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Synthesis, structure, redox properties and theoretical calculation of copper(I)-triphenylphosphine halide complexes of arylazopyridines, and their reaction with H_2O_2

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ABSTRACT

Reaction of CuX (X = Cl, Br, I), PPh_3 and 2-(arylazo)pyridine, R-H_4C_6—N=N—C_5H_4N (aap, **1** where R = H (pap), *p*-Me (*p*-tap), *m*-Me (*m*-tap)) has synthesized [Cu((aap)(PPh_3)X]. The structure has been established by spectroscopic (UV–Vis, ^1H NMR) data and by single crystal X-ray diffraction of [Cu((pap)(PPh_3)Br]. Addition of H_2O_2 to [Cu((aap)(PPh_3)Cl] has afforded blue Cu(II) complexes, [Cu(aapO)(PPh_3)Cl]. These complexes have been characterized by elemental analyses, IR, UV–Vis spectral and magnetic data. Upon addition of H_2S saturated dil. H_2SO_4 solution to [Cu(aapO)(PPh_3)Cl] free aapOH is separated and has been characterized by spectral data. Cyclic voltammogram of [Cu((aap)(PPh_3)X] shows Cu(II)/Cu(I) response at 1.00–1.15 V and azo reduction at negative to SCE. DFT calculation of optimized structure of a representative complex has been used to determine the composition and energy of molecular levels and data have been used to explain the electronic spectral and redox properties.

1. Introduction

The chemistry of azopyridine has started with a publication in 1953 by Taylor and co-workers [1] and second report has appeared, after 23 years, in 1976 by Chakravorty and co-workers [2]. The coordination chemistry of azopyridine with different metal ions has extensively been started from the last quarter of twentieth century [3–21]. 2-(Arylazo)pyridine (aap, **1**) serves as N(azo), N(pyridyl) bidentate chelating ligand and has been used to synthesize various types of metal complexes [7–12]. These ligands can stabilize low oxidation states of metal ions like M(0) (M = Cr, Mo, W) [7], Cu(II/I) [8], Ag(I) [9], Fe(II) [2], Ru(II) [10], Os(II) [11] etc. The coordination complexes of azopyridine show different chemical transformation such as, the N—N bond cleavage reactions and their combination with other organic moieties to form organic products and/or cluster frameworks [12], the activation of the C—H bond *ortho* to the azo group of pendant aryl ring followed by hydroxylation [13], thiolation [14] and amination [15]. Ruthenium chemistry of 2-(arylazo)pyridine has attracted vastly because of different isomeric structures [10], interesting redox chemistry, photophysical properties and currently explored cytotoxicities against a series of tumor cell lines [16]. Redox chemistry and azo anion radical generation are another area of azopyridine chemistry [17]. Ruthenium–azopyridine complexes are successfully used in water oxidation [18] and epoxidation [19] type catalytic processes. Non-transition metal complexes of arylazopyridine are less popular than transition cousin. Few mercury(II) [20] and tin(IV) [21] complexes appear in literature. This brief literature review accounts that although transition metal chemistry is widely explored from different views and scientific manner but copper chemistry appears only once [8]. This has inspired us to re-examine the copper-arylazopyridine chemistry. Copper is one of the biologically very important metal ions and constituent of many metalloproteins and regulate bio-redox reactions [22,23]. Copper(I) complexes of azoimidazoles are reported recently by us [24–26]. This work is focused to Cu(I) complexes of 2-(arylazo)pyridine (aap) and exploring their chemistry. Herein we report the synthesis, structure, redox properties of copper(I)-triphenylphosphine halide complexes of 2-(arylazo)pyridine, [Cu(aap)(PPh_3)X]

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(X = Cl (**2**), Br (**3**), I (**4**)) and their reaction with H_2O_2. The product so obtained has been characterized spectroscopically as regiospecific aromatic hydroxylated copper(II) complexes, [Cu(aapO)(PPh_3)Cl] (**5**). The quantum chemical calculation using density functional theory (DFT) has been used to study the structural, electronic, spectroscopic, and thermodynamic properties of different type of compounds. Time-dependent density functional theory (TD-DFT) is used to explain the electronic properties of the molecules [27–29]. The calculations have been performed on the optimized geometries of the selected complexes. The complexes are characterized by spectroscopic studies and the structural confirmation by single crystal X-ray diffraction has been achieved in one case only.

