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Synthesis, characterization, structure, catalytic and redox property of (NNN) tridentate azopalladium (II) andplatinum(II) complexes

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ABSTRACT

Reaction of the ligands, bis-2,2'-(N-alkylamino)azobenzene1a & b, with $K_2[PdCl_4]$ and $K_2[PtCl_4]$in a 1:1 ratio in methanol afforded Pd(II), Pt(II) complexes 2a -2d. Both the complexes were characterized by ^{1}H NMR, IR spectroscopy and elemental analysis. Furthermore, the solid-state structures of complex (2b and 2c) was determined using single crystal X-ray diffraction analysis. The diffraction analysis revealed that the ligand 1a binds with Pt(II) in monoanionicterdentate (N,N,N) fashion offering distorted square planar geometry where fourth coordination site is satisfied by one chloride ligand. Redox properties of the new complexes were examined.

Keywords- Pt(II), Bis-2,2'-(N-alkylamino)azobenzene, Crystal structure, Suzuki & Heck coupling,Palladium(II),Platinum(II)

I. INTRODUCTION

Selective c-c bond-formation by palladium-catalyzed reactions are known as versatile tools in organic synthesis. Suzuki coupling is an efficient method for the production of biaryls, which are important in agrochemistry, pharmaceutical, herbicides, materials and synthetic chemistry [1-3].

After the discovery of cis-platin, Pt(II) complexes supported by nitrogen donor ligands have attracted greatly attention both in research and biological applications [4-14]. Platinum complexes incorporating nitrogen and oxygen or sulfur donor ligands with azo functionality have attracted a great deal of attention because of their potential interest in C-H bond activation, redox property, oxidative addition, reductive elimination, regioselective ring amination and invitro cytotoxicity [15-25]. In last few years, research containing platinum complexes has concentrated on the study of their photophysical properties and their anticancer activity and interest in biological chemistry [12-14, 4-11]. Orthometallatedplatinum compounds containing nitrogen donor ligands have attracted a great deal of attention because of their use in functionalization of organic molecules [26-27], luminescence / phosphorescence [28-30], mesogenic materials [31-33] and antitumour agents [5, 8-13]. For this reason, the development of new approaches for the synthesis of new platinated compounds containing nitrogen donor ligands is a pursued goal. A very limited phosphine free palladium azo-imine complexes have been found to useful as homogeneous catalyst in Suzuki and Heck coupling reactions [19, 34-35].

Herein, we report the synthesis of palladium and platinum complexes incorporating bis-2,2'-(N-alkylamino)azobenzene ligands. Both the complexes were characterized by UV-Vis, IR and ^{1}H NMR spectroscopy. The structure of the complex **2b** and **2d** were determined by X-ray crystallography. Catalytic activityinSuzuki and Heck coupling reactions of palladium **2a** complexes and redox behavior of the new complexes were examined.

II. EXPERIMENTAL

A. Materials and Physical measurements

The solvents used in the reactions were of reagent grade (Merck, Kolkata, India) and were purified and dried by general procedure [31]. Sodium chloride, Methyl iodide, ethyl bromide and potassium carbonate were purchased from Merck, India. Methyl iodide was purchased from SRL, Mumbai, India. Potassium tetrachloropalladate, Potassium tetrachloropltinate was purchased from Sigma-Aldrich. 2,2'-diaminoazobenzene and (2-((2-aminophenyl)diazenyl)-N-alkylaniline) were prepared following reported procedure [16, 30]. 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 BX-1 FT-IR spectrometer with the samples prepared as KBr pellets. Electronic spectra were recorded on a Shimadzu UV- 1800 PC spectrophotometer. ^{1}H NMR spectra were obtained on Bruker 400 NMR spectrometers in $CDCl_3$ using TMS as the internal standard.

B. Synthesis of complex

Palladium complexes 2a &2b was prepared following similar procedures. A representative procedure for 2a is given below.

