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THEORETICAL COMPARISON OF THE BONDING IN $\text{CpCr}(\text{CO})_2(\text{NX})$ [$X = \text{O}, \text{S}, \text{Se}, \text{Te}$]

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Molecular orbital calculations employing the PM3 model have been used to examine the bonding in the complexes $\text{CpCr}(\text{CO})_2(\text{NX})$ ($X = \text{O}, \text{S}, \text{Se}, \text{Te}$). The previously established trend of increasing Cr–N interaction as X changes from O to S is demonstrated by these calculations, and found to extend to Se and Te. Bond lengths, bond orders, vibrational frequencies, and heats of reaction are used to support the conclusion that metal to ligand π -backbonding increases down the periodic chart from NO to NTe.

Keywords: Nitric oxide; Nitrosyl; Thionitrosyl; Selenium; Tellurium; Molecular orbital calculation

INTRODUCTION

The nitrosyl ligand, NO^+ , bonds more strongly to metal atoms than does the carbonyl, CO, ligand [1]. There are several types of evidence supporting this concept. One type is that substitution reactions preferentially result in replacement of CO rather than NO in complexes containing both [2–5]. Other evidence comes from mass spectra of compounds containing both CO and NO ligands where CO is lost more readily than NO [6,7]. Significantly shorter bond lengths from metal to NX than metal to CO also indicate the stronger bonding to metals by NX [2]. There is a considerable body of work that has been done on NS complexes, indicating stronger bonding to metal atoms by NS compared to NO. This work consists of theoretical studies of the electronic structure of complexes [8], measurement of IR positions in NO and NS complexes [7,9] and mass spectral data on such complexes [7–9]. Much less is known about the bonding of NSe and NTe to metal atoms due to lack of experimental data.

A previous computational study on the ligand series CO, CS, CSe, and CTe [10], showed that ligand metal bond strength was greatest for CTe and weakest for CO. That study was done using the Fenske–Hall approach which involved neither geometry optimization of the complexes nor calculation of the vibrational frequencies. It does, however, suggest an expected trend for this series of ligands. The current study, using the PM3 model, involves geometry optimizations as well as frequency calculations and thermodynamic considerations to establish comparative bond strengths.

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EXPERIMENTAL

PM3 semi-empirical molecular orbital calculations in the Spartan Pro package [11] were done on the complexes $\text{CpCr}(\text{CO})_2(\text{NX})$ where $X = \text{O}, \text{S}, \text{Se}, \text{Te}$. The known structures of $\text{CpCr}(\text{CO})_2(\text{NO})$ [2] and $\text{CpCr}(\text{CO})_2(\text{NS})$ [6,9] served as a starting point for all ground state geometry optimization calculations. All ground states were verified by frequency calculations, which showed the existence of no imaginary frequencies. Thermodynamic quantities were also computed so that ΔH_{rxn} values could be calculated.

RESULTS AND DISCUSSION

A bond distance for an NO ligand bound to chromium has been measured by x-ray diffraction of the complex $(^5\eta\text{-C}_{13}\text{H}_{19})\text{Cr}(\text{CO})_2\text{NO}$ [2]. The Cr–N bond length found in that study, 1.687 Å, is similar to that found in $\text{Cr}(\text{H}_2\text{O})_5\text{NO}$ [12]. Other reported values are 1.63 Å in $[(^5\eta\text{-C}_5\text{H}_5)\text{Cr}(\text{NO})(\text{NMe}_2)]_2$ [13] and 1.72 Å in $(^5\eta\text{-C}_5\text{H}_5)\text{Cr}(\text{NO})_2(\text{NCO})$ [14]. The PM3 structure of $\text{CpCr}(\text{CO})_2(\text{NO})$, computed here compares favorably with the experimental results. The Cr–N distance of 1.674 falls within the range of such distances that have been experimentally determined. In addition, the distance from the Cr atom to the center of the ring, i.e., the centroid, 1.873 Å, also compares well with known values of 1.844 and 1.884 [2].

