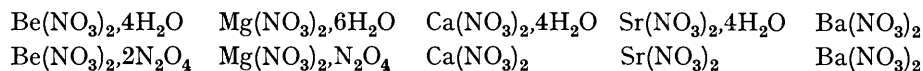## 227. *Anhydrous Nitrates of the Group* II *Metals.*

By C. C. ADDISON and A. WALKER.

Reaction of beryllium chloride with a mixture of dinitrogen tetroxide and ethyl acetate gives the addition compound $Be(NO_3)_2,2N_2O_4$. Thermal decomposition yields successively beryllium nitrate and beryllium oxide nitrate $Be_4O(NO_3)_6$. Beryllium nitrate is strongly covalent, and is unusual in that it gives nitrite ions as well as nitrate ions on dissolution in water or alkali; possible mechanisms are discussed. By similar reactions with Grignard magnesium, the 1 : 1 adduct $Mg(NO_3)_2,N_2O_4$ is obtained. This loses dinitrogen tetroxide irreversibly at 52—54°, in contrast to the reversible dissociation of $Cu(NO_3)_2,N_2O_4$. Calcium, strontium, and barium nitrates form no stable adducts at room temperature. The infrared spectra of all five metal nitrates are reported and discussed.

THE nitrates of barium, strontium, and calcium have long been known in both anhydrous and hydrated forms. Until recently, little was known of anhydrous magnesium nitrate; a convenient method for its preparation has now been found, and some of its properties have been studied. Furthermore, anhydrous beryllium nitrate has been prepared in pure form. We are now able, therefore, to review the nitrates of this group as a whole. This paper is concerned with the anhydrous nitrates of beryllium, magnesium, calcium, strontium, and barium, and their relative tendency to form addition compounds with dinitrogen tetroxide. This tendency decreases from beryllium to barium, with respect to solvation by either water or dinitrogen tetroxide: thus we can list the solvates separating at 20° from an aqueous or dinitrogen tetroxide medium as follows:

$Be(NO_3)_2,4H_2O$	$Mg(NO_3)_2,6H_2O$	$Ca(NO_3)_2,4H_2O$	$Sr(NO_3)_2,4H_2O$	$Ba(NO_3)_2$
$Be(NO_3)_2,2N_2O_4$	$Mg(NO_3)_2,N_2O_4$	$Ca(NO_3)_2$	$Sr(NO_3)_2$	$Ba(NO_3)_2$

Beryllium Nitrate, Bis(dinitrogen tetroxide) Solvate.—Pure metallic beryllium does not react with liquid dinitrogen tetroxide, or with mixtures of the tetroxide with ethyl acetate or methyl cyanide. Some solvolysis of anhydrous beryllium chloride probably occurs in dinitrogen tetroxide, but this is inefficient owing to the insolubility of the product. Reaction of beryllium chloride was vigorous in a 1 : 1 v/v mixture of dinitrogen tetroxide and ethyl acetate, and from the resultant solution pale straw-coloured crystals of the addition compound $Be(NO_3)_2,2N_2O_4$ were isolated.

Thermal decomposition. The addition compound (2 g.) was heated in an evacuated vessel (200 ml.) and the pressure of the evolved gas was determined over a temperature range by means of a glass-spiral gauge. The results (obtained by B. F. G. Johnson in these laboratories) are shown in Fig. 1. At each temperature, the pressure recorded is the equilibrium value. The part CD of the curve follows the gas law, and indicates the presence of a solid product which is stable up to 125°. In separate experiments in which

the addition compound was heated under a vacuum at temperatures in the range CD, the loss in weight corresponded to the evolution of two mol. of dinitrogen tetroxide:

$$Be(NO_3)_2,2N_2O_4 \longrightarrow Be(NO_3)_2 + 2N_2O_4 \qquad (1)$$
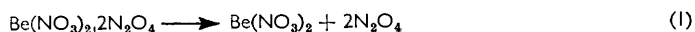
and analysis of the solid product showed it to be pure beryllium nitrate. The successive loss of the two molecules of dinitrogen tetroxide in the temperature range AC is indicated by the break in the curve (Fig. 1) at B. When the decomposition (reaction 1) was carried out in a closed vessel heated to the temperature range CD, and the vessel was allowed to cool, the pressure remained high, so that reaction (1) is not reversible to any appreciable extent.

