THE CHEMISTRY OF THE NITROSYL GROUP (NO)

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The unique features in the properties and reactions of the nitric oxide molecule arise largely from its ability to exist in the three forms NO^+, NO, and NO^-. In many reactions the NO group loses or gains an electron, but otherwise retains its identity. Other atoms or groups which show this versatility are : H^+, H, H^- ; I^+, I, I^- ; NO_2^+, NO_2, NO_2^- ; ClO_2^+, ClO_2, ClO_2^-, but examples of such behaviour are rare in chemistry. Since the monomeric NO group contains an odd electron, much of its chemical behaviour is analogous to that of the hydrogen atom ; the simplest modes of compound formation are (a) the sharing of an electron pair to give a covalent compound X·NO, (b) the gain of one electron to form the anion NO^-, and (c) the loss of one electron to form the cation NO^+. In this Review the term " nitrosyl " is employed as a general name for compounds of the NO group, the term " nitrosonium " being used only when it is desired to imply the presence of the discrete NO^+ ion. The nitrosyl halides are typical of class (a). These compounds are non-electrolytes in solution, although structural studies frequently indicate that an ionic structure makes an important contribution to the resonance state ; they show the high volatility and ready hydrolysis typical of covalent compounds. Compounds of the type X·NO are invariably highly coloured. The colour depends upon the electron shift introduced by the atom or group X, but blue or red predominates. The NO^+ ion itself does not absorb in the visible region of the spectrum, and in the absence of other chromophoric groups the presence of intense colour is taken as an indication of predominantly covalent bonding. Compounds containing the ion NO^- are believed to exist, but are relatively few. They are produced by reaction of nitric oxide with elements (or solutions such as sodium in liquid ammonia) having very strong electron-donor properties.

Compounds containing the NO^+ ion have been clearly established. The ionisation potential for the process $NO \rightarrow NO^+ + e$ is 9·5 ev ;[1] this is much less than that for $N_2 \rightarrow N_2^+ + e$, for which values in the range 15·5—17·2 ev have been obtained,[2] or for $O_2 \rightarrow O_2^+ + e$, for which the ionisation potential is in the range 12·2—18·2 ev depending on the electronic

[1] Tate, Smith, and Vaughan, *Phys. Rev.*, 1935, **48**, 525 ; Hagstrum and Tate, *ibid.*, 1941, **59**, 354.

[2] Angus and Leckie, *Trans. Faraday Soc.*, 1935, **31**, 958.

state of the ion.[3]   The lower ionisation potential in the case of NO reflects the more ready loss of an electron from an odd-electron molecule, and the fact that the NO^+ ion produced is isoelectronic with CO and N_2 suggests that it should have some degree of stability.   Again, the nitric oxide molecule exists in two excited states having internuclear distance 1·06 and 1·07 Å ; since the sum of the radii for a triple bond is 1·06 Å, Pauling [4] considers that these states must be based on the structure $[:N\equiv O:]^+$ in which the remaining electron occupies an outer orbital.   Hantzsch [5] first postulated the existence of the NO^+ ion in 1909, as a result of cryoscopic measurements of the compound $NO \cdot HSO_4$ in sulphuric acid ; the perchlorate [6] and hydrogen sulphate [2] behave as electrolytes in nitromethane solution, and are formulated as $NO^+HSO_4^-$ and $NO^+ClO_4^-$.[6]   A Raman displacement of 2330 cm.$^{-1}$ has been assigned to the NO^+ ion.[7]   From X-ray powder photographs of the isomorphous ammonium, hydroxonium, and nitrosonium perchlorates and fluoroborates Klinkenberg [8] has shown that the NO group acts as a univalent positive ion having about the same volume as H_3O^+, but somewhat smaller than NH_4^+.

The NO^+ ion is quite stable in non-hydroxylic solvents such as sulphur dioxide [9] and nitromethane.[2, 6]   Nitrosonium compounds may be prepared in liquid dinitrogen tetroxide (see p. 129), and bromine trifluoride has also been used as a preparative medium.[10]   It is mainly in hydroxylic solvents that the question of the instability arises.   In such solvents, the chemical reactivity is governed by the equilibria [5]

$$NO^+ + OH^- \overset{(1)}{\rightleftharpoons} HNO_2 \overset{(2)}{\rightleftharpoons} NO_2^- + H^+ \qquad . \qquad . \qquad (1)$$
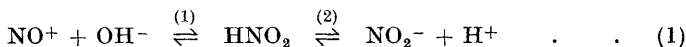
In strongly acid media the equilibrium is displaced completely to the left, and nitrites, or dinitrogen trioxide, dissolve in sulphuric acid to give nitrosonium ions according to the equation

$$N_2O_3 + 3H_2SO_4 = 2NO^+ + 3HSO_4^- + H_3O^+$$

in almost quantitative yield.[11]   As the acid concentration is reduced, equilibrium (1) moves towards the right, and it is only in the presence of covalent nitrous acid molecules that the solutions are unstable.   When the pH of the solution approaches 7, equilibrium (2) becomes significant, and in alkaline solutions this equilibrium is displaced completely to the right.   The full equilibrium can be investigated by examination of the change in ultraviolet absorption spectra of nitrite solutions with pH.   At

[3] Landolt–Börnstein :   " Tabellen ", Band I, Teil 3 (Atom-u. Molecularphysik), 1951, p. 359.

[4] " The Nature of the Chemical Bond ", Cornell Univ. Press, 2nd edn., p. 267.

[5] Z. phys. Chem., 1909, **65**, 57.

[6] Hantzsch and Berger, Z. anorg. Chem., 1930, **190**, 321.

[7] Angus and Leckie, Proc. Roy. Soc., 1935, A, **149**, 327.

[8] Rec. Trav. chim., 1937, **56**, 749 ;   Chem. Weekblad, 1938, **35**, 197.

[9] Seel, Bolz, and Nogradi, Z. anorg. Chem., 1951, **264**, 298 ;   Seel and Nogradi, ibid., p. 311.

[10] Woolfe, J., 1950, 1053.

[11] Gillespie, Graham, Hughes, Ingold, and Peeling, J., 1950, 2504 ;   Nature, 1946, **158**, 480.

$pH > 7$, the only absorption is that due to the nitrite ion.   At $pH < 7$, strong absorption due to HNO_2 molecules occurs, and in sulphuric acid of 80—90% concentration only the NO^+ absorption occurs.[12]   Nitrosonium hydrogen sulphate is hydrolysed in solutions containing less than 80% of sulphuric acid [13] and hydrolysis is not complete until the sulphuric acid concentration is decreased below 40%.[14]   The vapour pressure of these solutions undergoes a sharp change on decreasing the sulphuric acid concentration below 73%, indicating the onset of hydrolysis, which is practically complete at 57% sulphuric acid.[15]
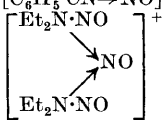
There is an equilibrium equation for covalent compounds which is similar to the ionic equation (1).   This may be written

$$NOX + ROH \rightleftharpoons RO \cdot NO + HX$$
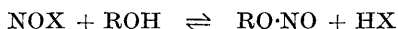
and many reactions of nitrosyl compounds illustrate this equilibrium.   For example, equilibrium constants have been determined for both the reactions

$$NOCl + HOH = HO \cdot NO + HCl \text{ [16]}$$

and $$NOCl + CH_3 \cdot OH = CH_3 \cdot O \cdot NO + HCl \text{ [17]}$$
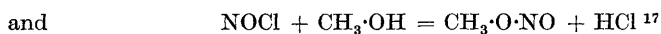
This type of relation has led to the formulation of covalent nitrites as nitrosyl compounds.   Acetyl and methyl nitrite react towards iodide and

Bond type	Nature of bonding	Examples
NO—X . . .	Sharing of an electron pair	NOCl
NO⁺ X⁻ . . .	Donation of one electron	$NO^+ClO_4{}^-$
M⁺ NO⁻ . . .	Acceptance of one electron	Na^+NO^-
NO⁺ Ẋ . . .	One-electron bond	$[NO \cdot NO_2]^+$
$[L \to NO]^+$ $[2L \to NO]^+$	NO^+ behaving as an electron-deficient group, accepting one or two pairs of electrons	$[C_6H_5 \cdot CN \to NO]^+$ $\begin{bmatrix} Et_2N \cdot NO \\ \searrow NO \\ \nearrow \\ Et_2N \cdot NO \end{bmatrix}^+$
M←N̈O	An electron pair donated to metal atom	A few metal co-ordination complexes
M̄←N̈≡O	Three electrons donated to metal atom	Metal nitrosyls Metal nitrosyl carbonyls Most co-ordination complexes
M̄←N=Ō	Electron-pair bond, but one electron also donated by metal to NO group	A few metal co-ordination complexes

[12] Addison and Lewis, unpublished results.
[13] Raschig, *Angew. Chem.*, 1905, **18**, 1281 ; *J. Soc. Chem. Ind.*, 1911, **30**, 166.
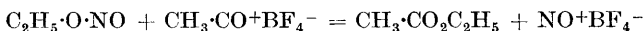[14] Schlesinger and Salathe, *J. Amer. Chem. Soc.*, 1923, **45**, 1863.
[15] Berl and Saenger, *Z. anorg. Chem.*, 1931, **202**, 113.
[16] Schmid and Maschka, *Z. physikal. Chem.*, 1941, **49**, B, 171.
[17] Leermakers and Ramsperger, *J. Amer. Chem. Soc.*, 1932, **54**, 1837.

azide ions as does nitrosyl chloride,[9, 18] and can also give rise directly to nitrosonium compounds, as in the reaction

$$C_2H_5 \cdot O \cdot NO + CH_3 \cdot CO^+BF_4^- = CH_3 \cdot CO_2C_2H_5 + NO^+BF_4^-$$

In the treatment which follows, the classification of compounds containing the NO group is designed to illustrate the ways in which this very versatile group can enter into chemical combination. The various bond types are summarised in the Table on page 117.

The Structure of Nitric Oxide

The nitric oxide molecule is paramagnetic, the molal magnetic susceptibility being $1 \cdot 46 \times 10^{-3}$ c.g.s. units at $20°$.[19] The magnetic moment varies with temperature; this variation is recorded for the temperature range $100—300°$ K, and has been interpreted by Van Vleck on the basis of the distribution of molecules between two electronic states of similar energy.[20] The absorption spectrum of NO is similarly explained.[21] The internuclear distance is $1 \cdot 14$ Å, which is interpreted by Pauling [4] as resulting from resonance among the three structures

$$^+N—O^- \qquad N{=}O \qquad ^-N{=}O^+$$

The two partially ionic structures make approximately equal contributions, and the resultant dipole moment [22] of the molecule is small ($0 \cdot 16$ D). Since nitric oxide is an odd-electron molecule it might be expected to dimerise readily. In fact, the resonance energy stabilises the monomeric form to such an extent that the heat of dimerisation becomes negative. The dimer is only obtained at low temperatures, and nitric oxide is the most stable of the odd-electron molecules. At high pressure and low temperature there is slight association in the gas, and bands are present in the ultra-violet which have been attributed to N_2O_2.[23] The heat of the dissociation $N_2O_2 \rightarrow 2NO$ in the gas is 2870 cal./mole.[24] In the liquid state nitric oxide exists almost entirely as the dimer, and infrared and Raman spectra indicate that this is a bent $ON \cdot NO$ molecule.[25] The dimer is diamagnetic, having molar susceptibility $- 0 \cdot 026 \times 10^{-3}$ c.g.s. unit,[26] so that the liquid consists of a mixture of para- and dia-magnetic molecules in a ratio which varies with temperature.[27] From magnetic-susceptibility measurements over the full liquid temperature range ($109 \cdot 4—121 \cdot 3°$ K), the degree of dissociation of N_2O_2 was found to vary from $2 \cdot 7\%$ at $110°$ K to 5% at

[13] Seel, Z. anorg. Chem., 1943, **250**, 331.

[19] Bauer and Picard, J. Physique, 1920, **1**, 97; Sone, Sci. Rep. Tohoku Univ., 1922, **11**, (3), 139.

[20] Phys. Rev. 1928, **31**, 587.

[21] Jenkins, Barten, and Mulliken, ibid., 1927, **30**, 150; Gillette and Eyster, ibid., 1939, **56**, 1113.

[22] Watson, Rao, and Ramaswamy, Proc. Roy. Soc., 1934, **143**, 558.

[23] Tarte, J. Chem. Phys., 1951, **19**, 1064.

[24] Rice, ibid., 1936, **4**, 1936.

[25] Smith, Keller, and Johnston, ibid., 1951, **19**, 189.

[26] Smith and Johnston, J. Amer. Chem. Soc., 1952, **74**, 4696.

[27] Bizette, Ann. Physik, 1946, **1**, 233; Chem. Zentr., 1947, I, 494.

