

## Adducts of Coordination Compounds. IV<sup>1</sup>.-Nitric Acid Adducts of Ammine Complexes of Trivalent Metals

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The solid adducts of the type  $[M(NH_3)_6](NO_3)_3 \cdot HNO_3$  and  $[M(NH_3)_5(H_2O)](NO_3)_3 \cdot HNO_3$ , where  $M = Cr, Co$  and  $Rh$ , have been characterized by means of analyses, solution studies and infra-red spectroscopy. The mode of attachment of the nitric acid molecule (through hydrogen bonds to nitrate ions) is discussed; supporting evidence from deuterated species is presented. It is suggested that the ion  $[H(NO_3)_4]^{3-}$  may be present in the solids, containing protons tetrahedrally surrounded by oxygen atoms.

### Introduction

A number of adducts of coordination compounds with protonic acids are reported, mostly in the older literature. The nature of these compounds has received some attention recently, and some novel hydrogen-bonded species have been found responsible for the presence of the «added» protonic acid. The added hydrogen halide in certain dihydrates of complex halides has thus been shown<sup>2</sup> to occur as the bis-aquo-hydrogen ion.

Nitric acid forms adducts with the nitrates of several coordination cations. In the seven nitric acid adducts represented (1) by<sup>3</sup>  $trans-[MA_4X_2]NO_3 \cdot HNO_3$ , where (a)  $M = Rh, A = py, X = Cl$  or  $Br$  (b)  $M = Rh, A = \frac{1}{2}$  bipy,  $X = Cl$ , (c)  $M = Co, A = py, X = Cl$  and (2) by<sup>1</sup>  $trans-[Coen_2XY](NO_3) \cdot HNO_3$ , where (a)  $X = Y = NO_2$ , (b)  $X = NO_2, Y = Cl$ , (c)  $X = NO_2, Y = NO_3$ , the nitric acid is present as the hydrogen dinitrate ion,  $[H(ONO_2)_2]^-$ . Another class of compounds of nitric acid is represented by  $[M(NH_3)_5L](NO_3)_3 \cdot HNO_3$ , where  $M = Cr, Co$  or  $Rh$ , and  $L = NH_3$  or  $H_2O$ . The present report concerns these latter compounds, where the bonding of the nitric acid added differs markedly from that in the hydrogen dinitrate salts.

The first example, hexamminecobalt(III) nitrate nitric acid, was described<sup>4a</sup> by S.M. Jørgensen in 1891; it was made by crystallising the parent nitrate from concentrated nitric acid; the other five were prepared by similar means. Wendt and Jander confirmed<sup>4b</sup> the

existence of the adducts containing  $[Co(NH_3)_6]^{3+}$  and  $[Cr(NH_3)_6]^{3+}$ . We have reprepared all six compounds, and confirm their stoichiometry. The association of the nitric acid is not quite so firm as in the hydrogen dinitrate salts earlier described; with these hexammine adducts, the nitric acid is very slowly lost in a dry atmosphere at ca. 50°; thermogravimetric analysis confirms that it is lost rather readily; the solid residue is the parent nitrate. The nitric acid is also readily removed by polar solvents. For example, all six adducts, when dissolved in water, give strongly acid solutions, whose conductivities (and pH's) correspond to a 1:1 mixture of the parent nitrate and nitric acid. We have not found a solvent which preserves the linkage between the nitric acid and the complex. The electronic spectra of solutions of the adducts in water are identical (in the regions due to d-d transitions) with those of the parent nitrates. The adducts are clearly salts of the unchanged parent cations, with nitric acid bonded in the crystal lattice. Since the stoichiometries are always 1:1, and since marked changes in infra-red spectra occur on forming the adducts, the compounds could not be clathrates, or inclusion compounds.

