

# SUBSTITUTED-NITRATOXYCARBON COMPLEXES OF SILVER(I): A DENSITY FUNCTIONAL COMPUTATIONAL INVESTIGATION

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## Abstract

Hydrogen, fluorine, chlorine, and methyl derivatives of the nitratocarbon group  $[\text{:N}(\text{-O-})_3\text{C-X}]$ ,  $\text{X} = \text{H, F, Cl, CH}_3$  were investigated as ligands for the silver(I) cation. This study was carried out to ascertain whether the complexation of the nitratocarbon group to a metal center would stabilize the group with respect to decomposition or rearrangement. While the energy of rearrangement for the nitratocarbon group as a ligand bound to silver(I) was somewhat lower than was found computationally for the group as a substituent on an organic alkane, the ligands are still predicted to rearrange highly exothermically to the nitrosoformate structure. Both the nitratocarbon and nitrosoformate systems were found to act as ligands to the silver(I) cation in much the same way that the ammonia molecule bonds to the silver(I) cation. The hydrogen- and methyl-substituents appear to lend slightly more stability to the ligand than do the fluoro- and chloro-substituents, indicating that classical electron donor groups may be preferred for stabilizing the nitratocarbon group as a ligand on a metal center.

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Keywords: Nitratocarbon, Density functional,  $\omega\text{B97X-D}$ , Silver(I) complexes, Ligand rearrangement, Ligand stabilization through metal complexation

## Introduction

The nitratocarbon (or the nitrate-*O,O,O*-carbon) group,  $[\text{:N}(\text{-O-})_3\text{C-}]$ , was initially investigated computationally and determined to produce “high-energy” organic materials with the formula  $\text{C}_n(\text{CO}_3\text{N})_{2n+2}$ .<sup>1</sup> However, the nitratocarbon moiety was also predicted to readily rearrange highly exothermically to nitrate-*O*-carbon-, nitrate-*O,O*-carbon-, or nitrocarbonyl-containing species when  $n=0$ . When  $n=1$  or 2, only decomposition to nitrocarbonyl-containing species was possible, but the rearrangements were still highly exothermic. More recently, the tetra-substituted tetrakis(nitratocarbon)methane was theoretically investigated as a potential explosive<sup>2</sup> and other molecules containing the nitratocarbon group, such as nitratocarbon derivatives of tetrahedrane,<sup>3</sup> have been computationally investigated. Further, the decomposition of the simplest model compound containing the nitratocarbon moiety,  $\text{HCO}_3\text{N}$ , has also been investigated computationally.<sup>2</sup>

The difference in energy between a nitratocarbon group and a nitrocarbonyl group bound to a carbon atom, based on previous calculations,<sup>1</sup> is estimated to be between 515 kJ/mol and 525 kJ/mol at the Hartree-Fock RHF/6-31G\* level of theory and between 457 kJ/mol and 465 kJ/mol at the density functional B3LYP/6-31G\* level of theory. Such extraordinarily large exothermic energy differences lent credence to the conclusion that the nitratocarbon group would be an exceedingly difficult synthetic target to achieve. However, the potential for the stabilization of the nitratocarbon group through complexation a metal center through the nitrogen atom in the group was advanced.<sup>1</sup> A canonical drawing of the nitratocarbon group places a lone pair of electrons on the nitrogen moiety, and these electrons could be involved in bonding to a metal center. Other examples of the stabilization of reactive ligands through metal complexation, although only tenuously-related to the nitratocarbon group, do

exist, such as cyclobutadiene complexed to an iron center<sup>4</sup> and carbon monosulfide complexed to a metal carbonyl complex.<sup>5</sup>

To investigate the potential for the stabilization of a nitratocarbon group through complexation to a metal center, the silver(I) cation was chosen. This cation is known to form strong (simple, linear) complexes with amines and ammonia. Because the substituted-nitratocarbon group may be considered as an oxygen-substituted amine, the silver(I) cation was hypothesized to also be able to form strong complexes with the substituted-nitratocarbon and -nitrocarbonyl groups, each bonding to silver through the nitrogen atom.