$120°$ K. The heat of dissociation of the dimer in the liquid state is 3710 ± 150 cal./mole,[26] compared with an earlier value of 3910 cal./mole obtained from the entropy of vaporisation of nitric oxide at its boiling point.[24] Association in the solid state is almost complete, although very feeble paramagnetism (3.53×10^{-6} c.g.s. units) has been observed at $100°$ K.[28] Single crystals of nitric oxide are monoclinic, with two molecules of N_2O_2 in the unit cell. The dimer molecule is approximately rectangular, the N–N bond length being 1.10 Å and the N–O bond 2.38 Å.[29]

Covalent Compounds of the Type NO—X

Nitric oxide combines directly with fluorine, chlorine, and bromine, although for the laboratory preparation of nitrosyl halides, indirect methods are often more convenient (e.g., NOF,[30] NOCl [31]). Nitrosyl fluoride, chloride, and bromide have m.p.s $-132.5°$, $-64.5°$, and $-55.5°$, and b.p.s $-59.9°$, $-6.4°$, and ca. $0°$, respectively. Nitrosyl fluoride is prepared by mixing streams of fluorine and nitric oxide gases in a copper tube ; [32] nitric oxide and chlorine combine at temperatures as low as $-80°$,[33] and nitrosyl bromide is produced [34] by passing nitric oxide into bromine at $-15°$. The stability of the nitrosyl halides decreases with increasing atomic number of the halogen, and nitrosyl iodide has not been prepared. Thus at room temperature nitrosyl chloride decomposes to the extent of 0.5% into nitric oxide and chlorine, while nitrosyl bromide undergoes 7% decomposition.[37] The thermodynamic constants for the reaction

$$2NO \text{ (g)} + X_2 \text{ (g)} = 2NO{\cdot}X \text{ (g)},$$
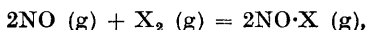
evaluated from equilibrium measurements, are

	$-G_{298}$ (cal.)	$-S_{298}$ (cal./deg.)
Nitrosyl chloride	9720 ± 60	28.0 ± 0.5
Nitrosyl bromide	2790 ± 30	29.0 ± 0.3

Early determinations of these values from spectroscopic data, using normal covalent radii, were not in agreement,[39] but more recently a vibrational assignment has been made which accounts for most of the discrepancy.[40] The rates of combination vary widely with the halogen employed. For nitrosyl chloride the value k in the expression

$$d[NOCl]/dt = k[NO]^2[Cl_2]$$

[28] Bizette and Tsai, *Compt. rend.*, 1938, **206**, 1288 ; Lips, *Helv. Phys. Acta*, 1934, **7**, 663 ; 1935, **8**, 247.
[29] Dulmage, Meyers, and Lipscomb, *J. Chem. Phys.*, 1951, **19**, 1432.
[30] Ruff and Stauber, *Z. anorg. Chem.*, 1905, **47**, 190.
[31] Whittaker, Lundstrom, and Metz, *Ind. Eng. Chem.*, 1931, **23**, 1410 ; Giraud and Pabst, *Bull. Soc. chim.*, 1878, **30**, 531 ; Scott and Johnson, *J. Phys. Chem.*, 1929, **33**, 1975.
[32] Ruff, Menzel, and Neumann, *Z. anorg. Chem.*, 1932, **208**, 293.
[33] Stoddart, *J.*, 1944, 388 ; Taylor and Denslow, *J. Phys. Chem.*, 1927, **31**, 374.
[34] Trautz and Dalal, *Z. anorg. Chem.*, 1920, **110**, 34.
[35] Welinsky and Taylor, *J. Chem. Phys.*, 1938, **6**, 466.
[36] Trautz and Dalal, *Z. anorg. Chem.*, 1918, **102**, 149.
[37] Belson and Yost, *J. Chem. Phys.*, 1939, **7**, 44.

is 0.897×10^7 cm.[6] mole[-2] sec.[-1] at $0°$ compared with 3.0×10^{10} for nitrosyl bromide.[35, 36]

A number of determinations of the structure of the nitrosyl halides have been made, and relevant data are given in Table 1. These structures

TABLE 1. *Structure of the nitrosyl halides*

	NOF	NOCl	NOBr
Bond distance (Å)			
X–N	1·52 [44]	1·95 ± 0·01 [41, 47]	2·14 ± 0·02 [41, 47]
N–O	1·13 [44]	1·14 ± 0·02 [41, 47]	1·15 ± 0·04 [41, 47]
Bond angle	110·2° [44]	116° ± 2° [41, 47]	117° ± 3° [41, 47]
Dipole moment (D) . .	1·81 [45]	1·83 [42]	1·87 [42]
Entropy, S_{298} (cal./deg.) . .	59·24 [44]	62·4 [40, 46, 47]	65·2 [38, 47]

are of interest for two reasons : they are among the few examples of bent molecules formed from three different atoms, and the X–N bond distance is much greater than the sum of the normal covalent radii (1·71 Å for ClNO, and 1·84 Å for BrNO). The exceptional bond length has been explained [42] on the basis of resonance between the homopolar bond structure Cl—N=O and an ionic structure Cl[-][N≡O][+]. The observed N–O bond length in nitrosyl chloride is smaller than the calculated double-bond value required by the homopolar structure, agreeing with partial triple-bond character. Calculation of force constants from the infrared spectrum of nitrosyl chloride supports this interpretation.[43]   Assuming a homopolar structure, Ketelaar [42] has calculated approximate values of 0·3 and 0·45 D for the dipole moments of nitrosyl chloride and bromide respectively ; the large difference between these and the observed values indicates that the ionic structure makes an important contribution to the stationary state.   The existence of a compound NOBr$_3$ has been regarded as further evidence for partial ionic character in nitrosyl bromide.[48]   However, the homopolar structure for the compound is analogous to that of the amine oxides R$_3$N→O, and there is no physical evidence available on which to assess the contribution made by the structure NO[+]Br$_3$[-]. The melting-point diagram for the NOBr–Br$_2$ system shows a maximum corresponding to NOBr$_3$, m.p. $-40°$.[34]   The compound is also formed as a dark red oil by interaction between nitric and hydrobromic acids.[49]

[38] Blair, Brass, and Yost, *J. Amer. Chem. Soc.*, 1934, **56**, 1916.
[39] Bailey and Cassie, *Proc. Roy. Soc.*, 1934, *A*, **145**, 336.
[40] Pulford and Walsh, *Trans. Faraday Soc.*, 1951, **47**, 347.
[41] Ketelaar and Palmer, *J. Amer. Chem. Soc.*, 1937, **59**, 2629.
[42] Ketelaar, *Rec. Trav. chim.*, 1943, **62**, 289.
[43] *Idem, Atti X. Congr. Intern. Chim.*, 1938, **2**, 301.
[44] Stephenson and Jones, *J. Chem. Phys.*, 1952, **20**, 135.
[45] Magnuson, *ibid.*, 1951, **19**, 1071.
[46] Wise and Elmer, *ibid.*, 1950, **18**, 1411.
[47] Burns and Bernstein, *ibid.*, p. 1669.
[48] Moeller, *J. Chem. Educ.*, 1946, **23**, 441.
[49] Datta and Chatterjee, *J. Amer. Chem. Soc.*, 1923, **45**, 480.

Self-ionisation in liquid nitrosyl chloride is small, as indicated by the specific conductivity κ ($2\cdot7 \times 10^{-6}$ ohm^{-1} cm.$^{-1}$ at $-10°$ [50, 51]). In solution in liquid sulphur dioxide [52] (dielectric constant $\varepsilon = 13\cdot5$) and liquid dinitrogen tetroxide [50] ($\varepsilon = 2\cdot42$), conductivity data indicate slight dissociation only. For an 0·02M-solution in sulphur dioxide, κ is 0·6 and $1\cdot5 \times 10^{-6}$ ohm^{-1} cm.$^{-1}$ at $-70°$ and $0°$ respectively, which is of the same order as for corresponding solutions of acetyl, benzoyl, or thionyl chloride ; over the full concentration range of NOCl–N_2O_4 mixtures the specific conductivity does not exceed 10^{-5} ohm^{-1} cm.$^{-1}$.

Dinitrogen trioxide may be regarded as a nitrosyl compound ; the covalent form of the molecule is accepted as

$$\begin{array}{c} {}^{-}O \qquad\qquad O \\ \diagdown \quad + \quad \diagup\!\!\diagup \\ N\!\!-\!\!N \\ \diagup\!\!\diagup \\ O \end{array}$$

, both by analogy with the tetroxide and on the basis of evidence collected by Ingold and Ingold.[53] The contribution of an ionic form [NO$^+$][NO$_2^-$] has been found to be insignificant [54] in media of low dielectric constant, and only homolytic fission of the N–N bond occurs. Thus metals (*e.g.*, sodium) react with liquid dinitrogen tetroxide to give the metal nitrate exclusively ; in the presence of up to 70% of dinitrogen trioxide the reaction is unchanged except in rate, and no nitrite is produced. However, in concentrated sulphuric acid the behaviour of dinitrogen trioxide is compatible with initial heterolytic fission to give the ionic form [NO$^+$][NO$_2^-$] in a medium of high dielectric constant, followed by the rearrangement

$$NO_2^- + H^+ \longrightarrow NO^+ + OH^-$$
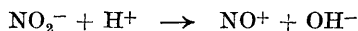
which is usual in acid solution. The disappearance of the intense blue colour on dissolution in sulphuric acid is consistent with this. A blood-red compound NO·SCN can be prepared by any of the following reactions : [56, 57]

$$NO\cdot OH + HSCN \longrightarrow NO\cdot SCN + H_2O$$
$$NOCl + AgSCN \longrightarrow NO\cdot SCN + AgCl \text{ (in CCl}_4)$$
$$EtO\cdot NO + HSCN \longrightarrow NO\cdot SCN + EtOH$$
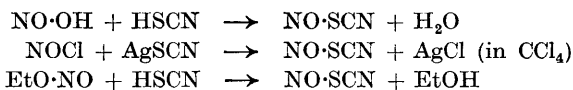
but is not obtained by direct interaction of thiocyanogen and nitric oxide. The compound gives typical nitrosyl group reactions with iodide and azide ions,[9] but is only known in solution, and in high concentration the solution decomposes into its components even at $-60°$. The solution converts cuprous into cupric thiocyanate and mercury into mercurous thiocyanate,

[50] Addison and Lewis, *J.*, 1951, 2843.

[51] Burg and Campbell, *J. Amer. Chem. Soc.*, 1948, **70**, 1964.

[52] Seel, *Z. anorg. Chem.*, 1943, **252**, 24 ; Seel and Bauer, *Z. Naturforsch.*, 1947, **126**, 397.
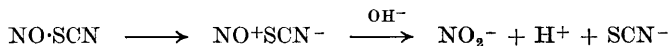
[53] *Nature*, 1947, **159**, 743.

[54] Addison, Lewis, and Thompson, *J.*, 1951, 2838.

[55] Rodebush and Yntema, *J. Amer. Chem. Soc.*, 1923, **45**, 332.

[56] Söderback, *Annalen*, 1919, **419**, 217.

[57] Lecher and Graf, *Ber.*, 1926, **59**, 2601.

and reacts with sodium hydroxide to form sodium thiocyanate and sodium nitrite :

$$NO \cdot SCN \longrightarrow NO^+SCN^- \xrightarrow{OH^-} NO_2^- + H^+ + SCN^-$$

More physical evidence is required before the structure of this compound can be established. It may occur in a co-ordination complex prepared when a solution of Reinecke's salt $K[Cr(NH_3)_2(SCN)_4], H_2O$ is treated with a mixture of nitric oxide and nitrogen dioxide. Werner and Richter [58] have assigned to it the formula $NO[Cr(NH_3)_2(SCN)_4]$, because of its similarity to nitrosonium hydrogen sulphate in its reactions with water, potassium hydroxide, and ammonia, but Seel and Nogradi [9] write the compound as $[Cr(NH_3)_2(SCN)_3(NCS \cdot NO)]$, and classify it as a non-electrolyte in liquid sulphur dioxide along with the nitrosyl halides.

### Ionic Compounds of the Type NO^+X^- (Nitrosonium Compounds)

Nitrosonium hydrogen sulphate and perchlorate are well known ; the first is produced (as chamber crystals) in the lead-chamber process for the manufacture of sulphuric acid, and the second is one of the most stable nitrosonium compounds. The compound $NO^+HSO_4^-$ melts at $73 \cdot 5°$, and is normally obtained in the form of rhombic prisms. It dissolves readily in absolute nitric acid and in concentrated sulphuric acid.[93] With alkalis, it reacts quantitatively :

$$NO \cdot HSO_4 + 2KOH = KNO_2 + KHSO_4 + H_2O$$

and this reaction is employed in the quantitative analysis of nitrosonium salts. The reaction with dry hydrogen chloride gas

$$NO \cdot HSO_4 + HCl = NOCl + H_2SO_4$$
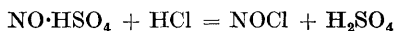
is reversible ; with ammonia, the reaction is

$$NO \cdot HSO_4 + 3NH_3 = (NH_4)_2SO_4 + N_2 + H_2O$$
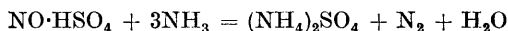
The evolution of nitrogen arises from the intermediate formation of ammonium nitrite. Ethers cannot be used as solvents, since reactions such as

$$NO \cdot HSO_4 + (C_2H_5)_2O = C_2H_5 \cdot HSO_4 + C_2H_5O \cdot NO$$
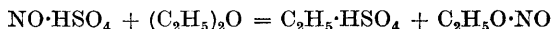
occur. A surprising feature in the chemistry of this compound is that it has not yet been possible to prepare normal salts, so that the HSO_4^- ion does not possess all the chemical properties with which it is usually associated. Nor can the hydrogen be replaced by another NO group ; nitrosonium hydrogen sulphate is formed in the reaction of dinitrogen tetroxide with chlorosulphonic acid, but attempts to synthesise the compound $(NO)_2SO_4$ by reaction of sulphuryl chloride with dinitrogen tetroxide, or with silver nitrite, were unsuccessful.[60] The compound $NO^+HSeO_4^-$ is formed by reaction of a large excess of dinitrogen trioxide with pure selenic acid ; [61] it forms white crystals which melt with decomposition at $80°$.

[58] Werner and Richter, *Z. anorg. Chem.*, 1897, **15**, 243.
[59] Jander and Wendt, *ibid.*, 1948, **257**, 26.
[60] Hart-Jones, Price, and Webb, *J.*, 1929, 312.
[61] Meyer and Wagner, *J. Amer. Chem. Soc.*, 1922, **44**, 1032.

Like the sulphur analogue, it is soluble without decomposition in absolute alcohol, but not in ether ; but unlike it, the hydrogen of the $HSeO_4^-$ ion has been replaced by a nitrosonium ion to give dinitrosonium selenate $(NO^+)_2SeO_4^{2-}$.[62] This compound was, in fact, prepared in 1906 before the mononitrosonium compound was known, by the addition of excess of liquid dinitrogen tetroxide to an 83% aqueous solution of selenic acid. If the mixture is kept below $-13°$, deep blue crystals are obtained ; although this compound has been generally accepted as a dinitrosonium salt, its blue colour is not in accord with this formulation, and it seems possible on present evidence that at least one of the NO groups is covalently bonded.

Nitrosonium hydrogen sulphate decomposes slowly above its melting point to give colourless crystals of nitrosonium disulphate $(NO^+)_2S_2O_7^{2-}$ (m.p. 217°). This compound dissolves unchanged in sulphuric acid, and is so stable that it boils at 360° without decomposition.[93] The disulphate has also been obtained by the action of dinitrogen tetroxide on liquid sulphur dioxide, disulphuric acid, disulphuryl chloride,[60] or nitrogen sulphide (N_4S_4),[63] and by submitting a mixture of air and sulphur dioxide to an electric discharge.[64] Nitrosonium hydrogen selenate decomposes on heating to give oxides of nitrogen and selenic acid,[61] and does not yield the corresponding diselenate. Nitrosonium salts of more complex sulphates have also been prepared. Vacuum-distillation of the reaction product of sulphur trioxide with sodium nitrite gives the compound $N_2O_3,3SO_3$ (b.p. 170°/13 mm., m.p. 143°)[65] and with dinitrogen pentoxide the compound $N_2O_4,3SO_3$.[66] Because of the hardness and thermal stability of these crystals, they are formulated as the ionic compounds $(NO^+)_2[S_3O_{10}]^{2-}$ and $(NO)^+(NO_2)^+[S_3O_{10}]^{2-}$; this structure for the latter compound is supported by its Raman spectrum.[66]

Nitrosonium perchlorate is prepared as a colourless crystalline solid by methods analogous to those for the hydrogen sulphate.[6, 7, 67] The compound hydrolyses immediately in water, and forms methyl nitrite with methyl alcohol. The solid decomposes, without melting, when heated to temperatures below 100° $(2NO \cdot ClO_4 = N_2O_4 + Cl_2 + 3O_2)$; its heat of formation is $-41·9$ kcal./mole.[68] A related compound, nitrosonium perrhenate $(NO^+ReO_4^-)$, is obtained as colourless, hygroscopic crystals on passing nitric oxide into a concentrated solution of per-rhenic acid.[69]

A number of nitrosonium salts of metal fluoro- and chloro-complex anions exist ; it is consistent with the stability of the corresponding nitrosyl halides that no salts of bromo- or iodo-complexes are known. The various

[62] Lenher and Mathews, *J. Amer. Chem. Soc.*, 1906, **28,** 516.

