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# A Density Functional Study of the Reactivity and Stability of Mixed Copper Complexes. Is Hardness the Reason?

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Mixed-ligand $Cu^{2+}$ ternary complexes, formed by an aromatic diimine and a second ligand with O donor atoms, show a higher than expected stability. To understand the factors affecting the stability of these systems, we performed a density functional study of $[Cu(H_2O)_5]^{2+}$, $[Cu(N\text{-}N)(H_2O)_3]^{2+}$, and $[Cu(N\text{-}N)(O\text{-}O)H_2O]$ {N-N is 1,10-phenanthroline, 5-nitro-1,10-phenanthroline, or 3,4,7,8-tetramethyl-1,10-phenanthroline; and O-O is oxalate}. In the present study, full geometry optimization (B3LYP/3-21G**) has been performed without symmetry constraints and a comparison with some available experimental results has been made. Bond distances, equilibrium geometries, harmonic frequencies, and net atomic charges from Mulliken populations are presented. Since the principle of hard and soft acids and bases has been widely used to explain the stability of these complexes, we also calculated and analyzed the global hardness and the local softness. The results of the global hardness do not support the commonly held idea that harder acids will preferably bind to harder ligands, while softer acids will bind to softer ligands. Interestingly, local softness and electron affinity correlate well with the formation constants of these compounds and provide an explanation of the reactivity behavior. The present results may help to rationalize the stability and reactivity of these systems.

## Introduction

Several systematic studies of mixed-ligand $Cu^{2+}$ ternary complexes show that the stability of those compounds formed by an aromatic diimine and a second ligand with O as donor atoms is unexpectedly high.[1−4] It has been stated that ligands containing O as donor atoms form more stable complexes with the $[Cu(N\text{-}N)]^{2+}$ than with the free (hydrated) $Cu^{2+}$ ion.[1,2] This feature is very surprising due to the fact that more coordination positions are available for bonding of the first ligand to a given metal ion than for the second ligand. Sigel et al.[1,2] explained this behavior based on the principle of hard and soft acids and bases.[5−7] A $\pi$-acceptor ligand bound to a copper ion will withdraw electron density from it. As a result, $[Cu(N\text{-}N)]^{2+}$ becomes a harder acid and will consequently be preferred by hard bases such as oxygen donors, over the simple aqueous $Cu^{2+}$ ion.

It is well-known that different substituents on a phenanthroline molecule affect its basicity, or $\sigma$-donor ability, in a way easily quantified by p$K_a$ values. A significant effect of the same substituents on the $\pi$-acceptor properties of phenanthroline is also expected. An experimental parameter widely accepted to indirectly measure this effect is the half wave potential ($E_{1/2}$). Sanna et al.[8] have obtained $E_{1/2}$ values for several phenanthrolines and reported an inverse correlation with p$K_a$ values.

There is no experimental data for stability constants for ternary Cu complexes with substituted phenanthrolines due, probably, to their low solubility. However, to evaluate the effect caused by the substituent on the phenanthroline molecule on the strenght of the interaction between Cu(x-phen) and (O-O), Gasque et al.[3] studied the variations on the Cu−O stretching frequencies in 32 isostructural mixed copper complexes containing different substituted phenanthrolines and oxygen donor bidentate ligands. They found differences in strength interactions of copper(II) with oxygen atoms and also reported a linear correlation between phenanthroline p$K_a$ values and the vibration frequencies, suggesting that an increase in phenanthroline basicity weakens Cu−O bonds in this type of compounds. These results are consistent with other quantitative analysis of ligand effects (QALE)[9−12] studies in which it has been established that

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the $\pi$-acceptor properties of a ligand decrease regularly as their basicity increases.

