Published in final edited form as:

Mol Phys. 2009 January 1; 107(8-12): 1251–1259. doi:10.1080/00268970902953596.

Assessment of the CCSD and CCSD(T) Coupled-Cluster Methods in Calculating Heats of Formation for Cu Complexes

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Abstract

Heats of formation for nine complexes of the form CuX_n ($X = \text{Cu}, \text{H}, \text{O}, \text{OH}, \text{S}, \text{F}, \text{F}_2, \text{Cl}, \text{Cl}_2$) were calculated using the CCSD and CCSD(T) coupled cluster methods with the 6-31G** and TZVP basis sets as well as the LANL2DZ basis set/pseudopotential on Cu with both the 6-31G** and TZVP basis sets applied to the nonmetal atoms. These values were compared with literature heat of formation values. A second order Douglas-Kroll-Hess relativistic correction was applied at the CCSD/TZVP and CCSD(T)/TZVP levels of theory. Overall, the CCSD(T)/TZVP level of theory with the relativistic correction was most suited for the heat of formation calculations possessing low absolute average error and RMSD and the ability to analyze each copper complex, except for the problematic case of copper(II) fluoride. Finally, experimental geometric parameters were compared with the calculated structures in such cases where these data were available. None of the investigated levels of theory predicted bond lengths consistently better than other methods, and it was determined that the most accurate bond length does not necessarily result in the most accurate calculated heat of formation value for a given complex.

Keywords

Copper; Heat of Formation; Coupled Cluster; Ab Initio

1. Introduction

Copper is an extremely relevant transition metal and is contained in a wide range of chemical systems, including biological molecules such as proteins, catalysts, reagents for enantioselective synthesis and building blocks for molecular magnets.¹⁻⁶ With its rich chemistry, copper containing systems have been the subject of much study both experimentally and theoretically.

Copper systems have been the subject of a wide range of theoretical treatments over the last two decades. Ahlrichs in 1990 studied small CuX systems and their dimers using coupled pair functional calculations, including first order relativistic effects.⁷ Other CuX systems, including tellurides, have been probed using pseudopotentials and MP2 calculations and such calculations were found to predict spectroscopic parameters that compared favorably with experiment.⁸ Terreux and coworkers probed the interactions of Cu^{2+} with glucosamine and *N*-acetylglucosamine using density functional methods and were able to successfully analyze

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Supporting Information Available: Spreadsheets detailing all heat of formation calculations at all investigated levels of theory.

the energetics of the various complex conformers.⁹ Further density functional calculations investigated the structure of copper clusters, structural and spectroscopic relationships in blue copper proteins and complexes of copper with dinitrogen.¹⁰⁻¹² DFT methods have additionally been applied in the mechanistic study of Cu-involving reactions, including alkene insertion into Cu—B bonds and cuprate conjugate addition.^{13,14} Cascella and coworkers applied hybrid TDDFT-Molecular Dynamics simulations to study the optical spectra of the Cu²⁺—azurin complex and found these methods appropriate for the faithful reproduction of experimental data.¹⁵ High level CCSD(T) calculations have been used to investigate the reactivity of copper atoms with CS₂.¹⁶ CCSD(T) calculations including relativistic effects have further been implemented in the study of metal fluorides, including CuF.¹⁷

Numerous high-quality heat of formation studies on small organic molecules are present in the literature. Of particular interest to us are methodologies incorporating coupled-cluster methods. In 2001, Dixon and coworkers showed that ΔH_f values for NH_x systems could be very accurately reproduced by CCSD(T) calculations extrapolated to the complete basis set (CBS) limit.¹⁸ A subsequent study by Feller and Dixon demonstrated the applicability of this powerful methodology to a larger set of small molecules in an excellent benchmark study.¹⁹ More recently, these calculations have been applied to the products of hydrocarbon oxidation²⁰ and *N*-alkanes²¹ containing 5, 6 and 8 carbon atoms. The most important limitation of this method pointed out in these papers is the associated computational cost as the system size is increased. This is particularly important when transition metal atoms will be incorporated in the target species, as the number of electrons present will quickly increase.