[63] Meuwsen and Kruger, *Z. anorg. Chem.*, 1938, **236,** 221.

[64] Wannagat, *ibid.*, 1952, **269,** 232.

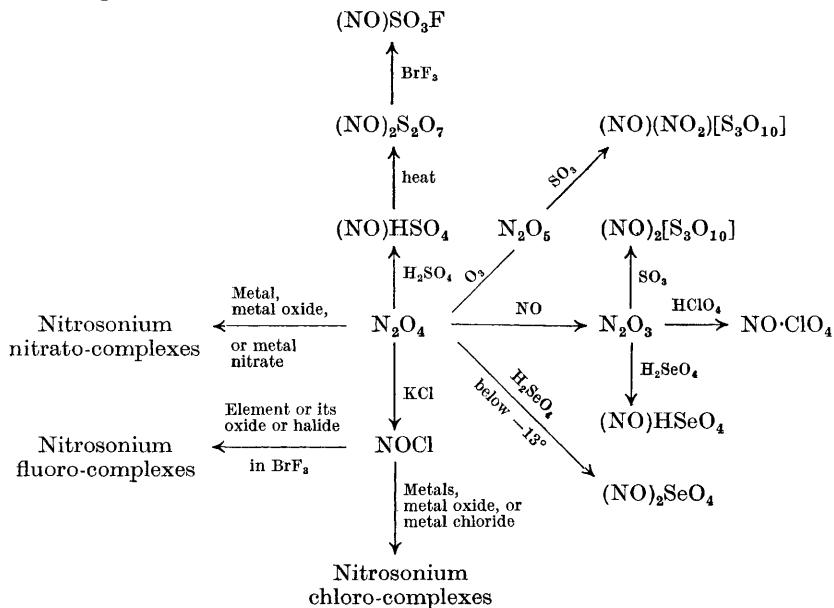[65] Lehmann and Kluge, *ibid.*, 1951, **264,** 120.

[66] Gerding and Eriks, *Rec. Trav. chim.*, 1952, **71,** 773.

[67] Cruse, Drobny, Huck, and Möller, *Z. anorg. Chem.*, 1949, **259,** 154.
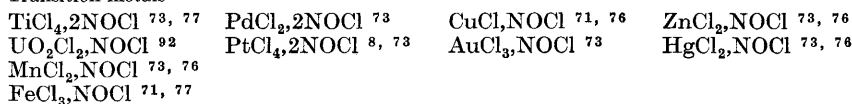
[68] Cruse, Huck, and Möller, *ibid.*, p. 173.

[69] Wilke-Dörfurt and Gunzert, *ibid.*, 1933, **215,** 369.

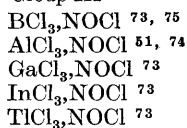nitrosonium compounds discussed in this section are correlated in the following scheme :

$$(NO)SO_3F$$

$\uparrow$ BrF$_3$

$$(NO)_2S_2O_7 \qquad\qquad (NO)(NO_2)[S_3O_{10}]$$

$\uparrow$ heat $\qquad\qquad$ SO$_3$ $\nearrow$

$$(NO)HSO_4 \qquad N_2O_5 \qquad (NO)_2[S_3O_{10}]$$

$\uparrow$ H$_2$SO$_4$ $\qquad$ O$_2$ $\nearrow$ $\qquad\qquad$ $\downarrow$ SO$_3$

Nitrosonium $\qquad$ Metal, metal oxide, $\qquad\qquad\qquad$ NO $\qquad\qquad$ HClO$_4$

nitrato-complexes $\longleftarrow$ or metal nitrate $\quad$ N$_2$O$_4$ $\longrightarrow$ N$_2$O$_3$ $\longrightarrow$ NO·ClO$_4$

$\downarrow$ KCl $\qquad$ $\searrow$ below $-13°$ H$_2$SeO$_4$ $\qquad\qquad$ $\downarrow$ H$_2$SeO$_4$

Nitrosonium $\qquad$ Element or its oxide or halide $\qquad\qquad\qquad\qquad$ (NO)HSeO$_4$

fluoro-complexes $\longleftarrow$ in BrF$_3$ $\qquad$ NOCl

$\downarrow$ Metals, metal oxide, or metal chloride $\qquad\qquad$ (NO)$_2$SeO$_4$

Nitrosonium
chloro-complexes

Nitrosonium Salts of Chloro-complexes.—These addition compounds of nitrosyl chloride and metal chlorides are prepared by the direct action of nitrosyl chloride on the free metal, metal oxide, or metal chloride. Some known compounds are listed below.
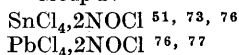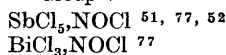
Transition metals

TiCl$_4$,2NOCl [73, 77]   PdCl$_2$,2NOCl [73]   CuCl,NOCl [71, 76]   ZnCl$_2$,NOCl [73, 76]

UO$_2$Cl$_2$,NOCl [92]   PtCl$_4$,2NOCl [8, 73]   AuCl$_3$,NOCl [73]   HgCl$_2$,NOCl [73, 76]

MnCl$_2$,NOCl [73, 76]

FeCl$_3$,NOCl [71, 77]

Group III	Group IV	Group V
BCl$_3$,NOCl [73, 75]	SnCl$_4$,2NOCl [51, 73, 76]	SbCl$_5$,NOCl [51, 77, 52]
AlCl$_3$,NOCl [51, 74]	PbCl$_4$,2NOCl [76, 77]	BiCl$_3$,NOCl [77]
GaCl$_3$,NOCl [73]		
InCl$_3$,NOCl [73]		
TlCl$_3$,NOCl [73]		

The existence of the NO$^+$ ion has not been established unequivocally in all these compounds, and the following discussion is concerned with the

[70] Addison and Thompson, *J.*, 1949, S 218.
[71] Burg and McKenzie, *J. Amer. Chem. Soc.*, 1952, **74**, 3143.
[72] Houtgraaf and De Roos, *Rec. Trav. chim.*, 1953, **72**, 963.
[73] Partington and Whynnes, *J.*, 1948, 1952 ; 1949, 3135.
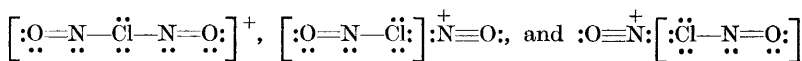[74] *Rec. Trav. chim.*, 1953, **72**, 21.
[75] Hewitt and Holliday, *J.*, 1953, 532.
[76] *Z. anorg. Chem.*, 1939, **243**, 127.
[77] Rheinbolt and Wasserfuhr, *Ber.*, 1927, **60**, 732.

various criteria which have been used to determine the nature of the bonding of the NO group.

(a) *Electrical properties of solutions.* Liquid nitrosyl chloride is an ionising solvent for a number of these compounds ; it has dielectric constant $\varepsilon = 19.7$ ($- 10°$) and 22.5 ($- 27°$).[71] Burg and Campbell [51] point out that whereas the chloride ion should not be appreciably solvated, the nitrosonium ion should be strongly solvated because of resonance involving the structures

$$\left[:\overset{..}{O}=N-\overset{..}{\underset{..}{Cl}}-N=\overset{..}{\underset{..}{O}}:\right]^{+}, \quad \left[:\overset{..}{O}=N-\overset{..}{\underset{..}{Cl}}:\right]:\overset{+}{N}\equiv O:, \quad \text{and} \quad :O\equiv\overset{+}{N}:\left[:\overset{..}{\underset{..}{Cl}}-N=\overset{..}{\underset{..}{O}}:\right]$$

In agreement with this, potassium chloride is insoluble in nitrosyl chloride, whereas a number of the addition products listed above are soluble. The aluminium, iron, and antimony compounds behave as strong electrolytes, and are formulated as $NO^+[AlCl_4^-]$, $NO^+[FeCl_4^-]$, and $NO^+[SbCl_6^-]$. With the first two compounds pressure–composition isotherms show the existence of further compounds $NO[AlCl_4],NOCl$ and $NO[FeCl_4],NOCl$ having dissociation pressures (at $0°$) of 180 mm. and 224 mm., respectively. Magnetic-susceptibility measurements on the iron compound confirm it as a solvate, of the type $[NO^+\cdot NOCl][FeCl_4^-]$.[71] Evidence for the compound $AlCl_3,2NOCl$ is also given by the freezing-point diagram ; it has an incongruent melting point, and a transformation temperature of $125°$.[72] Some conductivity values at $- 20°$ are given below :

| Solute	Molar concn.	Sp. conductivity (ohm^{-1} cm.$^{-1}$)
$NO^+[AlCl_4^-]$	0·098	$1·17 \times 10^{-2}$
$NO^+[FeCl_4^-]$	0·0099	$1·34 \times 10^{-3}$
$NO^+[SbCl_6^-]$.	0·14	$2·35 \times 10^{-2}$

Assuming the applicability of the Debye–Huckel theory, Burg and McKenzie [16] calculated the following degrees of ionic dissociation for the salt $NO^+[FeCl_4^-]$ dissolved in nitrosyl chloride :

Concn. (10^{-4} mole/l) .	3·28	7·04	15·3	21·9	46·5	61·3
Dissociation (%) . . .	93·7	88·5	82·0	79·2	71·7	69·3

The ions involved have been identified by electrolysis, nitric oxide being evolved at the cathode and chlorine at the anode. Tentative values for the transport numbers of the ions are 0·12 ($FeCl_4^-$) and 0·88 (NO^+).[71] The very high NO^+ value is surprising and, if true, must imply some chain mechanism analogous to the transport of the H^+ ion in water.

The acid–base equilibrium in the nitrosyl chloride solvent system may be represented as $NO^+ + Cl^- \rightleftharpoons NOCl$, and radioactive chloride ions dissolved in liquid nitrosyl chloride exchange rapidly with the medium.[119] Nitrosonium salts therefore function as acids in this system, and chlorides

as bases.   The following acid–base reaction has been established by conductometric titration :

$$NO^+[FeCl_4^-] + Me_4N^+Cl^- = Me_4N^+[FeCl_4^-] + NOCl$$
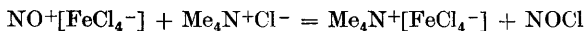
In keeping with the high transport number of the NO^+ ion, the shape of the conductivity curves is similar to that obtained on addition of a base to a strong acid in the aqueous system.   When antimony pentachloride is added to a solution of nitrosyl chloride in liquid sulphur dioxide, the conductivity increases.[52]   A break in the conductivity curve occurs when the ratio $SbCl_5 : NOCl$ is $1 : 1$, after which there is no further increase, indicating the reaction $NOCl + SbCl_5 = NO^+ + SbCl_6^-$.   The molar conductivity of concentrated solutions of the nitrosonium salt in liquid sulphur dioxide is of the same order as that of strong electrolytes such as $K^+[SbCl_6^-]$, and varies in a significant manner with temperature ;   the following Table shows this variation for 0.02M-solutions of the potassium and nitrosonium salts :

Molar conductivities $(ohm^{-1}\ cm.^{-1})$ *in liquid sulphur dioxide*

	$-70°$	$-60°$	$-50°$	$-40°$	$-30°$	$-20°$	$-10°$	$0°$
$NO^+[SbCl_6]^-$	50·0	57·7	63·9	68·1	70·5	71·2	70·0	67·5
$K^+[SbCl_6]^-$	49·6	57·8	65·7	73·5	80·0	85·6	90·0	92·8

At low temperatures the conductivities are almost identical.   In interpreting the maximum in the conductivity curve for the nitrosonium salt, Seel [52] has suggested that this compound is not to be regarded under all conditions as a true salt, but that an equilibrium exists between the ionic form and a molecular addition compound, *i.e.*,

$$NO^+[SbCl_6^-] \ \rightleftharpoons \ SbCl_5 \cdots Cl \cdot NO$$
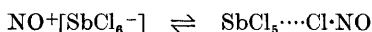
and that there is a shift in this equilibrium within the above temperature range.   In agreement with this, the pure solid is bright yellow and is readily sublimed.

(b) *Raman spectra.*   This was one of the first physical methods to be applied to the study of the structure of nitrosonium salts.[7]   Gerding and Houtgraaf [74] have compared the Raman spectra of the compounds $NaCl,AlCl_3$ and $NOCl,AlCl_3$.   Earlier preparations [73] of the latter gave a lemon-yellow product melting at 108—$112°$, with decomposition.   Gerding and Houtgraaf obtained a white substance, melting at $180°$ to give a yellow liquid which showed no decomposition during several days.   The difference in melting points is too wide to be accounted for by impurities, and the compound probably exists in two allotropic forms, the metastable form having the lower melting point.   Measurements on the stable liquid show that the strongest Raman line of low frequency is identical with that for the compound $NaCl,AlCl_3$, indicating the presence of the $[AlCl_4]^-$ ion in the compound $NOCl,AlCl_3$ also.   Measurements on the solid showed an intense Raman line corresponding to a frequency shift of 2236 cm.$^{-1}$.   The

Table below lists the frequency shifts (ν NO) found for different inorganic compounds containing the NO group:[74]

Compound	(ν NO) cm.$^{-1}$	N–O bond length (Å)
NO$^+$[HSO$_4^-$]	2340	1·107
NO$^+$[ClO$_4^-$]	2313	1·11
NO$^+$[AlCl$_4^-$]	2236	1·12
NO (gas)	1877	1·15
NOCl	1800	1·14

On the basis of this comparison, Gerding and Houtgraaf's conclusions regarding the compound NO$^+$[AlCl$_4^-$] resemble those of Seel [52] with respect to the corresponding antimony complex, the compound being intermediate between an ionic and a molecular compound,

$$NO^+[AlCl_4^-] \rightleftharpoons AlCl_3\cdots Cl\cdot NO$$
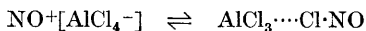
with the ionic form making much the greater contribution. The physical properties of the corresponding gallium, indium, and thallium compounds indicate that they are in a similar physical state.[73]

(c) *X-Ray crystallography.* This technique has been little used in recent studies of the structure of nitrosonium compounds. Klinkenberg [8] found the complexes SnCl$_4$,2NOCl and PtCl$_4$,2NOCl to contain the nitrosonium ion, and to be isomorphous with the corresponding ammonium salts (NH$_4$)$_2$SnCl$_6$ and (NH$_4$)$_2$PtCl$_6$.

