

Stability Studies of Transition-Metal Linkage Isomers Using Quantum Mechanical Methods. Groups 11 and 12 Transition Metals

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Several hypotheses to elucidate the linkage isomer preference of the thiocyanate (SCN^-) ion have been offered. For complexes with small coordination numbers (i.e., 1 and 2) and groups 11 (Cu-triad) and 12 (Zn-triad) metals, different levels of theory and a variety of basis sets have been employed to study linkage isomerism. Similar results are obtained for all density functionals tested, pure and hybrid. Overall, good agreement, vis-à-vis experimentally identified linkage isomers, is achieved for ab initio techniques, whereas semiempirical quantum mechanical methods show a bias toward S-ligated isomers. Despite the seeming ease for the a priori prediction of the most stable thiocyanate isomers using acid/base principles, this research highlights the sensitivity of quantitative calculations of transition-metal linkage isomerism to the choice of basis set and electron correlation, particularly with post-Hartree–Fock treatments.

INTRODUCTION

Linkage isomerism is a type of isomerism that is distinctive of transition-metal complexes, where ligands are capable of bonding through different atoms. Jorgensen reported the first example of linkage isomerism in 1893¹ for nitro ($\text{Co}-\text{NO}_2$) and nitrito ($\text{Co}-\text{ONO}$) cobalt(III) ammine complexes. A large variety of linkage isomers involving ligands such as NCS^- , NCO^- , CN^- , NO^- , NO_2^- , NCS^- , SO_3^{2-} , CO_2^- , and so forth were reported² in subsequent years. From all possible ligands that readily form linkage isomers, the thiocyanate group, with two different isomers exemplified by SCN^- (S bonding) and NCS^- (N bonding), was selected for the present research as there is considerable experimental data with which to compare theoretical results.

Turco and Pecile reported the first thiocyanate linkage isomers³ in 1961. One of their hypotheses for linkage preference was based on the electronic effect of ancillary ligands. For example, they proposed that a phosphine ligand trans to a thiocyanate would monopolize the π -bonding d orbitals of the square-planar Pt(II) complex, yielding an N-bonded thiocyanate in the trans position, as the Pt–N linkage is preponderantly σ in character. In the absence of competition for Pt d π orbitals from the trans ligand (e.g., NH_3), the S-bonded thiocyanate was proposed to be favored because a Pt–S linkage can maximize π bonding (Figure 1).

Using this hypothesis, Basolo et al.⁴ prepared and identified (e.g., through IR spectra) both thiocyanate linkage isomers in the following complexes: $\text{Pd}(\text{AsPh}_3)_2(\text{SCN})_2$, $\text{Pd}(\text{AsPh}_3)_2(\text{NCS})_2$, $\text{Pd}(\text{bipy})(\text{SCN})_2$, and $\text{Pd}(\text{bipy})(\text{NCS})_2$. In all cases, the S-bonded isomer, which is stable at room temperature, is converted to the N-bonded isomer upon warming. Electronic effects in linkage isomerism were also

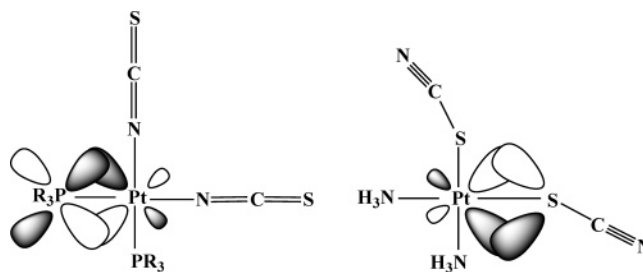


Figure 1. Ligand competition for Pt π orbitals

experimentally tested by Bertini and Sabatini,⁵ who stated that thiocyanates are N-bonded in $[\text{Pd}(5\text{-nitrophen})(\text{NCS})_2]$ and S-bonded in $[\text{Pd}(1,10\text{-phenanthroline})(\text{SCN})_2]$. Their explanation is based on the electronic properties of the 5-nitro-phenanthroline ligand, whereby the nitro group is presumably π -bonded to the arene ring, inducing π character to the bond between Pd and N, thus enforcing the σ -bonded thiocyanate in the trans position. It was proposed that by increasing the temperature, that π bonding between the nitro group and ring would be removed, inducing the S-bonded linkage isomer in the trans position, in accord with experimental observations.⁵

The combined influence of electronic and steric factors upon thiocyanate linkage isomerism has been investigated for bidentate ligands⁶ that have one σ -donor functionality (e.g., an amine) and one π -bonding functionality (e.g., phosphine), namely, $[\text{Ph}_2\text{P}-(\text{CH}_2)_3-\text{NMe}_2]\text{Pd}(\text{NCS})(\text{SCN})$, where the S-bonded thiocyanate is trans to the amine and the N-bonded isomer is trans to the phosphine (Figure 2).

