Review

The electronic structure and photochemistry of transition metal thionitrosyl complexes

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ABSTRACT

A review of the electronic structure of transition metal thionitrosyl complexes is given. The optical spectra and EPR spectra of the complexes are discussed along with the results of theoretical calculations of the electronic structure including geometry optimizations. The σ donor and π donor/acceptor properties of the NS ligand are compared with the isovalent NO ligand. The photochemistry of thionitrosyl complexes is presented. The reactivity of the photoreleased NS radical in solution is discussed.

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1. Introduction

Nitrogen sulfide NS is, unlike the isovalent compound NO, highly unstable in the free state due to the ready polymerization to $(NS)_x$ and it has accordingly only been studied in the gas phase at low pressure. Photolysis at $\lambda = 248$ nm of the "tetramer" N_4S_4 produces NS which has therefore been used as a source for NS [1,2]. Selected properties of NS are listed in Table 1 and for comparison NO is included. The values of the first ionization energy are similar whereas NS has a higher electron affinity. Few salts of the cation NS^+ have indeed been isolated [13], but no crystal structures have so far been reported. Dyke [4] has published the value $r_e = 1.440$ Å based on photoelectron spectroscopy. Salts containing the anion NS^- (isovalent with O_2) have not been isolated but a value $r_e = 1.589$ Å in the $X^3\Sigma^-$ ground state has been obtained from photoelectron spectra [6]. The values of the electric dipole moment differ significantly with NO being almost nonpolar and with NS having a high dipole moment with the negative charge residing on the nitrogen atom. Numerous calculations of the molecular properties

Table 1
Equilibrium internuclear distance (r_e), vibrational frequency (ω_e), first ionization energy (IE_1), electron affinity (E_{ea}), electric dipole moment (μ), dissociation energy (D_o), and enthalpy of formation ($\Delta_f H^\circ$) of NS and NO.

	NS	NO	Reference
r_e (Å))	1.494	1.1508	[3]
ω_e (cm^{-1})	1218.7	1904.2	[3]
IE_1 (eV)	8.87	9.26	[4,5]
E_{ea} (eV)	1.19	0.026	[6,7]
μ (D)	1.83	0.16	[8,9]
D_o (kJ mol^{-1})	468	626.8	[3,10]
$\Delta_f H^\circ$ (kJ mol^{-1})	283	90.3	[11,12]

of NS have been published during the years and it will be beyond the scope of the present article to review those. A few recent articles will, however, be mentioned in the following. Gao [14] calculated by ab initio methods the values $r_e = 1.498$ Å and $\omega_e = 1220.9$ cm^{-1} in excellent agreement with the experimental values in Table 1. In another ab initio study Zhu [15] obtained the values $r_e = 1.4962$ Å and $\omega_e = 1216.4$ cm^{-1}, also very close to the experimental values. Furthermore Zhu calculated the spin orbit coupling constant to 223.64 cm^{-1} which is very close to the experimental value of 223.37 cm^{-1} [16]. From the coupled cluster method Czernek [17] obtained the $E_{ea} = 1.13$ eV, and $IE_1 = 8.86$ eV in excellent agreement with the experimental values. The hyperfine coupling constants $A(^{14}N) = 6.2 \times 10^{-4}$ cm^{-1} and $A(^{33}S) = 1.8 \times 10^{-4}$ cm^{-1} were calculated by Boeré [18] by DFT methods. Finally Denis [19] calculated the value $\Delta_f H(298\,K) = 282$ kJ mol^{-1} by the coupled cluster method in good agreement with the experimental value.

The very reactive molecule NS can be stabilized by coordination to a metal centre M(NS)L$_n^z$. The first example of a thionitrosyl complex Mo(NS)(S$_2$CNR$_2$)$_3$ was reported by Chatt in 1974 [20]. Since then several thionitrosyl complexes have been isolated, mainly of the middle 4d and 5d transition metals. However, compared with the number of nitrosyl complexes M(NO)L$_n^z$ reported in the literature, thionitrosyl complexes are still scarce. The chemistry of NS has earlier been reviewed several times in the years 1982–1992 by Pandy, Roesky, Woollins, and Chivers [21–25] and recently by Døssing [26]. The main focus in those reviews has been on the syntheses and structures of the complexes.

From the fact that the electric dipole moment of NS being $\mu = 1.83$D with the negative charge located on the nitrogen atom is much higher than in NO (0.16D), it must be expected that the σ donor and/or π donor/acceptor properties of NS and NO molecules differ significantly. In this regard DFT calculations have been used in order to understand the electronic structure of thionitrosyl complexes with special emphasis on comparison with analogous nitrosyl complexes. Since 2009 the results of such calculations have been published for the metals Cr, V, Fe, Mn, Tc, Re, and Ir. This review will cover the results of these studies, and relevant results of earlier experimental EPR studies and photochemical studies of M(NS)L$_n^z$, will be discussed in the light of the new insight gained from such DFT calculations.