(d) *Magnetic susceptibility.* Nitrosyl chloride is diamagnetic in the liquid and the gaseous state.[78] Asmussen [76] used magnetic-susceptibility measurements to study nitrosyl chloride addition compounds, which were found to fall into three distinct groups:

Compound	Temp.	$-\chi_M \times 10^6$	$-\chi_{NOCl} \times 10^6$
ZnCl$_2$,NOCl	2°	68·6	−0·9
HgCl$_2$,NOCl	5	67·4, 70·8	3·8
AlCl$_3$,NOCl	5	101·5, 83·6	0·5
SbCl$_5$,NOCl	2	138·7, 142·4	15
SnCl$_4$,2NOCl	5	133, 137	23
PtCl$_4$,2NOCl	10	196	—
MnCl$_2$,NOCl	21	Paramagnetic	
CuCl,NOCl	21	Diamagnetic, becoming paramagnetic on illumination	

Col. 3 gives values for the molar susceptibility of the compound, and col. 4 the apparent molar susceptibility of the combined nitrosyl chloride. Subdivision into the first two groups is in accord with the observed thermal

[78] Beeson and Coryell, *J. Chem. Phys.*, 1938, **6**, 656.

stability. Members of the first group readily lose nitrosyl chloride on being heated, and were considered by Asmussen to be molecular addition compounds. Compounds in the second group are more stable to heat, and were classified as nitrosonium salts. The aluminium compound used by Asmussen was yellow, and was probably the metastable form mentioned earlier. The copper compound is discussed later. The manganese compound is formulated [76] as $[MnNO]Cl_3$ by analogy with the copper compound, but paramagnetism in this case gives no direct evidence in support of this structure, since the manganese ion is itself paramagnetic.

Nitrosonium Salts of Fluoro-complexes.—These compounds have not been investigated to the same extent as the chloro-complexes. The chief method of preparation involves the reaction of the element itself, or its oxide or halide, with nitrosyl fluoride ; the following compounds have been prepared :

Transition metals : $(NO)_2TiF_6$ [10] $(NO)VF_6$ [81] $(NO)AuF_4$ [10]

Group III	Group IV	Group V	Group VI
$(NO)BF_4$ [8, 10, 18]	$(NO)_2GeF_6$ [10]	$(NO)PF_6$ [10, 82]	$(NO)SO_3F$ [10]
	$(NO)_2SnF_6$ [10]	$(NO)AsF_6$ [10]	
		$(NO)SbF_6$ [10]	

Many of these compounds are white crystalline solids, readily hydrolysed by water. They have been formulated as above by analogy with the chloro-complexes, and relatively few studies of structure have been carried out. The compound $(NO)PF_6$ has been shown to be a salt by virtue of its conductivity in nitromethane solutions,[82] and the observed equilibrium

$$(NO)BF_4 + Me_4NCl = NOCl + Me_4NBF_4$$
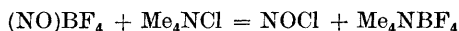
in liquid nitrosyl chloride is consistent with an ionic formulation for the fluoroborate.[71]

Nitrosonium Nitrates.—The simplest member of this group is dinitrogen tetroxide, the structure of which has been the subject of considerable discussion. Much physical evidence (*e.g.*, crystallographic study of the solid,[83] and infrared spectra [84]) is in support of a symmetrical structure for the molecule, while its chemical reactions favour its formulation as nitrosonium nitrate. In the liquid state, the molar refraction and molar polarisation are 15·2 and 26·5 c.c., respectively.[85] This difference is attributed to the presence in the liquid of the dipolar constituent $[NO^+][NO_3^-]$; because of the low dielectric constant (2·42) these ions are associated as ion-pairs. The equilibrium $N_2O_4 \rightleftharpoons [NO^+][NO_3^-]$ lies almost entirely on the left in the pure tetroxide,[86] but in solution in liquids

[79] Sudborough, *J.*, 1891, **59,** 655.
[80] Manchot, *Annalen*, 1910, **375,** 308.
[81] Sharpe and Woolfe, *J.*, 1951, 798.
[82] Seel and Gössl, *Z. anorg. Chem.*, 1950, **263,** 253.
[83] Broadley and Robertson, *Nature*, 1949, **164,** 915.
[84] Sutherland, *Proc. Roy. Soc.*, 1933, *A*, **141,** 342.
[85] Addison, Bolton, and Lewis, *J.*, 1951, 1294.
[86] Addison and Lewis, *J.*, 1953, 1869.

of high dielectric constant (*e.g.*, pure nitric acid) dissociation into these ions is complete.[90]   Some support for the presence of the nitrate group in liquid dinitrogen tetroxide is also given by an isotope-exchange reaction, in which the compound $Me_4N\cdot^{15}NO_3$ was dissolved in the tetroxide ; the latter when separated was found to contain the ^{15}N isotope.[87]   This exchange probably results from the presence of nitrate ions in the tetroxide, although it could occur by oxide-ion transfer between the added nitrate ions and nitrogen dioxide molecules.   Kinetic studies of the reaction of metals with liquid dinitrogen tetroxide indicate that electron transfer involving the ion-pair occurs, *e.g.*, $Zn + 2[NO^+][NO_3^-] \rightarrow Zn(NO_3)_2 + 2NO$. This reaction has an activation energy of 4500 cal., which is of the same order as that for reaction of zinc with aqueous mineral acids.[88]

Liquid dinitrogen tetroxide is a useful medium for the preparation of nitrosonium salts of metal nitrato-complexes.   In the above reaction, zinc nitrate separates as the compound $Zn(NO_3)_2,2N_2O_4$.   The reaction of this compound with organic solvents (*e.g.*, ethyl ether) is vigorous, and quite different in character from that of its components ;   the compound is formulated as the salt $(NO^+)_2[Zn(NO_3)_4]^{2-}$.[89]   Electrolysis of its solutions in nitromethane shows the presence of the NO^+ ion,[91] and other salts of the tetranitratozincate ion may be obtained by such metathetical reactions as

$$(NO^+)_2[Zn(NO_3)_4]^{2-} + 2EtNH_3^+NO_3^- = (EtNH_3^+)_2[Zn(NO_3)_4]^{2-} + 2N_2O_4$$
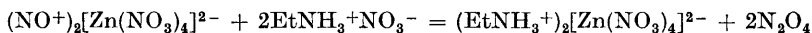
This is an acid–base reaction in the dinitrogen tetroxide solvent system. Reaction of uranium metal with nitromethane–dinitrogen tetroxide mixtures gives the compound $(UO_2)(NO_3)_2,N_2O_4$ as yellow transparent crystals. However, in nitromethane solution the equilibrium

$$NO^+[UO_2(NO_3)_3]^- \rightleftharpoons UO_2(NO_3)_2 + N_2O_4$$
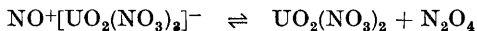
must lie far to the right, since the ultraviolet absorption spectrum of the solution indicates the presence of a negligible quantity of the $[UO_2(NO_3)_3]^-$ ion.[92]

Ionic Compounds of the Type M^+NO^-

When a stream of slow electrons (accelerated by potentials of less than 1 v) is passed through nitric oxide under a pressure of a few mm. of mercury, NO^- ions are formed.[94]   If an electron filter is placed between cathode and anode, the change in anode current shows the NO molecule to have a definite electron affinity.[95]   Compounds which probably contain the NO^- ion are formed by reaction of nitric oxide with the most electropositive

[87] Clusius and Vechi, *Helv. Chim. Acta*, 1953, **36,** 930.
[88] Addison and Lewis, *J.*, 1951, 2833.
[89] Addison, Lewis, and Thompson, *J.*, 1951, 2829.
[90] Goulden and Millen, *J.*, 1950, 2620.
[91] Addison and Hodge, *J.*, 1954, 1138.
[92] *Idem*, unpublished results.
[93] Elliott, Kleist, Wilkins, and Webb, *J.*, 1926, 1219.
[94] Bradbury, *J. Chem. Phys.*, 1934, **2,** 827.
[95] Pritchard, *Chem. Rev.*, 1953, **52,** 529.

metals. Some reactions have been carried out in pyridine,[102] but liquid ammonia is normally used as reaction medium. Joannis [96] first observed that when nitric oxide was passed into a solution of sodium in liquid ammonia, the blue colour disappeared, leaving a white gelatinous suspension which on evaporation of the ammonia gave a white amorphous solid ; the ratio of the nitric oxide absorbed to the sodium dissolved was 1 : 1. Potassium solutions behaved similarly. Zintl and Harder [97] established the empirical formula NaNO, and suggested a monomeric structure ; they compared the Debye–Scherer photographs with those of sodium hyponitrite, and in this way showed that the product differed from the dimer $Na_2N_2O_2$. More recently, Frazer and Long [98] have shown the product to be diamagnetic, and suggest the structure Na^+NO^-. There is, nevertheless, a close relation between this compound (sodium nitrosyl) and sodium hyponitrite. The latter dissolves in water or alkali without immediate decomposition ; sodium nitrosyl dissolves with vigorous effervescence of nitrous oxide. This hydrolysis probably involves first the reaction

$$NaNO + H_2O \longrightarrow NaOH + HNO$$

followed by

$$2HNO \longrightarrow H_2N_2O_2 \longrightarrow N_2O + H_2O$$
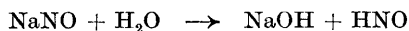
The relative amounts of nitrous oxide or sodium hyponitrite in the hydrolysis product depend upon the alkalinity of the solution, since hyponitrous acid is unstable ; in dilute sodium hydroxide solution the two are formed in comparable quantities.[99] Solutions of hydrogen chloride in dry ether react with sodium nitrosyl to give nitrous oxide only, which no doubt results from complete decomposition of the hyponitrous acid initially produced. The action of nitric oxide on solutions of barium in liquid ammonia gives a white solid $Ba(NO)_2$.[100] This product also evolves nitrous oxide on reaction with water.

A compound which may be sodium nitrosyl is formed by direct reaction of nitric oxide with sodium metal. No reaction occurs at room temperature, but at 160—170° sodium reacts to give a yellow solid $(NaNO)_x$.[101] This gives nitrous oxide with water, and the aqueous solution contains hyponitrite ; the presence also of considerable quantities of nitrite in the solution has been considered to distinguish it from sodium nitrosyl, but it is possible that this by-product may result from some thermal decomposition at the high reaction temperature employed.

These compounds have received little attention and merit further investigation. They may be regarded as salts of the parent acid HNO, of which little is known. Reaction of nitric oxide with atomic hydrogen at low pressures and at the temperature of liquid air gives a pale yellow,

[96] Ann. Chim. Phys., 1906, **7**, 84.
[97] Ber., 1933, **66**, 760.
[98] J. Chem. Phys., 1938, **6**, 462.
[99] Addison and Thompson, unpublished results.
[100] Mentrel, Compt. rend., 1902, **135**, 740.
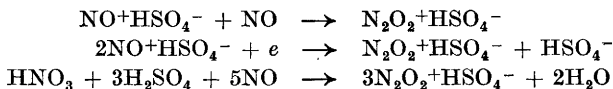[101] Gehlen, Ber., 1939, **72**, 159.
[102] Wertz and Vollmer, Ber., 1924, **57**, 1015.

explosive, hygroscopic solid having empirical formula HNO. On rise of temperature the product becomes white, and at $-95°$ decomposes slowly, evolving nitrous oxide. Explosive decomposition occurs according to the process $2HNO \rightarrow H_2 + 2NO$. Hydrolysis and precipitation with silver nitrate gave 50—70% of the equivalent quantity of hyponitrous acid.[103] This compound clearly differs from hyponitrous acid, which forms white crystals at room temperature.

Complex Ions containing One-electron Bonds

Several compounds exist in which the nitrosonium ion may be regarded as attached to another atom or group by a one-electron bond; they may of course be considered alternatively to involve addition of nitric oxide to a positive ion. The Raman spectrum of pure nitric acid containing nitrosonium ions shows the presence of an ion $N_2O_3^+$ which may be written as $\overset{+}{N}O\cdot\overset{\cdot}{N}O_2$ (I) or $\overset{\cdot}{N}O\cdot\overset{+}{N}O_2$ (II). The frequency of the complex (2240 cm.$^{-1}$) is displaced only one-seventh of the way from that of the nitrosonium ion (2300 cm.$^{-1}$) towards that of nitric oxide (1880 cm.$^{-1}$), so structure (I) makes much the greater contribution.[104]

The existence of the ion $N_2O_2^+$ is of particular interest. Under a pressure of 20 atm. of nitric oxide, solutions containing nitrosonium salts take up nitric oxide according to the scheme $NO^+ + NO \rightarrow N_2O_2^+$, and the following reactions have been studied:

$$NO^+HSO_4^- + NO \quad \rightarrow \quad N_2O_2^+HSO_4^-$$
$$2NO^+HSO_4^- + e \quad \rightarrow \quad N_2O_2^+HSO_4^- + HSO_4^-$$
$$HNO_3 + 3H_2SO_4 + 5NO \quad \rightarrow \quad 3N_2O_2^+HSO_4^- + 2H_2O$$

The " blue acid " formed during the lead-chamber process for sulphuric acid is attributed [107] to the first of these reactions. The ion is stable for short periods at atmospheric pressure in viscous solutions (such as phosphoric acid). Salts of this complex with other anions are available; for example, in liquid sulphur dioxide medium under a pressure of nitric oxide, the reactions

$$NO^+[AlCl_4]^- + NO = N_2O_2^+[AlCl_4]^-$$
and
$$Al + 4NOCl = N_2O_2^+[AlCl_4]^- + 2NO$$
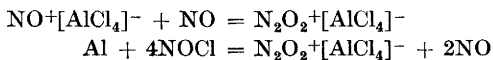
occur, but nitrosyl chloride does not give a compound $N_2O_2^+Cl^-$ under these conditions. $N_2O_2^+[SbCl_6]^-$ is prepared similarly. The structure of the nitric oxide–nitrosonium ion is probably $[ON\cdot NO]^+$, with the two groups united by a one-electron bond. The hydrogen sulphate and a compound NO,SO_3 have both been mentioned in connection with " blue acid "; they can be related in the following way:

$$N_2O_2^+HSO_4^- \rightleftharpoons NO\cdot SO_3 + NO^+OH^-$$
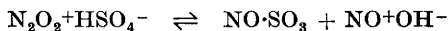
[103] Harteck, *Ber.*, 1933, **66,** 425.
[104] Goulden and Millen, *J.*, 1950, 2620.
[105] Berl and Saenger, *Z. anorg. Chem.*, 1932, **208,** 113.
[106] Meyer and Gulbins, *Ber.*, 1926, **59,** 456.
[107] Seel, Ficke, Riehl, and Wölkl, *Z. Naturforsch.*, 1953, **86,** 607.

