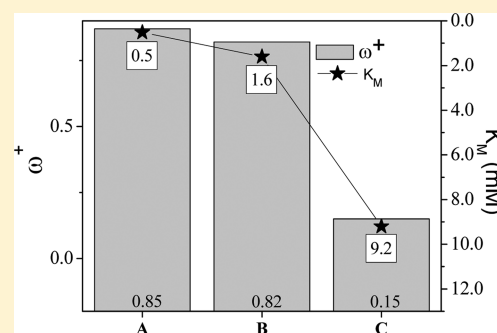


Dinuclear Copper Complexes with Imidazole Derivative Ligands: A Theoretical Study Related to Catechol Oxidase Activity

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Supporting Information

ABSTRACT: Catechol oxidase is a very important and interesting metalloprotein. In spite of the efforts to understand the reaction mechanism of this protein, there are important questions that remain unanswered concerning the catalytic mechanism of this enzyme. In this article, dinuclear copper compounds are used as biomimetic models of catechol oxidase to study plausible reaction paths. These dinuclear copper(II) complexes have distant metal centers (of 7.5 Å approximately) and superior catalytic activity to that of many dicopper complexes with shorter Cu–Cu distances. One mononuclear copper(II) complex is also analyzed in this investigation in order to see the influence of the two metal centers in the catalytic activity. Density functional theory calculations were performed to obtain optimized structures, vertical ionization energies, vertical electron affinities, the electrodonating power (ω^-), the electroaccepting power (ω^+) and the energy difference of several reaction paths. The K_M experimental results that were previously reported compare well with the electroaccepting power (ω^+) of the copper compounds that are included in this article, indicating that this index is useful for the interpretation of the electron transfer capacity and therefore the catalytic activity. The catechol moiety coordinates to only one Cu ion, but two metal atoms are needed in order to have a good electron acceptor capacity of the biomimetic models.



INTRODUCTION

Nearly half of all proteins in nature are metalloproteins, and many of these are enzymes that contain one or more metal ions and catalyze crucial biological processes, such as photosynthesis and respiration, among others.^{1–4} Even though the whole macromolecule is necessary for an optimal catalytic activity, the active site is centered in the metal ion(s) of these biological catalysts.^{1–7} Particularly, proteins containing dinuclear copper centers play crucial roles in several reactions that are very important for survival, such as electron transfer reactions and the oxidation of a large variety of substrates.^{5,6} In these reactions, the role of the metal is dominated by its redox properties, which in turn depend strongly on the nature of its coordination environment. This has motivated many attempts to reproduce, at least partially, the catalytic function of metalloenzymes, using low molecular weight coordination complexes as models.

Catechol oxidase (or catecholase) is a dinuclear copper enzyme present in most plants, which catalyzes the oxidation of a broad range of *ortho*-diphenols to *ortho*-quinones in the presence of dioxygen.^{8,9} Interestingly, its dinuclear copper site is EPR-silent due to a strong antiferromagnetic coupling between the bridged copper(II) ions. The crystal structure of catechol oxidase was reported in 1998 by Krebs and co-workers;¹⁰ from then, we know that this enzyme contains two

Cu atoms, with a Cu–Cu distance close to 2.9 Å. These two Cu atoms are close enough to bind simultaneously to a single catecholate molecule. In fact, this is the most accepted mechanism for this enzyme.^{7,11–15}

In an approach that has been called biomimetic catalysis, many of the efforts to understand the reaction mechanism of this protein, have involved dinuclear copper complexes with some resemblance to the active site of catecholase.^{16–29} Since the active site of many enzymes presents one or more copper ions bound to imidazole groups from histidine residues, numerous dicopper complexes involving heteroaromatic nitrogen donors have been reported including their catalytic activity toward oxidation reactions.^{15,30–41} Given that the Cu–Cu bond length in catechol oxidase is close to 2.9 Å, most of these biomimetic models have focused mainly on obtaining dinuclear complexes with this Cu–Cu bond distance. The study of dimetallic coordination compounds has generated great interest due to the expectation of potential cooperativity between metal ions since it is well-known that the chemical properties of these dimetallic compounds are not additive by comparison with two equivalents of the corresponding mononuclear analogues.

