850. *Volatile and Anhydrous Nitrato-complexes of Metals: Preparation by the Use of Dinitrogen Pentoxide, and Measurement of Infrared Spectra.*

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New volatile anhydrous nitrato-complexes of hafnium, indium, palladium, and zinc have been prepared by the reaction of liquid dinitrogen pentoxide at room temperature with the metal, or its anhydrous chloride, or its hydrated nitrate. All of these complexes and also the volatile nitrato-complexes of beryllium, copper, iron, mercury, titanium, and zirconium, have been shown by infrared spectroscopy to contain the co-ordinated nitrato-group, and their structures are interpreted in terms of bridging and non-bridging nitrato-groups.

WEBER reported in 1872[1] that gaseous dinitrogen pentoxide reacted vigorously with arsenic and mercury, and slightly with cadmium, magnesium, and zinc, but that many other metals were passive. Guntz and Martin[2] used a solution of dinitrogen pentoxide in nitric acid to prepare anhydrous nitrates of cobalt(II), copper(II), manganese, and nickel, and Misciattelli[3] isolated anhydrous thorium nitrate by dehydrating the hydrate with dinitrogen pentoxide.

Schmeisser and his co-workers[4,5] studied the reaction of liquid dinitrogen pentoxide with a number of oxides and salts of metals and non-metals and discovered that certain compounds containing the nitrate group were volatile, *e.g.*, $CrO_2(NO_3)_2$, b. p. 28°/0·001, $VO(NO_3)_3$, b. p. 55—60°/vac. They were unable to obtain a volatile tin(IV) nitrate with liquid dinitrogen pentoxide, but prepared it from chlorine nitrate and tin(IV) chloride.[6] Addison and his co-workers independently showed the anhydrous nitrates of copper(II),[7] iron(III),[8] beryllium,[9] and mercury[8] to be volatile; these they made from the metals or their anhydrous chlorides and dinitrogen tetroxide in an ionising non-aqueous solvent, for instance ethyl acetate or methyl cyanide.

We have extended our previous work[10-13] on anhydrous and volatile compounds containing the nitrate group and now report the preparation of a number of new anhydrous compounds of metals containing the covalently bonded nitrato-group; we find that those of gold, hafnium, indium, palladium, and zinc can be sublimed *in vacuo*. We propose to term these *nitrato-complexes* to distinguish them from compounds which contain the nitrate ion. We have measured the infrared spectra of these complexes, and of a number of previously reported nitrato-complexes, and discuss their structure in terms of bridging and non-bridging nitrato-groups.

EXPERIMENTAL AND RESULTS

Preparation of Anhydrous Metal Nitrato-complexes.—A 1—10 g. sample of the metal, metal chloride, or metal nitrate hydrate, was placed in the bottom of a glass reaction tube of about 3 cm. inside diameter and 15 cm. long with a B29 socket connected to an adaptor with two B19

[1] Weber, *Sitzber. akad. Berlin*, 1872, 454; *Pogg. Ann.*, 1872, **147**, 113; *J. Prakt. Chem.*, 1872, **6**, 342.
[2] Guntz and Martin, *Bull. Soc. chim. France*, 1909, **5**, 1004; 1910, **7**, 313.
[3] Misciattelli, *Gazz. chem. ital.*, 1930, **60**, 882.
[4] Schmeisser and Lützow, *Angew. Chem.*, 1954, **66**, 230.
[5] Schmeisser, *Angew. Chem.*, 1955, **67**, 493.
[6] Schmeisser and Brändle, *Angew. Chem.*, 1957, **69**, 781.
[7] Addison and Hathaway, *Proc. Chem. Soc.*, 1957, 19.
[8] Addison, Hathaway, and Logan, *Proc. Chem. Soc.*, 1958, 51.
[9] Addison and Walker, *Proc. Chem. Soc.*, 1961, 242.
[10] Field and Hardy, *Proc. Chem. Soc.*, 1962, 76.
[11] Field and Hardy, *Proc. Chem. Soc.*, 1963, 11.
[12] Field and Hardy, *J.*, 1963, 5278.
[13] Hardy and Field, *J.*, 1963, 5130.

