Inorganica Chimica Acta, 169 (1990) 207–210

Comparison of the Electronic Structures of Osmium–Thionitrosyl and Osmium–Nitrosyl Complexes

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(Received April 26, 1989; revised October 5, 1989)

Abstract

The electronic structure of the isoelectronic complexes $[Os(NX)Cl_5]^{2-}$ (X = S or O) and $[Os(NS)Cl_4(H_2O)]^{1-}$ has been investigated within a CNDO/2 formalism in order to investigate the nature and energetics of the interaction between osmium and isoelectronic NS and NO ligands. The computed trends for Os–N, NS and NO bond strengths in the complexes, as measured by Wiberg indices, charge distribution and orbital population suggest that the strength of the Os–NS bond is greater than that of the Os–NO bond and the NS ligand is a better electron remover from the central metal atom than the NO ligand. The strength of the Os–Cl bond *trans* to the NS ligand is weaker than the Os–Cl bond *trans* to the NO ligand. The calculations confirm the experimental observations that the chlorine atom positioned *trans* to a NS ligand is more labile and, hence, more susceptible to replacement.

Introduction

Considerable progress has been made recently in the synthesis and structural determination of transition metal thionitrosyl complexes [1–9]. A number of complexes has been structurally characterized [10–20], but little is known about their electronic structures [21, 22]. Owing to the isoelectronic nature of NS and NO, the comparative bonding properties of thionitrosyl and nitrosyl ligands is of special interest. The 7σ-donor orbital of NS is at higher energy than the 5σ-donor orbital of NO, while the $3\pi(\pi^*)$-acceptor orbital of NS is at lower energy than the $2\pi(\pi^*)$-acceptor orbital of oxygen [23]. There is a weaker P_π–P_π bonding for sulfur compared to oxygen. The above results lead one to expect that M–NS bonds should be stronger than M–NO bonds. In this paper we report the comparison of the electronic structures of $[Os(NX)Cl_5]^{2-}$ (X = S or O) and $[Os(NS)Cl_4(H_2O)]^{1-}$ complexes using CNDO/2 molecular orbital calculations. In this investigation, particular attention was focused on the nature of the *trans* effect and, hence, on the electronic composition of the molecules. This is obtained from the calculated electron densities and Wiberg bond indices.

Computational Details

Molecular orbital calculations were done using a CNDO/2-U method [24]. The orbitals 6s, 6p and 5d of osmium were included in the calculation. Wave functions for these orbitals were those given by Burns [25]. The wave functions used for S(3s and 3p), Cl(3s and 3p) and N(2s and 2p) were slater type orbitals. Atomic charges and overlap populations were obtained by Mulliken population analysis [26]. The coordinate system adopted for $[Os(NS)Cl_4L]^{n-}$ ($L = H_2O$, $n = 1$; $L = Cl$, $n = 2$) is given in Fig. 1.

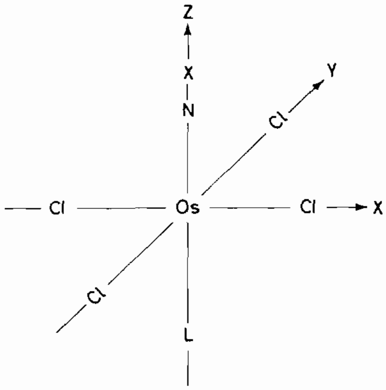

Fig. 1. Coordinate system for $[Os(NX)Cl_4L]^{n-}$; *z* axis is out of plane.

Interatomic distances were estimated on the basis of the X-ray structures of octahedral osmium thionitrosyl complexes $[Os(NS)Cl_3(PPh_3)_2]$ [12] and $[Os(NS)Cl_4(H_2O)]^-$ [13] and osmium nitrosyl complexes $[Os(NO)Cl_2(HgCl)(PPh_3)_2]$ [27] and $[Os(NO)Cl_3(SnCl_3)_2]$ [28]. In spite of the deviation from 180° reported for the Os–N–X angle, this was disregarded in the present calculations and C_{4v} symmetry maintained. The estimated distances

0020-1693/90/$3.50

in $[Os(NO)Cl_5]^{2-}$ are: Os–N = 1.734, N–O = 1.166, *trans*-Os–Cl = 2.364, *cis*-Os–Cl = 2.380 Å and in $[Os(NS)Cl_5]^{2-}$ are: Os–N = 1.779, N–S = 1.503, *trans*-Os–Cl = 2.399, *cis*-Os–Cl = 2.387 Å. Distances reported for $[Os(NS)Cl_4(H_2O)]^-$ [13] are used: Os–N = 1.731, N–S = 1.514, Os–Cl = 2.356, Os–O = 2.165, O–H = 0.95 Å. All computations were performed using the QCPE474 program [29], implemented on an ICIM-6000 computer.