*Infra-red Spectra. General.* The new absorptions arising from the added nitric acid molecule are similar throughout the range of six complexes studied (the new bands in the region ca. 800  $cm^{-1}$  for the protonated complexes of chromium(III) are obscured by the  $NH_3$  deformation mode at 774  $cm^{-1}$ , but are apparent in the complexes containing  $ND_3$ ). The new bands are shown for the complexes  $[M(NH_3)_6](NO_3)_3 \cdot HNO_3$  in Figure 1 (those for the aquo-complexes  $[M(NH_3)_5(H_2O)](NO_3)_3 \cdot HNO_3$  show minor differences, notably around 2500  $cm^{-1}$  and 1040  $cm^{-1}$ ).

The assignments given are based on those<sup>5</sup> of Cohn, Ingold and Poole, for the  $HNO_3$  molecule. The absorption around 2500  $cm^{-1}$  arising from overtones and combination bands is discussed below in detail. The absorption at ca. 1040  $cm^{-1}$  arises from the formally forbidden  $\nu_1$  mode of the nitrate ions but again changes markedly on formation of the adduct, as discussed below.

The absorption bands, (1)-(4) and (6) of Figure 1 correspond closely to those<sup>5</sup> of nitric acid itself. How-

(1) Part III: K. Garbett, R. D. Gillard and R. Ugo, *J. Chem. Soc., A*, 1137 (1966).

(2) D. Dollimore, R. D. Gillard and E. D. McKenzie, *J. Chem. Soc.*, 4479 (1965).

(3) R. D. Gillard and R. Ugo, *J. Chem. Soc., A*, 549 (1966).

(4) (a) S. M. Jørgensen, *J. prakt. Chem.*, 44, 63-6 (1891).

(4) (b) H. Wendt and G. Jander, *Z. Anorg. Chem.*, 259, 309 (1949).

(5) H. Cohn, C. K. Ingold and H. G. Poole, *J. Chem. Soc.*, 4272 (1952).

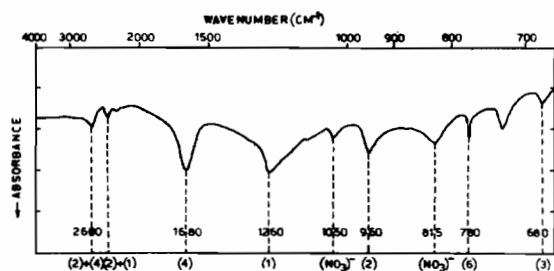
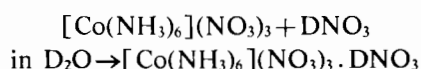


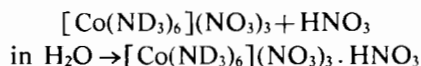
Figure 1. New absorption arising from the presence of nitric acid in the adducts. The diagram was constructed by subtracting the spectrum of  $[\text{M}(\text{NH}_3)_6](\text{NO}_3)_3 \cdot \text{HNO}_3$ . The assignments are based on those given in ref. 5.

ever, two facts lead us to believe that the O-H bond of the nitric acid is closely involved in the bonding of the acid. First, we are unable to find any absorption which can reasonably be assigned to O-H stretching. The frequencies<sup>5</sup> for the stretching mode in  $\text{HNO}_3$  and  $\text{DNO}_3$  are 3560 and 2627  $\text{cm}^{-1}$ . In our compounds with deuterated ligands, such as  $[(\text{Co}(\text{ND}_3)_6)(\text{NO}_3)_3]\text{HNO}_3$  discussed below, any band due to OH above 3000  $\text{cm}^{-1}$  would have been detected. Similarly, in  $[\text{Co}(\text{NH}_3)_6](\text{NO}_3)_3 \cdot \text{DNO}_3$  we would expect to have seen any new band due to O-D stretching around 2600  $\text{cm}^{-1}$ , but in fact the spectrum is essentially identical with that of  $[\text{Co}(\text{NH}_3)_6](\text{NO}_3)_3 \cdot \text{HNO}_3$ . Presumably this stretching band is concealed under one of the bands below 2000  $\text{cm}^{-1}$ . Secondly, the only other frequency of the nitric acid molecule which is grossly shifted in the adduct is the stretching of N-O(H), (2) in the earlier nomenclature.<sup>5</sup> This occurs at  $950 \pm 10 \text{ cm}^{-1}$  in the six adducts, but at 886  $\text{cm}^{-1}$  in  $\text{HNO}_3$  vapour.