Another electronic explanation of thiocyanate bonding preferences was proposed by Jorgensen⁷ and is called “symbiosis theory.” This theory is based on the “hard” or “soft” acid/base character of the metal and ligands and has been applied mainly to octahedral complexes. Symbiosis theory asserts that hard ligands will make the metal cation to which they are connected “harder,” which will, in turn,

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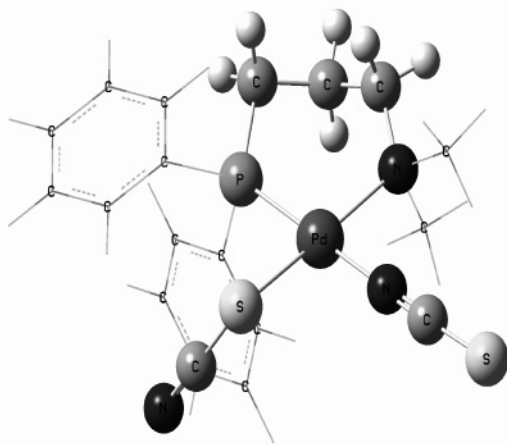


Figure 2. Meek's complex.⁶ (Amine and phosphine substituents are shown in the wireframe.)

promote further coordination of additional hard ligands; similarly, "soft" ligands will lead the metal ion to favor additional "soft" ligands. This theory was supported by Guterman and Gray,⁸ who, on the basis of spectroscopic and theoretical data, suggested that $-\text{SCN}$ would prefer to bind soft metals, whereas $-\text{NCS}$ would prefer to bind hard metals.

Palenik et al.⁹ proposed an analysis of linkage isomerism based solely on steric effect for Pd complexes of the type $[\text{Ph}_2\text{P}-(\text{CH}_2)_n-\text{PPh}_2]\text{Pd}(\text{NCS})_2$. The electronic environment at the phosphorus is essentially constant throughout this series, and thus, by adding a CH_2 group, only the steric effect is changed, which should make it possible to delineate steric and electronic influences upon linkage isomerism. By varying the number of CH_2 groups from 1 to 3, the $\text{P}-\text{Pd}-\text{P}$ bite angle increases, and both thiocyanate groups, thus, change from both being S-bonded ($n = 1$) to a mixture of S-bonded and N-bonded ($n = 2$) to only N-bonded ($n = 3$) because the linearly coordinated NCS is sterically less hindering than the bent SCN isomer.

At first glance, "symbiosis theory" and " π -bonding theory" appear to contradict each other. In addition, the possibility that multiple factors (e.g., both electronic *and* steric) are involved in determining linkage isomer preferences seems plausible. To incorporate all effects, Pearson¹⁰ proposed that two soft ligands connected to a soft transition metal would destabilize each other. He also indicated that symbiosis theory is predominant in octahedral complexes, whereas π -bonding theory is more applicable to square-planar species. Furthermore, small energy differences between both linkage isomers have been identified in solutions, where the bonding mode is decided by the nature of the solvent.¹¹ For the majority of transition metals, thiocyanate complexes are preponderantly S-bonded in solvents with a high dielectric constant, whereas in solvents with a low dielectric constant, N-bonded isomers are preferred.¹¹

To better understand linkage isomer complexity for the thiocyanate ion, and to fill in existing gaps in experimental data, we performed theoretical calculations to elucidate factors that influence linkage to a transition metal through the S or N atom. In many cases, experimental methods encounter difficulties in differentiating between the S and N linkage isomers of thiocyanate. Furthermore, small energy differences between both possible coordination isomers will present an extremely challenging task to identifying the most