outlet sockets; all joints were lubricated with PTFE sleeves. The tube was connected by one B19 socket to the side-arm of a 1 l. glass flask containing about 200 g. of phosphoric oxide and fitted with a glass dropping funnel. A few ml. of AnalaR fuming nitric acid was added from the funnel and the apparatus was purged with the gaseous dinitrogen pentoxide produced by dehydration of the acid. The second B19 socket was then stoppered and the dinitrogen pentoxide condensed into the reaction tube by cooling in liquid nitrogen. Fresh additions of 10 ml. of fuming nitric acid were made about every 10 min. until the tube contained about 20 g. of solid dinitrogen pentoxide.

The tube with its adaptor was disconnected from the flask and stoppered and the liquid nitrogen trap removed. The tube was clamped upright and provision made for venting excess of dinitrogen pentoxide and gaseous reaction products; for this purpose stoppers and sockets were all fitted with PTFE sleeves to ensure that they did not " stick " and the stoppers were spring-loaded.

When the cream-white solid dinitrogen pentoxide was warmed to 30° it immediately melted to a pale amber liquid and the reaction started; the liquid dinitrogen pentoxide did not re-solidify at room temperature because of supercooling and dissolution of the products. With some starting materials (*e.g.*, $ZrCl_4$ [10]) reaction was complete in a few minutes at room temperature, with others [*e.g.*, $ZrO(NO_3)_2, xH_2O$] several hours were required to complete the dehydration at 21°. After gas ceased to be evolved or the reaction had proceeded overnight, the apparatus was attached to a vacuum line and the excess of dinitrogen pentoxide was distilled off at low pressure. Some of the nitrato-complexes, *e.g.*, those of zinc and zirconium, dissolved readily in liquid dinitrogen pentoxide and remained as very viscous liquid addition complexes, *e.g.*, $Zn(NO_3)_2, 2N_2O_5$, at room temperature. The complexes whether liquid or solid were slowly heated under vacuum to remove the nitrogen oxides of addition, care being taken to minimise " bumping." The liquids eventually solidified and pumping was continued until the residue showed a vapour pressure of about 10^{-3} mm., indicating that all the nitrogen oxides of addition had been removed. Dry nitrogen was admitted to the apparatus and the reaction tube removed from the vacuum line, stoppered, and transferred to a dry-box with phosphoric oxide desiccant for all subsequent manipulations.

An attempt was made to sublime each of the metal nitrato-complexes in a tube similar to the one in which they were prepared but fitted with a water-cooled finger and having a glass-wool plug between the finger and the solid to prevent material sputtering on the condenser. The tube was evacuated and the material slowly warmed and kept at about 30° above the temperature at which a condensate first appeared on the finger. Table 1 gives the actual temperatures and pressures of sublimation together with chemical analyses, and other information. Standard analytical methods were used for the metals, and the nitron method for the nitrate group.

Hydrated gold nitrate was prepared by heating gold oxide with concentrated nitric acid and evaporating the solution to dryness *in vacuo*, and the product was treated with liquid N_2O_5 at 25°, whereupon a liquid addition complex was obtained. The excess of N_2O_5 was removed *in vacuo*, and a small amount of a golden-yellow sublimate was obtained at $80°/4 \times 10^{-3}$ (gold content, 52·5% by weight by ignition to metal). We suggest that this compound is $Au(NO_3)_3$ (theory, 51·5% Au), but have been unable to determine the nitrate content quantitatively, or to measure its infrared spectrum because of its reaction with the mulling agents.

