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Absorption and Fluorescence Spectral Studies of some Binuclear Copper Complexes

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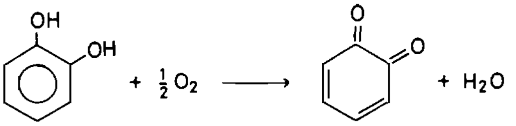
Several dicopper complexes which were previously prepared with the binucleating ligand 2,6-diformyl-4-methylphenol were found to possess extensive fluorescence spectra despite their paramagnetism. The absorption and fluorescence of the dicopper complexes are compared in water and dimethylsulfoxide. The effect of CN$^-$ ion on the fluorescence spectra is discussed.

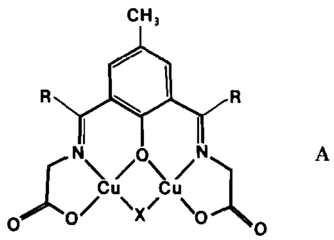
Introduction

Binuclear copper(II) complexes are currently of great interest as catalysts in industrial processes [1–3] and as models which mimic the oxidase behavior of metalloenzymes [4]. Recent studies in this laboratory have shown that the complexes of the type given in Fig. 1 (A & B) catalyze the air oxidation of catechols (eqn. 1) [5, 6]. Mechanistic studies of the catalyzed catechol oxidation reaction involving the interactions of dioxygen (O_2, O_2^-, O_2^{-2}), dicopper complexes and catechols were attempted by absorption spectroscopy. These studies were unsuccessful because of the growth of an intense *o*-quinone band which developed from catechol oxidation. The band tailed off into the visible region obscuring the diagnostic copper d–d and charge transfer bands.

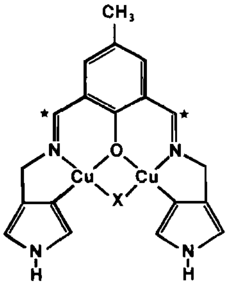


(1)

Fluorescence studies were proposed as a method to get around the obstacles presented by absorption spectra methods. The literature however held out little hope that one could observe the fluorescence of complexes containing copper(II) ions principally because of their ion size and paramagnetism [7, 8]. Surprisingly, however, the dicopper complexes were found to give extensive fluorescence spectra. In this work, we report the fluorescence spectra of several dicopper complexes of the type in Fig. 1.



FSAL(GLY)$_2$Cu$_2$Cl	R=H, x=Cl
FSAL(ALA)$_2$Cu$_2$Cl	R=CH$_3$, x=' Cl
FSAL(GLU)$_2$Cu$_2$OH·2H$_2$O	R=CH$_2$-CH$_2$-COOH, x=OH
FSAL(ARG)$_2$Cu$_2$Cl$_3$·2H$_2$O	R=CH$_2$-CH$_2$CH$_2$NH-$\underset{NH}{C}$-NH$_2$, x=Cl
FSAL(LYS)$_2$Cu$_2$Cl$_3$·2H$_2$O	R=CH$_2$-CH$_2$-CH$_2$-CH$_2$-NH$_2$, x=Cl



F (HIS)$_2$Cu$_2$OH·(ClO$_4$)$_2$, x=OH
F (HIS-RED)$_2$Cu$_2$OH·(ClO$_4$)$_2$·H$_2$O, x=OH

★ AZOMETHINE GROUPS ON HIS-RED COMPLEX ARE REDUCED

Fig. 1.

Experimental

Synthesis

The syntheses of the complexes were performed by methods given in the indicated references:

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Complex	Abbreviation	Ref.
2,6-diformyl-4-methylphenol	[diformyl ligand]	5
$\mathrm{FSAL(Gly)_2Cu_2Cl}$	[FSAL Gly]	9
$\mathrm{FSAL(Ala)_2Cu_2Cl}$	[FSAL Ala]	9
$\mathrm{FSAL(Glu)_2Cu_2(OH)\cdot 2H_2O}$	[FSAL Glu]	5
$\mathrm{FSAL(Arg)_2Cu_2Cl\cdot 2HCl\cdot 2H_2O}$	[FSAL Arg]	5
$\mathrm{FSAL(Lys)_2Cu_2Cl\cdot 2HCl\cdot 2H_2O}$	[FSAL Lys]	5
$\mathrm{[(Cu_2(HA)_2IPA)OH](ClO_4)_2}$	[FSAL His]	10
$\mathrm{[(Cu_2(H_2HA)_2IPA)OH](ClO_4)_2\cdot H_2O}$	[FSAL His-red]	10

Spectral Studies

The spectral studies were performed in water buffered by phosphate buffer, pH = 7.0 and spectral grade dimethylsulfoxide (DMSO). The absorption spectra were recorded on a Cary 17 Spectrophotometer. The fluorescence spectra were recorded on a Perkin Elmer 650-4D Fluorescence Spectrometer. The spectrometer cells were maintained between 20–22 °C using a constant temperature water bath.

