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Synthesis, Crystal Structure and Properties of (1,3-(Bis(*N*-methylimidazolimine)-propan-2-ol)Cu(II))·perchlorate

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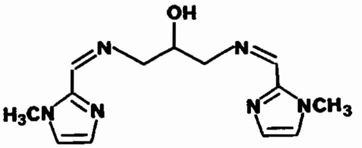
Abstract

The synthesis, crystal structure and physical properties of a mononuclear Cu(II) complex of 1,3-bis(*N*-methylimidazolimine)propan-2-ol is described. The complex crystallizes in the triclinic space group $P\bar{1}$ with $a = 11.343(5)$, $b = 11.770(4)$, $c = 8.452(2)$ Å, $\alpha = 109.71(2)°$, $\beta = 91.25(2)°$, $\gamma = 98.24(3)°$, $V = 1048.4$ Å^3 and $Z = 2$. The structure of the complex is a distorted square pyramid consisting of the N_4 basal plane resulting from coordination of the 1,3-bis(*N*-methylimidazolimine)propan-2-ol ligand and a weak coordinated apical water molecule. The complex displays quasireversible electrochemical behavior in both aqueous and acetonitrile solutions. In addition, the complex has been studied by UV–Vis and EPR spectroscopies.

Introduction

Galactose oxidase (D-galactose: oxygen oxidoreductase, EC 1.1.3.9) is a copper containing metalloprotein which catalyzes the oxidation of several primary alcohols to aldehydes [1]. The catalytic site of the protein is thought to contain only one type II copper center and no additional prosthetic group. The mechanism of catalytic activity has received much interest recently [2] and is thought to involve displacement of a coordinated H_2O molecule by the alcohol substrate prior to its two-electron oxidation. The active site is thought to contain two histidine imidazole nitrogens, a labile H_2O solvent molecule, and additional O or S containing ligands [3] coordinated to the Cu(II) ion. The coordination environment around the copper(II) ion has been proposed to be either tetragonal or square pyramidal [4]. Several attempts to model the active site of galactose oxidase (GOase) and its catalytic activity utilizing simple inorganic compounds have been reported [5].

We wish to describe herein the synthesis, crystal structure and characterization of a mononuclear Cu(II) complex of 1,3-bis(*N*-methylimidazolimine)-propan-2-ol (2-MeImPrO) (I) which may be considered to be a structural model of the active site of GOase. The complex is quite soluble in both aqueous and non-aqueous solutions and crystallizes readily from water.



I

Experimental

All manipulations were performed under dried-nitrogen. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, TN.

Physical Measurements

^1H and ^{13}C NMR spectra were recorded on a Varian XL-300-MHz spectrometer. All chemical shifts are referenced relative to $Si(CH_3)_4$ in deuterochloroform (Aldrich) and are recorded as δ units in ppm. Visible absorption spectrum was recorded on a Shimatzu 600 spectrophotometer using quartz cells of 1 cm thickness. Spectroscopic grade acetonitrile (Baker) was used as a solvent for all measurements. Extinction coefficients are reported in units of M^{-1} cm^{-1}. Room temperature solid-state magnetic susceptibilities were recorded on a PAR Model 155 Vibrating Sample Magnetometer which has been calibrated with $HgCo(NCS)_4$. Pascal constants were used to correct all data for diamagnetism [6]. EPR spectra were recorded at X-band on a Varian E-109 spectrometer equipped with an Oxford Instruments, Inc. cryostat. Spectra were recorded as powdered samples and frozen acetonitrile solutions. X-ray crystallographic data were obtained on an Enraf-Nonius CAD-4 diffractometer. Data reduction and solution were performed on a VAX-11/750 using the SDP package of programs [7]. Electrochemical measure-

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ments were made at room temperature using PAR 175 universal programmer, a PAR 179 digital coulometer, and PAR 173 potentiostat interfaced with a Houston Instrument Model 2000 X-Y recorder. A conventional three-electrode configuration consisting of a Ag/AgCl reference electrode and platinum wire working and auxiliary electrodes was used to obtain cyclic voltammograms. Melting points were determined using a Thomas Hoover capillary melting point apparatus and are reported as uncorrected values.

Reagents

All solvents used were either reagent or spectroscopic grade and were dried by conventional procedures prior to use. The *N*-methylimidazole and 1,3-diamino-propan-2-ol (Aldrich) were used as received. *N*-Methylimidazole-2-carboxaldehyde was prepared by the method of Iverson and Lund [8]. Copper(II) bromide was purchased from Merck and used as received.

