

Synthesis and Characterization of Copper(II) Complexes of a Tetradentate N_3O Ligand: Mononuclear Analogs for Phenolate-bridged Dinuclear Complexes

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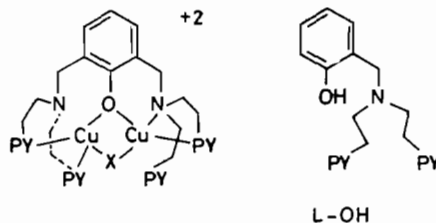
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Received February 28, 1985

Copper(II) Complexes of a potentially tetradentate ligand L-OH, which contains two pyridines, a tertiary amine and a phenol group have been synthesized and characterized. The coordination environment provided by this ligand closely resembles that found in a number of phenolate-bridged dinuclear Cu(II) complexes which have been synthesized as analogs for the ligand probe derivatives of the active sites of hemocyanin and tyrosinase. These complexes fall into two categories, $[(L-O)Cu-X]$ ($X = Cl^-$, N_3^-) where L-OH is deprotonated and acts as a tetradentate ligand and $[(L-OH)Cu-X_2]$ ($X = Cl^-$, NO_3^-) where L-OH behaves as a tridentate ligand. In addition, a dinuclear complex $[(L-O)_2-Cu_2](BF_4)_2$ has been isolated. The formulation and characterization of these complexes have been carried out using UV-Vis and IR spectroscopy as well as conductometric methods. The complexes $[(L-OH)Cu-X_2]$ are shown to dissociate and deprotonate in solution, resulting in phenoxide coordinated species. The spectral properties of these mononuclear complexes are compared and contrasted to each other and to their dinuclear analogs.

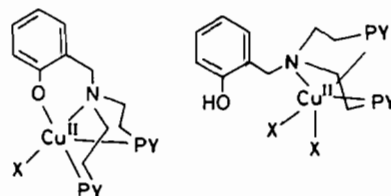
Spectroscopic and chemical investigations of the interactions of small molecules with the copper-containing active sites of hemocyanin (dioxygen carrier) and tyrosinase (mono-oxygenase) have been extremely useful in defining the coordination environment in these proteins [1–3]. For example, the azide anion (N_3^-) has been a particularly informative probe due to: (a) the occurrence of strong ligand to metal charge-transfer (LMCT) absorptions in the visible region, (b) accessibility by IR and EPR spectroscopic techniques, and (c) its variable mode of binding [3, 4]. We have previously reported the synthesis and characterization of a number of phenolato-bridged complexes serving as models for ligand probes of met-hemocyanin and met-tyrosinase derivatives [3, 5, 6].

These contain tetragonally coordinated Cu(II) ions, also bridged by 'exogenous' ligands (X) such as hydroxide [6], chloride [3, 5] and μ -1,1-azide [3, 5].



In order to fully understand the physico-chemical properties of these dinuclear systems, we sought to examine the chemistry of a mononuclear analog of these binucleating ligands. Thus, we are studying the properties of derivatives of the ligand L-OH. Here, coordination to copper from a phenolate oxygen, tertiary amino nitrogen and two pyridine nitrogen atoms may occur in a manner closely resembling that found in the dinuclear complexes. Studies of these derivatives may facilitate the assignment of UV-Vis absorptions by allowing us to sort out those bands due to phenoxide absorption compared to those due to exogenous ligand binding. In addition, the effects (structural and spectroscopic) of bridging of phenoxide or exogenous ligands to two copper(II) ions may be examined. Here, we describe the properties of a number of Cu(II) complexes containing L-OH which also possess chloride, azide or nitrate ligands.

The ligand L-OH was prepared by the reaction of bis(2-(2-pyridyl)ethyl)amine (py2) [7] with 2-bromomethylphenylacetate [8] followed by hydrolysis to the phenol. Two types of compounds were formed in the synthesis of Cu(II) derivatives of L-OH, depending on whether base was added to the ligand before addition of copper(II) salts. These include tetradentate-containing complexes I–III, in which the phenolate oxygen atom is coordinated to the copper, and tridentate-containing complexes IV–V, where the phenol oxygen is not deprotonated and is uncoordinated. The formulation and characterization of these complexes are based on elemental analysis, IR and UV-Vis spectroscopy and electrical conductance measurements.



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Tetradentate-containing Complexes, I–III

Stoichiometric reaction of cupric chloride with L–OH and NaOH in methanol (MeOH), followed by precipitation with diethylether affords complex I, containing coordinated chloride. Initially, we attempted to make the azide derivative by reaction of sodium azide with a solution containing cupric nitrate and L–OH. However, this resulted in the deposition of a polymeric azide containing material. The successful synthesis of II, $[(L-O^-)Cu-N_3]$, was achieved by direct reaction of I with one equivalent of NaN_3 in MeOH. We have determined the structure of this azide complex II via a single crystal X-ray diffraction study. This confirms the formulation and shows the Cu(II) ion to be pentacoordinate (square-based pyramid), with basal ligation to the azide, phenoxide oxygen, tertiary amine and one pyridine nitrogen. The other pyridine is coordinated in the axial position. The full structural details along with a direct comparison to the dinuclear μ -1,1-azido complex will be reported elsewhere [9].