**Ammine frequencies.** The adducts precipitate very rapidly at room temperature from an aqueous solution of the parent nitrate treated with concentrated nitric acid. We took advantage of this as follows :



and



The exchange of the ammine protons or deuterons in the acid conditions is negligible. The isotopic purity of the two products was also revealed by their infrared spectra as discussed below.

The vibrations of the coordinated  $\text{NH}_3$  unit in these hexammines are well known; they have been assigned<sup>6</sup> as shown in Table I, which also includes the corresponding absorptions of the adducts.

The nomenclature is that of Nakamoto;<sup>6</sup> only those bands which can be assigned with some certainty are given, i.e.  $\delta_s(\text{NH}_3)$  at ca. 1250  $\text{cm}^{-1}$  is omitted in nearly all cases because of overlap with nitrate absorption, and, for the complexes  $[\text{M}(\text{NH}_3)_5(\text{H}_2\text{O})](\text{NO}_3)_3$  and their adducts, the deformation frequency at ca. 1600  $\text{cm}^{-1}$  is composite [ $\delta_d(\text{NH}_3)$  and  $\delta(\text{H}_2\text{O})$ ]. The order  $\nu_3 > \nu_1$  for the  $\text{NH}_3$  stretching frequencies is based on

Table I. Vibrations of coordinated ammonia in parents and adducts

Complex	$\nu(\text{NH}_3)$ <sup>a</sup>		$\delta_d(\text{NH}_3)$	$\nu_r(\text{NH}_3)$
	$\nu_{as}$	$\nu_s$		
$[\text{CoA}_6](\text{NO}_3)_3$ <sup>c</sup>	3290	3200	1625 <sup>b</sup>	849
$[\text{CoA}_6](\text{NO}_3)_3 \cdot \text{HNO}_3$	3290	3195	1630	861
$[\text{CoA}_6](\text{NO}_3)_3$	3300	3200	1620	765
$[\text{CrA}_6](\text{NO}_3)_3 \cdot \text{HNO}_3$	3290	3190	1625	764 <sup>d</sup>
$[\text{RhA}_6](\text{NO}_3)_3$	3300	3200	1660	860
$[\text{RhA}_6](\text{NO}_3)_3 \cdot \text{HNO}_3$	3300	3200	1660	860
$[\text{CoA}_3\text{W}](\text{NO}_3)_3$	3270	3200	1625 <sup>c</sup>	774
$[\text{CoA}_3\text{W}](\text{NO}_3)_3 \cdot \text{HNO}_3$	3270	3200	1635	775
$[\text{CrA}_3\text{W}](\text{NO}_3)_3$	3300	3200	—	771
$[\text{CrA}_3\text{W}](\text{NO}_3)_3 \cdot \text{HNO}_3$	3310	3215	—	772
$[\text{RhA}_3\text{W}](\text{NO}_3)_3$	3330	3225	—	860
$[\text{RhA}_3\text{W}](\text{NO}_3)_3 \cdot \text{HNO}_3$	3325	3225	—	860

<sup>a</sup> Values in  $\text{cm}^{-1}$ , notation from ref. 6. <sup>b</sup> Ref. 6 gives 1618; however, all the bands are rather broad. <sup>c</sup> A denotes  $\text{NH}_3$ , W denotes  $\text{H}_2\text{O}$ . <sup>d</sup> A band at 1245  $\text{cm}^{-1}$  is probably  $\delta_s(\text{NH}_3)$ . <sup>e</sup> As mentioned in the text, this region is complex in the aquo-ammine complexes.

the isotopic shift experiments with hexamminecobalt(III) nitrate discussed in detail below.