A solution of 1a (0.135 g, 0.34mmol) in 10 cm^{3}methanolwas added to a solution of $Na_2[PdCl_4]$ (0.1 g, 0.34mmol) in 10 cm^3 methanol. The mixture was stirredfor 6 h. The dark solid precipitate was separated by filtrationand purified by column chromatography using silicagel (60–120 mesh). The eluent was toluene-acetonitrile (80/20 v/v) mixed solvent. Upon evaporation of the solvent,a blue solid of pure 2a was obtained.Yield: 2a, 70%. Anal. Calc. for $C_{14}H_{15}N_4ClPd$: C, 44.11; H, 3.97; N, 14.70.Found: C, 44.24; H, 4.07; N, 14.52%. UV/VIS (λ_{max}/nm (ε/ dm^2 mol^{-1}), dichloromethane): 575 (10420), 360(8325), 260(24450), 230(36730). IR (KBr, cm^{-1}): 3062ν(NH), 1739ν(C=N), 1400ν(N=N).^{1}H NMR (300 MHz, $CDCl_3$):3.22 (CH_3, d, 3H), 3.45-3.53 (CH_3, m, 3H), 5.30 (NH, s, 1H), 6.58 (ArH, t, 1H), 6.99 (ArH, t, 1H), 7.20-7.28 (ArH, m, 2H), 7.32 (ArH, t, 1H), 7.39 (ArH, d, 1H), 7.57 (ArH, d, 1H), 8.07 (ArH, d, 1H).Yield: 2c, 64%. Anal. Calc. for $C_{16}H_{19}N_4ClPd$: C, 46.96; H, 4.68; N, 13.69. Found: C, 46.58; H, 4.54; N, 13.47%. UV/VIS (λ_{max}/nm (ε/ dm^2 mol^{-1}), dichloromethane): 610 (9380), 575(11510), 360(8715), 260(22955), 230(36530). IR (KBr, cm^{-1}): 3071 ν(NH), 1744ν(C=N), 1403ν(N=N).^{1}H NMR (300 MHz, $CDCl_3$):1.21 (CH_3, t, 3H), 1.26 (CH_3, t, 3H), 3.16-3.21 (CH_2, m, 2H), 4.01-4.07 (CH_2, m, 2H), 6.0 (NH, s, 1H), 6.53 (ArH, t, 1H), 6.96 (ArH, d, 1H), 7.16-7.21 (ArH, m, 2H), 7.25-7.28 (ArH, m, 1H), 7.36 (ArH, d, 1H), 7.52 (ArH, d, 1H), 7.97 (ArH, d, 1H).

Similarly, blue platinum complexes 2c & 2d were synthesized by same procedure. Yield: 2c, 60%. Anal. Calc. for $C_{14}H_{15}ClN_4Pt$: C, 35.79; H, 3.22; N, 11.93. Found: C, 35.32; H, 3.45; N, 11.84%. UV/VIS (λ_{max}/nm (ε/ dm^2 mol^{-1}), dichloromethane): 630 (14040), 585 (14500), 355 (14900), 265 (40050). IR (KBr, cm^{-1}): 3134 ν(NH), 1614 ν(C=N), 1405 ν(N=N). 1H NMR (400 MHz, $CDCl_3$): 7.90 (m, ArH, 1H), 6.58 (d, 1H, ArH), 7.50 (d, 1H, ArH), 7.43-7.47 (m, 1H, ArH), 7.20-7.23 (m, 2H, ArH), 6.71-6.76 (d, 2H, ArH, NH), 6.55 (t, 1H, ArH), 3.38 (t, 6H, CH3). E1/2 [V]: 1.58, -1.22, -0.85. Yield: 2d, 65%. Anal. Calc. for $C_{16}H_{19}ClN_4Pt$: C, 38.60; H,3.85; N, 11.25. Found: C, 38.44; H, 3.65; N, 11.36%. UV/VIS (λ_{max}/nm (ε/ dm^2 mol^{-1}), dichloromethane): 625 (14500), 585 (15540), 360(16630), 270(41350). IR (KBr, cm−1): 3052 ν(NH), 1615 ν(C=N), 1410 ν(N=N). ^1H NMR (400 MHz, $CDCl_3$): 7.90 (b, s, ArH, 1H), 7.63 (d, ArH, 1H), 7.41(t, ArH, 2H), 7.13-7.16(m, ArH, 3H), 6.86 (b, NH, 1H), 6.51 (t, 1H, ArH), 4.23-4.31 (m, 2H, CH_2), 1.06-1.11 (m, 6H, CH_3).