Several groups have undertaken the task of performing high quality calculations on transition metal containing systems. Balabanov and Peterson describe accurate basis sets (extracted towards the CBS limit) for transition metals Sc through Zn.^{22,23} Further work by Peterson and coworkers describes the application of the correlation consistent Composite Approach to the thermochemistry of transition metal systems.²⁴ Finally, Lu and coworkers have recently published high level calculations on transition metal-ammonia complexes at the CCSD(T) level extrapolated to the CBS limit in order to accurately predict ionization potentials.²⁵ While it may not be practical to apply the highly accurate CCSD(T)-CBS extrapolated model to larger transition metal containing systems, we desired to probe the efficacy of CCSD and CCSD(T) calculations with smaller basis sets in predicting the heats of formation of such systems, since to our knowledge this has not been examined closely.

Recently, we have conducted density functional studies incorporating twelve popular DFT methods on a series of 94 transition metal complexes using the 6-31G** and triple- ζ quality TZVP basis sets as well as the pseudopotential based LANL2DZ.^{26,27} We have also conducted studies on a series of nine ZnX_n complexes using the coupled cluster methods CCSD and CCSD(T) with the 6-31G** and TZVP basis sets alone and in combination with LANL2DZ.²⁸ Herein we extend our coupled cluster treatment to include a series of nine CuX_n complexes and report calculated ΔH_f values. We additionally compare the copper-nonmetal bond lengths with literature geometries where available.

Table 1 contains a summary of the best density functional and basis set combination for each of the nine CuX_n complexes where in each case “best” is taken as the density functional/basis set pairing producing the heat of formation closest to the experimental value. As was observed with Zn complexes, there is no universal best density functional for use in the prediction of heats of formation for CuX_n systems, with the mostly widely applicable combination being BB1K/6-31G** for five of the nine systems considered. While it is simple for small systems to choose a best functional from the list or even test several, it is desirable to have a computational methodology that is effective for a larger range of compounds. This is especially important when considering the study of larger, more substituted systems. We hypothesized

that utilizing more computationally elaborate coupled-cluster methods will provide a more broad approach to the calculation of these values in Cu complexes and test this on the nine selected CuX_n complexes.

2. Computational Methodology

All calculations were carried out on a SUN cluster featuring dual 2.5GHz Opteron nodes using the Gaussian 03³¹ suite of programs. All geometry optimizations incorporated standard gradient methods. For all single point calculations, the SCF=TIGHT keyword was used. Additionally, the SCF=XQC keyword was applied in all instances, as SCF convergence was often problematic, especially for higher energy multiplets and this is a standard procedure for attempting to correct such difficulties. CCSD and CCSD(T) calculations were run as implemented in Gaussian 03.³²⁻³⁷ Where applicable, calculations were done at the UCCSD at UCCSD(T) levels. All other calculations are closed shell. Frequency calculations were conducted on all geometries (at the minimum energy multiplicity) to insure all calculated lowest energy structures resided at local minima on the potential energy surface. The results of the frequency analysis, once deemed acceptable minima, were used in the heat of formation calculation. The 6-31G** and triple- ζ quality TZVP basis sets were used as implemented in Gaussian 03.³⁸⁻⁴⁰ LACVP** calculations were run using the GEN keyword for the basis set. In these calculations, the LANL2DZ basis/pseudopotential was used for copper and the 6-31G** basis set for the nonmetal atoms. A second set of calculations was run which applied the TZVP basis set to the nonmetals while retaining LANL2DZ on the copper atom.

For all CuX_n species considered, it was initially desired to optimize the 1, 3, 5 and 7 multiplicities for even electron species and the 2, 4, 6 and 8 multiplicities for odd electron species as done in our previous DFT work.²⁶ This worked well for most CCSD calculations, although high energy multiplicities were sometimes difficult to converge. CCSD(T) calculations failed for a large number of high energy multiplicities especially in the larger systems, although the CCSD ground state could always be converged for smaller complexes using CCSD(T) calculations.

Heats of formation (ΔH_f) for all complexes were computed using the method outlined in the Gaussian white paper on Thermochemistry in the Gaussian 03 online manual.⁴¹ These calculations follow equation (1) that simplifies to equation (2), derived from the procedures outlined in the Gaussian white paper. The 'M' and 'X' designations in equation one correspond to the molecule and individual atoms, respectively.

$$\Delta H_f(M, 298K) = \Delta H_f(M, 0K) + ((H_M(298K) - H_M(0K)) - \sum x(H_x(298K) - H_x(0K))) \quad (1)$$

$$\Delta H_f(298K) = 627.5095(E_{\text{CORR}}) + 80.64 - 627.5095(E_{\text{Cu}}) + (\Delta H_f(\text{atom}, 298K) - 627.5095(E_{\text{atom}})) \quad (2)$$