The bonding in NO,SO_3 is not certain, and it may resemble the boron trifluoride addition compound NO,BF_3.[108]

One-electron bonding may occur in the complex formed by nitric oxide with hydrochloric acid. When a mixture of the two gases is condensed at $120°$ K, a deep blue liquid is obtained which has a maximum conductivity of 10^{-3} ohm^{-1} cm.$^{-1}$ when the components are in equimolecular quantities.[55] The complex NO,HCl is considered to be $[NOH]^+Cl^-$; the cation may be written $\overset{+}{N}O\overset{\bullet}{H}$ or $\overset{\bullet}{N}O\overset{+}{H}$. Reduction of nitrosonium hydrogen sulphate gives the compound NH_2SO_5,[105] and reduction of nitrosonium hydrogen selenate with mercury gives an analogous selenium compound.[106] The structures of these compounds are not established, but $[NOH]^+HSO_4^-$ and $[NOH]^+HSeO_4^-$ seem to be highly probable.

Complex Ions $L{\rightarrow}NO^+$ and $2L{\underset{\rightarrow}{\rightarrow}}NO^+$
(where L is an electron-pair donor)

The first evidence for the existence of ions of this type was obtained during the study of " basic " solutions in the dinitrogen tetroxide solvent
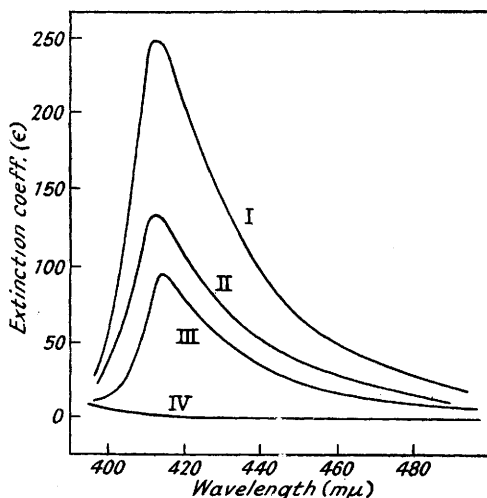
FIG. 1. *Absorption spectra*

I, $NO^+HSO_4^-$ in $Et_2N·NO$ III, N_2O_4 in $Et_2N·NO$
II, $(NO)_2[Zn(NO_3)_4]$ in $Et_2N·NO$ IV, N_2O_4 in CCl_4

system. Solutions of diethylammonium nitrate decompose slowly: $Et_2NH_2·NO_3 + N_2O_4 \rightarrow Et_2N·NO + 2HNO_3$. If the NO^+ ion be regarded here as analogous to the H^+ ion in the aqueous system, then the change $Et_2NH \rightarrow Et_2N·NO$ represents the conversion of diethylamine into the corresponding compound in the dinitrogen tetroxide solvent system, and this stimulated a search for secondary base behaviour involving N_2O_4.

[108] Bues, *Angew. Chem.*, 1952, **64**, 421.

The phase diagram [109] and the viscosities [110] for diethylnitrosamine–dinitrogen tetroxide mixtures give clear evidence for a 2 : 1 compound. This is supported by conductivity data [109] which show also that the molecular complex is ionised. Ultraviolet absorption spectra [110] (Fig. 1) leave no doubt that the $Et_2N\cdot NO$ molecules are associated with NO^+ ions, and all evidence therefore supports the equation

$$N_2O_4 + 2Et_2N\cdot NO \rightleftharpoons \begin{bmatrix} Et_2N\cdot NO \\ \downarrow \\ NO \\ \uparrow \\ Et_2N\cdot NO \end{bmatrix}^+ + NO_3^-$$
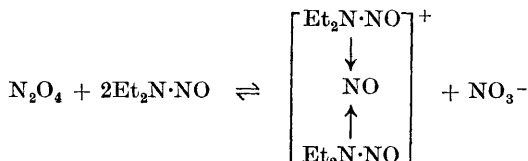
It is now known that this is but one member of a family of such compounds ; NO may be regarded as an electron-deficient group which forms the central unit in a co-ordination complex.[111] The NO^+ ion has 10 valency electrons ; the donation of electron pairs from suitable ligands can take place in two stages :

$$:N{\equiv}O:^+ \rightarrow \begin{bmatrix} L \\ \downarrow \\ :N{=}O: \end{bmatrix}^+ \rightarrow \begin{bmatrix} L \\ \downarrow \\ :N{-}O: \\ \uparrow \\ L \end{bmatrix}^+$$
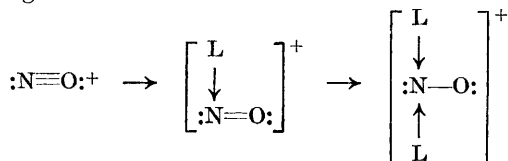
Depending on the structure of the ligand, one or both of the 1 : 1 and 2 : 1 complexes may be formed. Acetonitrile forms both 1 : 1 and 2 : 1 complexes, whereas benzonitrile forms the 1 : 1 complex only.[114] The final stage represents completion of the electron octet of both N and O atoms, with the two atoms united by a single bond, so that complexes having ratios greater than 2 : 1 are not to be expected ; this is normally the case. A wide range of compounds can serve as ligands. Suitable nitrogen compounds include trimethylamine, dimethylaniline, triethylamine, diethylaniline, p-nitrosodimethylaniline, and N-methyldiphenylamine ;[112] the first two gave 1 : 1 addition compounds with dinitrogen tetroxide or nitrosyl chloride and were formulated as $[R_3\overset{+}{N}\cdot NO]X^-$. Addition compounds of general formula $2L,N_2O_4$ have also been isolated where L is pyridine, quinoline, isoquinoline, acridine, α- or β-picoline, or triethylamine.[113] These compounds are stable at sufficiently low temperatures, but decompose vigorously at room temperature. The relative stability of the 1 : 1 and 2 : 1 complexes depends upon the nature of the ligand and the experimental conditions. Many of the features governing the formation of

[109] Addison, Conduit, and Thompson, J., 1951, 1298, 1303.
[110] Addison and Conduit, J., 1952, 1390.
[111] Addison, Hodge, and Sheldon, Chem. and Ind., 1953, 1338.
[112] Comyns, Nature, 1953, 172, 491.
[113] Davenport, Burkhardt, and Sisler, J. Amer. Chem. Soc., 1953, 75, 4175.
[114] Addison and Sheldon, unpublished results.

I

nitrosonium co-ordination complexes are also those observed in the formation and stability of metal co-ordination complexes ; the nature and position of groups substituted into aromatic ligands have a pronounced effect on complex formation in each case. Complexes involving dinitrogen tetroxide and some ethers have been described, which are stable only at low temperatures,[115] but the addition compound with dioxan, $N_2O_4,C_4H_8O_2$, is stable and crystallises readily on mixing the components at room temperature. Nitrosonium complexes are formed with many other oxygen ligands such as carboxylic acids, esters, aldehydes, and ketones. These
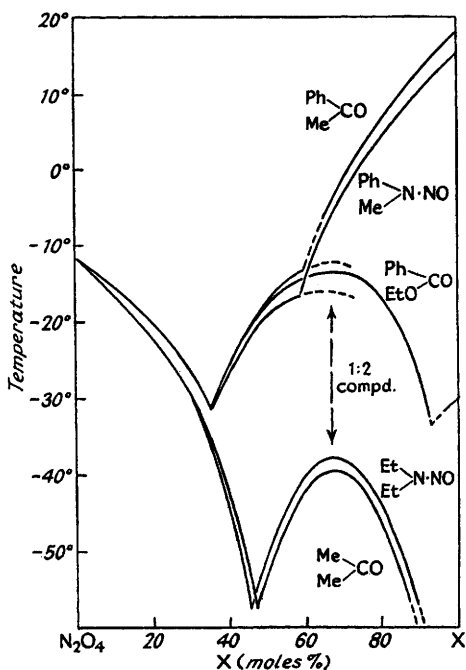
Fig. 2

compounds mostly give 2 : 1 complexes. Fig. 2 illustrates the close similarity in the phase diagrams obtained with ketones R_2CO and nitrosamines $R_2N{\cdot}NO$; [114] while acetic acid gives the 2 : 1 complex only, acetic anhydride gives a 1 : 1 complex with no evidence of the 2 : 1 ratio (Fig. 3). The formulation of the anhydride complex as a chelate compound thus :

$$\left[\begin{array}{c} CMe{=}O \\ \diagup \qquad \searrow \\ O \qquad\qquad NO^+ \\ \diagdown \qquad \nearrow \\ CMe{=}O \end{array}\right] NO_3{}^-$$
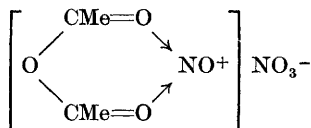
is therefore an attractive possibility. The replacement of oxygen and

[115] Rubin, Shechter, and Sisler, *J. Amer. Chem. Soc.*, 1952, **74**, 877.
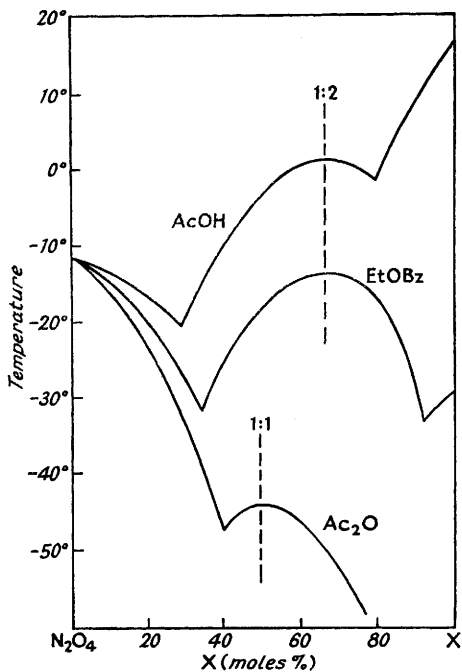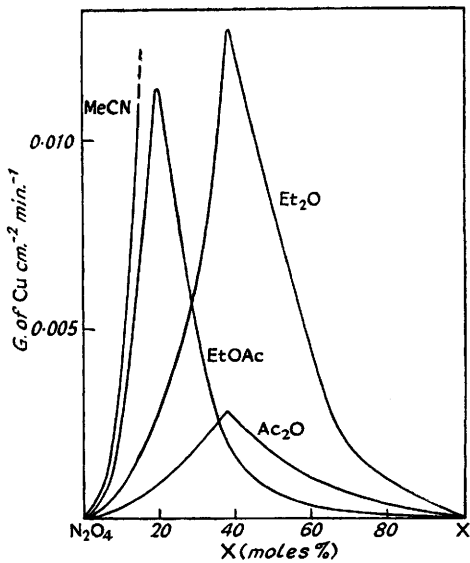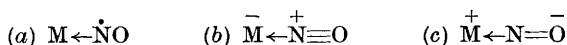
Fig. 3

Fig. 4. *Rates of reaction with copper.*

nitrogen ligands by alkyl or aryl sulphides and phosphides leads to the formation of complexes of high stability.[114]

The ionic nature of the complexes discussed above is illustrated by the fact that they react with metals much more rapidly than do the separate components. Metallic copper reacts at a negligible rate with dinitrogen tetroxide, yet in the presence of ligands such as ether or ethyl acetate (Fig. 4) reaction rates are high [114] and cannot be accounted for by change in dielectric constant. The high rates are considered to result from a high concentration of the nitrosonium complex ion $[L_2NO]^+$. In the cases cited this complex is not sufficiently stable to resist acceptance of an electron, so that it breaks down after electron transfer ; with more stable complexes the rates of reaction with metals are reduced.

Metal Complexes containing the NO Group

General.—A wide range of such complexes is known, and because of the different possible methods of bonding to the metal, the NO group is one of the most interesting of ligands. Nitrogen is the donor atom ; the nitroprusside ion $[Fe(CN)_5NO]^{2-}$ gives the corresponding nitro-compound on hydrolysis and the ammine on reduction. The three possible methods of combination are :

$$(a)\ \text{M} \leftarrow \overset{.}{\text{N}}\text{O} \qquad (b)\ \overset{-}{\text{M}} \leftarrow \overset{+}{\text{N}} \equiv \text{O} \qquad (c)\ \overset{+}{\text{M}} \leftarrow \text{N} = \overset{-}{\text{O}}$$

Type (a) involves no change, (b) a reduction of one unit, and (c) an increase of one unit, in the oxidation state of the metal. Structure (b) is in resonance with the alternative double-bonded structure $\text{M}=\text{N}=\text{O}$.

In type (a) NO donates two electrons to the metal, and co-ordinates as an electrically neutral unit. This should give rise to paramagnetic complexes, with perhaps a temperature variation in magnetic susceptibility associated with the nitric oxide. Type (a) is converted into type (b) when the unpaired electron in the nitrogen p-orbital couples with an unpaired electron in a d-orbital of the metal to give a π-type bond. Alternatively, type (b) may be considered to involve first the donation of the odd electron to the metal, leaving a nitrosonium ion which then acts as a normal ligand by donating an electron pair ; a π-bond is formed by donation of electrons from the metal atom. Type (c) involves donation of an electron from the metal to the NO group, the NO^- ion then behaving as a normal ligand.

Most compounds fall into type (b). The ion NO^+ is isoelectronic with CO and CN^-, and a close analogy is therefore to be expected between corresponding complexes. The variation in the charge on a complex on replacement of one group by another is illustrated by the series

$$K_2[Fe(CN)_5NO] \qquad K_3[Fe(CN)_5CO] \qquad K_4[Fe(CN)_5CN]$$
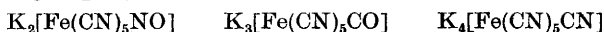
The relation between the metal carbonyls and the metal nitrosyl carbonyls is similarly explained, and simple members of both series obey the effective atomic number rule. The simplest cobalt carbonyl is $Co_2(CO)_8$ since the monomer $Co(CO)_4$ does not satisfy this rule. However, replacement of

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[116] Mellor and Craig, *Proc. Roy. Soc. N.S. Wales*, 1944, **78**, 25.

one CO group (which donates two electrons) by NO [which provides three electrons under bond type (b)] furnishes the missing electron, and cobalt nitrosyl carbonyl is the monomer $Co(NO)(CO)_3$.   In the series

$$Ni(CO)_4 \qquad Co(NO)(CO)_3 \qquad Fe(NO)_2(CO)_2$$
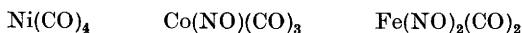
the decrease in atomic number of the metal is compensated by supply of the additional electron from each NO group.   The cobalt and the iron compound have been termed " pseudo-nickel " carbonyls.   The three compounds have similar properties,[117] the gradation resulting from increase in polarity of the nitrosyl group.   Each is tetrahedral,[118] with linear metal-donor atom–oxygen bonds.   Bond-distance measurements show that, as required by structure (b) shown above, the double-bonded form $M{=}N{=}O$ makes some contribution ; the M–N distance is intermediate between those for a single and a double bond, and the N–O distance intermediate between those for a double and a triple bond.