III. CRYSTALLOGRAPHY

Single crystal of 2band2cwas grown by diffusion of dichloromethane into petroleum ether at room temperature. Data were collected by ω- scan technique on a Bruker Smart CCD diffractometer with Mo-K_α radiation monochromated by graphite crystal. Structure solution was done by direct method with SHELXS–97 program [32, 33]. Full matrix least square refinements on F^2 were performed using SHELXL–97 program [32, 33]. All non-hydrogen atoms were refined anisotropically using reflections $I > 2\sigma(I)$. The C-bound hydrogen atoms were included in calculated positions and refined as riding atoms and N-bound hydrogen atoms were assigned and refined.

IV. RESULTS AND DISCUSSION

Reactions of 1a-b with $K_2PdCl_4$and K_2PtCl_4separately in methanol water at room temperature afforded blue coloured complexes of composition 2a-2d. In all complexes the ligand binds in tridentate fashion through amido nitrogen, azo nitrogen and amino nitrogen atoms. The fourth coordination site of the complexes is occupied by a chloride ligand.

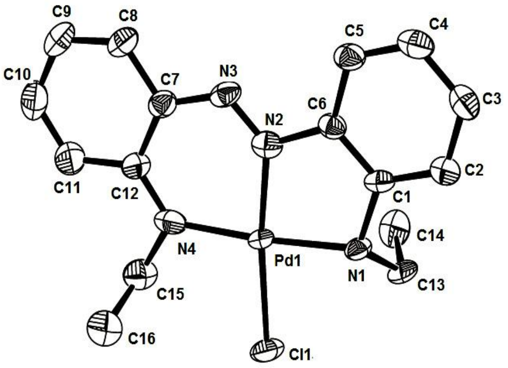
Fig. 1: Synthesis of ligands and palladium and platinum complexes

All the palladium(II) and platinum (II) complexes are soluble in common organic solvents, producing blue-violet and intense blue colour solutions. UV–visible spectra of the complexes were recorded at room temperature in dichloromethane solvent. Spectral data are presented in the Experimental Section. The absorption bands observed in the spectra of the free ligand have shifted to lower energy region in the spectra of all palladium complexes due to the coordination of the ligand with metal ion. All the transitions are majorly due to intra ligand charge transfer transitions [19, 33, 39]. A Characteristic low energy absorption band for **2c**at 570-575 nm is assigned as mixed metal ligand charge transfer The absorption spectra of the platinum compounds contains of four intense absorption bands at ~275, ~355, 585 and ~630 nm, the first two bands can be assigned to the π–π* transitions of the phenyl rings and n–π^* transitions of azo (–N=N–) [19,33, 39]. Characteristic low energy absorption peaks observed at 585 nm and 630 nm could be assigned to mixed metal ligand charge transfer transition [19,33,39].

