Research Article

Ruthenium (II)-arylazoimidazole (RaaiR')-catecholates (CA) : Synthesis, Spectral study, Solvatochromism and Electrochemistry

Prithwiraj Byabartta

Departmento de Quimica Inorganica-Instituto de Ciencia deMateriales de Aragon, Universidad de Zaragoza-CSIC, Zaragoza-50009, Spain
Present Address: Department of Chemistry, Jogesh Chandra Chaudhuri College, 30- Prince Anwar Shah Road, Kolkata-700033
Corresponding Author: pribatta@rediffmail.com

Abstract

Ag^+- assisted dechlorination of blue *cis-trans-cis* $Ru(R\text{-aai-}R')_2Cl_2$ followed by the reaction with catecholes (H_2CA) in presence of Et_3N gives a neutral mononuclear violet complex $[Ru(R\text{-aai-}R')_2(CA)]$. [$R\text{-aai-}R'$ = *p*-$R\text{-}C_6H_4\text{-}N\text{=}N\text{-}C_3H_2\text{-}NN$, abbreviated as N,N' chelator where N(imidazole) and N(azo) represent N and N', respectively; R = H (**a**), Me (**b**), Cl (**c**) and R' = Me (**4**), Et (**5**), Bz(**6**)]. All the complexes exhibit strong intense MLCT transition in the visible region. Visible transition (580-595 nm) shows negative solvatochromic effect. The cyclic voltammograms show two quasireversible to irreversible couples at positive to SCE and are due to CA^-/CA^{2-} (1.2-1.35 V) and Ru(III)/Ru(II) (1.6-1.8 V) redox processes. Three couples negative to SCE are assigned to CA^{2-} / CA^{3-} (-0.2 to –0.3 V) and azo reductions (-0.5 to –0.7, -0.8 to –0.9 V) of the chelated $R\text{-aai-}R'$.

Keywords: $Ru(R\text{-aai-}R')_2Cl_2$, Synthesis, Spectral study, Solvatochromism and Electrochemistry

Introduction

The coordination chemistry of quinonoid systems are important because of their existence in various redox state (catechole (CQ)/semiquinone (SQ)/quinone (RQ)), optoelectronic communication, biological model study, DNA intercalation etc [(Francesco Caruso, Elena Monti, et al., March 11, 2014 (Article), Benjamin J. Coe, Madeleine Helliwell, et al., March 10, 2014; Daniel B. Pardue, Jiajun Mei, et al., February 26, 2014; Atsushi Kobayashi, Tadashi Ohba, et al., February 21, 2014). A common feature of the metal-RQ chemistry is delocalization of active electrons beween the metal and the quinonoid ligand. Thus transition metals are good candidates to stabilize different redox states of the quinonoid system. This is mainly due to closer energy of quinonoid based ligands to those of metal based $d\pi$-orbitals and recently much effort has been devoted to the study of the electrochemical and spectroscopic

properties of ruthenium complexes. The presence of π-acidic co-ligands like CO, pyridines (R-Py), α-diimines (bpy, phen, tpy), PPh_3, and 2-(arylazo) pyridines efficiently control the energy of metal $d\pi$ levels. As a result of this, the electron delocalization between ruthenium and RQ is perturbed in the mixed ligand complexes. Various approaches have been chosen to establish the participation of metal, coligand and RQ orbitals in the spectroscopic and redox states (Anna Rathgeb, Andreas Böhm, et al., 2014, ; Sarat Chandra Patra, Thomas Weyhermüller, and Prasanta Ghosh, 2014, Stephan Sinn, Benjamin Schulze, et al., , Inorg. Chem., 2014, Stephan Sinn, Benjamin Schulze, Christian Friebe, Douglas G. Brown, Michael Jäger, Joachim Kübel, Benjamin Dietzek, Curtis P. Berlinguette,et al.,., 2014, 53). The modification has been carried out by the synthesis of ruhenium-RQ

system using electron donor/acceptor coligands; RQ may be modified by putting substituents of different electronic properties or by replacing one or both O-donor centers by NH or S. Polyoxo carbon compounds like 2,5-dihydroxy-1,4-benzoquinone (H_2L) and other derivatives like catechols are also good candidates to synthesise metal-RQ series of complexes (Robert Staehle, Lianpeng Tong, Lei Wang, Lele Duan, Andreas Fischer, Mårten S. G. Ahlquist, Licheng Sun, and Sven Rau 2014, Amlan K. Pal, Samik Nag, Janaina G. Ferreira, Victor Brochery, Giuseppina La Ganga, Antonio Santoro, Scolastica Serroni, Sebastiano Campagna, and Garry S. Hanan, 2014, Joaquín Alós, Tamara Bolaño, Miguel A. Esteruelas, Montserrat Oliván, Enrique Oñate, and Marta Valencia, , 2014, Zahra Almodares, Stephanie J. Lucas, Benjamin D. Crossley, Aida M. Basri, Christopher M. Pask, Andrew J. Hebden, Roger M. Phillips, and Patrick C. McGowan,, 2014,). Because of the presence of equivalent O,O-donor centers on either side of the aromatic backbone of L^{2-} the isolation of monomeric complexes are difficult. However, some mononuclear complexes are summarized in the references 26 and 32-35. They are all considered as candidates for a synthon of supramolecular assemblies because of metal free oxygen sites. The complexes of arylazoheterocycles have been of special interest in the coordination chemistry of ruthenium and osmium (Katharine A. Smart, Mary Grellier, Yannick Coppel, Laure Vendier, Sax A. Mason, Silvia C. Capelli, Alberto Albinati, Virginia Montiel-Palma, Miguel A. Muñoz-Hernández, and Sylviane Sabo-Etienne , 2014, 53 (2), pp 1156, Sumit Saha and Burjor Captain , 2014, , Melissa V. Werrett, Sara Muzzioli, Phillip J. Wright, Antonio Palazzi, Paolo Raiteri, Stefano Zacchini, Massimiliano Massi, and Stefano Stagni 2014, Christi L. Whittington, Lukasz Wojtas, and Randy W. Larsen, 2014,). Pseudo-octahedral dichloro-bis-chelated arylazoheterocycles of ruthenium(II) can exist, in principle, in five isomeric forms and out of them three isomers have structurally been characterized (Nathir A. F. Al-Rawashdeh, Sayandev Chatterjee, Jeanette A. Krause, and William B. Connick, , 2014, Rongwei Zhou, Baburam Sedai, Gerald F. Manbeck, and Karen J. Brewer , 2013, Wei Su, Quanquan Qian, Peiyuan Li, Xiaolin Lei, Qi Xiao, Shan Huang, Chusheng Huang, and Jianguo Cui , 2013, Michael R. Norris, Javier J. Concepcion, Christopher R. K. Glasson, Zhen Fang, Alexander M. Lapides, Dennis L. Ashford, Joseph L. Templeton, and Thomas J. Meyer, 2013,). Ruthenium is a component of mixed-metal oxide (MMO) anodes used for cathodic protection of underground and submerged structures, and for electrolytic cells for chemical processes such as generating chlorine from salt water. The fluorescence of some ruthenium complexes is quenched by oxygen, which has led to their use as optode sensors for oxygen. Ruthenium red, $[(NH_3)_5Ru-O-Ru(NH_3)_4-O-Ru(NH_3)_5]^{6+}$, is a biological stain used to stain polyanionic molecules such as pectin and nucleic acids for light microscopy