Ligand synthesis

The Schiff base ligand was prepared by condensation of 2.192 g (0.022 mol) of *N*-methylimidazole-2-carboxyaldehyde [8] with 1.007 g (0.011 mol) of 1,3-diaminopropan-2-ol in dry methanol. The solvent was removed and the resulting yellow oil was dissolved in chloroform, dried with magnesium sulfate, and the solvent removed *in vacuo*. An off-white precipitate of 1,3-bis(*N*-methylimidazolimine)propan-2-ol (2-MeImPrO) (**1**) was obtained upon removal of an ether solution of the oil (70% yield). Melting point (m.p.) = 132–134 °C. ^{1}H(δ, CDCl$_3$): 3.74(m, 2H), 3.81(m, 2H), 3.94(s, 6H), 4.25(s, 1H), 4.90(s, 2H), 7.07(s, 2H), 8.34(s, 2H).

Preparation of [Cu(2-MeIm$_2$PrO)H$_2$O]·2ClO$_4$ (2)

Compound **1** (0.6488 g, 0.024 mol) and CuBr$_2$ (1.056 g, 0.024 mol) were dissolved in 250 ml of ethanol and stirred for 2 h at 55 °C. The purple solution was cooled to room temperature and stirred overnight whereupon a purple solid was isolated by filtration. Approximately 1.0 g of this purple solid was dissolved in 8 ml of hot H$_2$O, filtered and added to an aqueous solution (30 ml) of NaClO$_4$ (2.4 g). The solution turned an aqua green color upon mixing. The volume of the solution was reduced *in vacuo* whereupon a blue–green microcrystalline sample precipitated. Crystals suitable for X-ray crystallographic analysis were isolated by slow evaporation of an aqueous solution of the complex. *Anal.* Calc. for C$_{13}$H$_{20}$CuCl$_2$N$_6$O$_{10}$: 11.3. Found: 10.9%(Cu).

X-ray Crystallography, Data Collection, Reduction of X-ray Data

A light blue plate having approximate dimensions of 0.23 × 0.32 × 0.48 mm was mounted on a glass fiber with epoxy and used for data collection. Cell constants and an orientation matrix for data collection were obtained by least-squares refinement of the diffraction data from 18 reflections in the range of $10.5 < \theta < 14°$. The reflections were measured using a computer controlled diagonal slit method of centering. All calculations were performed on a VAX-11/750 computer using SDP/VAX. Choice of the triclinic space group, $P\bar{1}$, was confirmed by Tracer [7] and by the successful solution and refinement of the structure. Data were collected at 295 K using Mo Kα radiation and the ω–2θ scan technique on an Enraf-Nonius CAD-4 automated diffractometer. As a check on crystal and electronic stability, three reflections were chosen as standards and their intensities were monitored every 40 min. The intensities of these standards remained constant within experimental error during data collection so no decay correction was applied. The data were corrected for Lorentz and polarization effects and an empirical absorption correction based on a series of psi scans was applied to the data. Relative transmission coefficients ranged from 0.752 to 1.000 with an average value of 0.896. A secondary extinction correction was applied. The final coefficient, refined in the least-squares cycle, was 3.0×10^{-7}. Intensities of equivalent reflections were averaged and all data were handled and the crystal structure solved using the SDP package [7]. A summary of the crystal data, experimental details and refinement results is listed in Table 1.

TABLE 1. Crystal Data for [Cu(2-MeIm$_2$PrO)(H$_2$O)]·2ClO$_4$

Formula	C$_{13}$H$_{20}$CuCl$_2$N$_6$O$_{10}$
Formula weight	554.78
Space group	$P\bar{1}$
Crystal system	triclinic
Temperature (K)	295
a (Å)	11.343(5)
b (Å)	11.770(4)
c (Å)	8.452(2)
α (°)	109.71(2)
β (°)	91.25(2)
γ (°)	98.24(3)
V (Å^3)	1048.4
Z	2
D_{obs} (g cm^{-3})	1.75(1)
D_{calc} (g cm^{-3})	1.76
F(000)	566
Crystal dimensions (mm)	0.23 × 0.32 × 0.48
μ (cm^{-1})	13.6
R, R_{w}	0.042, 0.053
No. unique reflections	4792
No. observed reflections	3832 ($I > 3\sigma\|I\|$)
GOF	2.17
Radiation, λ (Å)	Mo Kα (0.71069)
Data collected	$\pm h, \pm k, +l$
Monochromator	graphite
Scan technique	ω–2θ
Scan range	0.8 + 0.340 tan θ