Herein are reported the density functional computational results for the gas-phase structures and properties of the complexes of substituted-nitratocarbon and -nitrocarbonyl groups with the silver(I) cation and, for comparison, for the ammonia complexes of silver(I) as well, in the gas phase. The eight parent ligands,  $:\text{N}(\text{-O-})_3\text{CX}$  and  $:\text{N}(\text{=O})\text{-OCX}(\text{=O})$ ,  $\text{X}=\text{H, F, Cl, CH}_3$ , were also investigated to establish the structures of these ligands before complexation to silver(I). These molecules were then investigated as ligands to silver(I) to delineate both complexation properties and the effect of electron-donating and -withdrawing groups on the these systems.

## Computational methods

The structures and properties of all cationic species were determined in the gas phase at the  $\omega\text{B97X-D}/6\text{-311++G}^{**}$  (for all atoms except silver)<sup>4</sup> and the  $\omega\text{B97X-D}/\text{def2-TZVP}$  (for the silver atom)<sup>5</sup> levels of density functional theory using the *Spartan '18* program package.<sup>6</sup> The density functional method was chosen due to the enhanced performance of  $\omega\text{B97X-D}$  for the calculation of the properties and geometries of species containing transition metals.<sup>7</sup> Multiple initial trial geometries were employed to confirm minima on the potential energy surfaces and the structures and

properties of the species were calculated without the imposition of any symmetry constraints. Vibrational frequencies were calculated for all species to ensure that the structure corresponded to a local energy minimum with no imaginary vibrations. When cationic species exhibited multiple conformational minima, only the most stable minimum structure has been reported herein.

## Results and Discussion

The DFT-calculated structures and properties of the neutral substituted-nitratocarbon and -nitrosoformate free ligands are listed in Table 1; the molecules are illustrated in Figure 1. As was

**Table 1.** Selected electronic and structural properties of the substituted-nitratocarbon and -nitrosoformate free ligands

Ligand	Electronic energy (a.u.)	Energy difference (kJ/mol)	Bond distances (pm)				N=O	C=O
			N-O	O-C	C-X <sup>a</sup>			
:NO <sub>2</sub> CH	-318.843869	448.93	147.9	141.8	108.8 <sup>H</sup>			
:N(O)OCHO	-319.014860	—	147.0	136.6	110.0 <sup>H</sup>	114.8	118.6	
:NO <sub>2</sub> CF	-418.096060	461.34	148.0	140.8	128.7 <sup>F</sup>			
:N(O)OCFO	-418.271777	—	158.2	132.8	133.2 <sup>F</sup>	112.8	118.0	
:NO <sub>2</sub> CCl	-778.450340	466.62	147.7	141.6	170.8 <sup>Cl</sup>			
:N(O)OCClO	-778.628068	—	159.8	132.7	177.1 <sup>Cl</sup>	112.6	118.2	
:NO <sub>2</sub> CCH <sub>3</sub>	-358.175612	430.58	147.3	142.9	147.8 <sup>CH<sub>3</sub></sup>			
:N(O)OC(CH <sub>3</sub> )O	-358.339611	—	148.3	137.8	150.1 <sup>CH<sub>3</sub></sup>	114.9	119.2	

<sup>a</sup> Superscript identifies the substituent "X".