The application of density functional theory (DFT) to a variety of problems in chemistry has increased dramatically in recent years.[13] DFT is a theory (in principle an exact theory) of electronic structure, based on the electron density distribution.[14,15] DFT methods compute electron correlation through functionals of the electron density. Since the functional of the density that exactly reproduces the ground-state energy of any molecular system is not known, different approximate forms of this functional have been developed. These functionals differ in their treatment of the exchange and correlation contributions. One of these approximate forms consists of a new class of hybrid Hartree–Fock/DFT functionals.[16] These hybrid functionals, such as B3LYP,[17] yield accurate results for many systems containing transition metal atoms.[16,18–20] As an example, Mire et al.[13] evaluated the performance of several density functionals on four problems in inorganic chemistry. They reported that B3LYP differs from MP2 by an average of 0.021% Å and discovered that DFT calculations can reproduce the G2 energies at least as well as MP4 calculations. In addition, density functional language has a great strength due to its definitions of important universal concepts of molecular structure and molecular reactivity. Recent works based on DFT[7,21] have developed the concepts of absolute electronegativity and absolute hardness. Within this theory, the operational and approximate definitions are

| abs electronegativity | abs (global) hardness | abs (global) softness |
|---|---|---|
| $X = {}^1/_2(I + A)$ | $\eta = {}^1/_2(I - A)$ | $S = 1/\eta$ |

where $I$ is the vertical ionization potential and $A$ is the vertical electron affinity. (See Methodology). It is also possible to use density functional theory and molecular orbital theory to calculate the local softness and the condensed local softness in order to carry out a more detailed analysis of the different effects that have an influence on the chemical reactivity. The local softness[22] is given by

$$s(\mathbf{r}) = Sf(\mathbf{r})$$

where $S$ is the global softness and $f(\mathbf{r})$ is the Fukui function.[23] Recently,[24,25] an alternative procedure to obtain information about $f(\mathbf{r})$ was reported. This procedure condenses the values around each atomic site into a single value that characterizes the atom in the molecule. With this approximation, the condensed Fukui function becomes

$$f^{+}_{\mathrm{AK}} = q_{\mathrm{AK}}(N_{\mathrm{A}} + 1) - q_{\mathrm{AK}}(N_{\mathrm{A}}) \text{ for nucleophilic attack}$$

$$f^{-}_{\mathrm{AK}} = q_{\mathrm{AK}}(N_{\mathrm{A}}) - q_{\mathrm{AK}}(N_{\mathrm{A}} - 1) \text{ for electrophilic attack}$$

$$f^{0}_{\mathrm{AK}} = {}^1/_2[q_{\mathrm{AK}}(N_{\mathrm{A}} + 1) - q_{\mathrm{AK}}(N_{\mathrm{A}} - 1)] \text{ for radical attack}$$

while the condensed local softness is given by

$$s^{+}_{\mathrm{AK}} = S_{\mathrm{A}}f^{+}_{\mathrm{AK}}$$

$$s^{-}_{\mathrm{AK}} = S_{\mathrm{A}}f^{-}_{\mathrm{AK}}$$

$$s^{0}_{\mathrm{AK}} = S_{\mathrm{A}}f^{0}_{\mathrm{AK}}$$

where $q_{\mathrm{AK}}$ is the charge of the $k$th atom in the molecule A. The systems with $N + 1$, $N$, and $N - 1$ electrons are calculated with the ground-state geometries of the $N$-electron system. The simplest procedure to determine the charge is to make use of a Mulliken population analysis. The Fukui function provides the same information as the local softness. The regions of a molecule where the Fukui function is large are chemically softer than the regions were the Fukui function is small.

To explain the behavior of mixed-ligand $\mathrm{Cu}^{2+}$ complexes, we have performed a density functional study of $[\mathrm{Cu(H_2O)_6}]^{2+}$, $[\mathrm{Cu(N\text{-}N)(H_2O)_3}]^{2+}$, and $[\mathrm{Cu(N\text{-}N)(O\text{-}O)H_2O}]$ {N-N is 1,10-phenanthroline (phen), 5-nitro-1,10-phenanthroline ($5\mathrm{NO_2}$-phen), or 3,4,7,8-tetramethyl-1,10-phenanthroline (3,4,7,8-phen); and O-O is oxalate (ox)}. These aromatic diimines were selected due to their p$K_\mathrm{a}$ values. For phen, the p$K_\mathrm{a}$ is 4.93, while for $5\mathrm{NO_2}$-phen it is 3.22 and for 3,4,7,8-phen it is 6.31. With these systems, it is possible to study the behavior of the Cu–O frequencies when the p$K_\mathrm{a}$ values increase.