stable linkage isomer with theory. Epps et al.¹² prepared and investigated $[\text{Co}(\text{DH})_2(\text{NCS})_2]^-$, DH is the monoanion of dimethylglyoxime, using IR spectral methods and molecular orbital calculations; they observed small energy differences (less than 1 kcal/mol) between S- and N-bonded linkage isomers. Moreover, the authors stated that π -bonding effects will be more pronounced for square-planar complexes than for octahedral complexes and that S-bonded isomers are more likely to form a π bond with fourth- and fifth-row transition metals than with third-row transition metals. Small energy differences between S- and N-bonded linkage isomers were also identified for $[\text{Co}(\text{NH}_3)_5(\text{NCS})]^{2+}$ and $[\text{Ru}(\text{NH}_3)_5(\text{NCS})]^+$ by Tuan et al.¹³ using extended Hückel calculations, consistent with the experimental observation of both linkage isomers resulting from small temperature variations. The electronic structure of the thiocyanate ion was investigated by Di Sipio et al.¹⁴ using SEQM (semiempirical quantum mechanics) methods in order to determine bonding preference. The ambidentate nature of the thiocyanate ion was explained as arising from the almost equally distributed charge over the terminal atoms, and thus, formation of N- or S-bonded linkage isomers was mainly attributed to the establishment of the most stable electron configuration during bond formation with the transition metal.

Reiher¹⁵ evaluated the performance of calculations [Hartree-Fock (HF) and density functional theory (DFT) methods] to determine spin-crossover and vibrational effects for $\text{Fe}(\text{phen})_2(\text{NCS})_2$, phen = phenanthroline. Reliable energy splittings compared with experimental results were provided by hybrid DFT functionals, particularly B3LYP, when one of the three parameters was modified (i.e., $c_3 = 0.15$ instead of the original $c_3 = 0.20$). The same DFT functional was then used by Tercero et al.¹⁶ to investigate the contribution of the thiocyanate ion to the magnetic coupling of $\text{Cu}(\text{II})-\text{Ni}(\text{II})$ supramolecular compounds. Theoretical results suggested that coupling through the thiocyanate ion is very small and antiferromagnetic. The stability of group 12 transition metals (Zn, Cd, and Hg) as four-coordinate complexes where all ligands are either N- or S-bonded thiocyanate was investigated by Fukushima et al.¹⁷ using DFT methods. For the first- and second-row metals Zn and Cd, respectively, the N-bonded isomer was found to be more stable, whereas for the heavier Hg, the S-bonded isomer is preferred; for the Cd complex, the difference in energy between the two linkage isomers was relatively small.

In this research, the accuracy of the "symbiosis theory" proposed by Jorgensen⁷ is investigated for a series of transition-metal thiocyanate complexes using several theoretical methods.

COMPUTATIONAL METHODS

The results of the faster PM3(tm) semiempirical method are compared with HF and DFT methods (e.g., pure BLYP and BP86 and hybrid B3LYP and B3PW91 functionals). The "B" functionals include Slater¹⁸ local and Becke¹⁹ nonlocal exchanges, whereas the "B3" functionals are formed from Slater + HF local and Becke¹⁹ nonlocal exchanges, along with the Vosko, Wilk, and Nusair²⁰ local correlation. The "LYP" functionals contain the Lee, Yang, and Parr²¹ local + nonlocal correlation functional; the designation "PW91" denotes the 1991 nonlocal correlation functional developed by Perdew and Wang,²² and the "P86" functional designates

Perdew 81²³ local correlation and Perdew 86²⁴ nonlocal correlation.

In cases in which DFT-calculated energy differences between linkage isomers are small, other geometry optimizations (e.g., MP2) and single point [CCSD(T)/MP2] calculations are performed to further differentiate isomer stability. The large majority of theoretical calculations employed the CEP-31G and CEP-121G effective core potential basis sets²⁵ with s and p diffuse and d polarization functions obtained from the 6-31+G* basis set for all p-block elements.²⁶ The LANL2DZ²⁷ scheme employs the Dunning/Huzinaga valence double- ζ basis set D95V²⁸ for the first-row main-group elements and the Los Alamos ECP/valence basis set for all elements between Na and Bi.

For some species, calculations with additional basis functions are performed to determine the most stable linkage isomer; in particular, the 3f and 2g polarization functions from the Ahlrichs coulomb fitting basis set²⁹ are added to all group 11 and 12 metals of the periodic table.²⁶ Moreover, extra diffuse s and p and polarization d and f functions are added to C, N, and S atoms, these being obtained from the aug-cc-pVTZ diffuse basis set.³⁰ To this are added additional polarization functions: 3d1f for S [from the cc-pV-(T+d)Z basis set³¹] and 2d1f for C and N atoms (from the cc-pVTZ basis set³²). Adding these diffuse and polarization basis functions to the existing CEP-121G yields a basis set designated "b₀."

