

STUDIES OF ANHYDROUS METAL NITRATES

V.* VIBRATIONAL SPECTRA OF $\text{In}(\text{NO}_3)_3$ AND $\text{Pd}(\text{bipy})(\text{NO}_3)_2$

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The vibrational spectra of nitrate complexes and anhydrous covalent metal nitrates have been used to investigate the nature of the metal–ligand bond.^{1,2} Recent studies have cast some doubt on the unidentate–bidentate classification of nitrate coordination and indicate that in most cases two oxygen atoms are involved in each coordinate linkage.^{3,4} The vibrational frequencies observed for the salts are, however, still useful in giving crude information concerning the bonding involved. This note reports the spectra of two anhydrous salts and demonstrates how the data may be usefully interpreted.

Experimental

The salts were prepared by standard methods as follows:

$[\text{Pd}(\text{bipy})(\text{NO}_3)_2]_4$ (Method Similar to that Described⁵)

Palladium(II) nitrate was prepared by dissolving palladium metal in excess fuming nitric acid to which a crystal of N_2O_5 had been added. On evaporation a black-brown solid was left. This was dissolved in dilute nitric acid and a solution of bipyridine in warm water was added (ratio by weight Pd/bipy = 1/3). Some of the water was boiled off and on cooling the solution yellow crystals of $\text{Pd}(\text{bipy})(\text{NO}_3)_2$ formed (Found: N, 14.4; Pd, 27.65. Calc. for $\text{Pd}(\text{bipy})(\text{NO}_3)_2$: N, 14.5; Pd, 27.5%).

$\text{In}(\text{NO}_3)_3$

Indium metal (B.D.H. 99.9%) was allowed to react with a solution of N_2O_4 (Matheson) in nitromethane. The concentration of N_2O_4 was kept high for fastest reaction.⁶ The reaction

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³ Cotton, F. A., and Bergman, J. G., *J. Am. chem. Soc.*, 1969, **86**, 2941; Cotton, F. A., and Soderberg, R. H., *Inorg. Chem.*, 1963, **85**, 2402; James, D. W., *Inorg. chim. Acta*, in press.

⁴ James, D. W., and Kimber, G. M., *Aust. J. Chem.*, 1969, **22**, 2287.

⁵ Livingstone, S. E., *Proc. R. Soc. N.S.W.*, 1952, **86**, 36.

⁶ Garner, C. D., and Wallwork, W. C., *J. chem. Soc.*, 1966, 1496; Addison, C. C., and Simpson, W. B., *J. chem. Soc.*, 1965, 598; Garner, C. D., Sutton, D., and Wallwork, S. C., *J. chem. Soc. (A)*, 1967, 1949.

required at least a week for completion. When N_2O_4 and solvent were removed under vacuum an oily residue was first formed which on further evacuation with heating solidified to a white powder. The white powder was purified by vacuum sublimation at 140° and the product was a glass which could not be induced to crystallize. This is in contrast to the findings of Field and Hardy¹ who sublimed $\text{In}(\text{NO}_3)_3$ and obtained a white powder (Found: In, 37.8; N, 13.85. Calc. for $\text{In}(\text{NO}_3)_3$: In, 38.2; N, 13.9%).

Spectra

The spectra were obtained on a Perkin-Elmer 457 spectrophotometer (i.r.) and a Perkin-Elmer L.R.I. (Raman). Particular attention was paid to ensuring that the samples remained anhydrous during the running of the spectra (see⁴).

TABLE 1
VIBRATIONAL SPECTRA OF $\text{Pb}(\text{bipy})(\text{NO}_3)_2$ AND $\text{In}(\text{NO}_3)_3$ (cm^{-1})

Infrared	$\text{Pd}(\text{bipy})(\text{NO}_3)_2$		Raman (CH_3CN)	Assignment	$\text{In}(\text{NO}_3)_3$	
	Raman (solid)	Raman (H_2O)			Infrared	Raman ^a (solid)
284w 350sh 363m 460-490w,br				metal-ligand vibrations		270s,br
655m 725m 801m 975sh				skeletal bend O-N-O bend (in plane) O-N-O bend (out of plane)	500-600vbr	
982sh 991s		1028sh	1026w,p	N-O stretch (sym)	722w 774sh 796m	800w,br
	1028m	1046s,p ^b			975sh 1005m,br	1000s,br
1250sh 1268sh 1274s 1296s 1320m ^c		1275vw,dp		N-O stretch (asym)	1250s,vbr	
	1330w	1325m,p	1324m,p			
1449s 1521s 1568w		1509w,dp		N-O stretch (terminal)	1520s,vbr 1598sh	1530m,br
	1562w	1568w,dp	1564w,dp			
	1604m	1605m,dp	1604dp	bipyridine band		

^a Raman spectrum of $\text{In}(\text{NO}_3)_3$ was masked by high fluorescence. The Raman shifts are thus not very precise.

