38 *(193)*	1.46 *(203)*	
$CsNO_3$	1.44 *(193)*	1.68 *(202)*	1.37 *(194)*	1.72 *(203)*
$Pb(NO_3)_2$	0.48 *(193)*	0.44 *(202)*	0.43 *(204)*	

The *G* values quoted in Table XV represent the initial decomposition rates before the change in density occurs. The values decrease as irradiation proceeds; with potassium nitrate, the value of *G* falls abruptly from 1.38 to 0.93 after the change in density has occurred. Of the nitrates tested, sodium nitrate has the smallest "free space" (i.e., the most closely packed structure) and the low *G* value is in accord with the view that the initial *G* values are proportional to the free space. The extent of decomposition has also been calculated. For potassium nitrate, a dose of 120×10^{20} ev/gm gives 3 mole % decomposition; corresponding values for caesium nitrate are 1.6 mole % (99×10^{20} ev/gm) and for lead nitrate 0.73 mole % (27×10^{20} ev/gm).

The fragments generated by irradiation of metal nitrates can recombine under the influence of heat, and this "annealing" process gives valuable information on the decomposition mechanism. Gamma irradiation of lead nitrate crystals *(191)* produces a yellow-brown coloration which fades on heating the crystals, the rate of fading increasing with temperature in the range 100–200°. The data may be interpreted in terms of a unimolecular recombination affecting only a proportion of the fragments, and a bimolecular process, with a higher energy of activation, governing the behavior of the remainder. On radiolysis, decomposition takes place at normal lattice sites and is not primarily associated with the original lattice defects

(194). The first annealing process is explained *(191)* by recombination of the primary fragments, i.e.,

$$NO_2^- + O \rightarrow NO_3^-;$$

it involves only those fragments which have separated a very short distance in the lattice, and thus have a small energy barrier to recombination. The second recombination process involves the remainder of the fragments. The oxygen atoms penetrate into the lattice, where they combine to produce molecular oxygen. This oxygen remains dissolved (except under extensive radiolysis, when gas bubbles may appear) and the second-order annealing reaction may be represented by the equation:

$$O_2 + NO_2^- \rightarrow NO_3^- + O$$

followed by the rapid reaction

$$NO_2^- + O \rightarrow NO_3^-.$$

Since the covalent metal nitrates are more readily decomposed than the ionic nitrates, study of their radiolysis has fascinating possibilities.

B. THERMAL DECOMPOSITION

Present knowledge of the mechanism of thermal decomposition of metal nitrates is very limited indeed. It is known, however, that a distinction can be drawn between the decomposition of the hydrates and that of the anhydrous compounds. Some hydrates [e.g., $Ca(NO_3)_2{\cdot}4H_2O$] first lose water of crystallization, followed by decomposition of the anhydrous nitrate, but with many hydrated nitrates of heavy metals the water present plays a major part in the decomposition. Both water molecules and nitrate groups are in the coordination sphere of the metal atom and react with one another to produce nitric acid as the main decomposition product; these reactions are not relevant to the present review. With the anhydrous compounds, we are concerned with the readiness with which the NO_3 group disintegrates and the various ways in which this can occur, but the scope of the work has been limited severely in the past by the very few such compounds available. Even so, investigations have concentrated almost exclusively on the solid phases involved. For example, in the well-known decomposition

$$2Pb(NO_3)_2 \rightarrow 2PbO + 4NO_2 + O_2$$

one might ask whether the ratio of nitrogen dioxide and oxygen evolved is constant throughout the decomposition. Are these gases primary products, or is some nitric oxide first produced and subsequently oxidized to nitrogen dioxide? Answers to these questions, together with thermogravimetric analysis, would give a useful indication of the decomposition mechanism, but the problem has been approached only recently from the point of view of the gas phase (*254*).

The more important factors influencing thermal stability include the following:

(1) The physical state of the nitrate (i.e., solid, liquid, or gas).
(2) The polarizing power of the cation.
(3) The type of metal-nitrate bond.
(4) The valency of the metal.
(5) The availability of higher valency states of the metal.
(6) The stability of intermediate decomposition products.
(7) Lattice energy.

In most instances several of these factors are operating together, and it is seldom that one factor can be isolated. The decomposition of the alkali metal nitrates is simplest to interpret. Each compound is ionic; each gives the metal nitrite as a first step in the decomposition (though lithium nitrite is by far the least stable), so that the polarizing power of the cation is the major variable. The alkali metal nitrate decomposition temperatures in Table XVI are those at which the decomposition vapor pressure of oxygen reaches 1 atmosphere, and polarizing power is defined as the ionic charge e divided by the square of the ionic radius r, following Goldschmidt (*205*). The stronger the polarizing power, the more is the electron distribution in the free nitrate ion distorted, and the lower is the thermal decomposition temperature. There is an obvious correlation between the two properties. With the nitrates of Group II, other factors must be considered also. The

TABLE XVI
CATION POLARIZING POWER AND DECOMPOSITION TEMPERATURES FOR THE ANHYDROUS NITRATES OF METALS OF GROUPS I AND II

Metal	e/r^2	Decomposition temperature of nitrate (°C)
Li	2.2	474
Na	1.0	529
K	0.57	533
Rb	0.46	549
Cs	0.36	584
Be	17	125 (*48*)
Mg	3.3	450 (*48*)
Ca	1.8	575 (*128*)
Sr	1.2	635 (*128*)
Ba	1.0	675 (*128*)

polarizing powers of Ba^{2+}, Sr^{2+}, and Ca^{2+} are comparable with those of Li^+ and Na^+; these nitrates are ionic and give nitrite as the first decomposition stage, and high decomposition temperatures are again observed. The increased polarizing power of Mg^{2+} is reflected in the lower decomposition temperature; on rapid heating, anhydrous magnesium nitrate can be induced to melt, but it then decomposes immediately. It is in the case of anhydrous beryllium nitrate that the most marked decrease occurs (Table XVI). The very high polarizing power of Be^{2+} should in itself lower the decomposition temperature; added to this, however, is the covalent nature of the metal-nitrate bond (as shown by its infrared spectrum) and the high thermal stability of the first decomposition product $Be_4O(NO_3)_6$, which has been described earlier.

