Synthesis, Structure and Properties of Tris(1-Ethyl-4-Isopropyl-Imidazolyl- κ N)Phosphine Copper(II)

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In this study we report the synthesis and characterization of $[\text{Cu}(\text{T1Et4iPrIP})(\text{CH}_3\text{OH})\text{Cl}]\text{Cl}$ (**1**) (T1Et4iPrIP = tris(1-ethyl-4-isopropyl-imidazolyl)phosphine). T1Et4iPrIP serves as a His_3 biomimetic ligand binding metals through the 3-nitrogen of the imidazolyl group. The structure of **1** features copper(II) bonded to three nitrogen ligands from T1Et4iPrIP along with an oxygen ligand from methanol and a chloride ligand to form slightly distorted square pyramidal geometry with an imidazole group occupying the axial position and the methanol and chloride ligands situated in the basal plane. The weak sigma donation of the ligand set results in low energy d-d electronic transitions and small $A_{\parallel}$ (131 G). Time-dependent DFT calculations (B3LYP, 6-311+G(d,p)) on the optimized structure of **1** in methanol solvent allowed for the assignment of specific electronic transitions in the UV-Vis spectrum. The highest occupied molecular orbital (HOMO) was noted to consist of 65% Cu-d character identified as the $d_{x^2-y^2}$ orbital.

1. Introduction

Metalloproteins possessing copper centers with N-ligation include dopamine β -monooxygenase, nitrite reductase, amine oxidase, hemocyanin, and tyrosinase.[1-6] The X-ray structures for copper(II) centers possessing 3His (nitrite reductase and amine oxidase) coordination are shown below.[7, 8] A hydroxide/water ligand occupies the fourth position yielding distorted tetrahedral geometry. Preparing accurate synthetic models for these sites requires ligands bearing imidazole groups.

Many synthetic copper model compounds have been prepared with a variety of saturated polydentate amine, pyridine, and pyrazolylborate-based ligands,[9-14] few groups, however, have incorporated the biologically most relevant bis/tris(imidazole) donors,[15-21] which have significantly different donor/acceptor properties.[22-25] Previously tris(imidazol-2-yl)phosphine tripodal ligands were employed as histidine mimics for synthetic model studies.[26-32] Steric bulk (*i*Pr or *t*Bu)[18, 31, 33] was introduced at the 4-position of the imidazole ring to prevent the formation of $[\text{Cu}(\text{ligand})_2]^{n+}$. [31] Tris(imidazol-2-yl)phosphine supported metal complexes using

Zn,[28, 30, 32, 34-39] Co,[38-43] Cd,[38] Hg,[38] Ni,[39] Sc,[44] and Fe[26, 27, 29, 45-47] have been reported in the literature. Despite their biological relevance, however, only five Cu(II) complexes possessing these ligands have been reported.[18, 33, 38] In order to correlate the structure-spectroscopic properties of model complexes with respective copper proteins, more studies are required. In this work, we report the synthesis, structure and characterization of a new Cu(II) complex supported by the tris-imidazolylphosphine ligand T1Et4iPrIP[31] which possesses *i*Pr groups at the 4-position of the imidazole ring (Scheme 1). EPR spectroscopy and time-dependent DFT calculations for the Cu(II) complex of T1Et4iPrIP are also reported. Structural and spectroscopic features will be compared with the oxidized forms of nitrite reductase and amine oxidase.

Scheme 1 Structure of T1Et4iPrIP

2. Experimental Section

2.1 Materials

Anhydrous cupric chloride (Alpha Aesar Chemical Co.) was obtained by warming cupric chloride dihydrate at 40 °C under high vacuum for 24 h. T1Et4iPrIP was synthesized according to a literature method.[31] Solvents were purified using an Innovative Technologies Inc. Solvent Purification System. Methanol was dried and distilled from magnesium methoxide. Elemental analysis was performed on pulverized crystalline samples that were heated under vacuum and sealed in a glass ampule prior to submission (Atlantic Microlabs, Inc., Norcross, GA).