Attempts to Prepare Volatile Nitrato-complexes of Other Metals.—Attempts have been made to sublime anhydrous nitrato-complexes (prepared generally from hydrated nitrates) of several elements not mentioned in Table 1. The materials were not analysed at the stage at which the anhydrous nitrato-complex was thought to be present, but were slowly heated to about 300° in a vacuum to detect volatile products condensable on a water-cooled surface. Neodymium, erbium, nickel, thorium, and uranium did not give volatile nitrato-complexes; all decomposed to oxides. Aluminium gave variable results depending upon the starting material, and its behaviour calls for comment. The pure metal foil was unattacked by liquid dinitrogen pentoxide; AnalaR anhydrous chloride dissolved readily but the sublimate at 100°/0·05 mm. contained, in addition to nitrate, traces of iron due to sublimation of $FeNO(NO_3)_4$, and chloride, which a large excess of dinitrogen pentoxide failed to displace; " specpure " hydrated aluminium nitrate was converted into an oxide-nitrate, and in some experiments gave poor yields (mg. amounts) of a white sublimate which contained aluminium and nitrate, but which could not be characterised definitely.

Anhydrous ruthenium nitrato-complexes were prepared from (*a*) commercial " ruthenium

TABLE 1.

Physical properties and analytical data.

Element	Starting material (Metal or hydrated nitrate)	Nature of addition complex at 25° in contact with excess of liquid N_2O_5	Sublimation conditions		Empirical formula found	Method for analysis of metal	Analytical data				Colour of anhydrous nitrato-complex
			Temp.°	Pressure (mm. Hg)			Metal (%) Found	Calc.	Nitrate (%) Found	Calc.	
Cu	Metal foil or hydrated nitrate	Liquid	150°	10^{-3}	$Cu(NO_3)_2$	α-Benzoinoxime	33·1	33·8	65·9	66·2	Blue-green
Fe	Metal powder	Liquid	120	10^{-3}	$FeNO(NO_3)_4$	Oxine	17·1	16·7	75·3	74·2	Brown
Zn	Metal shot	Liquid	275	3×10^{-2}	$Zn(NO_3)_2$	Pyridine-CNS^-	33·2	34·5	64·0	65·5	White
Be	$BeCl_2$ or hydrated nitrate	Solid	125/150	5×10^{-2}	$Be_4O(NO_3)_6$	Beryllon	8·1	8·5	87·5	87·6	White
Hf	Hydrated nitrate	Liquid	100	10^{-2}	$Hf(NO_3)_4,N_2O_5$	Oxide	33·7	33·5	66·1	69·6	White
Pd	Hydrated nitrate	Liquid	80	3×10^{-3}	$Pd(NO_3)_2$	Reduction by formic acid to Pd metal	45·9	46·2	54·0	53·8	Brown
In	$InCl_3$	Liquid	130	10^{-3}	$In(NO_3)_3$	Oxide	36·8	38·2	63·8	61·8	White
Hg	Metal	Liquid	240	7×10^{-2}	$Hg(NO_3)_2$	As $Hg_5(IO_6)_2$	62·2	61·7	37·9	38·3	White

TABLE 2.

Infrared spectra of anhydrous nitrato-complexes of metals.

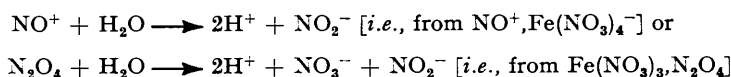| Complex	Ref.	Frequency, cm^{-1}, and strength of absorption peaks.
$Be_4O(NO_3)_6$	a *	1620s; (1345, 1305, *1270*, *1222*)mb; 1140w; 1031sb; 855s, 827w, 795mb, 760mb
$Cu(NO_3)_2$	a	*1570*sh, 1489vs; 1324vs, *1285*vs; 1038m, 1015s; 814vw, 796w, 768m, 759m
Cf.	18	1565vs, 1546vs, 1504m; 1344vsb, *1289*vs, sh, 1264vsb; 1038m, sh, 1016sb; 907w, 795w, 787sb, 770s
$FeNO(NO_3)_4$	a	1620—*1480*vsb; *1320*—*1200*vsb; 1030—1000sb; 795b, 760sb; 2310m (NO$^+$)
$Hg(NO_3)_2$	a	1540—1150s, vb; 1020mb; 789m, 736w
Cf.	18	1495m; 1376s; 1027vsb; 788vs, 750m
$In(NO_3)_3$	a	(*1599*, 1574, *1538*)vsb; *1270*—*1169*vsb; 1030m, sh, 982vsb; 793s, 777s, 692w, 665w; *570m*; 2330w
$Pd(NO_3)_2$	a	1630m, 1506s; 1275s, *1170*vs; 1000m; 775m, 762m, 734m, 647m
$Zn(NO_3)_2$	a	1557m; (*1340*, 1310, 1285, 1260)s; (1097, 1054, 1026)m; 809m, 796w, 769w
Cf.	18	1546s, 1502m; 1359vs, 1300vs; 1050sh, 1040s; 905w; 800s, 793s, 763s, 746m