The decomposition temperatures given in Table XVI for barium, strontium, and calcium nitrates are those at which decomposition becomes visible; where melts are concerned, the onset of decomposition can usually be recognized to within about 20°, and the temperatures quoted are sufficiently accurate to illustrate the arguments outlined above. Where detailed comparisons of thermal behavior are required, it is necessary to define experimental conditions more precisely. This results from the fact that it is usually difficult to select the exact temperature at which thermal decomposition first begins, and this is particularly the case where solid nitrates are concerned. In a typical experiment, a stream of dry oxygen was passed over anhydrous zinc nitrate controlled at various temperatures, and oxides of nitrogen produced by decomposition were carried over with the gas stream into a trap containing sodium hydroxide, which was titrated at intervals (*68*). The following results were obtained:

Temperature (°C):	100	150	240	285	310
Decomposed per minute (%):	*0*	*(just detectable)*	*0.033*	*0.33*	*0.66*

The decomposition rate approaches zero asymptotically as temperature decreases. Baekeland (*206*) studied the same effect with lead nitrate. The reaction

$$Pb(NO_3)_2 = PbO + 2NO_2 + \tfrac{1}{2}O_2$$

is reversible, and a sample of lead nitrate heated at various temperatures in an evacuated vessel gave the following equilibrium dissociation pressures (p):

Temperature (°C):	223	230	250	274	297	357	448
p (mm Hg):	6.2	6.9	11.8	32.6	78.4	514	1180

This behavior is typical of the decomposition of all solid nitrates, and it is obvious that the term "decomposition temperature" has no significance unless the experimental conditions under which it was determined are defined. Decomposition temperatures are usually determined by thermogravimetric analysis, in which the solid is heated at a constant rate of about 0.5–3° per minute; the decomposition temperature is then defined as that temperature at which change in weight is first detected.

Using this technique, Wendlandt (*1*) determined decomposition temperatures for the anhydrous nitrates of lanthanum, praseodymium, and neodymium (Table XVII). These nitrates give intermediate decomposition products of composition $MONO_3$, and their decomposition temperatures are also recorded. The hydrated nitrate of each of the lanthanide elements has been studied by thermogravimetric analysis (*6*, *207*), but the lanthanum, praseodymium, and neodymium compounds were the only cases in which a plateau corresponding to the anhydrous trinitrate was obtained (*1*). These nitrates are essentially ionic; the infrared spectrum of praseodymium trinitrate indicates the presence of symmetrical D_{3h} nitrate ions (*208*). The infrared spectra of solid decomposition products suggest that the decomposition proceeds via an intermediate nitrite structure (*208*). This is not necessarily in conflict with thermogravimetric analysis (which indicated the intermediate $PrONO_3$) since praseodymium nitrite may have only transitory existence, in which case it would not be recognized on the thermobalance. This is another instance in which a study of the gaseous products also would be desirable. Table XVII shows that the thermal stability of lanthanum, praseodymium, and neodymium nitrates is quite high, as would be expected from their ionic character. The polarizing power (e/r^2) of the M^{3+} cations is 2.27 (i.e., between lithium and magnesium) and the decomposition temperatures also lie between those for lithium and magnesium nitrates. However, a direct comparison of this nature is not fully justifiable since the lanthanide nitrates decompose in the solid state.

TABLE XVII
DECOMPOSITION TEMPERATURES (°C) FOR ANHYDROUS NITRATES OF SOME LANTHANIDE ELEMENTS

Metal (M)	T for $M(NO_3)_3$	T for $MONO_3$	Final product
Lanthanum	420	575	La_2O_3
Cerium	—	—	CeO_2
Praseodymium	375	480	Pr_6O_{11}
Neodymium	380	475	Nd_2O_3

The fact that anhydrous cerium(III) nitrate is not obtained on heating the hexahydrate has special interest. The thermogravimetric curve shows a steady loss in weight, with no plateau corresponding to either $Ce(NO_3)_3$

or $CeONO_3$. Since cerium falls in the series La, Ce, Pr, Nd, it might have been expected to show a behavior resembling that of its congeners. The difference is attributed to the higher valency, Ce(IV), which is available in cerium, and to which Ce(III) can readily be oxidized on breakdown of the nitrate group; the final decomposition product is the oxide CeO_2 (*1*, *209*).

As examples of covalent nitrates we may refer to the anhydrous compounds of general formula $M(NO_3)_2$ which are now known for manganese (*75*), cobalt (*103*), nickel (*77*), copper (*171*), and zinc (*58*, *68*). The decomposition temperatures of these nitrates do not differ greatly from one another, and it is therefore necessary to define precisely the stage of decomposition at which comparison is to be made. Each compound was therefore heated in a thermobalance, in an atmosphere of dry nitrogen at a heating rate of 0.7° per minute, and an accurate weight-temperature curve obtained. The variation in the decomposition rate with temperature was then derived from the slope of the curve, and the results are given in Fig. 11.

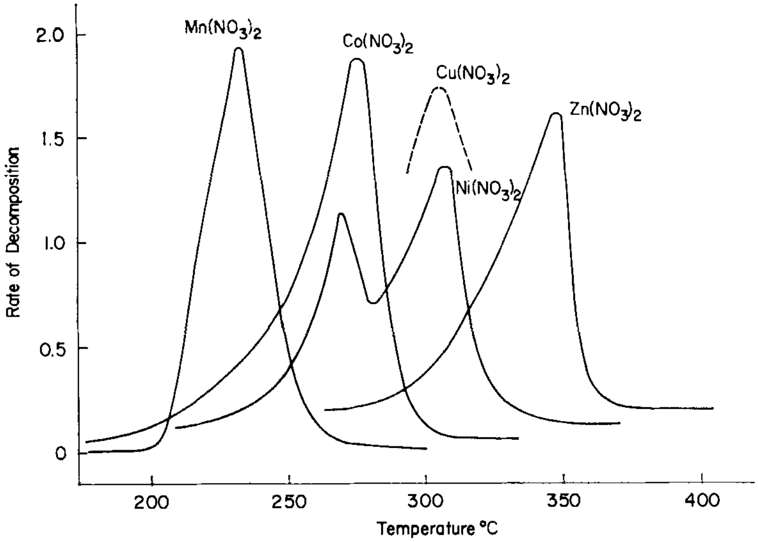


FIG. 11. Rates of thermal decomposition of some transition metal nitrates. (Rates of decomposition are expressed in molecular weight units lost per minute, assuming each experiment began with 1 gram mole of metal nitrate; for clarity, the values for cobalt, nickel, and zinc nitrates are raised progressively by 0.07 unit on the rate axis.)