The principal point is that little change occurs, even in the deformation frequency at ca. 800  $\text{cm}^{-1}$ , which is highly sensitive to hydrogen bonding. We therefore conclude that hydrogen bonding involving coordinated amines is unimportant in giving stability to the adducts.

The spectrum of the completely deuterated parent nitrate,  $[\text{Co}(\text{ND}_3)_6](\text{NO}_3)_3$  gave rise to three points requiring comment.

Judging by the complete absence of the bands at 1618 and 840  $\text{cm}^{-1}$ , due to  $\text{NH}_3$ , deuteration is complete. However, there appears a band of medium strength at 3200  $\text{cm}^{-1}$ , which we initially thought was due to N-H stretching of unsubstituted ligands. This is not the case, since we have exhaustively crystallized the salt from pure heavy water and have confirmed the absence of the other  $\text{NH}_3$  bands. Further, the position of this band (3200  $\text{cm}^{-1}$ ) differs from that of the  $\text{NH}_3$  ligand bands ( $\sim 3250 \text{ cm}^{-1}$ ). We assign the band at 3200  $\text{cm}^{-1}$  to a combination band of nitrate or possibly an overtone.

The second feature in the deuterated compounds is the strong splitting of the N-D stretching frequencies, by ca. 150  $\text{cm}^{-1}$ . There is no splitting of this size in the corresponding N-H stretching region at 3250  $\text{cm}^{-1}$  (so that coupling with a lattice mode is ruled out). Comparing our results for isotopic shifts with those of  $\text{NH}_3$  and  $\text{ND}_3$  vapours, we can assign the bands as shown (Table II) to the two infra-red active N-D stretching frequencies. This is, to our knowledge, the only evidence that the order  $\nu_3 > \nu_1$  in ammonia is maintained on complexing.

In fully deuterated  $[\text{Co}(\text{ND}_3)_6](\text{NO}_3)_3$ , a small band at ca. 1750  $\text{cm}^{-1}$ , which appears as a shoulder in all twelve protonated parent nitrates and adducts, is now sharply defined, though weak. It is not shifted in the deuterated compound. It therefore does not arise from an ammine vibration, but from nitrate ion, and is presumably a combination band, perhaps ( $\nu_1 + \nu_4$ ), in the notation of a recent review.<sup>7</sup>

(6) K. Nakamoto, «Infra-red Spectra of Inorganic and Coordination Compounds», John Wiley, New York, 143 (1963).

(7) B. O. Field and C. J. Hardy, *Quart. Revs.*, 18, 361 (1964).

**Table II.** Isotope shifts in ammine stretching frequencies

	$[\text{Co}(\text{NH}_3)_6](\text{NO}_3)_3$	$[\text{Co}(\text{ND}_3)_6](\text{NO}_3)_3$	$\nu_{\text{H}} : \nu_{\text{D}}$	$\text{NH}_3$	$\text{ND}_3$	$\nu_{\text{H}} : \nu_{\text{D}}$
$\nu_3$	3290 <sup>a</sup>	2480	1.32	3414 <sup>a</sup>	2556 <sup>a</sup>	1.33
$\nu_1$	3200 <sup>a</sup>	2310	1.39	3336 <sup>a</sup>	2420 <sup>a</sup>	1.38
$(\nu_3 - \nu_1)$	90	170		78	136	

<sup>a</sup> From Ref. 6.

