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Theoretical insights into M–SO bonds in transition metal-sulfur monoxide complexes $[\{N(SPMe_2)_2\}_2M(SO)]$ (M = Fe, Ru, Os): Assessment of density functionals and dispersion interactions

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ABSTRACT

Geometry, electronic structure and bonding analysis of the sulfur monoxide complexes $[\{N(SPMe_2)_2\}_2M(SO)]$ (M = Fe, Ru, Os) have been investigated with the DFT, DFT-D3 and DFT-D3(BJ) methods using density functionals BP86, PW91, BLYP, PBE, revPBE, and TPSS. The BP86 and PBE optimized geometries of complex $[\{N(SPMe_2)_2\}_2Ru(SO)]$ are in good agreement with the reported experimental values. The Mayer and Gopinathan–Jug bond orders confirm the presence of M–SO and S–O multiple bond characters. Hirshfeld charge analysis shows transfer of electron density from metal fragments to antibonding π^* orbital of SO ligand. Significant noncovalent interactions between metal fragment and SO ligand are observed in the studied sulfur monoxide complexes. Noncovalent M---O and S---SO interactions have been justified by molecular orbital analysis. The M–SO bond dissociation energies vary in the order Fe < Ru < Os and depends on the choice of density functionals. The BP86/D3(BJ) dispersion corrections add 38% to the bond dissociation energy of Fe–SO bond, while only 22% and 17% to Ru–SO and Os–SO bonds, respectively. The π-bonding contributions to the total M–SO bonds are relatively smaller (22.6–27.0%) than the σ-bonding contribution.

1. Introduction

The chemistry of transition metal complexes with sulfur dioxide ligand has been known for decades [1–3]. The use of simple chemical methods to generate and study reactive molecules has attracted some attention, but relatively little attention has been paid to sulfur monoxide (SO) and disulfur monoxide complexes S_2O [3–5]. Sulfur monoxide is unstable and generally rapidly disproportionate to S_2O and SO_2 [6], but it is an important intermediate in sulfur oxide chemistry. The first example of a μ-SO complex, $[(\eta^5\text{-}C_5H_5)Mn(CO)_2\}_2(\mu\text{-}SO)]$ has been introduced by Höfler and Baitz [7]. Synthesis, structure and bonding of transition metal sulfur monoxide complexes have been explored [8–21]. Sulfur monoxide ligand shows mainly bridged-coordination to transition metals and can be prepared by oxidation of corresponding μ^2-S or μ^3-S complexes, for example, 2-electron-4-centre (*2e-4c*) bonding in $[Fe_3(CO)_9(\mu_3\text{-}SO)]$ [22], *2e-3c* bonding in or *4e-3c* bonding in several dinuclear transition-metal complexes [23,24]. In contrast to the bridged-SO complexes, little attention has been paid to the synthesis and characterization of the complexes with terminal sulfur monoxide. To the best of our knowledge, only three complexes with terminal sulfur-monoxide ligand have been characterized by X-ray crystallography (Chart 1). The first X-ray characterized terminal SO complex $[Ir(SO)Cl(P\textit{i}\text{-}Pr_3)_2]$ was reported by Schenk et al. [9]. Heyke et al. reported the ruthenium complex $[RuCl(NO)(SO)(PPh_3)_2]$ [15] while another example of a ruthenium complex containing a terminal SO ligand $[\{N(SP^iPr_2)_2\}_2Ru(SO)]$ has been reported by Leung et al. [16].

The bonding nature of the SO ligand has been investigated in limited quantum-chemical studies [10,25,26]. Extended Hückel calculations have been performed for the model complex $[Ir(SO)Cl(PH_3)_2]$ [10] which revealed that the upper valence orbital of free SO are largely similar in energy and size to those of CO. It has been suggested by CNDO/2 molecular orbital calculations for the complex $[Rh(SO)Cl(PH_3)_2]$ that the SO ligand acts as relatively a better σ donor and poorer π acceptor [25]. The optimized geometries and electronic structures of the iron sulfur monoxide complexes have been studied by Silaghi-Dumitrescu and coworkers [26]. However, detailed quantum chemical analysis of the transition metal-sulfur monoxide complexes in terms of their electronic structures,

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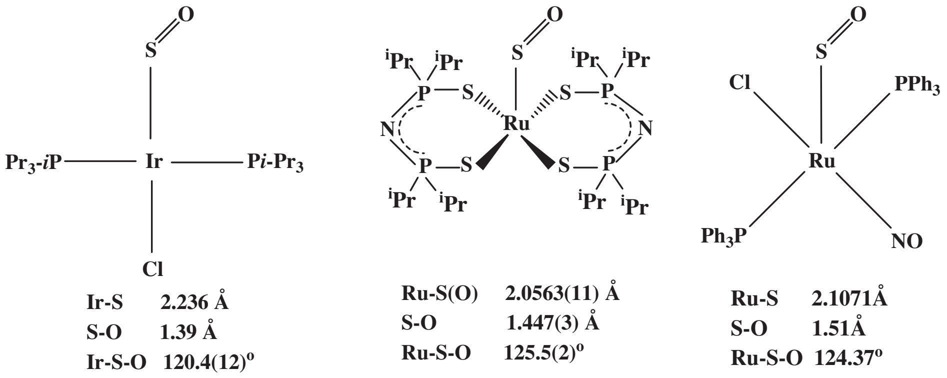

Chart 1. Experimentaly known terminal sulfur monoxide complexes of iridium and ruthenium.

molecular orbital analysis, bonding energy analysis of M–SO bond and impact of dispersion interactions on M–SO bonding have not been discussed till date.

