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Complexes of Molecular Nitrogen

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The review deals with problems associated with the formation and structure of complexes of molecular nitrogen with transition metal compounds, metals, and other active species. Nitrogen interacts very weakly with acceptors of the type BF_3 but is capable of forming more stable systems (of the type of diazo-compounds) with species having both acceptor and donor properties (CH_2, CH, O).

On the surface of metals (nickel, palladium, platinum), nitrogen forms complexes with the linear configuration of the fragment M-N≡N.

A large number of stable complexes (nitrogenyls), also with a linear configuration of the M-N≡N fragment and analogous to the carbonyls and diazo-compounds, have been obtained recently with compounds of iron(II), ruthenium(II), osmium(II), cobalt(I), rhodium(I), iridium(I), and nickel(0). In addition, dinitrogenyl compounds $L_n M(N_2)_2$ and dinuclear complexes M-N≡N-M are known.

In nitrogenyl compounds nitrogen behaves as a π-electron acceptor ligand and therefore donor ligands stabilise the $M-N_2$ bond in the complex and acceptor ligands weaken it.

The method of synthesis of nitrogenyl complexes, their properties, and the mechanism of their formation have been examined. The possibility of the involvement of dinuclear complexes in nitrogen fixation under mild conditions is discussed.

The bibliography includes 121 references.

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I. INTRODUCTION

In the last three years the chemistry of a new class of coordination compounds, complexes of molecular nitrogen with transition metal compounds, has arisen and has been developing vigorously. Although the first such complex was synthesised as late as 1965, at the present time dozens of similar compounds are known and some of them are surprisingly stable. By analogy with the carbonyls, it has been suggested that they be called nitrogenyl complexes.

It is noteworthy that, even before the preparation of these complexes, hypotheses were put forward concerning the possibility of the coordination of molecular nitrogen and the probable structure of the complexes. The great interest in the complexes of molecular nitrogen is due to the fact that they are probably intermediates in reactions involving the binding of molecular nitrogen, in particular in biological nitrogen fixation. Chemisorption and hydrogenation of nitrogen on the surface of various metals are closely associated with the formation of the complexes.

Studies in recent years have shown that molecular nitrogen is capable of interacting not only with transition metals and their compounds but also with a number of other active species in the gas phase and in solution, the reactions being to a considerable degree related. Therefore such investigations are also included in the review.

The range of studies involving the formation of the complexes and reactions of molecular nitrogen under mild conditions has been rapidly developing recently and it is likely that new reviews will be necessary in the near future.

II. PHYSICOCHEMICAL PROPERTIES OF MOLECULAR NITROGEN

Table 1 lists certain physicochemical characteristics of molecular nitrogen. It is readily seen that the nitrogen molecule has very high dissociation energies and ionisation potentials and exhibits an appreciable quadrupole moment and polarisability.

Table 1. Physicochemical properties of molecular nitrogen

Interatomic distance r_e	1.0975 Å
Quadrupole moment	-1.4×10^{-26}
Anisotropy of the polarisability ($\alpha_{\parallel} - \alpha_{\perp}$)	0.696×10^{-24} cm^3
Ionisation potential	367 kcal mole^{-1}
Electron excitation energy	
$^1\Sigma_g^+ \rightarrow {}^3\Sigma_u^+$	142 kcal mole^{-1}
$^1\Sigma_g^+ \rightarrow \Pi_g$	196 kcal mole^{-1}
Dissociation energy ($^1\Sigma_g^+$)	225 kcal mole^{-1}
Vibration frequency (gas)	2331 cm^{-1}
Anharmonicity constant	0.006
Rotational constant	1.9983
Solubility:	
in water (20°C)	1.7×10^{-2} cm^3 cm^{-3}
in benzene (20°)	1.11×10^{-1} cm^3 cm^{-3}

The inertness of molecular nitrogen is attributed to the high stability of the first bond to be dissociated in the N_2 molecule. The energy of this bond amounts to about 130 kcal mole^{-1},[1] which greatly exceeds the corresponding values for other multiple bonds. For example, in acetylene the dissociation of the first bond requires only 53 kcal mole^{-1}.[1] Pauling[1] explains the deviation from linearity of the variation of the dissociation energy of the nitrogen–nitrogen bond with increasing bond order (Fig. 1) by the lower repulsion energy of the unshared electron pair in molecular nitrogen compared with the N=N and N–N bonds.

The positions of the upper filled and lower unfilled molecular levels of the interacting molecules play a significant role in the formation of the complexes, since they determine the donor–acceptor properties of the interacting species.

Let us now consider the system of molecular orbitals of the N_2 molecule. Eight molecular orbitals are formed from the eight sp^3 orbitals of the two nitrogen atoms. The sequence of the filled molecular orbitals of the nitrogen molecule ($^1\Sigma_g^+$) with increasing energy (Fig. 2) is as follows: $1\sigma_g^2$, $1\sigma_u^2$, $2\sigma_g^2$, $2\sigma_u^2$, $1\pi_u^4$, and $3\sigma_g^2$. The highest filled level is the bonding $3\sigma_g$ level, since ionisation of N_2 results in the formation of the N_2^+ ion ($^2\Sigma_g^+$) by removal of a $3\sigma_g$ electron[2,3]. It is noteworthy that, in contrast to N_2, the upper filled 3σ level of carbon monoxide is of the non-bonding type[4] and this is precisely the reason for the significant difference between N_2 and CO as ligands in complex formation (see pp. 360 and 367).

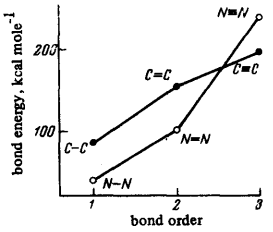


Figure 1. Dependence of the energy of the nitrogen–nitrogen and carbon–carbon bonds on bond multiplicity.

The removal of electrons from bonding orbitals weakens the nitrogen–nitrogen bond while their removal from antibonding orbitals strengthens the bond. In diatomic molecules this affects the interatomic distances and frequencies of the stretching vibrations.

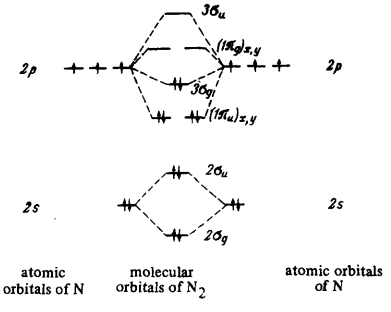


Figure 2. Molecular orbitals of N_2 (arbitrary scale).

The ionisation potentials, interatomic distances, and vibration frequencies (Table 2) confirm the sequence of molecular orbitals presented in Fig. 1. The removal of an electron from the strongly antibonding $2\sigma_u$ level leads to a decrease in the interatomic distance and an increase in the vibration frequency, while the removal of $3\sigma_g$ and $1\pi_u$ electrons greatly weakens the N≡N bond. The $3\sigma_g$, $1\pi_u$, and $2\sigma_u$ molecular orbitals of nitrogen are located relatively close to one another and small changes in interatomic distance can alter the sequence of these levels[5].

The ionisation potential of N_2 is 360 kcal mole^{-1}† and the dissociation energy of N_2^+ remains fairly high (201 kcal mole^{-1}). The electron affinity of molecular nitrogen, which characterises the position of the lower unfilled level,

† All the energy values quoted in the review without a reference were taken from Ref. 9.

is important. In this connection studies[6,7] on the scattering of slow electrons by molecular nitrogen, which showed that electrons with energies of 53 kcal mole^{-1} collide inelastically with N_2, are of interest. The observed low-energy resonance is probably associated with the excitation of the short-lived virtual negative ion N_2^- ($^2\Pi_g$), the potential energy minimum of which is higher by 34 kcal mole^{-1} than the lowest vibrational state of N_2($^1\Sigma_g^+$).[8] These data lead to the conclusion that in the excited state N_2 possesses considerable electron affinity.

Table 2. Physical constants of N_2 in various electronic states*

	N_2			N_2^+		
	$^1\Sigma_g^+$	$^3\Sigma_u^+$	$^1\Pi_g$	$^2\Sigma_g$	$^2\Pi_u$	$^2\Sigma_u^+$
Interatomic distance r, Å	1.09			1.12	1.17	1.07
Vibration frequency ν_e, cm^{-1}	2358			2207	1902	2419
Dissociation energy D_e, kcal mole^{-1}	225	83	138	201		
Ionisation potential of the N_2 molecule ($^1\Sigma_g^+$), kcal mole^{-1}	360 ($3\sigma_g$); 390 ($1\Pi_u$); 430 ($2\sigma_u$)					

* The interatomic distances and the vibration frequencies have been taken from Ref. 5 and the ionisation potentials from Ref. 3.

We may note that in carbon monoxide, which is isoelectronic with respect to nitrogen, resonance is observed at an electron energy of about 39 kcal mole^{-1}. The dissociation energy of "hot" nitrogen molecules in long-lived states is greatly reduced (Table 2).

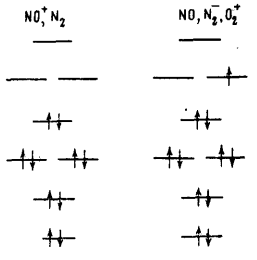


Figure 3. The system of molecular orbitals of NO^+ and N_2 and of NO, N_2^-, and O_2^{2+} (arbitrary scale).

In order to obtain some idea about the weakening of the nitrogen–nitrogen triple bond in the N_2^- ion, we shall compare the dissociation energies of the isoelectronic molecules NO^+ and N_2, and also NO, N_2^-, and O_2^+ (Fig. 3). The dissociation energy of NO^+ is 252 kcal mole^{-1}. The introduction of an electron into the antibonding $1\pi_g$ orbital reduces the strength of the nitrogen–oxygen bond and the dissociation energy of NO is 152 kcal mole^{-1}. The dissociation energy of the O_2^+ molecule, isoelectronic with NO and N_2^-, is 153.5 kcal mole^{-1}. Assuming that in the transition from N_2 to N_2^- the dissociation energy diminishes in proportion to the energy change on going from NO^+ to NO, we obtain about 140 kcal mole^{-1} for the dissociation energy of the N_2^- ion. On the basis of this value, it is possible to estimate the electron affinity (EA) of N_2 from the following cycle:

$$\begin{aligned} &N_2 + e \rightarrow N_2^- && +EA,\\ &N_2^- \rightarrow N^- + N && -140 \text{ kcal mole}^{-1},\\ &N^- \rightarrow N + e && -1 \text{ kcal mole}^{-1},\\ &N + N \rightarrow N_2 && +225 \text{ kcal mole}^{-1},\\ &\overline{EA = -84 \text{ kcal mole}^{-1}}. \end{aligned}$$

Thus, in accordance with this estimate, the affinity of the nitrogen molecule for an electron is a large negative quantity. The electron affinity obtained and the ionisation potential of the N_2 molecule show that the ionic states N_2^+ and N_2^- are difficult to achieve on energetic grounds, i.e. reactions with complete electron transfer

$$N_2 + D \rightarrow N_2^- + D^+$$
$$N_2 + A \rightarrow N_2^+ + A^-$$

are very unlikely (here D is an electron donor and A an acceptor).

III. REACTIONS OF N_2 WITH NON-METAL DERIVATIVES

Several examples of non-elastic collisions of N_2 with the molecules of other gases are known at present.

1. Collision Complexes in the Gas Phase

In a mixture with carbon dioxide, H_2, and other gases under a pressure of several tens of atmospheres, nitrogen absorbs infrared radiation. Then the spectrum of the gaseous mixture shows both the frequency corresponding to the fundamental vibration of N_2 and the sum and difference frequencies with the colliding molecules. Such vibrational transitions are due to the simultaneous excitation of the two interacting molecules by a single light quantum[10].

In an inelastic collision the electrical charges of the molecules are redistributed, as a result of which vibration frequencies corresponding to forbidden transitions appear in the infrared spectrum. Thus Fahrenfort and Ketelaar[11] observed absorption bands at 2331, 2995, and 4670 cm^{-1} in the spectrum of a mixture of N_2 with CO_2. The last two are combination frequencies:

$$\nu(N_2) + \nu'(CO_2) = 2331 + 2349 = 4680 \text{ cm}^{-1},$$
$$\nu(N_2) + \nu''(CO_2) = 2331 + 667 = 2998 \text{ cm}^{-1}.$$

It has been shown experimentally that the intensity of infrared absorption corresponding to simultaneous transition in a complex of two molecules is proportional to the pressures of both mixture components, i.e. the transitions occur in bimolecular collisions.

Under normal conditions, the lifetime of collision complexes should not exceed 10^{-13} s, since the interaction energy of the components of the complex is very low.

2. Interaction of Molecular Nitrogen with Water, Hydrogen Chloride, and Boron Trifluoride

Van der Waals forces play a significant role in the formation of "collision complexes" of molecular nitrogen. However, it has been shown[12] that the formation of complexes as a result of exchange interactions, similar to hydrogen bonding, is possible. In the study of the broadening

of the rotational lines of the R- and P-branches of the rotational vibrational bands of water, hydrogen chloride, and methane in a mixture with different gases, it was found[12] that the effect of the gases in the broadening of the water and hydrogen chloride lines increases in the sequence He, Ar, O_2, and N_2. N_2 is almost twice as effective as argon, although the effect of argon and nitrogen on the methane molecule is almost the same (Table 3).