*Other features.* (a) As shown in Figure 2, in the complexes  $[\text{M}(\text{NH}_3)_6](\text{NO}_3)_3$ , there are absorptions at ca. 2400-2600  $\text{cm}^{-1}$  which may be attributed to overtones and combination bands of the nitrate ions (they are absent in the chlorides,  $[\text{M}(\text{NH}_3)_6]\text{Cl}_3$ ). In the adducts  $[\text{M}(\text{NH}_3)_6](\text{NO}_3)_3 \cdot \text{HNO}_3$ , this region alters completely (Figure 2). This further suggests that the nitrate ions are modified by the addition of nitric acid. Further, the new absorptions in this region correspond closely to the overtone  $[2 \times (1)]$  and combination band  $[(2) + (4)]$  observed<sup>5</sup> in nitric acid vapour at 2627  $\text{cm}^{-1}$  and 2585  $\text{cm}^{-1}$ . The region 2400-2600  $\text{cm}^{-1}$  also changes for  $[\text{M}(\text{NH}_3)_5(\text{H}_2\text{O})](\text{NO}_3)_3$  on formation of the adduct, but not in such a clear-cut way (though the changes are similar).

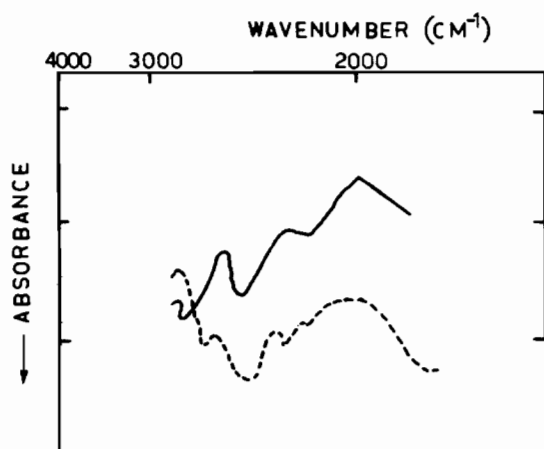


Figure 2. The region of the spectrum from 3000 to 2000  $\text{cm}^{-1}$ . — Parent nitrate,  $[\text{Rh}(\text{NH}_3)_6](\text{NO}_3)_3$ . - - - - Adduct,  $[\text{Rh}(\text{NH}_3)_6](\text{NO}_3)_3 \cdot \text{HNO}_3$ .

The spectra of the adducts also differ markedly from those of the parents in the region around 1000  $\text{cm}^{-1}$ , where, in the complexes  $[\text{M}(\text{NH}_3)_6](\text{NO}_3)_3$ , a sharp absorption of low intensity occurs at ca. 1040  $\text{cm}^{-1}$ . It arises from the  $\nu_1$  mode of nitrate ion, infra-red forbidden for the isolated ion, but appearing weakly here, presumably through the operation of site symmetry lower than  $D_{3h}$ . This band becomes much stronger and broader in the adducts of the hexamine cations. In the three compounds,  $[\text{M}(\text{NH}_3)_5(\text{H}_2\text{O})](\text{NO}_3)_3 \cdot \text{HNO}_3$  it actually becomes complex, as shown in Figure 3. This change again presumably arises because the nitrate ions have now acquired sites of differing symmetry, i.e. they are involved in bonding the proton.

