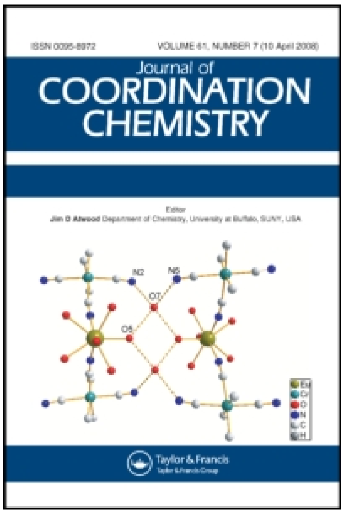

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

Impact of Geometric Changes on the Oxidation of Catechol by Copper(II) Complexes

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To cite this Article Malachowski, Mitchell R. , Tomlinson, Laura J. , Davidson, Marilyn G. and Hall, Mary J.(1992) 'Impact of Geometric Changes on the Oxidation of Catechol by Copper(II) Complexes', Journal of Coordination Chemistry, 25: 2, 171 — 174

To link to this Article: DOI: 10.1080/00958979209409749

URL: http://dx.doi.org/10.1080/00958979209409749

J. Coord. Chem. 1992, Vol. 25, pp. 171-174
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NOTE

IMPACT OF GEOMETRIC CHANGES ON THE OXIDATION OF CATECHOL BY COPPER(II) COMPLEXES

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(Received January 17, 1991; in final form March 19, 1991)

Keywords: Copper, catechol, oxidation, catalysis

The synthesis of transition metal complexes which can serve as catalysts for the oxidation of organic molecules involves the search for both more efficient and more selective catalysts.[1] The design of complexes in which structural and electronic features are selectively varied allows the analysis of structure/activity relationships in the study of their oxidation chemistry. Successful probing of these features would therefore allow a more fundamental understanding of the catalysts' properties.

We are particularly interested in the air oxidation of catechol to quinone (shown below), since this is one of the reactions catalyzed by the copper-containing enzyme tyrosinase.[2]

At the active site of the enzyme, there are two copper atoms each ligated by either two or three imidazole nitrogen atoms and possibly a bridging oxygen group. We have undertaken the synthesis of nitrogen-containing ligands and their copper complexes along with a study of their catalytic properties in order to better understand the function of tyrosinase and to develop more effective catalysts.

In earlier work, we focussed on the effect of changing exogeneous donors[3] on the rate of oxidation of catechol and compared mononuclear to dinuclear complexes.[4] In this study, we report the kinetics of the oxidation of catechol to quinone using Cu(II) complexes of the tripodal ligands tris(3,5-dimethylpyrazol-l-ylmethyl)amine and tris(3,5-dimethylpyrazol-l-ylethyl)amine. The catalytic ability of the complexes was determined and shown to be dependent on the changes in geometry of the metal complexes.

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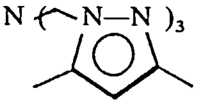
When substrate and/or intermediates are bound, evidence suggests that the copper atoms in tyrosinase are five-coordinate.[5] Current knowledge of the reaction of synthetic Cu(II) complexes towards catechol does not include an understanding of the difference in reactivity between the possible geometries in which five-coordinate complexes can exist.[6] Therefore, we are in the process of probing the effect that changing the geometry around the copper atom in mononuclear and dinuclear Cu(II) complexes has on oxidation properties.

The tripodal ligands tris(3,5-dimethylpyrazol-l-ylmethyl)amine (tpzma)[7] (**1**) and tris(3,5-dimethylpyrazol-l-ylethyl)amine[8] (tpzea) (**2**) were prepared along with a variety of their Cu(II) complexes using modifications of literature methods.



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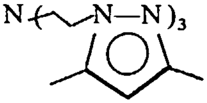

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The tetradentate ligand tpzma was used to prepare[9] $[Cu(tpzma)NO_3]NO_3$, $[Cu(tpzma)Cl]BPh_4$, and $[Cu_2(tpzma)_2F(H_2O)_2]$ $(BF_4)_3$, while tpzea formed $[Cu(tpzea)NO_3]NO_3$, $[Cu(tpzea)Cl]$ BPh_4, and $[Cu(tpzea)H_2O]$ $(BF_4)_2$[8] when treated with the appropriate copper salts.[10] These complexes allow the study of both the impact of changes in the geometry and the nature of the fifth donor on the rate of oxidation.

It has been shown[8] that Cu(II) complexes formed from tpzea (which has three atoms separating donors) are five-coordinate mononuclear species with square pyramidal geometry. X-ray crystallographic studies of the unmethylated analogue (formed from tris(pyrazol-l-ylethyl)amine) of $[Cu(tpzea)H_2O](BF_4)_2$ showed that the ligand coordinates as a tetradendate donor with water occupying an equatorial site.[8] It was also shown by a combination of electronic and EPR spectroscopy that $[Cu(tpzea)H_2O](BF_4)_2$ and $[Cu(tpzea)Cl]BF_4$ have similar geometries.[8]

By way of comparison, complexes of tpzma (which has two atoms separating donors) form Cu(II) complexes of two types. In the case of $[Cu_2(tpzma)_2F(H_2O)_2]$ $(BF_4)_3$, a dimeric complex was formed, while $[Cu(tpzma)\ Cl]\ BPh_4$ and $[Cu(tpzma)\ NO_3]\ NO_3$ are monomeric with trigonal bipyramidal geometry, as shown by conductivity studies, IR, electronic, and EPR spectroscopy.[9] An X-ray structure of the analogue $[Co(tpzma)H_2O]\ ClO_4$ showed the complex to exist as a trigonal bipyramidal monomeric complex with the amino nitrogen and a water molecule in the apical positions.[11]