Some discrepancies between results provided by the preceding "b₀" basis set and experimental data are observed for mercury bis(thiocyanate) complexes, and thus, four additional smaller basis sets are employed for further calculations. First, "b₁" is obtained from "b₀" by removing polarization functions for N, C, and S atoms that came from the cc-pV-(T+d)Z basis set.³¹ Second, "b₂" is obtained from "b₀" by removing diffuse functions for N, C, and S atoms that came from the aug-cc-pVTZ diffuse basis set³⁰ and then adding the polarization and diffuse functions from the cc-pVTZ basis sets³² for N, C, and S atoms. Third, "b₃" is similar to "b₂" except for the S atom, for which the extra polarization and diffuse basis functions came from cc-pV-(T+d)Z³¹ instead of cc-pVTZ. The last, and largest, basis set employed in the study of linkage isomers, "b₄", included the same extra basis functions for N, C, and S atoms as "b₃" and included the complete Ahlrichs coulomb fitting basis set²⁹ for the Hg atom.

This research employs the PM3(tm) method as implemented in the Spartan 04³³ package, whereas the Gaussian 98 and Gaussian 03³⁴ programs are used for all ab initio and DFT calculations. Reported energies quoted below are differences in electronic energies; the inclusion of zero-point, enthalpy, and entropic corrections does not affect the linkage isomer preference.

RESULTS AND DISCUSSION

The preference for S- versus N-bonded linkage isomers for thiocyanate complexes of different transition metals, with various coordination numbers and ligand environments, is investigated using theoretical calculations. To determine the accuracy of each individual method, theoretical results are compared with crystallographic data when available.

When the principle first proposed by Jorgensen is considered,⁷ it is expected that transition metals will favor the

coordination of the N or S atom of thiocyanate on the basis of complementarity to the metal's own acid/base properties. Thus, first-row transition metals are expected to be preponderantly "hard" and should, thus, prefer to be ligated to the "hard" N atom of the thiocyanate ion, whereas third-row transition metals are primarily "soft" and would favor a "soft" S atom. For second-row transition metals, both isomers may be feasible with small energy differences between them.¹⁷ Of course, metal cation softness and hardness is also a function of formal oxidation state.

Analysis of the Cambridge Structural Database (CSD³⁵) reveals that transition metals exhibit a strong preference for the formation of N-ligated thiocyanates, in a ratio of 7:1 (1782 samples) as compared to S-ligated thiocyanates. Surprisingly, even though Jorgensen's symbiosis theory predicts that third-row transition metals will form predominantly S-ligated thiocyanates, the CSD shows an approximately equal distribution between the two isomers (N:S = 108:133 \approx 0.81). Thus, only the first and second-row transition metals follow the expected acid/base prediction; the ratios between the two isomers are \sim 42:1 (N:S = 1271:30) and \sim 3:1 (N:S = 176:64), respectively, favoring the N-ligated thiocyanates over the S-ligated thiocyanates.

Group 11 Thiocyanate Complexes. Thiocyanate complexes of group 11 ions (Cu⁺, Ag⁺, and Au⁺) are chosen on the basis of their reduced isomeric complexity, resulting from the low coordination numbers (CN = 1 and 2). For one-coordinate complexes, MN (N-thiocyanato) and MS (S-thiocyanato) linkage isomers are considered (M = Cu, Ag, Au; N \rightarrow NCS, S \rightarrow SCN), whereas for two-coordinate complexes, M(thiocyanate)₂⁻, MN₂, MNS, and MS₂ are investigated at disparate levels of theory.

The performance of different DFT functionals (e.g., pure BP86 and BLYP and hybrid B3LYP and B3PW91) is investigated for both one- and two-coordinate thiocyanate complexes of group 11 ions to establish the sensitivity of the results to functional choice. All DFT functionals tested are associated with two pseudopotential basis sets, CEP-121+G(d)²⁵ and LANL2DZ(d)²⁷ ($\xi_{sp}S = 0.0405$, $\xi_{sp}C = 0.0438$, $\xi_{sp}N = 0.0639$, $\xi_dS = 0.65$, and $\xi_dC,N = 0.80$).²⁶ Less expensive methods exemplified by HF with the same basis sets and PM3(tm) semiempirical quantum mechanics are also assessed. More expensive MP2 and CCSDT//MP2 calculations are carried out with the CEP-121+G(d) basis set. Calculated bond lengths and bond angles for optimized geometries are consistent with available experimental data. Table 1 organizes the relative energies of the different linkage isomers at the different levels of theory investigated.