Table 3. Collisional broadening cross-sections (10^{-16} cm^2) of molecules[12] with Ar and N_2

Molecule	λ, nm	Ar	N_2
H_2O	1.45	41 (30) *	85 (32)
HCl	1.7	62 (50)	116 (53)
CH_4	1.7	50 (28)	50 (30)

* The gas-kinetic cross sections are indicated in brackets.

The difference in the broadening effects of argon and molecular nitrogen on the rotational lines of water and hydrogen chloride has been attributed to the formation of the hydrogen bonds N_2...HCl and N_2...HOH.

In order to investigate the donor–acceptor interaction of nitrogen with powerful acceptors, the infrared spectra of mixtures of nitrogen with boron trifluoride were investigated[13]. A change in the contour and integral intensities of the $\nu_2(A'')$ and $\nu_3(E)$ bands of boron trifluoride, corresponding to an increase in the moment of inertia and the dipole moment of the B–F bond in the BF_3 molecule, were observed.

Table 4. Electro-optical parameters $\partial\mu/\partial Q$ and the dipole moments μ_{B-F} of boron trifluoride mixed with various gases[13]

Gas	$\partial\mu/\partial Q$, CGSU/cm^{-1} g$^{-1/2}$	$10^{18}\mu_{B-F}$, CGSE
BF_3 *	101.5	1.7
BF_3+He **	103	1.75
BF_3+H_2 (D_2)	104.5	1.77
BF_3+Ar	111	1.9
BF_3+N_2	116.5	2.0

* The pressure of BF_3 was in all cases 20–30 mmHg.
** The pressure of the gas interacting with BF_3 was 70 atm.

Compared with other gases (helium, hydrogen, deuterium, and argon), nitrogen has the greatest effect on the integral intensity and the dipole moment of the B–F bond; argon is the next most effective gas in this respect (Table 4).

The increase of the moment of inertia and of the polarity of the B–F bond in mixtures of boron trifluoride with argon and nitrogen is evidence of the formation of donor–acceptor molecular complexes in which N_2 behaves as an electron donor by virtue of its unshared electron pair or the π electrons of the triple bond and BF_3 behaves as an acceptor by virtue of the unfilled $2p_z$ orbital of boron. The complexes of boron trifluoride with argon were known even earlier[14].

It is noteworthy that the intensities $\mathcal{I}\nu_2$ and $\mathcal{I}\nu_3$ vary little in the nitrogen pressure range 1–70 atm and therefore a very low concentration of the complexes is formed even at high pressures.

Evidently, by itself donor–acceptor interaction, even with powerful acceptors such as boron trifluoride, leads to the formation of complexes with only a very weak bond, i.e. nitrogen may be regarded as a very weak base.

So far there is no information about the structure of the unstable donor–acceptor complexes of molecular nitrogen in the gas phase.

3. Interaction of Nitrogen with Carbenes and Related Species

Organic diazo-compounds and diazonium salts may be arbitrarily regarded as complexes of molecular nitrogen with carbenes and aryl cations respectively[15]. Nitrous oxide (N_2O) and hydrazoic acid (HN_3) may be included among these compounds. In fact the interatomic distance r_{NN} and the stretching vibration frequency $\nu(N_2)$ in these compounds are close to the corresponding values in molecular nitrogen. The C–N_2, O–N_2, and HN–N_2 fragments have a linear configuration‡ (which, as will be shown below, is characteristic of the complexes of nitrogen with metals and their compounds).

The C–N_2, O–N_2, and HN–N_2 bonds are fairly stable: thus in diazomethane $D(H_2C-N_2)$ = 21 kcal mole^{-1} [16] and in nitrous oxide $D(O-N_2)$ = 40 kcal mole^{-1}. The higher energy of the bond of N_2 with carbenes (and the related species O, NH, etc.) and aryl cations, compared with "pure" acceptors such as BF_3, can be accounted for by the additional interaction of the antibonding N_2 orbital and the unshared pairs of p electrons in CH_2, O, or NH. In diazonium salts this role is fulfilled by the π electrons of the aromatic ring, which explains the higher stability of aromatic diazonium salts compared with the aliphatic salts.

It has been shown recently that in many cases the decomposition of diazo-compounds may be reversible. This confirms that it is valid to regard these compounds as "complexes" of molecular nitrogen.

It is now known that certain species are capable of reacting with nitrogen to form diazo-compounds, the process involving a small activation energy. Thus the oxygen atom formed in the singlet state by the photolysis of ozone reacts with N_2 to form N_2O.[17–19] The yield of nitrous oxide varies significantly with reaction conditions: in the gas phase it is only 0.01%,[17] in liquid nitrogen it is 7%,[18] and in solid nitrogen it reaches 35%.[19] This increase in the yield is accounted for by the fact that the energy of the excited N_2O molecule formed in the reaction between N_2 and O is more readily eliminated in the condensed phase.

Moore and Pimentel[20] observed in 1964 the reaction of methylene with N_2 in the solid nitrogen matrix at 20°K. In the photolysis of $CH_2{}^{15}N^{14}N$ in solid molecular nitrogen[14] the infrared spectrum of the products showed, in addition to the absorption bands at 2053 and 2072 cm^{-1}, which are

‡ A cyclic form, as in diazirine $H_2C\begin{smallmatrix}N\\ \|\\ N\end{smallmatrix}$, is also known. However, linear diazomethane is thermodynamically more stable.

due to the $\nu(N\equiv N)$ vibrations in $CH_2{}^{15}N^{14}N$ and $CH_2{}^{14}N^{15}N$ respectively, a band at a frequency of 2096 cm^{-1}, corresponding to the $\nu(N\equiv N)$ vibrations in $CH_2{}^{14}N^{14}N$.

The light diazomethane is formed in the reaction

$$CH_2{}^{15}N^{14}N \rightleftarrows CH_2 + {}^{15}N^{14}N \rightleftarrows CH_2{}^{15}N^{14}N$$

$$CH_2 + {}^{14}N^{14}N \rightarrow CH_2{}^{14}N^{14}N$$

It may be supposed that in this case "hot" CH_2 species formed in the photolysis of diazomethane react with nitrogen.

The reaction of methylene with molecular nitrogen in the gas phase was first observed and investigated in detail by Shilov and coworkers [15,21,22]. Both diazomethane and keten, diazirine, and phenylcyclopropane, subjected to photolysis or pyrolysis in an atmosphere of labelled $^{15}N_2$, were employed as sources of methylene in these investigations. In all cases the formation of linear diazomethane ($CH_2{}^{15}N_2$) molecules was observed; the isomeric cyclic diazirine did not form. It was shown that both singlet [$CH_2(s)$] and triplet [$CH_2(t)$] methylene are capable of interacting with nitrogen, the activation energies for the reactions of $CH_2(s)$ and $CH_2(t)$ being respectively about 8 and 16 kcal $mole^{-1}$. Here we may note that, although these quantities are in fact small, they nevertheless exceed the activation energy for the formation of nitrogen complexes with transition metals and their compounds (see p.369). Among the carbenes investigated, methylene proved to be the more active with nitrogen. The rates of the reactions of $(CF_3)CH$ and $(CN)CH$ with N_2 are lower at least by a power of ten than that of CH_2. The remaining carbenes investigated, CH_3CH, C_5H_4, and $CHCOOC_2H_5$, do not react with nitrogen at an appreciable rate.

Recently it was shown that the CH radical [23] and the C atom [24] are also capable of reacting with molecular nitrogen.

An interesting case of the formation of a diazo-compound in the reaction of nitrogen with benzenesulphenium ($C_6H_5S^+$) was recently described [25]. This reaction (if the data are correct) is the first and so far unique example of a reaction of nitrogen with non-metal derivatives in solution at room temperature and at atmospheric pressure of nitrogen. Although the reaction product was not identified, the authors noted that it is capable of entering into the azo-coupling reaction. This suggests that a diazonium salt is formed.

IV. COMPLEXES OF N_2 ON THE SURFACE OF METALS

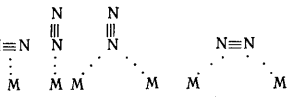
In the reaction of N_2 with metals there is rapid reversible low-temperature chemisorption and slow high-temperature chemisorption [26]. Surface complexes of molecular nitrogen are then formed together with surface nitrides. Measurements of the heat of chemisorption show that the values of ΔH_{ads} vary in the range between −2 and −20 kcal $mole^{-1}$.

It has been established [27] that several states of chemisorbed nitrogen molecules are realised in the chemisorption of N_2 on the surface of tungsten purified in an ultrahigh vacuum. In one of these states (molecular) nitrogen is completely desorbed at 300°K, while in the other it is desorbed only above 1100°K. If the initial nitrogen is a mixture of $^{14}N_2$ and $^{15}N_2$, the gas desorbed above 1100°K contains $^{14}N^{15}N$. Kinetic studies showed that the desorption of some of the molecules is a second-order process and that of others is a first-order process with respect to the concentration of N_2 on the surface. This finding has been explained [27] by the existence on the surface of both "atomic" (i.e. evidently nitride) nitrogen and its "molecular" form. Possibly isotopic $^{14}N^{15}N$ molecules are formed in the decomposition of the four-membered surface complexes



The possibility of the existence of four-membered nitrogen rings, stabilised by complex formation with transition metals, was demonstrated theoretically in a recent paper [28].

Several structures may be put forward for the surface complexes of molecular nitrogen in low-temperature chemisorption, for example:



So far there has been no direct experimental evidence for the structure of the surface complexes and various authors put forward different considerations in favour of one or other of the structures given above.

By analogy with the bonds of other unsaturated molecules with metals, it may be assumed [29] that the M–N_2 bond forms via the filled π or σ orbitals of N_2 and the free p orbitals of the metal (donor–acceptor interaction) and also the unshared pairs of d electrons of the metal and the antibonding orbitals of N_2 (dative interaction). In this treatment it is of course assumed that the behaviour of the d levels of the surface metal atoms is equivalent to that of free metal atoms.

It may be expected that the polarity of the M–N_2 bond in the surface complex will be different for different metals depending on the relative contributions of the dative and donor–acceptor bonds. In most cases the charge of N_2 should then be negative. It has been shown electrochemically [30,31] that nitrogen undergoes cathodic polarisation on cobalt, copper, silver, and iron. The authors believe that this is associated with the cathodic reduction of the nitrogen molecule: N_2^- ions are formed on the surface of porous metallic films.

Eischens and Jacknow [32], who investigated the chemisorption of N_2 on nickel, observed infrared absorption in the region of 2196 cm^{-1}. With the aid of the $^{14}N_2$ and $^{15}N_2$ isotopes, they showed that this absorption is due to the stretching vibration of the N≡N bond, the frequency of which is greatly reduced compared with that in gaseous nitrogen. The authors believe that the vibration of the N_2 molecule is active in the infrared spectrum because of the formation of the complex Ni–N≡N. Subsequently the infrared spectra of N_2 chemisorbed on different metals (nickel, cobalt, palladium, platinum, iridium) were investigated by other workers [15,33,34,120].

To elucidate the structure of the surface Ni–N_2 complex, molecular nitrogen $^{14}N^{15}N$ was employed [35] (see p. 364). Analysis of the contours of the observed absorption bands of the isotopic molecules $^{14}N^{14}N$, $^{14}N^{15}N$, and $^{15}N^{15}N$ confirmed the linear structure of the complex. In the same study the enthalpy of formation of the complex, Ni + N_2 ⇌ Ni–N_2, was measured and found to be −9.2 kcal $mole^{-1}$ for a surface coverage $\Theta \simeq 0.05$ and −5 kcal $mole^{-1}$ for $\Theta \simeq 0.2$.

According to the data of Eischens and Jacknow [32] and Chernikov and Borod'ko [36], the Ni–N_2 complex is sensitive to molecular hydrogen: when hydrogen is admitted to the system comprising nickel and N_2, the nitrogen absorption band is displaced to higher frequencies, up to 2260 cm^{-1} and then up to 2275 cm^{-1}. Under the action of argon and krypton, the absorption band is displaced towards lower

frequencies[36], to 2170 and 2080 cm^{-1} respectively. It follows from these data that, on being chemisorbed on nickel, hydrogen and the inert gases alter the state of the surface of the metal and the strength of the nickel–nitrogen bond. The direction of the displacement of the vibration frequency of the N≡N bond shows that H_2 behaves as an electron acceptor and argon and krypton behave as electron donors (see p. 365).

The surface complexes of N_2 with palladium and platinum were investigated by van Hardeveld and van Montfoort[34]. Since the extinction coefficients of the bands corresponding to the ν(N≡N) vibration of nitrogen chemisorbed on nickel, palladium, and platinum are similar, one may conclude that the structure of the N_2 complexes with palladium and platinum is also linear.

It is interesting that the complex formation is influenced by the dimensions of the palladium and platinum crystallites: N_2 complexes are formed on particles with effective diameters in the range 15 Å $< d_{eff} <$ 70 Å. Virtually no complexes are formed on metal particles with $d >$ 200 Å and the amount formed on particles with $d <$ 10 Å is very small. These features of the surface nitrogen compounds distinguish them from individual coordination compounds containing a nitrogen molecule as the ligand.