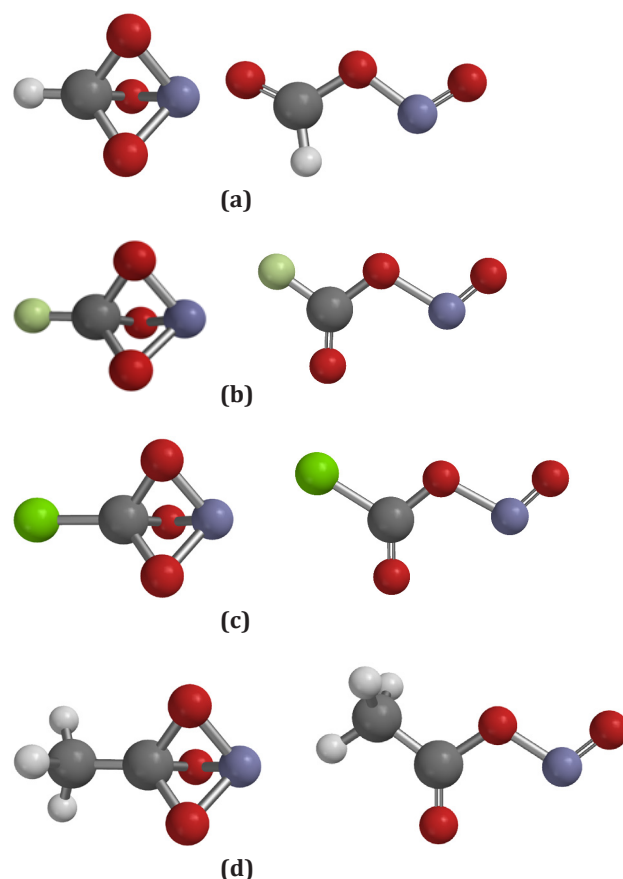
observed previously,<sup>1</sup> the substituted-nitratocarbon isomers are much less stable than the substituted-nitrosoformate isomers. For these free ligands, the energy differences are about 430 kJ/mol or more, in line with the energy differences noted previously.<sup>1</sup> Interestingly, the ligands with the electron-withdrawing fluoro- and chloro-substituents exhibit the highest energy difference, perhaps indicating that electron-donating groups might better stabilize the nitratocarbon moiety.

Structurally, the substituted-nitratocarbon systems are extremely similar, most likely due to the highly strained and constrained trigonal bipyramidal arrangement of the five-atom core. On the other hand, the substituted-nitrosoformate molecules, while also very similar in structure, differ in the arrangement about the carbonyl carbon atom when the substituent is hydrogen: The hydrogen substituent is in a *syn*-orientation with respect to the nitrogen atom, while the fluorine, chlorine, and methyl substituents are in an *anti*-orientation, in the lowest energy conformations. (For all of the substituted-nitrosoformate molecules, multiple initial trial geometries were used to investigate the energies of the conformations; only the lowest energy conformations have been reported herein.)

The reasons for the difference in orientation for the hydrogen-substituted nitrosoformate from that of the fluoro-, chloro-, and methyl-substituted molecules may not be straightforward. Some steric factors may be involved, as indicated by the hydrogen atom being bent toward the nitrogen atom in nitrosoformate, while the methyl-substituted nitrosoformate has the larger methyl group rotated away from the nitrogen atom, with no distortion of the carbonyl oxygen atom toward the nitrogen atom. (The N...H distance is 233.1 pm in nitrosoformate, while the N...O=C

distances range from 266.8 pm in the methyl compound to 272.3 pm in the fluoro compound. Electronic factors may also play a role, in that the electronegative fluorine atom is rotated away from the nitrogen atom; the same is true for chlorine, but the chlorine atom is larger than fluorine and steric factors may play a role as well.

The structure of the diamminesilver(I) complex, [H<sub>3</sub>N-Ag-NH<sub>3</sub>]<sup>+</sup>, as a salt in the solid state, has been determined in combination with a number of different anions. Among these reports, as early as 1934 the Ag-N distances for the sulfate tetrammoniate



**Figure 1.** The structures of the neutral free ligands in the gas phase: (a) nitratocarbon-O-O-O-methane and nitrosoformate, (b) nitratocarbon-O-O-O-fluoromethane and nitrosofluoroformate, (c) nitratocarbon-O-O-O-chloromethane and nitrosochloroformate, and (d) nitratocarbon-O-O-O-ethane and nitrosomethylformate. Large, dark-gray spheres represent carbon; small, light-gray spheres, hydrogen; blue spheres, nitrogen; red spheres, oxygen; pale-green spheres, fluorine, and green spheres, chlorine.