Equation 2 is in terms of the output provided by Gaussian, for convenience, where E_{CORR} is the sum of electronic and thermal enthalpies provided in output of the frequency calculation (which includes thermal and ZPE corrections to the energy). E_{Cu} and E_{atom} are the energies of the copper and nonmetal atoms at a given level of theory. The constant 80.64 (kcal/mol) in Equation 2 is the $\Delta H_f(\text{Cu}, 298K)$ taken from the NIST chemistry WebBook⁴² and the respective $\Delta H_f(\text{atom}, 298K)$ values for the nonmetals are found there as well. Finally, equation 3 was implemented in the calculation of root mean squared deviations (RMSD).

$$\sqrt{\frac{1}{n} \sum_i^n (x_i - \bar{x})^2} \quad (3)$$

3. Results and Discussion

The results of calculations using the CCSD and CCSD(T) coupled-cluster methods with the 6-31G** and LACVP** basis sets are summarized in table 2 and figure 1. CCSD(T) calculations failed for $^2\text{CuF}_2$ using both basis sets, but were successfully completed for all remaining entries. Generally, the CCSD(T) level was an improvement over CCSD level calculations. Excluding $^1\text{CuF}_2$ values, as these were not obtainable at the CCSD(T) level, the average unsigned error at CCSD(T)/6-31G** was a 3.4 kcal/mol improvement over CCSD/6-31G**, although the RMSD was actually slightly larger at the CCSD(T) level, by 1.3 kcal/mol. The same trend was observed using the LACVP** basis set, with CCSD(T) improving the average unsigned error by 1.3 kcal/mol, with a 0.5 kcal/mol higher RMSD value. For this set of calculated ΔH_f values, the CCSD(T)/6-31G** level of theory provides the best results in five of the eight studied CuX_n complexes. The three complexes for which CCSD(T)/6-31G** is not the best method are $^1\text{Cu}_2$, ^1CuH and ^2CuO . The predicted value for CuO is significantly off at the CCSD(T)/6-31G** level of theory, and it should be pointed out that this is the lone instance in the study where the incorrect ground state multiplicity was predicted by the calculations. At the CCSD(T)/6-31G** level, CuO was predicted to be a ground state quartet, with a significantly elongated C—O bond (*vide infra*). At all other theory levels, the doublet ground state was predicted for this species, in concord with the expected ground state. Langhoff and Bauschlicher pointed out in a 1986 paper the importance of using diffuse functions with copper sulfides and oxides due to the ionic nature of the bond.⁴³ Indeed, calculations at the CCSD(T)/6-31+G** level of theory were found to correctly predict the ground state and the calculated heats of formation (85.4 and 90.3 kcal/mol respectively for the oxide and sulfide) were in closer agreement with the experimental value for the oxide, while poorer for the sulfide.

The failure in predicting the heat of formation for $^2\text{CuF}_2$ at the CCSD(T)/6-31G** theory level is due to lack of convergence in the SCF on submitting the frequency job. Efforts to alleviate this problem included taking the initial guess from the checkpoint file, enforcing maximal symmetry and the removal of all symmetry constraints, to no avail. For the methods where $^2\text{CuF}_2$ could be evaluated, the results were not very good. The errors associated with these values approached 20 kcal/mol. Methods excluding CCSD(T)/6-31G** were also very poor at evaluating the heat of formation in ^2CuS , with very large errors. Conversely, the error in ^2CuS with CCSD(T)/6-31G** was very low at 2.2 kcal/mol. In the table 2 data set, nearly all calculated ΔH_f values are overestimates when compared to the literature values, with two exceptions. $^1\text{CuOH}$ is underestimated at the CCSD(T)/6-31G** level of theory and $^2\text{CuF}_2$ at the CCSD/6-31G** level.

