

Electron Donor & Acceptor Abilities of Thionitrosyl(NS) & Nitrosyl(NO) Ligands

K K PANDEY*, S R AHUJA & M GOYAL

Department of Chemistry, Devi Ahilya Vishwavidyalaya, Indore 452 001

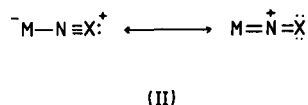
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The atomic charge and core binding energies of the complexes $[M(NX)Cl_5]^{2-}$, $[M(NX)Cl_4(H_2O)]^-$ and $M(NX)Cl_3(PPh_3)_2$ ($M = Ru, Os$; $X = O, S$) have been calculated. The electron donating property of NS ligand is found to be superior to that of NO ligand.

Synthesis and characterisation of transition metal thionitrosyl (NS) complexes have attracted much attention recently¹. In view of the resemblance between the ligands NS and NO, comparative studies on the coordinated thionitrosyl and nitrosyl ligands are of much interest. A number of studies have been made; however, the reported results have generated much controversy, specially those concerning the relative ratio of σ -donor to π -acceptor abilities of these ligands²⁻⁸. (a) A comparison of molecular orbitals^{3,4} of NS and NO indicates that 7σ -donor orbital of NS is ~ 3.8 eV higher in energy than 5σ donor orbital of NO. On the other hand 3π acceptor orbital of NS is ~ 1.1 eV lower in energy than the 2π acceptor orbital of NO. This suggests that $(\sigma\text{-donor}/\pi\text{-acceptor})_{NS} > (\sigma\text{-donor}/\pi\text{-acceptor})_{NO}$. (b) On the basis of IR spectra of $CpCr(CO)_2(NX)$ [$X = S$, ν_{CO} 2033 and 1962 cm^{-1} ; $X = O$, ν_{CO} 2028 and 1955 cm^{-1}], Greenhough *et al.*² have concluded that NS ligand is more effective in removing electron density from the metal centre than the NO ligand², that is, $(\sigma\text{-donor}/\pi\text{-acceptor})_{NS} < (\sigma\text{-donor}/\pi\text{-acceptor})_{NO}$. The spectra of the same complexes have been reported by Herberhold *et al.*⁵ also. The 1H NMR and ^{13}C NMR spectra of $CpCr(CO)_2(NX)$ indicate more deshielded proton and carbon resonances of carbonyl and cyclopentadienyl ring in thionitrosyl complex. This supports the increased $Cr \rightarrow CO$ and $Cr \rightarrow C_5H_5$ back-donation resulting from greater electron density on the metal in thionitrosyl complex and suggests that $(\sigma\text{-donor}/\pi\text{-acceptor})_{NS} > (\sigma\text{-donor}/\pi\text{-acceptor})_{NO}$. (c) On the basis of XPS studies of $CpCr(CO)_2(NX)$ complexes, Jolly *et al.*⁷ have stated that NS group must be stronger σ -donor and better π -acceptor than NO group. (d) The shortening of bond *trans* to NO^+ ligand and the lengthening of bond *trans* to NS^+ ligand have been observed⁶. (e) The reactions of NOX with metal thionitrosyl complexes having linear NS group result in the displacement of NS group by NO group while

the reverse is not true^{6,8}. In this note we wish to report the results of our studies which indicate superior electron donating ability of NS ligand than that of NO ligand; our study is based on a calculation of atomic charges and core binding energies of some thionitrosyl and nitrosyl complexes of ruthenium and osmium.

The atomic charges of the complexes $[M(NX)Cl_5]^{2-}$, $[M(NX)Cl_4(H_2O)]^-$ and $M(NX)Cl_3(PPh_3)_2$ ($M = Ru, Os$; $X = O, S$) were calculated by an electronegativity equalization procedure⁹. In free NX^+ , the nitrogen atom has formal charge zero and X atom has a formal positive charge (I).