Table 5. Effect of chemisorption on the stretching vibration frequencies of N_2 and CO

Compound	$\nu(N\equiv N)_{ads}$, cm^{-1}	$(\nu_{gas}-\nu_{ads})/\nu_{gas}$	Compound	$\nu(N\equiv N)_{ads}$, cm^{-1}	$(\nu_{gas}-\nu_{ads})/\nu_{gas}$
Ni—N_2	2204	0.055	Ni—CO	2033	0.051
Pd—N_2	2260	0.031	Pd—CO	2085	0.027
Pt—N_2	2230	0.041	Pt—CO	2071	0.034

Carbon monoxide, which is isoelectronic with nitrogen, is also known to form linear complexes on the surface of metals. Comparison of the ν(N≡N) and ν(C≡O) stretching vibration frequencies (Table 5) shows that the reduction of the ν(N≡N) frequency of chemisorbed nitrogen from its frequency in the gas phase is greater than the corresponding shift for carbon monoxide. This is probably associated with the different nature of the upper filled levels of N_2 and carbon monoxide, namely the $3\sigma_g$ orbital of N_2 is bonding and the $3\sigma_g$ orbital of carbon monoxide is non-bonding[4]. While the formation of the π bonds, by which the electron density is displaced to the antibonding orbitals of N_2 and carbon monoxide, lowers the stretching vibration frequencies, the formation of σ bonds has different effects[37] on the N≡N and C≡O bond strengths and hence the ν(N≡N) and ν(C≡O) frequencies. In the coordination of N_2 the formation of a σ bond leads to an electron shift from the bonding $3\sigma_g$ orbital and an additional lowering of the ν(N≡N) frequency, while in the case of carbon monoxide the formation of a σ bond is associated with a decrease of electron density in the non-bonding 3σ orbital§.

§ Carbon monoxide in the gas phase is characterised by absorption at 2146 cm^{-1} in the infrared spectrum, while in the complex BH_3...CO (formed via a σ bond) the ν(C≡O) vibration frequency is 2164 cm^1. Possibly this is due to the fact that the 3σ(CO) level is weakly antibonding.

In the interaction of carbon monoxide with transition metals the displacement of the ν(C≡O) frequency is a result of the superposition of two opposed effects, and the fact that ν(C≡O) is reduced on complex formation is evidence that the π dative component makes a greater contribution to the bond with the transition metal than the σ donor component. For the nitrogen molecule, both types of interaction lead to a decrease of frequency. Therefore, in contrast to carbon monoxide, in the case of N_2 one should always expect a bathochromic shift of the ν(N≡N) frequency on complex formation[37].

V. COMPLEXES OF NITROGEN WITH TRANSITION METAL COMPOUNDS (NITROGENYLS)

1. SYNTHESIS AND CHEMICAL PROPERTIES OF NITROGENYLS

Nitrogenyl Complexes of Ruthenium

$[RuN_2(NH_3)_5]X_2$. This, the first of the known complexes of molecular nitrogen with transition metal compounds, was obtained by Allen and Senoff[38] in 1965 by the reaction of $RuCl_3$ with hydrazine hydrate in aqueous solution; it is then possible to isolate from the solution the saltlike compounds $[RuN_2(NH_3)_5]X_2$ (X = Cl^-, Br^-, I^-, or BF_4^-). Subsequently the same complexes were obtained by the action of hydrazine hydrate on other ruthenium(III) and ruthenium(IV) salts and in the reaction of sodium azide with aquopentammineruthenium(III) methanesulphonate[39].

The complexes $[RuN_2(NH_3)_5]X_2$ were also obtained when all the ligands, except nitrogen, were substituted by ammonia[40] in the non-saltlike complexes $RuN_2Cl_2(H_2O)$THF (see p. 361)[THF = tetrahydrofuran (Ed. of Translation)], by passing nitrogen[41] into an aqueous solution of $[Ru(NH_3)_5H_2O]Cl_2$, and by the action of ammonia[42] and zinc dust on $RuCl_3.3H_2O$.

The salts of pentammineruthenium nitrogenyls have been isolated in a crystalline state. They are thermally stable and relatively stable in aqueous solutions, but, under the action of a number of compounds, molecular nitrogen may be displaced by other ligands[39].

The infrared spectra of the complexes show an absorption band in the region 2105–2167 cm^{-1} (Table 6), which corresponds to the N≡N stretching vibration, and in the electronic spectra there are absorption bands with maxima at 221 and 463 nm.

According to the data of Allen and Senoff[38], under the action of $NaBH_4$ nitrogen in the complex may be reduced to ammonia either completely or, as stated subsequently[39], partially. However, these results were not confirmed[40]. It has been established by mass-spectrometric analysis that ammonia in the product of the reaction of $[Ru^{15}N_2(NH_3)_5]X_2$ with $NaBH_4$ is not enriched in labelled $^{15}NH_3$ in excess of the natural content, i.e. N_2 in the complex is not reduced.

It also proved impossible to reduce the nitrogen in the complex by reducing agents such as $CrCl_2$, EtMgBr, $Na_2S_2O_4$, and zinc and hydrochloric acid[40]. Allen and coworkers[38,39] and subsequently Chatt and coworkers[45] stated that, under the action of sulphuric and hydrochloric acids, only part of the coordinated nitrogen in the nitrogenyl complex is evolved in the form of N_2 (i.e. the coordinated nitrogen reacts at least partially with the acid), but these results appear very doubtful, particularly in view of

the negative findings of Borod'ko et al.[40] in the study of the reduction of a nitrogenyl complex¶.

$RuN_2Cl_2L_3$ (L = H_2O, NH_3, Py, THF, etc.). These complexes were the first to be obtained directly from molecular nitrogen. They are formed[40,43,44] by the reduction of $RuCl_3$ and $RuCl_3OH$ with amalgamated zinc in the presence of nitrogen in tetrahydrofuran (THF). The yield of the nitrogen complex increases with the N_2 pressure and becomes almost quantitative at pressures in excess of 40–60 atm.

Table 6. Stretching vibration frequencies of the N≡N bond in nitrogenyl complexes

Compound	ν (N≡N), cm^{-1}	References
$FeN_2(PPh_2Et)_3H_2$	2055	59
$FeN_2(PPh_2Et)_2H_2$	1939	59
$FeN_2(PPh_3)_3H_2$	2074, 2053, 2039 *	85
$FeN_2(PPh_3)_3H_2$ (in toluene)	2068	
$[RuN_2(NH_3)_5]Cl_2$	2105	38, 39
$[RuN_2(NH_3)_5]Br_2$	2114	38, 39
$[RuN_2(NH_3)_5]I_2$	2129	38, 39
$[RuN_2(NH_3)_5](BF_4)_2$	2144	38, 39
$[RuN_2(NH_3)_5](BF_6)_2$	2167	38, 39
$[RuN_2(NH_3)_5]^{2+}$ (в H_2O)	2130	38, 39
$RuN_2(NH_3)_3Cl_2$	2080	40, 44
$RuN_2(NH_3)_2H_2OCl_2$	2090	40, 44
$RuN_2(H_2O)Cl_2$ THF	2153	40, 44
$RuN_2(PPh_3)_3H_2$	2147	49, 50
cis-$[RuN_2(en)_2H_2O][B(C_6H_5)_4]_2$	2130	51
cis-$[Ru(N_2)_2(en)_2][B(C_6H_5)_4]_2$	2220, 2190	51
$[OsN_2(NH_3)_5]Cl_2$	2012**	52, 53, 54
$[OsN_2(NH_3)_5]Br_2$	2028**	52, 53, 54
$[OsN_2(NH_3)_5]I_2$	2033**	52, 53, 54
$[OsN_2(NH_3)_5](ClO_4)_2$	2051**	53
$[OsN_2(NH_3)_5](BF_4)_2$	2055	53
$[OsN_2(NH_3)_5](BPh_4)_2$	2061	53
$[OsN_2(NH_3)_5]^{2+}$ (в H_2O)	2032	54
$[Os(N_2)_2(NH_3)_4]Cl_2$	2120, 2175	54, 55
$CoHN_2(PPh_3)_3$	2088	61,62,63,64
$CoHN_2(PPh_3)_2(PBu_3)$	2075	84
$CoHN_2(PPh_3)(PBu_3)_2$	2061	84
$CoHN_2(PBu_3)_3$	2048	84
$CoHN_2[P(p\text{-}CH_3C_6H_4)_3]_3$	2073	68
$CoHN_2[P(Ph_2C_6H_5)]_3$	2060	68
$CoHN_2[P(p\text{-}C_6H_5)_3]_3$	2032	68
$CoHN_2[P(C_2H_5)_3]_3$	2032	68
$RhN_2Cl(PPh_3)_2$	2152	37, 76
$IrN_2Cl(PPh_3)_2$	2185	37, 74, 75
$NiN_2[P(C_6H_{11})_3]_2$	2028	77

* The vibration frequencies ν(N≡N) of the crystalline complex due to Davydov splitting.
** The vibration frequency of the Davydov component with maximum intensity.

The composition of the complex obtained in tetrahydrofuran solution corresponds to the formula $RuN_2Cl_2(H_2O)_2THF$. This complex is thermally much less stable than the pentammine and decomposes slowly with evolution of hydrogen even at room temperature. It has been established[40,44] that, when the complex is acted upon by bases (ammonia, pyridine, ethylenediamine, etc.), the ligands at the ruthenium atom are substituted with retention of part of the nitrogen in the coordination sphere. A whole series of $RuN_2Cl_2L_3$ with different ligands L were obtained in this way, which permitted certain conclusions about the nature of the ruthenium–nitrogen bond. It again proved impossible to reduce the nitrogen in the complex by various reducing agents.

¶ In fact, recently Chatt and coworkers[46,47] found that the results of earlier studies[38,39,45] showing the reduction of N_2 in the complex and also the interaction of nitrogenyl complexes with acids are erroneous, due to the presence of large amounts of hydrazine as an impurity in the complex obtained by Allen's method.

Other Complexes of Nitrogen with Ruthenium Compounds

It has been established[44,48] that nitrogen is coordinated to ruthenium when $RuCl_3$ is reduced by reducing agents such as C_2H_5MgBr, C_6H_5MgBr, $TiCl_3$, Na_2S_2, and Na_2S. The complexes formed under these conditions were not isolated but there are indications that in some cases they contain ligands other than those discussed above. Thus, when sulphides are used, the complexes probably contain sulphur together with nitrogen.

$RuN_2(PPh_3)_3H_2$. It has been found[49] that nitrogen forms a complex on interaction with the ruthenium compound having the hypothetical formula $Ru(PPh_3)_4H_2$. This complex was isolated[50] after the reaction of $(PPh_3)RuHCl$ with $AlEt_3$ in the presence of nitrogen in ether. The complex corresponds to the formula $RuN_2(PPh_3)_3H_2$. It is sensitive to air and is stable in an atmosphere of nitrogen at room temperature.

Dinitrogenyl complex of ruthenium(II). The interaction of *cis*-$[Ru(en)_2N_3N_2]^+$ with HNO_2 yielded a complex containing two nitrogen molecules in the coordination sphere of ruthenium in the *cis*-position[51]. The reaction takes place according to the equation

$$cis\text{-}[Ru(en)_2N_3N_2]^+ + HNO_2 \rightarrow cis\text{-}[Ru(en)_2(N_2)_2]^{2+} + N_2O.$$

The infrared spectrum of the complex shows two absorption bands at 2220 and 2190 cm^{-1}. In aqueous solution the dinitrogenyl complex decomposes irreversibly with formation of *cis*-$[Ru(en)_2H_2ON_2]^{2+}$; the product of this reaction was isolated as the tetraborate [ν(N≡N) = 2130 cm^{-1}].

Osmium Complexes

Ammine nitrogenyls. The first complexes of nitrogen with osmium compounds were obtained[52] by the reaction of hydrazine with osmium compounds such as K_2OsCl_6, $OsCl_4$, $OsCl_3OH$, i.e. a reaction analogous to that whereby ruthenium nitrogenyls are synthesised by the method of Allen and Senoff. If is interesting that, in contrast to ruthenium compounds, the formation of several complexes of molecular nitrogen with osmium was observed in this case. Subsequently it was established[53,54] that the main product is the analogue of pentammineruthenium nitrogenyl $[OsN_2(NH_3)_5]X_2$ with ν(N≡N) at 2012 cm^{-1} in the infrared spectrum. The less stable dinitrogenyl complex $[Os(N_2)_2(NH_3)_4]X_2$ probably forms at the same time.

In a recent communication[55] the synthesis of the dinitrogenyl complex of osmium by another method was described. When nitrous acid acts on an aqueous solution of $[OsN_2(NH_3)_5]X_2$, a crystalline product is formed, whose composition corresponds to the formula $[Os(N_2)_2(NH_3)_4]X_2$ (X = Cl^-, Br^-, or I^-) according to elemental analysis. The infrared spectrum of this compound shows absorption bands at 2120 and 2175 cm^{-1}, which is evidence of the *cis*-configuration of this dinitrogenyl complex.

