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670. *The Infrared Spectrum of the Nitrosonium Ion.*

By D. W. A. Sharp and J. Thorley.

Compounds containing the nitrosonium ion have an infrared absorption peak between 2150 and 2400 cm.$^{-1}$. The changes in absorption frequency are discussed and some correlation is noted with the covalent character and with charge effects in the lattice.

The compounds $NOClO_4$ and $NOBF_4$ have been shown to be isomorphous with the salts NH_4ClO_4 and NH_4BF_4 and to contain nitrosonium, NO^+, ions which have achieved spherical symmetry by rotation.[1] The evidence for the presence of nitrosonium ions in other compounds has been summarised by Addison and Lewis [2] and has involved studies of conductivity, magnetic susceptibility, and Raman spectra; the present report describes the infrared spectra of a series of compounds which, on the basis of their stoicheiometry, might be expected to contain the nitrosonium ion. The free nitrosonium ion is generally considered to absorb at about 2300 cm.$^{-1}$; this is to be compared with a value of 1700—1900 cm.$^{-1}$ when the NO^+ ion is co-ordinated to a metal [3] and of 1050—1200 cm.$^{-1}$ when the NO^- ion is co-ordinated to a metal.[4]

The results of the present study are shown in Table 1. There is good agreement between the present results and the Raman spectral measurements which have been previously made on some of these derivatives. In all the examples given in the Table there was a strong absorption band between 2150 and 2400 cm.$^{-1}$. It is considered that this band is characteristic of the nitrosonium (NO^+) ion. With the exception of $2NOCl,SnCl_4$, $NOCl,SbCl_5$, and $2NOCl,PtCl_4$, samples of the adducts between nitrosyl chloride and chlorides tended to give additional absorption bands in the region of 1800 cm.$^{-1}$. These bands were absent in freshly prepared samples and increased in intensity as the sample was kept. It is considered that these bands are due to the presence of nitrosyl chloride formed by dissociation of the complexes—ClNO absorbs at 1799 cm.$^{-1}$,[5] but there is the possibility of isomeric change in the compounds so that an NO^+ group becomes co-ordinated to the metal. Most of the nitrosonium peaks are sharp singlets but some compounds gave additional shoulders. It has previously been shown [6] that $(NO)(NO_2)S_3O_8$ gives two Raman peaks at 2277 and 2308 cm.$^{-1}$ and the former peak has

[1] Klinkenberg, *Rec. Trav. chim.*, 1937, **56**, 749.
[2] Addison and Lewis, *Quart. Rev.*, 1958, **9**, 115.
[3] Lewis, Irving, and Wilkinson, *J. Inorg. Nuclear Chem.*, 1958, **7**, 32.
[4] Griffith, Lewis, and Wilkinson, *J. Inorg. Nuclear Chem.*, 1958, **7**, 38.
[5] Burns and Bernstein, *J. Chem. Phys.*, 1950, **18**, 1669.
[6] Gerding and Eriks, *Rec. Trav. chim.*, 1952, **71**, 773.

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TABLE 1.

Vibrational spectra of compounds containing NO^+ ions.

$(NO)_2GeF_6$	2391 s	shoulder at 2336	$(NO)(NO_2)S_3O_{10}$	2308, 2277 R ‡	
$NOVF_6$	2391 s	shoulder at 2328	$(NO)_2S_2O_7$	2278 s	shoulder at 2294
$NOBF_4$	2387 s		$NOMnCl_3$	2271 b	
$NOSbF_6$	2385 b	shoulder at 2342	$NOCuCl_2$	2271 b	
$NOPF_6$	2379 s		$NOHgCl_3$	2268 b	
$NOSO_3F$	2377 b		$NOAlCl_4$	2242 s	shoulder at 2370
$(NO)_2SnF_6$	2342 s			2236 * R	
$NOAsF_6$	2340 s		$(NO)_2PtCl_6$	2201 s	
$NOHSO_4$	2340 * R		$NOFeCl_4$	2200 s	shoulder at 2275
$NOUF_6$	2333 † }	measured as sublimed	$(NO)_2SnCl_6$	2191 b	
$NOMoF_6$	2331 † }	films	$NOSbCl_6$	2189 b	
$NOBiCl_4$	2331 b		$NOZnCl_3$	2187 b	
$NOClO_4$	2313 ‡ R		$(NO)_2TiCl_6$	2165 b	

All present work except where marked; spectra measured as mulls in Fluorube grease; all figures in $cm.^{-1}$; s, sharp; b, broad; R, Raman spectra.

* Gerding and Houtgraaf, *Rec. Trav. chim.*, 1953, **72**, 21. † Geichman, Smith, Trond, and Ogle, *Inorg. Chem.*, 1962, **1**, 661. † Gerding and Eriks, *Rec. Trav. chim.*, 1952, **71**, 773.

been considered to be due to the antisymmetrical stretching vibration of the NO_2^+ ion which has been rendered Raman-active by the ion-site symmetry. In view of the analytical figures for the compounds studied in the present work a similar explanation is unlikely to hold for the two bands which are observed in the spectra of some of the compounds. It seems more likely that the splitting of the main band is due to the presence of more than one nitrosonium ion in the unit cell, so that the different ions are, in fact, in positions of different local symmetry and in different chemical environments.