Full geometry optimization has been performed without symmetry constraints, and a comparison with some available experimental results has been made. Bond distances, equilibrium geometries, harmonic frequencies, ionization potential, and electron affinity are presented. Since the principle of hard and soft acids and bases was used previously to explain the stability of these complexes, the global hardness and the local softness of these systems were calculated and analyzed. The present results allow the experimental behavior of these systems to be rationalized, providing a better understanding of the electronic structure, the stability, and the reactivity of mixed copper complexes.

## Methodology

Full geometry optimization without symmetry constraints was performed using Gaussian 94[26] at the B3LYP level. The basis used was 3-21G** for all the atoms. Optimized geometries were verified performing frequency calculations. For $[\mathrm{Cu(H_2O)_5}]^{2+}$ and $[\mathrm{Cu(N\text{-}N)(H_2O)_3}]^{2+}$ the "anion" and the cation are charged 1+ and 3+, respectively, as the double charge compound is the reference system for the calculation of the ionization potential and the electron affinity. No optimization was performed either for the anion or for the cation, because the global hardness is defined with the vertical ionization potential and the vertical electron affinity. To obtain the vertical ionization potential and electron affinity, single point calculations were performed for the cation and the anion with the optimized geometry

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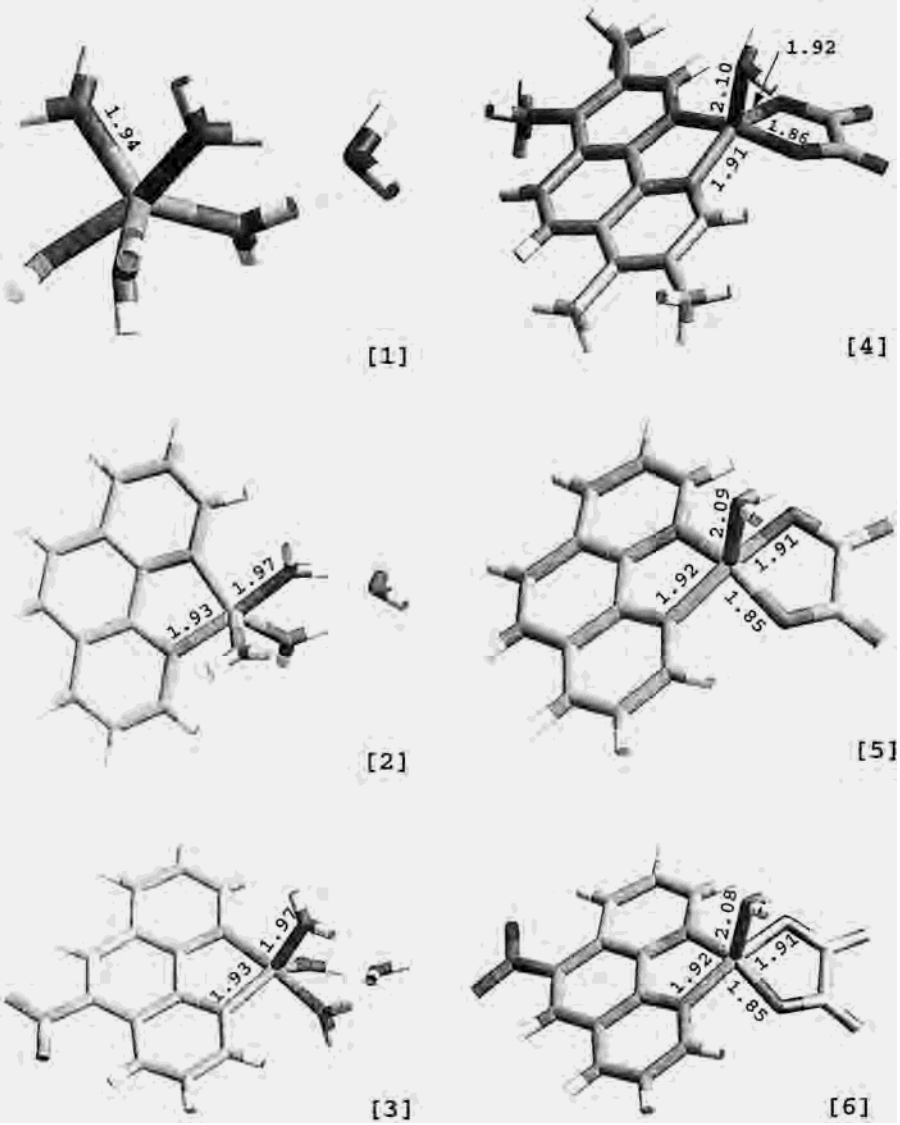