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Recently, Gasque et al. reported a series of dinuclear copper complexes as biomimetic models for the catechol oxidase that present a Cu–Cu distance close to 7.4 Å.^{20,21} These two Cu atoms do not have the steric possibility to bind simultaneously to a single catechol unit, as required in the most accepted mechanism for this enzyme.¹⁵ Nonetheless, the reported catalytic activity is similar or even superior to several dinuclear complexes described in the literature for copper dinuclear complexes with Cu–Cu bond distances close to 3 Å,^{15,38,39,42–50} as well higher than some mononuclear analogues also synthesized by this group.⁵⁰ One very interesting feature of these complexes is that, in spite of the long Cu–Cu separation, their experimental EPR spectra indicates that the two metal atoms are magnetically coupled.

Notwithstanding these results, many questions concerning the reaction mechanism between these molecules and catechol remain unanswered. On the basis of the scarce information about the reaction mechanism of these dinuclear copper compounds with catechol, it is the main goal of the present work to provide some theoretical data on such processes. To that purpose, we report a theoretical investigation about two dinuclear copper complexes with imidazole derivatives that were recently prepared. One mononuclear copper compound was also analyzed to explain the experimental results concerning their low reactivity when compared with the dinuclear ones. Some reactivity indexes previously reported are used in order to explain the differences in the reactivity of dinuclear and mononuclear copper complexes. A comparison with the electron donor–acceptor capacity of catechol allows us to classify these compounds as good electron donors or acceptors, and with this information, it is possible to determine the thermodynamically feasible reaction paths.

■ COMPUTATIONAL DETAILS

Density functional approximation⁵¹ as implemented in Gaussian 03⁵² was used for all calculations. The hybrid, three parameter B3LYP⁵³ functional was used for the calculation of complete optimizations, without symmetry constraints. Two basis sets were employed: LANL2DZ for Cu, and DSDV⁵⁴ for C, H, O, and N. Harmonic frequency analyses permitted us to verify optimized minima. In order to compute the vertical ionization energy (IE) and vertical electron affinity (EA), further single-point calculations were necessary. IE is calculated as the difference between the energy of the cation and the neutral molecule, assuming that both of these have the ground-state nuclear configuration of the neutral molecule. EA is also calculated as vertical and represents the energy difference between the neutral and the anion, calculated with the ground-state nuclear configuration of the neutral molecule. To compare with other density functional theory approximations, complete optimizations were also obtained with M06-2X functional⁵⁵ and the same basis sets.

■ RESULTS AND DISCUSSION

Two dinuclear copper complexes ($[\text{Cu}_2\text{dimp}(\text{H}_2\text{O})_4]^{4+}$ (A) and $[\text{Cu}_2\text{dimeim}(\text{H}_2\text{O})_4]^{4+}$ (B)) and one mononuclear copper compound ($[\text{Cuemitrim}(\text{OH})(\text{H}_2\text{O})]^{1+}$ (C) with imidazole derivatives were selected for this study and are shown in Figure 1. A and B are used in order to analyze the influence of the Cu–Cu distance and the coordination environment. Compound C is selected with the intention of investigating the

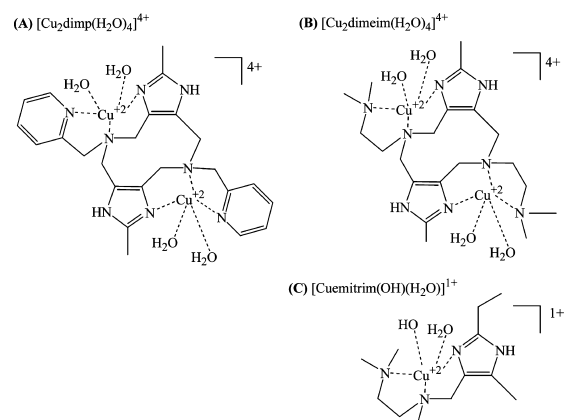


Figure 1. Schematic representation of copper complexes with imidazole derivatives that were used in this study.

differences between mononuclear and dinuclear copper complexes.

Given that, in the experimental conditions, these complexes may display various degrees of hydrolysis as a function of pH, and it has been established²⁰ that the catalytically active form involves some degree of hydrolysis; in the present work, the following species were optimized: $[\text{Cu}_2\text{dimp}(\text{H}_2\text{O})_4]^{4+}$, $[\text{Cu}_2\text{dimp}(\text{H}_2\text{O})_3(\text{OH})]^{3+}$, $[\text{Cu}_2\text{dimeim}(\text{H}_2\text{O})_4]^{4+}$, $[\text{Cu}_2\text{dimeim}(\text{H}_2\text{O})_3(\text{OH})]^{3+}$, $[\text{Cu}_2\text{dimeim}(\text{H}_2\text{O})_2(\text{OH})_2]^{2+}$, and $[\text{Cuemitrim}(\text{H}_2\text{O})(\text{OH})]^{1+}$. For simplicity reasons, the substrate used in the experimental studies, 3,5-diterbutylcatechol, was substituted in the calculations for catechol; this simplification is justified due to the similar reactivity of both substrates toward copper complexes.