2. Experimental

2.1. Materials

2-(Arylazo)pyridines (aap) were synthesized according to the published procedure [30]. CuX (X = Cl, Br, I) and triphenyl phosphine (PPh_3) were purchased from E. Merck India. All other chemicals and solvents were of reagent grade and used as received.

2.2. Physical measurements

Microanalytical (C, H, N) data were obtained from a Perkin–Elmer 2400 CHNS/O elemental analyzer. Spectroscopic data were obtained using the following instruments: UV–Vis, Perkin–Elmer Lambda-25; IR (KBr disc, 4000–200 cm^{-1}), Perkin–Elmer RX-1 spectrophotometer, and ^{1}H NMR, Bruker 300 MHz FT-NMR spectrometer. Electrochemical measurements were performed using computer-controlled CHI Electrochemical Workstation with Pt-disc electrodes. All measurements were carried out under nitrogen environment at 298 K with reference to saturated calomel electrode (SCE) in acetonitrile using [nBu_4N][ClO_4] as supporting electrolyte. The reported potentials are uncorrected for junction potential.

2.3. Synthesis

2.3.1. [Cu(pap)(PPh_3)Br] (**3a**)

To methanol solution (25 ml) of 2-(phenylazo)pyridine (pap) (89.4 mg, 0.49 mmol) acetonitrile solution of CuBr (70 mg, 0.49 mmol) and triphenyl phosphine (127.8 mg, 0.99 mmol) were added, stirred and refluxed for 3 h. The solution was filtered through G4 crucible and was allowed to evaporate slowly in air. Block shaped dark microcrystals deposited on the wall of beaker. These were collected by filtration. X-ray quality block shaped crystals were obtained by recrystallising from DMF-MeOH solution (1:2 v/v). Yield, 0.19 g (66%).