Inspection of any particular curve shows that there is the usual difficulty in deciding, with any accuracy, the temperature at which decomposition commences, but the temperature corresponding to maximum rate of decomposition is clearly defined and forms an excellent basis on which to compare the thermal properties of the compounds. Nickel nitrite has an unusually high thermal stability for a transition metal nitrite (*78*), and the formation of nickel nitrite on thermal decomposition of the nitrate is shown by the double peak for this compound in Fig. 11. The curve for copper nitrate could not be determined by thermogravimetric analysis since the compound sublimes. The broken curve in Fig. 11 was determined by differential thermal analysis (*194*) and is placed at an arbitrary position on the rate axis. There is satisfactory agreement between the two techniques; the maximum decomposition rate for cobalt(II) nitrate was found to occur at 270° by each method (*70, 76*).

We have already mentioned that the temperature at which decomposition occurs can be defined much more sharply for a molten nitrate than for a solid nitrate. This is presumably because in a melt the ions are kinetically more free, so that their response to increase in temperature is more nearly the same. In a solid, the lattice environment may not be the same for all ions; ions in different environments are subject to different lattice forces and will decompose at different temperatures. The influence of physical state should be even more marked when a metal nitrate is decomposed in the vapor and in the solid state, and this is illustrated clearly by the behavior of copper nitrate. In the absence of other gases there is no evidence for decomposition of the vapor below 226°. At this temperature decomposition occurs suddenly; all the vapor decomposes within a temperature range of a few degrees, and the walls of the containing vessel are covered by a dark-colored deposit. In contrast, decomposition of the solid occurs at a maximum rate at 305° (Fig. 11), is measurable at 190° (*171*), and is detectable at temperatures as low as 100°.

Infrared and ultraviolet spectra show that in each of the compounds referred to in Fig. 11 the nitrate groups are covalently bonded to a greater or lesser extent. It is consistent with this that thermal decomposition should occur over a lower temperature range than that for the ionic nitrates discussed earlier. In this connection the temperature of maximum decomposition rate for zinc nitrate, 350°, may be compared with the 420° found for cadmium nitrate (*210*), which is fully ionic (*211*). The 4-valent state of manganese is readily available, and for this reason it is understandable that manganese(II) nitrate, which decomposes according to the equation:

$$Mn(NO_3)_2 \rightarrow MnO_2 + 2NO_2$$

should have the lowest decomposition temperature. The oxide Co_3O_4 is obtained on decomposition of cobalt(II) nitrate (*76*), which also decomposes at a lower temperature than do the nitrates of nickel, copper, or zinc; the latter have no higher valency which is readily accessible under these conditions. However, in the present state of our knowledge it is somewhat surprising that such factors as variable valency and the pronounced differences in degree of covalency among these nitrates are not reflected more obviously in the decomposition temperatures; the peaks in the rate curves (Fig. 11) all lie within a fairly narrow temperature range (230–350°) and are arranged in the order of the atomic numbers of the metals.

The anhydrous nitrates of chromium(II) and iron(II) have not been isolated. The thermal stability of the simple Cr(III) nitrate, which is strongly covalent, is much lower than that of any other anhydrous nitrate studied; sudden decomposition occurs at 60°, and decomposition rate is maximum at 100° (*248*). In view of the high stability of the ionic nitrates of La(III), Pr(III), and Nd(III), it would seem that the ionic or covalent character of the bond has a pronounced influence on stability so far as the trivalent metals are concerned.

VIII. Systematic Survey of Anhydrous Metal Nitrates

In previous sections the various metal nitrates referred to have been those which most appropriately illustrated preparative methods or chemical properties. The purpose of this final section is to correlate the known anhydrous nitrates on the basis of the Periodic Table. The position is summarized in Fig. 12.

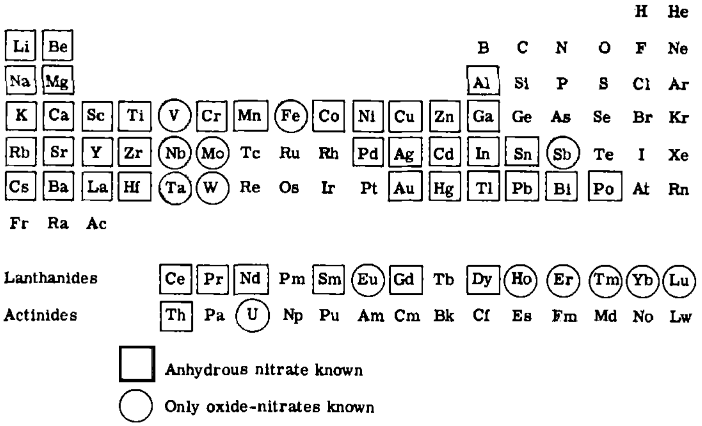


FIG. 12. The known anhydrous nitrates arranged on the basis of the Periodic Table.

A. MAIN GROUPS

Group I

All relevant aspects have been discussed in Sections II, III, IV, and VII.

Group II

Following the recent isolation of anhydrous beryllium nitrate, it is now possible to view the nitrates of this group as a whole, and a comparative account has been recently published (*48*). The preparation of the ionic nitrates of barium, strontium, calcium (Section II,B), and magnesium (Section II,F,H,I) has been discussed. Only beryllium nitrate is covalent; its preparation (Sections II,I and V,D), its decomposition to the basic nitrate (Section V,D), and its solution properties in water (Section VI,C) have already been treated in detail.