Most of the compounds prepared were examined by *X*-ray powder photography and the unit-cell dimensions found are given in Table 2. It was confirmed that nitrosonium fluoroborate, chlorostannate, and chloroplatinate are isomorphous with their potassium analogues; the last two salts have been briefly mentioned [7] as isomorphous with their potassium analogues but no cell dimensions were given. The cell dimensions determined for nitrosonium fluoroborate in the present work are somewhat different from those of

TABLE 2.

Unit cell dimensions (Å).

$NOBF_4$ orthorhombic	$a = 7{\cdot}88$, $b = 5{\cdot}72$, $c = 7{\cdot}40$ *	$(NO)_2SnCl_6$ cubic	$a = 10{\cdot}24$ *
	$a = 8{\cdot}79$, $b = 5{\cdot}66$, $c = 7{\cdot}10$ †	K_2SnCl_6 cubic	$a = 10{\cdot}14$ ‡
KBF_4 orthorhombic	$a = 7{\cdot}83$, $b = 5{\cdot}67$, $c = 7{\cdot}35$ *	$(NO)_2PtCl_6$ cubic	$a = 11{\cdot}27$ *
	$a = 7{\cdot}85$, $b = 5{\cdot}68$, $c = 7{\cdot}37$ ‡	K_2PtCl_6 cubic	$a = 11{\cdot}18$ ‡
$NOSO_3F$ orthorhombic	$a = 8{\cdot}59$, $b = 5{\cdot}99$, $c = 7{\cdot}37$ *		
KSO_3F orthorhombic	$a = 8{\cdot}56$, $b = 5{\cdot}95$, $c = 7{\cdot}33$ §		

* Present work. † Ref. 1. ‡ Wyckoff, "Crystal Structures." § Sharp, *J.*, 1957, 3761.

Klinkenberg.[1] Nitrosonium fluorosulphate is isostructural with potassium fluorosulphate, both compounds being isomorphous with potassium fluoroborate.[8] The results from powder photography strongly support the presence of an ionic lattice in the four compounds where lattice dimensions were established and, by comparison of infrared spectra, in all the compounds listed in Table 1. In each case the lattice dimensions of the nitrosonium salts are slightly greater than those found for the corresponding potassium salts; it has been estimated that, when the nitrosonium ion is in free rotation and is acting as a sphere, the effective radius is 1·40 Å (cf. K^+ 1·33 Å; ref. 1). No nitrosonium salt of a complex fluoro-acid other than the fluoroborate has been found to be isomorphous with the corresponding potassium salt. Complex halides generally have structures which are based on close-packing of halide ions and cations.[9] The fluoride ion ($r = 1{\cdot}33$ Å) is

[7] Klinkenberg, *Chem. Weekblad*, 1938, **35**, 197.
[8] Sharp, *J.*, 1957, 3761.
[9] Wells, *Quart. Rev.*, 1954, **8**, 380.

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smaller than the nitrosonium ion, and the formally asymmetrical ion can probably not attain full spherical symmetry. The chloride ion ($r = 1{\cdot}81$ Å) is larger and would be more able to accommodate the nitrosonium ion and to allow it to attain spherical symmetry. Nitrosonium fluoroborate and fluorosulphate, which are isomorphous with the potassium salts, do not have close-packed structures.

The vibrational frequency of the nitrosonium ions varies widely, as has previously been noted by Gerding and Houtgraaf [10] who explain the variation in terms of polarisation of the anion by the cation, such polarisation having also been postulated by Seel [11] and by Burg and McKenzie.[12] In the present work, however, it has been shown that some salts which absorb near both the high- and the low-frequency ends of the range are isomorphous with the corresponding potassium salts and are hence unlikely to be appreciably polarised. This does not mean, however, that the other salts in Table 1 are not polarised. The only generalisation that it is possible to make about the trends in values of the NO^+ vibrational stretching frequency is that salts of complex fluoro-acids tend to give the highest frequency, followed by salts of oxy-acids, followed by salts of complex chloro-acids. There is a vague trend in that the salts containing larger anions tend to give lower NO^+ vibrational frequencies than do salts of smaller anions. It is apparent that the factors governing the NO^+ vibrational frequency are complex, but it is suggested that interaction both between the nitrosonium ion and the halogens of the complex anion and between the nitrosonium ion and the central metal atom of the anion may be factors of importance in lowering the frequency of the N–O vibration. This frequency probably also depends on the effect of the electrostatic charges in the lattice on the nitrosonium ion; such an effect would depend upon the size of the anion. There appears to be little correlation between the position of the nitrosonium ion absorption and the stability of the compound.

