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Synthesis, characterization, structure and properties of copper and palladium complexes incorporating azo-amide ligands

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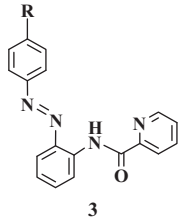
ABSTRACT

The reaction of the multidentate ligand N-(2-(aryldiazenyl)phenyl)picolinamide, HL (**3a**, **3b** and **3c**) [HL is ArN = $NC_6H_4NHC(O)Py$, where Ar is C_6H_5 for HL^1 (**3a**), *p*-MeC_6H_4 for HL^2 (**3b**) or *p*-ClC_6H_4 for HL^3 (**3c**), and Py stands for pyridyl], with $Cu(CH_3COO)_2{\cdot}H_2O$ and Na_2PdCl_4 separately afforded the complexes $[(L)_2Cu]$ (**4a**, **4b** and **4c**) and [(L)PdCl] (**5a**, **5b** and **5c**) respectively, where the deprotonated ligand L^- binds copper(II) and palladium(II) in a tridentate (N,N,N) fashion. X-ray structures of $[(L^3)_2Cu]$ (**4c**) and $[(L^1)PdCl]$ (**5a**) were determined to confirm the molecular structures. The newly synthesized complex **4a** exhibits catalytic activity toward the oxidation of alcohols to the corresponding carbonyl compounds and oxidation of organic thioethers to sulfoxide and sulfone, whereas the complex **5a** is an active catalyst for Suzuki and Heck reactions.

1. Introduction

This work stems from our interest in the coordination chemistry of transition metals incorporating 2-(arylazo)aniline and related ligands [1–5]. The synthesis of several ligands exploiting the reactivity of the free amine function of the 2-(arylazo)aniline backbone (Chart 1) have been reported earlier [1–5]. The ligands **1** and **2** were synthesized by the reaction of alkyl halides or by the condensation of aldehydes with the free $-NH_2$ group of 2-(arylazo)aniline, respectively (Chart 1) [2–5]. In continuation of our endeavor, we contemplated the use of the amide (CONH) derivative of 2-(arylazo)aniline as a ligand, as shown in **3** [2–5]. The biological relevance of transition metal complexes containing amide nitrogen donors ligands and the rich catalytic activity of copper complexes *in vivo* and *in vitro* encouraged us to prepare the Cu(II) complexes of the azo-amide ligands, **3** [6–13].

Development of a suitable environmentally benign catalyst for the catalytic oxidation of organic substrates is a challenge in current chemical research [6–13].



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Researchers have been using copper(II) complexes as catalysts for oxidative organic transformations involving the oxidation of alcohols, alkanes, alkenes and thioethers [10–31]. Air, tertiary butylhydroperoxide (TBHP) and hydrogen peroxide have been used as oxidants in the presence of Cu(II) catalysts for such catalytic oxidations [10,11,25–30]. However, the advantages of using H_2O_2 as the oxidant prompted us to prepare catalysts that are active for oxidations with H_2O_2 [32,33]. Thus, the newly synthesized Cu(II) complexes would be screened to search for such catalytic properties.

In addition to the synthesis and studies on copper complexes, we targeted the preparation of Pd(II) complexes using the same ligand system, **3**, to study the catalytic activity in Heck and Suzuki reactions, with the purpose of comparing the results with the catalytic activities of the Cu(II) complexes. C–C coupling reactions

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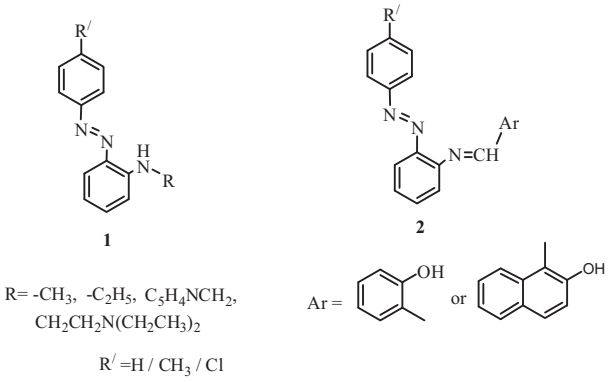

Chart 1.

catalyzed by Pd(II) complexes have drawn much attention during the last few decades. Notable examples are Suzuki, Heck and Sonogoshira coupling reactions [34–46]. C–C coupling reactions catalyzed by Cu(I) complexes, and in a few cases Cu(II) complexes, have been used for C–C coupling. In the later cases, the initial conversion of Cu(II) to Cu(I) species were proposed to occur *in situ* to generate the active catalyst [47–50]. Therefore, we envisaged that studies on the catalytic properties of the newly synthesized Pd(II) complexes towards Suzuki and Heck coupling and a comparison with such (if any) activity of Cu(II) complexes toward these later reactions would be interesting.

