125. *The Infrared Spectra of Anhydrous Transition-metal Nitrates.*

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Infrared spectra for the anhydrous nitrates of manganese, copper, zinc, and mercury indicate the presence of covalent metal–nitrate bonds. The anhydrous nitrates of cobalt, silver, cadmium, and lead have spectra characteristic of the nitrate ion. Frequencies for the hydrated nitrates of iron, cobalt, nickel, copper, zinc, and cadmium are given for comparison. Hydrated thorium nitrate exhibits bands characteristic of a co-ordinated nitrato-group.

A BRIEF report [1] has already been made concerning the infrared spectra of some anhydrous transition-metal nitrates; this work is now described in detail. Following the observations that anhydrous cupric nitrate [2] and ferric and mercuric nitrates [3] are volatile, the infrared spectra of some anhydrous transition-metal nitrates have been examined to obtain evidence concerning the covalent nature of the metal-to-nitrate bond in these compounds. Recent work on the infrared spectra of nitrato-co-ordination complexes [4,5] has shown that it is possible, by examination of the spectra, to distinguish between the nitrate ion and the covalently bound nitrato-group.

EXPERIMENTAL

Determination of Spectra.—A Grubb-Parsons double-beam infrared spectrometer, equipped with an S3A monochromator and a rock-salt prism, was used. The mulling agents were Nujol (2—15 μ) and hexachlorobutadiene. The latter was used for the region obscured by Nujol absorption bands.

The cell windows were of sodium chloride coated with polystyrene; [6] use of coated windows has been found to be essential for work with complex nitates [4] since some of these compounds react with the windows to give the spectrum of the nitrate ion.

The samples were prepared in a dry box which was dried (overnight) with phosphorus pentoxide and flushed out with dry nitrogen during use.

Preparation of Compounds.—Anhydrous copper nitrate [2] and zinc nitrate [7] were prepared as already described. Manganese, cobalt, cadmium, and mercury nitrates were prepared from the metals and dinitrogen tetroxide–organic solvent mixtures. These reactions yielded metal nitrate–dinitrogen tetroxide addition compounds, from which the anhydrous metal nitrates were obtained by heating them under vacuum. Details of these preparations will be published in later papers.

RESULTS AND DISCUSSION

The frequencies of observed absorption bands are listed in Tables 1, 2, and 4. The anhydrous transition-metal nitrates examined can be divided into two groups, those whose infrared spectra indicate the presence of an ionic nitrate group (NO_3^-, symmetry D_{3h}) and those whose spectra indicate the presence of co-ordinated nitrato-groups (ONO_2, symmetry C_{2v}). The latter group can be further subdivided, since anhydrous cupric and mercuric nitrates exhibit volatility,[2,3] whereas anhydrous zinc and manganous nitrates do not. The frequencies of the ionic nitrates are listed in Table 1, those of the covalent nitrates in Table 2, and those of some hydrated transition-metal nitrates in Table 4.

Arising out of the different symmetries of the nitrate ion and the nitrato-group, two

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[1] Addison and Gatehouse, *Chem. and Ind.*, 1958, 464.
[2] Addison and Hathaway, *Proc. Chem. Soc.*, 1957, 19; *J.*, 1958, 3099.
[3] Addison, Hathaway, and Logan, *Proc. Chem. Soc.*, 1958, 51.
[4] Gatehouse, Livingstone, and Nyholm, *J.*, 1957, 4222.
[5] Gatehouse and Comyns, *J.*, 1958, 3965.
[6] Meister *et al.*, *Research Publications, Illinois Institute of Technology*, 1948, **6**, No. 1.
[7] Addison, Lewis, and Thompson, *J.*, 1951, 2829.

TABLE 1. *Anhydrous nitrates containing the nitrate ion* (NO_3^-).