Results of CCSD and CCSD(T) calculations with the TZVP and LANL2DZ basis sets are presented in table 3 and figure 2. All calculated values are overestimations of the literature heats of formation in this data set, with no exceptions as were observed in the 6-31G** and LACVP** data. Of the four methodologies, the CCSD(T)/TZVP level provides the best predictions of the ΔH_f values with an average unsigned error of 14.1 kcal/mol and an RMSD value of 4.8. The CCSD(T)/TZVP results are systematic improvements over their CCSD counterparts. CCSD(T)/LANL2DZ-TZVP results showed a similar improvement over their CCSD/LANL2DZ-TZVP counterparts, with average unsigned errors of 17.6 and 19.1 kcal/mol respectively. These average errors were larger than those observed using only the TZVP basis set. For each of the nine CuX_n complexes studied, the CCSD(T)/TZVP result was the

closest to the experimental value. As was observed in the 6-31G** results, the copper dihalides and copper sulfide generally had the largest associated errors, although with the exception of ${}^1\text{CuOH}$ (-6.3 kcal/mol) all calculated errors were at least 10 kcal/mol. Unlike the CCSD(T)/6-31G** case, there was no combination of a coupled-cluster method and TZVP incorporating basis set which provided a good heat of formation value for ${}^2\text{CuS}$. There were no convergence issues in the SCF with any calculations involving the TZVP or LANL2DZ-TZVP basis sets and the nine CuX_n complexes.

Overall, for the eight methodologies employed, the best ΔH_f values are calculated with the CCSD(T) coupled-cluster method and the 6-31G** and TZVP basis sets. A comparison of these two levels of theory is shown in figure 3. CCSD(T)/6-31G** ΔH_f values are superior for ${}^2\text{CuCl}_2$, ${}^1\text{CuF}$, ${}^1\text{CuOH}$ and ${}^2\text{CuS}$. The CCSD(T)/TZVP level of theory is most accurate for ${}^1\text{Cu}_2$, ${}^2\text{CuO}$, ${}^1\text{CuH}$ and ${}^1\text{CuCl}$. The latter theory level is also the only for which ${}^2\text{CuF}_2$ could be properly calculated. The unsigned average error is 13.0 kcal/mol at the CCSD/6-31G** level of theory and 14.1 at CCSD(T)/TZVP however the latter value includes the result for ${}^2\text{CuF}_2$. Removal of this entry results in an average unsigned error of 13.1 kcal/mol, so both levels of theory are comparable in that respect. The largest and smallest overall errors are calculated using the 6-31G** basis set whereas less of a range is predicted with TZVP. This is reflected in the twofold decrease in RMSD error upon switching from 6-31G** to TZVP (10.9 to 4.8 kcal/mol). These observations are consistent with previous DFT work on metal containing systems, where increasing the basis set size did not necessarily correspond to an increase in the predicted ΔH_f value.²⁶

Relativistic Correction

We decided to further our investigation by applying a Douglas-Kroll-Hess 2nd order relativistic correction (DKH) to calculations at the CCSD/TZVP and CCSD(T)/TZVP levels of theory as implemented in Gaussian 03.⁴⁴⁻⁴⁸ This correction was applied during the course of both the geometry optimizations and frequency analyses and these results are summarized in tables 4 and 5. At the CCSD/TZVP theory level, the average unsigned error drops by 2.7 kcal/mol with the addition of this correction, with eight of the nine calculated values improving over the uncorrected values. The lone entry that does not improve is ${}^2\text{CuS}$, whose predicted ΔH_f value worsens by 0.6 kcal/mol. It should be pointed out that the experimental error bar in ${}^2\text{CuS}$ is relatively high at 5.0 kcal/mol, or 6.7% of the reported literature value. The amount of improvement observed in the remaining eight entries varies, with ${}^1\text{CuF}$ and ${}^1\text{CuCl}$ only improving by 0.4 kcal/mol, while ${}^2\text{CuCl}_2$ and ${}^2\text{CuF}_2$ improve by 7.5 and 7.2 kcal/mol respectively. The ${}^1\text{Cu}_2$ ΔH_f value improves by 2.8 kcal/mol with the addition of the relativistic correction and the calculated ${}^1\text{CuH}$ ΔH_f value is 2.7 kcal/mol closer to the experimental. There is also good improvement in both corrected ΔH_f values calculated for the oxygen-containing species, 2.2 kcal/mol for ${}^2\text{CuO}$ and 2.5 kcal/mol in ${}^1\text{CuOH}$. These two oxygenated Cu species also have high experimental errors associated with their reported heat of formation value, 10 kcal/mol (13.1%) in ${}^2\text{CuO}$ and 4 kcal/mol (13.9%) in ${}^1\text{CuOH}$. Still, as both the corrected and uncorrected CCSD/TZVP ΔH_f values are overestimates, it is safe to conclude that the improvement observed in each of the eight cases reported is indeed real and not a statistical anomaly.