Group III

In view of the preparation of a compound $B(HSO_4)_3$ from boron tetrachloride and anhydrous sulfuric acid (*212*), the existence of boron trinitrate is an attractive possibility. However, reaction of boron trichloride with dinitrogen pentoxide (*27*), dinitrogen tetroxide (*50*), or absolute nitric acid (*17*) gave only boric oxide or addition compounds of boron trichloride. The formation of $B(NO_3)_3$ by the BCl_3—$ClNO_3$ reaction has been mentioned, but no confirmatory evidence is available. It decomposes even at −78° to give $BO(NO_3)$ (*37*). A similar reaction carried out at −7°, using aluminum bromide in liquid bromine as reaction medium, is said to give anhydrous aluminum trinitrate, which sublimes with some decomposition, when heated above room temperature in vacuum. Solvolysis of aluminum chloride in dinitrogen tetroxide does not give the simple nitrate. A product $Al(NO_3)_3{\cdot}0.38N_2O_4$ has been described (*60*); the simple nitrate cannot be isolated from this product, which may in fact be an oxide-nitrate. Using the same reaction, Addison *et al.* (*175*) isolated a product of composition $Al(NO_3)_3{\cdot}AlO(NO_3){\cdot}2N_2O_4$, which could not be converted to the simple nitrate. The preparation of the compounds $Ga(NO_3)_3$ (Section II,B) and $In(NO_3)_3$ (Section II,I) has already been mentioned.

In view of the similarity in the behavior of Tl^+ to Ag^+ and the alkali metal cations, the isolation of anhydrous thallium(I) nitrate from aqueous solution is not surprising. The salt melts at 206°, and decomposition sets in rapidly at 450°; according to Thomas (*213*), a little thallium(I) nitrate may be volatilized unchanged. Anhydrous thallium(III) nitrate is unknown, but an anhydrous double salt $Tl(NO_3)_3{\cdot}2TlNO_3$ has been described (*214*).

Group IV

The action of dinitrogen pentoxide (*27*), chlorine nitrate (*37*), or nitric acid (*17*) on silicon tetrachloride produces only silica. Silicon tetranitrate may well be the primary product in these reactions, but decomposes immediately. However, an addition compound of the tetranitrate with pyridine was obtained by first mixing solutions of silver nitrate in methyl cyanide and silicon tetrachloride in ether at −40°; on addition of pyridine to the supernatant liquor, a white precipitate of the compound $Si(NO_3)_4{\cdot}2C_5H_5N$ was obtained which evolved oxides of nitrogen at room temperature (*215*). Oxy-acid salts of germanium are rare, and no nitrate has yet been described; moderately concentrated nitric acid converts germanium to hydrated germanium dioxide. The reactions of germanium compounds with the nitrogen oxides and their derivatives do not appear to have been studied, and may well prove fruitful. The preparation of tin tetranitrate has been discussed (Section II,G). It can also be prepared by reaction of tin tetrachloride with dinitrogen pentoxide (*27*). Tin(II) nitrate has not yet been prepared; its instability is probably due to the ready oxidation of Sn(II) to Sn(IV), especially in the presence of nitrate groups, and it is relevant that even the basic tin(II) nitrate $Sn_3(OH)_4(NO_3)_2$ explodes on heating (*216*). With lead, the higher stability is in the +2 oxidation state; the tetranitrate has not been prepared.

Group V

In this group, only antimony and bismuth are sufficiently electropositive to form salts with oxy-acids. A simple nitrate of antimony has not been obtained, though some oxide-nitrates are known. The basic salt $SbONO_3$ separates from solutions in nitric acid on dilution with water; the same product is obtained as the addition compound $SbONO_3{\cdot}(CH_3)_2SO$ from the reaction of metallic antimony with a mixture of dinitrogen tetroxide and dimethyl sulfoxide (*102*). The oxide-nitrate of Sb(V), $SbO(NO_3)_3$, is the product of the reaction between antimony pentachloride and dinitrogen pentoxide (*27*), and is highly unstable at room temperature. In contrast to antimony, bismuth forms an oxide-nitrate and a simple nitrate. The action of heat on the hydrate $Bi(NO_3)_3{\cdot}5H_2O$ gives the oxide-nitrate $BiO(NO_3)$, whereas slow dehydration at room temperature (Section II,B) gives $Bi(NO_3)_3$. Bismuth metal also reacts with a mixture of methyl cyanide and excess dinitrogen tetroxide to give an adduct $Bi(NO_3)_3{\cdot}0.25N_2O_4{\cdot}0.25MeCN$, which can be thermally decomposed in vacuum to give the anhydrous nitrate (*102*). From the infrared spectrum, the nitrate groups would appear to be covalently bonded.

Group VI

The formation of a compound $Te(NO_3)_2$ by reaction of silver nitrate and tellurium tetrabromide in boiling benzene has been claimed (*250*). The only other known nitrate compound of tellurium has the empirical formula $2TeO_2{\cdot}HNO_3$ (*249*); its structure is unknown.

The preparation of anhydrous polonium(IV) nitrate (*217*, *218*) is of considerable interest. Treatment of polonium(IV) chloride or hydroxide with dilute nitric acid gives rise to basic salts, one of which is the analogue of $2TeO_2 \cdot HNO_3$. A basic salt is also obtained on keeping polonium metal in a gaseous mixture of nitrogen dioxide and oxygen. Polonium metal is not attacked by either pure liquid dinitrogen tetroxide or its mixture with ethyl acetate; however, both polonium dioxide and polonium tetrachloride react with liquid dinitrogen tetroxide to give the white crystalline addition compound $Po(NO_3)_4 \cdot N_2O_4$, from which dinitrogen tetroxide is easily removed to give polonium(IV) nitrate. This decomposes to give a basic salt slowly in air at room temperature, or more rapidly (1.5–2 hours) under vacuum.