salt were determined to be 190 pm (with emphasis reported by the authors of the low accuracy of the determination),<sup>8</sup> while, as the dinitroargentate salt in 1977, the Ag-N distances were found to be 211.2(6) and 211.7(6) pm.<sup>9</sup> Later, the nitrate salt was shown to exhibit Ag-N distances of 212(1) pm,<sup>10</sup> and a re-determination of the crystal structure of the sulfate provided Ag-N distances of 211.0(3) pm.<sup>11</sup> While these distances are all from solid-state investigations, the calculated gas-phase distances of 216.9 pm (Table 2) for the isolated cation [H<sub>3</sub>N-Ag-NH<sub>3</sub>]<sup>+</sup> are reasonable considering the crystal packing forces and the cation-anion interactions that occur in the solid phase but which are absent in these calculations.

Selected properties for all silver(I) cations investigated are found in Table 2. The Ag–N distances are remarkably constant for any particular ligand, *i.e.*, the Ag–NH<sub>3</sub> distances lengthen by less than 1.0 pm compared to the homoleptic system when a substituted-nitroxycarbon ligand is also bound to the silver(I) center. Similar small variations for the Ag–N distance are observed for the substituted-nitroxycarbon ligands when compared to the homoleptic analogs (Figure 2), but the Ag–N distances are longer. Bond orders are also similar: For the homoleptic systems, the Ag–N Löwdin bond orders are 0.630 (:NH<sub>3</sub>), 0.466 (:NO<sub>3</sub>CH), 0.449 (:NO<sub>3</sub>CF), 0.460 (:NO<sub>3</sub>CCl), and 0.479 (:NO<sub>3</sub>CCH<sub>3</sub>), indicating weaker bonds to silver for the nitroxycarbon ligands. The slightly electron-donating methyl-substituted nitroxycarbon and the parent appear to exhibit somewhat stronger bonds than do the electron-withdrawing fluoro- and chloro-substituted systems.

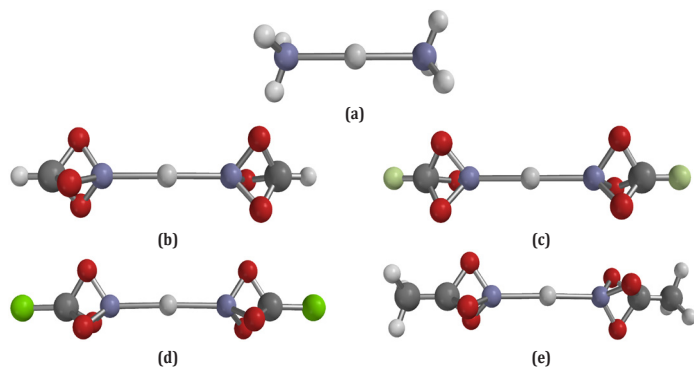
**Table 2.** Selected electronic and structural properties of the gas phase silver(I) complexes