In IR spectra for the complexes **2a–2b**, the $\nu_{N\text{-}H}$ band appeared within the range 3076–3062 cm^{-1} [42,48]. The $\nu_{N=N}$ band (1508–1504 cm^{-1}) of all the ligands shifted to lower frequency (1406–1400 cm^{-1}) in the complexes, consistent with coordination of the azo nitrogen [34-35, 40]. A new band, near 1744–1736 cm^{-1},in the IR spectra of the complexes unlike the ligands, has been attributed to imine formation [34-35, 40]. For the complexes 2c &2d of in solid KBr pellet displayed $\nu_{N\text{-}H}$ absorption as a singlet band at 3134 cm^{-1} and 3047 cm^{-1} respectively due to coordination with amino nitrogen [15,19,33,39]. The $\nu_{N=N}$ band (1508–1504 cm^{-1}) of all the ligands shifted to lower frequency ~1408 cm^{-1} in the complexes, indicating the coordination of the azo nitrogen[15,19,33,39]. A new band, near ~1616 cm^{-1}, in the IR spectra of the complexes has been signifying to imine (–C=N–) formation [12, 34-35]. The spectral data for the complexes are collected in experimental section.

The NMR spectra of the complexes were recorded in $CDCl_3$ at room temperature. The complexes shows highly resolved ^{1}H-NMR spectra, which are in complete agreement with the X-ray structures. All aromatic protons signals appeared in the range 6.72-7.91 ppm. Two $-CH_3$ and $-CH_2CH_3$ signals of complexes 2a and 2b appeared as multiplate due to formation of two unsymmetrical chelate rings with ligands. A broad singlet at 6.76 ppm and 6.86 ppm is assigned for NH proton of the complexes 2a and 2b respectively. The spectral data for the complexes are collected in experimental section.

The structure of **2b** & **2d** has been determined by single crystal x-ray analysis. Overall view of the molecules of 2a with the atom-labeling scheme is shown in Fig. 2 and selected bond lengths and bond angles are given in Tables 1 & 2. Complexes **2b** & **2d** is monoclinic and crystallize in the space group $P2_{1/n}$and $P2_1/c$ with Z=8 and Z = 4. The both palladium and platinum metal centre is bonded to the amido nitrogen, azo nitrogen and amino nitrogen of the tridentate (N,N,N) donor system along with a chloride ion which is trans to azo nitrogen. The tetra-coordination geometry of the platinum(II) atom is distorted square planar (mean deviation 0.076 Å), deviation from the idealized geometry is mainly due to geometric constraints imposed by the tridentate ligand. The maximumdeviation is represented by the bite angle N(1)-Pt(1)-N(3) of 83.4(2). The Pt(1)–N(1), Pt(1)–N(3), Pt(1)–N(4), Pt(1)–Cl(1) and N(1)-N(2) bond lengths 1.935(5), 2.068(6), 1.991(6), 2.350(2) and 1.285(7) Å are within the normal range similar to relatedplatinum complexes of terdentate nitrogenous ligands [12,15-17]. The C(8)-N(2) and C(13)-N(4) lengths (~1.34Å) is comparatively shorter than the C-N single bond C(1)-N(1) and C(6)-N(3), 1.423(8) and 1.475(9) Å) in the same molecule is close to the imine distance [12,15-17]. Furthermore, the elongation of four bonds (C(8)–C(9) (1.412(10) Å), C(10)–C(11) (1.403(11) Å), C(12)–C(13) (1.444(9) Å) and C(8)–C(13) (1.451(9) Å)) and compression of two bonds (C(9)-C(10) (1.354(10) Å)



andC(11)–C(12) (1.336(10) Å)) adjacent to six membered chelate rings of this molecule is attributed to extensive delocalizationof the negative charge along the ligand backbone [19].The geometry about Pd(II)isnear square planar with N(1)–Pd–N(4), N(3)–Pd–Cl(1) bond angles 174.29(8) and 169.53(6). The Pd–N(1), Pd–N(4),Pd–N(3) and Pd–Cl(1) bond lengths 2.001(2), 2.063(19), 1.947(2), 2.3512(6) Å are within the normal range [40-42, 49-50].The C(1)-N(1) and C(6)-N(2) lengths (~1.34Å) is shorter than the C-N single bond C(7)-N(3) and C(12)-N(4), (~1.44Å) in the same molecule is close to the imine distance [19, 34-35, 40]. Thus the carbon–carbon bond lengths on phenyl ring (adjacent to six membered chelate rings) ofthe ligand (C(2)-C(3) (1·353(4)Å) and C(4)–C(5) (1·351(4) Å))are appreciably shorterthan that of other four bonds (C(1)–C(2) (1·445(3) Å), C(3)–C(4) (1·407(4), C(5)–C(6) (1·421(4)Å) and C(6)–C(1) (1·446(3) Å))[16, 34].