B. TRANSITION ELEMENTS

Scandium Group and Lanthanides

The preparation of anhydrous nitrates of scandium, yttrium, and lanthanum has been referred to in Section II,B,I,J, and the thermal decomposition of lanthanum nitrate in Section VII,B. No anhydrous nitrate of actinium has been described. So far as the lanthanides are concerned, the position is indicated in Fig. 12. The earlier members form anhydrous nitrates; thermogravimetric analysis of the 4-hydrates of europium, holmium, erbium, thulium, ytterbium, and lutecium indicates that these metals form only oxide-nitrates (*6*). It seems quite likely, however, that the simple nitrates could be prepared by appropriate methods. The nitrate chemistry of promethium and terbium does not appear to have been studied.

Titanium Group

All the elements of this group form anhydrous nitrates $M(NO_3)_4$. The titanium compound has been prepared (*a*) by reaction of the tetrachloride with chlorine nitrate (Section II,G) or with dinitrogen pentoxide in carbon tetrachloride solution (*27*), and (*b*) by reaction of hydrated titanium nitrate with dinitrogen pentoxide (*26*). The compound melts at 58.5°, sublimes in high vacuum, and decomposes at about 100° to the nonvolatile oxide-nitrate $TiO(NO_3)_2$. Titanium tetrachloride reacts in a different way with dinitrogen tetroxide. The reaction:

$$TiCl_4 + 4N_2O_4 \rightarrow Ti(NO_3)_4 + 4NOCl$$

does not go to completion, since the nitrosyl chloride formed reacts with the remaining tetrachloride to give the stable complex $(NO)_2[TiCl_6]$ (*54*). Reaction with titanium tetraiodide,

$$TiI_4 + 4N_2O_4 \rightarrow Ti(NO_3)_4 + 4NO + 2I_2$$

is more satisfactory. There is a vigorous reaction on addition of the tetraiodide to liquid dinitrogen tetroxide in carbon tetrachloride at −17°. Zirconium tetraiodide reacts in the same way. The tetranitrates are no doubt present in the solution, but were not isolated since at temperatures above 10° brown fumes were evolved, and the only compounds which could be isolated were the oxide-nitrates $TiO(NO_3)_2$ and $ZrO(NO_3)_2$.

Anhydrous zirconium tetranitrate has now been prepared by reaction of zirconium tetrachloride with dinitrogen pentoxide (*32*). The initial product had the composition $Zr(NO_3)_4 \cdot 0.4N_2O_5 \cdot 0.6N_2O_4$, but the nitrogen oxides could be removed by heating at 100° for 4 hours under vacuum (0.01 mm). On continued heating, the tetranitrate slowly sublimed onto a cold finger in the form of colorless crystals. The compound has a high solubility in water and in polar aliphatic solvents; it is insoluble in toluene, with which it reacts rapidly to produce nitro compounds. The infrared spectrum of the solid includes bands in the ranges 1224–1284 (ν_1), 1575–1631 (ν_4), and 983–1015 (ν_2) cm^{-1}. The high ν_4 frequency suggests that the metal-nitrate bonds are strongly covalent, and that the nitrate groups are bidentate or bridging (Section V,C,D). This would also be consistent with the high reactivity towards aromatic solvents (Section VI,D). If all nitrate groups are bidentate, a structure represented by a cubic arrangement of eight oxygen atoms, with the zirconium atom at the center, is attractive. The corresponding hafnium compound $Hf(NO_3)_4$ has been prepared by the reaction of dinitrogen pentoxide with hydrated hafnium nitrate. Its properties resemble those of the zirconium compound (*30*).

The preparation of the thorium compound $Th(NO_3)_4$ has been described (Section II,E). The covalent bonding must again be strong, since it persists even in the tetrahydrate. The infrared spectrum of the latter compound includes bands at 1292, 1323 (ν_1), 1506, 1520 (ν_4), and 1030, 1036 (ν_2) cm^{-1}, but no frequency corresponding to an ionic nitrate (*211*).

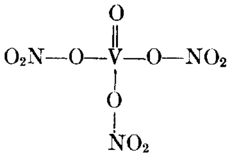
Vanadium Group

At this position in the Periodic Table it is to be expected that nitrate groups will again be covalently bonded. In view of the oxidizing properties of such groups, it is also to be expected that the metals concerned will normally be present, in covalent nitrates, in their highest oxidation states. However, with the metals of the vanadium group this would involve either the unfavorable coordination number of 5 (if all nitrate groups were unidentate) or a coordination number too high to be acceptable on steric grounds (if nitrate groups were bonded in bidentate fashion). It is not surprising, therefore, that no simple nitrates $M(NO_3)_5$ are known for the metals of this group. This is the hypothetical initial product in a number of reactions, but we may consider that decomposition to oxide-nitrates then occurs; this reduces the coordination number while retaining the maximum oxidation state.

Dinitrogen pentoxide reacts with vanadium pentoxide according to the equation

$$V_2O_5 + 3N_2O_5 \rightarrow 2VO(NO_3)_3$$

and reaction with $VOCl_3$ gives the same product (*27*, *219*). Vanadium oxide trinitrate is yellow, melts at 2°, and boils at 68–70° in high vacuum. Further study of the physical and chemical properties of this compound should be rewarding. The fact that it is a liquid at room temperature indicates a covalent molecule. If the nitrate groups are monodentate, the structure would then be



$$\mathrm{O_2N{-}O{-}}\underset{\underset{\underset{\displaystyle \mathrm{NO_2}}{|}}{\underset{\displaystyle \mathrm{O}}{|}}}{\overset{\overset{\displaystyle \mathrm{O}}{\|}}{\mathrm{V}}}\mathrm{{-}O{-}NO_2}$$

Rupture of the molecule may occur either at the V—O or the O—N bonds in the V—O—N links, as discussed in Section VI. Depending on the reaction conditions, the compound may therefore behave as vanadyl nitrate, $VO^{3+}(NO_3^-)_3$, or as nitronium vanadate, $(NO_2^+)_3VO_4^{3-}$. Reactions with dinitrogen tetroxide give a different product (*220*). Chips of electrolytic vanadium metal react readily with a mixture of liquid dinitrogen tetroxide and methyl cyanide at 0°:

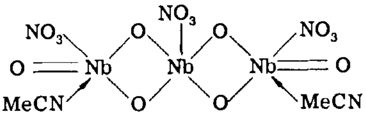
$$V + 2N_2O_4 \rightarrow VO_2NO_3 + 3NO.$$

The mononitrate was obtained as a brick-red free-flowing powder; it is highly soluble in water to give an orange-colored solution, but is insoluble in common organic solvents.