For one-coordinate species, complete agreement is found among all DFT functionals using both CEP-121+G(d) and LANL2DZ(d) basis sets; the linkage isomers calculated to be most stable are CuN, AgS, and AuS, Table 1. The S-bonded linkage isomer is always found to be more stable by PM3(tm). When HF/CEP-121+G(d) and HF/LANL2DZ(d) methods are used, the DFT results are reproduced, although the smaller basis set predicts the CuS linkage isomer to be more stable than the CuN isomer by 0.3 kcal/mol. MP2/CEP-121+G(d) and CCSDT/CEP-121+G(d)//MP2/CEP-121+G(d) predicted CuN, AgS, and AuS to be the more stable linkage isomers, supporting the consensus DFT and HF predictions, Table 1.

Table 1. Relative Energies (kcal/mol) of the Linkage Isomers Investigated^a

Group 11 Metals									
	<i>E</i> rel	B3LYP/CEP-121+G(d)	B3LYP/LANL2DZ(d)	B3LYP/CEP-121G(b ₀)	HF/CEP-121+G(d)	HF/LANL2DZ(d)	MP2/CEP-121+G(d)	CCSDT/CEP-121+G(d)//MP2/CEP-121+G(d)	
Monothiocyanate									
Cu	S–N	1.2	2.4	2.2	0.0	–0.3	6.2	2.5	
Ag	S–N	–3.1	–2.2	–1.9	–2.9	–4.3	–2.7	–4.4	
Au	S–N	–7.4	–4.5	–6.7	–9.8	–9.9	–9.5	–11.9	
Bis(thiocyanate)									
Cu	NS	10.2	9.8	9.8	6.0	4.7	8.6	6.0	
Cu	S ₂	18.6	17.5	18.4	10.8	8.7	20.8	14.5	
Ag	NS	3.8	3.6	3.5	1.4	0.3	1.8	0.7	
Ag	S ₂	6.7	5.9	6.5	2.6	0.5	3.6	1.6	
Au	NS	4.3	5.5	3.9	1.1	1.3	2.5	1.1	
Au	S ₂	6.2	7.8	6.0	1.1	1.2	3.9	1.2	
Group 12									
	<i>E</i> rel	B3LYP/CEP-121+G(d)	B3LYP/b ₀	B3LYP/LANL2DZ(d)	HF/CEP-121+G(d)	HF/LANL2DZ(d)	MP2/CEP-121+G(d)	MP2/b ₀	CCSDT/CEP-121+G(d)//MP2/CEP-121+G(d)
Bis(thiocyanate)									
Zn	NS	11.4	11.3	14.1	6.7	9.7	8.4	13.1	6.7
Zn	S ₂	21.1	21.5	27.1	12.5	18.3	19.0	29.2	15.1
Cd	NS	4.4	5.1	8.0	1.0	2.6	2.4	5.7	0.9
Cd	S ₂	8.0	9.7	15.2	1.8	5.0	4.9	11.1	1.8
Hg	NS	0.1	–0.1	2.8	–3.9	–3.8	–1.4	0.7	–3.1
Hg	S ₂	–0.4	1.2	4.8	–8.1	–8.0	–3.0	1.0	–6.6
	<i>E</i> rel	B3LYP/b ₁	B3LYP/b ₂	B3LYP/b ₃	B3LYP/b ₄				
Hg	NS	6.5	1.7	1.8	1.8				
Hg	S ₂	10.8	2.5	2.7	2.8				

^a For the group 11 monothiocyanates, the energy difference between MN and MS (e.g., S–N) linkage isomers is given; a negative number indicates the $E_{\text{MS}} < E_{\text{MN}}$. For group 11 and group 12 bis(thiocyanate) complexes, the energy differences are relative to the MN₂ (e.g., NS–N₂ and S₂–N₂) linkage isomer. Basis sets are described in the Computational Methods section.