The Cu–Cu bond distances of the optimized structures of $[\text{Cu}_2\text{dimp}(\text{H}_2\text{O})_4]^{4+}$ and $[\text{Cu}_2\text{dimeim}(\text{H}_2\text{O})_4]^{4+}$ are compared with available experimental^{20,21} values in Table 1. Two density

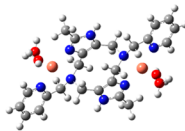

Table 1. Two Density Functional Approximations Were Used for the Optimization (B3LYP and M06-2X) and Two Different Spin Multiplicities (Singlet and Triplet)^a

cmpd	Cu–Cu singlet	Cu–Cu triplet	ΔE_s^t [$E(s) - E(t)$]
$[\text{Cu}_2\text{dimp}(\text{H}_2\text{O})_4]^{4+}$			
B3LYP	7.64	7.61	1.82
M06-2X	7.56	7.54	
experimental		7.34	
$[\text{Cu}_2\text{dimeim}(\text{H}_2\text{O})_4]^{4+}$			
B3LYP	7.72	7.68	1.65
M06-2X	7.65	8.34	2.93
experimental		7.52	

^aCu–Cu bond distances (in Å) and energy difference between singlets and triplets (in eV) are reported. Experimental Cu–Cu bond lengths^{20,21} are also included for comparison.

functional approximations were used for the optimization (B3LYP and M06-2X) and two different spin multiplicities (singlet and triplet). In all cases, triplets are more stable than singlets by more than 1.6 eV. Cu–Cu bond distances are in good agreement with the experimental values (the maximum errors are 4% for B3LYP and 10% for M06-2X). It is well-known that M06-2X functional describe transition metal systems better than B3LYP, but in these compounds, the Cu–Cu bond distances are too long and the errors with the B3LYP are smaller than the errors obtained with the M06-2X.

Table 2. Optimized Structures (B3LYP), Cu–Cu Bond Distances (in Å), and the Energy Difference between Singlets and Triplets (in eV) Are Reported; Mulliken Atomic Charges Are Also Included

Compound		Cu–Cu	Atomic charge	$\Delta E'_s$ [E(s)-E(t)]	Optimized Structures
[Cu ₂ dimp(H ₂ O) ₄] ⁴⁺	Singlet	7.64	0.54	1.82	
	Triplet	7.61	0.63		
[Cu ₂ dimp(OH)(H ₂ O) ₃] ³⁺	Singlet	7.60	0.49	0.94	
	Triplet	7.34	0.60		
[Cu ₂ dimeim(H ₂ O) ₄] ⁴⁺	Singlet	7.72	0.50	1.65	
	Triplet	7.68	0.57		
[Cu ₂ dimeim(OH)(H ₂ O) ₃] ³⁺	Singlet	7.75	0.44	1.25	
	Triplet	7.23	0.45		
[Cu ₂ dimeim(OH) ₂ (H ₂ O) ₂] ²⁺	Singlet	7.38	0.34	1.72	
	Triplet	7.40	0.39		
[Cuemitrim(OH)(H ₂ O)] ¹⁺			0.46		

It is important to mention that the following results are similar and do not depend on the methodology. For this reason, both functionals can be used for the purpose of this investigation. In what follows, we will report the results obtained with B3LYP because there is less error in the Cu–Cu bond distance obtained with this functional.

The Cu–Cu bond distances, the atomic charges, and the singlet–triplet energy differences are reported in Table 2 for all the compounds under study. As expected, atomic charge of the Cu atoms is positive, and it is decreasing as the global positive charge decreases. However, there is not a great difference. Mono and dinuclear complexes show more or less the same copper atomic charge, and therefore, the difference in the reactivity of these complexes can not be explained with the atomic charges. The Cu–Cu bond distances are smaller for triplets than for singlets with the exception of [Cu₂dimeim(OH)₂(H₂O)₂]²⁺. Optimized structures are very similar for both spin state multiplicities. These results indicate that triplets are more stable than singlets by more than 0.9 eV, and for this reason, in the following analysis, we will present the results for the triplets.