Infrared spectra of both I and II exhibit broad bands in the 3300 – 3400 cm^{-1} region due to the presence of solvated water. The water can be removed by heating ($90\text{ }^\circ\text{C}$) the compounds under vacuum for 24 h, as verified by IR spectroscopy. No peak attributable to a phenolic O–H stretch is observed. This contrasts with what is observed for compounds IV–V, where an uncoordinated phenol is proposed to exist (see below). A strong single IR band is observed at 2041 cm^{-1} for II, which is assigned to the asymmetric stretch of coordinated azide. This compares with the value of 2068 cm^{-1} found for the μ -1,1-azido-bridged dinuclear complex [3].

In the electronic spectrum of I, a band at 440 nm ($\epsilon = 1940\text{ (M}\cdot\text{cm)}^{-1}$) is observed. We assign this to the phenoxide to Cu(II) charge-transfer (CT) transition, which occurs in the region expected [2b, 6, 10]. This is on the basis that no absorptions in this region are expected due to CT transitions from the nitrogen donor ligands. Chloride to Cu(II) CT bands may be expected to contribute only weakly in this region.

We have confirmed that a chloro-copper(II) complex of the tridentate ligand py2, $Cu(py2)Cl_2$ [11], shows only a weak absorption at 475 nm ($\epsilon = 15\text{ (M}\cdot\text{cm)}^{-1}$). In a mull spectrum of the solid, I also exhibits a broad strong absorption centered around 450 nm suggesting that the phenoxide oxygen is also coordinated in the solid state (Table I).

For the azide complex II, two absorption bands are observed in the visible region at 405 ($\epsilon = 2310\text{ (M}\cdot\text{cm)}^{-1}$) and 465 nm (shoulder, $\epsilon = 1380\text{ (M}\cdot\text{cm)}^{-1}$). A comparison of the position and intensity of these bands to those observed for I–V suggests that the 405 nm band may be assigned to the azido- to Cu(II) CT absorption, while the 465 absorption can be ascribed to the phenoxide to Cu(II) CT transition. The solid state mull spectrum of II corresponds to the solution spectrum with a weak broad absorption in the 600 – 700 nm region and distinct and stronger absorbance transitions *ca.* 410 and 460 nm (Table I).

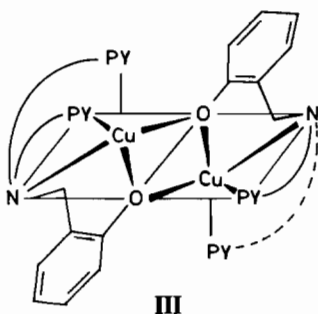
If $Cu(BF_4)_2\cdot 6H_2O$ is added to a methanolic solution containing stoichiometric quantities of L–OH and NaOH, a complex formulated as $[(L-O^-)_2Cu_2](BF_4)_2$, III, is isolated. The dimeric nature of III is suggested by conductivity measurements at 10^{-3} M in DMF and by the examination of Onsager plots for this and the other complexes (Table I). The molar conductance, Λ_M , for III falls in the range expected for a 2:1 electrolyte [12], and contrasts with the non-conducting nature of the neutral compounds I and II. The slope of the Onsager plot for III is $667\text{ ohm}^{-1}\text{M}^{1/2}$, consistent with values expected for a 2:1 electrolyte. Complex III also exhibits a strong absorption at 440 nm ($\epsilon = 5730$), assignable to a phenoxide to Cu(II) CT transition. When compared to the corresponding bands in the other complexes, the intensity of this transition is also consistent with the dimeric formulation and the occurrence of two bridging Cu(II)-phenoxide units. The observed magnetic moment of 1.6 BM per Cu atom (Evans method in DMF [13]) is not unreasonable for the proposed bridged $Cu_2(O^-Ph)_2$ unit. Such compounds are known [14]; variable temperature magnetic

TABLE I.

Complex	$\Lambda(10^{-3}\text{ M})$ ($\text{ohm}^{-1}\text{cm}^2\text{mol}^{-1}$)	Ion Type (slope)	pH	UV-Vis (CH_3CN)	
				$\lambda_{\text{max}}(\epsilon)^a$ solution	λ_{max} solid
$[(L-O^-)Cu-Cl]$ (I)	38.0		7.96	440 (1940)	450
$[(L-O^-)Cu-N_3]$ (II)	16			405 (2310) ^b 465 (1380)	410 460
$[(L-O^-)_2Cu_2](BF_4)_2$ (III)	133	2:1 (667)		440 (5730)	440
$[(L-OH)Cu-Cl_2]$ (IV)	33		6.57	445 (520)	–
$[(L-OH)Cu-(NO_3)_2]$ (V)	100	1:1	4.06	435 (2570)	–

^aAbsorption maxima are given in nm. Peaks given are those assigned to the phenoxide to Cu(II) CT transition; ^bAssigned to the azide to Cu(II) CT transition.

studies and/or an X-ray structural investigation would aid in the elucidation of the detailed coordination occurring in **III**.