The particular oxide-nitrate of niobium obtained again depends upon the oxide of nitrogen used. Reaction of anhydrous niobium pentachloride with liquid dinitrogen pentoxide at 30°

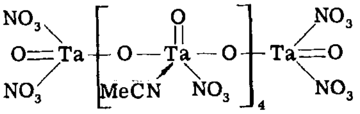
$$NbCl_5 + 4N_2O_5 \rightarrow NbO(NO_3)_3 + 5NO_2Cl$$

gives the oxide trinitrate as a white powder which is immediately hydrolyzed by water to nitric acid and hydrated niobium pentoxide (*29*). It is slightly soluble in some organic solvents. It is not volatile, and decomposes in vacuum at about 120°. These properties, together with the infrared spectrum, are considered to indicate that the complex contains a niobium-oxygen double bond, and that the monomeric units are linked together by bridging nitrate groups (*29*). From the reaction of niobium pentachloride with dinitrogen tetroxide in methyl cyanide solution, a complex is obtained which has a higher oxide: nitrate ratio, and is believed to have the structure



This compound is stable at 70°, is insoluble in organic solvents, and takes up one molecule of water (for each trimer unit) in moist air (*221*). The reaction has an induction period, and probably proceeds via intermediate species such as $Nb(NO_3)_5$ and $NbO(NO_3)_3$ (*222*). The analogous complex with *N*,*N*-dimethylacetamide is polymeric. Using ethyl acetate or nitrobenzene as solvent, products are isolated which by analysis appear to be $NbO_2(NO_3)$ with varying amounts of combined solvent. These products are much less stable, and probably contain monomeric $NbO_2(NO_3)$ units.

A complex of the tantalum oxide-nitrate $TaO(NO_3)_3$ with methyl cyanide is prepared by the same reaction as for the niobium complex (*221*). The structure



has been proposed. No anhydrous nitrates or oxide-nitrates of protactinium have been described.

Chromium Group

Under this heading we shall treat the nitrate chemistry of chromium, molybdenum, tungsten, and uranium. Simple chromium(III) nitrate $Cr(NO_3)_3$ has recently been isolated by reaction of chromium carbonyl with dinitrogen pentoxide in carbon tetrachloride solution (*248*). The addition compound $Cr(NO_3)_3{\cdot}2N_2O_4$ is formed when dinitrogen tetroxide reacts with chromium carbonyl (Section II,I) or with chromyl chloride. The latter reaction is of particular interest, both in comparison with the corresponding reaction with dinitrogen pentoxide and because it is one of the few instances in which liquid dinitrogen tetroxide acts as a reducing agent. When chromyl chloride vapor is passed into a N_2O_4—CH_3NO_2 mixture, reaction is vigorous, and green crystals of the compound $Cr(NO_3)_3{\cdot}2N_2O_4$ separate (*51*). The infrared spectrum of the solid is highly complex, indicating the presence of unidentate, bidentate, and (possibly) bridging nitrate groups; frequencies assignable to the NO^+ ion as well as the coordinated N_2O_4 molecule are also present. The fact that the simple nitrate cannot be obtained by thermal decomposition of the N_2O_4 addition compound is to be related to the complex nature of the latter.

Each of the four metals forms a compound of formula $MO_2(NO_3)_2$. Reaction of chromyl chloride with dinitrogen pentoxide (Section II,F) or chlorine nitrate (Section II,G)

$$CrO_2Cl_2 + 2N_2O_5 \rightarrow CrO_2(NO_3)_2 + 2NO_2Cl$$
$$CrO_2Cl_2 + 2ClNO_3 \rightarrow CrO_2(NO_3)_2 + 2Cl_2$$

gives chromyl nitrate as a brown volatile liquid which melts at −70°, boils at 28–30° at a pressure of 10^{-3} mm, and can be distilled unchanged. It is a violent oxidizing and nitrating agent, and inflames on contact with benzene (*219*, *246*). Like vanadium oxide trinitrate, this compound merits further detailed study, since it may behave either as chromyl nitrate or as nitryl chromate $(NO_2)_2CrO_4$. By similar preparative methods, the corresponding molybdenum and tungsten compounds $MoO_2(NO_3)_2$ and $WO_2(NO_3)_2$ are believed to be formed (*27*). These appear to be much less stable than the chromium compound, and have not been fully characterized. Reaction of molybdenum and tungsten hexacarbonyls with dinitrogen tetroxide results in the formation of amorphous yellow powders having the empirical formulas $MoNO_6$ and $W_2N_3O_{11}$, respectively. These products contain nitrate groups, but are probably polymeric; they begin to decompose at 95° and 67°, respectively (*70*).

The existence of anhydrous uranyl nitrate, $UO_2(NO_3)_2$, as a distinct compound is now well established. Section II,E,F,I deals with its preparation, and Section VI,E with some of its chemical properties. Its infrared spectrum shows that the nitrate groups are bonded covalently (*51*), and its thermal stability is much higher than that of the corresponding chromium, molybdenum, or tungsten compounds. When the addition compound $UO_2(NO_3)_2{\cdot}N_2O_4$ is heated in a thermobalance at a heating rate of 1° per minute, a plateau corresponding to $UO_2(NO_3)_2$ is obtained, and decomposition is not apparent, under these conditions, below 240° (*51*). The ultraviolet absorption spectrum of solutions of anhydrous uranyl nitrate in a number of organic solvents has been measured. The spectrum retains the vibrational band structure in acetone, 2-heptanone, dioxan, formamide (*223*), nitromethane (*83*), ethyl acetate, and methyl cyanide (*70*). The compound forms a very large number of adducts with organic compounds containing oxygen, sulfur, or nitrogen donor atoms (*224*); essential features in the structure of such compounds have been discussed in Section V,C.