Gas-phase ion	Electronic energy (a.u.)	Energy difference (kJ/mol)	Ag–N distances, <sup>a</sup> pm	$\nu(\text{Ag–N})$ , <sup>b</sup> cm <sup>-1</sup>
[Ag(NH <sub>3</sub> ) <sub>2</sub> ] <sup>+</sup>	-260.013952	—	216.9	354 <sup>sym</sup> , 429 <sup>asym</sup>
[Ag(NO <sub>3</sub> CH) <sub>2</sub> ] <sup>+</sup>	-784.501341	—	223.8	130 <sup>sym</sup> , 219 <sup>asym</sup>
[Ag(NO <sub>3</sub> CF) <sub>2</sub> ] <sup>+</sup>	-982.986575	—	225.7	108 <sup>sym</sup> , 198 <sup>asym</sup>
[Ag(NO <sub>3</sub> CCl) <sub>2</sub> ] <sup>+</sup>	-1703.705762	—	224.2	105 <sup>sym</sup> , 199 <sup>asym</sup>
[Ag(NO <sub>3</sub> CCH <sub>3</sub> ) <sub>2</sub> ] <sup>+</sup>	-863.179535	—	222.0	125 <sup>sym</sup> , 220 <sup>asym</sup>
[(H <sub>3</sub> N)Ag(NO <sub>3</sub> CH)] <sup>+</sup>	-522.258706	402.94	217.4 <sup>NH3</sup> , 222.1 <sup>NO3CH</sup>	169 <sup>sym</sup> , 397 <sup>asym</sup>
[(H <sub>3</sub> N)Ag(N(O)OCHO)] <sup>+</sup>	-522.412178	—	217.2 <sup>NH3</sup> , 224.8 <sup>N(O)OCHO</sup>	179 <sup>sym</sup> , 380 <sup>asym</sup>
[(H <sub>3</sub> N)Ag(NO <sub>3</sub> CF)] <sup>+</sup>	-621.501788	430.57	217.5 <sup>NH3</sup> , 223.4 <sup>NO3CF</sup>	153 <sup>sym</sup> , 396 <sup>asym</sup>
[(H <sub>3</sub> N)Ag(N(O)OCFO)] <sup>+</sup>	-621.665784	—	217.1 <sup>NH3</sup> , 223.2 <sup>N(O)OCFO</sup>	165 <sup>sym</sup> , 387 <sup>asym</sup>
[(H <sub>3</sub> N)Ag(NO <sub>3</sub> CCl)] <sup>+</sup>	-981.861005	429.94	217.8 <sup>NH3</sup> , 222.1 <sup>NO3CCl</sup>	149 <sup>sym</sup> , 395 <sup>asym</sup>
[(H <sub>3</sub> N)Ag(N(O)OCClO)] <sup>+</sup>	-982.024760	—	217.6 <sup>NH3</sup> , 222.2 <sup>N(O)OCClO</sup>	175 <sup>sym</sup> , 400 <sup>asym</sup>
[(H <sub>3</sub> N)Ag(NO <sub>3</sub> CCH <sub>3</sub> )] <sup>+</sup>	-561.597565	404.90	216.9 <sup>NH3</sup> , 220.4 <sup>NO3CCH3</sup>	167 <sup>sym</sup> , 397 <sup>asym</sup>
[(H <sub>3</sub> N)Ag(N(O)OC(CH <sub>3</sub> )O)] <sup>+</sup>	-561.751782	—	217.1 <sup>NH3</sup> , 219.8 <sup>N(O)OC(CH3)O</sup>	175 <sup>sym</sup> , 382 <sup>asym</sup>
[(HCO <sub>2</sub> N)Ag(NO <sub>3</sub> CF)] <sup>+</sup>	-883.744017	—	224.1 <sup>NO3CH</sup> , 225.3 <sup>NO3CF</sup>	118 <sup>sym</sup> , 210 <sup>asym</sup>
[(HCO <sub>2</sub> N)Ag(NO <sub>3</sub> CCH <sub>3</sub> )] <sup>+</sup>	-823.840622	—	223.5 <sup>NO3CH</sup> , 222.1 <sup>NO3CCH3</sup>	127 <sup>sym</sup> , 219 <sup>asym</sup>
[(HCO <sub>2</sub> N)Ag(NO <sub>3</sub> CCl)] <sup>+</sup>	-1244.103519	—	223.8 <sup>NO3CH</sup> , 224.0 <sup>NO3CCl</sup>	116 <sup>sym</sup> , 211 <sup>asym</sup>
[(FCO <sub>2</sub> N)Ag(NO <sub>3</sub> CCH <sub>3</sub> )] <sup>+</sup>	-923.083545	—	225.2 <sup>NO3CF</sup> , 222.3 <sup>NO3CCH3</sup>	116 <sup>sym</sup> , 210 <sup>asym</sup>
[(FCO <sub>2</sub> N)Ag(NO <sub>3</sub> CCl)] <sup>+</sup>	-1343.346233	—	225.4 <sup>NO3CF</sup> , 224.2 <sup>NO3CCl</sup>	107 <sup>sym</sup> , 199 <sup>asym</sup>
[(ClCO <sub>2</sub> N)Ag(NO <sub>3</sub> CCH <sub>3</sub> )] <sup>+</sup>	-1283.442876	—	223.9 <sup>NO3CCl</sup> , 222.3 <sup>NO3CCH3</sup>	114 <sup>sym</sup> , 211 <sup>asym</sup>