and electron microscopy (Wang Yuan, Yang Zheng-Yin, (October 2005),) . The beta-decaying isotope 106 of ruthenium is used in radiotherapy of eye tumors, mainly malignant melanomas of the uvea. Ruthenium-centered complexes are being researched for possible anticancer properties. Compared with platinum complexes, those of ruthenium show greater resistance to hydrolysis and more selective action on tumors. NAMI-A and KP1019 are two drugs undergoing clinical evaluation against metastatic tumors and colon cancers. Because of its ability to harden platinum and palladium, ruthenium is used in platinum and palladium alloys to make wear-resistant electrical contacts. In this application, only thin plated films are used to achieve the necessary wear-resistance. Because of its lower cost and similar properties compared to rhodium, the use as plating material for electric contacts is one of the major applications. The thin coatings are either applied by electroplating or sputtering. Ruthenium dioxide and lead and bismuth ruthenates are used in thick-film chip resistors. These two electronic applications account for 50% of the ruthenium consumption. Only a few ruthenium alloys are used other than those with other platinum group metals. Ruthenium is often used in small quantities in those alloys to improve some of their properties. The beneficial effect on the corrosion resistance of titanium alloys led to the development of a special alloy containing 0.1% ruthenium. Ruthenium is also used in some advanced high-temperature single-crystal superalloys, with applications including the turbine blades in jet engines. Several nickel based superalloy compositions are described in the literature. Among them are EPM-102 (with 3% Ru) and TMS-162 (with 6% Ru), as well as TMS-138 and TMS-174. both containing 6% rhenium. Fountain pen nibs are frequently tipped with alloys containing ruthenium. From 1944 onward, the famous Parker 51 fountain pen was fitted with the "RU" nib, a 14K gold nib tipped with 96.2% ruthenium and 3.8% iridium. A wide number of ruthenium complexes containing heterocyclic nitrogeneous molecules and related ligands have been reported to date (Maiti Nilkamal, et. al, (2001); Pal Chandan Kumar et al. (1996), Chakraborty Indranil, et al, (2005),) They are of considerable interest primarily due to variable oxidation states, building blocks for supramolecular assemblies, photo-physical properties, directional electron and energy transfer, potential anticancer property. Modification of heterocyclic ligands may be carried out by incorporating new donor centers, spectator groups, change of ring size and number of Heteroatoms. They can significantly influence the physical and chemical properties of the complex molecules. Since the discovery of important redox, photophysical and photochemical properties of ruthenium complexes having 2,2-bipyridine (bipy) as ligand, there has been continuous research activity in the direction of developing newer ruthenium–bipyridine systems with the perspective of interesting physicochemical properties (Ghosh Pradip, Samanta Subhas, et al.,(2013), Shivakumar Maya, Pramanik

Kausikisankar, et al. , (2000) ; Pramanik Kausikisankar, Shivakumar Maya, et al., (2000), Das Chayan, Saha Amrita, et al., (2002), Shivakumar Maya, et. al., (1998)). In this context different kinds of mixed ligand ruthenium–bipyridine complexes have been synthesized and studied over the last fifteen years [Rasmussen S. C., Thompson D. W., Singh V. and Petersen J. D., (1996 medical aspects), Krause Ronald A., Krause Kirsten, 1984]. The basic strategies behind all these activities are either to incorporate different groups within the bipyridine moiety itself or use other types of donor sites like azoimine function along with the Ru(bipy)$_2$ core to form mixed-ligand tris-chelates to modulate the photo-redox activities of this class of complexes [Santra B. K., Thakur G. A., Ghosh P., Pramanik A. and Lahiri G. K., Inorg. Chem., 1996]. The present work originates in preparing new mixed-ligand ruthenium–arylazoimidazole complexes of type [Ru(RaaiR)$_2$L], where L is a ligand which can form a four membered chelate ring on co-ordination and in studying the redox and spectroscopic properties of the Ru(RaaiR)$_2$ core [Bag N., Lahiri G. K., Bhattacharya S., Falvello L. R. and Chakravorty A., Inorg. Chem., 1988,]. I have chosen pyridine-2-thiol and pyridin-2-ol as ligand L. This work demonstrates example of [Ru(RaaiR)$_2$(X-Pyridine)] [RaaiR$'$ = p-R-C$_6$H$_4$-N=N-C$_3$H$_2$-NN-1-R$'$, (1-6), abbreviated as N,N$'$-chelator, where N(imidazole) and N(azo) represent N and N$'$, respectively; R = H (a), Me (b), Cl (c) and R$'$ = Me (1,4), CH$_2$CH$_3$ (2,5), Bz(3,6), X=S, 2-mercaptopyridine(1-3), X=O, 2-hydroxy-pyridine(4-6)] systems. Herein I report the synthesis of two complexes having RuN$_5$S and RuN$_5$O chromophores, their spectroscopic characterisation, electron-transfer properties, preliminary photophysical aspects. The stereoisomeric forms having cis-RuCl$_2$ moiety in cis-trans-cis–RuCl$_2${2-(arylazo)pyridine)}$_2$ exhibit potential antitumor activity even better than cisplatin. (The cis-trans-cis refers to the coordination sequence of pairs of Cl; N(heterocycle) and N(azo), respectively). The cis-RuCl$_2$ fragment in these complexes may be substituted by other donor centers either directly or Ag$^+$- assisted route to synthesise hetereoleptic tris-chelates. The compounds having cis-MCl$_2$ configuration have been used to synthesise catecholato complexes. In continuation of comprehensive studies on chemistry of catecholato system in this article I describe some ruthenium(II) 1-alkyl-2-(arylazo)imidazole complexes of catecholates.

Experimental

RuCl$_3$.nH$_2$O was obtained from Arrora Matthey. 1-Alkyl-2-(arylazo)imidazole was synthesized by the reported procedure. ctc–RuCl$_2$(R-aai-R$'$)$_2$ was prepared by a known method. Microanalytical data (C, H, N) were collected using a Perkin Elmer 2400 CHN instrument. Solution electronic spectra were recorded on a JASCO UV-VIS-NIR V-570 sprctrophotometer. Infrared (IR) spectra were obtained using a JASCO 420 spectrophotometer (using KBr disks, 4000-200 cm^{-1}).

The ^{1}H NMR spectra in CDCl$_3$ were obtained on a Bruker 500 MHz FT NMR spectrometer using SiMe$_4$ as internal reference. Electrochemical work was carried out using EG & G PARC Versastat computer controlled 250 electrochemical system. All experiments were performed under a N$_2$ atmosphere at 298K using a Pt-disk milli working electrode at scan rate 50 mVs^{-1}. All results were referenced to a saturated calomel electrode (SCE). Reported potentials are uncorrected for junction effect.

