Nitrogen Complexes of the Platinum Metals

POINTERS TO A MECHANISM OF FIXATION

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The discovery three years ago of the first well-defined complex compound containing the nitrogen molecule – a complex of ruthenium – aroused great interest in such compounds and in their relation to nitrogen fixation. Since then a number of other nitrogen complexes have been obtained, but as yet, despite reports to the contrary, attempts to reduce their nitrogen to ammonia have been unsuccessful. In this article the author, who is Director of the Agricultural Research Council's Unit of Nitrogen Fixation, puts into perspective the considerable amount of work now being done in this field, which may eventually point the way to a mechanism by which atmospheric nitrogen may be fixed and then reduced to yield ammonia and, for example, amines for the plastics industry.

Since the 1930s chemists have thought that co-ordination compounds containing the nitrogen molecule as a ligand might exist. They were stimulated into this line of thought by the discovery, in 1930, that nitrogen-fixing bacteria metabolised nitrogen gas only in the presence of traces of molybdenum. Nevertheless, the bacteria would grow without molybdenum if they were provided with a source of fixed nitrogen such as urea or ammonia (1). Molybdenum is evidently involved in the nitrogen fixing process, and it was thought that the nitrogen molecule was activated directly by a molybdenum ion in nitrogenase, the nitrogen fixing enzyme. This led to attempts, using nitrogen under pressure, to obtain complexes of molybdenum containing the nitrogen molecule, but of no avail, and the work went largely unpublished.

The formal analogy between the triple bond in acetylene and nitrogen molecules also led chemists to attempt the preparation of nitrogen complexes of the platinum metals, analogous to the acetylene and olefin complexes. It was again of no avail. We now know that the electronic energy levels in the nitrogen and acetylene molecules are completely different. Thus the highest filled electronic level in nitrogen is a σ-molecular orbital at -15.6 electron volts, whereas in acetylene it is a much more accessible degenerate pair of π-molecular orbitals at -11.4 electron volts (2).

Chemists were beginning to accept the view that nitrogen did not form stable complex compounds, when by chance, just three years ago, Allen and Senoff in Toronto obtained indirectly the first nitrogen complex, $[Ru(NH_3)_5(N_2)]^{2+}$ (3). Its discovery revived world-wide interest in nitrogen complexes generally and in their relation to nitrogen fixation by bacteria. Since then experiments in widely separated laboratories in various parts of the world have thrown up some dozen nitrogen complexes. These vary in stability from the thermally stable and chemically inert osmium complex $[Os(NH_3)_5(N_2)]^{2+}$ to the highly reactive and thermally labile uncharged complexes of iron, cobalt and nickel.
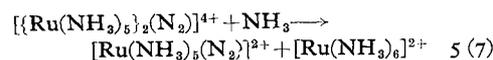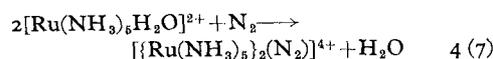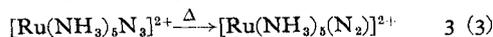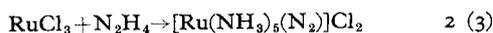
Despite reports to the contrary, the nitrogen ligand has not been reduced to ammonia in any complex (4).

So far only the Group VIII metals are known to form nitrogen complexes, and those of cobalt, ruthenium and iridium have received most study. This article is not concerned with nitrogen complexes of the first transition series. They are difficult to obtain pure, owing to their extreme lability and sensitivity to oxidation, but the cobalt compound formulated, perhaps incorrectly, as $[Co(N_2)(PPh_3)_3]$ is important. It was the first nitrogen complex reported to be obtained rapidly in high yield from gaseous nitrogen at atmospheric pressure (5). The hydride $[CoH(N_2)(PPh_3)_3]$ is equally important because it was the first nitrogen complex to be obtained in a protic solvent. It is obtained by passing nitrogen gas through a solution of a cobalt hydride complex in ethanol according to the following reversible reaction (6). There is some doubt as to whether the two cobalt nitrogen

$$[CoH_3(PPh_3)_3] + N_2 \rightleftharpoons [CoH(N_2)(PPh_3)_3] + H_2 \quad \text{1}$$

complexes are different, but our experience suggests that both exist, although the non-hydridic complex is usually contaminated with not less than 15 per cent of the hydride.