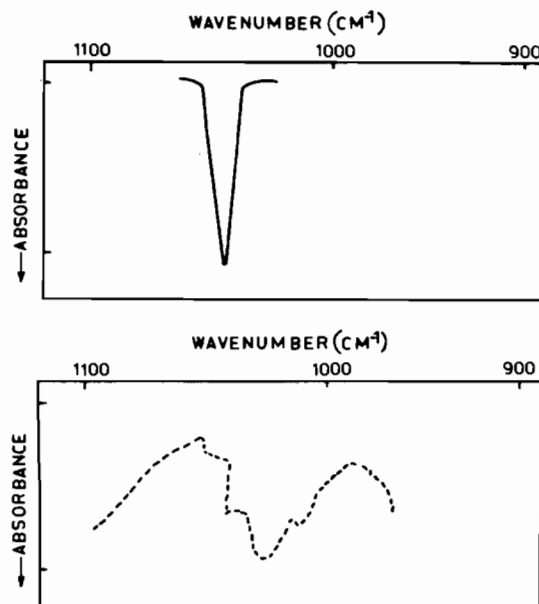


Figure 3. The change in the absorption at ca. 1040  $\text{cm}^{-1}$ . — Parent,  $[\text{Rh}(\text{NH}_3)_5(\text{H}_2\text{O})](\text{NO}_3)_3$ . - - - - Adduct,  $[\text{Rh}(\text{NH}_3)_5(\text{H}_2\text{O})](\text{NO}_3)_3 \cdot \text{HNO}_3$ .

*The Bonding of the Nitric Acid Molecule.* As outlined above, all the major changes in the vibrational spectrum on passing from parent nitrate to adduct arise from nitrate ions and nitric acid—the ammonia vibrations are almost unchanged. The bonding of the nitric acid therefore involves hydrogen bonding  $(\text{O}_2\text{N})\text{O}-\text{H}-\text{O}(\text{NO}_2)$  and not  $(\text{M})-\text{N}-\text{H}-\text{O}(\text{HNO}_2)$ . However, the spectrum of the «added» nitric acid is not similar to that of either form<sup>3,4</sup> of the hydrogen dinitrate ion, so that a more complicated scheme is required, involving the nitric acid molecule and more than one nitrate ion. There is added indication that this is the case in the identity of the spectra of  $[\text{Co}(\text{NH}_3)_6](\text{NO}_3)_3 \cdot \text{HNO}_3$  and  $[\text{Co}(\text{NH}_3)_6](\text{NO}_3)_3 \text{DNO}_3$ . The infrared spectra in the present adducts may suggest the presence of the hydrogen tetranitrate anion, as in  $[\text{M}(\text{NH}_3)_5\text{L}][\text{H}(\text{ONO}_2)_4]$ . In view of the absence of recognisable O-H stretching modes, the complex anion may be tetrahedral,<sup>8</sup> with the proton more or less equally bonded to the four monodentate nitrate group. A single crystal X-ray analysis is being undertaken to determine the stereochemistry of the complex anion.

The present and earlier papers<sup>2,3,9</sup> represent a useful approach to identifying species,  $\text{B}^{n-}$ , present (possibly in extremely low concentration) in solutions at labile

(8) G. Dobinson, R. Mason and D. R. Russel, *Chem. Comm.*, 62 (1967).

(9) B. D. Faithful, R. D. Gillard, D. G. Tuck and R. Ugo, *J. Chem. Soc., A*, 1185 (1966).

equilibrium. The charge and geometry of cations,  $A^{n+}$ , occasionally serves to make the solubility of the 1:1 salt, AB, very low, and, as precipitation of AB occurs, the equilibrium in solution shifts, thereby effectively concentrating B in the solid phase. In the present case, the triply charged  $[H(NO_3)_4]^{3-}$  is precipitated by the triply charged  $[M(NH_3)_5L]^{3+}$ .

We have been unable to make adducts with nitric acid from a range of nitrates of cobalt ammine complexes,  $[Co(NH_3)_5X]^{2+}$ , where  $X = Cl, NO_3$  or  $NO_2$ . The charge type of the cation is therefore important among these factors. Further, no adduct could be obtained from the bisquo species  $[Co(NH_3)_4(H_2O)_2](NO_3)_3$ .

**Deuteration.**  $[Co(NH_3)_6](NO_3)_3$  was recrystallised five times from heavy water, giving  $[Co(ND_3)_6](NO_3)_3$ . As discussed in the text, the isotopic substitution was essentially complete. A solution of  $[Co(ND_3)_6](NO_3)_3$  in water was then treated with nitric acid, and the precipitated  $[Co(ND_3)_6](NO_3)_3 \cdot HNO_3$  collected as rapidly as possible.