Synthesis of bis-{1-methyl-2-(p-chlorophenylazo)imidazole} catecholato-ruthenium(II) monohydrate

To a methanolic suspension of ctc-Ru(Cl-aai-Me)$_2$Cl$_2$ (0.6 g, 1.02 mmol), aqueous AgNO$_3$ solution (0.347 g, 2.04 mmol) was added and refluxed for 15 min, the blue solution changed to blue violet colour. AgCl so precipitated was filtered off over a G4 crucible. This solution was kept in N$_2$-atmosphere. To a methanolic solution of catechol (0. 213 g, 1.02 mmol) two drops of NEt$_3$ added and the colour changes from orange to pink. This pink solution was then added to the above solution and the resulting mixture was heated to reflux for 1h under nitrogen. The blue-violet solution changed to violet. The solution was then evaporated to half its original volume by N$_2$ bubbling, cooled to room temperature, filtered and then washed thoroughly with plenty of water, methanol and finally with diethyl ether and dried in vacuo over P$_4$O$_{10.}$ The dry mass was then dissolved in minimum vol. of CH$_2$Cl$_2$ and subjected to chromatography on a silica gel column (60-120 mesh). A violet band was eluted with C$_7$H$_9$-CH$_3$CN (1:1, v/v). This was collected and evaporated slowly in air. The crystals so obtained were dried over P$_4$O$_{10}$. The yield was 70%.

All other complexes were prepared similarly; yield, 65-80%. Analysis for [Ru(H-aai-Me)$_2$(CA)], **4a**, [C$_{26}$H$_{24}$N$_8$RuO$_2$], Calc(found): C, 53.74 (53.8), H, 4.2 (4.1), N, 19.36(19.30); IR ν(N=N) 1370 ν(C=N) 1590 ν(C=O) 1525,1360,1297, ES/MS, 581 [M$^+$], Proton n.m.r., ^{1}H, ppm, 8.07(d, J = 8Hz, H(7,11)), 8.01(d, J=6.5Hz, H(8,10)), 7.09(m, 9-H), 7.26(d, J=6Hz, H(4)), 7.34(d, J=5Hz, H(5)), 1.5(s, N-Me); ^{13}C {^{1}H}, ppm ,134.5(C2), 124(C4), 125(C5), 125.3(C7,11), 129.2(C8,10), 134(C6), 42 (Me Gr.); UV-Vis (nm), 580, 370, 480, 300, 710(sh); Electrochemistry, Ru(III)/Ru(II), 1.65 V, azo reductions -0.52, -0.83; Analysis for [Ru(Me-aai-Me)$_2$(CA)], **4b**, [C$_{28}$H$_{28}$N$_8$RuO$_2$], Calc(found): C, 55.4 (55.8), H, 4.6(4.6), N, 18.36(18.30); IR ν(N=N) 1379 ν(C=N) 1599 ν(C=O) 1525,1368,1297, ES/MS, 609[M$^+$], Proton n.m.r., ^{1}H, ppm, 8.0(d, J = 8Hz, H(7,11)), 8.1(d, J=6.5Hz, H(8,10)), 7.0(m, 9-H), 7.2(d, J=6Hz, H(4)), 7.3(d, H(5)), 1.5(s, N-Me); ^{13}C {^{1}H}, ppm ,134.5(C2), 125(C5), 125.3(C7,11), 129.2(C8,10), 134(C6), 42 (Me Gr.); UV-Vis (nm), 588, 370, 489, 309, 709(sh); Electrochemistry, Ru(III)/Ru(II), 1.69 V, azo reductions -0.59, -0.89; Analysis for [Ru(Cl-aai-Me)$_2$(CA)], **4c**, [C$_{26}$H$_{22}$N$_8$RuCl$_2$O$_2$], Calc(found): C, 47.74 (47.8), H, 3.2 (3.1), N, 17.36(17.30); IR ν(N=N) 1377 ν(C=N) 1594 ν(C=O) 1520,1360,1290, ES/MS,

651 [M⁺], Proton n.m.r., ¹H, ppm, 8.0(d, J = 8Hz, H(7,11)), 8.1(d, J=6Hz, H(8,10)), 7.2(d, J=6Hz, H(4)), 7.34(d, H(5)), 1.5(s, N-Me); ^{13}C {¹H}, ppm ,134.5(C2), 125(C5), 125.3(C7,11), 129.2(C8,10), 134(C6), 42 (Me Gr.); UV-Vis (nm), 580, 379, 480, 303, 700(sh); Electrochemistry, Ru(III)/Ru(II), 1.65 V, azo reductions -0.62, -0.83; Analysis for [Ru(H-aai-Et)₂(CA)], **5a**, [C₂₈H₂₈N₈RuO₂], Calc(found): C, 55.4 (55.8), H, 4.6(4.6), N, 18.36(18.30); IR ν(N=N) 1379 ν(C=N) 1599 ν(C=O) 1525,1368,1297, ES/MS, 609[M⁺], Proton n.m.r., ¹H, ppm, 8.0(d, Analysis for [Ru(Me-aai-Et)₂(CA)], **5b**, [C₃₀H₃₂N₈RuO₂], Calc(found): C, 56.4 (56.8), H, 4.9(5.0), N, 17.6(17.3); IR ν(N=N) 1378 ν(C=N) 1599 ν(C=O) 1525,1368,1297, ES/MS, 637[M⁺], Proton n.m.r., ¹H, ppm, 8.0(d, H(7,11)), 8.1(d, J=6.5Hz, H(8,10)), 7.0(m, 9-H), 7.2(d, J=6Hz, H(4)), 7.3(d, H(5)), 1.5(s, N-Me); ^{13}C {¹H}, ppm ,134.5(C2), 125(C5), 125.3(C7,11), 129.2(C8,10), 134(C6); UV-Vis (nm), 588, 370, 489, 309, 709(sh); Electrochemistry, Ru(III)/Ru(II), 1.69 V, azo reductions -0.59, -0.89; H(7,11)), 8.1(d, J=6.5Hz, H(8,10)), 7.0(m, 9-H), 7.2(d, J=6Hz, H(4)), 7.3(d, H(5)), 1.5(s, N-Me); ^{13}C {¹H}, ppm ,134.5(C2), 125.3(C7,11), 129.2(C8,10), 134(C6); UV-Vis (nm), 588, 370, 489, 309, 709(sh); Electrochemistry, Ru(III)/Ru(II), 1.69 V, azo reductions -0.59, -0.89; Analysis for [Ru(Cl-aai-Et)₂(CA)], **5c**, [C₂₈H₂₆N₈RuClO₂], Calc(found): C, 49.4 (49.8), H, 3.6(3.8), N, 16.6(16.30); IR ν(N=N) 1379 ν(C=N) 1599 ν(C=O) 1520,1368,1297, ES/MS, 679[M⁺], Proton n.m.r., ¹H, ppm, 8.0(d, J = 8Hz, H(7,11)), 8.1(d, J=6.5Hz, H(8,10)), 7.2(d, J=6Hz, H(4)), 7.3(d, H(5)), 4.4,1.5(s, N-Et); ^{13}C {¹H}, ppm ,134.5(C2), 125.3(C7,11), 129.2(C8,10), 134(C6), 42,53(Et Gr.); UV-Vis(nm),588, 370, 489, 309, 709(sh); Electrochemistry, Ru(III)/Ru(II), 1.69 V, azo reductions -0.59, -0.89; Analysis for [Ru(H-aai-Bz)₂(CA)], **6a**, [C₃₈H₃₂N₈RuO₂], Calc(found): C, 62.4 (62.2), H,