When beryllium nitrate was heated above 125° (part DE of curve in Fig. 1) rapid decomposition occurred; nitrogen dioxide was evolved copiously, and a white solid
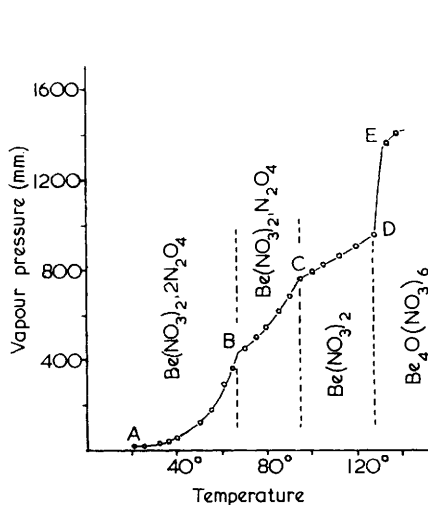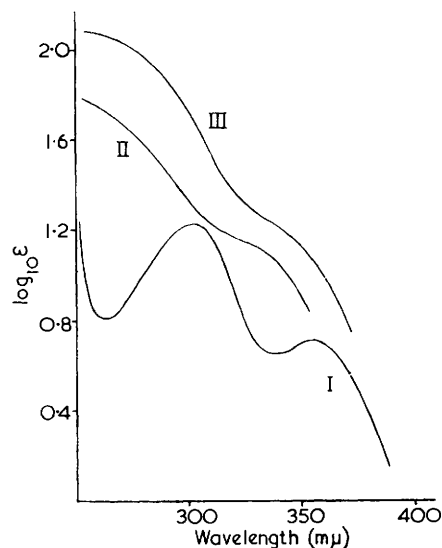

FIG. 1. Decomposition vapour pressure of $Be(NO_3)_2,2N_2O_4$.

FIG. 2. Ultraviolet absorption spectra of $Be(NO_3)_2$ solutions in (I) 2N-NaOH, (II) EtOAc, and (III) MeCN.

condensed on the cool part of the vessel in the form of cubic crystals. This volatile compound is beryllium oxide nitrate, $Be_4O(NO_3)_6$, with a structure analogous to the well-known beryllium oxide acetate $Be_4O(OAc)_6$. Brief reference has already been made to beryllium oxide nitrate,[1] and its properties will be described in detail in a later paper.

Anhydrous Beryllium Nitrate.—This compound is obtained as a white, amorphous solid which is very hygroscopic. From the analysis and infrared spectrum of the solid there is no doubt that it is a true anhydrous nitrate in which there is strong covalent bonding between the nitrate group and the metal, but in solution it shows behaviour which is at present unique amongst simple metal nitrates. When beryllium nitrate is added to water, brown fumes are evolved and a slight turbidity remains which is immediately clarified by acid. When it is hydrolysed in 2N-sodium hydroxide solution, both nitrate and nitrite ions are produced. The ultraviolet absorption spectrum of the resulting solution is shown in Fig. 2; in addition to the nitrate peak at 302 mμ, the peak at 355 mμ characteristic of nitrite is also observed. The nitrite present in solution has been determined by titration with ceric sulphate solution; the amount of nitrite present was ~5% of the original nitrate added, and this amount was largely independent of the concentration of sodium hydroxide used, within the range 0·05—2N.

¹ Addison and Walker, *Proc. Chem. Soc.*, 1961, 242.