Complex anions corresponding to those required for the nitrosonium salts of the complex fluoro-acids considered in this study are well known, as are the hydrogen sulphate and pyrosulphate anions. Amongst the chloro-complexes the $BiCl_4^-$, $AlCl_4^-$, $PtCl_6^{2-}$, $FeCl_4^-$, $SnCl_6^{2-}$, $SbCl_6^-$, and $TiCl_6^{2-}$ ions are well established.[13] The elements manganese, mercury, and zinc have previously been recorded as giving salts of the type $M'MCl_3$ (M' = alkali-metal or ammonium; M = Mn, Hg, or Zn), but the nature of the anions present does not appear to be known. The $ZnCl_3^-$ and $HgCl_3^-$ ions have been postulated as occurring as intermediates during chlorine exchange between nitrosyl chloride and the metal chlorides; it was suggested that such anions are, in fact, polymeric.[14]

There has been a great deal of previous work on the nitrosyl complexes of copper. Solutions of cupric halides react with nitric oxide to give blue covalent adducts which are in equilibrium with colourless ionic forms. It has been suggested that the solvated nitrosonium ion is present in such solutions,[15] but an infrared study taken in conjunction with older electrolysis experiments has been interpreted to favour the presence of $[Cu^I(C_2H_5OH)_3NO]^{2+}$ ions in solution in ethanol.[16] It is difficult to relate precisely the compound formed by the reaction between nitrosyl chloride and cuprous chloride and those formed in solution by the action of nitric oxide on cupric halides, but the present work appears to demonstrate that the former adduct contains a nitrosonium ion and must be formulated $NO^+Cu^ICl_2^-$.

Experimental

Infrared spectra were measured as mulls in Fluorube grease between calcium fluoride windows. It was found that any other mulling agent caused immediate decomposition of

[10] Gerding and Houtgraaf, *Rec. Trav. chim.*, 1953, **72**, 21.
[11] Seel, *Z. anorg. Chem.*, 1950, **261**, 75.
[12] Burg and McKenzie, *J. Amer. Chem. Soc.*, 1952, **74**, 3143.
[13] Sidgwick, "Chemical Elements and their Compounds," Oxford Univ. Press, 1950.
[14] Lewis and Sowerby, *J.*, 1956, 150.
[15] Fraser, *J. Inorg. Nuclear Chem.*, 1961, **17**, 265; Fraser and Dasent, *J. Amer. Chem. Soc.*, 1960, **82**, 348.
[16] Griffith, Lewis, and Wilkinson, *J.*, 1958, 3993.

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the nitrosonium salt, as did the use of windows of sodium chloride. All preparations of mulls were carried out in the dry-box. Spectra were measured on a Grubb-Parsons model DB1 spectrophotometer with sodium chloride optics. Each spectrum was calibrated against a spectrum of polystyrene.

TABLE 3.

	Ref. to prepn.	Calc. N	Calc. Cl	Found N	Found Cl		Ref. to prepn.	Calc. N	Calc. Cl	Found N	Found Cl
$(NO)_2GeF_6$	18	11·4		10·9		$NOMnCl_3$ ...	22	7·3	55·6	7·1	55·0
$NOVF_6$ ...	19	7·0		6·2		$NOCuCl_2$ ...	12, 23	8·5	43·1	8·3	42·6
$NOBF_4$ ...	18	12·0		11·6		$NOHgCl_3$ ...	22, 23	4·2	31·6	3·8	30·1
$NOSbF_6$ ...	18	5·2		5·0		$NOAlCl_4$ ...	10, 12	7·0	71·3	6·7	70·6
$NOPF_6$ ...	18	8·0		7·8		$(NO)_2PtCl_6$	22	6·0	45·5	5·9	45·6
$NOSO_3F$ ...	18	10·8		10·5		$NOFeCl_4$ ...	12	6·2	62·3	6·1	62·0
$(NO)_2SnF_6$	18	9·6		9·3		$(NO)_2SnCl_6$	12, 22	7·2	54·4	6·8	54·0
$NOAsF_6$ ...	18	6·4		6·1		$NOSbCl_6$ ...	12	3·8	58·3	3·7	58·2
$NOBiCl_4$ ...	20	3·7	37·0	3·6	36·2	$NOZnCl_3$ ...	22, 23	6·9	52·7	6·6	52·0
$(NO)_2S_2O_7$	21	10·2		10·0		$(NO)_2TiCl_6$	22	8·7	66·3	8·2	65·4

X-Ray powder photographs were taken in Lindemann glass capillaries with Cu-K_α radiation. Photographs were measured visually, but calculation of $\sin^2\theta$ values and indexing of powder lines were carried out on a Ferranti Sirius computer by means of programmes developed in these laboratories.[17]

Compounds were prepared by the known methods given in Table 3. Analysis for nitrogen was carried out by Dr. A. C. Syme and his colleagues of the Microanalytical Section of the Chemistry Department, Royal College of Science and Technology, by reduction with Devarda's alloy followed by distillation and estimation of the ammonia produced. Chlorine was estimated as silver chloride.

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[21] Hart-Jones, Price, and Webb, *J.*, 1951, 798.
[22] Partington and Whynnes, *J.*, 1948, 1952; 1949, 3135.
[23] Asmussen, *Z. anorg. Chem.*, 1939, **243**, 127.