4.6(4.4), N, 15.36(15.3); IR ν(N=N) 1370 ν(C=N) 1590 ν(C=O) 1525,1360,1290, ES/MS, 733[M⁺], Proton n.m.r., ¹H, ppm, 8.0(d, H(7,11)), 8.1(d, J=6.5Hz, H(8,10)), 7.0(m, 9-H), 7.2(d, J=6Hz, H(4)), 7.3(d, H(5)), ^{13}C {¹H}, ppm ,134.5(C2), 125(C5), 125.3(C7,11), 129.2(C8,10), 134(C6); UV-Vis (nm), 580, 379, 489, 309, 704(sh); Electrochemistry, Ru(III)/Ru(II), 1.59 V, azo reductions -0.57, -0.89; Analysis for [Ru(Me-aai-Bz)₂(CA)], **6b**, [C₄₀H₃₆N₈RuO₂], Calc(found): C, 63.1(63.1), H, 4.6(4.7), N, 14.6(14.7); IR ν(N=N) 1379 ν(C=N) 1599 ν(C=O) 1525,1368,1297, ES/MS, 761[M⁺], Proton n.m.r., ¹H, ppm, 8.0(d, H(7,11)), 8.1(d, J=6Hz, H(8,10)), 7.2(d, J=6Hz, H(4)), 7.3(d, H(5)), 4.95(s, N-Bz); ^{13}C {¹H}, ppm ,134.5(C2), 125(C5), 125.3(C7,11), 129.2(C8,10), 134(C6); UV-Vis (nm), 588, 377, 489, 309, 700(sh); Electrochemistry, Ru(III)/Ru(II), 1.69 V, azo reductions -0.53, -0.89; Analysis for [Ru(Cl-aai-Bz)₂(CA)], **6c**, [C₃₈H₃₀N₈RuClO₂], Calc(found): C, 56.84 (56.8), H, 4.76(3.6), N, 13.6(13.90); IR ν(N=N) 1379, ν(C=N) 1599, ν(C=O) 1525,1368,1290, ES/MS, 803[M⁺], Proton n.m.r., ¹H, ppm, 8.0(d, H(7,11)), 8.1(d, J=6Hz, H(8,10)), 7.2(d, J=6Hz, H(4)), 7.3(d, H(5)), ^{13}C {¹H}, ppm ,134.5(C2), 125(C5), 125.3(C7,11), 129.2(C8,10), 134(C6); UV-Vis (nm), 588, 377, 480, 309, 709(sh); Electrochemistry, Ru(III)/Ru(II), 1.69 V, azo reductions -0.59, -0.80.
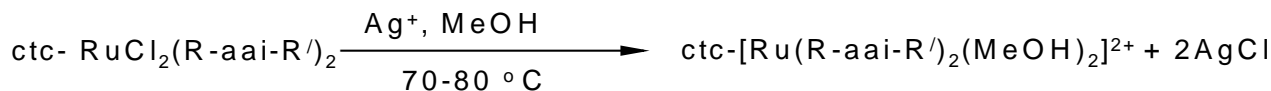
Results and Discussion

Silver⁺- assisted dechlorination of *ctc*-RuCl₂(R-aai-R′)₂ (*1-3*) in methanol has prepared a solvated species, [Ru(R-aai-R′)₂(MeOH)₂]²⁺ at 70-80° C. Addition of catechol (H₂CA) (one equivalent)
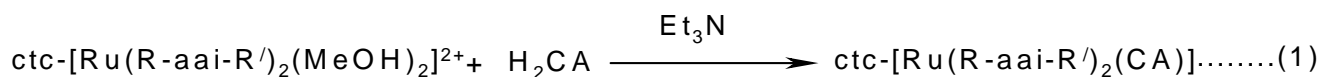

Heteroleptic tris chilates

Cat or Catechol
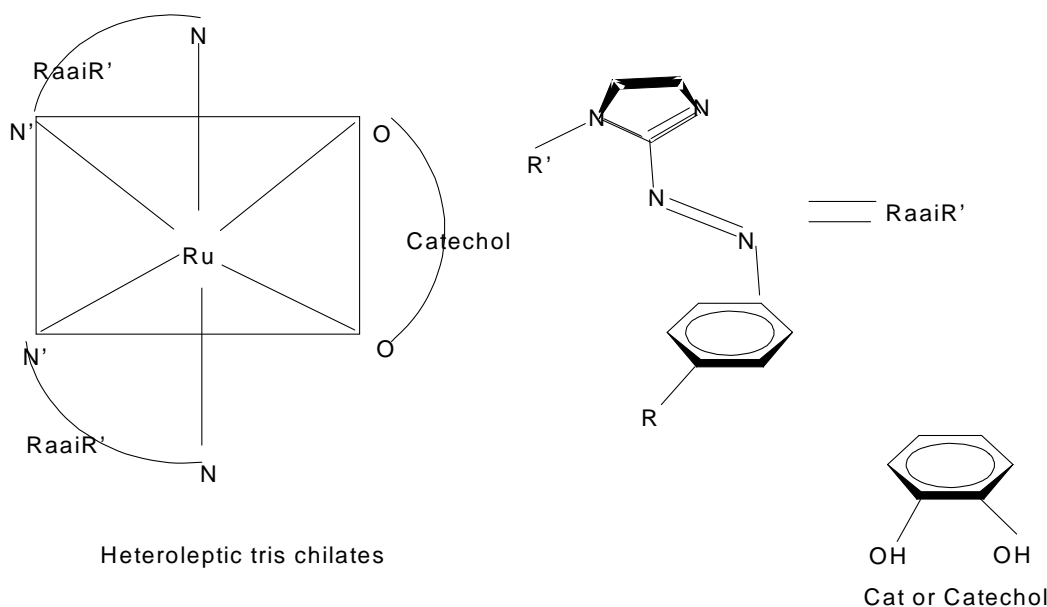
Scheme 1

to this solution followed by Et$_3$N (2.5 equivalent) under stirring condition has synthesized the title compound [Ru(R-aai-R$^{/}$)$_2$(CA)] (**4-6**) (*Scheme 1*). The products were purified by chromatographic process. Reaction temperature should be strictly maintained to optimize the yield of the product. At higher temperature (>100^{0}C) the reaction gives some unidentified products. The ligand, R-aai-R$^{/}$, refers to 1-alkyl-2-(arylazo)imidazole. They are N, N$^{/}$-donor ligands where N and N$^{/}$ are abbreviated to N(imidazole) and N(azo), respectively. The composition of **4 - 6** were formulated by elemental analyses. The complexes are diamagnetic (d^6, S=0) and non-electrolytic in nature in MeCN.

$$ctc\text{-}RuCl_2(R\text{-}aai\text{-}R^{/})_2 \xrightarrow[\text{70-80 }^oC]{Ag^+, MeOH} ctc\text{-}[Ru(R\text{-}aai\text{-}R^{/})_2(MeOH)_2]^{2+} + 2AgCl$$

1-3

$$ctc\text{-}[Ru(R\text{-}aai\text{-}R^{/})_2(MeOH)_2]^{2+} + H_2CA \xrightarrow{Et_3N} ctc\text{-}[Ru(R\text{-}aai\text{-}R^{/})_2(CA)]........(1)$$

4-6

The infrared spectra of **4 – 6** have been assigned on comparing with the spectra of the precursors Ru(R-aai-R$^{/}$)$_2$Cl$_2$ and catechol. Important part of IR spectra (KBr disc) of the complexes, **4 – 6** are the disappearance of stretching at 325-340 and 310-320 cm^{-1} correspond to *cis*-RuCl$_2$ configuration of the precursors, **1-3**. The characteristics stretchings at 1395-1410 and 1620-1630 cm^{-1} are assigned to ν (N=N) and ν (C=N) + ν (C=O), respectively of coordinated R-aai-R$^{/}$ in the complex, **4 - 6**. A broad weak stretch at 3170-3180 cm^{-1} may be assigned to the stretching of water of crystallization in the solid state. The ν (C-O) appears at 1525, 1360, 1297 cm^{-1} in the complexes, (**4-6**) and the free catechol values are 1664, 1630, 1360, 1265 cm^{-1}.