In the crystalline state the complex $[OsN_2(NH_3)_5]X_2$ is exceptionally stable: it decomposes above 200°C. In aqueous solution the evolution of nitrogen is catalysed by various metal ions (Ag^+, Cu^{2+}).[56] The thermal decomposition of the complex in aqueous solution is inhibited by carbon monoxide[57]. This is probably due to the binding of catalytically active species into inactive carbonyls.

Other Complexes of Osmium with Molecular Nitrogen

Nitrogenyl complexes of osmium have been obtained[44] directly from molecular nitrogen in the reduction of $OsCl_3OH$ by amalgamated zinc in tetrahydrofuran solution. Examination of the vibration spectra of the reduction products led to the conclusion that several nitrogen-containing complexes are formed. The complexes were not identified but it may be supposed that they are similar in composition to the ruthenium complexes formed under analogous conditions†.

Dinuclear Complexes of Ruthenium and Osmium

It has been stated[58] that the formation of a complex in which two metal atoms are linked to nitrogen is possible. The dinuclear ruthenium complexes are formed when the pentammineruthenium nitrogenyl $[RuN_2(NH_3)_5]X_2$ reacts with the aquopentammine complex $[Ru(NH_3)_5H_2O]X_2$. In aqueous solution the complex $[(NH_3)_5RuN_2Ru(NH_3)_5](BF_4)_4$ has an intense absorption band at 262 nm.

The formation of dinuclear complexes in aqueous solutions is an equilibrium process: when the concentration of $\{[Ru(NH_3)_5]_2N_2\}^{4+}$ is reduced, the complex dissociates into the mononuclear nitrogenyl and $[Ru(NH_3)_5H_2O]^{2+}$.

It has been suggested[56] that the decomposition of $[OsN_2(NH_3)_5]^{2+}$ in the presence of silver(I) and copper(II) salts takes place via the intermediate formation of the complexes $[(NH_3)_5OsN_2Cu]$ and $[(NH_3)_5OsN_2Ag]$.

Nitrogenyl Complexes of Iron

The complexes of nitrogen with iron compounds are of interest, since their formation in the enzyme systems of nitrogen-fixing bacteria probably constitutes the first stage in the biological fixation of nitrogen.

A complex of a dihydride derivative of iron(II) with nitrogen was synthesised by Sacco and Aresta[59] by the reaction of N_2 with $FeH_2[P(C_6H_5)_2R]_3$ (R = ethyl or butyl). A yellow crystalline complex, decomposing at 80°C with evolution of nitrogen and hydrogen, was then isolated. The complex is diamagnetic and is characterised by an intense absorption band in the infrared at 2055–2060 cm^{-1}. The interaction of this complex with triethylaluminium gave the compound $FeH_2N_2[P(C_6H_5)_2R]_2$, whose infrared spectrum shows a band at a frequency of 1989 cm^{-1}, which has been assigned[59] to the stretching vibrations of the nitrogen–nitrogen bond.

The formation of nitrogen complexes with iron compounds, produced by the action of N_2 on low-valence derivatives of iron, has also been described[60]. Thus the reaction of nitrogen with the iron(0) complex of cyclooctadiene or with tris-π-allyliron in the presence of phosphines yields nitrogen-containing complexes (a band at 2038 cm^{-1} is observed in the infrared spectrum), which, however, could not be isolated in a pure state.

Complexes of Nitrogen with Cobalt Compounds

The formation of complexes of molecular nitrogen with cobalt compounds has been described[61–65]. Yamamoto et al.[61] obtained the cobalt complex at atmospheric nitrogen pressure by the reaction of cobalt(III) acetylacetonate with ethoxydiethylaluminium in the presence of triphenylphosphine in ether or toluene. In accordance with the results of elemental analysis, the formula $CoN_2(PPh_3)_3$ was ascribed to the yellow crystals isolated from the solution. In the absence of air the complex is comparatively stable, but decomposes with evolution of nitrogen at 80°C.

A nitrogenyl complex of cobalt was also obtained by Misono and coworkers[63,64] by the action of nitrogen on a hydride derivative of cobalt. The hydride was synthesised by passing H_2 into a mixture of cobalt(III) acetylacetonate, triphenylphosphine, and tri-isobutylaluminium in ether at 10°C. In the interaction of this hydride solution with nitrogen the colour of the former changes from yellow to red and orange crystals can be isolated from the reaction mixture; their infrared spectrum shows absorption at 2088 cm^{-1}. Evidently this complex is identical with that obtained by Yamamoto and the reaction involves the displacement of hydrogen by nitrogen from cobalt hydride. It was concluded[63,64] that the product of the reaction with nitrogen is a mixture of $CoN_2(PPh_3)_3$ and $CoHN_2(PPh_3)_3$.

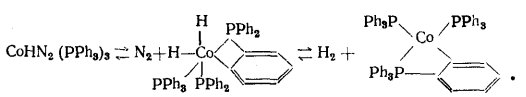
The Italian workers Sacco and Rossi[65,66] stated that nitrogen reacts reversibly with the trihydride complex of cobalt to form a cobalt(I) nitrogenyl complex:

$$CoL_3H_3 + N_2 \rightleftarrows CoHN_2L_3 + H_2.$$

where L = PPh_3 or PPh_2Et. This complex consists of orange crystals, which are fairly stable in air and soluble in non-polar solvents. An intense absorption band at 2080–2084 cm^{-1} in the infrared spectrum of the complex corresponds to the stretching vibrations of the nitrogen. The complex is diamagnetic; in accordance with the formula quoted, 1.5 moles of gas consisting of nitrogen and hydrogen in the proportions $N_2 : H_2 = 2 : 1$ are evolved per mole of the complex in its decomposition at 100–150°C.

Since the complex of Sacco and Rossi is very similar in its properties to the complex obtained by the Japanese workers[61–64], it may be supposed that the two are identical. Indeed X-ray diffraction analysis showed[67] that the complex obtained by a similar procedure[61] has the formula $CoHN_2(PPh_3)_3$. In a recent study by NMR Misono and coworkers[68] obtained further confirmation that this complex contains a hydride hydrogen atom and therefore the previously proposed formula[61] $CoN_2(PPh_3)_3$ may be regarded as erroneous.

The study of the isotope exchange of deuterium with the complex showed[69] that not only the hydride hydrogen atom but also the hydrogen atoms in the *ortho*-positions of the phenyl ring of triphenylphosphine participate in the reaction, possibly according to the mechanism



The complex $CoHN_2(PPh_3)_3$ reacts reversibly with H_2, ethylene, and ammonia with displacement of nitrogen[62]; it reacts irreversibly with carbon monoxide to form a carbonyl[70], and also with carbon dioxide to form the formate complex[71] $CoHCO_2(PPh_3)_3$.

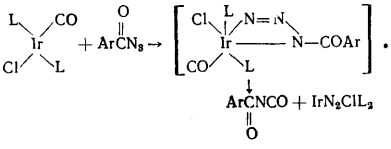
The cobalt nitrogenyl complex catalyses the hydrogenation of ethylene[72], the oxidation of triphenylphosphine to triphenylphosphine oxide, and the dimerisation of ethylene and propene[73].

† Recently a number of nitrogenyl complexes of osmium(II) of the type $OsN_2X_2(PR_3)_3$, where X = Cl or Br, were obtained[121] by the method of Borod'ko et al.[44]

The Nitrogenyl Complexes of Indium(I)

Collman and Kang[75] synthesised the complex $IrN_2Cl(PPh_3)_2$ by the reaction of azides with the carbonyl complex of iridium. The band at 2105 cm^{-1} in the infrared spectrum of this complex corresponds to the N≡N stretching vibrations. The complex is stable in the crystalline state at room temperature, but its solutions in chloroform and toluene decompose slowly with evolution of nitrogen.

A study of the mechanism of the formation of the complex IrN_2L_3 showed[75] that the reaction takes place in the coordination sphere of iridium without liberation of N_2 and CO molecules into the solution. The reaction also yields the isocyanate:



The Nitrogenyl Complex of Rhodium(I)

Using a procedure similar to that employed in the synthesis of the iridium complex of N_2, the analogous N_2 complex of rhodium(I) $RhN_2Cl(PPh_3)_2$ was synthesised[76]. A band at 2152 cm^{-1} in the infrared spectrum of the complex corresponds to the N_2 vibrations. The complex is less stable than its iridium analogue. Although in the solid state (yellow crystals) the complex remains unchanged at room temperature in the absence of air, its solutions in chloroform, benzene, or toluene decompose rapidly with evolution of nitrogen

Complexes of Nickel(0)

The first nitrogen complex of zerovalent nickel was synthesised in 1968[77]. This is a dinuclear complex which is formed on mixing nickel acetylacetonate with trimethylaluminium in the presence of nitrogen and tricyclohexylphosphine. The reaction proceeds according to the equation

$$2Ni(acac)_2+4(C_6H_{11})_3P+4Al(CH_3)_3+N_2\longrightarrow N_2[Ni(P(C_6H_{11})_3)_2]_2+ +4(CH_3)_2Al(acac)+4CH_3.$$

The yield of the complex, which consists of dark red crystals, reaches 40%.

In benzene solution the dinuclear complex dissociates reversibly to the mononuclear complex $NiN_2[P(C_6H_{11})_3]_2$ and $Ni[P(C_6H_{11})_3]_2$. The infrared spectrum of the mononuclear nitrogenyl shows absorption at 2028 cm^{-1}, which has been assigned to the vibration of the N≡N bond.

Nitrogen Complexes of Manganese(II)

It has been stated[78] that oxygen, carbon monoxide, and nitrogen combine reversibly with manganese(II) compounds forming 1 : 1 adducts. In contrast to all the mononuclear nitrogenyl complexes known hitherto, the infrared spectrum of the adduct with nitrogen does not contain a band in the region 2000–2200 cm^{-1}. It is surprising that the infrared spectrum of the carbon monoxide complex also lacks a band corresponding to the CO vibration. This finding is so unusual, that its validity appears questionable.

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Thus several methods are known at present for the synthesis of complexes containing molecular nitrogen in the coordination sphere of the metal and the complexes can be obtained both by the addition of molecular nitrogen and by indirect methods, in which nitrogen is formed directly in the coordination sphere of the metal.

The coordination of molecular nitrogen can occur at the instant of the reduction of transition metal salts (as in the synthesis of carbonyls) by the substitution of ligands in certain low-valence metal derivatives, and by direct interaction with coordination-unsaturated systems.

Although considerable advances have in fact been achieved in the synthesis of nitrogenyl complexes, many features of these compounds still remain obscure. For example, the failure to synthesise the complex by one of the standard methods may imply either that the complex is unstable or that the method is unsuitable for the given compound.

2, THE STRUCTURE OF THE COMPLEXES AND THE NATURE OF THE M–N_2 CHEMICAL BOND

X-Ray Diffraction Analysis of Nitrogenyls

At present only two compounds have been analysed by X-ray diffraction: $[RuN_2(NH_3)_5]X_2$,[79,80] and $CoHN_2(PPh_3)_3$.[67] The ruthenium complexes crystallise with a cubic lattice containing four molecules per unit cell. Bottomley and Nyburg[79,80] showed that the ruthenium ion is surrounded octahedrally by nitrogen atoms [r(Ru–N) = 2.10 Å], molecular nitrogen is coordinated to the two metals almost linearly, and the distance between two adjacent nitrogen atoms in the RuNN fragment is 1.12 Å. While the linear coordination of the N_2 molecule has been established unambiguously, the interatomic r(Ru–N) and r(N–N) distances have been determined only approximately due to the statistically disordered arrangement of the molecules in the lattice.

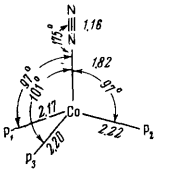


Figure 4. The structure of $CoHN_2(PPh_3)_3$.

The $CoHN_2(PPh_3)_3$ crystals were obtained[67] in two modifications, one of which is not susceptible to accurate analysis, while the other (it is noteworthy that subsequently it could not be synthesised again) has the structure of a distorted trigonal bipyramid (Fig. 4).

It should be noted that both in the cobalt complex and probably in the ruthenium nitrogenyl the M–N–N fragment is not rigorously linear. The Co–N–N angle is[67] 175° ± 4°.

In the nitrogenyl complexes of ruthenium and cobalt the r(N–N) bond length is greater than in the nitrogen molecule in the gas phase [r(N≡N) = 1.097 Å]. However, it is

significantly smaller than the nitrogen–nitrogen interatomic distance in azo-compounds; therefore it can be assumed that the multiplicity of the nitrogen–nitrogen bond in $[RuN_2(NH_3)_5]X_2$ and $CoHN_2(PPh_3)_3$ is close to three.

Infrared Absorption Spectra of Nitrogenyl Complexes

Infrared spectroscopy has found wide application in the identification and study of nitrogenyl complexes. As a result of the coordination of the N_2 molecule, an intense absorption band due to the stretching vibrations of the NN bond appears in the spectrum (2000–2200 cm^{-1}).

The vibration frequency of the N≡N bond in the nitrogen molecule is known to be 2331 cm^{-1}, while those of the N=N bonds in azo-compounds are in the range 1400–1600 cm^{-1}.[81,82] Thus the frequency range of the NN bond vibrations in nitrogenyl complexes (Table 6) corresponds to a bond order close to 3, in agreement with the X-ray diffraction studies.