Deuteronitric acid was made by the interaction<sup>5</sup> of dinitrogen pentoxide (made in a stream of ozone) and heavy water. This deuteronitric acid was used to precipitate the salt  $[Co(NH_3)_6](NO_3)_3$  dissolved in  $D_2O$ . The product,  $[Co(NH_3)_6](NO_3)_3 \cdot DNO_3$ , was collected as rapidly as possible.

**Table III.** Analytical data and properties

Complex <sup>e</sup>	Calc.				Found				$\Lambda^b$
	H	N	HNO <sub>3</sub>	pH <sup>b</sup>	H	N	HNO <sub>3</sub>	pH <sup>b</sup>	
$[CoA_6](NO_3)_3 \cdot HNO_3$	4.66	34.30	15.45	3	4.62	34.10	15.10	3.1	800
$[CoA_6](NO_3)_3$									430
$[CrA_6](NO_3)_3 \cdot HNO_3$	4.74	34.90	15.70	3	4.74	34.79	15.50	3	810
$[CrA_6](NO_3)_3$									430-5
$[RhA_6](NO_3)_3 \cdot HNO_3^c$	4.18	30.80	13.85	3	4.27	31.30	13.90	3	850
$[RhA_6](NO_3)_3^c$									450
$[CoA_5W](NO_3)_3 \cdot HNO_3$	4.42	30.97	15.45	3	4.17	30.49	15.73	2.9-3.0	835
$[CoA_5W](NO_3)_3$									450
$[CrA_5W](NO_3)_3 \cdot HNO_3$	4.49	31.20	15.60	3	4.22	30.67	15.65	2.8-2.9	825
$[CoA_5W](NO_3)_3$									440
$[RhA_5W](NO_3)_3 \cdot HNO_3^d$	3.97	27.80	13.90	3	4.11	27.60	14.05	3	830
$[RhA_5W](NO_3)_3^d$									470

<sup>a</sup> Adducts were prepared following ref. 4a. <sup>b</sup>  $10^{-3}M$  solution, 20°C. <sup>c</sup> Absorption maxima (aqu. soln.), 303 and 258 (sh) m $\mu$ .  
<sup>d</sup> Absorption maxima (aqu. soln.), 309 and 259 (sh) m $\mu$ . <sup>e</sup> A = NH<sub>3</sub>, W = H<sub>2</sub>O.

## Experimental Section

Microanalyses were by the Microanalytical Laboratory of Milan University. Conductivities were measured using a Philips Conductivity Bridge Type 9500. Infra-red spectra were measured (as mulls in Nujol or hexachlorobutadiene) using first a Perkin-Elmer Infra-cord Spectrometer (where, as pointed out by earlier workers,<sup>10</sup> broad bands are more easily located) and then a Unicam SP 100 Spectrometer. Electronic spectra were measured using a Unicam SP 700 spectrometer.

**Adducts.** These were prepared from the well-known parent nitrates by treatment with nitric acid. References to the original preparations are given in Table III, with analytical data and conductivities. The adducts were stable *in vacuo* ( $10^{-3}$  mm) at room temperature, though at 100° they readily lose nitric acid.

(10) D. F. Evans, D. Jones and G. Wilkinson, *J. Chem. Soc.*, 3164 (1964).

## Conclusion

Nitric acid adducts of nitrates are known with formulae (1)  $[M](NO_3) \cdot HNO_3$ , where e.g. M = Rb, Cs, *trans*  $[Rhpy_4Cl_2]^+$ , and  $[P(C_6H_5)_4]^+$ ; (2)  $[M](NO_3) \cdot 2HNO_3$ , where M = NH<sub>4</sub><sup>+</sup>; (3)  $[M](NO_3)_3 \cdot HNO_3$ , where M =  $M(NH_3)_5L^{3+}$ . In each of the cases, 1, 2 and 3, the bonding of the extra nitric acid is of a different type. A search is now under way for yet further modes of combination between simple inorganic species, such as that of nitric acid with nitrate ion.

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