^b The Raman shift at 1046 cm^{-1} is attributed to the presence of ionic nitrate.

^c Sharp.

Results

The spectra obtained for the two salts are given in Table 1. In both cases the infrared spectra are very much more intense than are the Raman spectra. This is due in part to the fluorescent nature of the complexes which partly masks the spectra in the solid state. However, because the spectra observed in solution for $\text{Pd}(\text{bipy})(\text{NO}_3)_2$ are also very weak it appears that the formation of covalent binding has reduced the polarizability of the group. The Raman band at 1028 cm^{-1} in the spectrum of $\text{Pd}(\text{bipy})(\text{NO}_3)_2$ is difficult to assign. It could possibly arise from the symmetrical stretch of NO_3 or from bipy. If the former assignment is assumed the

reason for the change in energy from that in the infrared spectrum ($975\text{--}991\text{ cm}^{-1}$) is hard to understand. It equally well does not appear to arise from ionic nitrate species as the salts are non-electrolytes except in aqueous solution where the ionic nitrate bands appear at quite different energies. We therefore chose to assign the band at 1028 cm^{-1} to a vibration of bipyridine but recognize that some contribution from the N-O stretching motion is possible. The general assignment of the remaining bands presents little difficulty and is represented in Table 1.

The metal-ligand vibration region has a number of bands in the infrared for $\text{Pd}(\text{bipy})(\text{NO}_3)_2$ while for $\text{In}(\text{NO}_3)_3$ it has a single broad band. As the structure of these compounds is not known it is not possible to make definite assignments of the bands. It might be expected however that the Pd-O and In-O stretching vibrations would be in the region of 250 cm^{-1} with the Pd-N stretching vibration at higher energy (350 cm^{-1}). The $450\text{--}500\text{ cm}^{-1}$ region is thought to involve the bending mode of the coordinated nitrate which is similar to a chelate ring vibration while the vibration at 656 cm^{-1} in the palladium complex is thought to arise from the bipyridine chelate system.

The stretching frequency region of the nitrate allows some comments on the nature of the coordination. For both compounds there are three regions of absorption: one at about 1000 cm^{-1} , the second at $1250\text{--}1300\text{ cm}^{-1}$, and the third at $1500\text{--}1550\text{ cm}^{-1}$. Disregarding the multiplicity of bands, this pattern is very similar to that observed for $\text{Ti}(\text{NO}_3)_4$ and $\text{Sn}(\text{NO}_3)_4$, the structures of which have been determined.⁶ For both of these salts the bonding to the metal was through two oxygen atoms; the nitrate stretching region was characterized by two frequencies involving the terminal oxygen (1630 cm^{-1}). The variation in energy of these vibrations was related to the length of the N-O bonds involved. Although the N-O (terminal) vibration is lower in energy the pattern is basically similar in the present study.

We feel that the marked lowering of the N-O symmetric stretch indicates that the N-O (bound) bond length has been considerably lengthened because of the formation of a strong metal-nitrato bond. In order for the palladium atom to have its usual square-planar coordination it is probable that the nitrato-planes are at right angles to the coordination plane. For $\text{In}(\text{NO}_3)_3$ on the other hand the persistent formation of a glassy mass indicates that random cross linking using bridging nitrate groups probably occurs with the symmetry of the indium atom being approximately tetrahedral.

The splitting of the bands observed strikingly in $[\text{Pd}(\text{bipy})(\text{NO}_3)_2]$ and to a much less extent in $\text{In}(\text{NO}_3)_3$ is undoubtedly due to factor group splitting due to the factor group containing several molecules. A similar occurrence in $[\text{Ce}(\text{NO}_3)_6]^{2-}$ has been discussed elsewhere.⁴

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