2.1.1 [Cu(T1Et4iPrIP)(CH₃OH)Cl]Cl (1). To a slurry of CuCl₂ (62 mg, 0.46 mmol) in MeCN (2 mL) was added T1Et4iPrIP (205 mg, 0.46 mmol) in CH₂Cl₂ (2 mL) drop wise with stirring. The resulting clear dark green solution was stirred for 1 h then filtered. The solvent was removed under reduced pressure. The compound was crystallized by ether diffusion into a methanol solution of **1** which afforded green blocks after 2 d. Yield: 159 mg (56.8 %). FTIR (KBr pellet, cm⁻¹): 3 475 (br, OH_{methanol}), 3 050 and 3 150 (Im), 2 964 (C-H). UV-vis (methanol; λ_{max}, nm (ε, M⁻¹ cm⁻¹): 809 (75.6). Anal. Calcd for C₂₅H₄₃N₆OPCuCl₂: C, 49.30; H, 7.12; N, 13.80. Found: C, 49.67; H, 6.95; N, 14.26. X-band EPR (77 K, methanol glass): g_{||} = 2.28 (A_{||} = 131 G); g_⊥ = 2.07. Magnetic measurements, μ_{eff} (polycryst, 298 K): 1.81 μ_B.

2.2. Physical measurements

A Cary 50 UV-vis spectrophotometer was used to collect optical spectra. FT-IR spectra were acquired on a Varian 3100 Excalibur Series. The EPR measurements were recorded in a suprasil quartz dewar (cat. no WG-850(-Q), WILMAD Glass co., Inc., Buena, NJ) at 77 K and at 13 mW using a Varian Century Series ESR spectrometer operating at 9.28 GHz with an E-4531 dual cavity, 9 in. magnet and with a 200 mW klystron. Calibration of the field was performed using

Fremy's salt (g (center of the spectrum) = 2.0056, A^N = 13.09 G). NMR spectra were monitored at 25 °C on a Bruker Avance II 400 MHz instrument and sample peaks were referenced to TMS (CDCl_3). Magnetic measurements on polycrystalline samples at 298 K were performed using a Johnson-Matthey magnetic susceptibility balance.

2.3. Crystallographic studies

Compounds **1** was crystallized by diffusion of ether into a methanolic solution of **1**. A light green block was attached to a glass fiber and mounted on a Siemens SMART Platform CCD diffractometer for data collection at 173(2) K.[48] The data collection was carried out using MoK_α radiation (graphite monochromator). A randomly oriented region of reciprocal space was surveyed to the extent of one sphere to a resolution of 0.84 Å. Four major sections of frames were collected with 0.30° steps in ω at four different φ settings and a detector position of -28° in 2θ . The intensity data were corrected for absorption and decay (SADABS).[49] Final cell constants were calculated from the xyz centroids after integration (SAINT).[50] Please Refer to Table 1 for additional crystal and refinement information. The structure was solved using SIR-97[51] and refined using SHELXL-97.[52] A direct-methods solution was calculated which provided most non-hydrogen atoms from the E-map. Full-matrix least squares/difference Fourier cycles were performed which located the remaining non-hydrogen atoms. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were placed in ideal positions and refined as riding atoms with relative isotropic displacement parameters. The function SQUEEZE, from the program PLATON,[53] was used to model solvent accessible void space in the unit cell. 1150.9 Å³ of void space, containing 364 electrons, per unit cell was detected. The crystalline lattice contains large pockets of disordered solvent. The second

chloride counter ion to the Cu(II) center is also contained within the large pockets. An attempt was made to model the position of the second chloride counter ion and use the SQUEEZE function to model the remaining electron density. After modeling the chloride ion over four positions (48:27:15:10) and running the SQUEEZE function, the total solvent accessible void space was calculated to be 859.7 Å³, containing 169 electron per unit cell. The largest residual density peak was 2.04 electrons/Å³. This resulted in an R1(observed) of 0.0797 and a wR2(all data) of 0.2550. The atomic coordinates (x10⁴) and equivalent isotropic displacement parameters (Å²x10³) of the four chloride atom positions were calculated (See Table S3). After modeling the positions of the second chloride ion, the atoms were removed from the atom list and the SQUEEZE function was used to model all of the electron density in the solvent accessible void space (see structure solution and refinement section), leading to the final refinement. The ethyl group containing carbon atoms C4 and C5 was modeled as disordered over two positions (79:21). The isopropyl group containing carbon atoms C14, C15 and C16 was modeled as disordered over two positions (74:26). The isopropyl group containing carbon atoms C22, C23 and C24 was modeled as disordered over two positions (65:35). The methyl group C13 was modeled as rotationally disordered over two positions. The proton on the coordinated methanol appears to form a hydrogen bond with an atom in the disordered solvent void space, however, attempts to determine the donor/acceptor atom pair were unsuccessful. CCDC 676115 contains the supplementary crystallographic data for **1** and can be obtained from the Cambridge Crystallographic Data Centre.

