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Five-electron donor bridging thionitrosyl groups in unsaturated binuclear manganese carbonyl derivatives

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ABSTRACT

Metal carbonyl thionitrosyls are potentially accessible by reactions of metal carbonyl anions and related nucleophiles with $N_3S_3Cl_3$ as illustrated by the reported synthesis of $(\eta^5\text{-}C_5H_5)Cr(NS)(CO)_2$ from $N_3S_3Cl_3$ and $NaCr(CO)_3(\eta^5\text{-}C_5H_5)$. Related manganese carbonyl thionitrosyls provide the opportunity to examine the behavior of the NS ligand in both mononuclear and binuclear systems that have a reasonable chance of experimental realization by related synthetic methods. In this connection the two low energy structures for $Mn_2(NS)_2(CO)_7$ are a doubly NS-bridged structure and an unbridged $(OC)_5Mn\text{–}Mn(NS)_2(CO)_2$ structure. A triply bridged $Mn_2(NS)_2(CO)_7$ structure analogous to the experimental triply bridged $Fe_2(CO)_9$ structure is not found at competitive energies. The lowest energy structures for the unsaturated $Mn_2(NS)_2(CO)_n$ ($n = 6, 5$) all have a five-electron donor bridging η^2-NS group, showing the propensity of a bridging NS group to bond to metals through both the nitrogen and sulfur atoms. The lowest energy $Mn_2(NS)_2(CO)_6$ structure of this type is a particularly attractive synthetic objective since it lies at least 15 kcal/mol below any other $Mn_2(NS)_2(CO)_6$ structures.

1. Introduction

Simple diatomic molecules have played an important role as ligands in the development of transition metal coordination chemistry. Initially the use of such ligands was restricted to stable species, such as CO [1], NO [2,3], CN^- [4–6], and N_2 [7,8], which represent various atom pairs chosen among the first row elements carbon, nitrogen, and oxygen. A major factor allowing the relatively simple synthesis of numerous metal complexes of ligands of this type is the stability of the free ligand, which allows it to be used as a reagent to synthesize metal complexes by reactions with suitable transition metal derivatives.

Other simple diatomic ligands are possible not corresponding to stable diatomic molecules. Typically such ligands contain either the first row elements boron and/or fluorine or the heavier chalcogens such as sulfur, selenium, or tellurium. The synthesis of metal complexes of such ligands requires indirect methods since the free ligand is not stable as a synthetic reagent. The ligand of this type that has been studied the most extensively is the thiocarbonyl ligand, CS [9]. Since free CS is not a stable species, the synthesis of metal thiocarbonyl complexes requires indirect methods using reagents such as CS_2 and $S{=}CCl_2$ as sources of thiocarbonyl groups. Other diatomic ligands which are not stable in the free state but which have been recently realized in stable transition metal complexes include the BF ligand [10] in $[(\eta^5\text{-}C_5H_5)Ru(CO)_2]_2(BF)$, the BO ligand [11] in $(R_3P)_2Pt(BO)Cl$, and the CF ligand [12] in $(\eta^5\text{-}C_5H_5)Mo(CO)_2(CF)$. The difficulties in synthesizing extensive series of metal complexes of diatomic molecules unstable in the free state make theoretical studies of such complexes particularly valuable in predicting the structures and energetics of the most promising synthetic targets.

The extensive series of metal carbonyls and nitrosyls of various types as well as the variety of metal thiocarbonyl complexes [9] that are now known make metal complexes of thionitrosyl (NS) ligands of interest. Starting more than a half century ago, reactions of S_4N_4 with suitable metal derivatives were found to give numerous metal complexes of general stoichiometry $M(NS)_n$ including the homoleptic $M(N_4S_4)$ derivatives (M = Ni, Co, Pd, Pt). For example, the reaction of $Fe(CO)_5$ with S_4N_4 was reported [13] to give a species of stoichiometry $Fe(CO)(N_4S_4)$. Initially these complexes were assumed to be metal thionitrosyl derivatives containing the NS ligand. However, subsequent experiments proved that these complexes derived from the reactions of N_4S_4 with metal derivatives were not true metal thionitrosyls containing the monomeric NS ligand [14]. The compound $H_2N_2S_2$, a product of reactions of N_4S_4, was also considered as reagent for the synthesis of metal thionitrosyl complexes, and a series of inner complex salts of metals of the eighth subgroup were obtained. However, the Zerevitinov method [15] unambiguously showed that such compounds contain