	$Co(NO_3)_2$	$AgNO_3$	$Cd(NO_3)_2$	$Pb(NO_3)_2$
	2558w		2545w	
	2494w			
	2475w		2469m	
	1969w	2375w	2410sh	
	1887w			
	1859w			
$\nu_1 + \nu_6$	1828w	1789w, sp	1828m	
		1767w, sp	1608w	
			1502w, sp	
	1404sh		1420m	
ν_3	1366s	1362vs, b	1381vs	1373vs
			1348vs, b	
ν_1	—	—	1028w	—
			906w	
ν_2	799vs	801vs, sp	805w, sh	836w, sp
	792s		802w, sp	807vw
ν_4	762w	733s, sp	751m	726w

vs very strong; m medium; sh shoulder; s strong; w weak; sp sharp; b broad.

TABLE 2. *Anhydrous nitrates containing the nitrato-group* ($-ONO_2$).

	$Mn(NO_3)_2$	$Cu(NO_3)_2$	$Zn(NO_3)_2$	$Hg(NO_3)_2$
		2710w	2717w	
		2618w		
$\nu_2 + \nu_4$		2591w	2591w	
$2\nu_1$		2525w	2513w, sp	
$3\nu_6$	2469w	2404w	2433w	2488w
		2392w	2410w	2432w
$\nu_1 + \nu_4$	2320w	2381w		
		2299w	2353w	
			2222w, b	
$2\nu_2$ (or $\nu_1 + \nu_6$)	2075w	2058w, b	2075w, b	
	1883w			
$\nu_2 + \nu_6$	1812w	1792m	1802m	
	1779w	1733m, sh		1773w
	1724w			
	1634s			
$2\nu_6$	1603vw	1592vs, sp	1600m, sp	1600w, sp
ν_4		1565vs		
	1553vs	1546vs	1546s	1495m
		1504m, sp	1502m, sp	
		1344vs, b	1359vs	
ν_1	1294vs	1289vs, sh	1300vs	1376s
		1264vs, b		
ν_2		1038m, sh	1050sh	
	1019vs	1016s, b	1040s, sp	1027vs, b
		907w	905w	
ν_6	805s	795s, sh	800s, sp	
	799vs	787s, b	793s, sp	788vs, sp
ν_3 or ν_5	759m	770s	763s, sp	750m, b
			746m	

TABLE 3.

NO_3^-	Type [a]	ν_1 (A_1^1)	ν_2 (A_2^{11})	ν_3 (E^1)	ν_4 (E^1)		
	Assignment	NO stretch	Out-of-plane	NO_2 stretch	NO_2 bend		
	Frequency (cm.$^{-1}$)	1050	831	1390	720		
$-ONO_2$	Type [a]	ν_2 (A_1)	ν_6 (B_2)	ν_1 (A_1)	ν_4 (B_1)	ν_3 (A_1)	ν_5 (B_1)
	Assignment	NO stretch	Out-of-plane	NO_2 stretch symmetric	NO_2 stretch asymmetric	NO_2 bend symmetric	NO_2 bend. asymmetric
	Frequency [b]	1034—970	800—781	1290—1253	1531—1481	~739	~713

[a] See reference 8. [b] See references 4 and 5.

different conventions are used in numbering the vibrations. To avoid any confusion the relations between the two sets of conventions are shown in Table 3. The symmetry types of the vibrations are given in parentheses and their approximate forms have been

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[8] Redlich and Nielson, *J. Amer. Chem. Soc.*, 1943, **65**, 654.

illustrated elsewhere.[8,9] The frequencies given, and characteristic of the nitrato-group, were determined in earlier investigations.[4,5]

TABLE 4. *Some hydrated transition-metal nitrate frequencies.*

Compound	NO_3^- ⟶	ν_3	ν_1	ν_2		ν_4
$Cu(NO_3)_2,3H_2O$		1387vs	—	836w		—
$Zn(NO_3)_2,6H_2O$		1377vs	—	835vs		—
$Cd(NO_3)_2,4H_2O$		1370vs, b	—	834vs		—
$Fe(NO_3)_3,9H_2O$		1361vs	—	835w		—
$Co(NO_3)_2,6H_2O$		1372vs	—	836w 807vw		—
$Ni(NO_3)_2,6H_2O$		1383vs	1048vw	837s		—
	$-ONO_2$ ⟶	ν_4	ν_1	ν_2	ν_6	ν_3 or ν_5
$Th(NO_3)_4,4H_2O$		1520vs 1506sh	1323s 1292vs	1036sh 1030vs	811m 805m	756m 744m