2.4. Computational methods

The time-dependent Density Functional Theory (TD-DFT) was employed to calculate the UV-vis spectrum for **1**. Initial coordinates for geometry optimization were taken from X-ray data. The optimized structure was used for vibration calculations to check for possible imaginary frequencies, which would indicate that the optimized structure is not at the minimum of the potential energy surface. Since no such normal modes were found this geometry was utilized as the ground state. These as well as the excited-state calculations were performed with the B3LYP functional and the 6-311+G(d,p) basis set for all atoms via Gaussian 09 program package.[54] The solvent was simulated with default method implemented in Gaussian 09 which use the Polarizable Continuum Model. In addition the population analysis was performed to assess the atomic contributions to the α - and β -spin molecular orbitals involved in the transitions obtained from TD-DFT calculations. To further analyze the nature of these spin orbitals the Natural Bond Orbital (NBO) program (ver. 3)[55-57] was employed. It is important to note that a typical error for the TD-DFT method in predicting excitation energies for an open-shell complexes is expected to be between 0.3 – 0.5 eV,[58, 59] hence the results presented here agree quite well with experiment.

3. Results and discussion

3.1. Synthesis

The synthesis of T1Et4iPrIP was achieved through a literature method.[31] The synthesis of the title compound, [Cu(T1Et4iPrIP)(CH₃OH)Cl]Cl (**1**), was carried out by addition of T1Et4iPrIP in dichloromethane to a slurry of CuCl₂ in MeCN. Crystallization of the product by ether diffusion into a solution of **1** in methanol afforded X-ray quality crystals.

3.2. Spectroscopic studies

3.2.1 UV-Vis spectroscopy

The electronic absorption spectrum of **1** was monitored in methanol. A broad ligand field band is observed with $\lambda_{\text{max}} = 809 \text{ nm}$ and $\varepsilon = 75.6 \text{ cm}^{-1} \text{ M}^{-1}$ tailing towards the near IR. The position of this band is lower in energy compared to other imidazole-containing copper(II) complexes[19, 60] consistent with a weaker ligand field. For the oxidized forms of amine oxidase, a band is observed in this region.[6]

3.2.2 EPR spectroscopy

The X-band EPR spectrum of **1** in methanol glass (77 K) is shown in Fig. 1. The spectrum ($g_{\perp} = 2.07$ and $g_{\parallel} = 2.28$ with $A_{\parallel} = 131 \text{ G}$) resembles the EPR spectra of a monomeric tetragonal Cu(II) complexes with $d_{x^2-y^2}$ ground state. Although no well-resolved superhyperfine coupling to first coordination sphere donor atoms is detected (Fig. 1), some structural information can be inferred from the EPR parameters. The g values of ~ 2 are indicative of a distorted square-pyramidal Cu(II) chromophore. The hyperfine coupling constant $A_{\parallel}$ of **1** however, is associated with *off-planar* distortion observed in the crystal structure of this complex and the weaker in-plane crystal field strength [61] as well as tetrahedral distortion of the Cu(II) site[62-64] compared to other imidazole-ligated Cu(II) complexes.[60] The $g_{\perp}$ and $g_{\parallel}$ values compare favorably to other imidazole copper(II) complexes [19, 65] and amine oxidase ($g_{\parallel} = 2.29$, $g_{\perp} = 2.06$, and $A_{\parallel} = 164 \text{ G}$)[66]

Fig. 1. X-band EPR spectrum (77 K) of **1** in methanol glass. Selected g and A values are indicated. Spectrometer settings: microwave frequency 9.43 GHz; microwave power, 13 mW; modulation frequency, 100 kHz; modulation amplitude, 4 G; gain, 1×10^4 .