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one hydrogen atom for each pair of NS units [14,16]. Thus the nitrogen-sulfur ligands in these complexes are the bidentate carbon-free monoanionic chelate ligands HN_2S_2 so that the $M(NS)_4$ derivatives mentioned above are really $M(HN_2S_2)_2$ derivatives with the central metal atom in the +2 formal oxidation state (Fig. 1).

The synthesis of true metal thionitrosyls is complicated by the instability of free NS in contrast to the very stable NO. Free NS is obtained in the gas phase at low pressures by reaction of atomic nitrogen with suitable sulfur derivatives such as SCl_2 [17]. Although NS is stable enough in the dilute gas phase to be found in comets and interstellar media, free NS readily polymerizes in condensed phases. An important difference between the NS and NO molecules is the much higher electric dipole moment of NS (μ = 1.83 D) [18] relative to NO (μ = 0.16 D) [19] with the negative charge in NS residing on the nitrogen atom. This suggests that the coordination chemistry of the NS group might be significantly different from that of the NO group.

The first transition metal complexes of the monomeric NS ligand were the molybdenum dithiocarbamate derivatives $Mo(NS)(S_2CNR_2)_3$, synthesized by Chatt and Dilworth in 1974 [20]. The first true transition metal carbonyl derivative of a monomeric NS ligand was the cyclopentadienylchromium derivative $(\eta^5\text{-}C_5H_5)Cr(CO)_2(NS)$, shown by X-ray crystallography to contain an NS ligand coordinated essentially linearly to the chromium through the nitrogen atom.[21,22] Octahedral chromium $[Cr(NS)L_5]^{2+}$ complexes (L = H_2O, CH_3CN, MeHNCHO, Me_2SO, etc.) were subsequently synthesized [23,24]. Other well-characterized metal thionitrosyls are rather limited in number and contain mainly the middle second and third row transition metals [25].

The successful synthesis of the first metal carbonyl thionitrosyl $(\eta^5\text{-}C_5H_5)Cr(CO)_2(NS)$ used the reaction of $NaCr(CO)_3(\eta^5\text{-}C_5H_5)$ with $S_3N_3Cl_3$ [21,22]. This reaction appears to involve dissociation of $S_3N_3Cl_3$ into monomeric NSCl [26] followed by nucleophilic substitution of the chlorine in NSCl with the $(\eta^5\text{-}C_5H_5)Cr(CO)_3^-$ anion. Related reactions of $S_3N_3X_3$ derivatives with metal carbonyl anions and related nucleophiles provide potential routes to similar metal carbonyl thionitrosyl derivatives.

Binuclear metal carbonyl thionitrosyls are of interest in connection with the exploration of possible ways for a thionitrosyl group to bridge a pair of metal atoms. In this connection the manganese carbonyl thionitrosyl systems $Mn(NS)(CO)_n$ (n = 4, 3) and $Mn_2(NS)_2(CO)_n$ (n = 7, 6, 5) derivatives were chosen for our initial theoretical exploration of metal thionitrosyls since the analogous monomeric nitrosyl $Mn(NO)(CO)_4$ has been synthesized [27] and structurally characterized by low-temperature X-ray crystallography [28]. In addition the binuclear derivative $Mn_2(NS)_2(CO)_7$ is isoelectronic with the known [29–31] $Fe_2(CO)_9$ and provides a chance to explore possible behavior of the thionitrosyl group in binuclear metal carbonyl derivatives that are potentially accessible experimentally. Related manganese carbonyl nitrosyls, including binuclear derivatives $Mn_2(NO)_2(CO)_n$ (n = 7, 6, 5), have been studied theoretically using similar methods [32].

