P.G. Sem-II
Sub - Inorganic chemistry
Paper — CC-VI
Unit — IV
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Dinitrogen Complexes :

Molecular nitrogen is isoelectronic with carbony and nitrosyl. Carbon monoxide and nitrosyl have many complexes with transition metals but dinitrogen have only few complexes, it is unable to act as a π acceptor.

Preparation :—

(1) ~~Pentaamine~~ Pentaammine dinitrogen ruthenium(II) is prepared by the direct reaction of nitrogen gas with pentaammine aqua ruthenium(II) complex.

$$[Ru(NH_3)_5H_2O]^{2+} + N_2 \rightarrow [Ru(NH_3)_5N_2]^{2+} + H_2O$$

$$[Mo(CO)_3(PCy_3)_2] + N_2 \xrightarrow{\text{at room temp}} [Mo(CO)_3(PCy)_3N_2]$$

$$2[Sm(C_5Me_5)_2] + N_2 \longrightarrow \cancel{[Sm(C_5Me_5)_2N_2Sm}$$

$$[Sm(C_5Me_5)_2N_2Sm(C_5Me_5)_2]$$

Properties :- Dinitrogen complexes are stable. Most dinitrogen complexes are rapidely oxidised by air and decomposed when heated.

The N_2 ligand of dinitrogen complexes are easily displaced by other ligands.

$$[Ir(PPh_3)_2Cl\,N_2] + PPh_3 \rightarrow [Ir(PPh_3)_3Cl] + N_2\uparrow$$

$$[Ir(PPh_3)_2Cl\,N_2] + PPh_3 \rightarrow [Ir(PPh_3)_2CO\,Cl] + N_2\uparrow$$

Metal ligand bonds in carbonyl and dinitrogen is similar but weaker in carbonyl complexes. The super π acceptibility of CO of carbonyl nitrogen complexes instable the complex, so the bond decomposes when warmed.

The unexpectly strong nucleophilicity of dinitrogen shown by its displacement of water from pentaammine aqua ruthenium(II) ion and formation of bridged dinitrogen complex.

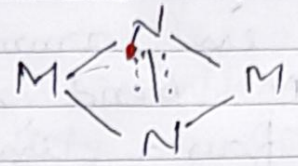
$$[Ru(NH_3)_5N_2]^{2+} + [Ru(NH_3)_5\text{-}H_2O]^{2+} \longrightarrow$$

$$[Ru(NH_3)_5\text{-}N_2\,Ru(NH_3)_5]^{4+} + H_2O.$$

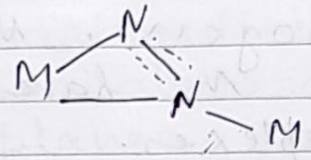
Structure and Bonding :-

There are two structure for terminal dinitrogen and two for bridged one.

Terminal dinitrogen ligand :

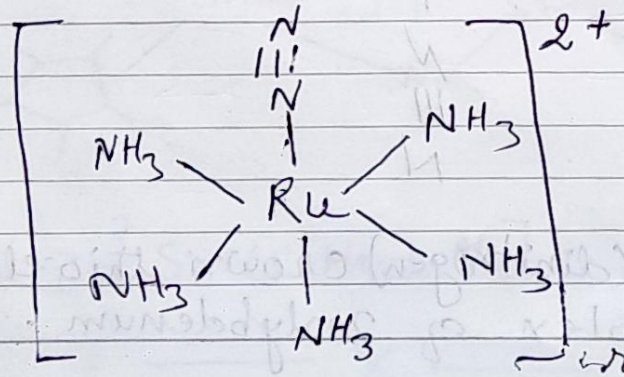
M – N ≡ N , 

end on terminal. side on terminal

M – N ≡ N – M 

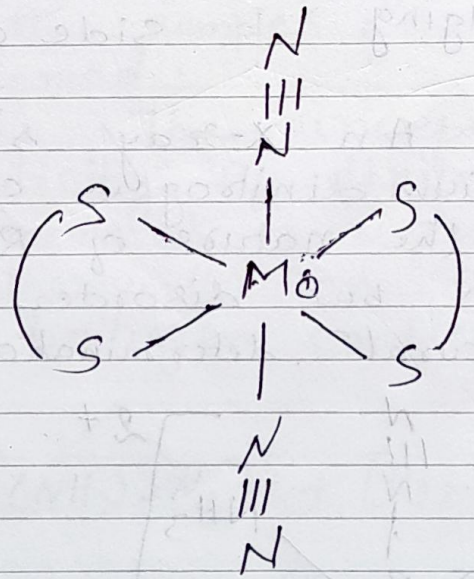
end on bridging side on bridging.

An X-ray study of the ruthenium dinitrogen complex indicate that the nature of Ru–N–N linkage was end on, but disorder in the crystal prevented accurate determination of bond length



Pentaammine dinitrogen ruthenium (II)

The result for complex bis(dinitrogen) crown thioether are typical and show that dinitrogen ligand resemble with carbonyl in its bonding to metal. Back donation of electron density from the metal into π antibonding orbitals is apparent from the short Mo-N bond, which is similar to Mo-CO bond, than to the Mo-NH_3 bond in ammine complexes. The mean N-N bond length is slightly greater that found in molecular nitrogen, which weaken the nitrogen-nitrogen triple bond from the donation of electron density into the π ~~bondi~~ antibonding orbitals of nitrogen. No examples of side on binding by N_2 have been confired in non-bridging complexes.

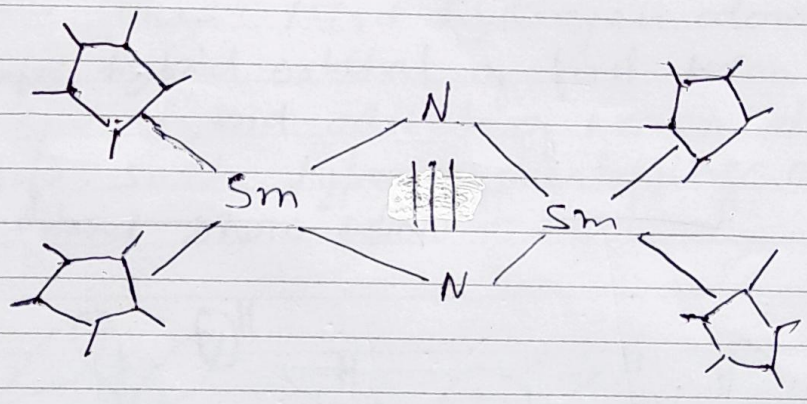


Bis(dinitrogen) crown thioether complex of molybdenum.

The Raman streching frequency of free di N_2 is 2331 cm^{-1}. After co-ordination this vibration becomes infrared active and shift to a lower frequency. Strong N-N streching bend appear at 2105 cm^{-1} for $[Ru(NH_3)_5N_2]Cl_2$ and at 1955 cm^{-1} and 1890 cm^{-1} for trans $[Mo(N_2)_2 Me_8[16]ane\ S_4]$.

The metal ligand bond in carbonyl and dinitrogen complexes are similar but weaker in dinitrogen complexes. The superior π-accepting ability of CO also account for the instability of carbonyl dinitrogen complexes.

When dinitrogen functions as a bridging ligand, it exhibits end-on co-ordination. In samarium dinitrogen complex, the two samarium atoms and two nitrogen atoms are planar. The Sm-N bond distance is shorter than that found in free nitrogen (N ≡ N).



$[Sm(C_5Me_5)_2N_2]$

— X —