3.3. X-ray Crystallography

The crystal structure for the cation of **1** (Fig. 2) reveals a copper(II) ion coordinated in a distorted square pyramidal geometry ($\tau = 0.19$)[67] with three nitrogens derived from T1Et4iPrIP, a chloride, and a methanol serving as the ligands. Selected bond distances and angles are listed in Table 2. The N(5) is the axial ligand since it is longer (2.212(3) Å) due to tetragonal distortion compared to the other Cu-N bond lengths (2.012(3) Å and 2.057(3) Å). The Cu-N bond distances are comparable to other mononuclear compounds containing Cu(II) bonded to imidazole nitrogens.[18, 21, 33, 38, 60, 68] Compound **1** contains three 6-membered chelate rings. The N-Cu-N angles range between 87.31° and 94.73° and are in line with other known copper(II)

complexes bonding to tris-imidazolylphosphine ligands.[18, 33] One of the chlorides is located in the void space of the crystal lattice and the function SQUEEZE, from the program PLATON,[53] was used to model its position over four positions (48:27:15:10). The atomic coordinates and equivalent isotropic displacement parameters of the four chloride atom positions were calculated (See Table S3).

Table 1. Crystallographic parameters for [Cu(T1Et4iPrIP)(CH₃OH)Cl]Cl (**1**).

	1
chemical formula	C ₂₅ H ₄₃ Cl ₂ Cu N ₆ O P
fw / g mol ⁻¹	609.06
Temperature / K	173(2)
λ / Å	0.71073
cryst. system	Monoclinic
space group	<i>P</i> 2 ₁ / <i>n</i>
<i>a</i> / Å	9.9164(12)
<i>b</i> / Å	13.0901(16)
<i>c</i> / Å	30.028(4)
α / °	90
β / °	96.641(2)
γ / °	90
Volume / Å ³	3871.7(8)
<i>Z</i>	4
μ / mm ⁻¹	0.766
<i>D</i> _{calcd} / Mg m ⁻³	1.045
GOF on <i>F</i> ²	1.032
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> 1 = 0.0583, <i>wR</i> 2 = 0.1557
<i>R</i> indices (all data)	<i>R</i> 1 = 0.0816, <i>wR</i> 2 = 0.1654

Table 2. Selected Angles (°) and bond distances (Å) For [Cu(T1Et4iPrIP)(CH₃OH)Cl]Cl (**1**).

Calculated data shown in brackets.

Cu(1)-N(3)	2.012(3) [2.049]	Cu(1)-Cl(1)	2.2497(11) [2.291]
Cu(1)-N(1)	2.057(3) [2.061]	P(1)-C(1)	1.827(4) [1.840]
Cu(1)-N(5)	2.212(3) [2.333]	P(1)-C(17)	1.811(4) [1.828]
Cu(1)-O(1)	2.068(3) [2.139]	P(1)-C(9)	1.823(4) [1.836]
N(3)-Cu(1)-N(1)	87.31(13) [86.718]	C(1)-N(1)-Cu(1)	117.0(3) [117.601]
N(3)-Cu(1)-O(1)	84.04(12) [84.739]	C(2)-N(1)-Cu(1)	135.9(3) [134.669]
N(1)-Cu(1)-O(1)	171.35(12) [170.478]	C(9)-N(3)-Cu(1)	119.8(3) [119.012]
N(3)-Cu(1)-N(5)	94.73(12) [92.135]	C(10)-N(3)-Cu(1)	133.4(3) [133.009]
N(1)-Cu(1)-N(5)	91.82(12) [94.080]	C(17)-N(5)-Cu(1)	116.6(2) [114.731]
O(1)-Cu(1)-N(5)	88.61(12) [90.438]	C(18)-N(5)-Cu(1)	137.1(3) [138.107]
N(3)-Cu(1)-Cl(1)	160.09(10) [166.281]	C(17)-P(1)-C(9)	101.53(17) [99.992]
N(1)-Cu(1)-Cl(1)	97.89(9) [97.192]	C(17)-P(1)-C(1)	96.80(17) [99.780]
O(1)-Cu(1)-Cl(1)	90.37(9) [90.189]	C(9)-P(1)-C(1)	95.05(17) [95.910]
N(5)-Cu(1)-Cl(1)	104.24(9) [100.660]

Fig. 2. Thermal ellipsoid plot of $[\text{Cu}(\text{T1Et4iPrIP})(\text{CH}_3\text{OH})\text{Cl}]^+$ (cation of **1**) (50% probability). H atoms have been removed for clarity.