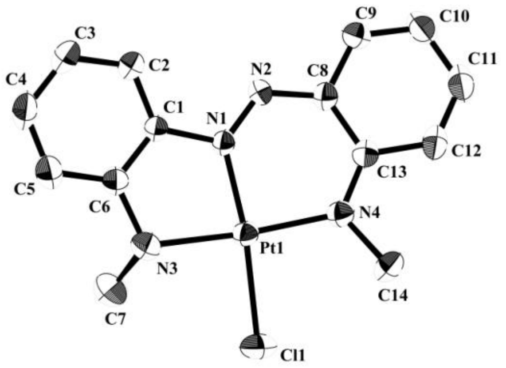


Fig. 2: Molecular structure of 2a & 2d (80% probability ellipsoids) with atom numbering scheme

TABLE 1

Selected Bond Distances (Å) and Angles (deg) for Compound **2a**.

Pd(1)-C(l1)	2.3476(15)
Pd(1)-N(1)	2.078(5)
Pd(1)-N(2)	1.932(5)
Pd(1)-N(4)	2.001(6)
N(1)-C(1)	1.454(7)
N(1)-C(13)	1.498(8)
N(2)-N(3)	1.265(7)
N(2)-C(6)	1.446(8)
N(3)-C(7)	1.372(8)
N(4)-C(12)	1.337(8)
C(7)-C(8)	1.418(9)
Cl(1)-Pd(1)-N(1)	89.09(13)
N(2)-Pd(1)-N(4)	91.0(2)
Cl(1)-Pd(1)-N(2)	172.98(16)
N(2)-N(3)-C(7)	120.3(5)
N(3)-N(2)-C(6)	112.6(5)

TABLE 2

Selected Bond Distances (Å) and Angles (deg) for Compound **2d**.

Pt(1)-Cl(1)	2.350(2)
Pt(1)-N(1)	1.935(5)
Pt(1)-N(3)	2.068(6)
Pt(1)-N(4)	1.991(6)
N(1)-N(2)	1.285(7)
N(1)-C(1)	1.423(8)
N(3)-C(6)	1.475(9)
N(3)-C(7)	1.455(11)
N(4)-C(14)	1.479(9)
N(4)-C(13)	1.340(9)
N(2)-C(8)	1.344(8)
Cl(1)-Pt(1)-N(1)	172.27(16)
Cl(1)-Pt(1)–N(4)	95.43(17)
N(1)-Pt(1)–N(3)	83.4(2)
N(1)-Pt(1)-N(4)	91.6(2)
Pt(1)-N(1)-N(2)	130.4(4)
Pt(1)-N(1)-C(1)	115.4(4)
N(1)-N(2)-C(8)	122.8(5)

V. The Suzuki and Heck coupling reactions

The active catalytic performance of **2a** in the Suzuki and Heck reaction cross coupling reaction (Equation 1 & 2) was investigated by the conversion of different substratein refluxing THF and MeOHsolvent and K_2CO_3 as base resulting good yields.All the reactions were carried out in presence of air moisture. This reusability of the catalyst was examined up to two times for a reactionwithout sufficient loss of its catalytic activity.