**Figure 1.** Optimized geometries for **[1]** $[Cu(H_2O)_5]^{2+}$, **[2]** $[Cu(phen)(H_2O)_3]^{2+}$, **[3]** $[Cu(5NO_2\text{-}phen)(H_2O)_3]^{2+}$, **[4]** [Cu(3,4,7,8-phen)(ox)$H_2O$], **[5]** [Cu(phen)(ox)$H_2O$], and **[6]** [Cu($5NO_2$-phen)(ox)$H_2O$]. All the calculations were performed with the B3LYP functional, 3-21G** basis.

for $[Cu(H_2O)_5]^{2+}$ and $[Cu(N\text{-}N)(H_2O)_3]^{2+}$, and the neutral optimized geometry for [Cu(N-N)(O-O)$H_2O$]. In all cases, we keep the spin multiplicity fixed.

Mulliken charges were used for computing the condensed Fukui functions. To see if the Mulliken charges are accurate, we have performed single point calculations for $[Cu(H_2O)_5]^{2+}$ and $[Cu(phen)(H_2O)_3]^{2+}$ with two other bases (3-21G and 6-311G**). The qualitative conclusions are unchanged, so the following discussion will be presented using the results with the 3-21G** basis set.

## Results and Discussion

This section is organized into three subsections. Section A describes the results of the geometry optimization and the harmonic frequencies. Section B discusses the results of the ionization potential and the electron affinity. In section C, we present an analysis of the global hardness and the local softness.

**A. Geometry Optimization and Harmonic Frequencies.** The optimized geometries for $[Cu(H_2O)_5]^{2+}$, $[Cu(phen)(H_2O)_3]^{2+}$, $[Cu(5NO_2\text{-}phen)(H_2O)_3]^{2+}$, [Cu(3,4,7,8-phen)(ox)$H_2O$], [Cu(phen)(ox)$H_2O$], and [Cu($5NO_2$-phen)(ox)$H_2O$] are shown in Figure 1.

When analyzing $[Cu(H_2O)_5]^{2+}$, it is important to mention that the initial geometry used for the optimization included six water molecules bonded to the copper atom. After optimization, only five water molecules remain bonded to the copper atom, no bond existing between the sixth water molecule and the metal atom. For $[Cu(phen)(H_2O)_3]^{2+}$ and $[Cu(5NO_2\text{-}phen)(H_2O)_3]^{2+}$ similar results are obtained, i.e., the initial geometries include four water molecules and after optimization only three bonded water molecules remain. Selected bond distances and angles for [Cu(phen)(ox)$H_2O$] and available experimental results[27] are shown in Table 1. As can be seen, in both cases Cu−$OH_2$ distances (between the copper and the oxygen atom of the water molecule) are longer than Cu−N and Cu−O. Experimental and theoretical bond distances and angles are similar. The distortion with respect to the square pyramid of the theoretical structure is bigger than the experimental one, as indicated by the angles and the Cu−O bond distances. For the calculated structure, the Cu−O1 bond distance is shorter than Cu−O2, while these distances have been shown to be equal. The calculation of the