Structure Solution and Refinement

The structure was solved using the Patterson heavy-atom method which revealed the position of the copper atom. The remaining atoms were located using successive difference Fourier syntheses. All non-hydrogen atoms were refined anisotropically. Two disorder problems were encountered during the solution and refinement of the structure. First, the position of O(1) was found to be disordered and was treated as 1/2 occupancy atoms for each tetrahedral site. Second, both of the perchlorate counter ions were found to contain rotational disorders about a three-fold symmetry axis. Atoms O(11) and O(21) were assigned occupancies of 1.0 during refinement while the remaining oxygen atoms were assigned the following occupancies: O(12), 0.65; O(13), 0.65; O(14), 0.65; O(112), 0.35; O(113), 0.35; O(114), 0.35; O(22), 0.75; O(23), 0.75; O(24), 0.75; O(122), 0.25; O(123), 0.25; O(124), 0.25. Final atomic positional parameters for all non-hydrogen atoms are given in Table 2. Hydrogen atoms were located and added to the structure factor calculations as fixed contributions and their positional parameters were not refined. The structure was refined using full-matrix least-squares on F where the function minimized was $\Sigma w(|F_o| - |F_c|)^2$ and the weight w is defined using the method of Killean and Lawrence [9] with terms of 6.020 and 3.0. Scattering factors were taken from Cromer and Waber [10] and anomalous dispersion effects were included in F_c with the values for $\Delta f'$ and $\Delta f''$ obtained from Cromer [11]. The final cycle of refinement included 353 variable parameters and resulted in final agreement factors of $R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o| = 0.042$ and $R_w = [\Sigma(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2} = 0.053$. The highest peak on the final difference Fourier had a height of 0.43 e/Å^3. Plots of $\Sigma(|F_o| - |F_c|)^2$ *versus* $|F_o|$, reflection order in data collection, sin θ/λ, and various classes of indices showed no unusual trends. See also 'Supplementary Material'.

Results and Discussion

Characterization of [Cu(2-MeIm$_2$PrO)(H$_2$O)]·2ClO$_4$

Previous studies have recognized the ability of pentadentate ligands such as 1,3-bis(*N*-methylimidazolimine)propan-2-ol(2-Im$_2$PrO) (I) to function both as tetradentate and binucleating ligands [5c, 12]. Borer *et al.* [5d] have described the synthesis of insoluble Cu(II) complexes of 1,3-bis(imidazolimine)-propan-2-ol, however these complexes are incompletely characterized and thought to be polymeric. [Cu(2-MeIm$_2$PrO)(H$_2$O)]$^{2+}$ on the other hand, is quite soluble in aqueous and some non-aqueous solutions and has been characterized by X-ray crystallography, electrochemical and spectroscopic techniques.

TABLE 2. Positional Parameters[a]