The dicopper complexes have already shown they can be considered as biomimetic models for catechol oxidase. Considering that, for a successful reaction between catechol

and a copper complex, two separate events need to take place, the present theoretical study analyzes each of these individually. One of these events is the charge transfer from the catechol to the copper center in each complex, while the other is the chemical bond formation between catalyst and substrate.

To analyze the viability of the charge transfer process involving these copper molecules and catechol, it is necessary to characterize all the compounds as electron donors or acceptors. To determine whether the electron transfer reaction will be exergonic or not, an energetic index (ΔE) for the full electron transferability was reported before.⁵⁶ Its definition involves the electronegativity (χ , a measure of the ability to accept electrons) and the chemical hardness (η , a measure of their resistance to donate electrons) as follows:

$$\Delta E = \chi_d - \chi_a + \frac{1}{2}(\eta_d + \eta_a) \quad (1)$$

In this equation, d refers to the electron donor and a to the electron acceptor. This index is negative for exergonic reactions ($\Delta G < 0$), indicating that the reaction is thermodynamically feasible. For the reaction between the copper compounds and catechol, the latter is the electron donor and former the electron acceptors.

With eq 1 and considering the definitions of electronegativity ($\chi = (IE + EA)/2$) and chemical hardness ($\eta = IE - EA$), it is feasible to propose that a necessary condition for the electron transfer process is

$$IEd < EAa \quad (2)$$

It is important to note that these values are the vertical ionization energy (IE) and the vertical electron affinity (EA). To analyze the electron transfer process, we obtained IE and EA for all the compounds under study. Given that the pK_a value⁵⁷ of catechol is close to 10, some deprotonated catechol (catecholate anion [(catechol-H)¹⁻]) might be present in the experimental conditions. For this motive, catechol and (catechol-H)¹⁻ were both considered. These results are reported in Table 3.

Table 3. Vertical Energy (IE), Vertical Electron Affinity (EA), Electrodonating Power (ω^-), and Electroaccepting Power (ω^+) Are Reported in eV; Dinuclear Copper Complexes Are Triplet Spin States

cmpds	IE	EA	ω^- (donor)	ω^+ (acceptor)
[Cu ₂ dimp(H ₂ O) ₄] ⁴⁺	0.67	0.46	1.85	1.28
[Cu ₂ dimp(OH)(H ₂ O) ₃] ³⁺	0.56	0.37	1.33	0.87
[Cu ₂ dimeim(H ₂ O) ₄] ⁴⁺	0.70	0.47	1.82	1.24
[Cu ₂ dimeim(OH)(H ₂ O) ₃] ³⁺	0.56	0.36	1.28	0.82
[Cu ₂ dimeim(OH) ₂ (H ₂ O) ₂] ²⁺	0.47	0.24	0.75	0.39
[Cuemitrim(OH)(H ₂ O)] ¹⁺	0.40	0.13	0.42	0.15
Catechol	0.30	-0.07	0.12	0.00
[Catechol-H] ¹⁻	0.08	-0.25	0.0	0.08

It can be seen that, as expected, neither catechol nor (catechol-H)¹⁻ are good electron acceptors (EA is negative). Moreover, there are four complexes acting as electron acceptors that satisfy condition 2 when they interact with the neutral catechol molecule (i.e., $0.30 < EA$): [Cu₂dimp(H₂O)₄]⁴⁺, [Cu₂dimp(OH)(H₂O)₃]³⁺, [Cu₂dimeim(H₂O)₄]⁴⁺, and [Cu₂dimeim(OH)(H₂O)₃]³⁺. On the basis of the ideas explained before, it can be considered that these compounds are more reactive toward catechol than the other two copper complexes, [Cu₂dimeim(OH)₂(H₂O)₂]²⁺ and [Cuemitrim(OH)(H₂O)]¹⁺. Comparatively, when we analyze condition 2 with the values for (catechol-H)¹⁻, results of Table 3 show that EA of all the compounds are larger than the IE value for (catechol-H)¹⁻. This means that all the copper complexes under study satisfy condition 2 and that also (catechol-H)¹⁻ is expected to be more reactive than catechol. Apparently, the charge transfer between copper complexes in Table 3 and (catechol-H)¹⁻ is feasible. Condition 2 only indicates if the electron transfer between two molecules proceeds, but one can expect the better electron acceptors to react more quantitatively. If this is the situation, the mononuclear copper complex will be less reactive than the dinuclear copper complexes because it is an inferior electron acceptor. This is in concurrence with the experimental results.