Anhydrous (ionic) nitrates of magnesium, calcium, strontium, and barium dissolve in water to give metal and nitrate ions only, and the unusual behaviour of beryllium nitrate is attributed to the strength of the metal–oxygen bond. Strong covalent bonding of the nitrate group occurs in the alkyl nitrates, and the dissociation

$$R-O-NO_2 \longrightarrow R-O\cdot + NO_2\cdot$$

is an important step in the chemistry (and the pyrolysis) of alkyl nitrates.[2] In principle, this dissociation may also occur in a nitrate group covalently bonded to a metal:

$$\overset{a}{M}-\overset{b}{O}-NO_2 \longrightarrow M-O\cdot + NO_2\cdot$$
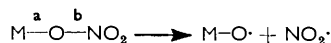
Dissociation may occur at bond (a) or bond (b) or at both bonds, depending upon their relative strengths. All metal nitrates so far studied have dissociated at (a) on dissolution in water, but the size and polarising power of the beryllium atom is presumably sufficient to raise the bond strength of (a) to the same order as that of (b). In addition to normal ionisation in solution, the dissociation

$$Be(NO_3)_2 \longrightarrow NO_3-Be-O\cdot + NO_2\cdot$$

is also considered to occur to a small extent. The NO_2 radicals so produced will hydrolyse to give equal quantities of nitrite and nitrate in solution, so that about 10% of the original nitrate dissociates in this way. The nature of the beryllium species remaining after fission of the O–N bond has not been investigated; it seems unlikely that both NO_3 groups in any one molecule will dissociate in this way.

It is of interest to compare the hydrolytic behaviour of the beryllium oxide nitrate $Be_4O(NO_3)_6$. In this compound, each nitrate group is part of a 6-membered ring (I). The NO_2 radical can no longer break away as in the simple nitrate, since two of its oxygen atoms are now bonded to beryllium atoms. This compound hydrolyses slowly in water or in alkaline solution to give nitrate ions only.

Several other observations support the mechanism postulated above. The fact that the nitrite produced is independent of alkali concentration suggests reaction with water rather than the hydroxyl ion. Again, all metal nitrates which by virtue of covalent bonding can release NO_2 radicals during reaction need not necessarily give nitrite on hydrolysis; the latter is a complicated process involving the co-ordination chemistry of the metal. For example, copper nitrate gives only nitrate ions in aqueous solution, but its vigorous reactions with some ethers[3] possess features[4] closely resembling those characteristic of nitrogen dioxide–ether reactions at high temperatures.[2] Direct support is provided by the nature of the solutions of beryllium nitrate in non-aqueous solvents. On its dissolution in ethyl acetate or methyl cyanide, a pale brown coloration due to nitrogen dioxide is observed, and the absorption spectra of these solutions are shown in Fig. 2. Many anhydrous nitrates give a nitrate peak in these solvents, though $\lambda_{max.}$ is reduced from 302 mμ to 280—285 mμ. With beryllium nitrate no actual peak is observed in this region, but an inflexion occurs at higher wavelengths which is clearly due to the known 333 mμ absorption by dinitrogen tetroxide in these solvents.[5]

Magnesium Nitrate–Dinitrogen Tetroxide Solvate.—A mixture of equal volumes of dinitrogen tetroxide with ethyl acetate or methyl cyanide reacts very slowly with magnesium ribbon, but reacts vigorously with Grignard magnesium at room temperature, and reaction is complete within a few hours. The analysis of the very pale yellow powder isolated from the mixture corresponded to $Mg(NO_3)_2,0\cdot92N_2O_4$ in contrast to the 1 : 2

[2] Gray and Yoffe, *Chem. Rev.*, 1955, **55**, 1069.
[3] Bauer and Addison, *Proc. Chem. Soc.*, 1960, 251.
[4] Addison, Proc. Symposium on Inorganic Free Radicals, Amer. Chem. Soc., Atlantic City, 1962.
[5] Addison and Sheldon, *J.*, 1958, 3142.
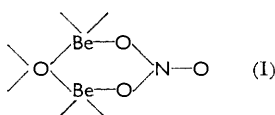
compound formed by beryllium nitrate. It is likely that at lower temperatures a precise 1 : 1 stoicheiometry can be obtained, but the compound has an appreciable vapour pressure of tetroxide at room temperature. Thermal decomposition yields pure anhydrous magnesium nitrate, and this method is believed to be more convenient than the two methods previously described.[6,7]