Atom	x	y	z	B(Å^2)[b]
Cu	0.23187(3)	0.22979(3)	0.09404(5)	3.096(6)
Cl1	0.66798(9)	0.78551(8)	0.3507(1)	4.73(2)
Cl2	0.83940(9)	0.37441(8)	0.2639(1)	5.05(2)
O1A	0.3858(6)	0.4899(6)	0.0006(8)	5.8(1)
O1B	0.3733(5)	0.6546(5)	0.2177(9)	6.8(2)
O2	0.1345(2)	0.2740(3)	0.3441(4)	5.21(6)
O11	0.6364(3)	0.7797(3)	0.1835(4)	6.05(7)
O12	0.5529(6)	0.776(1)	0.4192(8)	11.5(3)
O13	0.7390(5)	0.8927(5)	0.4321(7)	9.2(1)
O14	0.7090(7)	0.6763(5)	0.3391(7)	9.0(1)
O21	0.9262(4)	0.4725(4)	0.2661(6)	9.6(1)
O22	0.7630(8)	0.3263(8)	0.1141(9)	14.6(3)
O23	0.7607(5)	0.4114(7)	0.3867(8)	11.3(2)
O24	0.8899(5)	0.2787(5)	0.276(1)	11.8(2)
O12′[c]	0.7959(8)	0.759(1)	0.364(1)	8.1(3)
O13′	0.604(1)	0.7179(8)	0.423(1)	8.2(2)
O14′	0.689(1)	0.9039(9)	0.487(1)	7.4(2)
O22′	0.850(1)	0.301(2)	0.113(2)	8.3(5)
O23′	0.735(1)	0.410(2)	0.275(2)	8.2(5)
O24′	0.854(3)	0.333(2)	0.390(2)	15.7(9)
N1	0.1010(2)	0.1297(2)	−0.0790(3)	3.18(5)
N2	−0.0380(2)	0.1366(2)	−0.2605(3)	3.66(5)
N3	0.1662(2)	0.3677(2)	0.0528(3)	3.28(5)
N4	0.3822(2)	0.3415(2)	0.2184(3)	3.37(5)
N5	0.3196(2)	0.1020(2)	0.1218(3)	3.31(5)
N6	0.4868(2)	0.0697(2)	0.2252(3)	3.80(5)
C1	0.0506(3)	0.0122(3)	−0.1740(4)	3.62(6)
C2	−0.0366(3)	0.0165(3)	−0.2862(4)	3.94(7)
C3	0.0446(2)	0.2023(3)	−0.1356(4)	3.13(5)
C4	0.0818(3)	0.3336(3)	−0.0617(4)	3.43(6)
C5	0.2094(3)	0.4977(3)	0.1418(5)	4.18(7)
C6	0.3450(3)	0.5265(3)	0.1562(5)	4.26(7)
C7	0.4040(3)	0.4749(3)	0.2776(5)	4.29(7)
C8	0.4614(3)	0.2846(3)	0.2519(4)	3.50(6)
C9	0.4269(3)	0.1540(3)	0.2015(3)	3.26(5)
C10	0.3103(3)	−0.0207(3)	0.0962(4)	4.01(7)
C11	0.4142(3)	−0.0408(3)	0.1599(4)	4.32(7)
C12	−0.1178(3)	0.1856(4)	−0.3528(5)	5.29(8)
C12	0.6043(3)	0.0947(4)	0.3181(5)	5.66(9)

[a] e.s.d.s given in parentheses. [b] Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as: $(4/3[a_2B(1,1) + b_2B(2,2) + c_2B(3,3) + ab(\cos \text{gamma})B(1,2) + ac(\cos \text{beta})B(1,3) + bc(\cos \text{alpha})B(2,3)]$. [c] Prime atoms correspond to atomic positions associated with disordered perchlorate oxygen atoms. See 'Experimental' for assignment of occupancy factors.

Compound **1** has been isolated from the Schiff base condensation of 2 equivalents of 1-methylimidazole-2-carboxaldehyde with 1,3-diaminopropan-2-ol in methanol. The mononuclear copper(II) complex [Cu(2-MeIm$_2$PrO)H$_2$O]·2ClO$_4$ (**2**) has been isolated as a blue–green crystalline solid from an aqueous methanolic solution of **1** and CuBr$_2$. A broad absorption at approximately 3400 cm^{-1} is observed in the IR spectrum of the copper complex

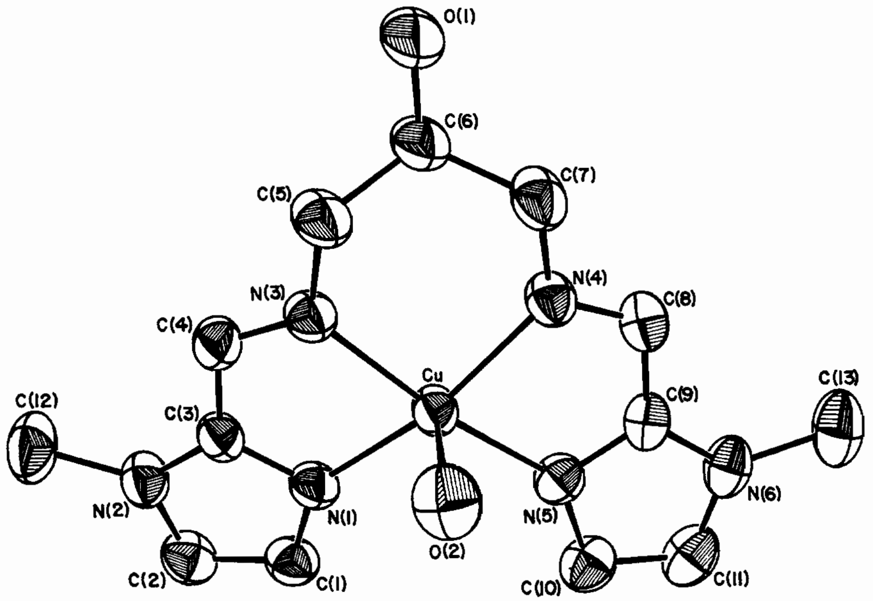

Fig. 1. A view of the coordination environment of the $[Cu(2\text{-}MeIm_2PrO)(H_2O)]^{2+}$ cation.