Results and Discussion

The absorption spectra of FSAL complexes show two bands of transitions in the region of 210–270 nm and 350–415 nm in water. The transitions in the 210–270 nm region are assigned to the $\pi \rightarrow \pi^*$ of the benzene ring of the 2,6-diformyl-4-methylphenyl moiety [9, 10]. The transitions in the 350–415 nm region are assigned to the azomethine in the complex formed by the Schiff Base reaction of the diformyl ligand and the amino acid [10–12].

Table I lists the absorption spectral data of the FSAL complexes in water and DMSO two solvents of decreasing polarity. Absorption transitions in the 210–270 nm region changed little if any with a change in solvent. The R groups on the amino acid moiety of the complexes had some effect on the absorption energies in this region but in a way which was not readily evident. The same can be said for the effect of the R groups of the amino acid moiety on the absorption energies in the 350–415 nm region. There was, however, a solvent effect in this region. In general, the absorption energies were redshifted with a decrease in solvent polarity. Spectral absorptions for FSAL His-red were absent in this region for both of the solvents. It should be remembered that the azomethine group in this complex was reduced by sodium tetraborohydride. The lack of spectral feature in FSAL His-red supports the assignment of the transitions in the 350–415 nm region to the azomethine group.

TABLE I. Absorption Spectral Data (nm) of the FSAL Complexes in Water and DMSO.

	λ nm	
	I	II
Complexes in Water		
FSAL Ala	410, 385	260, 240, 207
FSAL Arg	380, 370	260, 240, 210
FSAL Gly	420, 485	255, 207
FSAL Glu	380, 372	260, 210
FSAL His	375, 365	240, 208
FSAL His-red	– , –	330, 280, 232
FSAL Lys	420, 390	260, 207
Complexes in DMSO		
FSAL Ala	420, 410	260, 207
FSAL Arg	388, 375	250, 210
FSAL Gly	420, 385	255, 207
FSAL Glu	390, 370	255, 210
FSAL His	385, 370	250, 210
FSAL His-red	– , –	330,
FSAL Lys	420, 390	260, 207

TABLE II. Emission (Excitation) Spectral Data (nm) of FSAL–Copper(II) Complexes in Water and DMSO.

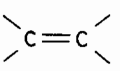
	Water	DMSO
FSAL Ala	531(453)	490(450)
FSAL Arg	540(465)	525(480)
FSAL Gly	537(454)	488(456)
FSAL Glu	532(440)	428(310)
FSAL His	535(440)	526(495)
FSAL His-red	none	NONE
FSAL Lys	518(468)	512(472)

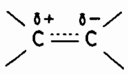
Emission (Excitation) Spectral Data (nm) of FSAL Gly in Water upon Addition of CN^-

FSAL Gly	FSAL Gly with CN^-
537(454)	534(470)

Table II lists the fluorescence (emission/excitation) spectral data (nm) of the FSAL complexes in the solvents water and DMSO. The R groups changed the fluorescence emission energies, and as in the case of the absorption spectra, reason for the change was not readily evident. The fluorescence excitation energies were found in the region of 400–470 nm, the same general region (although somewhat lower in energy) in which the absorption bands of the azomethine were assigned. We learned earlier that the FSAL His-red complex whose (C=N) group was reduced to the single bonded (C–N) group possessed no spectrum. Table II also shows a lack of fluorescence spectral features in this region. It is thus likely that the absorption energies around 365–420 nm and the fluorescence excitation energies around 400–470 nm have the same origin.

Changes in solvent are seen to have an effect on both the absorption and fluorescence spectral region assigned to the azomethine group. Table I indicated a general blue shift in the absorption energies with an increase in solvent polarity. Table II, however, shows a general red-shift in the emission energy of the (C=N) group with an increase in solvent polarity. The solvent affected blue shift of the azomethine group absorption is expected to result from an electronic excitation from the ground state to an excited state which is reasonably non-polar; one which has decreased in dipole moment with increase in solvent polarity. The excited state would resemble structure *a* below [13].


a


b

In as much as fluorescence studies reveal information about the ground state, a destabilization of the ground state must result in the presence of a more polar solvent. The solvent affected red-shift of the fluorescence emission would be consistent with the dipolar structure, *b*, above as the ground state [13].

The above explanation is not the only one which can be used to explain the observed shifts. The metal orbitals overlap with the complex chromophores, especially the nitrogen atom of the azomethine group. Perturbation of copper orbitals which couple with the fluorescence chromophore would be expected to reflect a change in the fluorescence spectra. NaCN Crystals were added to a solution of FSAL Gly to observe their effect on the fluorescence spectra. The color of the solution changed from a light green to an intense yellow green. The results of the fluorescence measurements are given in Table II. They show a large redshift in the excitation energy but only a moderate blue shift in the emission energy when compared with the FSAL Gly values. The most significant feature is a two fold increase in the intensities of both the emission and excitation spectra. These brief experiments have demonstrated that fluorescence studies may be expected to be a sensitive probe for the investigation of substrate interactions with copper ions of the binuclear complexes without the difficulties encountered using the absorption spectral methods. The study of phenol interaction with FSAL copper complexes using fluorescence spectroscopy is presently underway.

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