The solution electronic spectra of the complexes were examined in CH$_2$Cl$_2$. There are two high intense absorptions in the region 580-595 and 370-380 nm along with two weak bands at 470-480 and 300-310 nm. The transition below 400 nm are due to intra-ligand charge transfer transitions and are not considered further. On comparing with the parent dichloro complexes, Ru(R-aai-R$^{/}$)$_2$Cl$_2$ two transitions 580-595 and 470-480 nm may be assigned to d(Ru) → π* (ligand) transitions. The concentrate solution of the complexes (~10^{-3} M) exhibit broad and weak absorption at 670-685 and 875-886 nm. In the complexes where metal ion is redox active with delocalisable dπ-orbitals and/or π-acidic co-ligands having vacant π*-orbitals can participate with additional charge transitions: 3b$_1$(catecho lato)→dπ(metal), 3b$_1$(catecholato) →π*(co-ligand). Usually these transitions appear at longer wavelength region (> 700 nm) and are high intense in nature (ε ~ 10^4) (Nathir A. F. Al-Rawashdeh, Sayandev Chatterjee, Jeanette A. Krause, and William B. Connick, , 2014, Rongwei Zhou, Baburam Sedai, Gerald F. Manbeck, and Karen J. Brewer , 2013, Wei Su, Quanquan Qian, Peiyuan Li, Xiaolin Lei, Qi Xiao, Shan Huang, Chusheng Huang, and Jianguo Cui , 2013, Michael R. Norris, Javier J.

Concepcion, Christopher R. K. Glasson, Zhen Fang, Alexander M. Lapides, Dennis L. Ashford, Joseph L. Templeton, and Thomas J. Meyer, 2013,). So, the transitions near 700 nm may be assigned to ligand-to-ligand charge transfer transitions, CA^{2-}→ π*(R-aai-R$^{/}$) / π*(Ru + R-aai-R$^{/}$).

The MLCT band at 580-595 nm is sensitive to solvent polarity. The effect has been examined for a series of non-hydroxylic and hydroxylic solvents. The hydroxylic solvents show higher values of E$_{MLCT}$ compared with non-hydroxylic solvents. The observation is corroborated with negative solvatochromism. This can be attributed to superior solvation of the dipolar ground state and inferior solvation of the less dipolar excited state by the polar solvent. If the electronic excitation is associated with decrease in dipole moment than the excited state will be in a strained solvent cage of oriented dipoles not correctly oriented so as to efficiently stabilize the excited state. Thus, with increasing solvent polarity the energy of the ground state is lowered to a greater extent than that of the excited state and this produces hypsochromic effect.

The nmr spectra are corroborated with *ctc*-isomer and suggest retention of strereo-configuration. Protons are assigned on the basis of spin-spin interaction, effect of substitution on R-aai-R$^{/}$ and on comparing with the spectra of precursor *ctc*-[Ru(R-aai-R$^{/}$)$_2$Cl$_2$] . Each R-aai-R$^{/}$ chelated fragment in the complexes [Ru(CA)(R-aai-R$^{/}$)$_2$] exhibits separate set of proton signals. Imidazole 4- and 5-H appear at 6.9-7.2 and 6.8-7.0 ppm respectively. They are broad singlet in spin interaction pattern. It may be due to charge delocalisation from coordinated chloranilate ion to π-acidic R-aai-R$^{/}$ *via* Ru(II). Aryl-H (7-H −11-H) are affected by substituent R; electron donating substituent –Me shifts the protons to lower δ while electron withdrawing –NO$_2$ group moves the protons to higher δ values

ISOMER-A

ISOMER-B

ISOMER -C
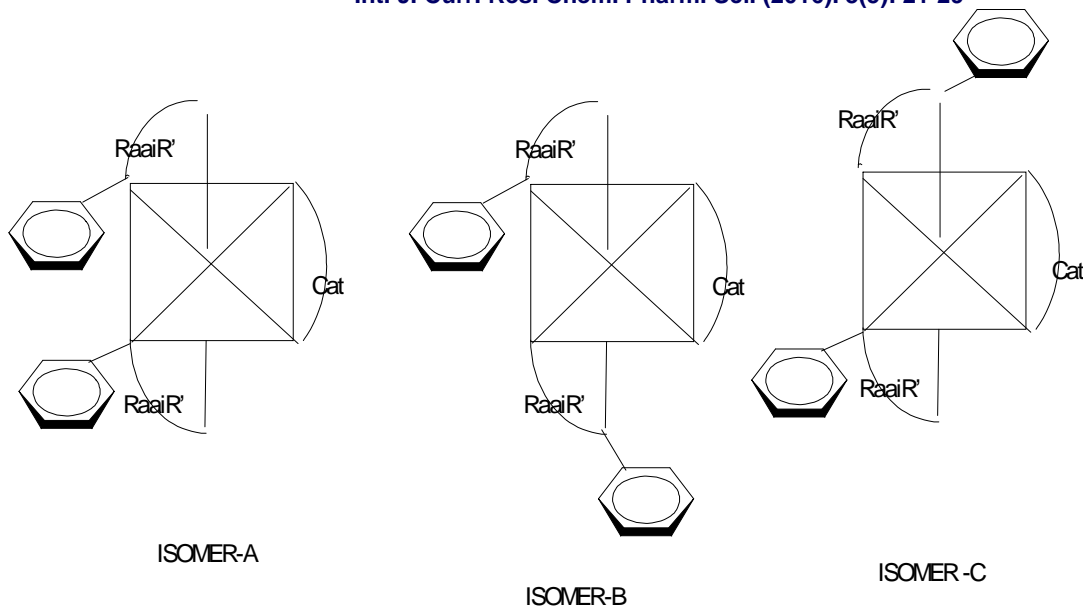
compared with phenyl group. 8,10-H ($8'$, $10'$-H) are severely affected by substituent R than that of 7-H ($7'$-H) and 11-H ($11'$-H). The 1-Me group of [Ru(R-aai-Me)$_2$(CA)] (*4a-6a*) shows two closely spaced singlet signals showing hetero symmetry of chelated R-aai-R' groups. Similar observations are also recorded in 1-Et and 1-CH$_2$Ph groups (Isomer A, B, C).