* *a*, this work.

Frequencies in italics are tentatively assigned to the bridging nitrato-group.   s, strong;   m, medium;   w, weak;   b, broad;   v, very;   sh, shoulder.

trichloride" [which has been shown to be a mixture of ruthenium-(IV) and -(VI) species [14]], and (b) nitrosylruthenium trihydroxide prepared by precipitation from a solution of nitrosylruthenium nitrato-complexes in nitric acid. When the product from either method was heated to 100° *in vacuo*, ruthenium tetroxide was produced and could be condensed out in the liquid-nitrogen trap. The product from (b), after being pumped at 25°/0·001 mm. for 2 days in an attempt to remove co-ordinated oxides of nitrogen, had the empirical formula $RuNO(NO_3)_5(N_2O_4)_{0.75}$ [by colorimetric analysis of Ru (18·5%), and nitrate, and cerate titration of nitrite; its infrared spectrum confirmed the presence of the NO radical and the co-ordinated NO_3 group].

Properties and Reactions of Certain Nitrato-complexes.—(a) *The iron complex.* This, $FeNO(NO_3)_4$, was first prepared by Addison, Hathaway, and Logan [8] from anhydrous ferric chloride and liquid dinitrogen tetroxide in dry ethyl acetate. The product fractionally sublimed when heated *in vacuo* at 120°, yielding a small quantity of white crystals (Fe : NO_3 ratio 1 : 3] in part of the apparatus and a large amount of brown needle-shaped crystals [analysed as $FeNO(NO_3)_4$] on a cooled condenser.

We have prepared $FeNO(NO_3)_4$ from iron powder and liquid dinitrogen pentoxide. On sublimation a hard brown film (not separate crystals) was obtained on the cold condenser and we did not observe white crystals in the apparatus. The infrared spectrum indicated the NO^+ group (2310 cm.$^{-1}$) and the strongly co-ordinated nitrato-group. Titration of a solution in water with ceric sulphate indicated 7% of the amount of nitrite expected from hydrolysis or reaction according to the equations

$$NO^+ + H_2O \longrightarrow 2H^+ + NO_2^- \text{ [}i.e.,\text{ from } NO^+, Fe(NO_3)_4^-\text{] or}$$

$$N_2O_4 + H_2O \longrightarrow 2H^+ + NO_3^- + NO_2^- \text{ [}i.e.,\text{ from } Fe(NO_3)_3, N_2O_4\text{]}$$

Thus the NO group is either strongly bound to the iron atom and not completely hydrolysed in water, or the small amount of nitrite arose from nitrato-groups as Addison and Walker found for beryllium nitrate.[15] Hydrolysis of the complex with *alkali* gives a ratio of nitrate ions to nitrite ions of 4 : 1.[8]

(b) *The beryllium complex*, $Be_4O(NO_3)_6$. Beryllium metal reacted too slowly with liquid dinitrogen pentoxide to be useful practically, but both anhydrous beryllium chloride and hydrated beryllium nitrate reacted readily with the reagent to give a good yield of the volatile complex $Be_4O(NO_3)_6$. Beryllium chloride gave a pale straw-coloured lower liquid phase from which removal of the solvent produced a cream powder, presumably $Be(NO_3)_2, xN_2O_5$. This decomposed *in vacuo* at 55°, first giving off oxides of nitrogen and frothing violently, and then setting to a pumice-like solid, presumably $Be(NO_3)_2$ (cf. Addison and his co-workers [9]). At 125°/0·05 mm. it sublimed rapidly and analysis of the sublimate agreed with the formula $Be_4O(NO_3)_6$.