The best-defined complexes of the platinum metals are listed in Table I. The most important are the ammine complexes of ruthenium, obtained in good yields by the following reactions in aqueous solution. In reaction 3 the co-ordinated azide ion decomposes to leave nitrogen on the metal.

$$RuCl_3 + N_2H_4 \rightarrow [Ru(NH_3)_5(N_2)]Cl_2 \quad \text{2 (3)}$$

$$[Ru(NH_3)_5N_3]^{2+} \xrightarrow{\Delta} [Ru(NH_3)_5(N_2)]^{2+} \quad \text{3 (3)}$$

$$2[Ru(NH_3)_5H_2O]^{2+} + N_2 \longrightarrow$$
$$[\{Ru(NH_3)_5\}_2(N_2)]^{4+} + H_2O \quad \text{4 (7)}$$

$$[\{Ru(NH_3)_5\}_2(N_2)]^{4+} + NH_3 \longrightarrow$$
$$[Ru(NH_3)_5(N_2)]^{2+} + [Ru(NH_3)_6]^{2+} \quad \text{5 (7)}$$

Ruthenium trichloride also picks up nitrogen to give a material of analysis, $RuCl_2(N_2)(H_2O)_2(THF)$, when its tetrahydrofuran (THF) solution is reduced by zinc amalgam under nitrogen. It has $v(N\equiv N)$ at $2153 cm^{-1}$

and is converted to $[Ru(NH_3)_5(N_2)]^{2+}$ by ammonia (8, 9).

The product of reaction 2 is grossly contaminated with a hydrazine complex, perhaps $[Ru(NH_3)_5(N_2H_4)]^{2+}$, which cannot be removed by re-crystallisation, but it can be destroyed by mercuric chloride oxidation leaving the relatively inert nitrogen complex untouched. This impurity was not suspected until recently and many of the chemical properties recorded as belonging to the ruthenium nitrogen complex are those of a hydrazine complex. The most important of these reactions was the supposed reduction of the nitrogen ligand to ammonia by sodium borohydride. However, tracer studies using $[Ru(NH_3)_5(^{15}N_2)]^{2+}$ show that no $^{15}NH_3$ is obtained by sodium borohydride, or any other tried reductant (4, 9). The ammonia previously reported as coming from the nitrogen ligand in this complex must have had its origin in the hydrazine.

The formation of the nitrogen complex by Harrison and Taube's method (Reactions 4 and 5) is important because it shows that nitrogen gas can compete successfully with
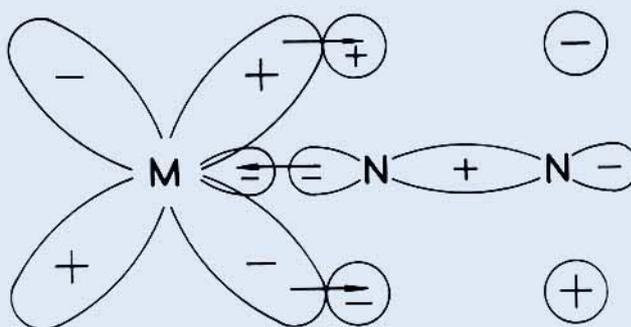
Table 1		
Nitrogen Complexes of Platinum Metals		
Ru	$v(N\equiv N)$†	Ref.
$[Ru(NH_3)_5(N_2)]^{2+}$	2105	3
$[\{Ru(NH_3)_5\}_2(N_2)]^{4+}$	—	7
$[Ruen_2(N_2)H_2O]^{2+}$	2130‡	19
Os		
$[Os(NH_3)_5(N_2)]^{2+}$	2010	11
$[Os(NH_3)_4(N_2)_2]^{2+}$	2175, 2120	12
Rh		
$[RhCl(N_2)(PPh_3)_2]$	2152	14
Ir		
trans-$[IrX(N_2)(PPh_3)_2]$	2095	13
(X = Cl, Br, N_3)		(see text)

A few other poorly defined complexes have been claimed, e.g. see ref. 20. No complex of Pd or Pt is known.

† of chloride, solid state spectra.

‡ $[BPh_4]^-$ salt.