The spontaneous decomposition of uranium tetranitrate has been referred to in Section II,C; it is known in the form of the *N*,*N*-dimethylacetamide complex $U(NO_3)_4{\cdot}2.5AcNMe_2$ (*15*).

Transuranium Elements

The preparation of simple anhydrous nitrates of the transuranium series is still awaited. The nitrate group decomposes under irradiation (Section VII,A), and for this reason the simple nitrates of the higher members of this series may not be available. The nitrates of neptunium are known only in solution, but the plutonium compounds $Pu(NO_3)_4{\cdot}5H_2O$ and $PuO_2(NO_3)_2{\cdot}6H_2O$ have been isolated (*225*). All the plutonium(IV) present in nitrate solutions above 1 *M* concentration or in 1–4 *M* nitric acid, is in the form of undissociated $Pu(NO_3)_4$, and the only Pu(IV) species present in concentrated nitric acid is $H_2[Pu(NO_3)_6]$ (*226*). The americium(VI) nitrate $AmO_2(NO_3)_2$ is extracted from aqueous solution by ether (*225*) [compare hydrated $UO_2(NO_3)_2$] and the heavier transuranium elements no doubt behave similarly; americium(III) nitrate, presumably hydrated, is known (*227*). Tri-*n*-butyl phosphate has, of course, one of its most extensive applications in separations of the transuranium elements. Disolvates are formed with plutonium(VI) and plutonium(IV) nitrates, and with neptunium(VI) and neptunium(IV) nitrates (*228*). Plutonium(III) (*229*, *230*) and americium(III) (*231*) nitrates form trisolvates. Trivalent curium forms a nitrate which has properties similar to americium(III) nitrate (*232*).

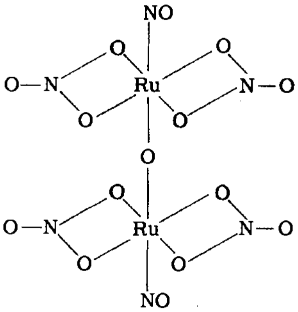
Manganese Group

In discussing nitrates of the vanadium and chromium group metals, it was seen that where the metal readily assumes a high oxidation state, oxide-nitrates rather than simple nitrates are usually produced, and that the higher the available valency state the more readily does complete decomposition to oxide occur. Thus, the oxide-nitrates of molybdenum and tungsten are less stable than those of niobium and tantalum. No nitrates or oxide-nitrates of technetium or rhenium are known, and this is now seen to be in accord with the general pattern. However, the manganese(II) oxidation state is stable because of its $3d^5$ electronic structure, and the anhydrous nitrate $Mn(NO_3)_2$ is well established. Its preparation has been mentioned in Section II(B,C,D,E,I) and its thermal decomposition has been discussed in Section VII,B. The compound $Mn(CO)_5NO_3$ is a key compound in connection with the infrared spectrum of the unidentate nitrate group (Section V,B), and the infrared spectrum of $Mn(NO_3)_2$ shows that in this compound also the nitrate groups are covalently bonded (*211*).

Iron Group

When ferric chloride is treated with a mixture of liquid dinitrogen tetroxide and ethyl acetate, the addition compound $Fe(NO_3)_3{\cdot}N_2O_4$ is obtained in the form of pale brown crystals (*49*). The same product is obtained by reaction of iron pentacarbonyl with excess liquid dinitrogen tetroxide (Section II,I) or by the action of dinitrogen pentoxide on metallic iron (*30*). Attempts to obtain the simple nitrate from this adduct have so far been unsuccessful. On heating at 80° in vacuum the compound vaporizes (Section VI,A); the first stage in the thermal decomposition under atmospheric pressure is the oxide-nitrate $FeO(NO_3)$ (*67*), which is also produced by reaction of iron pentacarbonyl and nitrogen dioxide vapors.

Ruthenium and osmium are known to form neither simple anhydrous nitrates nor oxide-nitrates, although a number of derivatives of these compounds are known. Ruthenium, in particular, forms a large number of nitrato-nitrosyl ruthenium complexes (*233*, *234*). For example, reduction of a nitric acid solution of ruthenium tetroxide with nitric oxide gives the dark red compound $Ru(NO)(NO_3)_3{\cdot}4H_2O$ (*235*). When this is held in vacuum at 50° for 12 hours, the dihydrate is obtained as the 6-coordinate complex $[Ru(NO)(NO_3)_3(H_2O)_2]$; the infrared spectrum of this compound shows that the nitrate groups are covalently bonded to the metal. A corresponding compound $Ru(NO)(NO_3)_3{\cdot}(Bu_3PO_4)_2$ has also been isolated. The anhydrous compound $Ru(NO)(NO_3)_3$ cannot be obtained; the dihydrate decomposes to RuO_2 on heating to 150° in vacuum (*236*). Again, when the RuO_4–NO reaction is carried out in carbon tetrachloride, an anhydrous product of composition $Ru_2N_6O_{15}$ is obtained in the form of a brown powder. The infrared spectrum indicates that the nitrate groups may well be bidentate, and the compound is believed to have the binuclear structure (*233*, *236*)



The known nitrate chemistry of osmium is negligible, but this is more likely to be the result of limited investigation than of any inherent reluctance of osmium to form such compounds. Osmium trinitrate is said to be deep brown, and sufficiently stable to be dried at 100° (*237*). However, these properties are actually those of a compound $Os(NO_2)_3$ described by Wintrebert (*238*), which has not itself been properly characterized. The only other nitrates described are those where the nitrate is the anion in salts in which coordination complexes of osmium form the cation.