Besides using IE and EA, the electron transfer reactions can be further analyzed with the electrodonating (ω^-) and electroaccepting (ω^+) power that has been described by Gázquez et al.⁸ These indexes were defined as follows and they represent the tendency to donate charge (ω^-) and the propensity to accept charge (ω^+), considering a partial charge transfer process:

$$\omega^- = \frac{(3IE + EA)^2}{16(IE - EA)} \quad (3)$$

$$\omega^+ = \frac{(IE + 3EA)^2}{16(IE - EA)} \quad (4)$$

Lower values of ω^- imply a greater capacity for donating charge; higher values of power ω^+ imply a greater capacity for accepting charge. These indexes are based on a simple charge transfer model, expressed in terms of chemical potential and chemical hardness, and they are helpful for the electron donor–acceptor characterization of the dicopper complexes that we are analyzing. It is important to say that IE and EA refer to one-electron transfer processes, while ω^- and ω^+ consider fractional charge transfer reactions. Since our approach proposes that a partial charge transfer is one of the intermolecular factors considered as fundamental for the reaction to take place, we prefer to use ω^- and ω^+ for the analysis of the reaction.

In order to analyze the relationship between these parameters and the experimental reactivity, in Figure 2, we

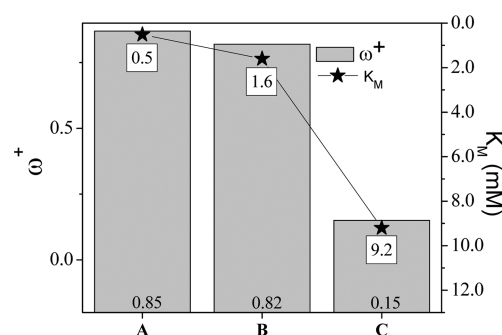


Figure 2. Electroaccepting power (ω^+ , in eV) and experimental values of K_M (dissociation constant of the enzyme–substrate complex in Michaelis–Menten kinetic model, in mM) previously reported.^{20,21,50} A corresponds to [Cu₂dimp(OH)(H₂O)₃]³⁺, B corresponds to [Cu₂dimeim(OH)(H₂O)₃]³⁺, and C is [Cuemitrim(OH)(H₂O)]¹⁺.

include these indexes for some of the compounds under study with the previously reported^{20,21,50} values of K_M (the Michaelis constant, an experimental index useful for comparing the relative stability of the enzyme–substrate complex). The species taken in consideration are only those that correspond to the predominant form of the catalyst in the kinetic experiments: [Cu₂L(H₂O)₃(OH)]³⁺ or [CuL(H₂O)(OH)]¹⁺.

As can be seen, there is a relationship between the copper compound's ability to accept electrons (ω^+) and the experimental K_M value, i.e., [Cuemitrim(OH)(H₂O)]¹⁺ is the least effective electron acceptor and also the least reactive compound. Since there is a good correspondence between ω^+ of the copper complexes and the experimental K_M values, it is acceptable to say that these indexes are useful for the description of the charge transfer process between a given copper complex and catechol molecule or catecholate anion.

As mentioned above, the other relevant event to the reaction between a copper complex and catecholate, apart from the charge transfer process, is the formation of a chemical bond between these two species. Several reaction mechanisms proposed in the literature for dicopper compounds consider that both Cu atoms bind simultaneously to a single catechol molecule.^{1,7} However, this reaction mechanism is not possible for the compounds discussed in this article, due to the large