Schematic representation of the metal to nitrogen bond. Electrons are donated from the $3\sigma_g$ orbital of the nitrogen molecule to the metal ($\leftarrow$) to form a σ M—N bond, and from two non-bonding d-orbitals of the metal into the degenerate $1\pi_g$ antibonding orbitals of the nitrogen molecule to form a pair of π-type M—N bonds (--)

water for a suitable metal site in aqueous solution. Reaction 4 even occurs when air is bubbled through the aqua-ruthenium complex solution, but oxidation of the ruthenium complex also occurs (10). It is the only known reaction of nitrogen at ordinary temperature and pressure in aqueous solution, and might well provide a model for the uptake of nitrogen, possibly by iron, in the enzyme nitrogenase. However, it does not lead to an easily reducible species, and if it provides a true model the reduction step still has to be worked out.

The osmium complexes are remarkably stable. The analogue of the ruthenium complex, $[Os(NH_3)_5(N_2)]^{2+}$ is obtained by reaction of hydrazine on aqueous ammonium chloro-osmate(IV) (11). The nitrogen is so strongly bound that it is not lost even in boiling hydrochloric acid but it yields to a mixture of hydroiodic acid and iodine to form $[Os(NH_3)_5I]^{2+}$. By diazotisation with nitrous acid the mononitrogen complex yields the only known stable di-nitrogen complex (12):

$$[Os(NH_3)_5(N_2)]^{2+} + HNO_2 \longrightarrow$$
$$cis\text{-}[Os(NH_3)_4(N_2)_2]^{2+} + 2H_2O \qquad 6$$
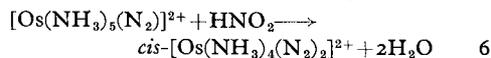
The planar iridium complex *trans*-$[IrCl(N_2)(PPh_3)_2]$ was the second nitrogen complex to be discovered. It is obtained very easily by the reaction of Vaska's compound, *trans*-$[IrCl(CO)(PPh_3)_2]$, with acid azides (13):

$$trans\text{-}[IrCl(CO)(PPh_3)_2] + PhCON_3 \xrightarrow[\text{0°C}]{\text{CHCl}_3}$$
$$trans\text{-}[IrCl(N_2)(PPh_3)_2] + PhCONCO \qquad 7$$
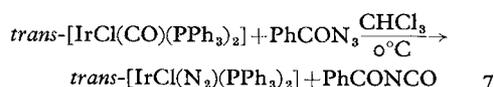
The complex reacts with π-bonding ligands, particularly acetylenes, to lose nitrogen. The corresponding rhodium complex is formed by an analogous reaction and is very unstable (14).

In addition to the reasonably-defined nitrogen complexes listed in the table and discussed above, a number of other nitrogen complexes too unstable to be identified have been reported but none containing platinum or palladium.

In the above mono-nuclear complexes the nitrogen is always bonded end-on to the metal as is carbon monoxide in the carbonyl complexes. The mode of bonding in nitrogen complexes is also very similar to that in carbonyl complexes with back donation of non-bonding d-electrons from the metal into the anti-bonding orbitals of the nitrogen molecule as shown in the diagram. The feedback of electrons into anti-bonding orbitals of the nitrogen molecule weakens the N–N bond and so lowers the stretching frequency, $\nu(N\equiv N)$. In nitrogen gas $\nu(N\equiv N)$ is observed at 2331 cm^{-1} in the Raman spectrum. In the complexes it is observed as a very strong sharp band in the infrared spectrum at 180–320 cm^{-1} lower than in nitrogen gas. The frequencies have been listed, together with the complexes in Table I. Because the band in the infrared spectrum is intense, the electrical asymmetry of the complexed nitrogen molecule is probably high. However, neither the electrical

asymmetry nor the reduction in bond order is sufficient to increase materially the reactivity of the nitrogen molecule in the complex and there is no evidence that it can be either hydrolysed or reduced in aqueous solution. Just as nitrogen reacts with the complex $[Ru(NH_3)_5H_2O]^{2+}$ to form the bridged compound, so the free end of the nitrogen molecule in $[Ru(NH_3)_5(N_2)]^{2+}$ reacts with the aqua-complex to form the bridged complex (7) (Reaction 8).

$$[Ru(NH_3)_5H_2O]^{2+} + [Ru(NH_3)_5(N_2)]^{2+} \longrightarrow$$
$$[\{Ru(NH_3)_5\}_2(N_2)]^{4+} \qquad 8$$
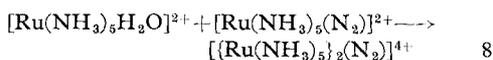
In this reaction the nitrogen complex has no greater affinity for the ruthenium of the aqua complex than has gaseous nitrogen itself (15). The nitrogen molecule is evidently symmetrically bonded in the dinuclear ruthenium complex because the intense N—N stretching band is missing from the infrared spectrum.