The ^{13}C NMR spectrum provides direct information about the carbon skeleton of the molecule. Assignment of different resonant peaks to respective carbon atoms are done on nine complexes and the datas are given on table 4. Considering two arylazoimidazole moities there are twenty different carbon atoms in the molecule which gives a total of twenty different peaks in the ^{13}C NMR spectrum. Carbon atoms neighbouring the nitrogen atom shifted to downfield due to an increased electron density resulting from the presence of electronegative nitrigen atom and pi electron delocalisation in the magnetic environment. The non-protonated carbon atoms at C(2) and C(6) of the arylazoimidazole moiety is shifted farthest downfield in the spectrum (δ = 170.12 ppm and 168 ppm) effected by the magnetic interection of two bulky phenyl rings environment and the two methyl substituted imidazole rings and the pi electron delocalization on the =N--CC=N-- and =N—CC=CC--. Similarly the carbon atom at e and e' position on bipyridine molecule in the complex resonance at a lower field of 165 ppm resulting of the conjugative effect of the –N=CC—CC=N--. The methyl carbon atom of the imidazole ring resonate at 160 ppm, resonably compare to the other carbon atoms resonance.

Two redox responses are observed at positive to SCE and are oxidative in nature. They are quasi-reversible in nature and E_{pa} of first response lies in the range 1.2 – 1.4 V and the second couple appears at 1.6-1.8 V ($\Delta E_P \geq$ 90mV). The reversal in the positive scanning at

1.2 V increases cathodic current height and on repeat cycles (5 cycles) within potential range 0.9 to 1.5 V do not change symmetry and position of the voltammogram at scan rate 50 mVs^{-1}. Thus, the redox couple 1.2–1.4 V is assigned to CA$^-$ / CA^{2-}. Second oxidation is assigned to metal centered oxidation, Ru (III)/Ru(II). One electron nature of oxidation and reduction are estimated on comparing with current height of Fe(CN)$_6^{4-}$/Fe(CN)$_6^{3-}$ couple. If we carry out experiment with going to negative potential first and reversed to positive then these two redox responses exhibit a broad overlapped voltammogram. However, subsequent scans are complicated and a broad cathodic peak is observed at 0.4-0.5 V. It may be due to stripping and adsorption behaviour resulting from deposition of reduced products on the electrode surface. There are three quasi-reversible reductive responses at negative to SCE and they are ligand centered reductions. A quasireversible reduction wave is observed at −0.2 to −0.3 V (ΔE_P = 80-120 mV) whose current height is comparable with 1e electrochemical response (current height is compared with Fe(CN)$_6^{4-}$/Fe(CN)$_6^{3-}$ couple). There is a second reduction step (E_{pc} = - 0.5 to - 0.7 V) which exhibits peak-to-peak separation, ($\Delta E_P \geq$ 100 mV). A third quasireversible one electron reduction is observed at - 0.8 to - 0.9 V. Azoimine function is second reducing centre where azo group (-N=N-) may accommodate 2e$^-$s. First couple at –ve to SCE appears at - 0.2 to - 0.3 V which is insufficiently negative to be attributed to R-aai-R' reduction process. On comparing with redox data of Ru(R-aai-R')$_2$Cl$_2$, Ru(bpy)$_2$(cat), Ru(aap)$_2$(cat) and H$_2$CA confirms it is localized to chelated catecholate group. Second and third reductions appear at -0.5 to −0.6 V and −1.0 to −1.3 V and are sufficient enough for azo reductions. Two chelated R-aai-R' may accept two electrons in a stepwise manner for first stage azo reduction. The potential difference between first and second reduction responses is ~0.3 V.

26

In conclusion, In this work I have synthesised nine mononuclear ruthenium(II) mixed ligand complexes using catecholate ion (CA^{2-}) and 1-alkyl-2-(arylazo)imidazole (RaaiR$^{/}$) and their full spectral and elemental characterisation. In this case it forms mononuclear ruthenium (II) complex with metal-free quinonoid end. ^{1}H NMR study suggests azoimine and catechol linkage. ^{13}C (^{1}H)NMR gives the molecular skeleton in solution phase. ^{1}H-^{1}H COSY spectrum suggest the contour peaks in the solution phase.

Acknowledgments

References

[1] Rasmussen S. C., Thompson D. W., Singh V. and Petersen J. D., (1996), , Inorg. Chem., , 35,3449;

[2] Wang Yuan, Yang Zheng-Yin, Synthesis, Characterization and DNA-binding Properties of Three 3d Transition Metal Complexes of the Schiff Base Derived from Diethenetriamine with PMBP, Transition Metal Chemistry, (October 2005), Volume 30, Issue 7, pp 902-906

[3] Maiti Nilkamal, Pal Satyanarayan, and Chattopadhyay Surajit, Reaction of 2-(Phenylazo)aniline with Na$_2$PdCl$_4$: Formation of a 2-(Phenylazo)imino Complex of Bivalent Palladium, Inorganic Chemistry (2001) 40 (9), 2204-2205

[4] Pal Chandan Kumar , Chattopadhyay Surajit , Sinha Chittaranjan , and Chakravorty Animesh *, A Bis(azo–imine)palladium(II) System with 10 Ligand Electrons. Synthesis, Structure, Serial Redox, and Relationship to Bis(azooximates) and Other Species, Inorg. Chem., (1996), 35 (9), pp 2442–2447 DOI: 10.1021/ic950361t, Publication Date (Web): April 24, 1996..

[5] Chakraborty Indranil, Panda Bikash Kumar, Gangopadhyay Jaydip, and Chakravorty Animesh, Rhenium Chemistry of Azooximes: Oxygen Atom Transfer, Azoimine Chelation, and Imine–Oxime Contrast, Inorganic Chemistry, (2005), 44 (4), 1054-1060

[6] Ghosh Pradip, Samanta Subhas, Roy Suman K, Joy Sucheta, Krämer Tobias, McGrady John E., and Goswami Sreebrata, Redox Noninnocence in Coordinated 2-(Arylazo)pyridines: Steric Control of Ligand-Based Redox Processes in Cobalt Complexes, Inorganic Chemistry, (2013), 52 (24), 14040-14049

[7] Shivakumar Maya, Pramanik Kausikisankar, Bhattacharyya Indranil, and Chakravorty Animesh, Chemistry of Metal-Bound Anion Radicals. A Family of Mono- and Bis(azopyridine) Chelates of Bivalent Ruthenium, Inorganic Chemistry, (2000) 39 (19), 4332-4338.

[8] Pramanik Kausikisankar, Shivakumar Maya, Ghosh Prasanta, and Chakravorty Animesh, Azo Anion Radical Complexes of Osmium and Related Nonradical Species, Inorganic Chemistry, (2000), 39 (2), 195-199

[9]. Das Chayan, Saha Amrita, Hung Chen-Hsiung, Lee Gene-Hsiang, Peng Shie-Ming, and Goswami Sreebrata, Ruthenium Complexes of 2-[(4-(Arylamino)phenyl)azo]pyridine Formed via Regioselective Phenyl Ring Amination of Coordinated 2-(Phenylazo)pyridine: Isolation of Products, X-ray Structure, and Redox and Optical Properties, Inorg. Chem., (2003), 42 (1), pp 198–204, Publication Date (Web): December 10, (2002), (Article), DOI: 10.1021/ic0203724

[10]. Shivakumar Maya, Pramanik Kausikisankar, Ghosh Prasanta, and Chakravorty Animesh, Isolation and Structure of the First Azo Anion Radical Complexes of Ruthenium, , Inorg. Chem., (1998), 37 (23), pp 5968–5969, Publication Date (Web): October 17, (1998) (Communication), DOI: 10.1021/ic980719w

[11]. Krause Ronald A., Krause Kirsten, Chemistry of bipyridyl-like ligands. 3. Complexes of ruthenium(II) with 2-((4-nitrophenyl)azo)pyridine, Inorg. Chem., (1984), 23 (14), pp 2195–2198, Publication Date: July 1, 1984 (Article), DOI: 10.1021/ic00182a042 Extra references

[12] Byabartta P., Dinda J., Santra P. K., Sinha C., Panneerselvam K., Liao F. –L. and Lu T. –H., Heteroleptic tris-chelates of ruthenium(II)-bipyridine-arylazoimidazoles: Synthesis, spectral characterisation and electrochemical properties. Single crystal X-ray structure of [(2,2$^{/}$-bipyridine)-bis-{1-methyl-2-(p-tolylazo)imidazole} ruthenium(II)] perchlorate J. Chem.Soc., Dalton Trans., 2001, 2825.