When this complex was prepared by the dehydration of hydrated beryllium nitrate with dinitrogen pentoxide the sequence of events was different and the hexanitrato-complex sublimed at 150°/0·05 mm. without a sharp intermediate decomposition stage; differences of this kind were also observed for volatile nitrato-complexes of other metals prepared from hydrates.

(c) *The zinc complex*, $Zn(NO_3)_2$. Zinc powder dissolved readily in liquid dinitrogen pentoxide and produced a viscous liquid below the excess of reagent. When the latter was pumped off at 20° a lemon yellow syrup was left which at 100°/0·01 mm. set to a white microcrystalline solid. At 200°/0·01 the solid melted and gave off oxides of nitrogen over a long period. When raised to 275°/0·03 the dinitrato-zinc complex sublimed on a cold finger at *ca.* 18°, 50 mg. of sublimate being collected in 1 hr. No evidence was found of the formation of the complex $Zn_4O(NO_3)_6$ under these conditions, although it might be expected to exist by analogy with the volatile basic acetate, $Zn_4O(Ac)_6$, which is thought to be isostructural with the volatile basic acetate of beryllium.

Addison, Lewis, and Thompson [16] prepared anhydrous zinc nitrate from powdered zinc and liquid dinitrogen tetroxide. By removing the excess of tetroxide at 21° they obtained the addition complex $Zn(NO_3)_2, 2N_2O_4$ as a freely flowing powder, which lost two molecules of N_2O_4 at 100°/760 mm. in 6 hr. The anhydrous $Zn(NO_3)_2$ decomposed rapidly above 240° under atmospheric pressure.

[14] Woodhead and Fletcher, UKAEA Document AERE-R4123 (1962).
[15] Addison and Walker, *J.*, 1963, 1220.
[16] Addison, Lewis, and Thompson, *J.*, 1951, 2829.

(d) *The hafnium complex.* Analyses of several preparations of this complex gave weight percentages of hafnium and nitrate which agreed with those expected for the formula $Hf(NO_3)_4,N_2O_5$, rather than $Hf(NO_3)_4$. Spectrographic analysis confirmed that the sublimate was not contaminated with zirconium, which would have led to an apparently low weight percentage of hafnium determined as the oxide. The hafnium complex therefore appears to sublime as an addition complex with one molecule of dinitrogen pentoxide, which behaviour is different to that of the volatile nitrato-complexes of titanium, zirconium and tin in the same periodic group.

Measurement of Infrared Spectra.—Specimens of the solid nitrato-complexes were made into mulls with Nujol, or with hexachlorobutadiene, and mounted between 1 mm. thick silver chloride plates. This was done in a dry-box to minimise absorption of water vapour. Spectra were measured in the 2—15 μ region with a Hilger H800 instrument with a rock-salt prism. Some spectra were measured in the 10—35 μ region for Nujol mulls between 3 mm. thick polythene plates with the aid of a cæsium bromide prism. Spectra were measured over a period to detect whether the complexes reacted with the mulling agent as we found with the titanium complex;[12] no significant reaction was detected during the time of measurement of the spectra except for $Ti(NO_3)_4$, for which complex the spectrum is corrected. Unusually broad bands were obtained for the complexes of Pd, Fe, Hg, and Be but this may have been due to large particle size, since these particular mulls were difficult to grind even in a dry-box. The instrument was calibrated with a polystyrene film.

DISCUSSION

Preparation and Uses of Volatile and Anhydrous Nitrato-complexes of Metals.—The use of liquid dinitrogen pentoxide for the preparation of anhydrous nitrato-complexes of metals has certain advantages over the other principal reagent, dinitrogen tetroxide.[7-9] Metals or metal salts usually fail to react with dinitrogen tetroxide unless an ionising solvent such as ethyl acetate or methyl cyanide is present; such solvents often co-ordinate strongly to the metal ion and render the pure anhydrous nitrato-complex or metal nitrate difficult to isolate. Liquid dinitrogen pentoxide on the other hand reacts directly with many metals, metal chlorides, and hydrated metal nitrates, and anhydrous nitrato-complexes can readily be isolated, particularly if they are volatile. It seems probable that anhydrous nitrato-complexes of many metals other than those so far reported, and also of non-metals, could be prepared with this reagent, and that certain of the complexes may be appreciably volatile.