Herein, we describe the synthesis of the ligands N-(2-(aryldiazenyl)phenyl)picolinamide, HL, and the reactions of these ligands with $Cu(OAc)_2{\cdot}H_2O$ and Na_2PdCl_4. Azo-amide chelates of the compositions $[(L)_2Cu]$, **4**, and [(L)PdCl], **5**, have been isolated and characterized unequivocally. The catalytic activity of $[(L)_2Cu]$ towards the oxidation of benzyl alcohol derivatives to aldehydes and organic thioethers to sulfoxides and sulfones have been examined. The catalytic activity of the [(L)PdCl] complexes toward Suzuki and Heck coupling reactions is also examined.

2. Experimental

2.1. Materials

The solvents used in the reactions were of reagent grade (E. Marck, Kolkata, India) and were purified and dried by reported procedures [51]. The 2-(arylazo)anilines were prepared according to the reported procedure [1,52,53]. Picolinoyl chloride was prepared according to the reported procedure [54]. Palladium chloride and potassium carbonate were purchased from E. Merck, Kolkata, India. $Na_2[PdCl_4]$ was prepared following a reported procedure [55]. Phenylboronic acid, iodobenzene, bromobenzene, 1-iodo-3,5-dimethylbenzene, 1-iodo-3,4-dimethylbenzene, 1-iodo-2-nitrobenzene, 1-iodo-3-nitrobenzene, 1-bromo-3,5-dimethylbenzene, 1-bromo-2-nitrobenzene and styrene were purchased from Aldrich. Copper(II) acetate, benzyl alcohol and hydrogen peroxide were purchased from E. Merck, Kolkata, India. 4-Iodobenzyl alcohol, 3-methoxybenzyl alcohol, 4-nitrobenzyl alcohol and phenyl benzyl alcohols were purchased from Spectrochem, India. Methyl phenyl sulfide, ethyl phenyl sulfide, allyl phenyl sulfide and benzyl phenyl sulfide were purchased from Sigma Aldrich.

2.2. Physical measurements

Microanalysis (C, H, N) was performed using a Perkin–Elmer 2400 C, H, N, S/O series II elemental analyzer. Infrared spectra were recorded on a Perkin–Elmer L120-00A FT-IR spectrometer with the samples prepared as KBr pellets. Electronic spectra were recorded on a Shimadzu UV-1800 PC spectrophotometer. ^1H and ^{13}C NMR spectra were obtained on Bruker 400 spectrometers in $CDCl_3$.

2.3. Synthesis of the ligands

All the ligands **3a**, **3b** and **3c** were prepared following similar procedures, modifying the previously reported method for **3a** [56]. A representative procedure for **3a** is given below.

2.3.1. *3a*

A mixture of 2-(phenylazo)aniline (0.788 g, 4.00 mmol), picolinoyl chloride (0.500 g, 3.98 mmol) and 0.3 g (3 mmol) of triethyl amine in 30 cm^3 dry dichloromethane was stirred for 24 h. An orange liquid was obtained after evaporation of the solvent. Column chromatographic purification of this orange liquid on silica gel (60–120 mesh) using petroleum ether:benzene (90:10 v/v) mixed solvent as the eluent afforded the desired ligand, **3a**. Yield: 60%. *Anal.* Calc. for $C_{18}H_{14}N_4O$ (302); C, 71.52; H, 4.63; N, 18.54. Found: C, 71.54; H, 4.60; N, 19.00%. UV–Vis (CH_2Cl_2) λ_{max} (ε, M^{-1} cm^{-1}): 376 (18520), 337 (24180), 293 (29520), 242 (25480). IR (KBr pellets, cm^{-1}) ν: 3275 (N–H), 1692 (C=O), 1533 (N=N). ^1H NMR ($CDCl_3$) δ: 12.52 (s, 1H), 8.89 (d, 1H), 8.73 (d, 1H), 8.33 (d, 1H), 8.13 (d, 1H), 8.03 (d, 2H), 7.89–7.94 (m, 2H), 7.49–7.54 (m, 2H), 7.37 (d, 2H), 7.21 (t, 1H). ^{13}C NMR ($CDCl_3$) δ: 162.45 (s, 1C), 152.64 (s, 1C), 150.29 (s, 1C), 148.21 (s, 1C), 139.86 (s, 1C), 137.55 (s, 1C), 136.21 (s, 1C), 132.81 (s, 1C), 131.29 (s, 1C), 129.18 (s, 1C), 126.44 (s, 1C), 123.63 (s, 1C), 123.10 (s, 1C), 122.48 (s, 1C), 120.19 (s, 1C), 119.53 (s, 1C).