Thermal decomposition. This has been studied by the technique used for the beryllium compound. The shape of the pressure–temperature curve is compared in Fig. 3 with that
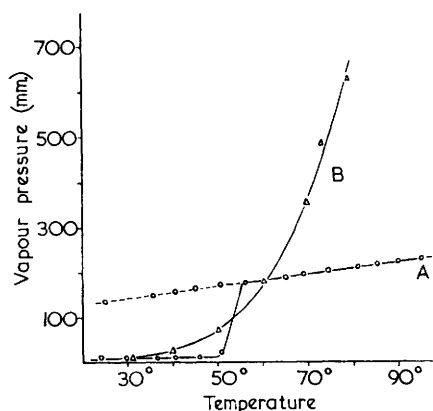

FIG. 3. Decomposition vapour pressures of (A) $Mg(NO_3)_2,N_2O_4$ and (B) $Cu(NO_3)_2,N_2O_4$.
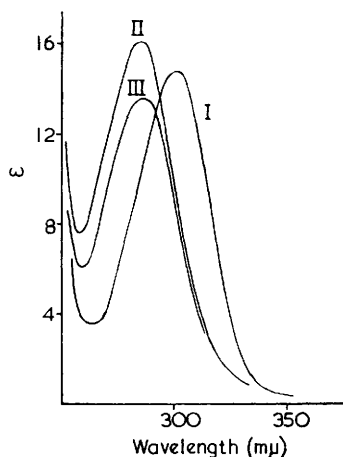
FIG. 4. Ultraviolet absorption spectra of $Mg(NO_3)_2$ solutions in (I) water, (II) methyl cyanide, and (III) ethyl acetate.

for the corresponding compound $Cu(NO_3)_2,N_2O_4$. (Actual pressure values should not be compared, since unweighed quantities of the two compounds were used.) The magnesium compound shows a sudden pressure increase at 52—54°. Thereafter, the pressure change follows the gas laws, so that the decomposition

$$Mg(NO_3)_2,N_2O_4 \longrightarrow Mg(NO_3)_2 + N_2O_4$$
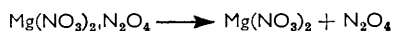
occurs over a very narrow temperature range. When the system was cooled below the decomposition temperature, pressures followed the broken line A (Fig. 3), indicating that this reaction is completely irreversible. This is in direct contrast to the decomposition of $Cu(NO_3)_2,N_2O_4$ which is represented by a smooth curve throughout the same temperature range and is completely reversible.[8] Magnesium nitrate is unchanged on immersion in liquid dinitrogen tetroxide, whereas copper nitrate is converted into the addition compound.

Experience with the transition-metal nitrates has led to the general conclusion that the more covalent the metal–nitrate bond, the more likely is the simple nitrate to form an adduct with dinitrogen tetroxide; thus, the ionic alkali-metal nitrates and cadmium nitrate give no such adduct. However, anhydrous magnesium nitrate is ionic (see below) and becomes the first ionic nitrate known to form an addition compound with dinitrogen tetroxide. The behaviour on decomposition (Fig. 3) indicates clearly that the dinitrogen tetroxide is bonded in quite different ways in the two solids. Neither structure is yet known, but the contrasting behaviour is almost certainly related to the widely differing abilities of the two metals to form co-ordination complexes. Both the copper [8] and the

[6] Archambault, Sisler, and Ryschkewitsch, *J. Inorg. Nuclear Chem.*, 1960, **17**, 130.
[7] Huebel, *Bull. Soc. chim. France*, 1952, 162.
[8] Addison and Hathaway, *J.*, 1960, 1468.

magnesium compound exhibit a sharp absorption band in the 2260—2300 cm.$^{-1}$ region characteristic of NO$^+$ in the solid. This, however, has been observed for all such adducts irrespective of their stability, and does not imply that these two compounds are nitrosonium salts.