Inclusion of the DKH relativistic correction at CCSD(T)/TZVP provides a slightly better improvement in the calculated ΔH_f values over their CCSD counterparts. ${}^2\text{CuO}$ and ${}^1\text{CuOH}$ had calculated heats of formation closest to the experimental, deviating by 5.6 and 4.6 kcal/mol respectively. The value for ${}^2\text{CuF}_2$ could not be determined due to convergence problems similar to those observed at the CCSD(T)/6-31G** and CCSD(T)/LACVP** levels of theory, but for the remaining entries the average unsigned error is 10.8 kcal/mol with a RMSD of 4.0 kcal/mol which represents an improvement over CCSD(T)/TZVP without the inclusion of the

relativistic correction, even if the error for $^2\text{CuF}_2$ is excluded from the average. As was the case with the CCSD/TZVP level, addition of the 2nd order DKH correction at CCSD(T)/TZVP resulted in a slight worsening of the predicted H_f value for ^2CuS . This was the lone instance in each data set where inclusion of relativistic effects worsened the calculated value.

Geometries

Calculated bond lengths are compared to available experimental values in Table 6. The CCSD/LACVP** level of theory most closely predicts the metal-nonmetal distance in ^2CuO , ^1CuF and $^2\text{CuF}_2$. The CCSD(T)/TZVP theory level is best at predicting this distance in $^1\text{Cu}_2$ and $^2\text{CuCl}_2$. The remaining closest values are scattered amongst the remaining levels of theory. It is worth pointing out that while CCSD/LACVP** may be suitable for predicting bond lengths closer to the experimental, the resulting heat of formation values in these instances were poor in comparison with some of the other methods that did not reproduce the bond length as well. In ^2CuS , while there is no experimental distance to compare with, it can be pointed out that the CCSD and CCSD(T) distances with the 6-31G** basis set are lower than the other six entries that are grouped more closely together.

For $^2\text{CuF}_2$ and $^2\text{CuCl}_2$ the experimental bond angles are 180 degrees and this was observed in most instances. The notable exceptions are in $^2\text{CuF}_2$ at the CCSD/6-31G** and CCSD(T)/6-31G** levels of theory. Here, the linear geometry was predicted to be a transition state and the optimized ground state structure possessed a F-Cu-F angle of approximately 172 degrees, a deviation of eight degrees from the experimental value. This geometric discrepancy surely contributed to the poorly predicted heats of formation for this complex. The Cu-O-H angle in $^1\text{CuOH}$ is 110.2 degrees. The calculated bond angles at CCSD/TZVP, CCSD(T)/LACVP** and CCSD(T)/LANL2DZ-TZVP were within 0.2 degrees of the experimental, and all other theory levels agreed within 2.4 degrees. There seems to be no trend relating accuracy in the geometry prediction with the determination of accurate ΔH_f values.

4. Conclusions

Heats of formation were calculated for nine CuX_n complexes using the CCSD and CCSD(T) coupled cluster methods in conjunction with the 6-31G**, LACVP**, TZVP and LANL2DZ-TZVP basis sets. The best correlation with experimental values were obtained with the CCSD(T)/6-31G** and CCSD(T)/TZVP levels of theory. Applying a second order Douglas-Kroll-Hess relativistic correction at the CCSD(T)/TZVP level of theory resulted in reduction of the absolute average error and RMSD, while a slightly lesser overall improvement was achieved applying the same correction at the CCSD/TZVP level. Clearly for determining ΔH_f values in these copper complexes the CCSD(T)/TZVP level of theory including a second order DKH relativistic correction is most appropriate when considering standard coupled cluster calculations in conjunction with reasonable basis sets. The fact that the best results were obtained at the CCSD(T)/TZVP level of theory with a relativistic correction for these copper systems is not a trivial observation. Previous DFT studies show that increasing the basis set does not always produce better results, nor does raising the quality of the applied density functional method.²⁶ The lone exception to this observation was in $^2\text{CuF}_2$, where no method was particularly appropriate; some due to lack of convergence in general and other methodologies due simply to poor predicted ΔH_f values.