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**Table 1.** Our Results and Available Experimental Results for $[Cu(phen)(ox)H_2O]$[a]

| | B3LYP (Å) | expt (Å) | | B3LYP (deg) | expt (deg) |
|---|---|---|---|---|---|
| Cu−OH$_2$ | 2.09 | 2.237 | N1−Cu−N2 | 84.3 | 82.8 |
| Cu−N1 | 1.92 | 2.010 | O1−Cu−O2 | 87.8 | 85.4 |
| Cu−N2 | 1.92 | 2.010 | N1−Cu−O2 | 88.9 | 94.2 |
| Cu−O1 | 1.85 | 1.94 | N2−Cu−O1 | 90.1 | 94.7 |
| Cu−O2 | 1.91 | 1.94 | | | |
| C14−O4 | 1.23 | 1.217 | | | |

[a] All the calculations were performed with the B3LYP functional and 3-21G** basis set. Experimental results from ref 27.

structure generally underestimates the bond distances. However, the differences between theoretical and experimental results are not very large and not very relevant for the stability analysis that we report below. These small differences may be attributed to the fact that the structure calculation is performed in the gas phase and is thus expected to vary from that obtained in the solid state. Nonetheless, the obtained results are quite satisfactory and they agree well with experimental data. We feel confident that the basis and the functional used in this study adequately perform the geometry optimization of these systems.

All the calculated vibration frequency values are positive, and it can be said that the optimized structures are local minima on the potential energy surface. Relevant calculated and obtained vibration frequencies are shown in Table 2. Cu−O related frequencies decrease as the substituted phenanthrolines' $\sigma$-donor strength (p$K_a$) increases, and both the calculated and experimental values follow this trend (experimental shifts are larger than the computed values). We are thus encouraged to say that reactivity and stability studies may be followed on the basis of the theoretical studies performed on these compounds in the gas phase. Cu−O vibrations are coupled with other vibrations that do not compromise the Cu−O bond as is generally the case in mixed-ligand systems. Regardless of this, the Cu−O frequencies correlate with substituted phenanthroline p$K_a$ values quite satisfactorily. The good agreement between theoretical and experimental values further confirms the obtained geometry optimization results.

**B. Ionization Potential and Electron Affinity.** In Table 3 the vertical ionization potential and the vertical electron affinity of $[Cu(H_2O)_5]^{2+}$, $[Cu(N\text{-}N)(H_2O)_3]^{2+}$, and $[Cu(N\text{-}N)(O\text{-}O)H_2O]$ are reported. As it was pointed out before in the Introduction, different substituents on a phenanthroline molecule affect its basicity (or $\sigma$-donor ability). Data presented in Table 3 show that the ionization potential values increase while the p$K_a$ values for the different substituted phenanthrolines decrease, indicating that the basicity of the diimine is related to the ionization potential of the compounds. The more basic phenanthrolines yield a lower ionization potential. In this way, ionization can be related with the $\sigma$-donor ability of the compounds.

As was established in the Introduction, a significant effect of the same substituents on the $\pi$-acceptor properties of phenanthroline is also expected. An experimental parameter widely accepted to indirectly measure these $\pi$-acceptor properties is the half-wave potential. For compounds with copper and different substituted phenanthrolines (L) an inverse correlation between the $E_{1/2}$ $[CuL_2]^{2+}/[CuL_2]^{1+}$ and p$K_a$ values of the diimine has been reported.[8] This means that there is an inverse correlation between the $\pi$-acceptor properties of the copper−diimine complexes and the p$K_a$ values of the diimine. The $\pi$-acceptor properties can be related with the electron affinity. For $[Cu(N\text{-}N)(H_2O)_3]^{2+}$, the LUMO is a $\pi$-orbital of phen and 5NO$_2$-phen. In $[Cu(N\text{-}N)(H_2O)_3]^{1+}$ this orbital is occupied, supporting the idea that the $\pi$-acceptor properties are related to the electron affinity. Table 3 shows an inverse correlation between the electron affinity ($\pi$-acceptor properties) of $[Cu(N\text{-}N)(H_2O)_3]^{+2}$ and the p$K_a$ values of the different substituted phenanthrolines, in agreement with the experimental results.[8] The same behavior was found for ternary compounds with diimines and oxalate, as can be seen in Table 3. The LUMO is a $\pi$-orbital of the diimine, and for this reason the $\pi$-acceptor properties can also be related to the electron affinity of the ternary compounds. These results confirm that the basicity of the diimine affects the electron affinity of the ternary compounds.

