Nitrosyl Complexes of the Platinum Metals

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In recent years much research has been carried out on platinum group metal complexes, especially those containing the carbonyl ligand. As the nitrosyl group is a nitrogen bonded ligand which in its normal mode of bonding is isoelectronic with carbon monoxide, the chemistry of complexes containing co-ordinated nitric oxide is interesting, and they may have similar potential uses to the carbonyl complexes. This article outlines our present knowledge of the nitrosyl complexes and their mode of bonding.

The nitric oxide molecule is unusual in that it has an odd number of electrons (namely 15), one of which is housed in an anti-bonding molecular orbital. It may lose this electron relatively easily to give NO^+, a species isoelectronic with molecular introgen as well as carbon monoxide. Simple nitrosonium salts such as $NO^+ClO^-_4$ are quite stable.

In the majority of nitrosyl complexes the ligand may be considered as NO^+ with the odd electron being transferred to the metal, thus decreasing its formal oxidation state by one. The nitrosonium ion co-ordinates to the metal by donation of an electron pair in an sp orbital of the nitrogen atom completing a bond in which three electrons are involved. This is a simplified picture of the bonding, for e.s.r. studies (1, 2) have indicated that the odd electron does spend a small amount of time on the nitrosyl ligand, and thus the true nature of the bonded ligand lies between neutral NO and NO^+ although very much

nearer the latter in most cases. The nitrosyl group is also a strong π-acceptor (stronger than CO) and the filled metal d orbitals will tend to overlap with the empty antibonding molecular orbital of the ligand to give the M-N bond a degree of multiple character. This is nicely demonstrated by a neutron diffraction study on $Na_2[Ru(NO)(OH)(NO_2)_4].2H_2O$ (3). The Ru-NO bond length of 1.748Å is much shorter than might be expected for single bonding as is shown in the same complex by the $Ru-NO_2$ bond which is 2.079Å in length. The $Ru-NO_2$ bond is very largely of single-bond character. All the platinum metal complexes are considered to be bonded in the NO^+ manner.

Nearly all nitrosyl complexes contain only one nitrosyl group and this is especially so for the platinum metals. The most likely explanation for this is that the π-acceptor ability of the ligand is so great that more than one group might remove an excessive amount of electron density from the metal. Simple binary compounds $M_x(NO)_y$, unlike the carbonyls, are unstable, the only reported one being prepared from $Ru_3(CO)_{12}$ with nitric oxide at 190°C and 320 atmospheres of pressure (4). There is considerable doubt as to the composition of the red crystals formed; they may be $Ru(NO)_4$ analogous to the iron nitrosyl, $[RuNO_5]_n$ or even a carbonyl nitrosyl. No definite carbonyl nitrosyl complexes have yet been prepared, which seems surprising considering the known compounds of nickel, iron and cobalt, and investigation into such compounds may well be rewarding. The only other compounds containing more than one nitrosyl group are the chloro-bridged species $Rh^{-1}(NO)_2X$ (X=Cl, Br, I),

the tetrahedral $Pd°(NO)_2Cl_2$ and also some nitrosyl phosphine complexes of iridium. The compounds $Rh^{-1}(NO)_2 X$ are prepared by the action of nitric oxide on the corresponding carbonyl halide $Rh(CO)_2X$ ($X=Cl$, Br, I) at 60°C (5, 6); they are black amorphous powders which are thought to be tetrameric. $Pd(NO)_2Cl_2$ is obtained by passing nitric oxide, laden with methanol vapour, over solid palladous chloride (7). It is unstable, evolving nitric oxide at high temperatures or in moist air. A sulphato complex $Pd(NO)_2SO_4$ is also known (7).

The mononitrosyl complexes will be considered metal by metal:

Ruthenium

Ruthenium nitrosyl complexes are more numerous than those of any other element (over one hundred are known). They are all octahedral with the Ru-NO group having a formal charge of $+3$. The metal-nitrogen bond is extremely difficult to break whether the complex is anionic, neutral or cationic, and reactions normally involve exchange of the other five ligands. The formation of the metal-nitrosyl bond is so favoured that reactions of ruthenium compounds with NO, NO_2^-, NO_3^- or HNO_3 almost always lead to its production. A very useful starting product for many other complexes is $Na_2[Ru\ NO(OH)(NO_2)_4]$ which is prepared from ruthenium trichloride and sodium nitrite in the presence of a small amount of hydrochloric acid (8). Treatment of these yellow crystals with the appropriate hydrohalic acid yields $[RuNOX_5]^{2-}$ ($X=Cl$, Br) and treatment of the latter with other ligands such as CN^- and NCS^- gives rise to further complexes of type $[RuNOL_5]^{2-}$ by ligand exchange. Reaction with ammonia gives hydroxy ammines $[Ru(NH_3)_4NO(OH)]X_2$ ($X=Cl$, Br, I); a pentammine may be prepared from either $[Ru^{II}(NH_3)_6]Cl_2$ or $[Ru^{III}(NH_3)_5Cl]Cl_2$ by reaction with sodium nitrite and hydrochloric acid. Nitrate complexes $[RuNO(NO_3)_y(OH)_{3-y}(H_2O)_2]$ ($y=$ 1, 2 or 3) are produced by the action of nitric acid on the nitrite complex. These species are particularly interesting as they are extremely soluble in organic solvents and have been used to remove ruthenium by solvent extraction. Trihalo complexes $[RuNOX_3]_n$ $.nH_2O$ are produced by evaporating RuO_4 with hydrochloric and nitric acids. A wide range of compounds of formulae $RuNOCl_3L_2$ (L=phosphines, arsines and stibines) may be prepared from $[RuNOCl_3]_n$ (9). Ruthenium (I) complexes $[RuNOX_2]_n$ ($X=Br$, I) can be made by the action of nitric oxide at 230°C on $[Ru(CO)_2X_2]_n$ (10).