Group-theoretical Analysis of the NN Bond Vibrations in Nitrogenyl Complexes

In principle molecular nitrogen can form with transition metals complexes having different structures (I)–(X) (Fig. 5). [So far compounds of types (I), (III), and (IX) have been synthesised.] On the basis of the local symmetry of these models, it is possible to determine under what conditions the nitrogen–nitrogen bond stretching vibrations will be active in the infrared absorption spectrum.

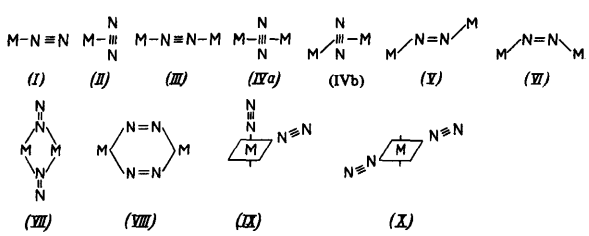


Figure 5. Possible structures of the nitrogen complexes.

The results of such analysis are presented in Table 7, which shows (fifth and sixth columns) that nitrogen–nitrogen bond vibrations in complexes of the type (I), (II), (IVb), (VI), and (VII)–(X) are active in the infrared spectrum, while the vibrations of complexes of the type (III), (IVa), and (V) are inactive. It should be noted that this conclusion was obtained on the assumption that in dinuclear complexes the ligands of both metal atoms and the metal atoms themselves are the same. On the other hand, when the ligands or the metal atoms are different, the symmetry is decreased and the stretching vibrations of the NN bond may be active in the infrared spectrum.

Spectra of Nitrogenyl Complexes Containing Nitrogen Isotopes

The validity of the assignment of the absorption bands in the range 2000–2200 cm^{-1} (Table 6) to the stretching vibrations of the N≡N bond is unambiguous, particularly since the replacement of $^{14}N{\equiv}^{14}N$ by $^{15}N{\equiv}^{15}N$ or $^{14}N{\equiv}^{15}N$ results in a decrease of the vibration frequency by 60–70 cm^{-1} or 30–35 cm^{-1} respectively, which agrees well with the calculated isotopic shift[40,43,44,49,52,54]. The ability to synthesise nitrogenyl complexes containing nitrogen-29 only, made it possible in some cases to establish the structure of the $M-N_2$ fragment.

Table 7. Types of stretching vibrations of the nitrogen–nitrogen bonds active in the infrared spectrum

Structure	Symmetry point group	Complete representation	Types of vibrations active in infrared spectrum	ν_s (NN)	ν_{as} (NN)
I	$C_{\infty v}$	$2A+E$	$2A+E$	A	—
II	C_{2v}	$2A_1+B_2$	$2A_1+B_2$	A_1	—
III	$D_{\infty h}$	$2A_{1g}+A_{1u}+E_{1g}+E_{1u}$	$A_{1u}+E_{1u}$	—	—
IVa	D_{2h}	$2A_g+B_{3g}+B_{1u}+B_{2u}+B_{3u}$	$B_{1u}+B_{2u}+B_{3u}$	—	—
IVb	C_{2v}	$3A_1+A_2+B_1+B_2$	$3A_1+B_1+B_2$	A_1	—
V	C_{2h}	$3A_g+A_u+2B_u$	A_u+2B_u	—	—
VI	C_{2v}	$3A_1+A_2+2B_2$	$3A_1+2B_2$	A_1	—
VII	D_{2h}	$3A_g+2B_{1u}+B_{2g}+2B_{2u}+2B_{3g}+2B_{3u}$	$2B_{1u}+2B_{2u}+2B_{3u}$	—	B_{3u}
VIII	D_{2h}	$3A_g+A_u+B_{1g}+2B_{1u}+2B_{2u}+2B_{3g}+B_{3u}$	$A_u+2B_{1u}+2B_{2u}+B_{3u}$	—	B_{3u}
IX	C_{2v}	$4A_1+A_2+3B_1+B_2$	$4A_1+3B_1+B_2$	A_1	B_1
X	D_{2h}	$2A_g+B_{2g}+B_{3g}+2B_{1u}+2B_{2u}+2B_{3u}$	$2B_{1u}+2B_{2u}+2B_{3u}$	—	B_{1u}

The spectra of ruthenium complexes containing $^{14}N^{14}N$ and $^{14}N^{15}N$ have been investigated[40,44]. The activity of the NN bond vibrations in the infrared spectrum may be evidence of the formation of complexes of type (I) or (II) (Fig. 5). If the complexes have the linear structure (I), then there are two equally probable possibilities of the coordination of nitrogen-29: either $Ru-{}^{14}N{\equiv}^{15}N$ or $Ru-{}^{15}N{\equiv}^{14}N$, and the $\nu(N{\equiv}N)$ vibration frequencies may differ by 3–10 cm^{-1}. For the structure of type (II), the band in the RuN_2 spectrum should of course not be split. Analysis[44] of the observed spectrum of the complex $RuN_2Cl_2(NH_3)_3$ showed that the absorption band corresponding to $\nu(^{14}N{\equiv}^{15}N)$ results from superposition of two bands with a splitting of 4–6 cm^{-1}. Hence it was concluded that the Ru–N≡N fragment is linear. Similar results were obtained[40] also for pentamminenitrogenylruthenium, in agreement with X-ray diffraction data[79,80]. The N≡N stretching vibration frequencies of the complexes $[RuN_2(NH_3)_5]I_2$ containing nitrogen isotopes proved to be as follows:

$$\left.\begin{array}{ll}[Ru(NH_3)_5N^{14}{\equiv}N^{14}]I_2 & 2132\\ [Ru(NH_3)_5N^{14}{\equiv}N^{15}]I_2 & 2098\end{array}\right\}\Delta\nu=4\ cm^{-1}$$

$$\left.\begin{array}{ll}[Ru(NH_3)_5N^{15}{\equiv}N^{14}]I_2 & 2094\\ [Ru(NH_3)_5N^{15}{\equiv}N^{15}]I_2 & 2060\ cm^{-1}\end{array}\right.$$

The force constants (10^6k, cm^{-2}) of the bonds in the Ru–N≡N fragment were calculated from these experimental values[40]: $k_{NN} = 29.3$, $k_{RuN} = 5.5$, and $k_{NN,RuN} = 1.2$.

It is interesting that these force constants of the bonds in the Ru–N≡N fragment of the nitrogenyl complex proved to be close to the corresponding force constants for the diazo-group C–N≡N in diazomethane[83]: $k_{NN} = 27.7$, $k_{CN} = 7.97$, and $k_{CN,NN} = 1.5$.

In the infrared spectra of the crystalline complexes $CoHN_2(PPh_3)_3$ [84] and $FeH_2N_2(PPh_3)_3$ [85] the half-widths of the bands due to the vibrations of the $^{14}N{\equiv}^{14}N$, $^{14}N{\equiv}^{15}N$, and $^{15}N{\equiv}^{15}N$ bonds are the same, the half-width amounting to

5–6 cm^{-1}. Thus one may conclude that the band corresponding to the $^{14}N\equiv{}^{15}N$ vibration in the complexes is not split. When the iron compounds are dissolved in toluene, the absorption bands corresponding to the N≡N vibration become appreciably broader (up to 16 cm^{-1}) (Fig. 6).

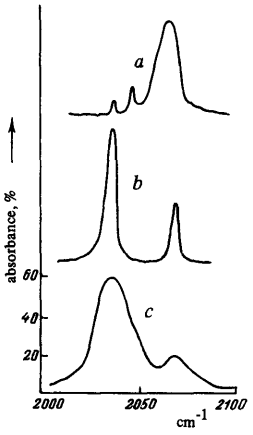


Figure 6. Absorption bands associated with the stretching vibrations of the N≡N bond in $FeH_2N_2(PPh_3)_3$: *a*) crystalline $FeH_2N_2(PPh_3)_3$; *b*) crystalline product containing $FeH_2(^{14}N^{15}N)(PPh_3)_3$ and $FeH_2(^{14}N^{14}N)(PPh_3)_3$; *c*) spectrum of a mixture of $FeH_2(^{14}N^{15}N)(PPh_3)_3$ and $FeH_2(^{14}N^{14}N)(PPh_3)_3$ in toluene solution at 10°C.

To account for the results obtained[85], it has been suggested that association complexes are formed in the crystals.

Borod'ko et al.[54] have quoted the vibration frequencies of a series of pentammineosmium nitrogenyls with different nitrogen isotopes in the range 60–3700 cm^{-1} and have given the assignments of these bands. The Os–N≡N fragment is characterised by three absorption bands corresponding to $\nu(NN) = 2010–2034\ cm^{-1}$, $\nu(Os–N_2) = 500–518\ cm^{-1}$, and $\delta(OsNN) = 245\ cm^{-1}$.

Absorption Band Intensities $\mathcal{J}$(N≡N)

The integral intensity of the absorption band corresponding to the stretching vibration of the N≡N bond can be used to assess the structure of the $M–N_2$ fragment. In the case of linear coordination of the type M–N≡N the nitrogen–nitrogen bond is appreciably polarised and probably in all nitrogen complexes with a linear structure the intensity $\mathcal{J}$(N≡N) will be high. By analogy with the π-complexes of symmetrical olefins and acetylenes, one may expect that the intensity $\mathcal{J}$(N≡N) in the spectra of π-complexes of the type $M-\overset{N}{\underset{N}{\|}}$ will be very low.

Table 8, where the intensities for a number of nitrogenyls are listed, shows that $\mathcal{J}$(N≡N) varies in the range 2.7×10^4–8.5×10^4 litre $mole^{-1}\ cm^{-2}$, which is characteristic of the intensities of the stretching vibrations of nitrogenyls known to have a linear structure and also of carbonyls. Hence one may conclude that the linear structure M–N≡N obtains in the complexes $[OsN_2(NH_3)_5]X_2$, $RhN_2Cl(PPh_3)_2$, $IrN_2Cl(PPh_3)_2$, and $Fe_2H_2N_2(PPh_3)_3$.

It is interesting that the surface complexes of nitrogen on metallic nickel, palladium, and platinum appear to have $\mathcal{J}$(N≡N) intensities similar to those quoted above.

Table 8. Integral intensities of the bands due to the stretching vibrations of the N≡N bond

Compound	$\nu_{(N\equiv N)}$, cm^{-1}	$\mathcal{J}_{(N\equiv N)}$, 10^4 litre $mole^{-1}$ cm^{-2}	Refs
$FeN_2H_2(PPh_3)_3$	2066	4.9	85
$[RuN_2(NH_3)_5]Br_2$	2106	2.9	54
$[OsN_2(NH_3)_5]Cl_2$	2012	6.1	54
$[OsN_2(NH_3)_5]^{2+}$	2030	8.5	54
$RhN_2(PPh_3)_2Cl$	2152	3.4	37
$IrN_2(PPh_3)_2Cl$	2095	2.7	37

Dependence of the ν(N≡N) Frequency on the Radii of the Anions and the Nature of the Ligands

The N≡N bond stretching vibration frequency in the salts $[RuN_2(NH_3)_5]X_2$ and $[OsN_2(NH_3)_5]X_2$ depends on the anion X^-: the greater the ionic radius of the anion the higher is the vibration frequency[87] (Fig. 7). This relation may be due to the fact that, as the radius of the X^- anion decreases, the effective electrostatic field strength increases. Accordingly there is an increase in the contribution of the more polar structure (b) which is characterised by a lower ν(N≡N) vibration frequency:

$$\underset{(a)}{L_5M-N\equiv N} \longleftrightarrow \underset{(b)}{L_5M=\overset{+}{N}=\overset{-}{N}}$$

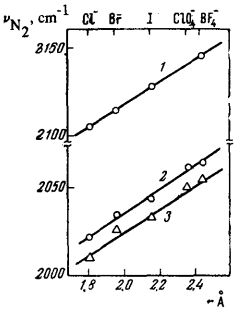


Figure 7. Dependence of the stretching vibration frequency ν(N≡N) on the radius of the anion: 1) $[RuN_2(NH_3)_5]X_2$; 2) and 3) $[OsN_2(NH_3)_5]X_2$. The variation of the frequencies of the two components of ν(N≡N), due to Davydov splitting, is shown for the osmium complex.

In the series of non-saltlike compounds of the type $RuN_2Cl_2L_3$ the N≡N stretching vibration frequency depends on the nature of the ligand L: the frequency falls with increasing basicity of the ligand[40] (Table 9). Misono et al.[87] who investigated the compounds $CoHN_2L_3$ in which L = $P(p\text{-}CH_3C_6H_4)_3$, $P[(C_6H_5)_2C_2H_5]_3$, $P(n\text{-}C_4H_9)_3$, or $P(C_2H_5)_3$ arrived at a similar conclusion; this dependence is evidence

of a significant contribution of the d_π–p_π interaction in the formation of the M–N_2 bond. Under the influence of donor ligands, the contribution of structure (b) falls.