and is assigned to the ν(OH) stretch of the uncoordinated secondary alcohol moiety. Other absorption bands in the infrared spectra occur in the 1600–1630 cm^{-1} region and are assigned to ligand ν(C=N) stretches for the complex. The complex is soluble in polar solvents and displays an electronic spectrum in acetonitrile consisting of a broad absorption band at 640 nm ($\epsilon = 53\ M^{-1}\ cm^{-1}$) and an additional band at 307 nm ($\epsilon = 13\,300\ M^{-1}\ cm^{-1}$). The solid-state room temperature magnetic moment of 1.8 BM is consistent with an $S = 1/2$ ground state configuration for the d^9 metal ion. In addition, compound **2** displays an axial EPR spectrum (77 K) for a frozen solution of the complex in acetonitrile giving $g_{\parallel} = 2.28, g_{\perp} = 2.08$ and $A_{\parallel} = 0.0159\ cm^{-1}$.

Description of Crystal Structure

The preparation and characterization of a few mononuclear complexes of binucleating ligands, similar to **1**, have been reported [5]. However, only the Cu(II) complexes containing pyrrole-2-aldimine [5c] and salicylaldimine [5a] moieties have been studied crystallographically. The structure of **2** (Fig. 1) consists of a '4 + 1' square pyramidal arrangement of the ligand **1** and a weakly coordinated water molecule. The $Cu{-}N_4$ unit is nearly planar with the metal ion displaced 0.185 Å from the chelate plane. The average Cu–N(imine) and Cu–N(imidazole) lengths of 2.014(3) and 1.992(3) Å (Table 3), respectively, are typical of copper(II) nitrogen bond lengths [13] and comparable to lengths reported for $[Cu(pyr_2PrO)]_2{\cdot}CH_3OH$ [5c]. The longer axial Cu–O2

TABLE 3. Selected Bond Distances (Å) and Angles (°)

Atom 1	Atom 2	Distance	Atom 1	Atom 2	Atom 3	Angle
Cu	N(1)	1.993(2)	N1	Cu	O2	102.5
Cu	N(3)	2.007(3)	N3	Cu	O2	87.9
Cu	N(4)	2.002(2)	N4	Cu	O2	90.9
Cu	N(5)	1.992(3)	N5	Cu	O2	98.7
Cu	O(2)	2.341(3)	N1	Cu	N3	82.2
N(1)	C(1)	1.374(3)	N3	Cu	N5	171.3
C(1)	C(2)	1.373(5)	N1	Cu	N4	165.2
C(2)	N(2)	1.358(5)	N3	Cu	N4	92.2
N(2)	C(12)	1.479(6)	N4	Cu	N5	82.2
N(2)	C(3)	1.337(3)	N1	Cu	N5	101.8
N(1)	C(3)	1.338(4)				
C(3)	C(4)	1.451(4)				
C(4)	N(3)	1.266(4)				
N(3)	C(5)	1.463(4)				
C(5)	C(6)	1.520(5)				
C(6)	O(1A)	1.353(8)[a]				
C(6)	O(1B)	1.404(6)				
C(6)	C(7)	1.541(7)				
C(7)	N(4)	1.460(5)				
N(4)	C(8)	1.275(4)				
C(8)	C(9)	1.441(4)				
C(9)	N(5)	1.335(3)				
N(5)	C(10)	1.374(5)				
C(10)	C(11)	1.369(5)				
C(11)	N(6)	1.365(4)				
N(6)	C(13)	1.471(5)				
N(6)	C(9)	1.345(5)				

[a] Lengths reported for two positions found for O(1).