[13] Byabartta P., Santra P. K., Misra T. K., Sinha C. and Kennard C. H. L., Synthesis, spectral characterization, redox studies of isomeric dichlorobis-[1-alkyl-2-(naphthyl-(α/β)-azo)imidazole]ruthenium(II). Single crystal X-ray structure of blue-green dichloro-bis-[1-ethyl-2-(naphthyl-α-azo)imidazole]ruthenium(II), Polyhedron, 2001, 20, 905.

[14] Byabartta P., Pal S., Misra T. K., Sinha C., Liao F. –L., Panneerselvam K. and Lu T. –H., Synthesis, spectroscopic and electrochemical studies of isomeric dichloro bis- [N(1)-alkyl-2-(arylazo)imidazole] osmium(II). Single crystal X-ray structures of blue-violet dichloro-bis-[N(1)-methyl-2-(arylazo)imidazole] osmium(II) species, J. Coord. Chem., 2002, 55(5), 479.

[15] Byabartta P., Jasimuddin Sk., Ghosh B. K., Sinha C., Slawin A. M. Z. and Woollins J. D.,Nitro-ruthenium(II)-arylazoimidazoles: Synthesis, spectra, crystal structure and electrochemistry of dinitro-bis-{1-alkyl-2-(arylazo)imidazole} ruthenium(II). Nitro-nitroso derivatives and

reactivity of electrophilic {Ru-NO}[6] system New Journal of Chemistry, 2002, 26, 1415.

[16] Byabartta P., Pal S., Ray U. and Sinha C., Synthesis, spectral characterization and electrochemical properties of osmium (II) complexes of 1-ethyl-2-(arylazo)imidazoles Indian J. Chem., 2001, 40A, 896.

[17] Byabartta P., Jasimuddin Sk., Mostafa G., Lu T. – H. and Sinha C., The synthesis, spectral studies and electrochemistry of 1,10-(phenanthroline)-bis-{1-alkyl-2-(arylazo)imidazole}ruthenium(II) perchlorate. Single crystal X-ray structure of [Ru(phen)(HaaiMe)$_2$](ClO$_4$)$_2$ [phen = 1,10-phenanthroline, HaaiMe = 1-methyl-2-(phenylazo)imidazole] Polyhedron, , Volume 22, Issue 6, 15 March 2003, Pages 849-859

[18] Santra P. K., Byabartta P., Falvello L. R. and Sinha C. Chemistry of azopyrimidines: Couplings of aromatic amines with the ortho C-H-function of the pendant phenyl ring in dichloro{2-(phenylazo)pyrimidine}palladium(II) complex, Eur. J. Inorg. Chem., 2001,

[19]. Jasimuddin Sk., Byabartta P., Mostafa G., Lu T. –H. and Sinha C.,Synthesis, spectral studies, crystal structure and redox properties of homoleptic tris-chelated ruthenium(II)– arylazoimidazoles Polyhedron, 2003, Polyhedron, Volume 23, Issue 5, 4 March 2004, Pages 727-733

[20] Francesco Caruso, Elena Monti, Julian Matthews, Miriam Rossi, Marzia Bruna Gariboldi, Claudio Pettinari, Riccardo Pettinari, and Fabio Marchetti, Synthesis, Characterization, and Antitumor Activity of Water-Soluble (Arene)ruthenium(II) Derivatives of 1,3-Dimethyl-4-acylpyrazolon-5-ato Ligands. First Example of Ru(arene)(ligand) Antitumor Species Involving Simultaneous Ru–N7(guanine) Bonding and Ligand Intercalation to DNA,Inorg. Chem., Articles ASAP (As Soon As Publishable), Publication Date (Web): March 11, 2014 (Article), DOI: 10.1021/ic403170y

[21] Benjamin J. Coe, Madeleine Helliwell, Martyn K. Peers, James Raftery, Daniela Rusanova, Koen Clays, Griet Depotter, and Bruce S. Brunschwig , Synthesis, Structures, and Optical Properties of Ruthenium(II) Complexes of the Tris(1-pyrazolyl)methane Ligand, Inorg. Chem., Articles ASAP (As Soon As Publishable), Publication Date (Web): March 10, 2014 (Article), DOI: 10.1021/ic500145r

[22] Daniel B. Pardue, Jiajun Mei, Thomas R. Cundari, and T. Brent Gunnoe , Density Functional Theory Study of Oxygen-Atom Insertion into Metal–Methyl Bonds of Iron(II), Ruthenium(II), and Osmium(II) Complexes: Study of Metal-Mediated C–O Bond Formation, Inorg. Chem., Articles ASAP (As Soon As Publishable), Publication Date (Web): February 26, 2014 (Article), DOI: 10.1021/ic402759w

[23] Atsushi Kobayashi, Tadashi Ohba, Erika Saitoh, Yui Suzuki, Shin-ichiro Noro, Ho-Chol Chang, and Masako Kato , Flexible Coordination Polymers Composed of Luminescent Ruthenium(II) Metalloligands: Importance of the Position of the Coordination Site in Metalloligands, Inorg. Chem., Articles ASAP (As Soon As Publishable), Publication Date (Web): February 21, 2014 (Article) DOI: 10.1021/ic402683j

[24] Anna Rathgeb, Andreas Böhm, Maria S. Novak, Anatolie Gavriluta, Orsolya Dömötör, Jean Bernard Tommasino, Éva A. Enyedy, Sergiu Shova, Samuel Meier, Michael A. Jakupec, Dominique Luneau, and Vladimir B. Arion , Ruthenium-Nitrosyl Complexes with Glycine, l-Alanine, l-Valine, l-Proline, d-Proline, l-Serine, l-Threonine, and l-Tyrosine: Synthesis, X-ray Diffraction Structures, Spectroscopic and Electrochemical Properties, and Antiproliferative Activity, Inorg. Chem., 2014, 53 (5), pp 2718–2729, Publication Date (Web): February 20, 2014 (Article), DOI: 10.1021/ic4031359

[25] Sarat Chandra Patra, Thomas Weyhermüller, and Prasanta Ghosh, Ruthenium, Rhodium, Osmium, and Iridium Complexes of Osazones (Osazones = Bis-Arylhydrazones of Glyoxal): Radical versus Nonradical States, Inorg. Chem., 2014, 53 (5), pp 2427–2440, Publication Date (Web): February 12, 2014 (Article), DOI: 10.1021/ic4022432