In co-ordination complexes the vacant d-orbitals of the metal are filled by electron-pair donation from the ligands.   If the stable valency state of the metal is such that an unpaired d-electron remains, then the third electron which the NO ligand supplies can complete the d-orbital.   Co-ordination complexes do not normally contain more than one NO group, and the complexes are of the inner orbital type involving d^2sp^3 hybridisation, rather than the outer orbital sp^3d^2 bonding.   Dinitrosyl complexes are only to be expected when the stable valency state of the metal involves two unpaired d-electrons ;   chromium forms the compound $(R_2NCS_2)_2Cr(NO)_2$ which is the only diamagnetic complex formed by chromium in a valency state less than six.[119]   Electron pairing in the final d-orbitals also increases to the maximum the number of such orbitals available for π-bonding, and practically all metal–nitrosyl co-ordination complexes are diamagnetic. The NO group is accompanied in the complexes by other donor atoms (e.g., S, C, Cl) which readily take part in inner-orbital type bonding.   The following metals are known to give such complexes :

V	Cr	Mn	Fe	Co	Ni	Cu
	Mo		Os		Pd	
			Ru		Pt	

and further research will no doubt add other metals to this list.   The tervalent state of ruthenium is particularly stable, and since it commonly forms inner orbital complexes, the range of nitrosyl complexes is unusually great.   No stable nitrosyl complexes are formed by those metals (e.g., Zn, Cd, Hg, and the metals in the main groups of the Periodic Table) which employ outer d-orbitals in complex formation.

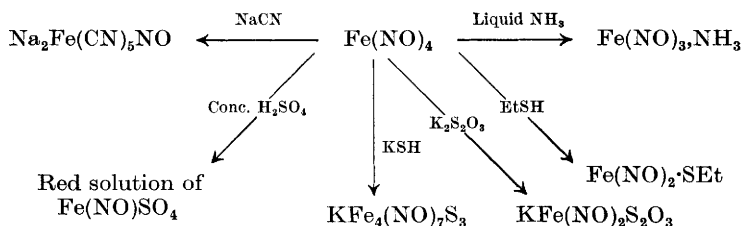### Metal Nitrosyls, Nitrosyl Carbonyls, and Related Compounds

Unstable metal nitrosyls are formed by iron, ruthenium, and nickel. The iron compound $Fe(NO)_4$ is the most stable, and is obtained as black

[117] Hieber and Anderson, Z. anorg. Chem., 1932, **208**, 238 ; 1933, **211**, 132.
[118] Brockway and Anderson, Trans. Faraday Soc., 1937, **33**, 1233.
[119] Lewis and Wilkins, J., 1955, 56.

crystals on heating iron carbonyl with nitric oxide under pressure at about 48°.[120]   It is non-volatile but is oxidised by air.   The following reactions show its relation with other complexes of iron :
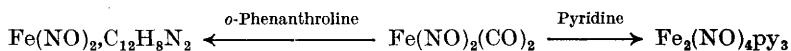
$$Na_2Fe(CN)_5NO \xleftarrow{\;NaCN\;} Fe(NO)_4 \xrightarrow{\;Liquid\ NH_3\;} Fe(NO)_3,NH_3$$

Conc. H_2SO_4 $\qquad$ $K_2S_2O_3$ $\qquad$ EtSH

KSH

Red solution of $\qquad\qquad$ $Fe(NO)_2 \cdot SEt$
$Fe(NO)SO_4$ $\qquad$ $KFe_4(NO)_7S_3$ $\qquad$ $KFe(NO)_2S_2O_3$

The structure of iron tetranitrosyl is not known.   An interesting suggestion [121] is that it is the nitrosonium salt $NO^+[Fe(NO)_3]^-$; this would agree with its non-volatility, and the iron atom has the effective atomic number of krypton.   The product of reaction with liquid ammonia may then be the ammonium salt $NH_4^+[Fe(NO)_3]^-$, and not the substitution compound shown above.

Reaction of ruthenium carbonyl $Ru_2(CO)_9$ with nitric oxide gave red cubic crystals of a ruthenium nitrosyl.[122]   There is some doubt about its original formulation as $Ru(NO)_5$, and it may be $Ru(NO)_4$, analogous to the iron compound.[121]   On passage of nitric oxide into pure nickel carbonyl or its solution in chloroform, a blue powder is deposited : [123] this decomposes violently above 60°, and its composition has not been determined with certainty ; its empirical formula is probably $Ni(NO)_2$, but it is likely to be polymeric.

Substitution of some of the NO groups greatly increases the stability of the metal nitrosyls.   Nitrosyl carbonyls are prepared from the higher carbonyls : [117]

$$Fe_2(CO)_9 \text{ or } Fe_3(CO)_{12} \xrightarrow{\;NO\;} Fe(NO)_2(CO)_2$$

$$KCo(CO)_4 + H_2O \xrightarrow{\;NO\;} Co(NO)(CO)_3$$
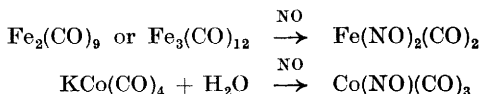
Iron nitrosyl carbonyl forms deep red crystals, m.p. 18·4°, and a red liquid, b.p. 110° ; it decomposes in a vacuum, is oxidised by air, and is soluble in organic solvents.   The cobalt compound (m.p. $-1°$, b.p. 78·6°) is monomeric in the vapour, and is diamagnetic at room temperature ($\chi_M = -45·9 \times 10^{-6}$).[124]   On reaction with compounds capable of substitution, the CO rather than the NO group is displaced :

$$Fe(NO)_2,C_{12}H_8N_2 \xleftarrow{\;\text{o-Phenanthroline}\;} Fe(NO)_2(CO)_2 \xrightarrow{\;\text{Pyridine}\;} Fe_2(NO)_4py_3$$

[120] Manchot and Enk, *Annalen*, 1929, **470,** 275.
[121] Sidgwick, " The Chemical Elements and their Compounds ", Oxford Univ. Press, pp. 1373, 1485.
[122] Manchot and Manchot, *Z. anorg. Chem.,* 1936, **226,** 385.
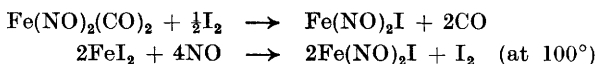[123] Mond and Wallis, *J.,* 1922, **121,** 32.
[124] Reiff, *Z. anorg. Chem.,* 1931, **202,** 375.

and iodine replaces the carbonyl group to give the metal nitrosyl iodide. An interesting series of compounds analogous to the nitrosyl carbonyls have been described recently in which the carbonyl groups are replaced by the electronically similar *iso*cyanide groups.[125] In the iron series $Fe(NO)_2(CNR)_2$, the methyl, phenyl, and *p*-tolyl *iso*cyanides were prepared, and in the cobalt series $Co(NO)(CNR)_3$ the phenyl, *p*-tolyl, and *p*-chlorophenyl *iso*cyanides. As with the corresponding nitrosyl carbonyls, these compounds are diamagnetic and soluble in organic solvents.

Metal Nitrosyl Halides.—An interesting series of halides of general formula $M(NO)_nX$ have been prepared by Hieber and his co-workers.[126, 127] A " nitrosyl displacement law " suggested by Seel [128] is useful in correlating these compounds. It develops the theme that metal–nitric oxide complexes may be regarded as pseudo-atoms ; atoms or groups in the same vertical column in the following scheme form corresponding halides :

Fe	Co	Ni	Cu
	Fe(NO)	Co(NO)	Ni(NO)
		$Fe(NO)_2$	$Co(NO)_2$
			$Fe(NO)_3$

The addition of n molecules of nitric oxide to a metal atom of atomic number A therefore forms a pseudo-atom of the metal of atomic number $A + n$. The ease of formation and the stability of these compounds fall in the order $Fe > Co > Ni$, and for the halogens $I > Br > Cl$. No fluorides are known. Compounds of the type $Fe(NO)_2X$, $Co(NO)_2X$, and $Ni(NO)X$ are best known ; the more stable compounds may be prepared by direct action of nitric oxide with the metal halide, but the less stable compounds require in addition the presence of a halogen acceptor such as iron, cobalt, nickel, or zinc metal powder. A very unstable trinitrosyl, $Fe(NO)_3Cl$, was obtained as dark needles by heating ferrous chloride with nitric oxide in the presence of iron powder at 70°. It sublimes at 110° and readily loses nitric oxide. Dinitrosyl iron iodide is prepared by either of the reactions

$$Fe(NO)_2(CO)_2 + \tfrac{1}{2}I_2 \longrightarrow Fe(NO)_2I + 2CO$$
$$2FeI_2 + 4NO \longrightarrow 2Fe(NO)_2I + I_2 \quad (\text{at } 100°)$$

and was the first known metal nitrosyl halide. The cobalt and the nickel compound are produced less readily ; nickel iodide reacts slowly with nitric oxide even in the presence of a halogen acceptor, but at 150° the reaction

$$2NiI + Zn + 2NO \longrightarrow 2Ni(NO)I + ZnI_2$$
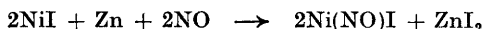
occurs. All the compounds of this class are non-polar, slightly soluble in organic solvents and readily sublimed. It is probable that their structures are such that the metal achieves the effective atomic number of the next
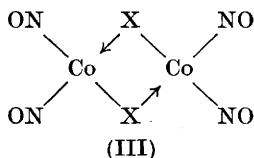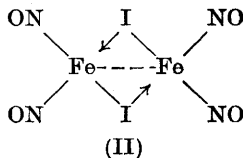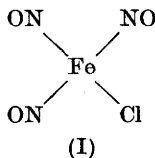
[125] Malatesta and Sacco, *Atti Accad. naz. Lincei*, 1952, **13**, 264 ; *Z. anorg. Chem.*, 1953, **274**, 341.
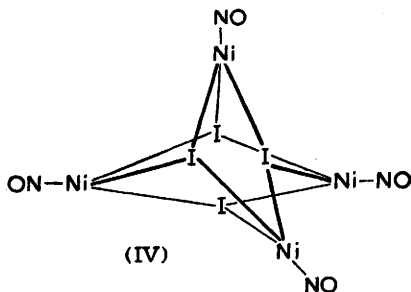[126] Hieber and Marin, *ibid.*, 1939, **240**, 241.
[127] Hieber and Nast, *ibid.*, 1940, **244**, 23.
[128] Seel, *ibid.*, 1942, **249**, 308.

inert gas, and they are in consequence diamagnetic. Suggested structures are (I)—(III). Donation of three electrons from each NO group being

$$
\begin{array}{ccc}
\text{ON} & & \text{NO} \\
& \diagdown \diagup & \\
& \text{Fe} & \\
& \diagup \diagdown & \\
\text{ON} & & \text{Cl}
\end{array}
\qquad
\begin{array}{ccccc}
\text{ON} & & \text{I} & & \text{NO} \\
& \diagdown & \downarrow & \diagup & \\
& \text{Fe}\text{-}\text{-}\text{-}\text{Fe} & \\
& \diagup & \uparrow & \diagdown & \\
\text{ON} & & \text{I} & & \text{NO}
\end{array}
$$

(I) \qquad\qquad\qquad\qquad (II)

$$
\begin{array}{ccccc}
\text{ON} & & \text{X} & & \text{NO} \\
& \diagdown & \downarrow & \diagup & \\
& \text{Co} & & \text{Co} & \\
& \diagup & \uparrow & \diagdown & \\
\text{ON} & & \text{X} & & \text{NO}
\end{array}
$$

(III)

assumed, iron trinitrosyl chloride (I) should be monomeric. A dimeric form (II) is necessary for iron dinitrosyl iodide, with the odd electrons on the metal atoms shared to form the metal–metal bond shown by a broken line, as has been suggested for Roussin's red salt (see p. 141). The effective atomic number rule does not require a metal–metal bond in the corresponding cobalt compounds (III), which are known to be dimeric.[131] Mononitrosyl nickel iodide has been considered to be tetrameric,[129] with a structure (IV) analogous to the copper–tertiary arsine compound $[Cu(AsR_3)I]_4$.[130] If each I atom forms one electron pair bond and two dative bonds, then each Ni atom satisfies the E.A.N. rule.

$$
\begin{array}{c}
\text{NO} \\
| \\
\text{Ni} \\
\text{ON—Ni} \underset{\text{I}}{\overset{\text{I}}{\diamondsuit}} \text{Ni—NO} \\
\text{Ni} \\
| \\
\text{NO}
\end{array}
$$

(IV)

These compounds are oxidised readily in air. On treatment with acids they decompose, evolving nitric oxide, nitrous oxide, and nitrogen. The last two are formed by reduction of nitric oxide in a quantity which corresponds with an increase of one in the oxidation state of the metal. Reaction between metal nitrosyl halides and nitrogen bases occurs in one of three possible ways : (a) an addition compound is formed, e.g., Ni(NO)I,2(o-phenanthroline), (b) the nitric oxide is partly replaced, as in the production of Fe(NO)I,6(pyridine) ; this behaviour contrasts with that of the nitrosyl

[129] Hieber and Nast, FIAT Review of German Science 1939—1946, Inorganic Chemistry, Part II, 146.
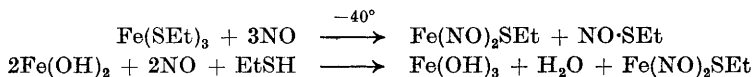
[130] Mann, Purdie, and Wells, J., 1936, 1503.

[131] Kelting, see ref. (129).

carbonyls, where the CO group is preferentially replaced, (c) complete decomposition may occur, with oxidation of the metal and the resultant formation of nitrous oxide and nitrogen. This type of reaction occurs when the nitrogen base can form a very stable co-ordination complex with the metal, e.g., with o-phenanthroline, $Fe(NO)_2I \rightarrow Fe(phen)_3^{2+}$.