The most accurate prediction of metal-nonmetal bond distances was scattered across the levels of theory investigated. There was also observed to be no correlation between accurate bond length prediction and the determination of an accurate ΔH_f value. Multiplicities in these CuX_n species were generally correctly predicted, with the lone exception of CuO which was found to be a ground state quartet at the CCSD(T)/6-31G** level of theory as opposed to the doublet predicted by all other levels. The ground state was properly predicted at the CCSD(T)/

6-31+G** level of theory. The resulting bond length was substantially elongated and the predicted ΔH_f value deviated greatly from the experimental, which reinforces the idea that accurate determination of the ground state spin multiplicity is critical in these endeavors.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

We thank the NIH (GM066859 and GM44974) for supporting this research. MNW wishes to thank the NIH for support in the form of an NRSA postdoctoral fellowship (F32GM079968).

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Figure 1. CCSD and CCSD(T) calculated vs. experimental ΔH_f values with the 6-31G** and LACVP** basis sets.

Figure 2.
CCSD and CCSD(T) calculated vs. experimental ΔH_f values with the TZVP and LANL2DZ-TZVP basis sets.

Figure 3.
Comparison of CCSD(T)/6-31G** and CCSD(T)/TZVP calculated ΔH_f values.

Table 1

Experimental^{29,30} and DFT ΔH_f values for Cu complexes

Best Density Functional Calculation ^d						
Experimental			6-31G**		TZVP	
Entry	ΔH_f	Error ^b	ΔH_f	Method	ΔH_f	Method
Cu ₂	113.8	2.6	113.33	PBE/PPBE	113.99	MPWPW91
CuH	65.9	2.0	63.83	TPSS/KCIS	67.95	TPSS/TPSS
CuO	76.5	10.0	68.79	BB1K	77.44	TPSS/KCIS
CuOH	28.7	4.0	17.41	BB1K	28.93	PBE/PPBE
CuS	75.1	5.0	78.41	BB1K	75.61	BB95
CuF	-3.2	2.0	0.75	BB1K	-0.53	BB95
CuF ₂	-66.0	---	-95.22	BB1K	-64.66	MPWPW91
CuCl	19.3	2.0	17.17	PBE/PPBE	23.74	TPSS/TPSS
CuCl ₂	-9.0	---	-19.39	B3LYP	-11.42	TPSS/KCIS

^aFrom Riley and Merz²⁶

^bError bars not provided for dihalides; all experimental values from ref. 29 except for CuCl₂ (ref. 30)

Table 2

CCSD and CCSD(T) ΔH_f Values for Cu Complexes; 6-31G**

Entry	ΔH_f (exp)	6-31G**			LACVP**a	
		CCSD	CCSD(T)	CCSD(T)	CCSD	CCSD(T)
¹ Cu ₂	113.8	144.91	138.4	128.25	128.25	125.74
¹ CuH	65.9	87.26	84.77	82.98	82.98	82.3
² CuO	76.5	88.31	105.87 ^q	93.99	93.99	92.05
¹ CuOH	28.7	32.06	26.18	41.21	41.21	39.2
¹ CuCl	19.3	37.92	35.92	37.05	37.05	36.3
² CuCl ₂	-9	-3.51	-5.65	34.29	34.29	34.2
¹ CuF	-3.2	7.96	2.89	15.01	15.01	14.52
² CuF ₂	-66	-83.88	---	-45.88	-45.88	---
² CuS	75.1	103.77	77.3	100.59	100.59	98.82
Average Unsigned Error ^b		16.6 (16.4)	13.0	20.7 (20.8)		19.5
RMSD		14.1 (9.6)	10.9	8.7 (9.2)		9.7

^aLANL2DZ on Cu; 6-31G** on nonmetal atoms^bNumbers in parentheses exclude ²CuF₂ for the purpose of comparison with CCSD(T) results^qQuartet ground state predicted

Table 3

CCSD and CCSD(T) ΔH_f Values for Cu Complexes; TZVP

Entry	ΔH_f (exp)	TZVP		LANL2DZ-TZVP ^a	
		CCSD	CCSD(T)	CCSD	CCSD(T)
¹ Cu ₂	113.8	128.43	125.06	128.25	125.74
¹ CuH	65.9	79.05	77.83	80.35	79.45
² CuO	76.5	91.17	87.74	93.92	91.16
¹ CuOH	28.7	38.83	34.96	39.60	36.08
¹ CuCl	19.3	31.88	30.79	34.33	33.45
² CuCl ₂	-9	12.75	10.85	28.36	28.20
¹ CuF	-3.2	13.17	11.41	13.62	12.02
² CuF ₂	-66	-40.47	-43.56	-43.54	-42.79
² CuS	75.1	95.56	93.21	98.27	96.34
Average Unsigned Error		16.6	14.1	19.1	17.6
RMSD		4.7	4.8	7.4	8.2

^a LANL2DZ on Cu; TZVP on nonmetal atoms

Table 4

CCSD/TZVP ΔH_f values with and without 2nd order DKH relativistic correction CuX_n complexes.