All other complexes were prepared by the same procedure. In all cases, crystalline products were obtained. The yield varied from 70% to 80% and microanalytical data of the complexes are as follows: [Cu(pap)(PPh_3)Cl] (**2a**) *Anal.* Calc. for $C_{29}H_{24}CuClN_3P$: C, 63.97; H, 4.44; N, 7.71. Found: C, 63.91; H, 4.47; N, 7.79%. . FT-IR (KBr disc, cm^{-1}), ν(N=N), 1437; ν(C=N), 1590; ν(PPh_3), 510 and 694 cm^{-1}. UV–Vis spectroscopic data in CH_3CN (λ_{max}(nm)(10^{-3} $\in$ ($dm^3\ mol^{-1}\ cm^{-1}$): 263 (10.51), 350 (12.94), 500 (1.60). [Cu(*p*-tap)(PPh_3)Cl]. (**2b**) *Anal.* Calc. for $C_{30}H_{26}CuClN_3P$: C, 64.51; H, 4.69; N, 7.52. Found: C, 64.60; H, 4.63; N, 7.57%. FT-IR (KBr disc, cm^{-1}), ν(N=N), 1436; ν(C=N), 1595; ν(PPh_3), 516 and 702 cm^{-1}. UV–Vis spectroscopic data in CH_3CN (λ_{max}(nm)(10^{-3} $\in$ ($dm^3\ mol^{-1}\ cm^{-1}$): 250 (9.24), 331 (13.56), 498 (1.52). [Cu(*m*-tap)(PPh_3)Cl] (**2c**) *Anal.* Calc. for $C_{30}H_{26}CuClN_3P$: C, 64.51; H, 4.69; N, 7.52. Found: C, 64.43; H, 4.63; N, 7.44%. . FT-IR (KBr disc, cm^{-1}), ν(N=N), 1435; ν(C=N), 1592; ν(PPh_3), 512 and 694 cm^{-1}. UV–Vis spectroscopic data in CH_3CN (λ_{max}(nm)(10^{-3} $\in$ ($dm^3\ mol^{-1}\ cm^{-1}$): 262 (17.15), 345 (19.25), 500 (2.30). [Cu(pap)(PPh_3)Br] (**3a**) *Anal.* Calc for $C_{29}H_{24}CuBrN_3P$: C, 59.14; H, 4.11; N, 7.13. Found: C, C, 59.11; H, 4.09; N, 7.19%. FT-IR (KBr disc, cm^{-1}), ν(N=N), 1435; ν(C=N), 1589; ν(PPh_3), 512 and 689 cm^{-1}. UV–Vis spectroscopic data in CH_3CN (λ_{max}(nm)(10^{-3} $\in$ ($dm^3\ mol^{-1}\ cm^{-1}$): 257 (17.52), 315 (24.72), 505 (1.69). [Cu(*p*-tap)(PPh_3)Br] (**3b**) *Anal.* Calc. for $C_{30}H_{26}CuBrN_3P$: C, 59.76; H, 4.35; N, 6.97. Found: C, 59.89; H, 4.40; N, 6.91%. . FT-IR (KBr disc, cm^{-1}), ν(N=N), 1435; ν(C=N), 1591; ν(PPh_3), 503 and 700 cm^{-1}. UV–Vis spectroscopic data in CH_3CN (λ_{max}(nm)(10^{-3} $\in$ ($dm^3\ mol^{-1}\ cm^{-1}$): 247 (12.34), 332 (15.26), 502 (1.78). [Cu(*m*-tap)(PPh_3)Br] (**3c**) *Anal.* Calc. for $C_{30}H_{26}CuBrN_3P$: C, 59.76; H, 4.35; N, 6.97. Found: C, 59.85; H, 4.38; N, 7.05%. FT-IR (KBr disc, cm^{-1}), ν(N=N), 1436; ν(C=N), 1593; ν(PPh_3), 519 and 693 cm^{-1}. UV–Vis spectroscopic data in CH_3CN (λ_{max}(nm)(10^{-3} $\in$ ($dm^3\ mol^{-1}\ cm^{-1}$): 255 (9.52), 329 (16.34), 515 (1.32). [Cu(pap)(PPh_3)I] (**4a**) *Anal.* Calc. for $C_{29}H_{24}CuIN_3P$: C, 54.77; H, 3.80; N, 6.61. Found: C, 54.70; H, 3.74; N, 6.70%. . FT-IR (KBr disc, cm^{-1}), ν(N=N), 1437; ν(C=N), 1589; ν(PPh_3), 522 and 691 cm^{-1}. UV–Vis spectroscopic data in CH_3CN (λ_{max}(nm)(10^{-3} $\in$ ($dm^3\ mol^{-1}$ Calc. for $C_{29}H_{24}CuIN_3P$: C, 54.77; H, 3.80; N, 6.61cm^{-1}): 246 (11.42), 315 (12.39), 518 (1.63). [Cu(*p*-tap)(PPh_3)I] (**4b**) *Anal.* Calc. for $C_{30}H_{26}CuIN_3P$: C, 55.44; H, 4.03; N, 6.46. Found: C, 55.49; H, 4.05; N, 6.49%. . FT-IR (KBr disc, cm^{-1}), ν(N=N), 1436; ν(C=N), 1593; ν(PPh_3), 510 and 701 cm^{-1}. UV–Vis spectroscopic data in CH_3CN (λ_{max}(nm)(10^{-3} $\in$ ($dm^3\ mol^{-1}$ Calc. for $C_{30}H_{26}CuIN_3P$: C, 55.44; H, 4.03; N, 6.46cm^{-1}): 249 (15.21), 333 (19.50), 494 (2.05). [Cu(*m*-tap)(PPh_3)I] (**4c**) *Anal.* Calc. for $C_{30}H_{26}CuIN_3P$: C, 55.44; H, 4.03; N, 6.46. Found: C, 55.38; H, 4.04; N, 6.52%. . FT-IR (KBr disc, cm^{-1}), ν(N=N), 1433; ν(C=N), 1590; ν(PPh_3), 519 and 691 cm^{-1}. UV–Vis spectroscopic data in CH_3CN (λ_{max}(nm)(10^{-3} $\in$ ($dm^3\ mol^{-1}\ cm^{-1}$): 244 (25.23), 320 (29.43), 445 (1.98).