2. Electronic structure of transition metal thionitrosyl complexes

2.1. Chromium

2.1.1. Optical absorption spectra

In the discussion about the electronic structure of complexes including the Cr(NS)^z core it is relevant to mention the well-studied, analogous nitrosyl complexes of chromium, Cr(NO)^z. A useful tool in the description of the electronic structure of transition metal nitrosyl complexes is the Enemark–Feltham notation [27] in which the complexes can be designated {M(NO)}^{n}. Here n is the total
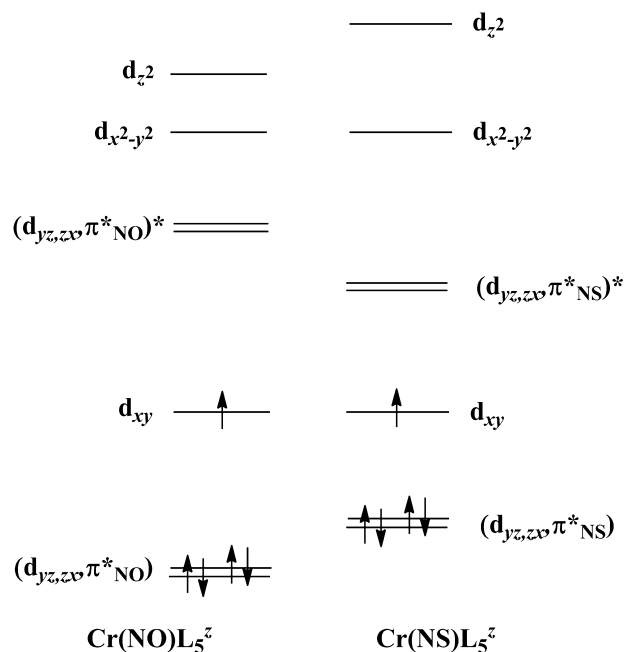

Fig. 1. Orbital splitting diagram for the $n = 5$ (Enemark–Feltham notation [27]) complexes Cr(NO)L$_5^z$ (proposed by Gray [29]) and Cr(NS)L$_5^z$.
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number of electrons in the metal d orbitals and the π^* orbitals of the NO ligand, or simply the number of d electrons if the nitrosyl ligand is regarded as a NO$^+$ ligand. This notation has proved useful in the prediction of the M—N—O bonding geometry (linear or bent). As an example, it can be shown from Walsh-diagrams that octahedral complexes contain a linear M—N—O core for $n \leq 6$. In accordance with this, nitrosyl complexes of chromium containing the Cr(NO)$^{2+}$ core ($n = 5$) indeed contains a linear Cr—N—O core. Another feature in the nitrosyl complexes is the oxidation state ambiguity. Complexes containing the Cr(NO)$^{2+}$ core might be described as Cr^I(NO$^+$) or Cr^{II}(NO) or Cr^{III}(NO$^-$). From magnetic measurements revealing a $S = \frac{1}{2}$ ground state it has often [28], and incorrectly, been concluded that the complexes are low-spin d^5 chromium(I) complexes. However, a $S = \frac{1}{2}$ ground state also occurs as a result of an antiferromagnetic coupling between a low-spin Cr^{II} ($S = 1$) and NO ($S = \frac{1}{2}$) and between a Cr^{III} ($S = 3/2$) and NO$^-$ ($S = 1$). Accordingly, the metal oxidation state in nitrosyl complexes cannot be found from magnetic measurements. Gray has earlier [29] proposed a qualitative molecular orbital splitting diagram for this type of nitrosyl complexes as shown in Fig. 1 (left). This splitting has been confirmed in later theoretical studies [30,31]. The unpaired electron resides in a metal d$_{xy}$ orbital and 4 electrons in the {d$_{yz,zx}$, π^*(NO)} orbitals. The chromium oxidation state cannot be assigned from this diagram either. It is the orbital parentage of the (d$_{yz,zx}$, π_{NO}^*) orbitals that determines the chromium oxidation state. If the orbitals have 50% d character, we have a d^3 system and thereby a chromium(III) complex. The oxidation state must therefore be determined through calculations of the electronic structure and/or various experimental methods. X-ray absorption near-edge structure spectra of a series of chromium nitrosyl complexes show that the oxidation state is +3 [32]. The UV–vis spectra of a series of complexes containing the Cr(NO)$^{2+}$ core are shown in Fig. 2 (top) [33]. A common feature in these spectra is an absorption band with an energy ($\sim$22,000 cm^{-1}) independent of the position of the other ligands in the spectrochemical series. At low temperature in the solid state this band displays a vibrational progression in some cases [29,34]. This has been assigned as a (d$_{yz,zx}$, π_{NO}^*) $\rightarrow$ (d$_{yz,zx}$, π_{NO}^*)* transition (see Fig. 1, left). The electronic transition takes place within the