3.4. Computational Studies

The twenty lowest excited states were calculated. The resulting spectra compare relatively well with absorption measurements and it is red-shifted with respect to the experimental. Results of the UV-Vis calculations can be found in the Table 3 and the corresponding spectrum is shown in Figure 3, which also show the experimental peaks for comparison. Based on the population analysis, results of which are presented in Table 4, the highest occupied molecular orbital has 65% of Cu-d character and it can be depicted as the $d_{x^2-y^2}$ orbital. This singly occupied MO (SOMO) is noted as *I* (Table 3) in the description of the molecular orbitals involved in the electron transitions of the theoretically predicted UV-Vis spectrum. From NBO analysis, Cu-d orbitals are not involved in the formation of the classical 2-center bond-orbitals with ligands

hence to determine their splitting, the energies of Natural Atomic Orbitals were used. Consequently the d orbital splitting is $d_{xy} > d_{x^2-y^2} > d_{yz} > d_{z^2} > d_{xz}$ which is different from expected $d_{x^2-y^2} > d_{xy} > d_{z^2} > d_{yz}, d_{xz}$ for classical square pyramidal geometry. Both $d_{x^2-y^2}$ and d_{z^2} , however, have only slightly higher energy than d_{xy} and d_{yz} , respectively, so it is possible that these orbitals are shifted energetically, when MOs are considered. For the sake of consistency we assigned SOMO (orbital 1) as $d_{x^2-y^2}$. The other molecular orbitals, which are considered to be Cu-d, possess higher than 40% of this character and are defined in the following way: orbital -2 as d_{xy} , orbital -3 as d_{z^2} , -4 as d_{yz} and -5 as d_{xz} .

The metal copper(II) center is formally d^9 and all the energetically deeper lying molecular orbitals are doubly occupied. Hence to mark their relative order with respect to the SOMO, these MOs will be denoted as: 0, -1, -2, *etc.* The lowest unoccupied molecular orbital (LUMO) in this notation is referred as 2 and the energetically higher lying MOs will have larger positive numbers (starting with 3).

In general the majority of the predicted spin allowed single electron excitations are of type-II,[59] *i.e.*, from a doubly occupied MO to the singly occupied HOMO. Most of these MOs are heavily mixed and the natural orbital analysis only slightly simplifies the description of the absorption bands. The ligand metal charge transfer (LMCT) transitions are present throughout the spectrum with the majority of peaks falling in the UV region of the spectrum (Figure 3). Absorption bands, with λ_{max} at 1153 nm, 780 nm, 741 nm, 513 nm, 444 nm and 428 nm are assigned as d-d transitions. Note that excited states: 13, 14 and 16 are highly spin contaminated and values of the oscillator strength are very low (see Table S1). Therefore these were omitted from Table 3.

Table 3. Wavelengths associated with calculated excitation energies, oscillator strengths (f), and assignments of transitions calculated with TD-DFT at the B3LYP/6-311+G(d,p) level of theory.