2.3.2. Hydroxylation of [Cu(pap)(PPh_3)Cl] by H_2O_2: [Cu(pap)(PPh_3)Cl] (**2a**) → [Cu(papO)(PPh_3)Cl] (**5a**)

The reaction is carried out by addition of H_2O_2 to acetonitrile solution of the complex. Detail of a representative reaction is given below.

To acetonitrile solution (20 ml) of [Cu(pap)(PPh_3)Cl] (**2a**) (0.05 g, 0.09 mmol) 30% H_2O_2 (1 ml) was added in drops and stirred in air for 6 h. The solution color changed slowly from brown red to blue and the solution was left for overnight and allowed to evaporate slowly. Dark mass was deposited on the wall of reaction vessel. It was then washed with water followed by toluene and then extracted by CH_2Cl_2. Hexane was layered over CH_2Cl_2 solution and allowed to diffuse. Dark mass was deposited after a week on wall of the crystallization tube. They were collected and used for analysis. Yield, 0.03 g (58%).

All other complexes were prepared by the same procedure. The yield varied from 50–60% and microanalytical data of the complexes are as follows: [Cu(papO)(PPh_3)Cl] (**5a**) *Anal.* Calc. for $C_{29}H_{23}CuClON_3P$: C, 62.25; H, 4.11; N, 7.51. Found: C, 62.11; H, 4.17; N, 7.39%. . FT-IR (KBr disc, cm^{-1}), ν(N=N), 1393; ν(C=N), 1595; ν(PPh_3), 693 and 722 cm^{-1}. UV–Vis spectroscopic data in CH_3CN (λ_{max}(nm)(10^{-3} $\in$ ($dm^3\ mol^{-1}\ cm^{-1}$): 378 (7.67), 394 (6.08), 568 (5.89). Magnetic moment, 1.57 BM. [Cu(*p*-tapO)(PPh_3)Cl] (**5b**) *Anal.* Calc. for $C_{30}H_{25}CuClON_3P$: C, 62.83; H, 4.36; N, 7.33. Found: C, 62.72; H, 4.28; N, 7.37%. FT-IR (KBr disc, cm^{-1}), ν(N=N), 1393; ν(C=N), 1595; ν(PPh_3), 693, 722 cm^{-1}. UV–Vis spectroscopic data in CH_3CN (λ_{max}(nm)(10^{-3} $\in$ ($dm^3\ mol^{-1}\ cm^{-1}$): 370 (8.23), 385 (6.27), 576 (5.28). Magnetic moment, 1.72 BM. [Cu(*m*-tapO)(PPh_3)Cl] (**5c**) *Anal.* Calc. for $C_{30}H_{25}CuClON_3P$: C, 62.83; H, 4.36; N, 7.33. Found: C, 62.68; H, 4.31; N, 7.41%. . FT-IR (KBr disc, cm^{-1}), ν(N=N), 1398; ν(C=N), 1590; ν(PPh_3), 683, 715 cm^{-1}. UV–Vis spectroscopic data in CH_3CN (λ_{max}(nm)(10^{-3} $\in$ ($dm^3\ mol^{-1}\ cm^{-1}$): 372 (7.88), 388 (5.97), 567 (5.45). Magnetic moment, 1.70 BM.