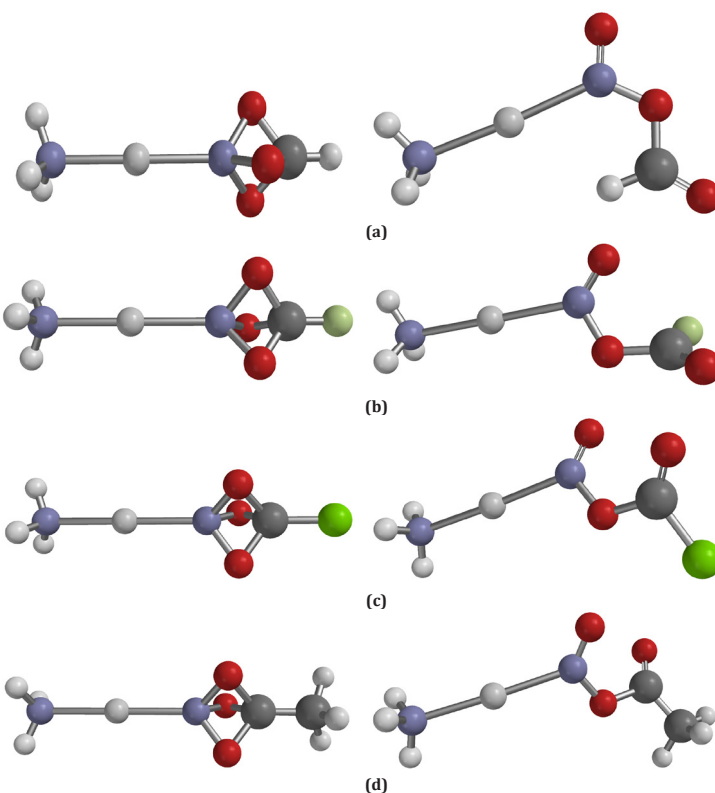
<sup>a</sup> Superscripts indicate to which ligand the distance refers. <sup>b</sup> Uncorrected frequencies. Superscripts indicate the symmetric stretch, sym, and the asymmetric stretch, asym. When the ligands are not identical, sym refers to the vibration in which both ligands move toward and away from the silver ion simultaneously, if not equally, and asym refers to the vibration in which one ligand moves toward and the other ligand moves away from the silver ion simultaneously, if not equally

The structures of the substituted-nitroxycarbon ligands upon complexation changes very little from that of the free ligands. In [Ag(NO<sub>3</sub>CH)<sub>2</sub>]<sup>+</sup>, for example, the N–O distance is 145.4 pm and the O–C distance is 143.4 pm, while in [Ag(NO<sub>3</sub>CF)<sub>2</sub>]<sup>+</sup>, the N–O distance is 145.5 pm and the O–C distance is 143.0 pm. Similar bond length changes upon complexation are seen in [Ag(NO<sub>3</sub>CCl)<sub>2</sub>]<sup>+</sup> and [Ag(NO<sub>3</sub>CCH<sub>3</sub>)<sub>2</sub>]<sup>+</sup>, indicating that, upon complexation, the N–O distance decreases by less than 2%, and the O–C distance increases by a similar percentage.

As was the case for the free ligands, the substituted-nitroxycarbon complexes are significantly less stable than the corresponding substituted-nitrosoformates. Complexation, however, lowers the energy difference by about 30 kJ/mol for all systems, and, again, the hydrogen- and methyl-substituted systems exhibit the lowest energy difference between the isomers (although still an enormous ~400 kJ/mol). Figure 3 illustrates the molecules investigated to determine the energy differences between the



**Figure 2.** The symmetrically-substituted silver(I) complexes: (a) [Ag(NH<sub>3</sub>)<sub>2</sub>]<sup>+</sup>, (b) [Ag(NO<sub>3</sub>CH)<sub>2</sub>]<sup>+</sup>, (c) [Ag(NO<sub>3</sub>CF)<sub>2</sub>]<sup>+</sup>, (d) [Ag(NO<sub>3</sub>CCl)<sub>2</sub>]<sup>+</sup>, and (e) [Ag(NO<sub>3</sub>CCH<sub>3</sub>)<sub>2</sub>]<sup>+</sup>. Large, dark-gray spheres represent carbon; small, light-gray spheres, hydrogen; medium-gray spheres, silver; blue spheres, nitrogen; red spheres, oxygen; pale-green spheres, fluorine, and green spheres, chlorine.