The reactivity of the Cu(II) complexes towards catechol (0.3 cm^3 of a 1×10^{-3} M methanol solution of catalyst and 2.0 cm^3 of a 0.1 M methanolic solution of catechol) was studied using electronic spectroscopy by following the appearance of quinone at 390 nm with time, as described elsewhere.[4] The results of the oxidations are presented graphically in Figure 1. As shown, the trigonal bipyramidal tpzma complexes were found to act as efficient catalysts towards the oxidation of catechol. On the other hand, none of the square pyramidal complexes formed from tpzea catalyze the oxidation of catechol.[12] Regardless of the various permutations (monomeric or dimeric structure, the nature of the fifth ligand or the counterion), Cu(II) complexes of tpzma catalyzed the oxidation of catechol while those of tpzea did not.

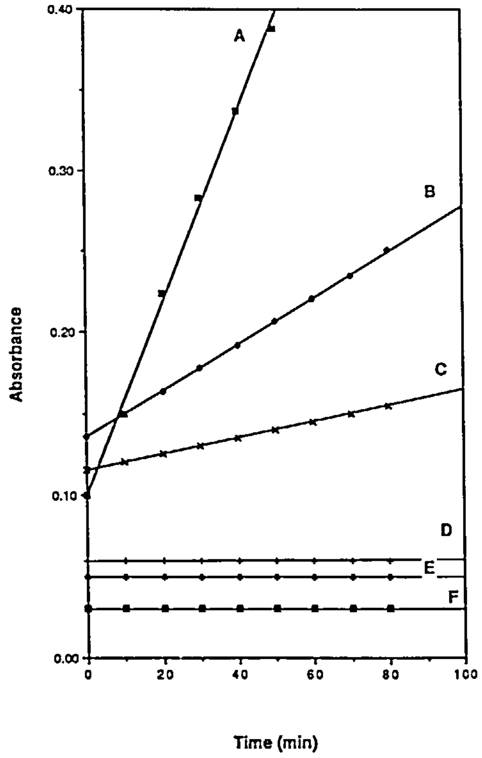

FIGURE 1 Plot of absorbance *vs* time for copper catalyzed oxidation of catechol: (A) $[Cu_2(tpzma)_2F(H_2O)_2](BF_4)_3$; (B) $[Cu(tpzma)NO_3]NO_3$; (C) $[Cu(tpzma)Cl]BPh_4$; (D) $[Cu(tpzea)NO_3]NO_3$; (E) $[Cu(tpzea)H_2O](BF_4)_2$; (F) $[Cu(tpzea)Cl]BPh_4$

It is not unusual for Cu(II) complexes to act as catalysts in this reaction since simple Cu(II) salts such as $CuCl_2$ will perform the task, but what is unusual is the fact that the tpzea complexes do not catalyze the reaction. Prior to complexation of catechol, dissociation of the fifth ligand needs to take place. One difference is that the complexes formed from tpzea leave a vacant equatorial site after dissociation of the fifth donor which would allow binding of the catechol to the half-empty $d_{x^2-y^2}$ Cu(II) orbital, while the tpzma complexes lose an axial donor allowing catechol to bind to the d_{z^2} orbital.

It is also notable that the $[Cu_2(tpzma)_2F(H_2O)_2](BF_4)_3$ complex is the most reactive species, since it is the only dinuclear system. This affirms the hypothesis that in tyrosinase, the two coppers need to be proximate in order to bind the two phenolic oxygens of the catechol, so that the two-electron redox reaction can efficiently proceed.

Along with these geometric effects, the nature of the fifth ligand in the tpzma complexes has a substantial effect on the rate of the reaction. This is in accord with our earlier study which focused on this feature in other catalysts.[3] The calculated rates for the tpzma complexes are shown in Table I. These are more efficient catalysts than other complexes of tripodal ligands which we have studied. It has been shown that electron transfer from catechol to Cu(II) can begin only after catechol and the Cu(II) species form a Cu(II) catecholate intermediate.[13] This infers that for the complexes with the greatest reactivity, either the fifth ligand dissociates faster or the dissociation constant for the loss of the fifth ligand is larger.

TABLE I
Catalytic activities of copper(II) complexes.

Complex	Activity (μmol substrate/mg catalyst per min)
$[Cu_2(tpzma)_2F(H_2O)_2](BF_4)_3$	0.567
$[Cu(tpzma)NO_3]NO_3$	0.213
$[Cu(tpzma)Cl]BPh_4$	0.050
$[Cu(tpzea)NO_3]NO_3$	No reaction
$[Cu(tpzea)H_2O](BF_4)_2$	No reaction
$[Cu(tpzea)Cl]BPh_4$	No reaction

The generality of the geometric effect demonstrated here has not yet been determined, but it has been suggested[5] that in the catalytic cycle of tyrosinase one of the copper atoms needs to rearrange from tetragonal to trigonal bipyramidal for effective oxidation to occur. Our results show this same preference for the tripod complexes studied. Work is in progress to ascertain the fundamental features which explain these variations in reactivity. Additionally, other complexes where these geometrical and electronic features can be varied are being studied in order to assess the implications with respect to the geometry of the active site of tyrosinase.

ACKNOWLEDGEMENTS

The support of this research by the Research Corporation is gratefully acknowledged.

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