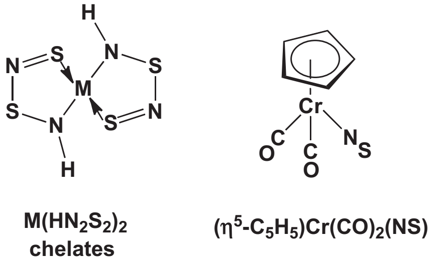

Fig. 1. (a) The $M(HN_2S_2)_2$ chelates, believed at one time to be $M(NS)_4$ derivatives; (b) The known [21,22] organometallic thionitrosyl $(\eta^5\text{-}C_5H_5)Cr(CO)_2(NS)$.

2. Theoretical methods

Electron correlation effects were considered using density functional theory (DFT) methods, which have evolved as a practical and effective computational tool, especially for organometallic compounds [33–39]. Two DFT methods were used in this study. The first functional is the B3LYP method, which is the hybrid HF/DFT method incorporating Becke's three-parameter exchange functional (B3) with the Lee, Yang, and Parr (LYP) correlation functional [40,41]. Another DFT method used in this paper is BP86, which combines Becke's 1988 exchange functional (B) with Perdew's 1986 gradient corrected correlation functional method (P86) [42,43]. It has been noted elsewhere [44–46] that the BP86 method may be somewhat more reliable than B3LYP for the type of organometallic systems considered in this paper.

The basis sets are similar to those used in our previous studies. The DZP basis sets used for carbon, nitrogen, oxygen, and sulfur add one set of pure spherical harmonic d functions with orbital exponents $\alpha_d(C)$ = 0.75, $\alpha_d(N)$ = 0.80, $\alpha_d(O)$ = 0.85, and $\alpha_d(S)$ = 0.70 to the standard Huzinaga–Dunning-Hay contracted DZ sets [47,48]. Therefore, the DZP basis sets for C, N, and O atoms are designated as (9s5p1d/4s2p1d), and that for the S atoms is designated as (12s8p1d/6s4p1d). For Mn, in our loosely contracted DZP basis set, the Wachters' primitive set [49] is used, but augmented by two sets of p functions and one set of d functions, contracted following Hood, Pitzer and Schaefer [50], and designated (14s11p6d/10s8p3d). For $Mn(NS)(CO)_4$ and $Mn(NS)(CO)_3$, there are 207 and 177 contracted Gaussian basis functions. For the binuclear manganese carbonyl thionitrosyls $Mn_2(NS)_2(CO)_7$, $Mn_2(NS)_2(CO)_6$, $Mn_2(NS)_2(CO)_5$, there are 384, 354, and 324 contracted Gaussian basis functions, respectively.

The geometries of all structures were fully optimized using the two DFT methods independently. The harmonic vibrational frequencies were determined by evaluating analytically the second derivatives of the energy with respect to the nuclear coordinates. The corresponding infrared intensities were also evaluated analytically. All of the computations were carried out with the GAUSSIAN 03 program [51], exercising the fine grid option (75 radial shells, 302 angular points) for evaluating integrals numerically [52], while the tight designation is the default for the self-consistent field (SCF) convergence.

In the search for minima using all currently implemented DFT methods, low magnitude imaginary vibrational frequencies are suspect because of significant limitations in the numerical integration procedures used in the DFT computations. Thus all imaginary vibrational frequencies with a magnitude less than $50i\ cm^{-1}$ are considered questionable and are given less weight in the analysis [52,53]. Therefore, we do not always follow such low imaginary vibrational frequencies.

The optimized structures and the relative energies are shown in Figs. 2–6. A given $Mn_a(NS)_a(CO)_b$ structure is designated as **abS-c** or **abT-c**, where **a** is the number of manganese atoms (the same as the number of NS groups); **b** is the number of CO groups; **S** or **T** refers to the spin multiplicity of the molecule as singlet or triplet, respectively; and **c** orders the structures according to their relative energies for a given spin state. Thus the lowest energy structure of singlet $Mn_2(NS)_2(CO)_7$ is designated **27S-1**.

3. Results

3.1. Binuclear derivatives

3.1.1. $Mn_2(NS)_2(CO)_7$

Five optimized $Mn_2(NS)_2(CO)_7$ structures were found (Fig. 2). The three low-lying $Mn_2(NS)_2(CO)_7$ structures **27S-1**, **27S-2**, and