In $M-NX$ the nitrogen atom has a formal positive charge and the X atom loses its formal positive charge in proportion to extent of back bonding (II),

The core binding energies (N_{1s} , O_{1s} and $S_{2p_{3/2}}$) were calculated by point charge potential model equation¹⁰ and the metal core binding energies ($E_{BM}(Ru\ 4d_{5/2}, Os\ 4f_{7/2})$) were calculated by the equation,

$$E_{BM} = M(O) + N + \sum_{\text{ligand}} \Delta M$$

where $M(O)$ is the bare metal binding energy¹¹, N is the metal oxidation state and the last term is the summation over all ligand group shifts. The important data are given in Table I.

A comparison of charges on metals in $M-NO$ and $M-NS$ complexes shows that the charge on the metal in $M-NS$ complexes is more negative than that in $M-NO$ complexes. The values of q_{ClM} (negative charge-transfer from chlorine to metal), q_{PM} (negative charge-transfer from phosphorus to metal) and q_{OM} (negative charge-transfer from oxygen to metal) are the same ($\Delta q = \pm 0.001$) for $M-NO$ and $M-NS$ complexes. This indicates that the difference in charges on the metals is due to difference in electron donor and acceptor abilities of NO and NS ligands. Slightly lower metal core binding energies on going from $M-NO$ to $M-NS$ are due to increase in electron density (increase in negative charge) on the metal. The more negative charge on the metal in $M-NS$ complexes suggests that

Table I—Atomic Charges and Core Binding Energies (eV) of the Complexes

Complexes	Atomic charges				Net charge on NO/NS	Core binding energies	
	Metal	N	O/S	Cl		Metal 3d _{5/2} or 4f _{7/2}	N _{1s}
Ru(NO)Cl ₃ (PPh ₃) ₂	-0.8078	0.4110	0.4150	-0.3386	0.8260	282.3	400.37
Ru(NS)Cl ₃ (PPh ₃) ₂	-0.8307	0.1466	0.7078	-0.3397	0.8544	282.1	393.08
[Ru(NO)Cl ₅] ²⁻	-1.0645	0.4014	0.4136	-0.3501	0.8150	283.7	399.96
[Ru(NS)Cl ₅] ²⁻	-1.0878	0.1375	0.7060	-0.3511	0.8435	283.5	392.68
[Ru(NO)Cl ₄ (H ₂ O)] ¹⁻	-0.8794	0.4082	0.4146	-0.3419	0.8228		400.26
[Ru(NS)Cl ₄ (H ₂ O)] ¹⁻	-0.9028	0.1441	0.7073	-0.3429	0.8513		392.97
[Os(NO)Cl ₅] ²⁻	-1.1198	0.4215	0.4166	-0.3437	0.8381	55.2	
[Os(NS)Cl ₅] ²⁻	-1.1297	0.1431	0.7071	-0.3441	0.8502	55.0	392.81
[Os(NO)Cl ₃ (PPh ₃) ₂]	-0.8492	0.4162	0.4158	-0.3316	0.8320	53.8	
[Os(NS)Cl ₃ (PPh ₃) ₂]	-0.8708	0.1504	0.7086	-0.3326	0.8590	53.6	393.18
[Os(NO)Cl ₄ (H ₂ O)] ¹⁻	-0.9202	0.4140	0.4155	-0.3348	0.8295		
[Os(NS)Cl ₄ (H ₂ O)] ¹⁻	-0.9438	0.1497	0.7084	-0.3358	0.8581		393.18

the NS ligand is better electron donor (not better electron remover from the metal atom) than NO ligand, i.e., NS ligand is more positive than NO ligand. The net charge on NS ligand is, in all the cases, approximately +0.03 electron charge greater than the net charges on the NO ligand. These observations support our spectral and X-ray studies⁶. The N_{1s} binding energy of NS ligand is lower than that of the NO ligand. The lowering of N_{1s} binding energy (approx. 7.3 eV) for the ruthenium thionitrosyl complexes is due to (a) lower electronegativity of sulphur compared to that of oxygen and (b) lower positive charge on the nitrogen atom in a coordinated NS group than that in a coordinated NO group (Table I).

On the basis of these data it can be concluded that NS ligand is a better electron donor than the NO ligand.

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