Compounds closely related to the metal nitrosyl halides are formed when nitric oxide is passed into solutions of nickel carbonyl in methyl or ethyl alcohol. From the resulting blue solutions, the compounds $Ni(NO)OH,2MeOH$ and $Ni(NO)OH,EtOH$ have been isolated.[132]

Metal Nitrosyl Complexes containing Sulphur.—Sulphur often features as the second donor atom in metal nitrosyl complexes, and the structure of these compounds has given rise to much conjecture. The best known members of this class are the Roussin " red " and " black " salts, of formulæ $K[Fe(NO)_2S]$ and $K[Fe_4(NO)_7S_3]$ respectively, which are conveniently prepared from ferrous sulphide, nitric oxide, and potassium polysulphide. Other metals may replace potassium, and the black precipitate of the cæsium compound may be used to detect the presence of the black salt. A series of esters of the red salt are prepared by such reactions as [133-135]

$$Fe(SEt)_3 + 3NO \xrightarrow{-40°} Fe(NO)_2SEt + NO \cdot SEt$$
$$2Fe(OH)_2 + 2NO + EtSH \longrightarrow Fe(OH)_3 + H_2O + Fe(NO)_2SEt$$

This ethyl ester is soluble in alcohol or ether, from which it crystallises in lustrous, odourless, black plates, m.p. 78°. The general formula being written as $Fe(NO)_2Y$, Y may be $-S^-K^+$, $-SEt$ [133-135], $-SPh$ [133], or $-S_2O_3^-K^+$ [133]. Corresponding thio-complexes of cobalt and nickel, $Co(NO)_2SR$ and $Ni(NO)SR$, are known.[134] Molecular-weight determinations on the esters of the red Roussin salt show them to be dimeric,[133, 135]

(V)   (VI)
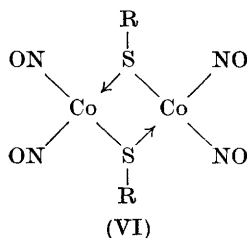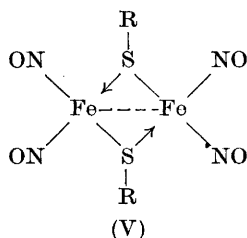
and they are readily formulated as in (V), with four groups arranged tetra-hedrally round each metal atom. This is analogous to the structure of the halide $Fe(NO)_2I$. The E.A.N. of each Fe atom is $26 + 3 + 3 + 2 + 1 = 35$; if we assume again that the odd electrons are paired in an $Fe \cdots Fe$ bond,[140] then each Fe atom has the E.A.N. of the inert gas, which is consistent with the diamagnetism of the compounds.[139] In the cobalt complex

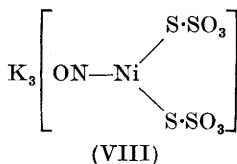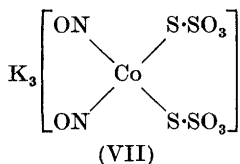[132] Anderson, *Z. anorg. Chem.*, 1936, **229**, 357 ; Reihlen, *ibid.*, 1937, **230**, 223.
[133] Hoffman and Wiede, *ibid.*, 1895, **8**, 318 ; **9**, 295.
[134] Manchot and Gall, *Ber.*, 1927, **60**, 2318 ; 1928, **61**, 2393.
[135] Reihlen and Friedolsheim, *Annalen*, 1927, **457**, 71.

(VI) it is unnecessary to assume a metal–metal bond.   The nickel compounds $Ni(NO)SR$ may perhaps be tetrameric as in the halide $Ni(NO)I$ (IV), p. 140. It is interesting that compounds are known having a structure analogous to (V), in which the four NO groups are replaced by six CO groups.[141]

The thiosulphate complexes of cobalt and nickel do not appear to conform to the Roussin red salt structure.   Nitric oxide reacts with cobalt and nickel salts in the presence of potassium thiosulphate to form the

$$K_3 \begin{bmatrix} ON & & S{\cdot}SO_3 \\ & \diagdown Co \diagup & \\ ON & \diagup & \diagdown S{\cdot}SO_3 \end{bmatrix}$$

(VII)

$$K_3 \begin{bmatrix} & & S{\cdot}SO_3 \\ ON{-}Ni & \diagup & \\ & & \diagdown S{\cdot}SO_3 \end{bmatrix}$$

(VIII)

compounds [137] (VII) and (VIII) ; in (VII) the cobalt atom achieves the inert gas E.A.N.   This is not the case with the nickel compound (VIII) ; it could be achieved by dimerisation, but there is as yet no evidence for this.   The low valency state of the metal is shown by the quantitative evolution of nitrous oxide in alkaline solution.

Roussin's black salt, $K[Fe_4(NO)_7S_3]$, is prepared from the red salt by the action of iron nitrosyl sulphate, $(FeNO)SO_4$.   It decomposes again in alkali to give the red salt

$$2K[Fe_4(NO)_7S_3] + 4KOH \longrightarrow 6K[Fe(NO)_2S] + Fe_2O_3 + N_2O + 2H_2O$$

and, as with all nitric oxide–iron complexes, reacts with cyanides to give the nitroprusside ion.   Molecular-weight determinations show it to be monomeric,[138] and its structure is of particular interest.   Seel [128] has suggested a structure (IX) for the ion based on a ferrous sulphide lattice ;

(IX)
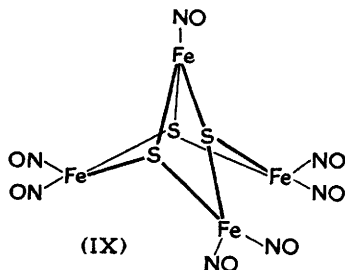
the iron atoms are at the corners of a tetrahedron, with each sulphur atom bonded to three iron atoms.   The black salt was written as early as 1926 [136] in the form $[(NO)_2Fe{-}S)_3{\equiv}Fe(NO)]K$.   We may now draw the ion as

[136] Manchot and Linckh, *Ber.*, 1926, **59**, 412.

[137] Manchot, *Ber.*, 1926, **59**, 2445 ; Spacci and Macarovici, *Bull. Soc. Stiinte Cluj,* 1939, **9**, 197.

[138] Marchlewski and Sachs, *Z. anorg. Chem.*, 1893, **2**, 175.

[139] Cambi and Szego, *Atti Accad. Lincei*, 1931, **13**, 168.

[140] Ewens, *Nature*, 1948, **161**, 530.

[141] Reihlen, Friedolsheim, and Oswald, *Annalen*, 1928, **465**, 72.

shown in (X), ignoring the broken lines. The iron atom at the apex has four tetrahedral bonds, but the three at the base have not. If nitric oxide was able to act as a bridge group, three bonds could be considered to exist

(X)
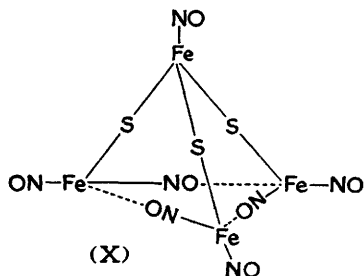
as shown by the broken lines, giving each Fe atom four tetrahedral bonds. This structure is an attractive modification of Seel's structure (IX), although no evidence for bridge-group behaviour in nitric oxide has yet been found. Neither structure gives the Fe atoms the inert-gas effective atomic number. This is not a serious criticism, since the same electron deficiency is observed in the higher carbonyls.

Cation Complexes of Iron and Copper

The metal–nitric oxide compounds already discussed have been for the most part covalent complexes. With iron, and probably with copper, complexes containing only the metal and nitric oxide are known in which the complex exists as a discrete cation. A well-known example is the compound responsible for the " brown ring " in the qualitative test for the nitrate ion. Ferrous sulphate solutions absorb nitric oxide reversibly in quantities up to $Fe^{2+} : NO = 1 : 1$.[142] The nitric oxide is removed again by low pressure, or by heating the solution. The ferrous salt remains, although in weakly acid or neutral solution some oxidation to the ferric state occurs, with production of nitrous oxide or nitrogen.[143] A hydrated salt $(FeNO)SO_4$ has been isolated by adding a concentrated aqueous solution of ferrous sulphate containing nitric oxide to ice-cold concentrated sulphuric acid saturated with nitric oxide.[144] It forms red leaflets which readily decompose, but the corresponding selenate and phosphate are more stable in the solid state. Addition of absolute alcohol to an aqueous solution of ferrous selenate (both cold and saturated with nitric oxide) gives brown-black crystals of $(FeNO)SeO_4,4H_2O$.[145] By similar methods a phosphate $(FeNO)HPO_4$ (m.p. 16°) is produced,[80] and electrolysis of these salts in dilute solutions of the appropriate acid shows the compounds to be ionic, the nitric oxide being associated with the Fe cation.[145]

[142] Manchot and Zechentmayer, *Annalen*, 1906, **350**, 368.
[143] Tarte, *Ind. chim. belge*, 1952, **17**, 42.
[144] Manchot and Huttner, *Annalen*, 1910, **372**, 153.
[145] Manchot and Linckh, *Z. anorg. Chem.*, 1924, **140**, 37.

From studies of the equilibrium $FeSO_4 + NO \rightleftharpoons [FeNO]SO_4$, the reaction has been found strongly exothermic.[146] Dissociation increases rapidly with increasing temperature, it being calculated that 80 atm. pressure would be required at 100° for the combination of 0·5 mole of nitric oxide.[147] The log $K_p-(1/T)$ graph is a straight line, and the calculated heat of reaction is 11·9 kcal./mole, compared with earlier experimental values of 10·5 for this reaction and 10·7 kcal./mole for reaction with ferrous chloride.[148]

The absorption of nitric oxide is influenced in an unusual way by the acidity of the ferrous salt solution. In the dilute acid range, addition of acid decreases the absorption, but this passes through a minimum and then a maximum corresponding to $NO : Fe = 1 : 1$ as acid concentration increases. With hydrochloric acid, the maximum occurs at 34% of acid ; [144] the change in absorption is accompanied by change in colour of the solution from brown in dilute to red in concentrated acid. With sulphuric acid, the brown form is stable below 55% of acid, and the red form above 65% of acid.[14] The absorption spectrum of solutions of the red nitric oxide complexes in the appropriate acid is independent of the anion. The probable explanation of these colour changes is that in solution aquo-nitrosyl iron co-ordination complexes $[Fe(NO)(H_2O)_n]^{2+}$ exist, and that the number of water molecules varies with acid concentration.[149] The presence of only one NO group supports this belief. Colour changes also occur in other solvents, e.g., in acetone and ethyl acetate the complex is green, but in pyridine it is brown.[144]

Less is known about the copper compounds. Cupric salts in concentrated ($> 70\%$) sulphuric acid absorb nitric oxide giving blue-violet solutions.[80] Absorption does not occur in weaker acid, and the complexes are clearly weaker than those of iron. Electrolysis in formic or glacial acetic acid shows the nitric oxide to be associated with the copper cation ; [150] in concentrated hydrochloric or sulphuric acid solution further addition compounds with the acid are formed and both the copper atom and nitric oxide group then occur in the anion. The compound prepared by the action of nitric oxide on cupric chloride [80] is that $(CuCl,NOCl)$ formed between cuprous chloride and nitrosyl chloride. It was first formulated as $Cu_2Cl_2,2NOCl$,[79] but on the basis of its apparent paramagnetism, Asmussen deduced the structure $[CuNO]Cl_2$, assuming the ion $[CuNO]^{2+}$ to be paramagnetic. However, the freshly prepared compound is diamagnetic [71] and becomes paramagnetic on standing ; diamagnetism would support the structure $NO^+[CuCl_2]^-$. The formulation $[CuNO]Cl_2$ appears to be the likely one, as it is reasonable to assume that the ion $[CuNO]^{2+}$ may be either diamagnetic or paramagnetic depending on conditions. In general, cupric salts absorb nitric oxide, whereas cuprous salts absorb carbon monoxide.

There is little evidence for the formation of nitrosyl ferric cations. A

[146] Manchot, *Annalen*, 1910, **372**, 179.
[147] Manchot and Haunschild, *Z. anorg. Chem.*, 1924, **140**, 22.
[148] Gay, Thesis, Paris, Faculté des Sciences, 1895.
[149] Schlesinger and Valkenburgh, *J. Amer. Chem. Soc.*, 1929, **51**, 1323.
[150] Manchot, *Ber.*, 1914, **47**, 1601.

solution of ferric sulphate in 90% sulphuric acid absorbs nitric oxide to give a deep red solution containing the complex $Fe_2(SO_4)_3,4NO$. The solution is unstable and the salt has not been isolated in the pure state.[146] Ferric halides in solution are reduced by nitric oxide to the ferrous state. Solid ferric, aluminium, and bismuth trichlorides absorb nitric oxide reversibly to give the compounds $FeNOCl_3$ (red), $AlNOCl_3$, and $BiNOCl_3$ (yellow), but their structure is unknown.

## Some 6-Co-ordination Complexes

Complexes containing other than cyanide ions are rare ; usually only one NO group occurs in the complex, and is combined (except in specific cases mentioned below) as $\overset{-}{M}{\leftarrow}\overset{+}{N}{\equiv}O$.

Anion Complexes.—The nitrosyl-pentacyano-complexes are most frequently encountered, the commonest example being the nitroprusside ion $[Fe(CN)_5NO]^{2-}$. Analogous ions are formed by ruthenium, manganese,[151] and molybdenum : [152] $[Ru(CN)_5NO]^{2-}$, $[Mn(CN)_5NO]^{3-}$, and $[Mo(CN)_5NO]^{4-}$. There are specific methods of preparation for these compounds, but the use of hydroxylamine for introducing the nitrosyl group has general application. With tripotassium hexacyanomanganate, hydroxylamine gives violet tripotassium nitrosylpentacyanomanganate, and with a mixture of molybdate and potassium cyanide it gives the violet complex $K_4[Mo(CN)_5NO],2H_2O$, which was the first nitrosyl-cyano-complex of a chromium group metal to be prepared. The pure nitroprussic acid $H_2[Fe(CN)_5NO]$ has been isolated, by reaction of the barium salt with sulphuric acid, as red-brown leaflets, very soluble in water to give an unstable solution.[153]

Molecular-weight and electrolytic studies show that sodium nitroprusside is monomeric, and gives three ions in solution. The complex may be considered to contain bivalent iron to which a nitrosonium ion is co-ordinated, so that replacement of the NO group by an uncharged ligand involves an increase of one in the negative charge on the complex :

$$Na_2[Fe(CN)_5NO] \xrightarrow{\text{Na amalgam}} Na_3[Fe(CN)_5NH_3]$$
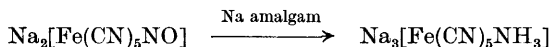
The equilibrium $NO^+ + OH^- \rightleftharpoons H^+ + NO_2^-$ (discussed on p. 116) also occurs when the NO^+ ion is co-ordinated, but whereas stabilisation of the free NO^+ ion requires very high acid concentrations, the ion is stabilised to such an extent by co-ordination that the NO_2^- ion is only formed in alkaline solution : [154]

$$[Fe(CN)_5NO]^{2-} + OH^- \rightleftharpoons [Fe(CN)_5NO_2]^{4-} + H^+$$
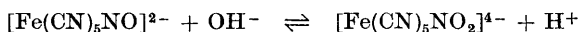
The decomposition of solutions of nitrosyl-pentacyano-complexes, to give the corresponding aquo-pentacyano-complexes with liberation of nitric

[151] Manchot and Schmid, *Ber.*, 1926, **59**, 2360 ; Blanchard and Magnusson, *J. Amer. Chem. Soc.*, 1941, **63, 2236.**
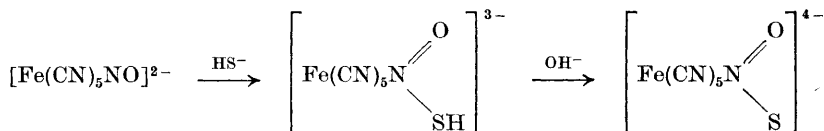
[152] Hieber, Nast, and Gehring, *Z. anorg. Chem.*, 1948, **256**, 169 (see also ref. 129).