The effect of the diimine's basicity on the ionization potential and the electron affinity of the copper ternary chelates is quite similar to the effect on the copper−phenanthroline complexes without the oxalate. The compounds with and without the oxalate present similar behavior. However, the ionization potential and the electron affinity are much higher for the complexes without the oxalate. This was expected due to the global charge of the compounds. Without the oxalate, the compounds have a charge equal to 2+, while with oxalate the compounds are neutral, and this also accounts for the reduced electron affinity values.

**C. Global Hardness and Local Softness.** In Table 3, the global hardness of the compounds is also reported.It was pointed out in the Introduction that ligands containing O as donor atoms form more stable complexes with the $[Cu(N\text{-}N)]^{2+}$ complex than with the free (hydrated) $Cu^{2+}$ ion. This surprising result was explained by Sigel et al.[1,2] based on the principle of hard and soft acids and bases.[5−7] If $[Cu(N\text{-}N)]^{2+}$ were to be a harder acid, it would consequently be preferred, over simple aqueous $Cu^{2+}$ ion, by hard bases such as oxygen donors. To corroborate this hypothesis, the global hardness of $[Cu(H_2O)_5]^{2+}$ and $[Cu(phen)(H_2O)_3]^{2+}$ was analyzed. The hardness of the fragments, i.e., those without two water molecules, was also investigated. This models the reaction that considers the separation of two water molecules prior to the reaction with the oxalate. These results are illustrated in Figure 2. As can be seen, the simple aqueous $Cu^{2+}$ ion is harder than the $[Cu(phen)(H_2O)_3]^{2+}$ cationic species. This is also observed with the fragments considered. This result is in agreement with the symbiotic effect described by Jørgensen[28] (harder ligands contribute to increase the global hardness). The water molecule is harder than the phenanthroline, and for this reason the hardness of the simple aqueous $Cu^{2+}$ ion is larger. With the global hardness, the principle of hard and soft acids and bases cannot explain the stability of these systems. A similar conclusion had been arrived at earlier by Martin.[29] He investigated the correlation between stability constants and quantitative values of a proposed hardness parameter for metal ions and found that metal ion electron affinity correlates much better than hardness or softness with metal complex stability constants. Following this approach, we analyzed the electron affinity of $[Cu(H_2O)_5]^{2+}$ and $[Cu(phen)(H_2O)_3]^{2+}$. The results shown in Table 3 indicate that the electron affinity of $[Cu(phen)(H_2O)_3]^{2+}$ is larger than the electron affinity of $[Cu(H_2O)_5]^{+2}$. Hence, $[Cu(phen)(H_2O)_3]^{2+}$ can accept electrons more easily during the reaction with anions like oxalate than $[Cu(H_2O)_5]^{2+}$. This favors the reaction between $[Cu(phen)(H_2O)_3]^{2+}$ and oxalate, in agreement with the stability constant values.

It is important to note that the calculations of the global hardness for ions can be troublesome because these calculations

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**Table 2.** Most Important Frequency Values (in $cm^{-1}$) of the Most Stable Structures[a]

| compound | description of the vibration | B3LYP | expt |
|---|---|---|---|
| [Cu(3,4,7,8-phen)(oxa)$H_2O$] | C=O (stretching) | 1671 | 1658 |
| p$K_a$ = 6.31 | Cu−O coupled with C−C | 498, 525 | 528 |
| | Cu−O coupled with the deformation of the ring (oxalate) | 455 | 412 |
| [Cu(phen)(oxa)$H_2O$] | C=O (stretching) | 1673 | 1663 |
| p$K_a$ = 4.93 | Cu−O coupled with C−C | 528, 534 | 546 |
| | Cu−O coupled with the deformation of the ring (oxalate) | 458 | − |
| [Cu(5$NO_2$-phen)(oxa)$H_2O$] | C=O (stretching) | 1675 | 1678 |
| p$K_a$ = 3.22 | Cu−O coupled with C−C | 531, 535 | 570 |
| | Cu−O coupled with the deformation of the ring (oxalate) | 460 | 436 |