The non-volatility of some of the anhydrous nitrates and nitrato-complexes, and the different degrees of volatility of others, enables separation processes to be devised, some of which may be useful for the purification of such rarer metals as beryllium, niobium, palladium, and gold. The volatility of nitrato-complexes may also enable ion beams of certain elements such as palladium to be produced, for which other sufficiently volatile compounds are not available, *e.g.*, for the electromagnetic separation of isotopes.

Infrared Spectra of Anhydrous Nitrato-complexes of Metals.—The infrared spectra of the anhydrous nitrato-complexes of metals prepared in this work and not previously described by us are in Table 2. In previous work on the infrared spectra of nitrato-complexes, band assignments have been made on the assumption that unidentate bonding occurs, and that the group has the form $-O'NO_2$, with C_{2v} symmetry and six fundamental vibrations ($\nu_1 - \nu_6$) with the following assignments and ranges of frequency:[17,18]

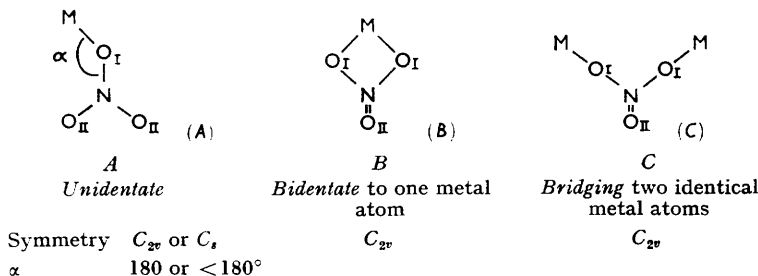| Species	$\nu_1\ (A_1)$	$\nu_2\ (A_1)$	$\nu_3\ (A_1)$	$\nu_4\ (B_1)$	$\nu_5\ (B_1)$	$\nu_6\ (B_2)$
Assignment	NO_2 stretch, symmetric	NO' stretch	NO_2 bend, symmetric	NO_2 stretch, asymmetric	NO_2 bend, asymmetric	Out of plane
Frequencies found (cm.⁻¹)	1290—1253	1034—970	~739	1531—1481	~713	800—781

[17] Gatehouse, Livingstone, and Nyholm, *J.*, 1957, 4222.
[18] Addison and Gatehouse, *J.*, 1960, 613.

The infrared spectra of all the anhydrous nitrato-complexes that we have prepared contain bands at frequencies which are broadly similar to those given above for the co-ordinated nitrato-group. However, the strong band usually assigned to the asymmetric stretching vibration (ν_4) in some of these occurs [10,11] at a frequency >1600 cm.$^{-1}$, and the difference between the frequency of this band and of that usually assigned to the symmetric stretching vibration (ν_1) is over 400 cm.$^{-1}$. These values are the highest reported for nitrato-complexes of metals and the separation of the two bands is greater than that found [19] for alkyl nitrates in which the nitrato-group is covalently bonded to a carbon atom. We propose to relate these high values to the presence of bridging nitrato-groups.

In comparing the different modes of bonding (A, B, C, below) quantitatively it will be necessary to take into account the M–O vibrations, and not to restrict discussion to the $-NO_3$ group alone.

	A	B	C
	Unidentate	*Bidentate* to one metal atom	*Bridging* two identical metal atoms
Symmetry	C_{2v} or C_s	C_{2v}	C_{2v}
α	180 or $<180°$		

The number, frequency, and assignment of the vibrations for models B and C has not yet been given, but is being studied.[20] However, it is possible to compare the bonding of the nitrato-group qualitatively with that of the carbonato-group, which (a) is isoelectronic with the nitrato-group, (b) has a similar mass-distribution, (c) is known to bond as a unidentate ligand, as a bidentate ligand, and by bridging between two other groups, and (d) has been studied in detail by Nakamoto and his co-workers.[21] Hathaway [22] postulated bidentate bonding for the perchlorato-ligand in anhydrous perchlorato-complexes, but the different symmetry and mass distribution of this ligand makes comparison with the nitrato-group more difficult.