Results and Discussion

Wiberg Indices

Bond strength results (as measured by Wiberg indices [30]) are summarized in Table 1. The values of the N–X Wiberg indices show the trend $[Os(NS)Cl_5]^{2-} < [Os(NS)Cl_4(H_2O)]^{1-} < [Os(NO)Cl_5]^{2-}$ which suggests that the Os–N π-backbonding is less for the osmium nitrosyl complex (the value of Os–N π-backbonding in $[Os(NS)Cl_5]^{2-}$ is 2.2755 as compared to 2.2416 in $[Os(NO)Cl_5]^{2-}$). The values of the Os–N Wiberg indices, which show the trend $[Os(NS)Cl_4(H_2O)]^{1-} > [Os(NS)Cl_5]^{2-} > [Os(NO)Cl_5]^{2-}$, confirm the above statement. Electron impact measurements at 70 eV for $[CpCr(CO)_2NX]$ (Cp = η^5-C_5H_5; X = O, S) also suggest that the thionitrosyl ligand is more tightly bound in $[CpCr(CO)_2(NS)]$ than is the nitrosyl ligand in $[CpCr(CO)_2(NO)]$ [31]. For $[Os(NX)Cl_5]^{2-}$ (X = S or O), the strength of the *trans*-Os–Cl bond is larger for the nitrosyl complex (W*trans*-Os–Cl = 0.9541) than the bond *trans* to the thionitrosyl complex (W*trans*-Os–Cl = 0.9186) and the *cis*-Os–Cl bond is stronger than the *trans*-Os–Cl bond in both the complexes. The calculations confirm the experimental observations that the chlorine atom positioned *trans* to a NS ligand is more labile and, hence, more susceptible to replacement than the chlorine atom positioned *trans* to a NO ligand.

Charge Distribution

Orbital charges and gross atomic charges are presented in Table 2. A comparison of charges on

TABLE 1. Bond strengths (Wiberg Indices) for $[Os(NX)Cl_5]^{2-}$ (X = S or O) and $[Os(NS)Cl_4(H_2O)]^{1-}$

Bond	$[Os(NS)Cl_5]^{2-}$	$[Os(NO)Cl_5]^{2-}$	$[Os(NS)Cl_4(H_2O)]^{1-}$
Os–N	2.2755	2.2416	2.3057
σ	0.7039	0.7193	0.7568
π	1.5716	1.5222	1.5489
N–X	1.0412	1.2618	1.0841
trans-Os–L	0.9186	0.9541	0.3098
cis-Os–Cl	0.9427	0.9607	0.9660

TABLE 2. Orbital charges and gross atomic charges for $[Os(NX)Cl_5]^{2-}$ (X = S or O) and $[Os(NS)Cl_4(H_2O)]^{1-}$

Complex	Orbital populations				Atomic charges
$[Os(NS)Cl_5]^{2-}$	Os		N		
	6s	0.8704	2s	1.1908	Os = −0.7033
	$6p_x$	0.8687	$2p_x$	1.2193	N = +0.0365
	$6p_y$	0.8687	$2p_y$	1.2193	S = −0.2923
	$6p_z$	0.8572	$2p_z$	1.3341	*cis*-Cl = −0.2060
	$5d_{z^2}$	0.6271			*trans*-Cl = −0.2165
	$5d_{xz}$	0.9971	S		
	$5d_{yz}$	0.9971			
	$5d_{x^2-y^2}$	0.6170	3s	1.6682	
	$5d_{xy}$	2.0000	$3p_x$	1.8020	
			$3p_y$	1.8020	
	cis-Cl		$3p_z$	1.0201	
	3s	1.5167	*trans*-Cl		
	$3p_x$	1.7908			
	$3p_y$	1.9565	3s	1.5272	
	$3p_z$	1.9420	$3p_x$	1.9311	

(continued)