Entry	ΔH_f (exp)	CCSD/TZVP		CCSD/TZVP w/ DKH	
		ΔH_f	Error	ΔH_f	Error
¹ Cu ₂	113.8	128.43	-14.6	125.6	-11.8
¹ CuH	65.9	79.05	-13.2	76.4	-10.5
² CuO	76.5	91.17	-14.7	89.0	-12.5
¹ CuOH	28.7	38.83	-10.1	37.3	-8.6
¹ CuCl	19.3	31.88	-12.6	31.5	-12.2
² CuCl ₂	-9	12.75	-21.8	5.3	-14.3
¹ CuF	-3.2	13.17	-16.4	12.8	-16.0
² CuF ₂	-66	-40.47	-25.5	-47.7	-18.3
² CuS	75.1	95.56	-20.5	96.2	-21.1
Average Unsigned Error		---	16.6	---	13.9
RMSD		---	4.7	---	3.7

Table 5

CCSD(T)/TZVP ΔH_f values with and without 2nd order DKH relativistic correction CuX_n complexes.

Entry	ΔH_f (exp)	CCSD(T)/TZVP		CCSD(T)/TZVP w/DKH	
		ΔH_f	Error ^a	ΔH_f	Error ^a
¹ Cu ₂	113.8	125.06	-11.3	121.92	-8.1
¹ CuH	65.9	77.83	-11.9	75.07	-9.2
² CuO	76.5	87.74	-11.2	85.06	-5.6
¹ CuOH	28.7	34.96	-6.3	33.25	-4.6
¹ CuCl	19.3	30.79	-11.5	30.36	-11.1
² CuCl ₂	-9	10.85	-19.8	3.56	-12.6
¹ CuF	-3.2	11.41	-14.6	11.03	-14.2
² CuF ₂	-66	-43.56	-22.4	---	---
² CuS	75.1	93.21	-18.1	93.54	-18.4
Average Unsigned Error ^a	---	---	14.1 (13.1)	---	10.8
RMSD	---	---	4.8 (4.0)	---	4.0

^aNumbers in parentheses exclude ²CuF₂ for the purpose of comparison

Table 6

Comparison of calculated and experimental²⁹ bond lengths. All values are in Ångstroms. Closest calculated values are in **bold** font.

CCSD					
Entry	M-X (Exp)	6-31G**	TZVP	LACVP**	LAN/TZVP ^a
¹ Cu ₂	2.220	2.052	2.323	2.357	2.357
¹ CuH	1.463	1.417	1.494	1.519	1.490
² CuO	1.724	1.619	1.803	1.732	1.770
¹ CuOH	1.769	1.706	1.812	1.808	1.834
¹ CuF	1.745	1.678	1.795	1.758	1.812
² CuF ₂	1.713	1.699	1.741	1.719	1.748
¹ CuCl	2.051	2.022	2.126	2.159	2.157
² CuCl ₂	2.036	2.096	2.092	2.115	2.107
² CuS	---	1.917	2.147	2.189	2.182
CCSD(T)					
Entry	M-X (Exp)	6-31G**	TZVP	LACVP**	LAN/TZVP ^a
¹ Cu ₂	2.220	2.043	2.304	2.342	2.342
¹ CuH	1.463	1.417	1.483	1.513	1.480
² CuO	1.724	2.018 ^q	1.786	1.713	1.747
¹ CuOH	1.769	1.707	1.810	1.809	1.836
¹ CuF	1.745	1.683	1.793	1.758	1.813
² CuF ₂	1.713	---	1.741	---	1.749
¹ CuCl	2.051	2.014	2.120	2.157	2.154
² CuCl ₂	2.036	2.095	2.090	2.117	2.108
² CuS	---	1.959	2.132	2.178	2.170

^a LANL2DZ on Cu; TZVP on nonmetal atoms

^q Quartet ground state predicted