Anhydrous Magnesium Nitrate.—This was prepared as a white amorphous powder by heating the N_2O_4 adduct under a vacuum for several hours at 150°, and it is stable up to 300°. In contrast to the anhydrous nitrates of calcium, strontium, and barium,[9] it is unstable in the molten state. On rapid heating, magnesium nitrate can be induced to melt, but it then decomposes immediately. The ultraviolet absorption spectra of solutions in three solvents are shown in Fig. 4. No nitrite is formed on dissolution of this nitrate in water; $\varepsilon_{max.}$ is 14·8 at 302 mμ, corresponding to the presence of two nitrate ions per molecule. Spectra in the two non-aqueous solvents (determined by D. Sutton in these laboratories) show nitrate peaks, with the expected decrease in $\lambda_{max.}$ from 302 to 285 mμ.[10] The magnesium nitrate solutions therefore show none of the unusual features observed for beryllium nitrate.

Anhydrous Nitrates of Calcium, Strontium, and Barium.—None of the metals concerned reacted with liquid dinitrogen tetroxide. Metallic barium and strontium were also inert to mixtures of the tetroxide with ethyl acetate or methyl cyanide. Reaction of calcium with these mixtures was found to be highly concentration-dependent. Reaction was vigorous with a mixture of equal volumes of dinitrogen tetroxide and ethyl acetate, but if the concentration of tetroxide was varied by only a few per cent on either side of 50%, the reaction rate decreased considerably. The effect is similar to that studied quantitatively for copper, zinc, and uranium reactions.[11] As reaction proceeded, a solid separated which had a pasty consistency on removal of mother-liquor and consisted of calcium nitrate with some loosely combined dinitrogen tetroxide. The latter is readily removed by vacuum-treatment at room temperature, to leave the free-flowing powder of calcium nitrate, but it appears that a distinct dinitrogen tetroxide adduct is formed at low temperatures. Strontium and barium nitrates were unaffected by immersion in dinitrogen tetroxide.

Infrared Spectra of the Anhydrous Nitrates.—Spectra for beryllium and magnesium nitrates have not previously been reported; the spectra of calcium, strontium, and barium nitrates have been discussed,[12,13] but in view of the possibility of exchange with unprotected sodium chloride windows we have also redetermined these spectra, using windows carefully protected with Polythene.

Beryllium nitrate. The following bands (cm.$^{-1}$) represent the full spectrum in the sodium chloride region: 1600s.sh, 1550vs.b, 1500s.sh, 1360s, 1280vs.b, 1074s.sp, 1020m.sh, 980w.sp, 857m.b, 790m, and 743m.

The spectrum differs considerably from those of the other Group II metal nitrates and indicates strong covalent metal–nitrate bonding. It is feasible with this compound that the nitrate group may act as a unidentate, bidentate, or bridging ligand. The beryllium atoms are probably 4-co-ordinate with respect to oxygen, so that more than one type of bonding may be present in the solid. Again, coupling will occur between nitrate and metal–oxygen vibrations, since the beryllium, oxygen, and nitrogen atoms are of comparable mass, and the symmetry of the nitrate group alone is not therefore a basis on which to evaluate the vibrations of the nitrate skeleton.

The strong band observed at 1550 cm.$^{-1}$ is of particular interest. In the compound Mn(CO)$_5$NO$_3$, which must possess only a unidentate nitrate group,[14] the asymmetric NO$_2$ stretch occurs at 1486 cm.$^{-1}$. The observed spectrum for beryllium nitrate at the higher

[9] Addison and Coldrey, *J.*, 1961, 468.
[10] Addison, Hathaway, Logan, and Walker, *J.*, 1960, 4308.
[11] Addison, Sheldon, and Hodge, *J.*, 1956, 3900.
[12] Ferraro, *J. Mol. Spectroscopy*, 1960, **4**, 99.
[13] Buijs and Schutte, *Spectrochim. Acta*, 1962, **18**, 307.
[14] Addison, Kilner, and Wojcicki, *J.*, 1961, 4839.

wave numbers is very similar to that for copper nitrate,[15] where half of the nitrate groups bridge copper atoms;[16] the 1550 cm.$^{-1}$ band may therefore arise from the N=O stretch of a bridging nitrate group. Since this is a symmetrical vibration, the problem should be resolved when the Raman spectrum is available. Alternatively, very strong covalency of a unidentate nitrate group to the beryllium atom may in itself move the asymmetric NO_2 stretch above 1500 cm.$^{-1}$, since this occurs at 1675 and 1672 cm.$^{-1}$ for nitric acid and methyl nitrate, respectively.