In general, the three fundamental stretching vibrations for models B and C (which are expected to have the same symmetry, C_{2v}) in the frequency range 950—1650 cm.$^{-1}$ are expected to be in the order:

$$\nu_{NO_{II}} > \nu_{O_I NO_I \text{ (asym)}} > \nu_{O_I NO_I \text{ (sym)}},$$

whereas in the unidentate model A (also symmetry C_{2v}) they are

$$\nu_{O_{II}NO_{II} \text{ (asym)}} > \nu_{O_{II}NO_{II} \text{ (sym)}} > \nu_{NO_I}$$
$$(1531–1481) \qquad (1290–1253) \qquad (1034–970)$$

We prefer to use these symbols to describe the high-frequency bands in Table 2, instead of the previous convention,[17] pending the publication of a more detailed analysis which is likely to require nine fundamental vibrations for models A and B (and probably twelve for model C) in a similar way to the treatment of carbonato-complexes by Nakamoto.[21]

The complexes $Be_4O(NO_3)_6$, $NbO(NO_3)_3$,[11] and $Ti(NO_3)_4$,[12] have strong bands, now tentatively assigned to the $\nu_{NO_{II}}$ stretching vibration in model C, at 1620, 1646, and 1628 cm.$^{-1}$, respectively, together with strong bands ($\nu_{O_I NO_I \text{ (asym)}}$ model C) at 1222—1270, 1213, and 1225 cm.$^{-1}$, respectively. These frequencies are outside the limits previously found [17]

[19] Bellamy, "The Infra-red Spectra of Complex Molecules," Methuen, London, 1954.
[20] Hardy, unpublished work; Addison and co-workers, personal communication.
[21] Nakamoto, "Infrared Spectra of Inorganic and Co-ordination Compounds," Wiley Sons, London, 1963, p. 159.
[22] Hathaway and Underhill, *J.*, 1961, 3091.

for complexes in which the unidentate nitrato-group is present, and it has been suggested [9] that the beryllium complex contains bridging nitrato-groups by analogy with the bridged acetato-complex, $Be_4O(Ac)_6$. We suggest that these three nitrato-complexes probably contain nitrato-groups only in the bridged form in the solid state.

The complexes, $Zr(NO_3)_4$, $Pd(NO_3)_2$, $In(NO_3)_3$, $Cu(NO_3)_2$, and $FeNO(NO_3)_4$ contain strong bands both within and outside the ranges previously found for unidentate nitrato-groups. The copper complex is thought [23] to contain bridging nitrato-groups and it is probable that they all contain bridging *and* either unidentate nitrato-groups, or nitrato-groups bidentate to one metal atom (since it has been shown that the frequencies found for nitrato-aquo-uranyl complexes containing bidentate nitrato-groups also fall within the ranges for unidentate nitrato-groups [24]).

We suggest that the occurrence of a strong band at a frequency greater than about 1560 cm.$^{-1}$ together with a strong band at a frequency less than about 1270 cm.$^{-1}$ may indicate a *bridging* nitrato-group. Much more information from X-ray, neutron, or electron diffraction measurements will be needed before the infrared spectra of these anhydrous nitrato-complexes can be explained quantitatively. The measurement of infrared spectra in the region of 300—450 cm.$^{-1}$ where the M—O stretching vibrations are expected to occur, would be particularly useful in determining whether a complex contains unidentate or bidentate nitrato-groups, but no information on this region has yet been published for nitrato-complexes of metals.

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        HARWELL, BERKS.

[23] Wallwork, *Proc. Chem. Soc.,* 1959, 311.
[24] Allpress and Hambly, *Austral. J. Chem.,* 1959, **12,** 569.