VI. Electrochemistry

The redox behavior of two complexes was examined in dichloromethane acetonitrile mixed solvent by cyclic voltammetry. Both the complexes exhibited two reductive responses, one irreversible and other quasireversible, reductive responses at negative to SCE and have assigned to reduction of azo (-N=N-) group [19]. One redox response appeared at positive side to SCE in the potential range 1.04–1.58 V and oxidative in nature. This redox response is quasireversible in nature and it also ligand centric [34].

VII. CONCLUSION

Newly designed, synhesized and characterized Pd(II) complexes incorporating tridendatebis-2,2'-(N-alkylamino)azobenzene1a & b ligands have excellent calytic activity towards industrially important Suzuki and Heck coupling reaction. Pt(II) complexes exhibit redox property. I thinkPt(II) complexes have biological activity towards cancer cell that will be further investigated.

VIII.Acknowledgements

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REFERENCES

[1]J-P. Corbet, G. Mignani, Selected patented cross-coupling reaction technologies,*Chem. Rev*.,*106(7), 2006, 2651-2710.*

[2]N. Selander, K.J. Szabá, Catalysis by palladium pincer complexes,*Chem. Rev., 111(3), 2011, 2048-2076.*

[3]A. Ghorbani-Choghamarani, A. Naghipour, H. Babaee, B. Notash, Synthesis, crystal structure study and high efficient catalytic activity....C–C coupling reactions, *Polyhedron,119(6), 2016, 517-524.*

[4]A. A. -Valdes, A. I. Matesanz, J. Perles, C. Fernandes, A. G. Quiroga, Novel structures of platinum complexes bearing N-bisphosphonates and study of their biological properties,*J. Inorg. Biochem., 191, 2019, 112-118.*

[5]M. V. Lunagariya, K. P. Thakor, R. R. Varma, B. N. Waghela, C. Pathak, Mohan N. Patel, Synthesis, characterization and biological application of 5-quinoline 1,3,5-trisubstituted pyrazole based platinum(II) complexes,*Med. Chem. Commun.,9, 2018, 282-298.*

[6]F. v. Nussbaum, B. Miller, S. Wild, C. S. Hilger, S. Schumann, H. Zorbas, W. Beck, W. Steglich, Synthesis of 1-(2-Aminophenyl)isoquinolines and the Biological Activity of Their cis-Dichloro Platinum(II) Complexes, *J. Medi. Chem., 42(18), 1999, 3478-3485.*

[7]N. Margiotta, P. Papadia, F. Lazzaro, M. Crucianelli, F. D. Angelis, C. Pisano, L. Vesci, G. Natile, Platinum-Based Antitumor Drugs Containing Enantiomerically Pure α-Trifluoromethyl Alanine as Ligand, *J. Med. Chem.,48(24), 2005, 7821-7828.*

[8] M. K. Raza, K. Mitra, A. Shettar, U. Basu, P. Kondaiah, A. R. Chakravarty, Pho toactive platinum(II) β-diketonates as dual action anticancer agents,*Dalton Trans., 45, 2016, 13234-13243.*

[9]K. Mitra, S. Patil, P. Kondaiah**,** A. R. Chakravarty,2-(Phenylazo)pyridineplatinum(II) Catecholates Showing Photocytotoxicity, Nuclear Uptake, and Glutathione-Triggered Ligand Release, *Inorg. Chem., 54(1), 2015, 253-264.*

[10]B. D. Palmer, Ho H. Lee, Paul Johnson, Bruce C. Baguley, G. Wickham, L. P. G. Wakelin, W. D. McFadyen, William A. Denny, DNA-directed alkylating agents. Synthesis and biological activity of platinum complexes linked to 9-anilinoacridine, J. Medi.Chem., *33, 1990, 3008-3014.*

[11]M. E. Cucciolito, A. D’Amora, G. De Feo, Giarita Ferraro, A. Giorgio, G. Petruk, Daria Maria Monti, A.Merlino**,** F. Ruffo, Five-Coordinate Platinum(II) Compounds Containing Sugar Ligands: Synthesis, Characterization, Cytotoxic Activity, and Interaction with BiologicalMacromolecules, *Inorg.Chem., 57, 2018, 3133-3143.*