All of the nitrogen complexes lose their nitrogen as gas on oxidation by such reagents as ceric sulphate. Even hydrochloric acid liberates the nitrogen and oxidises the metal to a higher oxidation state, in most cases evolving hydrogen as well as nitrogen, but no ammonia (4). Only the mononitrogen complex of osmium has failed to give up its nitrogen on treatment with hydrochloric acid.

Since the nitrogen complexes of ruthenium, osmium, rhodium and iridium are known to contain ammonia or tertiary phosphines as ligands it might be thought that analogues of these complexes could be prepared and also homologues containing amines or other tertiary phosphines. However, this is true to only a very limited extent indeed. Even the minutest change in the ligands of the complex is usually sufficient to render it completely unstable. Thus the iridium complex $[IrCl(N_2)(PPh_3)_2]$ is very easily prepared, but the corresponding bromide is less easy and the iodide is too unstable to be obtained pure (16), as is the thiocyanate, although the azide has been obtained. Similarly, if one attempts to use other tertiary phosphines in place of triphenylphosphine the nitrogen complex is obtained, if at all, only as a very unstable and impure material. Its presence can be established, from the N_2 stretching band in the infrared spectrum of the crude product, but it decomposes on attempted isolation. This applies even when one attempts to make such close derivatives as the ethyldiphenylphosphine analogue. It is evident that some critical and perhaps rather extreme arrangement of energy levels is necessary in the metal atom before nitrogen can be held strongly, and the minutest change in the ligands often causes sufficient re-adjustment of the levels to render the nitrogen complex unstable. In our own work we have found evidence of other unstable nitrogen complexes of the platinum metals and rhenium, but these have been too unstable to isolate in a pure condition, although when the correct ligands are found one or two stable complexes should be isolable.

The structures of two nitrogen complexes have been determined by X-rays but neither is entirely satisfactory because of the difficulty in getting good crystals. The structure of $[Ru(NH_3)_5(N_2)]Cl_2$ is disordered and so exact bond distances could not be obtained, but it was shown that the complex is an octahedral one in which the Ru—N—N bond system is linear (17). The other structure is that of the cobalt complex $[CoH(N_2)(PPh_3)_3]$ (18). In this the molecule is essentially a trigonal bi-pyramid with the phosphine ligands in the three equivalent equatorial positions, the hydrogen on one apex and the nitrogen molecule on the other. The cobalt is out of the plane of the three phosphorus atoms, being displaced slightly towards the nitrogen molecule which is bonded end-on to the cobalt; the Co—N—N bond system is bent from linearity by 5°. In these complexes the N—N distances are slightly longer than in the nitrogen molecule and comparable with that in the aliphatic diazo-compounds. Indeed the nitrogen complexes may be regarded as inorganic diazo-compounds, and similarly their main reactions result in the liberation of nitrogen, rather than the incorporation of

Table II

Bond Distances in some Diazo-compounds

(Ångstrom Units)

Nitrous oxide	$O \overset{1.187}{-\!-} N \overset{1.129}{-\!-} N$
Hydrazoic acid	$HN \overset{1.240}{-\!-} N \overset{1.134}{-\!-} N$
Diazomethane	$H_2C \overset{1.32}{-\!-} N \overset{1.12}{-\!-} N$
$[Ru(NH_3)_5(N_2)]Cl_2$	$(NH_3)_5Ru \overset{2.11}{-\!-} N \overset{1.12}{-\!-} N$†
$[CoH(N_2)(PPh_3)_3]$	$(PPh_3)_3HCo \overset{1.80}{-\!-} N \overset{1.16}{-\!-} N$†
Nitrogen	$N \overset{1.098}{-\!-} N$

† Subject to rather high possible error (see text).

nitrogen into other molecules. Table II shows a comparison of bond lengths in a series of diazo-compounds and nitrogen complexes.