The anhydrous nitrates listed in Table 1 all have spectra characteristic of the nitrate ion, with a strong broad band at about 1360—1380 cm.$^{-1}$ arising from the doubly degenerate vibration ν_3, a sharp band of varying intensity at about 800 cm.$^{-1}$ which arises from the out-of-plane bending mode ν_2, and a weak band at about 720—760 cm.$^{-1}$ which arises from the doubly degenerate vibration ν_4. Only with cadmium nitrate was the totally symmetric vibration (ν_1) apparent as a weak absorption, due presumably to some distortion of the nitrate ion resulting in a lowering of symmetry. A list of the frequencies of six hydrated transition-metal nitrates is given in the upper section of Table 4 for comparison with the ionic nitrate frequencies. It is interesting to note that on heating nickel nitrate hexahydrate in a drying pistol with phosphorus pentoxide some of the water was removed and very strong bands characteristic of the co-ordinated nitrato-group were then observed in the spectrum.

Anhydrous cupric nitrate has [2] a vapour pressure of 3 mm. at 214° and is very stable in the vapour state at temperatures below 225°. The infrared spectrum (Table 1) shows strong bands in the regions 1565—1546 cm.$^{-1}$ (ν_4) and 1289—1264 cm.$^{-1}$ (ν_1) which indicate the presence of co-ordinated nitrato-groups,[4] of C_{2v} symmetry. A strong band at 1016 cm.$^{-1}$ corresponds to ν_2 of the ONO_2 group. The fact that this compound exists in the vapour and that the spectrum indicates C_{2v} symmetry for the nitrato-group indicates that the metal–nitrate bond possesses a considerable degree of covalent character. Since this study was commenced the mass spectrum of anhydrous cupric nitrate has been examined,[10] and the compound shown to exist as a monomer in the vapour.

The spectra of anhydrous manganous, zinc, and mercuric nitrates (Table 2) show bands in the same regions as cupric nitrate, indicating that these compounds also contain the nitrato-group. The difference between the anhydrous nitrates of cadmium and zinc is consistent with the general observation that cadmium co-ordinates less readily with oxygen than does zinc. A large number of oxygen complexes of zinc are known but relatively few with cadmium; this has been regarded as evidence that the Cd–O bond is considerably weaker than the Zn–O bond.[11] Some tentative assignments of combination and overtone bands are also made in Table 2 on the basis of previous work.[5]

Thorium nitrate tetrahydrate was also examined, and its frequencies are listed in the lower part of Table 4. It clearly exhibits those bands characteristic of a co-ordinated nitrato-group, even in the hydrated form. Co-ordinative bonding of this nature was suggested by Katzin [12] to explain effects noted in a spectrophotometric study involving thorium and nitrate ions. Thorium is known to form many complex oxygen compounds, including double nitrates.[13]

[9] Cohn, Ingold, and Poole, *J.*, 1952, 4272.

[10] Porter, Schoonmaker, and Addison, *Proc. Chem. Soc.*, 1959, 11.

[11] Sidgwick, " Chemical Elements and their Compounds," Oxford University Press, 1950, p. 281.

[12] Katzin, *J. Chem. Phys.*, 1950, **18**, 789.

[13] Ref. 11, p. 641.

Clearly, the nitrate compounds examined can be grouped into three categories, (*a*) those which are covalent and volatile, (*b*) those which are covalent and involatile, and (*c*) those which are ionic. The infrared spectra of these compounds are very useful in that they give the apparent symmetry of the nitrate group in the crystal, and a definite indication of the covalent or ionic nature of the bonding.

However, from data at present available it is clear that there is no simple correlation between the covalency of the bonding and electronic structure (particularly the number of *d* electrons) of the transition-metal concerned. Again, the fact that the nitrates of zinc, cadmium, and mercury are covalent, ionic, and covalent respectively shows that pronounced variations can occur within a vertical group. In any attempted correlation, the influence of crystal environment must also be taken into account. Work is therefore in hand to prepare a wider range of transition-metal nitrates, and to examine their infrared spectra and crystal structures.

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