It also follows from the work of Misono et al.[87] that the steric factor plays a major role in the formation of nitrogen complexes. Thus nitrogen complexes are not formed with $P(C_6H_5)_2H$ and $P(C_6H_5)_2CH_3$ and only the compound $CoHL_4$ (L = phosphine) is produced. Thus in the more bulky phosphines (PPh_3, $PPh_2C_2H_5$, etc.) one coordination site is occupied by molecular nitrogen because it is inaccessible to the phosphine molecule, although the metal–phosphine bond is probably stronger than the metal–nitrogen bond.

Table 9. Variation of the stretching vibration frequency ν(N≡N) of ruthenium nitrogenyls $RuN_2Cl_2L_3$ with the basicity of the ligand (L)

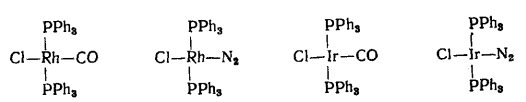
$RuN_2Cl_2L_3$	
ligand (L),	ν (N≡N), cm^{-1}
$3H_2O$	2163
$2H_2O \cdot$ THF	2153
$(CH_3)_2NCHO$*	2123
C_5H_5N *	2115
$2NH_3 \cdot H_2O$	2090
$3NH_3$	2080
$C_2H_4(NH_2)_2$	2085

* The number of ligands was not determined.

On the basis of the infrared absorption spectra of the square complexes $IrN_2(PPh_3)_2Cl$ and $IrCO(PPh_3)_2Cl$, Collman et al.[88] concluded that molecular nitrogen is a more powerful π-electron acceptor than carbon monoxide. This conclusion is based on the fact that in the formation of the complex the ν(N≡N) stretching vibration frequency falls more than does ν(C≡O) relative to the corresponding vibration frequencies of the gaseous N_2 and CO molecules. Collman et al.[88] do not take into account the fact that in the formation of the CO complex the ν(C≡O) stretching vibration frequency may actually increase, since the upper filled molecular orbital 3σ(CO) is non-bonding (see p. 360).

In fact, in agreement with the qualitative quantum-chemical treatment, carbon monoxide gives rise to stronger σ and π bonds with a transition metal atom than does molecular nitrogen, i.e. CO is a stronger "π-acid" than N_2.

The study of the nitrogen complexes of rhodium(I) and iridium(I)



showed[37] that the ν(M–Cl) stretching vibration frequency is higher by 12–15 cm^{-1} for the *trans*-position with respect to N_2 than for the *trans*-position with respect to CO (Table 10). Since the replacement of the CO molecule by N_2 does not alter the kinematic parameters of the complexes, the masses of molecular nitrogen and carbon monoxide being the same, the difference in the ν(M–Cl) frequencies is undoubtedly due to the difference in the M–Cl bond strengths.

Electron transfer from CO or N_2 via the σ bond to the hybrid ($d_{z^2} + p_z + s$) orbital of the metal hinders the formation of the M–Cl bond (which is the reason for the *trans*-effect).

Dependence of the ν(N≡N) Frequency on the Nature of the Metal

Since the nature of the ligand has a very significant influence on the vibration frequency of the N≡N bond, it is useful to compare the frequencies only for complexes having the same structures and the same ligands. Table 11 lists the values of the ν(N≡N) frequencies for certain nitrogenyl complexes of ruthenium(II), osmium(II), rhodium(I), and iridium(I). Evidently on going from complexes of metals with 4*d* electrons to those of metals with 5*d* electrons, the ν(N≡N) frequency is reduced by 60–90 cm^{-1}, while the ν(M–N_2) frequency is increased by 18 cm^{-1}.

Table 10. Stretching vibration frequencies ν(N≡N), ν(C≡O), and ν(M–Cl) in the square complexes of rhodium(I) and iridium(I)

Compound	ν (N≡N), cm^{-1}	ν (C≡O), cm^{-1}	ν (M–Cl), cm^{-1}
$RhN_2Cl(PPh_3)_2$	2152	—	315
$RhCOCl(PPh_3)_2$	—	1967	304
$IrN_2Cl(PPh_3)_2$	2095	—	329
$IrCOCl(PPh_3)_2$	—	1955	315

Probably the nitrogenyls of the transition elements in the lower periods have a structure close M=N=N, since with increase in the principal quantum number, there is an increase in the overlap of the molecular orbitals and therefore the d_π–p_π interaction is stronger (see p. 367).

Table 11. Dependence of the stretching vibration frequencies ν(N≡N) and ν(M–N) on the nature of the metal

Compound	ν (N≡N), cm^{-1}	ν (M–N_2), cm^{-1}	Compound	ν (N≡N), cm^{-1}
$[RuN_2(NH_3)_5Cl_2$	2102	500	$RhN_2Cl(PPh_3)_2$	2152
$[OsN_2(NH_3)_5]Cl_2$	2012	518	$IrN_2Cl(PPh_3)_2$	2095

Kinetic studies of the breakdown of nitrogenyl complexes confirm an increase in the strength of the M–N_2 bond on transition to metals in the lower periods. Thus the Os–N_2 bond energy in $[OsN_2(NH_3)_5]^{2+}$ is not less than 39 kcal $mole^{-1}$,[97] while in the corresponding ruthenium cation $D(Ru-N_2)_2 \simeq$ 25 kcal $mole^{-1}$. In the complex $RuN_2Cl_2THF(H_2O)_2$ the energy of the RuN_2 bond amounts to 22 kcal $mole^{-1}$.[95]

Other Results Obtained by Vibrational Spectroscopy

In the infrared spectra of $[OsN_2(NH_3)_5]X_2$ crystals the absorption band corresponding to the ν(N≡N) frequency results from the superposition of a number of components[37,53,54]. Thus in the spectrum of $[OsN_2(NH_3)_5]Cl_2$ the asymmetric band splits into three components: at 2012, 2022, and 2033 cm^{-1}. At the same time the infrared spectra of solutions of the complex in H_2O and D_2O are characterised by a single symmetrical absorption band at a frequency of 2030

cm^{-1}. In the spectra of the corresponding ruthenium complexes, both in the crystalline state and in aqueous solution, there is a single line. The splitting of the $\nu(N\equiv N)$ band of osmium nitrogenyls has been explained[37,54] by the resonance interaction of the translationally non-equivalent molecules in the unit cell of the crystal (the Davydov effect). In view of the splitting, it was concluded that the crystals of osmium nitrogenyls, in contrast to the ruthenium compounds, have a lattice with a lower symmetry than cubic.

In the spectra of the crystalline compounds $FeH_2N_2(PPh_3)_3$ and $FeH_2N_2(PPh_2Et)_3$ the absorption bands corresponding to the N≡N stretching vibrations are split into three components[85] (Fig. 6) which are displaced towards lower frequencies by 65–70 cm^{-1} when $^{14}N_2$ is replaced by $^{15}N_2$. In the spectra of crystals containing a mixture of the isotopic molecules $[FeH_2{}^{14}N^{14}N(PPh_3)_3]$ and $[FeH_2{}^{14}N^{15}N(PPh_3)_3]$ the band corresponding to the isotope present at a low concentration is not split, while that corresponding to the isotope at a high concentration is split.

These results show that the splitting of the infrared band due to the N≡N stretching vibrations is due to the resonance interaction of the translationally non-equivalent molecules in the unit cell of the crystals[86]. Due to the statistical distribution of the isotopic molecules containing nitrogen-28 and nitrogen-29 with different $\nu(N\equiv N)$ vibration frequencies, in the mixed crystals the resonance conditions are not realised and the Davydov components are absent.

The occurrence of Davydov splitting and the presence of three $\nu(N\equiv N)$ components shows that $FeH_2N_2(PPh_3)_3$ and $FeH_2N_2(PPh_2Et)_3$ crystallise with a lattice whose symmetry is lower than cubic and the number of molecules in the unit cell of the crystals is not less than three. Probably this effect can also account for the splitting associated with the stretching vibration of the N≡N bond in the crystalline complex $CoHN_2(PPh_3)_2$ into two components[66] with frequencies of 2101 and 2087 cm^{-1}.

The frequencies of the first and second overtones of the stretching vibration of the N≡N bond in the complex $[OsN_2(NH_3)_5]Br_2$ have been observed[57] at 3998 and 5904 cm^{-1}. The calculated anharmonicity constant X_e of the N≡N bond vibration in the complex is about 0.0125, while for gaseous nitrogen $X_e \simeq 0.0063$. According to an approximate estimate based on the convergence of the vibrational levels, the energy of the NN bond in the complex is about 120 kcal $mole^{-1}$. Unfortunately the accuracy of this estimate is low and the error is unknown. At the same time such a sharp increase of bond energy compared with the nitrogen molecule is not surprising, since the dissociation of the NN bond in the complex should result in the formation of a strong Os≡N bond. The range of values of the M≡N bond energies for various metals in the gas phase is 96–145 kcal $mole^{-1}$.[89] Thus the reduction of the N≡N bond energy in the complex should indeed be appreciable.

Raman Spectra. $\{[Ru(NH_3)_5]_2N_2\}(BF_4)_4$ and $[Ru(NH_3)_5N_2](BF_4)_2$

It has been shown[58] that in the infrared spectrum of the dinuclear complex $\{[Ru(NH_3)_5]_2N_2\}^{4+}$ there is no absorption characteristic of the stretching vibration of the N≡N bond. In view of this finding, a symmetrical structure was postulated[58], in which the N≡N molecule behaves as a bridge ligand.

Study of the Raman spectra of the crystalline tetrafluoroborate salt of this complex[90], containing $^{14}N_2$ and $^{15}N_2$, showed that the spectrum includes intense bands at frequencies of 2100 and 2030 cm^{-1} for the light and heavy nitrogen respectively. Therefore these lines should be assigned to the stretching vibration of the nitrogen–nitrogen bond {belonging to the symmetry type A_{1g}, which is allowed in the Raman spectrum and forbidden in the infrared spectrum [see Fig. 5 and Table 7, structure (III)]} and the order of this bond is close to three.

It should be noted that the formation of the complex with the linear structure Ru–N≡N–Ru leads to a decrease of the vibration frequency of the N≡N bond compared with the mononuclear complex. Thus the Raman spectrum of $[Ru(NH_3)_5N_2](BF_4)_2$ shows an intense line at 2133 cm^{-1}, while in the dinuclear complex the vibration frequency falls to 2100 cm^{-1}.

The Nature of the M–N_2 Bond

Even before the synthesis of the first complexes of molecular nitrogen with transition metal compounds, the question of the possibility of their formation and of the nature of their chemical bond was discussed. Orgel[91] compared transition metal carbonyls with the nitrogenyls, which were hypothetical at the time. According to Orgel, electron transfer from the σ orbital of N_2 to the metal and from the metal to the antibonding π orbital of N_2 leads to the transition of the neutral N_2 molecules to an excited state identical with the highest states of the $n-\pi$ transition. For N_2, the energy of the $n-\pi$ transition is 7.3 eV, while in the case of carbon monoxide the energy is 6 eV, the energies of the $\pi-\pi$ transitions for the two molecules being 6–8 and 7–8 eV respectively. Hence it was concluded that the configuration $M-\overset{N}{\overset{\|}{N}}$ is more favoured compared with $M-N\equiv N$ than is $M-\overset{C}{\overset{\|}{O}}$ compared with $M-C\equiv O$.

However, all the transition metal nitrogenyls known at the present time and also the surface complexes of nitrogen evidently have a linear structure like the carbonyls and diazo-compounds. As already mentioned, this has been established by X-ray diffraction analysis and by infrared and Raman spectroscopy.

Furthermore examination of the experimental data for the nitrogenyl complexes permits the following preliminary generalisations: (1) molecular nitrogen complexes are formed by compounds of transition metals in lower oxidation states, which have unshared pairs of d electrons; (2) the contribution of the $d\pi-p\pi$ interaction is significant in the formation of the M–N_2 bond, N_2 behaving as a π-electron acceptor ligand; (3) donor ligands enhance the stability of molecular nitrogen complexes and π-acceptors reduce it‡; (4) other conditions being equal, the complexes of metals in the lower Periods of the Periodic System are more stable than those in the higher Periods; (5) the nitrogenyl complexes known at the present time are diamagnetic, i.e. stable complexes are probably formed with metals in low-spin states.

‡ This explains the finding that each new N_2 molecule weakens the M–N_2 bond and polynitrogenyl complexes are less stable than mononitrogenyl complexes. We may also note that this distinguishes polynitrogenyls from polycarbonyls, many of which are very stable. Probably this is because carbon monoxide is not only a powerful π-electron acceptor ligand but also a much stronger σ-electron donor than nitrogen (see p. 360). Therefore the introduction of several CO molecules does not alter significantly the electron density at the metal.

We may note that N_2 complexes have been obtained for compounds of ruthenium and osmium [metals in Periods (V) and (VI)] with ligands which give rise to both weak (H_2O, NH_3, C_4H_8O, etc.) and strong (PR_3, H) crystal fields. For metals of Period (IV) (iron, cobalt, and nickel), covalent nitrogenyl complexes have been obtained (and these are probably the most stable) with ligands giving rise to a powerful field. This is evidently because low-spin states of metals of Periods (V) and (VI) are realised with both types of ligand, while for iron, cobalt, and nickel compounds spin-paired states can be obtained only with strong-field ligands.