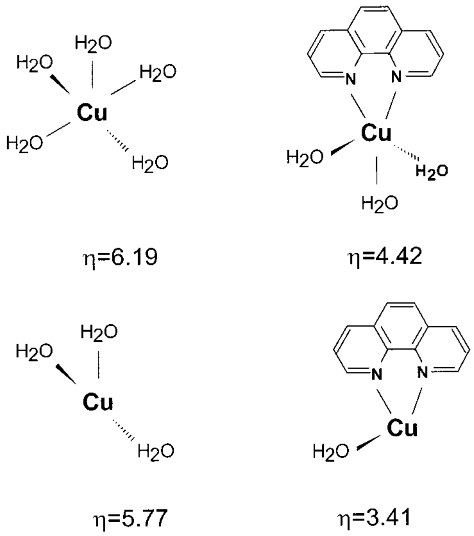
[a] All the calculations were performed with the B3LYP functional and 3-21G** basis set. Some available experimental results are included for comparison. (The p$K_a$ values correspond to the substituted phenanthrolines.)

**Table 3.** Ionization Potential (*I*), Electron Affinity (*A*), and Global Hardness ($\eta$, Calculated as $^1/_2(I - A)$) of the Compounds under Study[a]

| | $[Cu(H_2O)_5]^{2+}$ | $[Cu(phen)(H_2O)_3]^{2+}$ p$K_a$ = 4.93 | $[Cu(5NO_2\text{-phen})(H_2O)_3]^{2+}$ p$K_a$ = 3.22 |
|---|---|---|---|
| *I* | 18.43 | 14.98 | 15.15 |
| *A* | 6.04 | 6.14 | 6.48 |
| $\eta$ | 6.19 | 4.42 | 4.33 |
| $f^{+}_{Cu}(r)$ | −0.60 | −0.27 | −0.24 |

| | [Cu(3,4,7,8-phen)(oxa)] p$K_a$ = 6.31 | [Cu(phen)(oxa)] p$K_a$ = 4.93 | [Cu(5$NO_2$-phen)(oxa)] p$K_a$ = 3.22 |
|---|---|---|---|
| *I* | 6.34 | 6.64 | 6.88 |
| *A* | −0.18 | 0.08 | 0.99 |
| $\eta$ | 3.26 | 3.28 | 2.94 |

[a] All the values are in eV, and all the calculations were performed with the B3LYP functional and 3-21G** basis set. (The p$K_a$ values correspond to the substituted phenanthrolines. Water molecule of the [Cu(N-N)(ox)] is not included for simplicity.) We also report the Fukui function of the Cu atom in $[Cu(H_2O)_5]^{2+}$, $[Cu(phen)(H_2O)_3]^{2+}$, and $[Cu(5NO\text{-phen})(H_2O)_3]^{2+}$, for nucleophilic attack (the charge of the oxalate is 2−). Mulliken population analyses were used to determine the charge of the Cu atom in $[Cu(H_2O)_5]^{2+}$, $[Cu(phen)(H_2O)_3]^{2+}$, and $[Cu(5NO\text{-phen})(H_2O)_3]^{2+}$.



η=6.19 η=4.42

η=5.77 η=3.41

**Figure 2.** Hardness of $[Cu(H_2O)_5]^{2+}$, $[Cu(phen)(H_2O)_3]^{2+}$, and the fragments without two water molecules used as a model of the reactive species.

are based on a finite difference approximation. This gives equal weight to the gain and loss of an electron,[30] even when this is not the case for ions. It might be that the global hardness fails because the dominant effect is the electron transfer.

The results of this analysis do not support the common idea that harder metal ions prefer harder ligands while softer metal ions prefer softer ligands. Instead, electron affinity correlates well with formation constants of the compounds. The fact that the electron affinity correlates well with the observed trend implies that the transfer of the electrons is the driving force of the reaction. The hardness is a second-order effect, and it is relatively unimportant here.

