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Synthesis, structure and properties of delocalized transition metal chelates: Diazoketiminato chelates of Co(III) and Pt(II)

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Abstract

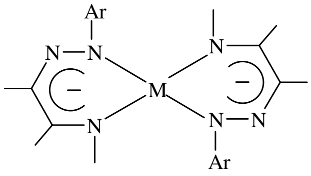
The reactions of HL **1** [where HL is 1*N*-(2-pyridyl-2-methyl)-2-arylazoaniline and is formulated as $ArN = NC_6H_4N(H)(CH_2C_5H_4N)$; $Ar = C_6H_5$ (for HL^1) or *p*-MeC_6H_4 (for HL^2) or *p*-ClC_6H_4 (for HL^3)] with K_2PtCl_4 and $Co(ClO_4)_3 \cdot 6H_2O$ afforded the (L)PtCl and $[(L)_2Co]ClO_4$ complexes, respectively. The HL ligands bind the platinum(II) and cobalt(III) centres in a tridentate (*N*,*N*,*N*) fashion, forming new diazoketiminato chelates upon dissociating the amino proton. The X-ray structures of $(L^3)PtCl$ and $[(L^3)_2Co]ClO_4$ were determined. Redox properties of the new complexes have been examined.

Keywords: 1*N*-(2-Pyridyl-2-methyl)-2-arylazo aniline; Potassium tetrachloroplatinate; Cobalt(III) perchlorate; Diazoketiminato species

1. Introduction

Syntheses of transition metal chelates incorporating delocalized ligands have emerged as an active area of chemical research in recent years, to obtain clarification of issues related to the oxidation states of the metal and ligand, the nature of electron transfer processes and metal assisted reactions [1–17].

Conjugated unsaturated organic ligands have been used for the preparation of such delocalized transition metal chelates [1–17]. Often deprotonation of a donor atom during complexation is necessary for the formation of delocalized chelates [14–17]. Earlier we reported that 2-(arylazo)aniline formed delocalized diazoketiminato chelates of Pd(II) and Pt(II), **A**, upon dissociation of one of the amino protons [14,16,17]. On the other hand, the *N*-alkylated derivatives of 2-(arylazo)aniline afforded orthopalladated complexes or delocalized diazoketiminato chelates of Pd(II) according to the proposed mechanism as shown in Scheme 1 [17,18].



M=Pd / Pt

A

Thus the donor atom, i.e. X within the *N*-alkyl group of **1**, plays an important role towards the exclusive formation of diazoketiminato chelates.

Herein, we report the reactions of the ligand **1b** with K_2PtCl_4 and $Co(ClO_4)_3 \cdot 6H_2O$.

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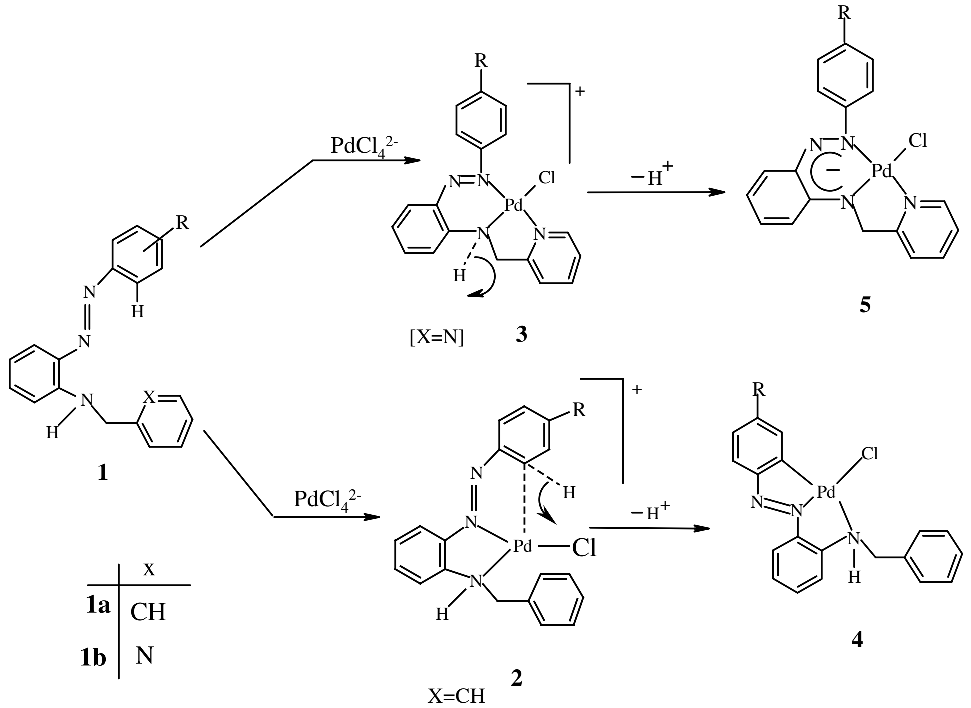
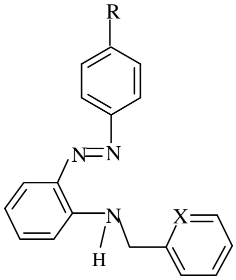


Scheme 1.