[26] Stephan Sinn, Benjamin Schulze, Christian Friebe, Douglas G. Brown, Michael Jäger, Esra Altunta , Joachim Kübel, Oliver Guntner, Curtis P. Berlinguette, Benjamin Dietzek, and Ulrich S. Schubert, Physicochemical Analysis of Ruthenium(II) Sensitizers of 1,2,3-Triazole-Derived Mesoionic Carbene and Cyclometalating Ligands, Inorg. Chem., 2014, 53 (4), pp 2083–2095, Publication Date (Web): January 28, 2014 (Article), DOI: 10.1021/ic402702z

[27] Stephan Sinn, Benjamin Schulze, Christian Friebe, Douglas G. Brown, Michael Jäger, Joachim Kübel, Benjamin Dietzek, Curtis P. Berlinguette, and Ulrich S. Schubert, A Heteroleptic Bis(tridentate) Ruthenium(II) Platform Featuring an Anionic 1,2,3-Triazolate-Based Ligand for Application in the Dye-Sensitized Solar Cell, Inorg. Chem., 2014, 53 (3), pp 1637–1645, Publication Date (Web): January 21, 2014 (Article), DOI: 10.1021/ic402701v

[28] Robert Staehle, Lianpeng Tong, Lei Wang, Lele Duan, Andreas Fischer, Mårten S. G. Ahlquist, Licheng Sun, and Sven Rau , Water Oxidation Catalyzed by Mononuclear Ruthenium Complexes with a 2,2′-Bipyridine-6,6′-dicarboxylate (bda) Ligand: How Ligand Environment Influences the Catalytic Behavior, Inorg. Chem., 2014, 53 (3), pp 1307–1319, Publication Date (Web): January 14, 2014 (Article), DOI: 10.1021/ic401701z

[29] Amlan K. Pal, Samik Nag, Janaina G. Ferreira, Victor Brochery, Giuseppina La Ganga, Antonio Santoro, Scolastica Serroni, Sebastiano Campagna, and Garry S. Hanan,

Red-Emitting [Ru(bpy)$_2$(N-N)]$^{2+}$ Photosensitizers: Emission from a Ruthenium(II) to 2,2 -Bipyridine ^{3}MLCT State in the Presence of Neutral Ancillary "Super Donor" Ligands, Inorg. Chem., 2014, 53 (3), pp 1679–1689, Publication Date (Web): January 13, 2014 (Article), DOI: 10.1021/ic4028332

[30] Joaquín Alós, Tamara Bolaño, Miguel A. Esteruelas, Montserrat Oliván, Enrique Oñate, and Marta Valencia, POP–Pincer Ruthenium Complexes: d^6 Counterparts of Osmium d^4 Species, Inorg. Chem., 2014, 53 (2), pp 1195–1209, Publication Date (Web): January 9, 2014 (Article), DOI: 10.1021/ic402795g

[31] Zahra Almodares, Stephanie J. Lucas, Benjamin D. Crossley, Aida M. Basri, Christopher M. Pask, Andrew J. Hebden, Roger M. Phillips, and Patrick C. McGowan, Rhodium, Iridium, and Ruthenium Half-Sandwich Picolinamide Complexes as Anticancer Agents, Inorg. Chem., 2014, 53 (2), pp 727–736, Publication Date (Web): January 7, 2014 (Article), DOI: 10.1021/ic401529u

[32] Katharine A. Smart, Mary Grellier, Yannick Coppel, Laure Vendier, Sax A. Mason, Silvia C. Capelli, Alberto Albinati, Virginia Montiel-Palma, Miguel A. Muñoz-Hernández, and Sylviane Sabo-Etienne , Nature of Si–H Interactions in a Series of Ruthenium Silazane Complexes Using Multinuclear Solid-State NMR and Neutron Diffraction, Inorg. Chem., 2014, 53 (2), pp 1156–1165, Publication Date (Web): January 6, 2014 (Article), DOI: 10.1021/ic4027199

[33] Sumit Saha and Burjor Captain , Synthesis and Structural Characterization of Ruthenium Carbonyl Cluster Complexes Containing Platinum with a Bulky N-Heterocyclic Carbene Ligand, Inorg. Chem., 2014, 53 (2), pp 1210–1216, Publication Date (Web): January 3, 2014 (Article) DOI: 10.1021/ic402832b

[34] Melissa V. Werrett, Sara Muzzioli, Phillip J. Wright, Antonio Palazzi, Paolo Raiteri, Stefano Zacchini, Massimiliano Massi, and Stefano Stagni , Proton-Induced Reversible Modulation of the Luminescent Output of Rhenium(I), Iridium(III), and Ruthenium(II) Tetrazolate Complexes, Inorg. Chem., 2014, 53 (1), pp 229–243, Publication Date (Web): December 20, 2013 (Article), DOI: 10.1021/ic402187e

[35] Christi L. Whittington, Lukasz Wojtas, and Randy W. Larsen, Ruthenium(II) Tris(2,2 -bipyridine)-Templated Zinc(II) 1,3,5-Tris(4-carboxyphenyl)benzene Metal Organic Frameworks: Structural Characterization and Photophysical Properties, Inorg. Chem., 2014, 53 (1), pp 160–166, Publication Date (Web): December 13, 2013 (Article), DOI: 10.1021/ic402614w

[36] Nathir A. F. Al-Rawashdeh, Sayandev Chatterjee, Jeanette A. Krause, and William B. Connick, Ruthenium Bis-diimine Complexes with a Chelating Thioether Ligand: Delineating 1,10-Phenanthrolinyl and 2,2 -Bipyridyl Ligand Substituent Effects, Inorg. Chem., 2014, 53 (1), pp 294–307, Publication Date (Web): December 10, 2013 (Article), DOI: 10.1021/ic4022454

[37] Rongwei Zhou, Baburam Sedai, Gerald F. Manbeck, and Karen J. Brewer , New Supramolecular Structural Motif Coupling a Ruthenium(II) Polyazine Light Absorber to a Rhodium(I) Center, Inorg. Chem., 2013, 52 (23), pp 13314–13324, Publication Date (Web): November 18, 2013 (Article), DOI: 10.1021/ic4006828

[38] Wei Su, Quanquan Qian, Peiyuan Li, Xiaolin Lei, Qi Xiao, Shan Huang, Chusheng Huang, and Jianguo Cui , Synthesis, Characterization, and Anticancer Activity of a Series of Ketone-N^4-Substituted Thiosemicarbazones and Their Ruthenium(II) Arene Complexes Inorg. Chem., 2013, 52 (21), pp 12440–12449, Publication Date (Web): October 21, 2013 (Article), DOI: 10.1021/ic401362s

[39] Michael R. Norris, Javier J. Concepcion, Christopher R. K. Glasson, Zhen Fang, Alexander M. Lapides, Dennis L. Ashford, Joseph L. Templeton, and Thomas J. Meyer, Synthesis of Phosphonic Acid Derivatized Bipyridine Ligands and Their Ruthenium Complexes, Inorg. Chem., 2013, 52 (21), pp 12492–12501, Publication Date (Web): October 21, 2013 (Article),DOI: 10.1021/ic4014976.

Access this Article in Online

Quick Response Code	**Website:** **www.icrcps.com**
	Subject: **Chemistry**

How to cite this article:
Prithwiraj Byabartta. (2016). Ruthenium (II)-arylazoimidazole (RaaiR)-catecholates (CA): Synthesis, Spectral study, Solvatochromism and Electrochemistry. Int. J. Curr. Res. Chem. Pharm. Sci. 3(5): 21-29.