The facts that the Cr–N distance is so much shorter than the Cr–C distance, 1.915 Å, indicates the stronger bonding between Cr and NO in agreement with those measured for $\text{CpCr}(\text{CO})_2(\text{NS})$ [9]. As expected, the other complexes have very similar structures. Table I shows data that indicate the trends in bonding as X varies from O down the periodic chart to Te.

The computed Cr–N bond length, 1.674 Å when $X = \text{O}$, gets shorter as one proceeds down the series until it is 1.642 Å when $X = \text{Te}$, direct evidence that NTe bonds best to the Cr atom. It is well known that the nitrosyl ligand competes effectively with most other ligands for π -backbonding electron density [1]. The bond length data suggest that this π -backbonding tendency increases down the series to Te. All of the other data in the table also support this concept.

If the NTe ligand is accepting more π -electron density than the other NX ligands, then the other ligands in $\text{CpCr}(\text{CO})_2(\text{NTe})$ will be getting less π -backbonding electron density. This is verified by the data in Table I. For example, the Cr–C bond distance is longest, 1.939 Å, when $X = \text{Te}$; and shortest, 1.915 Å, when $X = \text{O}$. This reflects less π -backbonding to the CO ligand when NTe is the ligand, and more π -backbonding

TABLE I PM3 computed properties of $\text{CpCr}(\text{CO})_2(\text{NX})$

	$\text{CpCr}(\text{CO})_2(\text{NO})$	$\text{CpCr}(\text{CO})_2(\text{NS})$	$\text{CpCr}(\text{CO})_2(\text{NSe})$	$\text{CpCr}(\text{CO})_2(\text{NTe})$
Cr–N	1.674	1.653	1.645	1.642
Cr–C	1.915	1.934	1.937	1.939
Cr–Cp	1.873	1.876	1.878	1.885
C–O	1.163	1.157	1.155	1.55
ν_{CO}	1949	1965	1970	1976
ΔH_{rxn}	–298.9	–310.7	–347.1	–379.4

Note: Frequencies have been scale to 0.90 of the computed value.

to CO when NO is the ligand. Similarly the distance to the center of the Cp ring, denoted by "Cr-Cp Distance" in Table I, is also longest, 1.885 Å, when $X = \text{Te}$; and shortest, 1.873 Å, when $X = \text{O}$. Note that the other values follow this trend with NO always at one extreme and NTe at the other.

Since π -backbonding to the CO ligand weakens the C-O bond, less π -backbonding should result in stronger, shorter C-O bonds. This is found to be the case when $X = \text{Te}$. The change in C-O bond strength is reflected by small changes in the C-O bond length computed for these complexes. But perhaps a more sensitive probe of the C-O bond strength is found in the computed frequencies for the symmetric C-O stretching motion. Again a nice trend is found with the NO compound having the lowest C-O stretching frequency, $\nu_{\text{CO}} = 1949 \text{ cm}^{-1}$, and NTe complex having the highest C-O stretching frequency, $\nu_{\text{CO}} = 1976 \text{ cm}^{-1}$.

All of the evidence noted above for increasing Cr-N bond strength and diminished N-X bond strength is verified by calculation of the bond order matrix for all four $\text{CpCr}(\text{CO})_2\text{NX}$ complexes. The strength of the interaction between the metal and ligand depends on a number of factors such as the energy match between the overlapping orbitals and the number of electrons transferred. The bond order matrix, which is given in Table II, accounts for all such factors. The bond order of Cr-N increases smoothly from 2.26 in $\text{CpCr}(\text{CO})_2\text{NO}$ to 2.72 in $\text{CpCr}(\text{CO})_2\text{NTe}$. The N-X bond order decreases from 1.47 in $\text{CpCr}(\text{CO})_2\text{NO}$ to 0.76 in $\text{CpCr}(\text{CO})_2\text{NTe}$. These results are easily explained, in the manner found in nearly all inorganic and organometallic textbooks [15-17], by increased π -backbonding between the Cr and N atoms in going from NO to NTe. This interaction simultaneously strengthens the Cr-N bond and weakens the N-X bond, as observed.