Excited State	Orbitals	Transition assignment ^b	f	λ (nm)
1	$-3 \rightarrow 1$ (37%)	$d_{z^2} \rightarrow d_{x^2-y^2}$	0.0001	1153
2	$-5 \rightarrow 1$ (26%)	$d_{xz} \rightarrow d_{x^2-y^2}$	0.0007	780
3	$-4 \rightarrow 1$ (27%)	$d_{yz} \rightarrow d_{x^2-y^2}$	0.0003	741
4	$-22 \rightarrow 1$ (20%)	$\pi(\text{Im}) \rightarrow d_{x^2-y^2}$ (LMCT)	0.0001	688
5	$0 \rightarrow 1$ (94%)	Cl-p $\rightarrow d_{x^2-y^2}$ (LMCT)	0.0003	630
6	$-1 \rightarrow 1$ (86%)	N-p/Cu-d $\rightarrow d_{x^2-y^2}$	0.0006	520
7	$-2 \rightarrow 1$ (89%)	$d_{xy} \rightarrow d_{x^2-y^2}$	0.0002	513
8	$-3 \rightarrow 1$ (89%)	$d_{z^2} \rightarrow d_{x^2-y^2}$	0.0019	444
9	$-4 \rightarrow 1$ (34%)	$d_{yz} \rightarrow d_{x^2-y^2}$	0.0079	428
10	$-7 \rightarrow 1$ (60%)	N-p/O-p/Cu-d $\rightarrow d_{x^2-y^2}$	0.0016	374
11	$-6 \rightarrow 1$ (45%)	N-p/Cu-d $\rightarrow d_{x^2-y^2}$	0.0009	365
12	$-8 \rightarrow 1$ (49%)	O-p/Cu-d $\rightarrow d_{x^2-y^2}$	0.0354	355
15	$-10 \rightarrow 1$ (34%)	O-p/Cl-p $\rightarrow d_{x^2-y^2}$	0.0079	331
17	$-11 \rightarrow 1$ (48%)	C-p $\rightarrow d_{x^2-y^2}$	0.0551	315
18	$-9 \rightarrow 1$ (42%)	O-p/Cl-p $\rightarrow d_{x^2-y^2}$ (LMCT)	0.0096	312
19 ^a	$\text{HOMO} \rightarrow \text{LUMO}$ (46%)	$d_{x^2-y^2} \rightarrow \text{C-p}$ (MLCT)	0.0525	285
20	$-11 \rightarrow 1$ (18%)	C-p $\rightarrow d_{x^2-y^2}$ (LMCT)	0.0303	280

^a HOMO (SOMO) $\rightarrow$ LUMO α -spin transition. ^bLMCT = ligand-to-metal-charge transfer; MLCT = metal-to-ligand charge transfer.

Table 4. Percent contribution of atomic orbitals for “paired” α - and β -spin MO.^a

MO	Atomic Contributions
143	Cu-d: 36%, O-p: 24%
144	Cu-d: 27%, O-p: 21%, N-p: 20%
145	Cu-d: 37%, N-p: 26%
146	Cu-d: 43%, O-p: 14%, N-p: 12%
147	Cu-d: 69%, N-p: 14%
148	Cu-d: 74%
149	Cu-d: 43%, N-p: 16%, N-p: 12%
150	Cu-d: 24%, N-p: 24%, Cl-p: 13%, C-p: 12%
151	Cl-p: 53%, Cu-d: 33%
152 ^b	Cu-d: 65%, Cl-p: 17%

^aCalculated in vacuum. ^bHOMO(SOMO).

Fig. 3. Comparison between theoretical and experimental UV-Vis spectra for **1** in methanol.

4. Conclusions

The ligand T1Et4iPrIP Ligand provides a tris-imidazolyl donor set and accurately models His₃ metal binding sites in metalloproteins. T1Et4iPrIP is not a strong σ donating ligand and results in minimal ligand stabilization. The weak ligand field results in low energy d-d electronic transitions which stretch into the near IR region. The solid state structure of crystals grown from methanol-ether exhibits copper(II) coordinated to 3-nitrogens of T1Et4iPrIP in a tridentate facial manner. Chloride and methanol ligands complete pentacoordination and yield distorted square pyramidal geometry ($\tau = 0.19$). Time-dependent DFT calculations on the BL3YP (6-311+G(d,p)) optimized structure of **1** reproduced the UV-Vis spectrum and allowed absorption bands to be assigned to specific transitions. The highest occupied molecular (HOMO) was noted to consist of 65% Cu-d character identified as the $d_{x^2-y^2}$ orbital.

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Appendix A. Supplementary Material

Computational and crystallographic information for **1** (PDF, 21 pages) is available.

Crystallographic Data for **4** (CCDC: 676115) has been deposited. These data can be obtained free of charge via <http://www.ccdc.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (.44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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Graphical abstract

The synthesis and structure of $[\text{Cu}(\text{T1Et4iPrIP})(\text{CH}_3\text{OH})\text{Cl}]\text{Cl}$ (T1Et4iPrIP = tris(1-ethyl-4-isopropyl-imidazolyl)phosphine) is reported. The copper center resides in distorted square pyramidal geometry and exhibits weak in-plane ligand field strength as evidenced by a small $A_{\parallel}$ value (131 G). TD-DFT calculations have been performed to assign the electronic transitions for this complex.