Cobalt Group

The preparation of cobalt(II) nitrate has already been mentioned (Section II,E,I); in spite of the fact that dinitrogen tetroxide or dinitrogen pentoxide are used as reagents, it is the nitrate of Co(II) which is obtained. When isolated from dinitrogen tetroxide medium, the adduct $Co(NO_3)_2{\cdot}2N_2O_4$ is first obtained as deep purple crystals. This decomposes in vacuum at about 50° to the 1:1 adduct $Co(NO_3)_2{\cdot}N_2O_4$. In this compound the infrared bands of dinitrogen tetroxide are no longer observed, but an NO^+ band remains (*76*). The compound may be represented in the form $NO^+[Co(NO_3)_3]^-$, though its structure has not been studied. Further heating in vacuum gives the pale purple anhydrous $Co(NO_3)_2$. The electrical conductivity (*67*, *76*) and ultraviolet spectrum (*76*) of solutions of this compound in nitromethane and methyl cyanide and its thermal decomposition (Section VII,B), suggest predominantly covalent bonding of the nitrate groups. The infrared spectrum of the solid (*211*) has been interpreted as indicating ionic bonding. However, on re-examination (*76*) the spectrum has been found to be compatible with the presence of both ionic and covalent nitrate groups.

No anhydrous nitrates or oxide-nitrates of rhodium or iridium appear to have been described; a hydrate of rhodium(III) nitrate is said to be formed on evaporation of a solution of the oxide Rh_2O_3 in nitric acid (*239*).

Nickel Group

The infrared spectrum of the anhydrous compound $Ni(NO_3)_2$ shows it to be a typical covalent nitrate. It can be prepared as a pale green powder by dehydration of the hydrate in an N_2O_5–HNO_3 mixture (Section II,E) or by reaction of nickel carbonyl with dinitrogen tetroxide (Section II,I). When the latter reaction was carried out with heptane, cyclohexane, or methylcyclohexane as diluent, the product always contained a small amount of an impurity containing carbon. This is attributed to attack of the covalent nitrate (or an intermediate carbonyl-nitrate) on the hydrocarbon (see Section VI,D); similar attack occurred during the preparation of cobalt nitrate from cobalt carbonyl. Anhydrous nickel nitrate may also be prepared by the solvolysis of nickel chloride in an ethyl acetate–dinitrogen tetroxide mixture; it is unique among transition metal nitrates in giving the metal nitrite on thermal decomposition (Section VII,B), and it is prepared from the nitrite by oxidation with liquid dinitrogen tetroxide (*78*). Anhydrous nickel nitrate is not volatile.

Palladium metal and palladium oxide dissolve in nitric acid solution;

it is stated in a number of textbooks that the compound $Pd(NO_3)_2$ separates as yellow-brown crystals from concentrated nitric acid, but this is now subject to considerable doubt. In contrast to nickel nitrate, palladium nitrate is readily volatile. When the dihydrate $Pd(NO_3)_2 \cdot 2H_2O$ is mixed with dinitrogen pentoxide and heated to 110° under a pressure of 0.1 mm, anhydrous palladium nitrate sublimes onto a cold finger (*30*). Manchot and Waldmuller (*240*) report the formation of palladium nitrite by reaction of the anhydrous nitrate with nitric oxide.

Consistent with the general reluctance of platinum to form simple salts of the oxy-acids, the nitrates of platinum are not so well characterized as is palladium nitrate. There are early references (*241*) to the existence of both $Pt(NO_3)_2$ and $Pt(NO_3)_4$, but further study is necessary to determine whether the products are correctly represented by these formulas.

Copper Group

The many unusual features in the chemistry of anhydrous copper(II) nitrate have already been discussed in some detail in various sections of this review. Copper(I) nitrate is unknown as the simple salt (Section II,C). In contrast, silver(I) nitrate is of course well known, but silver(II) nitrate has not yet been isolated as the simple salt; on the basis of calculated values for the free energy of formation, Morris (*242*) has predicted that $Ag(NO_3)_2$, if formed, would be thermodynamically unstable. If the Ag^{2+} cation is coordinated, as in the orange-red compound $[Ag(py)_4](NO_3)_2$, then the nitrate is stable (*243*). The dark brown solution obtained by dissolving the oxide AgO in concentrated nitric acid may contain silver(II) nitrate or nitrato complexes of silver(II), but no corresponding solid has been isolated from the solution (*244*). In an attempt to achieve this, dinitrogen tetroxide was added to this solution, but mutual decomposition occurred and silver(I) nitrate was deposited (*67*). The simple nitrate of Au(I) is not known, but $Au(NO_3)_3$ has recently been prepared (*30*). When a solution of gold(III) nitrate in concentrated nitric acid is diluted with water, immediate hydrolysis occurs with deposition of hydrated gold(III) oxide. The nitrates $[Au\{(CH_2NH)_2CS\}_2]NO_3$ (*245*) and $[Au(NH_3)_4](NO_3)_3$ have been isolated; the complex acid $H[Au(NO_3)_4] \cdot 3H_2O$ and its salts with K^+, Rb^+, and NH_4^+ are known, as well as salts of hexanitratogold(III) acid, e.g., $K_2H[Au(NO_3)_6]$.

Zinc Group

Anhydrous nitrates $M(NO_3)_2$ are known for each of the metals zinc, cadmium, and mercury. Their preparation has been referred to (Section II), and the thermal decomposition of zinc and cadmium nitrates compared (Section VII). Anhydrous mercurous nitrate, $Hg_2(NO_3)_2$, is unknown. There are some pronounced differences in the chemistry of the nitrates of these three metals for which no fully satisfactory reason exists at present. For example, their infrared spectra show zinc and mercury(II) nitrates to contain coordinated nitrate groups, whereas cadmium nitrate gives a typically ionic nitrate spectrum (*211*). Again, the readiness with which these nitrates form N_2O_4 adducts is quite different. The compound $Zn(NO_3)_2{\cdot}2N_2O_4$ decomposes slowly at 100°, $Hg(NO_3)_2{\cdot}N_2O_4$ decomposes rapidly even at room temperature, while $Cd(NO_3)_2$ separates as the simple salt from media containing dinitrogen tetroxide. Zinc nitrate (*30*) and mercury(II) nitrate (*70*) show slight volatility in vacuum.

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