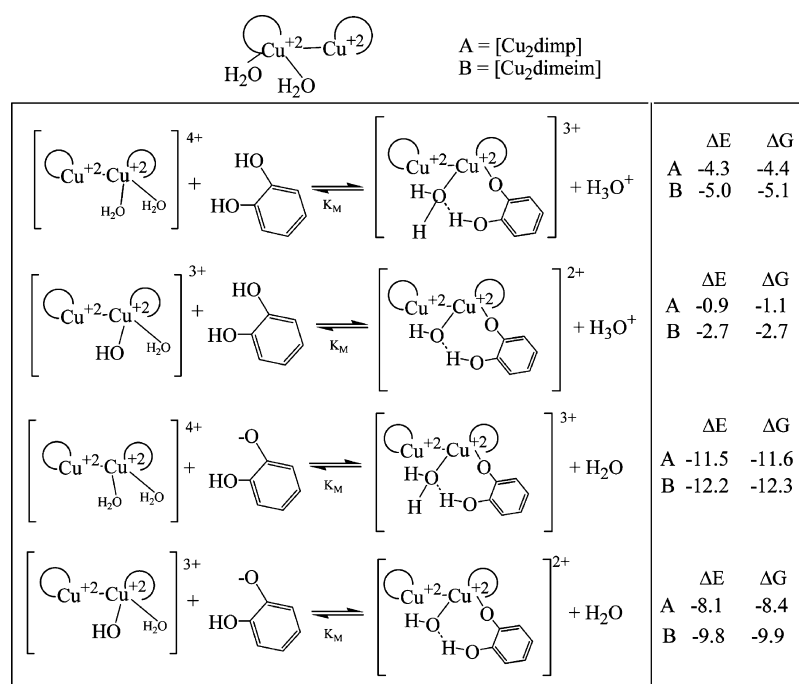


Figure 3. Schematic representation of the proposed reactions between $[\text{Cu}_2\text{dimeim}(\text{H}_2\text{O})_4]^{4+}$ and $[\text{Cu}_2\text{dimeim}(\text{OH})(\text{H}_2\text{O})_3]^{3+}$, with catechol or catecholate anion is shown. ΔE and ΔG (in eV) are included.

Cu–Cu distance. In order to give more insight about the possible reaction steps between these compounds and catechol (or catecholate anion), we calculate the energetic of feasible reaction paths. Two compounds, $[\text{Cu}_2\text{dimeim}(\text{H}_2\text{O})_4]^{4+}$ and $[\text{Cu}_2\text{dimeim}(\text{OH})(\text{H}_2\text{O})_3]^{3+}$, are used as an example since they are both good electron acceptors and they satisfy condition 2. $[\text{Cuemtrim}(\text{OH})(\text{H}_2\text{O})]^{1+}$ is also analyzed in order to see the differences between the dimetallic and the monometallic compounds. In what follows, we will describe the results obtained for these three compounds.

It is possible to study the viability of these reaction steps considering the energy difference (ΔE) and the free energy (ΔG) difference between reactants and products. The values of these two parameters calculated for the complexation reactions between catechol or catecholate with $[\text{Cu}_2\text{L}(\text{H}_2\text{O})_4]^{4+}$ or $[\text{Cu}_2\text{L}(\text{H}_2\text{O})_3(\text{OH})]^{3+}$ (L = dimp or dimeim) are shown in Figure 3.

In view of the fact that these complexation reactions are strictly ligand substitution processes, water molecules or H_3O^+ are released upon catechoate or catechol coordination, respectively. All of the reactions in Figure 3 are thermodynamically feasible as ΔE and ΔG are all negative. Moreover, ΔE and ΔG are similar indicating that entropic effects are not crucial. As expected, the reaction with catecholate anion is energetically more favorable than the reaction with catechol, due to the electrostatic interaction between the catecholate anion and the cationic copper complexes. It is possible to associate these values with the K_M value obtained experimentally for these reactions, considering that the catecholate anion is more reactive than catechol.

As can be seen in Figure 3, ΔE and ΔG of the reaction are larger for $[\text{Cu}_2\text{dimeim}(\text{H}_2\text{O})_4]^{4+}$ than for $[\text{Cu}_2\text{dimeim}(\text{OH})(\text{H}_2\text{O})_3]^{3+}$. This agrees with the electroaccepting power, which is greater for the former than for the latter. However, since there are two Cu atoms in the molecule, it could be considered that two catechol molecules or two catecholate anions attached

to two Cu atoms. For the reaction paths with two catechol moieties, it is necessary to consider the simultaneous interaction of three molecules, something far less probable than the two-molecule interaction needed for the reaction path in Figure 3. Gasque et al.⁵⁹ recently proved the involvement of only one copper ion, by detecting the catecholate radical during the anaerobic interaction of some of these dinuclear species with catechol. Considering that only one copper atom participates in the reaction, since the most plausible reaction path considers only one catechol molecule or one catecholate anion binding to the dicopper complex, it is easy to imagine that the monometallic complex could also react with the catechol molecule or with the catecholate anion. However, the K_M value indicates that the mononuclear compound is less reactive than the dicopper complex. Figure 4 displays the ΔE