A final bit of evidence for the strong interaction when $X = \text{Te}$ is found in the computed values of ΔH for the reaction forming the complexes from NX^+ and the $\text{CpCr}(\text{CO})_2^-$ fragment:

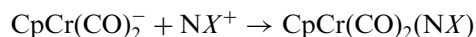


Table I contains these values, which range from -299 kcal/mol for the NO complex to -379 kcal/mol for the NTe complex. The calculations of the ΔH_{rxn} values include Zero Point Energy values.

The reactions of electrophiles with NO-containing complexes have been studied [18]. It is known that oxygenation occurs at the O atom of the coordinated NO ligand. Protonation is thought to occur at the N atom of the coordinated NO ligand. Our calculations show that the HOMO is spread out over the carbon and oxygen atoms of the CO and NO groups. There is very little nitrogen contribution to the HOMO of $\text{CpCr}(\text{CO})_2(\text{NO})$. On the other hand, the center of largest negative charge is the nitrogen atom with $q = -0.59$. This situation allows for different sites of attack, as has been observed, depending on the electrophile.

TABLE II PM3 computed bond orders for Cr-N and N-X in $\text{CpCr}(\text{CO})_2(\text{NX})$

	$\text{CpCr}(\text{CO})_2(\text{NO})$	$\text{CpCr}(\text{CO})_2(\text{NS})$	$\text{CpCr}(\text{CO})_2(\text{NSe})$	$\text{CpCr}(\text{CO})_2(\text{NTe})$
Cr-N	2.26	2.51	2.58	2.72
N-X	1.47	1.22	1.09	0.76

The reaction chemistry of the NS, NSe, and NTe species has not been studied as much. Our PM3 calculations suggest that the reactions of these complexes with electrophiles should be better defined than for NO complexes. The reason for this is that both orbital and charge considerations favor reaction at the *X* atom of the *NX* ligand in all three cases. In all three complexes the atomic orbital with the largest contribution, by far, to the HOMO is on the *X* atom. This is in contrast to the NO complex. In addition the negative charge is also largest on *X* [$q_{CO} = -0.17$ – -0.22 ; $q_X = -0.59$ (O), -0.53 (S), -0.47 (Se), and -0.37 (Te)].

Less can be said about the reactions of $\text{CpCr}(\text{CO})_2(\text{NX})$ with nucleophiles. In all four complexes the LUMO is spread out just about equally over the Cr atom and the CO and *NX* ligands. There is no orbitally dominant site for attack utilizing the LUMO. Charge considerations do not help much either. In the NO complex the largest positive charge is on the N atom, +1.11 compared with +0.50 on the C atoms. But in the NS complex the charges are much closer in value: $q_N = +0.68$, $q_C = +0.52$. By the time we reach NTe the charges have reversed: $q_N = +0.42$, $q_C = +0.53$.

We conclude that when more NSe and NTe complexes are prepared their reactions with electrophiles will generally occur at the Se and Te atoms. Their reactions with nucleophiles will exhibit a variety of sites of attack.

CONCLUSIONS

The series of ligands NX^+ ($X = \text{O}, \text{S}, \text{Se}, \text{Te}$) have a valence shell that is isoelectronic and an electronic structure that is similar to carbonyl ligand, CO. It is known [1] that NO^+ bonds more strongly to transition metals in complexes, possibly because it is formally a three-electron donor cationic ligand. These calculations reaffirm that idea and extend it to the other *NX* ligands. The concept of ever stronger ligand–metal interaction as one proceeds down the periodic chart from NO to NTe is supported by several quantities calculated herein. The Cr–N distances, the Cr–C distances, the C–O distances, the Cr–Centroid distances, the ν_{CO} values, the bond orders, and the ΔH_{rxn} values all indicate weakest bonding to Cr by NO and strongest bonding to Cr by NTe.

The chemical reactions of NX ($X = \text{S}, \text{Se}, \text{Te}$) complexes with electrophiles should occur at the *X* atom. Reactions with nucleophiles will have a variety of mechanisms.

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