[12] K. G. Samper, S. C. Marker, P. Bayón, S. N. MacMillan, J.J. Wilson, Reprint of Anticancer activity of hydroxy- and sulfonamide-azobenzene platinum(II) complexes in cisplatin-resistant ovarian cancer cells, *J. Inorg.Biochem., 174, 2017, 102-110.*

[13] P. Wang, C-H.Leung, D-L.Ma, R.W-Y.Sun, S-C.Yan, Q-S.Chen, C-M.Che, Specific Blocking of CREB/DNA Binding by CyclometalatedPlatinum(II) Complexes, *Angew. Chem. Int. Ed.,50, 2011, .2554-2558.*

[14] G. Mu, L.Cong, Z. Wen, J. I-Chia Wu, K. M. Kadish, T. S. Teets,Homoleptic Platinum Azo-iminate Complexes via Hydrogenative Cleavage of Formazans,*Inorg. Chem.,57(14), 2018, 9468-9477.*

[15] P. Chandrasekaran**,** A. F. Greene, K. Lillich, Stephen Capone, J. T. Mague, S. D. Beer, J. P. Donahue,A Structural and Spectroscopic Investigation of Octahedral PlatinumBis(dithiolene)phosphine Complexes:Platinum DithioleneInternal RedoxChemistry Induced by Phosphine Association, *Inorg. Chem.,53, 2014, 9192-9205.*

[16]J. Abildgaard, P. E. Hansen, J. Josephsen, B. K. V. Hansen, H. O. Sørensen, S. Larsen, Synthesis and characterization of nickel-, palladium- and platinum(II) complexes …results from NMR and X-ray experiments with theoretical *ab initio* calculations,*Inorg. Chim.Acta, 359(24), 2006, 4493-4502.*

[17]K. K. Kamar, S. Das, C-H. Hung, A. Castiñeiras, M. D. Kuz'min, C. Rillo, J. Bartolomé, S. Goswami, Metal promoted aromatic ring aminaton and deamination,*Inorg. Chem., 42 2003, 5367-5375.*

[18]P. Mandal, C-H. Lin, P. Brandão, D. Mal, V. Felix, J. L. Pratihar, Synthesis, characterization, structure and catalytic activity of (NNN) tridentate azo-imine nickel(II), palladium(II) and platinum(II) complexes, *Polyhedron,vol. 106, 2016, 171-177.*

[19]B. Shee, J. l. Pratihar, S. Chattopadhyay, Synthesis and characterization of new Pt(II) and Pt(IV) orthometallated complexes incorporating 1-arylazo-2-ethyl sulfanyl benzene,*Polyhedron, 25(13), 2006, 2513-2518.*

[20]M. Panda, S. Das, G. Mostafa, A. Castiñeiras, S. Goswami, Platinum complexes of diazo ligands. Studies of regioselective …… halogen elimination reactions, *Dalton Trans., 2005, 2005, 1249-1255.*

[21]S. Senapoti, Sk. Jasimuddin, G. Mostafa, T. -H. Lu, C. Sinha, Coupling of arylamine with coordinated arylazopyrimidine in platinum(II) complexes. …spectra and electrochemistry,Polyhedron, *25, 2006, 1571-1578.*

[22]S. Chattopadhyay, C. Sinha, P. Basu, A. Chakravorty, Platinum(IV)-azobenzenecyclometalation products and related species, *Organometallics, 10, 1991, 1135-1139.*

[23]D. N. Neogi, A. N. Biswas, P. Das, R. Bhawmick, P. Bandyopadhyay,Regiospecific C(naphthyl)–H bond activation by platinum(II): Isolation, characterization, reactivity and TD-DFT study of the platinum(II) and platinum(IV) organometallates having [C,N,S] donor set, J. *Organomet. Chem., 724, 2013, 147-154.*