The bands at lower frequency have not yet been assigned. In this region, metal–oxygen and nitrogen–oxygen vibrations occur, and may couple. Ring deformation frequencies will also occur if bidentate or bridging nitrate groups are present. Further discussion is deferred to a later paper dealing with beryllium oxide nitrate.

Magnesium nitrate. The spectrum is assigned under D_{3h} symmetry as follows:

$$\nu_2 = 812 \text{ cm.}^{-1} \text{ (s)}; \quad \nu_3 = 1380 \text{ cm.}^{-1} \text{ (v.s.)}; \quad \nu_4 = 762 \text{ cm.}^{-1} \text{ (m).}$$

No ν_1 frequency was observed, but strong absorption also occurred at 1475 cm.$^{-1}$. The nitrate is thus ionic, but has a symmetry somewhat lower than D_{3h} and may be grouped together with the nitrates of calcium, strontium, and barium.

Compound	ν_1	ν_2	ν_3	ν_4	Other bands
$Ca(NO_3)_2$	1040vw	815s	1350vs	741s	1460s
$Sr(NO_3)_2$	Absent	815s	1365vs	738s	1440s
$Ba(NO_3)_2$	Absent	818s	1344vs	730s	1410m

Calcium, strontium, and barium nitrates. With careful protection of windows (see below) these nitrates gave spectra closely supporting those previously reported.[12,13] Our results are annexed, the frequencies being classified under D_{3h} symmetry.

Ferraro [12] considers that these nitrates show possible transition to a C_{2v} symmetry. On that basis, the lowering of symmetry below D_{3h} causes some loss of degeneracy in the ν_3 vibration, giving rise to the observed peaks at 1460, 1440, and 1410 cm.$^{-1}$, respectively. No loss in degeneracy is observed for ν_4. Except for the very weak calcium nitrate band, no ν_1 absorption is observed, suggesting that the distortion of the free nitrate ions in all three salts is small. In a recent paper, Buijs and Schutte [13] offer an extension of Ferraro's interpretation, based on the fact that X-ray studies show these three nitrates to have C_3 symmetry for the nitrate ion; this symmetry is between D_{3h} and C_{2v}. In C_3 symmetry no degeneracy is lost, and the vibrations above 1400 cm.$^{-1}$ were assigned to interaction of $2\nu_4$ with ν_3.

There appears to be little doubt that with these three compounds the lattice field will distort the planar nitrate ion somewhat, with consequent lowering of symmetry below D_{3h}. Whether a loss of degeneracy has also occurred is less clear. It would appear that the interpretation involving interaction of $2\nu_4$ with ν_3 should also apply to the alkali-metal nitrates, whereas a single absorption at 1380 cm.$^{-1}$ is observed. Secondly, if the symmetry is C_3, then all four fundamental frequencies are infrared active. However, the ν_1 vibration observed by Buijs and Schutte was very weak for calcium, strontium, and barium nitrates, and in our measurements and those of Ferraro no ν_1 frequency was detected for either barium or strontium nitrate.

EXPERIMENTAL

Beryllium Chloride.—A single piece (2—3 g.) of pure beryllium metal was placed in a 1-l. flask, and dry chlorine passed through. The metal ignited on heating, and reaction then continued without further heating. Pure beryllium chloride settled as a flocculent white deposit on the walls of the flask.