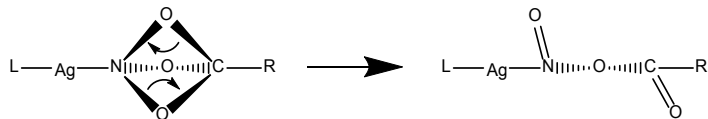


**Figure 3.** The structures of the nitroxycarbon ligand rearrangement products: (a) [(H<sub>3</sub>N)Ag(NO<sub>3</sub>CH)]<sup>+</sup> @ [(H<sub>3</sub>N)Ag(N(O)OCHO)]<sup>+</sup>, (b) [(H<sub>3</sub>N)Ag(NO<sub>3</sub>CF)]<sup>+</sup> @ [(H<sub>3</sub>N)Ag(N(O)OCFO)]<sup>+</sup>, (c) [(H<sub>3</sub>N)Ag(NO<sub>3</sub>CCl)]<sup>+</sup> @ [(H<sub>3</sub>N)Ag(N(O)OCClO)]<sup>+</sup>, and (d) [(H<sub>3</sub>N)Ag(NO<sub>3</sub>CCH<sub>3</sub>)]<sup>+</sup> @ [(H<sub>3</sub>N)Ag(N(O)OC(CH<sub>3</sub>)O)]<sup>+</sup>. Large, dark-gray spheres represent carbon; small, light-gray spheres, hydrogen; medium-gray spheres, silver; blue spheres, nitrogen; red spheres, oxygen; pale-green spheres, fluorine, and green spheres, chlorine.

substituted-nitroxycarbon molecules and the substituted-nitrosoformates. Note that, similarly to the free ligands, only the hydrogen-substituted nitrosoformate structure has the substituent rotated toward the silver(I) cation, while all of the other structures have the substituents rotated away from the metal center.

Thus, complexation of the substituted nitroxycarbon molecules to the silver(I) ion does slightly improve the stability of the nitroxycarbon with respect to rearrangement to the nitrosoformates. While the mechanism of this rearrangement is unknown, a

simple “electron-pushing” argument could be made for the mechanism, as illustrated below. Support for such a mechanism has not been addressed in this project and, unfortunately, the improvement in stability for the nitratocarbon-substituted silver(I) complexes is certainly insufficient to prevent such a rearrangement or to readily allow the synthesis of these interesting and fragile molecules.



## Conclusions

The novel hydrogen-, fluorine-, chlorine-, and methyl-substituted nitratocarbon and nitrosoformate molecules were investigated as ligands on the silver(I) cation. Complexation to silver(I) lowers the energy difference between the higher energy nitratocarbon and the more stable nitrosoformate isomers, but only by about 30 kJ/mol in comparison to the energy differences of the free ligands. The nitratocarbon ligands alter their structure only slightly upon complexation, but the nitrosoformate ligands rearrange to structures that differ from the free ligand molecules.

## Acknowledgements

The National Science Foundation's Course, Curriculum, and Laboratory Improvement Program, Adaptation and Implementation Section (NSF-9950344), is acknowledged for generous support for the initial purchase of computers and computational chemistry software. Matching funds and additional support have been received at various times from the Humboldt State University Department of Chemistry, the College of Natural Resources and Sciences, the Office for Research and Graduate Studies, the Office of the Vice-President for Academic Affairs, and the Office of the President, as well as from the Humboldt State University Sponsored Programs Foundation.

## Supplementary data

Supplementary data associated with this article containing final atomic coordinates for all molecules is available from the corresponding author on request.

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