SUBJECT- CHEMISTRY
CLASS - B.Sc (Hons) PART-III
PAPER - V
TOPIC - The ir spectra of nitrosyl Complexes

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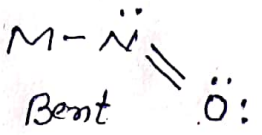
Q Discuss the ir spectra of nitrosyl Complexes.

Ans Nitrosyl (NO) ligand loses one extra electron which is present in π^* molecular orbital to form NO^+ ion By doing so, its bond order is increased from 2.5 to 3

$$N=O \xrightarrow[-e]{} [N\equiv O]^+$$

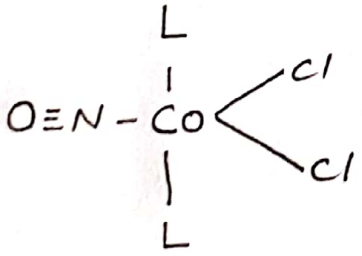
This is shown by the increase in N-O stretching frequency from 1878 cm^{-1} in free NO to 2200 - 2300 cm^{-1} in NO^+ i.e nitrosyl Compounds. in nitrosyl Complexes, N-O stretching frequency ranges from 1900 - 1500 cm^{-1}. X-ray data have shown the presence of linear and bent M-NO groups in such Complexes -

$N-N\equiv O$:
Linear

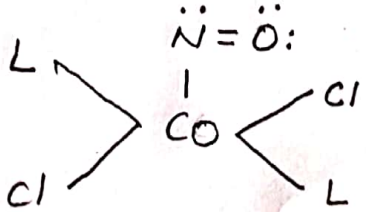


Bent

$CoCl_2(NO)L_2$ [where $L = P(CH_3)Ph_2$] exists in two isomeric forms-



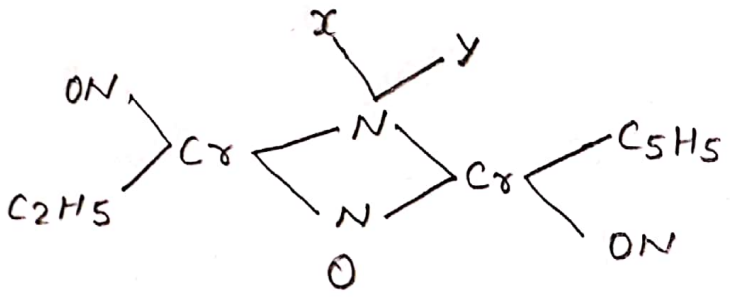
($\nu_{NO} = 1750 cm^{-1}$)



($\nu_{NO} = 1650 cm^{-1}$)

Although M-NO group is expected to show ν_{N-O}, ν_{M-N} and δ_{MNO}; only ν_{NO} is observed. The latter two modes are often Coupled since their frequencies are close to each other.

The ν_{NO} of bridging nitrosyl is much lower than that of the terminal nitrosyl group e.g $(C_5H_5)_2Cr_2(NO)_3(NXY)$ (X = OH and Y = t-Bu) shown below exhibits the terminal ν_{NO} at 1683 and 1625 cm^{-1} and the bridging ν_{NO} at 1499 cm^{-1}



$M_3(CO)_{10}(NO)_2$ where M = Ru & Os Contains double nitrosyl bridges. The ν_{NO} of these nitrosyl groups are very low : 1517 and 1500 cm^{-1} for Ru Compounds and 1503 and 1484 cm^{-1} for Os Compounds.