The structure of the dinuclear ruthenium-nitrogen complex has not yet been established. It may be written $[(NH_3)_5Ru-N=N-Ru(NH_2)_5]^{4+}$ which at first sight appears analogous to aromatic azo-compounds, for example azobenzene, Ph—N=N—Ph, but the ruthenium complex cannot be reduced to ammonia by sodium borohydride, sodium dithionite or other such reagents. It is evident, therefore, that the nitrogen, even in this complex, still retains the inactivity which is characteristic of gaseous nitrogen. It seems, therefore, that the complex should be represented as containing two ruthenium(II) atoms bridged by a neutral nitrogen molecule rather than two ruthenium(III) atoms bridged by the $[N=N]^{2-}$ ion, as would be required for formal analogy with azobenzene. The ruthenium(II) type structure would require a linear Ru—N≡N—Ru bond system whereas the ruthenium(III) would require a bent Ru—N≡N—Ru bond system capable of giving cis and trans isomers, analogous to cis and trans-azobenzene.

The nitrogen complexes of the transition metals are only just in process of being discovered. Their reactions have not been very thoroughly investigated. Undoubtedly more nitrogen complexes will be found, but many long series of analogues and homologues are never likely to be obtained. To the present no complexes have been obtained containing nitrogen which can be easily reduced to ammonia, but perhaps these may also be found. Also, to the present, there is no evidence of complexes containing nitrogen bonded sideways to the metal as dialkyl acetylenes are in their complexes. Such nitrogen complexes may be just possible, but they seem unlikely because the electrons in the π-bonding molecular orbital are so low in energy that the orbital can have little donor capacity. Such complexes, however, would be rather difficult to detect because the more symmetrical N≡N bond, which they would contain, would not give a strong band in the infrared spectrum. If they do exist they are not likely to be found until the taking of Raman spectra becomes as much a routine as taking infrared spectra is at present.

What is the significance of nitrogen complexes? Their preparation from gaseous nitrogen has shown that nitrogen can react readily at atmospheric temperature and pressure with reagents so mild that they attack neither water nor other protic solvents. They may eventually serve to point the way to the design of catalysts for reactions involving nitrogen under ambient physical conditions, and leading to useful products such as ammonia, and amines for the plastics industry.

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Maintaining Accurate Temperature Control

THE CARE OF PLATINUM THERMOCOUPLES

The use of carefully prepared thermocouples, the exercise of care and attention to details of installation, and the maintenance of calibration by frequent checking, all demand infinite patience, but are essential to the assurance of accurate and consistent furnace temperature control. That this is of primary importance in the semiconductor industry is emphasised in a paper by Ivan O. Nielson of Fairchild Semiconductor (*Solid State Technology*, 1968, **11**, (10), 29). A typical example of the diffusion process for introducing controlled impurities into silicon or germanium wafers requires a furnace operating at 1020°C±2°. Wider temperature variation produces variance in the beta characteristics of the devices.

The thermocouples used for control are platinum: 13 per cent rhodium-platinum in the form of wire 0.014 inch diameter to give quick response. The junction, formed by a butt weld, is little larger than the wire diameter. Before use each thermocouple is electrically annealed at about 1350°C for one hour to remove work hardness and volatile surface impurities. The thermocouple is insulated with double-bore refractory tubing and protected in the furnace with a quartz sheath. Leads are terminated with a crimp spade lug to ensure good mechanical connections.

Working-standard thermocouples are calibrated at known points of reference, and are used to calibrate the furnace thermocouples by comparison, using a heat-sink block in the calibration furnace and connecting the couples so as to give a difference reading. Working-standards are calibrated every four weeks and are used only for one week at a time.

Owing to the quicker deterioration of thermocouple e.m.f. at higher temperatures, the frequency of calibration varies according to the temperature being measured, ranging from every two weeks to every six months. Each diffusion furnace has a thermocouple that is used only in that furnace.

The temperature profile of each furnace is carefully checked before use. A period of 10 to 15 minutes is allowd to equalise the temperature at each point and for the system to become thermally stable. The furnaces are wound in three zones and thermocouple controls are so arranged that variations in the centre zone control the end zones. A diffusion furnace is only as good as the instrumentation system which controls it.

Advancements in technology, not only in the semiconductor field, demand higher productivity, and the accurate control of temperature is a means to this end. Particular care must, therefore, be given to frequent calibration of working thermocouples and measuring instruments, to constant checking of all connections in the system, and to allowing sufficient time for thermal sensing devices to reach stability.

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