[24]B. Tylkowski, A. Trojanowska, V. Marturano, M. Nowak, L. Marciniak, M. Giamberini, V. Ambrogi, P. Cerruti, *Coord. Chem. Rev., 351, 2017, 205-217.*

[25]M. S. Chen, M. C. White, *Science, vol. 318(5851), 2007, 783-787.*

[26] M. C. White, *Science, 335(6070), 2012, 807-809.*

[27]J.R. Berenguer, A. Diez, E. Lalinde, M.T. Moreno, S. Ruiz, S. Sanchez, Luminescent cycloplatinated complexes containing Poly(pyrazolyl)-borate and -methane ligands, *Organometallics, 30, 2011, 5776-5792.*

[28]W. Wu, W. Wu, S. Ji, H. Guo, J. Zhao, *Eur. J. Inorg. Chem. 49, 2010. 4470-448.*

[29]A. Diez, E. Lalinde, M.T. Moreno, *Coord. Chem. Rev., 255, 2011, 2426-2447.*

[30]J. L. Pratihar, P. Mandal, C. -H. Lin, C.-K. Lai, D. Mal, "Azo-amide palladium(II) complexes: Synthesis, characterization and application in C–C cross-coupling reactions",*Polyhedron, 135, 2017, 224-230.*

[31]V.N. Kozhevnikov, B. Donnio, D.W. Bruce, Phosphorescent, Terdentate, Liquid-Crystalline Complexes of Platinum(II): Stimulus-Dependent Emission,*Angew. Chem. Int. Ed., 47(33), 2008, 6286-6289.*

[32]H.-C. Chang, K. Komasaka, K. Kishida, T. Shiozaki, T. Ohmori, T. Mastusomo, A. Kobayashi, M. Kato, S. Kitagawa, Chromic Behaviors of Hexagonal Columnar Liquid Crystalline Platinum Complexes with Catecholato, 2-Thiophenolato, and Benzenedithiolato, *Inorg. Chem., 50, 2011, 4279-4288,*

[33]W. L. F. Armarego, Purification of laboratory chemicals, *8th edn, Butterworth-Heinemann, 2017*

[34] P. Pattanayak, S. P. Parua, D. Patra, C.-K. Lai, P. Brandão, V. Felix, S. Chattopadhyay, Ruthenium and palladium complexes incorporating amino-azo-phenol ligands: Synthesis, characterization, structure and reactivity,*Inorg. Chim.Acta, 429, 2015, 122-131.*

[35] J. L. Pratihar, P. Pattanayak, D. Patra, C-H.Lin, S. Chattopadhyay,Synthesis, characterization and structure ……of palladium(II): Potential catalyst for C–C coupling reactions,*Polyhedron, 33, 2012, 67-73.*

[36]G. M. Sheldrick, *ActaCrystallogr A., 64 (2008) 112-122*

[37]G. M. Sheldrick, *ActaCrystallogr., Sect. C 71 (2015) 3-8*

[38]J. L. Pratihar, P. Mandal, P. Brandão, D. Mal, V. Felix, Synthesis, characterization, spectral and catalytic activity of….. Schiff base copper(II) complexes,*Inorg. Chim. Acta, 479. 2018, 221-228.*

[39]K. Nakamoto, Infrared and Raman Spectra of ….Compounds.Part B. Applications in coordination, Organometallic and Bioinorganic Chemistry, *5th ed., Wiley, New York, (1997) 116.*

[40]J. L. Pratihar, B. Shee, P. Pattanayak, D. Patra, A. Bhattacharyya, V. G. Puranik, C-H. Hung, S. Chattopadhyay, Regiospecific ortho-Aromatic Hydroxylation via Cyclonickelation Using Hydrogen Peroxide and Other Oxygen Donors: Synthesis of Metalloazosalophens, *Eur. J. Inorg. Chem.,27, 2007, 4272-4281.*