[153] Burrows and Turner, *J.*, 1919, **115**, 1429 ; 1921, **119,** 1450.

[154] Cambi and Szego, *Atti Accad. Lincei*, 1927, **5**, 737.

oxide, is accelerated by light. The nitrosyl group in the nitroprusside ion is activated by light, and certain nitroprusside reactions only occur in the presence of light.

Two important reactions of the nitroprusside ion, for which the NO group is responsible, are the Gmelin reaction (used for the detection of sulphur in organic compounds) and the Bödeker reaction with sulphites. In the former, a purple-violet coloration is obtained in alkaline solution in the presence of sulphides. Electro-titrations of the solutions are interpreted on the basis of a two-stage reaction :

$$[Fe(CN)_5NO]^{2-} \xrightarrow{HS^-} \left[Fe(CN)_5N\begin{smallmatrix} \diagup O \\ \diagdown SH \end{smallmatrix} \right]^{3-} \xrightarrow{OH^-} \left[Fe(CN)_5N\begin{smallmatrix} \diagup O \\ \diagdown S \end{smallmatrix} \right]^{4-}$$

The stable solid $Na_4[Fe(CN)_5NOS]$ has been isolated from solution in absolute alcohol.[155] In Bödeker's reaction,[156] sulphites give a deep red colour due to the presence of the ion $\left[Fe(CN)_5N\begin{smallmatrix} \diagup O \\ \diagdown SO_3 \end{smallmatrix} \right]^{4-}$, and some stable addition compounds with hexamethylenetetramine, having the composition $M_2[Fe(CN)_5NO·SO_3],12H_2O,2C_6H_{12}N_4$ (where M = Ni, Cd, Zn), have been isolated.

Cation Complexes.—The nitrosyl pentammine complexes of cobalt, $[Co(NH_3)_5NO]X_2$, are unusual in that the mode of bonding of the NO group appears to vary with change in anion. The salts are prepared by bubbling nitric oxide through ammoniacal cobalt salt solutions ; from cobalt chloride, a black salt is obtained, but cobalt nitrate or sulphate gives a pink salt. The two cations have the same empirical formula, and since NO is the only group in which bond type can vary, it is clearly this variation which gives rise to the two complexes. Consistent with this, the chemical properties of the two complexes are different ; on acidification the black salt evolves nitric oxide, whereas the pink salt is unaffected. The pink complex is diamagnetic,[116, 157, 158] and this is one of the few cases where the NO group may be considered to function in a complex as a negative group NO^-. To give bonding of the type $M{\leftarrow}N{=}\overset{+}{O}$, the NO group must receive one electron from the cobalt atom, which thereby becomes tervalent, and the complex then involves inner orbital bonding $3d^24s4p^3$.

The magnetic moment of the black complex is 1·6—1·7 Bohr magnetons,[116, 157, 158] corresponding to one unpaired electron. Mellor and Craig [116] suggest that the nitric oxide in this case donates two electrons only ($M{\leftarrow}\overset{..}{N}O$), and that an inner orbital complex is formed, with cobalt

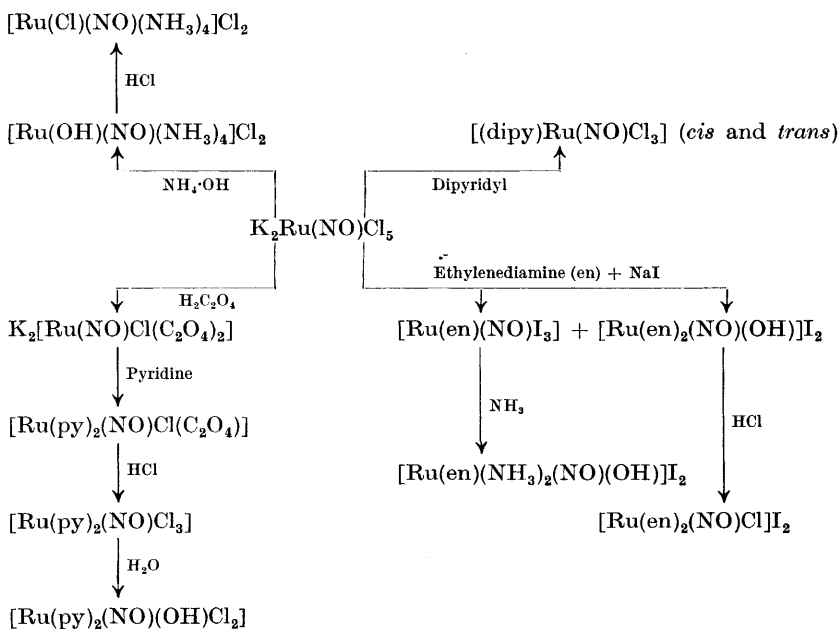[155] Scagliarini and Gentile, *Atti Accad. Lincei*, 1933, **17**, 398.
[156] *Annalen*, 1861, **117**, 193.
[157] Milward, Wardlaw, and Way, *J.*, 1938, 233.
[158] Ghosh and Ray, *J. Indian Chem. Soc.*, 1943, **20**, 409.

bivalent. Such a complex then has two unpaired electrons (one on the NO group and one on the cobalt atom), and to decrease this to one as required by the magnetic moment it is suggested that pairing of the odd electrons on the nitric oxide occurs to give the quadrivalent dimer ion $[Co(NH_3)_5NO—NO(NH_3)_5Co]^{4+}$. The low solubility of the salt makes it difficult to confirm this structure, which is somewhat inconsistent with general nitric oxide chemistry, but infrared absorption spectra appear to agree with this interpretation.[159] An alternative suggestion [158] is that in the complex the nitric oxide may exist either in a singlet state (the complex being diamagnetic) or in a triplet state (the complex being paramagnetic). The chloride is stable in a dry atmosphere but readily decomposes to the aquopentammine complex on exposure to moisture.[159] The possible complications which the presence of the NO group introduces are further illustrated by the preparation of a pentahydrate $[Co(NH_3)_5NO]Cl_2,5H_2O$; this has a magnetic moment of 4·12 Bohr magnetons, corresponding to between 3 and 4 unpaired electrons.[98] The complex presumably contains bivalent cobalt, and may be a dimer involving outer orbital bonding $4s4p^34d^2$, though this is highly unusual in nitrosyl complexes.

Ruthenium Compounds.—These compounds merit special mention because a wider range of nitrosyl complexes (cationic, neutral, and anionic) is formed with ruthenium than with any other element. The stability of the nitrosyl group is illustrated in the following chart, which shows that many other ligands may enter the complexes ; they are replaced without interference with the nitrosyl group.

$[Ru(Cl)(NO)(NH_3)_4]Cl_2$

↑ HCl

$[Ru(OH)(NO)(NH_3)_4]Cl_2$ $[(dipy)Ru(NO)Cl_3]$ (*cis* and *trans*)

↑ $NH_4·OH$ Dipyridyl   ↑

$K_2Ru(NO)Cl_5$

Ethylenediamine (en) + NaI

↓ $H_2C_2O_4$ ↓

$K_2[Ru(NO)Cl(C_2O_4)_2]$ $[Ru(en)(NO)I_3] + [Ru(en)_2(NO)(OH)]I_2$

↓ Pyridine

$[Ru(py)_2(NO)Cl(C_2O_4)]$ | NH_3 | HCl

↓ HCl

$[Ru(py)_2(NO)Cl_3]$ $[Ru(en)(NH_3)_2(NO)(OH)]I_2$

↓ H_2O $[Ru(en)_2(NO)Cl]I_2$

$[Ru(py)_2(NO)(OH)Cl_2]$

---

[159] Short, *Rev. Pure Appl. Chem.*, 1954, **4**, 44.

When ruthenium chloride is refluxed with concentrated nitric acid the 4-co-ordinate compound $Ru(NO)Cl_3$ is formed, which with potassium chloride gives $K_2[Ru(NO)Cl_5]$. This compound may be heated to 250° without decomposition, and on further heating simultaneous evolution of nitric oxide and chlorine occurs ; [160] its aqueous solutions are stable to sulphur dioxide, acid peroxide, or permanganate. Conversion of the nitrosyl into the NO_2^- group in alkaline solution, which occurs in nitrosyl-cyano-complexes of other metals (see p. 145), is not observed in ruthenium complexes. With alkali the OH^- ion is introduced : [161]

$$[Ru(NH_3)_5(NO)]Cl_3 \xrightarrow{\;OH^-\;} [Ru(NH_3)_4(OH)(NO)]Cl_2$$
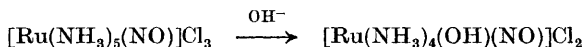
and the NO and OH groups can co-exist in the same complex without interaction.

5-Co-ordination Complexes

These nitrosyl complexes are amongst the very few examples of five-co-ordination. They are nitrosyl derivatives of metal dialkyldithiocarb-amates, of general formula $(NO)M(R_2N\cdot CS_2)_2$ where $M = V$,[162] Fe,[163] or Co,[163] and $R = Me$, Et, etc. They are prepared by saturating an alkali dialkyldithiocarbamate solution containing a salt of the metal M (usually in the bivalent state) with nitric oxide. The structure is not known with certainty. Calculations by Daudel and Bucher [164] indicate that dsp^3 hybridisation leads to a tetragonal pyramid structure, with the metal atom near the centre of the base. This is the structure of the complex $Ni(Et_3P)_2Br_3$ examined by Jensen,[165] and by analogy the nitrosyl complexes may have the structure :
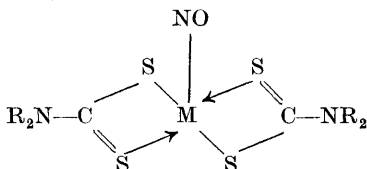
The alternative is a trigonal bipyramid structure as occurs with iron pentacarbonyl. The stability of the compounds falls in the order $Fe > Co \gg V$, the last two being readily oxidised by air. They are covalent in nature, and soluble in benzene, chloroform, and carbon disulphide.

Other 4-Co-ordination Complexes

There are two compounds in this class, one of nickel and one of platinum, which have particular interest. The action of nitric oxide on Belucci's

[160] Howe, *J. Amer. Chem. Soc.*, 1894, **16**, 389.

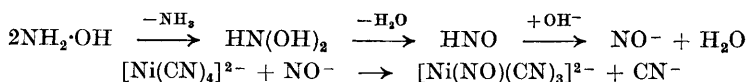[161] Gleu and Büddeker, *Z. anorg. Chem.*, 1952, **268**, 202.

[162] Malatesta, *Gazzetta*, 1941, **71**, 615.

[163] Cambi and Gagnasso, *Atti Accad. Lincei*, 1931, **13**, 254, 404.

[164] Daudel and Bucher, *J. Chim. phys.*, 1945, **42**, 6.

[165] Jensen and Nygaard, *Acta Chem. Scand.*, 1949, **3**, 481.

salt, $K_4[Ni_2(CN)_6]$, in liquid ammonia or absolute alcohol gives the compound $K_2[Ni(NO)(CN)_3]$ as permanganate-coloured crystals.[166]   The same product is obtained when hydroxylamine reacts with the complex $K_2[Ni(CN)_4]$.[132, 137]   The equality of charge on the nitrosyl-tricyano- and the tetracyano-complexes indicates that the NO group enters the complex in the first instance as the negative NO^- group, and Hieber and Nast [127] explain this by the following series of reactions:

$$2NH_2 \cdot OH \xrightarrow{-NH_3} HN(OH)_2 \xrightarrow{-H_2O} HNO \xrightarrow{+OH^-} NO^- + H_2O$$

$$[Ni(CN)_4]^{2-} + NO^- \longrightarrow [Ni(NO)(CN)_3]^{2-} + CN^-$$

The conversion of the NO^- into the NO^+ ion in the complex involves transfer of two electrons to the nickel atom.   The planar (dsp^2) tetracyano-complex thus gives a tetrahedral (sp^3) nitrosyl-tricyano-complex; the nickel atom has the inert gas configuration, and this was the first ionic tetrahedral diamagnetic complex of nickel to be prepared.   The low valency of nickel in the complex is shown by the evolution of nitrous oxide when the compound is decomposed by water or acid:

$$2[Ni(NO)(CN)_3]^{2-} + 2H^+ \longrightarrow [Ni(CN)_4]^{2-} + Ni(CN)_2 + N_2O + H_2O$$
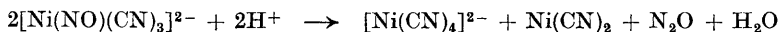
A saturated solution of potassium or ammonium tetrachloroplatinate absorbs nitric oxide to give a green solution containing the salt $K[Pt(NO)Cl_3]$, from which the derivatives $[Pt(NH_3)_4][PtNOCl_3]_2$ and $[Pt(py)(NO)Cl_2]$ have been prepared.   With carbon monoxide the salt $K[Pt(CO)Cl_3]$ is obtained, so that in this case nitric oxide and carbon monoxide form two exactly analogous ions $[Pt(NO)Cl_3]^-$ and $[Pt(CO)Cl_3]^-$, which is highly unusual. If the nitrosyl complex is a monomer, the NO group donates two electrons only to the platinum.   Replacement of CO by NO following the normal pattern would result in a non-ionic complex $Pt(NO)Cl_3$.   The platinum has no unusual valency, since the complex $[Pt(NO)Cl_3]^-$ is not readily oxidised, and is even less readily hydrolysed than is the corresponding carbon monoxide complex.

[166] Nast and Proeschel, *Z. anorg. Chem.*, 1948, **256**, 145.

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