Preparation of $Be(NO_3)_2,2N_2O_4$.—The reaction was carried out in two ways. (*a*) Beryllium

[15] Addison and Gatehouse, *J.*, 1960, 613.
[16] Wallwork, *Proc. Chem. Soc.*, 1959, 311.

chloride (2 g.) was dissolved in ethyl acetate (50 ml.) and dinitrogen tetroxide was added dropwise. At each addition, effervescence of nitrosyl chloride occurred; this was continued until effervescence no longer occurred. (*b*) Beryllium chloride was suspended in liquid dinitrogen tetroxide, and ethyl acetate was added dropwise. This was continued until effervescence ceased, when all the beryllium chloride had dissolved. The clear solution obtained by either method was warmed gently under a vacuum, thus removing the excess of dinitrogen tetroxide, nitrosyl chloride, and most of the ethyl acetate, until a viscous gum remained. An excess of liquid dinitrogen tetroxide (70 ml.) was added to this gum; pale yellow crystals of the *solvate* $Be(NO_3)_2,2N_2O_4$ gradually separated [Found: Be, 2·85; total N, 26·0; N_2O_4, 57·9; $Be(NO_3)_2,2N_2O_4$ requires Be, 2·84; total N, 26·5; N_2O_4, 58·0%]. They contained no chlorine.

A weighed quantity of the product in a phial was hydrolysed by breaking the phial in a closed bottle almost filled with 2N-sodium hydroxide. In this solution, total nitrogen was determined by a reductive Kjeldahl technique involving Devarda's alloy, and nitrite was determined by titration with ceric sulphate solution.

Beryllium content was determined by ignition to beryllium oxide. The product cannot be heated initially in the dry state since it is converted into beryllium oxide nitrate which vaporises. The weighed sample was first moistened with water, after which it could readily be ignited.

Beryllium Nitrate.—Analyses were carried out as described above [Found: Be, 6·8%; N, 20·7. $Be(NO_3)_2$ requires Be, 6·8%; N, 21·0%].

Preparation of $Mg(NO_3)_2,N_2O_4$.—Grignard magnesium (2—3 g.) was dissolved in a mixture of equal volumes (20 ml. each) of liquid dinitrogen tetroxide and ethyl acetate. The solution was filtered, and the excess of solvent removed under a vacuum until a viscous gum remained. On addition of an excess (70 ml.) of dinitrogen tetroxide, the adduct separated as a pale yellow powder. This was filtered off in a closed system and washed with dinitrogen tetroxide [Found: Mg, 10·4; total N, 22·1; N_2O_4, 36·2. Calc. for $Mg(NO_2)_2,N_2O_4$: Mg, 10·1; total N, 23·3; N_2O_4, 38·3%. The analyses are consistent with the formation of a product $Mg(NO_3)_2,0·92N_2O_4$]. N_2O_4 and total nitrogen contents were determined as for the beryllium compounds. Magnesium was determined by ignition to the oxide; it was not possible to obtain a satisfactory end-point when solutions in which this compound had been hydrolysed were titrated with solutions of EDTA.

Magnesium nitrate. Titration with solutions of EDTA was satisfactory for magnesium determinations on the simple *nitrate* [Found: Mg, 16·3; N, 18·7. $Mg(NO_3)_2$ requires Mg, 16·4; N, 18·9%].

Infrared Spectra.—These were determined by using an S.P. 100 Unicam spectrophotometer. Mulls were prepared in Nujol and in Halocarbon Oil, series 11—14. All transfers, and cell assembly, were carried out in a dry-box filled with argon. Exchange between covalent nitrates and the sodium chloride cell windows can produce erroneous bands in the spectrum which are typical of ionic nitrates. To avoid this possibility, the windows were protected by sheets (0·001 in. thick) of Polythene. The mull was placed between two sheets of Polythene, and the compensating cell also carried Polythene and mulling agent. To avoid the formation of interference patterns, it was also found necessary to put mulling oil between the windows and the Polythene sheets, so that in all there were three layers of mulling oil and two Polythene sheets between each pair of sodium chloride windows. Nevertheless, complete blanking of mulling agent and Polythene was readily achieved.

Ultraviolet Spectra.—All solutions in organic solvents were prepared in a dry-box. Spectra were recorded on a Unicam S.P. 500 spectrophotometer, with optically matched fused silica cells.

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