Osmium

Osmium complexes are far less numerous than those of ruthenium, which is somewhat surprising as recent work in these laboratories has indicated that the Os-NO bond may be stronger than Ru-NO and more stable to certain types of reaction, especially reduction (11). A nitrite complex $K_2[OsNO(OH)(NO_2)_4]$ may be prepared by the prolonged action of potassium nitrite on K_2OsCl_6, and reaction of this with hydrohalic acids gives halides $[OsNOX_5]^{2-}$ ($X=Cl$, Br, I) (12). An intermediate in the chloro reaction $K_2[OsNO(NO_2)_2Cl_3]$ has recently been isolated in these laboratories (11). It seems likely that other osmium(II) nitrosyl compounds will be prepared, probably in a similar manner to the ruthenium analogues but using more extreme conditions to overcome the kinetic inertness to substitution of the third row transition metal complexes.

Rhodium

Very few compounds are known; the only reported ones are from the reaction of $[Rh(NO)_2Cl]_n$ and phosphine type ligands giving $[Rh\ NO\ L_3]$ and $[Rh\ NO\ L_2Cl_2]$ (13). It is believed that $[RhNOCN_5]^{3-}$ is formed in the reaction of $[Rh(NO)_2Cl]_n$ with alkali cyanides (14). No rhodium(III) complexes are known; the reaction of hydrochloric acid with the nitro complexes $[Rh(NO_2)_yX_{6-y}]^{3-}$ ($y=6$, 4, 2) yields only the hexachloro compound.

Iridium

The nitrosyl chemistry is again limited and the only simple complexes are the halides [Ir NOX$_5$]$^-$ (X=Cl, Br) which are prepared by the action of hydrohalic acid on the nitro complexes [Ir(NO$_2$)$_y$ X$_{6-y}$]$^{3-}$ (y=2, 3, 4 or 6) (11, 15). Although anionic, these complexes (especially the bromide) are soluble in organic solvents. Some interesting nitrosyl phosphines are also known and these contain iridium in formal oxidation states varying from II to −II (16). The action of nitric oxide on [Ir H$_3$(PPh$_3$)$_3$] ClO$_4$ gives [Ir^{-1}(NO)$_2$(PPh$_3$)$_2$] ClO$_4$. Subsequent reaction with lithium halides gives [Ir^{-1}(NO)$_2$(PPh$_3$)$_2$X] (X=Cl, Br, I), with bromine gives [Ir^{II}(NO)Br$_3$ (PPh$_3$)$_2$] and hydrohalic acids (Ir^I(NO) X$_2$(PPh$_3$)$_2$] (X=Cl, Br, I). Nitric oxide with [Ir H$_3$(PPh$_3$)$_2$] gives (Ir^{-II}(NO)$_2$PPh$_3$].

Palladium

Apart from Pd(NO)$_2$Cl$_2$ only a bridged polymer [PdNOCl]$_n$ and a mixed nitro-nitrato complex are known. The former is prepared by the action of nitric oxide on palladous chloride or by the interesting re-action between palladous chloride, sodium nitrite and an olefin, where the intermediate nitro complex reacts with the olefin, to produce a ketone (17).

$$[Pd (Cl) (NO_2) X_2]^{2-} + R\ CH{=}CH_2 \rightarrow$$
$$PdNOCl + 2X^- + RCOCH_3$$

(X=Cl or OH) (R=H or alkyl)
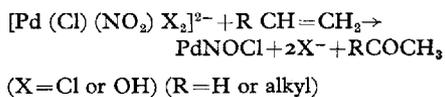
[PdNOCl]$_n$ reacts with ammonia and cyanide ion to lose the nitrosyl ligand and form complexes [Pd(CN)$_4$]$^{2-}$ and [Pd(NH$_3$)$_4$]$^{2+}$.

K$_2$[Pd(NO$_2$)$_4$(NO$_3$)NO] is formed by the action of nitric acid on K$_2$Pd^{II}(NO$_2$)$_4$ and is a red-brown air stable substance (18).

Platinum

Platinum forms a number of unstable octahedral complexes with the metal formally in the divalent state. Potassium chloroplatinite(II) reacts with nitrosyl chloride NOCl in chloroform on long shaking to give green crystals of K$_2$[PtNOCl$_5$] (18). A similar pentacyano compound has been made by ligand exchange. Other complexes containing ammine, nitro and nitrato ligands have been similarly prepared; [PtNO(NH$_3$)$_4$Cl]Cl$_2$ may be made from NOCl and [Pt(NH$_3$)$_4$]Cl$_2$, K$_2$[PtNO(NO$_2$)$_4$Cl] from NOCl and K$_2$[Pt(NO$_2$)$_4$] and K$_2$[Pt NO(NO$_2$)$_4$NO$_3$] from K$_2$Pt(NO$_2$)$_4$ and nitric acid (18). The general instability of these compounds is not surprising as they are the only known examples of six co-ordinate platinum (II).

For further reading the following excellent reviews are recommended:

Transition Metal Nitrosyl Complexes, B. F. G. Johnson and J. A. McCleverty. Progress in Inorganic Chemistry, Vol. 7 (Interscience, 1966)

Organometallic Nitrosyls, W. P. Griffith. Advances in Organometallic Chemistry, Vol. 7. Shortly to be published.

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