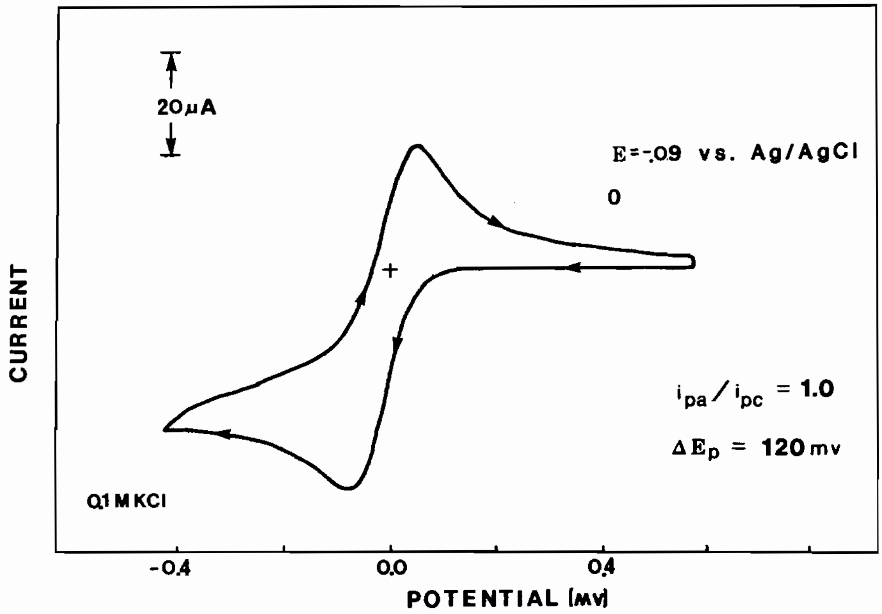

Fig. 2. Cyclic voltammogram of $[Cu(2\text{-MeIm}_2PrO)(H_2O)]^{2+}$ (1×10^{-3} M) in 0.1 M KCl at a glassy carbon electrode referenced against a Ag/AgCl electrode.

length of 2.341(3) Å is consistent with lengths observed for other tetragonally distorted structures [14]. The water molecule is not involved in hydrogen bonding and is considered to be weakly coordinated. Bond angles (Table 2) within the coordination sphere of the metal ion indicate moderate distortion of the square-pyramidal geometry of the complex. Bond distances and angles within the chelated $(2\text{-Im})_2PrO$ ligand are normal.

The alcoholic O(1) atom is not coordinated to the copper ion and its position is disordered (50:50) due to a weak hydrogen bonding interaction with O12 (occupancy of 0.65) of a disordered perchlorate counter ion. The O1–O12 and O1–H···O12 bond lengths of 2.923(3) and 1.752(3) Å, respectively, and O1–H···O12 angle of 167.9° are typical of moderately strong hydrogen bonding interactions. The other perchlorate ion is not involved in hydrogen bonding but also is disordered. A description of how the disorder problem was treated is contained in 'Experimental'.

Electrochemistry

Cyclic Voltammetry of Copper(II) Complex

The cyclic voltammogram of 2 in aqueous solution at a glassy carbon electrode is shown in Fig. 2. The mononuclear copper(II) complex displays a single quasireversible one-electron (i_{pa}/i_{pc} = 1.0, ΔE_p = 80 mV) reduction wave at −0.020 V *versus* Ag/AgCl. In acetonitrile the electochemical behavior of 2 is similar to that reported for the mononuclear pyrrole derivative [12c], except the redox potential of 2 is significantly more anodic. Essentially identical redox behavior is observed in aqueous solution ($E_{1/2}$ = −0.09 V, i_{pa}/i_{pc} = 1.0, ΔE_p = 120 mV), indicating that the axial H_2O molecule is most likely not coordinated strongly in solution. The low reduction potential and general reversibility of the redox reaction of 2 indicates that 1 is flexible enough to stabilize both Cu(II) and Cu(I) forms of the complex. The formation of the Cu(I) complex upon reduction will mostly require concomitant distortion of the square plane arrangement of the complex toward a tetrahedral geometry.

Conclusions

A new pentadentate bis-imidazolyl ligand has been synthesized and found to form a mononuclear Cu(II) complex whose structural features resemble those proposed for the active site of galactose oxidase. A crystal structure of the complex shows the Cu(II) is five-coordinate in the solid state with a water molecular weakly bonded in the fifth coordination site. The compound displays quasireversible electrochemical properties with a potential close to 0 V *versus* Ag/AgCl in both water and acetonitrile solutions. Evaluation of the catalytic properties of 1 toward various alcohols is in progress and will be reported elsewhere.

Supplementary Material

Tables of positional parameters of non-hydrogen atoms, anisotropic thermal parameters, fractional coordinates for H atoms, bond distances and angles, least-square planes, torsional angles and structure factors can be obtained from either the author or Cambridge Crystallographic Data Center.

Acknowledgements

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