Following the ideas of Méndez and Gázquez[24] and in order to analyze other parameters that can have some influence on the formation constant, the condensed Fukui functions of the Cu atom in $[Cu(H_2O)_5]^{2+}$, $[Cu(phen)(H_2O)_3]^{2+}$, and $[Cu(5NO\text{-phen})(H_2O)_3]^{2+}$ for nucleophilic attack (the charge of the oxalate is 2−) were calculated. The results of this analysis are shown in Table 3 (Mulliken population analysis was used to determine the charge of the Cu atom in $[Cu(H_2O)_5]^{2+}$, $[Cu(phen)(H_2O)_3]^{2+}$, and $[Cu(5NO\text{-phen})(H_2O)_3]^{2+}$). The data shown indicate that the condensed Fukui function of the Cu atom on $[Cu(H_2O)_5]^{2+}$ is larger than on $[Cu(phen)(H_2O)_3]^{2+}$ and $[Cu(5NO\text{-phen})(H_2O)_3]^{2+}$. This means that the Cu atom on $[Cu(H_2O)_5]^{2+}$ is chemically softer than on $[Cu(phen)(H_2O)_3]^{2+}$ and $[Cu(5NO\text{-phen})(H_2O)_3]^{2+}$, which implies that the Cu atom is harder on $[Cu(phen)(H_2O)_3]^{2+}$ and $[Cu(5NO\text{-phen})(H_2O)_3]^{2+}$. With these results, it can be concluded that a $\pi$-acceptor ligand bond to a copper ion will withdraw electron density, and as a consequence, the Cu atom on $[Cu(phen)(H_2O)_3]^{2+}$ and $[Cu(5NO\text{-phen})(H_2O)_3]^{2+}$ becomes harder; consequently it will be preferred by hard bases such as oxygen donors over the simple aqueous $Cu^{2+}$ ion where the Cu atom is softer. With the local softness it is possible to use the principle of hard and soft acids and bases to clarify the reasons for the differences observed in the formation constants of these compounds.

## Summary and Conclusions

A density functional study of mixed copper complexes is presented, and full geometry optimization without symmetry constraints was performed. The agreement between the theoretical and experimental values further supports the results obtained by the geometry optimization performed.

Different substituents on the diimines affect their basicity (or $\sigma$-donor ability). As a consequence, the values of the ionization potential of the compounds increase while the p$K_a$ values for the different substituted phenanthrolines decrease. The p$K_a$ values of the diimine are related to the ionization potential of the copper complexes.

On the other hand, the $\pi$-acceptor properties are related to the electron affinity. An inverse correlation between the electron affinity ($\pi$-acceptor properties) of $[Cu(N\text{-}N)(H_2O)_3]^{+2}$ and the p$K_a$ values of the different substituted phenanthrolines was found, in agreement with experimental results. The same behavior was found for ternary compounds with diimines and

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(30) Pearson, R. G. *Inorg. Chim. Acta* **1995**, *240*, 93.

oxalate. The basicity of the diimine affects the electron affinity of the ternary compounds.

Ligands containing O as donor atoms form more stable complexes with the $[Cu(N\text{-}N)]^{2+}$ complex than with the free (hydrated) $Cu^{2+}$ ion. This unexpected result cannot be explained with the global hardness of $[Cu(H_2O)_5]^{2+}$ and $[Cu(phen)(H_2O)_3]^{2+}$ because the simple aqueous $Cu^{2+}$ ion is harder than the $[Cu(phen)(H_2O)_3]^{2+}$ complex, in agreement with the symbiotic effect described by Jørgensen. With the local softness it is possible to use the principle of hard and soft acids and bases to clarify the reasons for a difference in the formation constants of these compounds.

In addition, the electron affinity of $[Cu(phen)(H_2O)_3]^{2+}$ is larger than the electron affinity of $[Cu(H_2O)_5]^{2+}$. For this reason, $[Cu(phen)(H_2O)_3]^{2+}$ can more easily accept electrons during the reaction with anions like oxalate than $[Cu(H_2O)_5]^{2+}$. This favors the reaction between $[Cu(phen)(H_2O)_3]^{2+}$ and oxalate, in agreement with the stability constants' values.

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**Supporting Information Available:** Listing of selected bond distances, angles, and total energies of the compounds. This material is available free of charge via Internet at http://pubs.acs.org.

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