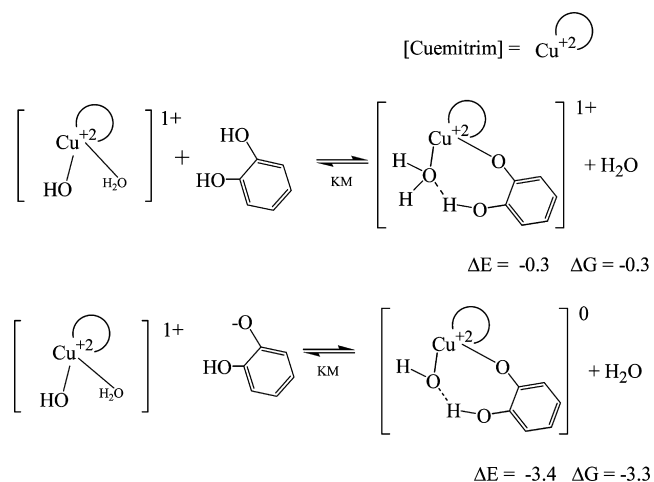


Figure 4. Schematic representation of the proposed second step of the reaction mechanisms with one catechol molecule reacting with the monometallic compound is shown. ΔE and ΔG (in eV) are included.

and ΔG values obtained for the complexation reaction between either the catechol molecule or catecholate anion to the mononuclear copper compound ($[\text{Cuemitrim}(\text{OH})(\text{H}_2\text{O})]^{1+}$). The reaction with catecholate anion is, again, as expected, more favorable than the reaction with the catechol molecule. However, the comparison of ΔE and ΔG reported in Figure 4 with those values reported in Figure 3 for the corresponding reaction paths indicate that these values are appreciably less negative for the mononuclear complex than for the dinuclear ones. These values support the experimental fact that the reaction with the mononuclear compound is less favorable than the reaction of the dinuclear complexes and is also in agreement with the electroaccepting power calculated for the involved species.

The main conclusion that can be drawn from these results is that the reaction of dinuclear complexes is more favorable than the reaction of mononuclear compounds since the former are better electron acceptors than the latter. The reaction proceeds on one Cu atom, but two metal atoms are needed in order to have a good electron acceptor capacity of the biomimetic models.

CONCLUSIONS

The reaction between a Cu(II) coordination complex and a catechol molecule or a catecholate anion is proposed to depend on two aspects: the electron donating-electron accepting properties of the reactant species and the formation of the chemical bond between Cu(II) and catecholate.

The study was done on two different dinuclear copper complexes and an analogous mononuclear complex. Since in the experimental conditions for the kinetic measurements the biomimetic catalysts are partially hydrolyzed, different hydrolysis degrees were considered for the dinuclear complexes: $[\text{Cu}_2\text{L}(\text{H}_2\text{O})_x(\text{OH})_y]^{4-y}$, ($x + y = 4$; $y = 0, 1, 2$).

For the charge transfer process, the reactants were quantitatively characterized as electron donors or acceptors. To this purpose, IE, EA, ω^+ , and ω^- of all the compounds under study were used, and it was found, as expected, that catechol and catecholate anion act as electron donors, while the copper compounds are the electron acceptors.

The K_M experimental results that were previously reported²⁰ compare well with the electroaccepting power (ω^+) of the copper compounds that are studied in this article. There is a good concordance between the ability to accept electrons (ω^+) and the experimental K_M value of the copper compound, being $[\text{Cu}_2\text{dimp}(\text{H}_2\text{O})_4]^{4+}$ the best electron acceptor with the highest catalytic activity and $[\text{Cuemitrim}(\text{OH})(\text{H}_2\text{O})]^{1+}$ the least effective electron acceptor and also the least reactive compound.

The substitution of a catecholate ion in the coordination sphere of a copper ion was found to be more energetically favorable for the dinuclear complexes than for the mononuclear one.

These two findings suggests that even though the reaction proceeds on one Cu atom, the presence of a second one improves the reactivity toward catechol in both of the analyzed aspects: first, by making the copper complex a better electron acceptor and, second, by favoring the substitution of a water molecule for an incoming catecholate in the coordination sphere of the copper ion.

ASSOCIATED CONTENT

Supporting Information

Cartesian coordinates of all the compounds. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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