TABLE 2. *(continued)*

Complex	Orbital populations				Atomic charges
$[Os(NS)(Cl)_4H_2O]^{1-}$	Os		$3p_y$	1.9311	
			$3p_z$	1.8271	
	6s	0.8656			Os = −0.7805
	$6p_x$	0.8679	N		N = +0.1031
	$6p_y$	0.8669			S = −0.1676
	$6p_z$	0.8462	2s	1.2055	*cis*-Cl = −0.1296
	$5d_{z^2}$	0.5592	$2p_x$	1.1569	*trans*-O = −0.0709
	$5d_{xz}$	1.0860	$2p_y$	1.1979	H = +0.2136
	$5d_{yz}$	1.0354	$2p_z$	1.3366	
	$5d_{x^2-y^2}$	0.6533			
	$5d_{xy}$	2.0000	S		
	cis-Cl		3s	1.6629	
			$3p_x$	1.7566	
	3s	1.4981	$3p_y$	1.7759	
	$3p_x$	1.7851	$3p_z$	0.9722	
	$3p_y$	1.9535			
	$3p_z$	1.8929	*trans*-O		
$[Os(NO)Cl_5]^{2-}$	Os		2s	1.3323	
			$2p_x$	1.2291	
	6s	0.8653	$2p_y$	1.9823	Os = −0.8524
	$6p_x$	0.8681	$2p_z$	1.5272	N = +0.1738
	$6p_y$	0.8681			O = −0.3485
	$6p_z$	0.8451	N		*cis*-Cl = −0.1964
	$5d_{z^2}$	0.5988			*trans*-Cl = −0.1876
	$5d_{xz}$	1.1093	2s	1.2954	
	$5d_{yz}$	1.1093	$2p_x$	1.1502	
	$5d_{x^2-y^2}$	0.5884	$2p_y$	1.1502	
	$5d_{xy}$	2.0000	$2p_z$	1.2304	
	cis-Cl		O		
	3s	1.5029	2s	1.6766	
	$3p_x$	1.7963	$2p_x$	1.7647	
	$3p_y$	1.9554	$2p_y$	1.7647	
	$3p_z$	1.9418	$2p_z$	1.1425	
			trans-Cl		
			3s	1.5013	
			$3p_x$	1.9297	
			$3p_y$	1.9297	
			$3p_z$	1.8269	

osmium in thionitrosyl and nitrosyl complexes shows that the charge on osmium in the nitrosyl complex is more negative than that in the thionitrosyl complex. The larger negative charge on the osmium in the nitrosyl complex suggests that the NO ligand is a poorer π-acceptor than the NS ligand. Photoelectron spectra of the core and valence electrons and molecular orbital calculations for $[CpCr(CO)_2(NX)]$ (X = S or O) also support the description of NS as a better π-acceptor [21, 32]. Both ^{95}Mo and ^{14}N NMR spectra have been measured for the purazoylborate thionitrosyl complexes and their nitrosyl analogues [33]. These studies revealed similar bonding features to those observed for osmium complexes.

For $[Os(NS)Cl_4(H_2O)]^{1-}$, upon substituting H_2O for Cl in the *trans* position, the charge on osmium decreases and those on NS increase. For $[Os(NO)Cl_5]^{2-}$, *cis*-Cl is a better electron acceptor from the central osmium atom than *trans*-Cl while the reverse is true for $[Os(NS)Cl_5]^{2-}$. For $[Os(NX)Cl_5]^{2-}$, the chloro ligand *trans* to a NS group is a better electron acceptor than the chloro ligand *trans* to a NO group.

Orbital Population

Upon substituting a NS ligand for a NO ligand in $[Os(NX)Cl_5]^{2-}$, there is an increase in the N $2P_\pi$ and X P_π populations and a decrease in the Os $5d_\pi$ population (Table 2). Similar changes have been observed upon substituting an aquo ligand for a chloro ligand in osmium–thionitrosyl complexes, $[Os(NS)Cl_4L]^{n-}$ ($L = H_2O$, $n = 1$; $L = Cl$, $n = 2$). For nitrogen, the lowest positive charge and larger $2P_\pi$ population in the $[Os(NS)Cl_5]^{2-}$ complex ion is indicative of greater π-backbonding in this complex.

The trans Effect

The *trans* effect in complexes containing NO or NS is usually discussed in terms of competition for σ- and π-electron density by groups *trans* to each other. A simple bonding model consistent with the observations discussed above, is that decreasing the strength of the σ-component and increasing the strength of π-component of a ligand increases the potential for bonding of the metal σ-orbital *trans* to it and shows shortening of the bond. On the other hand, increasing the strength of the σ-component and decreasing the strength of the π-component reduces the potential for bonding of the metal σ-orbital *trans* to it and shows lengthening of the bond. The shortening of the bond *trans* to the NO^+ ligand [for example: M—*trans*-L and M—*cis*-L bond distances (Å) in $Cs_2[Os(NO)F_5]\cdot H_2O$ [34] 1.947(5), 1.986(9)[a]; $Os(NO)(HgCl)Cl_2(PPh_3)_2$ [27] 2.37(2), 2.42(2); $(PPh_4)_2[Os(NO)Cl_3(SnCl_3)_2]$ [28] 2.364(4), 2.380(1)[a]] and lengthening of bond *trans* to NS^+ ligand [for example: M—*trans*-L and M—*cis*-L bond distances (Å) in $[Os(NS)Cl_3(PPh_3)_2]$ [12] 2.399(3), 2.387(3)[a]; $(PPh_4)[Os(NS)Cl_4(H_2O)]$ [13] 2.178(2), 2.0–2.1 (calculated from the covalent radius of Os(II) and O)[a], average of *cis* values] have been observed.

Acknowledgement

We are grateful for the support given by the University Grants Commission, New Delhi.

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