During the last decade, there has been a considerable interest in the development of approximate density functional theory (DFT) methods, which couple the computational efficiency of DFT with an improved description of dispersion interactions [27–40]. Grimme et al. have developed efficient methods, DFT-D3 with zero-damping [41] and DFT-D3(BJ) [42] with Becke and Johnson (BJ) damping [43,44] for the computation of the dispersion interactions in molecules. Dispersion effects are important for an adequate description of noncovalent interactions and for obtaining accurate bonding energies [38,39].

To the best of our knowledge, a dispersion-corrected DFT study of transition metal sulfur monoxide complexes has not been investigated. In the present study, we report for the first time geometries and bonding energy analysis as well as the nature of M–SO bonds in metal complexes [{N(SPMe$_2$)$_2$}$_2$M(SO)] (**I**, M = Fe; **II**, M = Ru; **III**, M = Os) at the DFT, DFT-D3 and DFT-D3(BJ) methods using density functionals BP86, PW91, BLYP, PBE, revPBE and TPSS. The pivotal issues regarding this study are (i) to determine the optimized structure and to analyze the nature of M–SO bonding in the transition metal sulfur monoxide complexes, (ii) to investigate the degree of ionic and covalent characters of the M–SO bonds, (iii) to evaluate the contribution of the M–SO σ-bonding and M–SO π-bonding to the total M–SO bonding energies, (iv) to determine the non-covalent M---O and O---H interactions, and (v) to evaluate the contribution of London dispersion energy to the M–SO binding energies. All these factors are addressed as a function of density functionals. The chemical bonding in these complexes can be considered as shared electron bonding, which is schematically presented in Fig. 1. The interaction of triplet [SO] ligand to the four coordinate planar triplet transition metal fragments results the formation of covalent σ and π-bonds. Energy decomposition analysis is performed to evaluate the various energy contributions to the M–SO bonding.

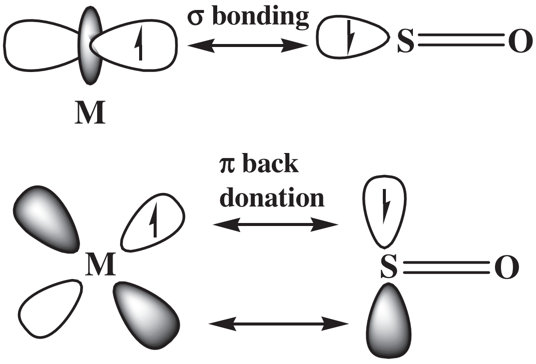

Fig. 1. Schematic representation of the orbital interaction between metal fragments [{N(SPMe$_2$)$_2$}$_2$M] and ligand fragment [SO].

2. Computational methods

Calculations on the sulfur monoxide complexes of the iron, ruthenium and osmium [{N(SPMe$_2$)$_2$}$_2$M(SO)] (**I–III**) have been carried out by DFT, DFT-D3 and DFT-D3(BJ) methods. Density functionals Becke-1988-Perdew-1986 (BP86) [45,46], Perdew–Wang 91 (PW91) [47], Becke–Lee–Yang–Peer (BLYP) [48], Predew, Burke, and Ernzerhof (PBE) [49], revPBE [50] and Tao–Perdew–Staroverov–Scuseria (TPSS) [51,52] were used for geometry optimization. Grimme's dispersion corrected DFT-D3 methods with zero damping and with BJ damping [43,44] were used to account for the dispersion interactions. All equilibrium geometries were optimized with C_s symmetry constraints. Uncontracted Slater-type orbitals (STOs) using triple-ζ basis sets augmented by two sets of polarization functions were employed for the self-consistent field (SCF) calculations [53]. Scalar relativistic effects have been considered using the ZORA formalism [54–57]. The (1s)^2 core electrons of carbon, nitrogen and oxygen, (1s2s2p)^{10} electrons of phosphorus, sulfur and iron, (1s2s2p3s3p3d)^{28} core electrons of ruthenium, (1s2s2p3s3p3d4s4p4d)^{46} core electrons of osmium were treated by the frozen-core approximation [58]. An auxiliary set of s, p, d, f and g STOs was used to fit the molecular densities and to present the Coulomb and exchange potentials accurately in each SCF cycle [57]. A numerical integration accuracy of INTEGRATION = 5 was used throughout. All open shell systems were treated with the unrestricted formalism without symmetry restriction. Frequency calculations were performed to determine whether the optimized structures were minima on the potential energy surface. The electronic structures of the complexes (**I–III**) were examined by Hirshfeld charges [59], Mayer bond order [60] and Gopinathan–Jug (G–J) bond order [61]. The calculations were performed utilizing the program package ADF-2013.01 [62]. The molecular orbitals were constructed using MOLDEN program [63].

The BP86 functional was used to perform the energy decomposition analysis (EDA). The bonding interactions between metal fragments [{N(SPMe$_2$)$_2$}$_2$M] and ligand fragment [SO] in their triplet states have been analyzed with C_s symmetry using the energy decomposition scheme of the program package ADF [64], which is based on the work of Morokuma [65] and Ziegler and Rauk [66,67]. It has been shown that the results of the energy decomposition analysis (EDA) give a quantitative insight into the nature of the metal–ligand interactions [68–71]. Details of the EDA method are given elsewhere [68–71].