It is striking that the electron shells of the metals in the complexes $FeH_2N_2(PPh_3)_3$ and $CoHN_2(PPh_3)_3$ are isoelectronic, as in the carbonyls $FeH_2(CO)_4$, $CoH(CO)_4$, and $Ni(CO)_4$, and in the nitrogenyls the number of outer electrons (18) corresponds to an inert gas shell. The number of electrons in $NiN_2[P(C_6H_{11})_3]_2$ is two less, but the complex may also include a solvent molecule with an electron pair.

Probably the stabilising effect of hydride bonds can be explained by the fact that nitrogen is a powerful electron donor. For a carbonyl hydride, this is illustrated by its acid dissociation in solution:

$$CoH(CO)_4 \rightleftarrows H^+ + [Co(CO)_4]^-.$$

We shall now examine the scheme of the molecular orbitals for the cation $[OsN_2(NH_3)_5]^{2+}$ shown in Fig. 8 (for clarity the energy scale has been extended).

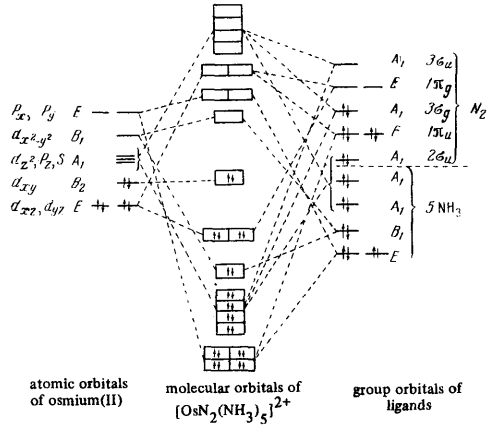


Figure 8. The system of molecular orbitals of $[OsN_2(NH_3)_5]^{2+}$ (arbitrary scale).

The $[OsN_2(NH_3)_5]^{2+}$ cation belongs to the point group C_{4V} and therefore the distribution of the atomic orbitals of osmium(II) corresponds to splitting in a tetragonal field. The ammonia molecules, which are σ-electron donors, are taken into account by the introduction of five groups of σ-orbitals. By taking into account the symmetry and the distribution of the osmium(II) and N_2 levels, it is seen that in the formation of the complex osmium cations there is, on the one hand, electron transfer from the bonding atomic orbitals of osmium of the type $E(d_{XZ}, d_{YZ})$ to the lower antibonding molecular orbital of nitrogen $(1\pi_g)_{XZ,YZ}$ and, on the other hand, the filled molecular orbitals of nitrogen of the type $A_1(3\sigma_g, 2\sigma_u)$ are capable of donating electrons to the antibonding hybrid osmium orbital $(d_{Z^2} + p_Z + s)$.

Fig. 9 gives a conventional representation of these two components of the metal–molecular nitrogen bonds in the complex $[OsN_2(NH_3)_5]^{2+}$ both for a linear and a non-linear configuration of the fragment. Fig. 9 shows that the overlapping of the orbitals is greater for the linear configuration of the $Os-N_2$ fragment, since in this case a dative bond is formed as a result of the overlapping of two pairs of orbitals, $d_{XZ}-(1\pi_g)_{XZ}$ and $d_{YZ}-(1\pi_g)_{YZ}$ in the mutually perpendicular planes xz and yz. In the π-complex with C_{2V} symmetry both dative and donor–acceptor interaction is less intense due to the smaller degree of overlapping of the orbitals.

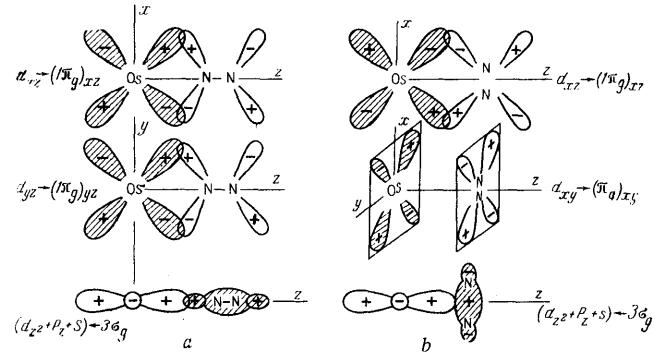


Figure 9. The overlapping of molecular orbitals in $[OsN_2(NH_3)_5]^{2+}$: *a*) for the linear coordination of molecular nitrogen, i.e. Os–N≡N (C_{4V}); *b*) for the π-complex (C_{2V}).

According to the principle of overlapping and orientation, the complex has the structure in which the overlap integrals are a maximum. Therefore it is evident that the complex with C_{4V} symmetry should be more stable than the complex with C_{2V} symmetry.

The hypothetical $Fe-N_2$ fragment, consisting of a neutral iron atom and a coordinated nitrogen molecule, has been examined quantum-chemically[92] for the two possible structures Fe–N≡N and $Fe-\overset{N}{\underset{N}{\|}}$. On the basis of the calculation, it was concluded[92] that the linear coordination of nitrogen is to be preferred and the charge distribution for the Fe–N′≡N″ model was obtained (Table 12). In this calculation the orbital energies calculated by the Hartree–Fock–Roothaan method were used as the diagonal elements of the effective Hamiltonian. As a result, the N_2 molecule was found to have an overall positive charge, i.e. nitrogen behaves as a donor in relation to the metal atom.

If the diagonal elements are approximated by the ionisation potentials of the valence states[93], one obtains for the linear model M–N′≡N″ (where M = Fe or Ru) a different charge distribution (Table 12), which agrees qualitatively with the experimental data concerning the π-electron acceptor properties of N_2 as a ligand.

Population analysis of the M–N and N–N bonds shows[93] that the contribution of the π-electron component to the metal–nitrogen bond is greater than that of the σ-electron

component, and the σ-components of the nitrogen–nitrogen bond in the coordinated and free N_2 molecules are almost indistinguishable. (The population of the bond may serve to some extent as a characteristic of its strength.)

Table 12. The atomic charges and electron populations for the fragment M–N′≡N″

Compound	Population of M–N′ bond		Population of N′–N″ bond		Atomic charges			Refs.
	σ-component	π-component	σ-component	π-component	M	N′	N″	
Fe–N′≡N″	0.433	0.254	0.845	0.746	−0.43	1.01	−0.58	92
	0.215	0.302	0.829	0.561	0.485	−0.188	−0.297	93
Ru–N′≡N″	0.255	0.313	0.832	0.590	0.426	−0.150	−0.276	93
N≡N			0.785	0.875				93

* The interatomic distances (Å) used in the calculation by Vinogradova et al.[93] were as follows: r(Fe–N) = 1.8; r(N–N) = 1.16; r(Ru–N) = 1.9.

3. THE MECHANISM OF THE FORMATION OF MOLECULAR NITROGEN COMPLEXES

Nitrogen is still an unusual ligand in the chemistry of coordination compounds and therefore it is interesting to examine how it becomes coordinated. There are very few data on this problem. The mechanism of the interaction of nitrogen in the reduction of $RuCl_3.nH_2O$ in tetrahydrofuran has been investigated in greatest detail[94,95]. As already stated, the main product of this reaction is $RuN_2Cl_2(H_2O)_2THF$; a certain amount of $RuN_2Cl_2(H_2O)_3$ is also formed. The study of the reaction kinetics led to the conclusion that nitrogen reacts with the coordination-unsaturated species RuL_5 formed as an intermediate in the reduction. The RuL_5 species may be coordinated not only to nitrogen but also to any other compound L′ present in the solution. For example, L′ may be water. The dependence of the yield of the nitrogenyl complex on nitrogen pressure is consistent with the mechanism

$$RuCl_3 \cdot nH_2O \xrightarrow{Zn} RuCl_2L_3$$

$$RuCl_2L_3 \begin{cases} \xrightarrow[N_2]{k_2} RuN_2Cl_2L_3, \\ \xrightarrow[L']{k_3} RuCl_2L_3L'. \end{cases}$$

The study of the exchange of molecular nitrogen with the nitrogen in the coordination sphere of ruthenium nitrogenyls[94,95] confirmed that nitrogen interacts with the coordination-unsaturated species RuL_5. It was established that the exchange of molecular nitrogen involves substitution by a dissociative mechanism of S_N1 type:

$$\begin{gathered} RuN_2L_5 \underset{k_2}{\overset{k_1}{\rightleftarrows}} RuL_5 + N_2, \\ RuL_5 + L' \xrightarrow{k_3} RuL_5L'. \end{gathered} \qquad (1)$$

In accordance with this mechanism, the exchange reaction takes place only in the thermal decomposition of the nitrogenyl complex. The application of the method of steady-states to mechanism (1) leads to the following expression for the rate of decomposition:

$$\frac{dz}{dt} = \frac{k_1k_2(a-z)L'}{k_2N_2 + k_3L'} = k_{\text{eff}}(a-z) \qquad (2)$$

where $z = [RuL_5L']$ and a is the initial $[RuN_2L_5]$. According to Eqn. (2), the decomposition of the nitrogenyl complex in an atmosphere of nitrogen is a first-order reaction, $1/k_{\text{eff}}$ varying linearly with the nitrogen pressure. The addition of water slows down the nitrogen exchange in the complex. It is reasonable to conclude that water competes with nitrogen in the reaction with RuL_5. The ratio of the rate constants (k_2/k_3) for the reactions of N_2 and H_2O with RuL_5 was determined from the kinetic data. The ratio is independent of temperature and equal to about 3.1. Tetrahydrofuran competes much less strongly than water. The results suggest that the difference in the reactivities of nitrogen and water is determined mainly by steric factors and the activation energy for the reaction of N_2 with RuL_5 is close to zero. Thus it has been shown[94,95] that nitrogen is coordinated only by a dissociative mechanism (S_N1) and not by an S_N2 mechanism (in contrast, for example, to the coordination of carbon monoxide) and that the rate constant for the reaction with a coordination-unsaturated compound is very high.

It may be supposed that the coordination of nitrogen in the reaction

$$[Ru(NH_3)_5H_2O]^{2+} + N_2 \rightarrow [RuN_2(NH_3)_5]^{2+} + H_2O$$

in aqueous solution at atmospheric nitrogen pressure[41] takes place by a similar mechanism. The kinetics of this reaction have been investigated recently[96] and the rate constants for the formation of the mono- and di-nuclear pentammineruthenium nitrogenyls have been measured, but the possibility of a dissociative mechanism was not discussed at all. Nevertheless it may be supposed that the water molecule in the aquopentammine-complex is weakly bound to the ruthenium atom and the following equilibrium exists in aqueous solution:

$$[Ru(NH_3)_5H_2O]^{2+} \rightleftarrows [Ru(NH_3)_5]^{2+} + H_2O$$

and the $[Ru(NH_3)_5]^{2+}$ ion interacts with molecular nitrogen.

Sacco and Aresta[59] obtained the complex $FeH_2N_2L_3$ (where L = PPh_2Et) in the reaction of N_2 with the iron dihydride compound FeH_2L_3. It was noted that the complex is formed readily not only in solution but also in the solid state. Here too nitrogen probably adds to the five-coordinated iron compound FeH_2L_3, which, however, is stable in this case. Further studies should show how general is the conclusion that nitrogen is incapable of reacting by an S_N2 mechanism.

4. COMPLEXES OF MOLECULAR NITROGEN AS INTERMEDIATES IN REDUCTIVE NITROGEN FIXATION

Several types of nitrogen reduction reactions with formation of ammonia or its derivatives are known at present.

The Formation of Nitrides in the Reaction of Nitrogen with Metals

Metals usually react with nitrogen at a high temperature; even lithium and the alkaline earth metals (calcium, strontium, and barium), which are known to form nitrides at room temperatures, react extensively with nitrogen only on heating. In many cases the necessity for severe reaction conditions is probably not due so much to the inertness of nitrogen as to the formation on the surface of oxide, nitride, etc. films; on clean surfaces nitrogen reacts with the metal at a high rate. Thus, if the reaction of lithium with ethyl bromide is carried out in nitrogen, the excess of lithium is converted into the nitride[97] at 30°C. Studies on the chemisorption of nitrogen on tungsten[27] and molybdenum[98] show that nitrogen is atomised (i.e. evidently forms surface nitrides) at a low temperature.

Heterogeneous-Catalytic Hydrogenation of Nitrogen

This process, which has been known for a long time and is widely used in technology, is carried out under comparatively severe conditions in the presence of metals such as iron, ruthenium, and osmium. Without considering this process in detail, to which numerous monographs and reviews have been devoted (see, for example, Kiperman[99]), we may note that for this process too the state of the catalyst surface is very important: on a clean iron surface, the synthesis of ammonia[100] takes place even at 80°C, albeit slowly.

Reduction of Nitrogen in Solutions

In 1964 Vol'pin and Shur[101] discovered a new nitrogen reduction reaction in hydrocarbon and ethereal solutions under the action of reducing agents such as organometallic compounds, metal hydrides, and metals [C_2H_5MgBr, Mg + MgI_2, C_6H_5Li, Al(iso-Bu)$_3$, etc.] in the presence of transition metal derivatives [$TiCl_4$, $(C_2H_5)_2TiCl_2$, $FeCl_3$, VCl_4, etc.]. A large number of examples of this reaction were subsequently observed in several studies[102,103].