The similarity of results among DFT functionals suggests that this parameter is not of overriding significance in determination of the preferred linkage isomer; therefore, B3LYP is chosen for further DFT investigations on the basis of its larger utilization for similar complexes in the literature.^{15,16} In combination with the larger b₀ basis set (see Computational Methods), the B3LYP functional reproduces the results provided by all DFT methods using the CEP-121+G(d) and LANL2DZ(d) basis sets. Thus, in the main, theoretical calculations predict CuN, AgS, and AuS to be the most stable linkage isomers, a result in accord with Jorgensen's hard/soft theory of linkage isomerism.⁷

For anionic group 11 bis(thiocyanate) complexes, M(thiocyanate)₂[–], all functionals and HF methods used in conjunction with both the CEP-121+G(d) and LANL2DZ(d) basis sets indicated N-linked thiocyanates (i.e., CuN₂, AgN₂, and AuN₂) to be more stable than the corresponding MNS and MS₂ linkage isomers, Table 1. Conversely, S-bonded linkage isomers are predicted to be more stable with the PM3(tm) method. Post-HF methods MP2 and CCSDT//MP2 coupled with the CEP-121+G(d) basis set provided predictions identical to those of the DFT and HF methods, the N-linked linkage isomer being more stable than the other possible isomers. When the CSD³⁵ was searched for bis(thiocyanate) complexes, five copper complexes corresponding to the CuN₂ isomer, one AgS₂ isomer, and one AuS₂ isomer were identified.

Although caution is needed in making conclusions about the stability of isomers on the basis of the existence or absence of structurally characterized complexes, particularly

for small sample sizes, the structurally characterized bis(thiocyanate) complexes are consistent with simple acid/base considerations. For copper bis(thiocyanate), the CuN₂ linkage isomer is always predicted to be more stable. However, an interesting trend is observed when comparing the energy differences between AgS₂–AgN₂ and AuS₂–AuN₂ linkage isomers using the CEP-121+G(d) basis set: B3LYP (6.7 and 6.2 kcal/mol for the silver and gold complexes, respectively) > MP2 (3.6 and 3.9 kcal/mol, respectively) > CCSDT//MP2 (1.6 and 1.2 kcal/mol, respectively). When more elaborate levels of electron correlation are incorporated, the S-linked isomer becomes more energetically competitive, consistent with the crystallographic data and the predictions of acid/base theory. It is remarkable that such extensive theoretical treatments are needed to properly describe what, a priori, would have been expected to be "simple" acid/base trends in linkage isomerism stability! A possible explanation for the need of such highly correlated calculations may result from an insufficient representation of relativistic effects for fourth- and fifth-row transition metals. Support for this inference arises from the method sensitivity encountered below for mercury complexes, for which relativistic effects are known to be substantial.

Group 12 Thiocyanate Complexes. For group 12 metals (Zn, Cd, and Hg) only neutral, two-coordinate thiocyanate complexes are investigated. On the basis of the agreement among DFT functionals for similar calculations performed on group 11 species, the B3LYP functional is used to model Zn-triad species.

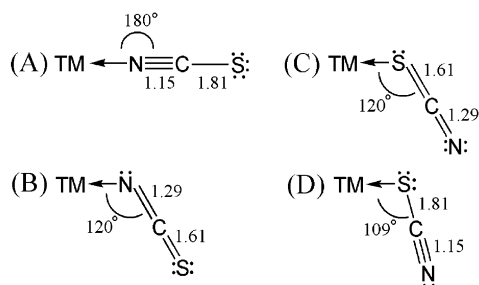


Figure 3. Resonance structures of N- and S-ligated thiocyanates with transition metals; bond lengths (Å) were estimated using the Pauling covalent radii.³⁸

In the CSD,³⁵ one CdN₂ (refcode ZIFKUU³⁶) and one HgS₂ (refcode REJNAV³⁷) (recall that N → N-ligated thiocyanate and S → S-ligated thiocyanate) bis(thiocyanate) complex are identified. No data were found for Zn, but “symbiosis theory”⁷ leads to the prediction that the “hard” N-bonded linkage isomer will be energetically preferred by the “hard” Zn²⁺ ion.