2.3.2. HL^2 and HL^3

The ligands HL^2 and HL^3 were prepared using 2-(p-tolylazo)aniline and 2-(p-chlorophenylazo) aniline in place of 2-(phenylazo)aniline, respectively. Yield: HL^2, 60% and HL^3, 55%.

HL^2, $C_{19}H_{16}N_4O$ (316), Calc.: C, 72.15; H, 5.06; N, 17.72. Found: C, 72.10; H, 5.10; N, 17.75%. UV–Vis (CH_2Cl_2) λ_{max} (ε, M^{-1} cm^{-1}): 375 (11867), 335 (14850), 308 (16400), 240 (15350). IR (KBr pellets, cm^{-1}) ν: 3288 (N–H), 1686 (C=O), 1522 (N=N). ^1H NMR ($CDCl_3$) δ: 12.45 (s, 1H), 8.86 (d, 1H), 8.61 (d, 1H), 8.33 (d, 1H), 8.00 (d, 2H), 7.90 (s, 1H), 7.50–7.56 (m, 2H), 7.37 (d, 2H), 7.21–7.28 (m, 2H), 2.47 (s, 3H). ^{13}C NMR ($CDCl_3$) 161.19 (s, 1C), 151.89 (s, 1C), 150.79 (s, 1C), 149.06 (s, 1C), 146.14 (s, 1C), 142.06 (s, 1C), 139.95 (s, 1C), 135.70 (s, 1C), 132.49 (s, 1C), 129.89 (s, 1C), 126.56 (s, 1C), 123.95 (s, 1C), 123.16 (s, 1C), 123.04 (s, 1C), 120.19 (s, 1C), 119.46 (s, 1C), 21.60 (s, CH_3).

HL^3, $C_{18}H_{15}N_4OCl$ (338.5), Calc.: C, 63.81; H, 4.43; N, 16.54. Found: C, 63.85; H, 4.45; N, 16.50%. UV–Vis (CH_2Cl_2) λ_{max} (ε, M^{-1} cm^{-1}): 378 (9550), 333 (15290), 296 (15610), 236 (15480). IR (KBr pellets, cm^{-1}) ν: 3290 (N–H), 1695 (C=O), 1522 (N=N). ^1H NMR ($CDCl_3$) δ: 12.49 (s, 1H), 8.90 (d, 1H), 8.71 (d, 1H), 8.34 (d, 1H), 8.07 (d, 2H), 7.89–7.96 (m, 2H), 7.51–7.58 (m, 4H), 7.20–7.24 (m, 1H). ^{13}C NMR ($CDCl_3$) δ: 161.18 (s, 1C), 151.77 (s, 1C), 151.01 (s, 1C), 149.05 (s, 1C), 146.27 (s, 1C), 139.80 (s, 1C), 137.31 (s, 1C), 135.96 (s, 1C), 133.21 (s, 1C), 129.50 (s, 1C), 126.70 (s, 1C), 124.21 (s, 1C), 124.01 (s, 1C), 123.26 (s, 1C), 120.31 (s, 1C), 119.63 (s, 1C).

2.4. Syntheses of the Cu complexes

The complexes $[(L^1)_2Cu]$, $[(L^2)_2Cu]$ and $[(L^3)_2Cu]$ were prepared following similar procedures. A representative procedure for $[(L^1)_2Cu]$ is given below.

2.4.1. $[(L^1)_2Cu]$

A solution of HL^1 (0.100 g, 0.331 mmol) in 15 cm^3 methanol was added to a solution of $Cu(CH_3COO)_2{\cdot}H_2O$ (0.302 g, 0.100 mmol) in