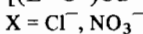
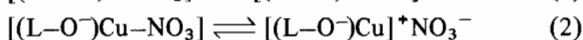
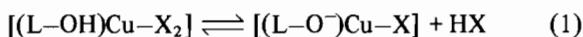


Tridentate-containing Complexes

Complexes **IV** and **V** are distinguished from **I–III** by the fact that they are all prepared in the absence of base. As solids, L–OH behaves as a tridentate ligand in these complexes and there exists an uncoordinated phenolic–OH group. However, in solution, it appears that phenolic group ionization occurs for the dichloride and dinitrate complexes **IV** and **V**, such that coordination to the phenoxide oxygen atom does occur.

Compounds **IV** and **V** are formulated as penta-coordinate Cu(II) complexes with coordination from the three nitrogen donors in L–OH. Neutral compounds are formed by further coordination to either two chloro (**IV**) or two nitrate (**V**) ligands. A broad absorption centered *ca.* 3500 cm^{-1} is observed in the IR region for both complexes and is assigned to the $\nu(\text{O–H})$ of the uncoordinated phenol group. In the mull UV-Vis spectrum (300–700 nm) of the solid complexes, no bands other than the broad weak d–d absorptions (>600 nm) are seen, consistent with the absence of phenoxide coordination.

However, the solution electronic spectra (in CH_3CN) of **IV** and **V** do exhibit absorptions at 445 nm and 435 nm respectively (Table I). Thus, we suggest that in solution these neutral complexes undergo phenolic group ionization; deprotonation of the phenol is accompanied by coordination of phenoxide to Cu(II) resulting in the observed CT transitions.



As noted above, a chloro–Cu(II) derivative of py2 exhibits no visible absorptions in the 300–600 nm range. Likewise, we find that a nitrate–Cu(II) complex ($\text{Cu}(\text{NO}_3)_2 + \text{py}_2$) also possesses no visible absorption bands in the 300–550 nm range. Thus, it is with confidence that we assign the strong 435–445 nm band to the phenoxide to Cu(II) CT transition.

Evidence for these dissociation reactions comes from several lines of additional data. Beer's Law plots (concentration dependence of the phenoxo to Cu(II) CT absorptions; 445 and 435 nm) for both complexes **IV** and **V** exhibit non-linear behavior, consistent with the occurrence of these equilibrium reactions. By contrast, a similar plot for complex **I** is well behaved. The chloro complex **IV** exhibits a molar conductance value in DMF lower than the range expected for a 1:1 electrolyte ($65\text{--}90 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$), but Λ_M for the nitrate compound **V** is $100 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$, indicative of a 1:1 (or greater) electrolyte [12b].

The deprotonation of L–OH and dissociation of the ligand X^- to form $[(\text{L–O}^-)\text{Cu–X}]$ (eqn. (1)) should also be accompanied by the formation of the strong acid HX, and this has been confirmed by pH measurements of complexes **I**, **IV** and **V** in CH_3CN solution. Relative to the 'apparent pH' of acetonitrile and complex **I**, both compounds **IV** and **V** show lower pH values (Table I) consistent with the increased acidity expected due to the dissociation reaction. Note that the nitrate complex **V** gives the most acidic solution suggesting that the dissociation equilibrium reaction lies further to the right compared to the chloro complex **IV** (eqn. (2)). This is also consistent with the intensities of the phenoxide to Cu(II) CT bands and the conductance at 10^{-3} M observed in these compounds. The nitrate complex **V** has a greater acidity, conductance and CT band intensity than the chloro complex **IV**. In fact, the extinction coefficient at 435 nm for **V** is comparable to those observed in **I–III** (per Cu), whereas that for the 445 nm band in **IV** is rather diminished.

It is apparent that the electronic spectral (position and intensity of CT transitions) and infrared spectral properties vary depending on whether the phenoxide group is bridging or non-bridging. Thus, in the dinuclear phenoxide bridged complexes where the second bridging group is OH^- or N_3^- , the phenoxide to Cu(II) CT band seems to occur below 400 nm [3, 6]. Here, it is found above 400 nm for all of the complexes **I–V**. It also has been recently reported that the $\nu(\text{C–O}, \text{phenoxide})$ stretching values in the resonance Raman spectra for phenoxide-bridged dinuclear Cu(II) complexes are observed at significantly higher frequencies than those of the corresponding mononuclear analogs [15].

The effects of 'exogenous' ligand binding and phenolate coordination in mono- vs. dinuclear copper complexes continue to be of interest because of the implications for structural and spectral assignments in other coordination compounds or protein active sites. Future investigations will focus upon detailed comparisons of the properties of analogous mono- and binuclear systems. We are also studying the copper(I) chemistry of L–OH since its dinucleating ligand analog forms a Cu(I)–Cu(I) system capable of binding dioxygen reversibly [16].

Acknowledgement

The authors wish to thank the National Institutes of Health (NIH GM28962) for support of this research.

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