At all levels of theory, the predicted energy ordering of the three possible linkage isomers for zinc and cadmium is MN₂ < MNS < MS₂, Table 1. Interestingly, the mercury complexes are much more sensitive to both the basis set and the electron correlation treatment. For example, the HgS₂ linkage isomer is calculated as the most stable species when the MP2/CEP-121+G(d) level of theory is used, Table 1. When the larger b₀ basis set is used, maintaining the MP2 method, the HgN₂ linkage isomer is now lowest in energy. For the B3LYP functional with these same basis sets, different ground state predictions are again obtained: HgS₂ [B3LYP/CEP-121+G(d)] and HgNS (B3LYP/b₀!). At the highest level of electron correlation employed in this study, the HgS₂ isomer is predicted to be the most stable linkage isomer. The expense of the CCSD(T) method precluded its use with augmented basis sets. However, B3LYP calculations and the augmented basis sets (b₂, b₃, and b₄) display a convergence to the HgN₂ complex as the most stable linkage isomer, being ca. 3 kcal/mol more stable than the HgS₂ isomer, Table 1.

Resonance Structures. Two resonance structures *seem plausible* for the N-ligated thiocyanates (Figure 3, **A** and **B**); bond lengths were estimated using the Pauling covalent radii.^{38,39} Investigation of the Cambridge crystallographic database³⁵ indicates that the average distance (537 samples) between N and C is 1.15 ± 0.01 Å (triple bond), whereas the average distance (547 samples) between C and S for N-ligated thiocyanates is 1.62 ± 0.01 Å (double bond). Moreover, the average transition-metal–N–C bond angle (558 samples) is 165.6 ± 7.9°, suggesting that both the **A** and **B** resonance structures contribute to the molecular structure of N-ligated thiocyanates, with perhaps a slightly higher percentage of **A** than **B**.

Likewise, when the sulfur of thiocyanate ligates the transition metal, two plausible resonance structures are expected (Figure 3, **C** and **D**). In this case, the experimental geometries show that the average distance (71 samples) between S and C for S-ligated thiocyanates is 1.66 ± 0.02 Å (double bond), whereas the average bond length (74 samples) between C and N is 1.14 ± 0.02 Å (triple bond). Again, both **C** and **D** resonance structures contribute to the molecular structure of the S-ligated thiocyanates, but the

average transition-metal–S–C bending angle (75 samples) of 103.0 ± 4.5° suggests that **D** is the dominant contributor.

Application of the natural bond order (NBO⁴⁰) analysis to the equilibrium geometry of the NCS anion at the B3LYP/aug-ccpVTZ level of theory reveals a triple bond (1.17 Å) between nitrogen and carbon and a single bond (1.67 Å) between carbon and sulfur. The NBO calculation indicates that nitrogen and carbon are s–p mixing, whereas the sp hybridization for sulfur is very small (20% s, 80% p); s character is primarily located in a sulfur lone pair. The NBO results are consistent with the experimental metric data. The predominant p character of sulfur with little s mixing is consistent with the value (103.0 ± 4.5°) for the bond angle of the S-ligated thiocyanates, which is greater than 90° (expected in the complete absence of s–p mixing) and smaller than 109° (expected for sp³ hybridization). A major reason for the S–C bond shortening (1.67 Å calculated compared to 1.81 Å expected³⁸) in thiocyanate is not multiple bonding, but rather, the nature of the C atom, which is sp hybridized. B3LYP/aug-ccpVTZ geometry optimizations of acetylene thiol (H–S–C≡C–H) and thiocyanic acid (HSCN) systems show C–S single bond lengths of 1.69 and 1.70 Å, respectively, that are comparable to the values obtained for thiocyanate complexes.

SUMMARY

To assess different theoretical methods, a series of calculations are performed for thiocyanate complexes of group 11 (Cu-triad) and group 12 (Zn-triad) metals. The PM3(tm) semi-empirical parametrization systematically predicted S-bonded linkage isomers to be more stable than the N-ligated counterparts. Thus, prediction of the stability of linkage isomers with PM3(tm) calculations is not always in agreement with experimental data. In general, predictions with ab initio methods are found to be reliable for neutral complexes in that the predicted ground-state linkage isomer did not change with the level of theory, although the magnitude of the energy differences is more sensitive to the basis set and the correlation method. For anionic complexes of group 11 bis(thiocyanates), the demands of the basis sets are more stringent and extensive correlation at the post-HF levels of theory is required to bring the calculations into correspondence with crystallographic data. However, it is remarkable to observe that the quantitative prediction of linkage isomer preferences for transition-metal thiocyanates, which can be done reliably using “symbiosis theory”, requires extended basis set augmentation and high levels of electron correlation.

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