The reaction takes place under very mild conditions, for example at room temperature and atmospheric nitrogen pressure. The reaction products yield ammonia on hydrolysis[101] and are probably nitride derivatives[104], although in most cases their structure is still unknown. It is interesting that in some cases the hydrolysis results also in the formation of aromatic amines[102]. Usually the yield of ammonia after the hydrolysis of the reaction products is smaller than or close to the stoichiometric value when calculated relative to the transition metal but titanium tetrachloride is a catalyst for the formation of aluminium nitride[105] (at least in the system Al–$AlBr_3$–$TiCl_4$).

In an attempt to simulate the biological fixation of molecular nitrogen, various workers investigated the reduction of nitrogen in aqueous solutions by powerful reducing agents in the presence of transition metal compounds, and some of them reported[106-108] the formation of small amounts of ammonia. These results could not, however, be reproduced[109].

Enzymic Fixation of Molecular Nitrogen

This extremely important biological process is carried out by many micro-organisms. Recently the mechanism of this reaction has been vigorously investigated and particularly important results have been obtained after the successful isolation of active cell-free extracts from the nitrogen-fixing bacteria. Without going into the details of these investigations (see the appropriate reviews[110,111]), we may note the following principal features of the mechanism of the biological fixation of nitrogen: (1) the reaction constitutes the reduction of nitrogen with intermediate formation of ammonia; (2) the enzymic system consists of two main components; one of them activates the nitrogen molecule and the other is responsible for electron (or hydrogen atom) transfer to the activated nitrogen molecule; metal atoms (iron and molybdenum) participate in both these processes; adenosinetriphosphoric acid, which is converted into adenosinediphosphoric acid and phosphate during the reaction, also plays an important role; (4) the part of the enzymic system activating the nitrogen is deactivated by carbon monoxide and hydrogen.

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Bearing in mind that metals or their compounds participate in all nitrogen reduction reactions, it is reasonable to suppose that the first stage involves the formation of an N_2 complex with the metal. In some of the earlier studies[15,29,101,112,113,114] it was also believed that the formation of a nitrogen complex is an essential intermediate stage in nitrogen fixation. The discovery of nitrogen complexes and the study of the complex-formation reactions have confirmed this view. Indeed, one may note in the first place that systems in which N_2 complexes are formed resemble those in which nitrogen is hydrogenated or reduced.

In many cases nitrogen complexes with ruthenium, osmium, cobalt, and iron compounds are formed in solution under the same conditions and under the action of the same reagents as the nitride derivatives in the reduction of nitrogen. Some examples are presented in Table 13.

Table 13. Examples of systems in which different products are formed with N_2

System	Nitrogen-containing product	Refs.
$RuCl_3$+EtMgBr+N_2	nitrogen complex	43
$FeCl_3$+EtMgBr+N_2	nitride derivative	95
Co (acac)$_3$+$AlEt_2OEt$+PPh_3+N_2	nitrogen complex	60—62
Ni (acac)$_3$+Al (iso-C_4H_9)$_3$ + N_2	nitride derivative	119

Ruthenium(II) complexes are formed in an aqueous medium and in the presence of oxygen, which explains why water is not an inhibitor of the biological fixation of nitrogen. Further reduction of nitrogen in the complexes formed in the first stage may consist in the formation of an "azo-complex" with two metal atoms:

$$M' + N_2 \rightarrow M'-N\equiv N,$$
$$M'-N\equiv N + M'' \rightarrow M'-N=N-M''.$$

The double bond –N=N– is further reduced to ammonia derivatives. A model for this mechanism of the biological fixation of nitrogen was proposed by Parshall[112], who considered the reduction of diazo-compounds (as analogues of the nitrogen molecule in the complex) in the presence of a hydride derivative of divalent platinum.

However, the formation of complexes is not a sufficient condition for the activation of nitrogen for further reactions. Indeed, the known nitrogenyl complexes are very stable with respect to nitrogen reduction reactions in the coordination sphere of the metal. As already pointed out, the reports[38,39] of the reduction of nitrogen in the ruthenium complex under the action of sodium borohydride were not subsequently confirmed[40].

In other nitrogenyl complexes nitrogen is also not reduced under the action of the usual reducing agents[46,47]. It can of course be supposed that the intermediate complexes in the reduction of nitrogen differ in structure from the stable nitrogenyls; for example, they could have the structure of the π-complex type $M-\overset{N}{\underset{N}{\|}}$. However, it is more likely that the reason lies in the necessity for a definite combination of properties in the metals comprising the complexes in order that the catalytic process may take place.

To establish what complexes can be intermediate in the catalytic reduction of nitrogen, it is necessary to bear in mind the exceptional stability of the first bond dissociated in the N_2 molecule (about 130 kcal mole^{-1}) and, on the other hand, the instability of the remaining two bonds. The addition of one H_2 molecule to a nitrogen molecule with formation of the di-imide N_2H_2 is endothermic to the extent of 49 kcal mole^{-1},[115] whereas the hydrogenation of acetylene to ethylene, for example, takes place with the evolution of 42 kcal mole^{-1}. Therefore the hydrogenation of nitrogen via the intermediate formation of free N_2H_2 is impossible under mild conditions. For this reason, the reaction involving "incorporation" in the M–H bond is unlikely for nitrogen:

$$M{-}H + N_2 \rightarrow M{-}N{=}N{-}H$$

This could be regarded as two-electron reduction (such a reaction might be put forward by analogy with the hydrogenation of acetylenes and olefins). Hence it is not surprising that nitrogen is not hydrogenated on the usual catalysts active in the hydrogenation of other unsaturated compounds.

In order to reconcile the ease of reduction of nitrogen in biological systems with the apparent necessity for the intermediate formation of di-imide (or its derivative), it has been suggested[116] that the formation of N_2H_2 is accompanied by a coupled reaction involving an energy gain, so that the overall free energy of the reaction decreases and the formation of N_2H_2 becomes possible.

However, in the formation of nitrogen complexes with transition elements there is a possibility, in principle, of another reduction pathway, not involving intermediate compounds with an N=N double bond.

In mono- and di-nuclear nitrogenyl complexes the order of the bond between the nitrogen atoms remains close to three. If the dinuclear complex is now acted upon by a two-electron reducing agent X_2, then two bonds in the nitrogen fragment may dissociate at once with formation of a hydrazine derivative as a result of the additional transfer of two electrons from the metal atoms constituting the complex:

$$M'\cdots N{\equiv}N\cdots M'' + X_2 \rightarrow \begin{matrix} & X & X & \\ & \diagdown & \diagup & \\ M' & & N{-}N & M'' \end{matrix}$$

Thus the intermediate formation of a dinuclear complex with molecules of nitrogen subsequently allows the four-electron reduction to a hydrazine derivative in one stage§.

The overall addition of two H_2 molecules to N_2 with formation of hydrazine in aqueous solution is endothermic only to the extent of 8 kcal mole^{-1}. Reducing agents only a little stronger than H_2, for example sodium dithionate, are capable of providing sufficient energy for the reduction of nitrogen to hydrazine or its derivatives. It is then necessary to remember that the metals comprising the complex must themselves be relatively powerful one-electron reducing agents. Furthermore, the complexes must not be too stable, since an increase in bond strength in the complex corresponds to a greater energy expenditure in its subsequent reduction.

In Vol'pin–Shur reactions these conditions are evidently fulfilled. Indeed in the presence of powerful reducing agents such as aluminium, RMgX, LiR, etc. transition metal compounds are reduced to low states of oxidation, becoming fairly powerful reducing agents. Since intermediate nitrogen complexes have not been detected in these reactions so far, their stability is probably low.

From this standpoint, it is not surprising that stable N_2 complexes of ruthenium, osmium, etc. cannot be reduced. The $M{-}N_2$ dissociation energy in these complexes reaches tens of kcal mole^{-1} and the capacity for electron transfer is low: osmium(II) and ruthenium(II) in these compounds are weaker reducing agents than H_2.

On the basis of the above considerations alone, three cases of the interaction of a metal or its compound (M) with an N_2 molecule have been examined[117]:

1. M is a very powerful reducing agent capable of transferring an electron to the N_2 molecule or forming a covalent bond by complete dissociation of one of the bonds in the nitrogen molecule in the absence of d_π–p_π interaction. The reduction potential of M in such a reaction must be not less than 2.5 eV. Even atomic hydrogen does not react with nitrogen, since the energy of the $H{-}N_2$ bond is negative. It may be supposed that a reaction of this kind takes place with lithium and certain other metals. Further addition of M to $M{-}N_2$ will occur very readily with the final formation of a nitride. At low temperatures M cannot be a catalyst for a reducing agent weaker than itself (for example H_2), since this would necessitate the expenditure of a large amount of energy on the dissociation of the M–N bond in the nitride. The reaction is of course impossible in an aqueous medium.

2. M is a weak reducing agent. The bond with nitrogen is formed mainly as a result of d_π–p_π interaction; the bond order in N_2 remains close to three. The formation of ruthenium(II) and osmium(II) complexes probably approaches this type. These complexes and the dinuclear complexes $M'N_2M''$ are formed readily but further reduction of nitrogen requires the use of a reducing agent almost as strong as for free nitrogen. The reaction largely terminates with formation of complexes stable to reduction.

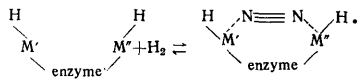
3. The intermediate case. The energy of the formation of the complexes M'N and $M'N_2M''$ includes a considerable contribution from d_π–p_π interaction, and at the same time M and M'' are comparatively powerful reducing agents capable of transferring one electron to an acceptor molecule. It is in fact in this case that we have the possibility of catalysis in the presence of M' and M'' of the reduction of molecular nitrogen by a reducing agent more powerful than M' and M'', although the reaction may of course terminate with formation of nitrides containing the M' and M'' atoms. The Vol'pin–Shur reaction and heterogeneous hydrogenation may be assigned to this case.

When a reducing agent active in an aqueous medium (of the type of sodium hydrosulphite) and with a reduction potential of about −0.2 eV is employed, the catalytic reaction can be achieved only for definite values of the reduction potential of M' and M'' and for definite strengths of the N_2–catalyst bond in the complex. These conditions are probably realised in the biological fixation of nitrogen, where M' and M'' are respectively both Fe atoms or Fe and Mo atoms present as constituents of the enzymes and forming a dinuclear complex with nitrogen in the course of fixation. It may be supposed[58] that the role of ATP in nitrogen fixation consists in its participation in the formation of hydride derivatives of molybdenum or iron.

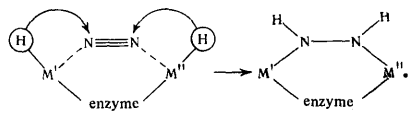
There are grounds for believing that in the biological fixation of nitrogen cyclic complexes with molybdenum and iron atoms linked by the enzyme molecule are formed, in contrast to the familiar "azo-complexes". Because of the

§ In principle one cannot exclude the possibility also of the six-electron reduction $M'...N{\equiv}N...M'' + X_2 \rightarrow M'{=}N{-}X + X{-}N{=}M''$. However, such a reaction, which cannot be regarded as a single elementary process, appears to be less likely.

more favourable entropy factor, this should lead to a higher concentration of the intermediate "azo-complex" and a correspondingly higher rate of reaction than in the case of the linear complex:



Further four-electron reduction can be readily represented, for example, as double "incorporation" in the M–H bond:



The formation of *cis*-dideuterioethylene[118] in the reduction of acetylene by the enzymic nitrogen-fixing system in D_2O provides indirect confirmation of the cyclic structure of the intermediate complex.

Further studies will show to what extent this hypothesis is correct.

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As already stated, nitrogenyl complexes with the compounds of seven metals of Group VIII of the Periodic System (iron, ruthenium, osmium, cobalt, rhodium, iridium, and nickel) have been isolated and characterised at the present time. There is no doubt that other transition metals are also capable of forming complexes with N_2 in a low-valence state. Although it may be supposed that the chemistry of nitrogenyls will prove to be less elaborate than the chemistry of the related more stable carbonyls, it will evidently undergo much further development. Probably it will be possible to isolate stable nitrogenyls of many metals (for example, platinum compounds), but unstable complexes with a low heat of formation, which can be observed at a low temperature and a high nitrogen pressure, will prove even more numerous.

The problem of the structure of the complexes is very interesting: it is still obscure whether we are dealing with π-complexes of N_2 or compounds with a structure analogous to that of the carbonyl bridge compound $\begin{matrix} M \\ N\equiv N \\ M \end{matrix}$, etc.

So far very little is known about dinuclear complexes of the type M–N≡N–M, which are of particular interest as possible intermediates in nitrogen reduction reactions. The mechanism of such reactions still requires serious revision and development. Evidently, it is possible to bind N_2 catalytically via unstable complexes (possibly by a process of the type of biological nitrogen fixation) or to synthesise other nitrogen-containing compounds (except ammonia).

It may be hoped that the development of the low-temperature chemistry of molecular nitrogen will lead to the creation of new highly effective catalytic systems and will thereby give rise to the discovery of new industrial methods for the binding of atmospheric nitrogen.

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