HL	R
HL^1	H
HL^2	CH_3
HL^3	Cl

1b

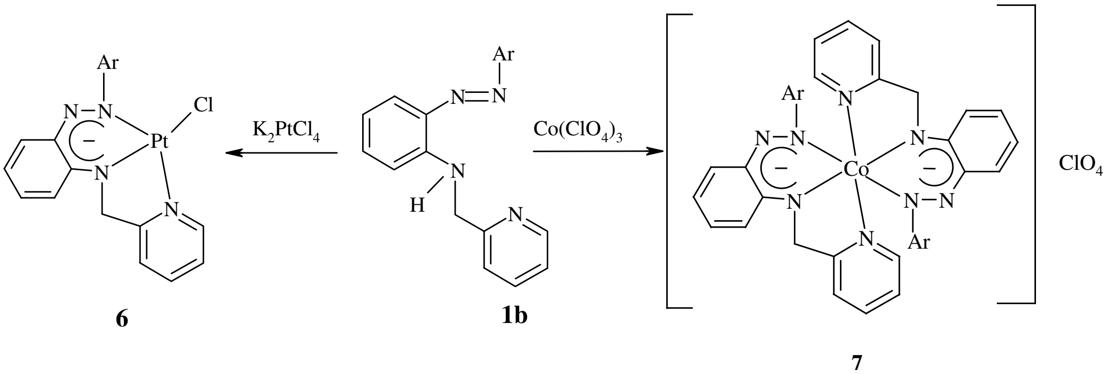
HL when X=N of **1b**

Formation of a diazoketiminato chelate, like **5**, supported our mechanistic proposal. The bis complex cation of Co(III) incorporating the tridentate diazoketimine ligand has been isolated for the first time. Synthesis, X-ray structures, redox properties and the plausible nature of the redox orbitals have been reported in this paper.

2. Results and discussion

2.1. Syntheses

The reaction of 1*N*-(2-pyridyl-2-methyl)-2-arylazo aniline, HL, with K_2PtCl_4 in methanol afforded a pink complex of platinum (II) of the composition (L)PtCl **6** incorporating the tridentate (*N*,*N*,*N*) ligand (Scheme 2). Reaction of HL **1b** with $Co(ClO_4)_3 \cdot 6H_2O$ in refluxing methanol afforded the blue-violet bis complex of the composition $[(L)_2Co]ClO_4$ **7** where L^- binds the metal in a tridentate (*N*,*N*,*N*) fashion (Scheme 2). In both cases the



Scheme 2.

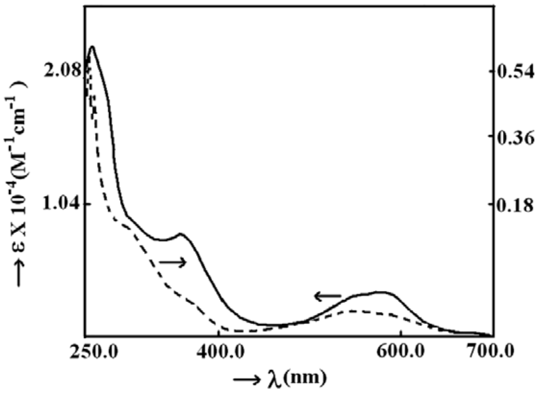


Fig. 1. UV–Vis spectra of $[(L^1)_2Co]ClO_4$ (---) and $(L^1)PtCl$ (—). The arrows indicate scales of the corresponding spectra.

deprotonated secondary amino nitrogen binds the metal forming a six-membered diazoketiminato chelate. Formation of a six-membered diazoketiminato chelate has been attributed to the delocalisation of the negative charge within the ligand backbone [14–17]. Complex **7** is diamagnetic and is consistent with a low spin t_{2g}^6 configuration.

2.2. Characterization

All the Pt(II) complexes, (L)PtCl, exhibited a characteristic low energy absorption near 580 nm which has been assigned to a MLCT transition [14–18]. The low energy absorption due to a MLCT transition for the $[(L)_2Co]ClO_4$ complexes has been observed near 570 nm. Representative UV–Vis spectra of $(L^1)PtCl$ and $[(L^1)_2Co]ClO_4$ are shown in Fig. 1. Relevant data are collected in Section 3.

The IR spectra of HL [17] displayed a sharp singlet near 3189 cm^{-1} for ν_{N-H} which was absent for both the complexes (L)PtCl and $[(L)_2Co]ClO_4$, indicating the dissociation of the amino proton upon complexation. The $\nu_{N=N}$ of the ligands (~1510 cm^{-1}) shifted to lower frequency upon complexation (1400–1410 cm^{-1}), consistent with coordination of the azo nitrogen [14–18]. The ν_{Pt-Cl} of the platinum complexes appeared at 325 cm^{-1} [19,20]. The cobalt complexes exhibited a broad absorption near 1100 cm^{-1}, characteristic of uncoordinated ClO_4^-. Relevant data are included in Section 3.

The N–H resonance of the free ligands (δ 9.37–9.55 ppm) [17] were absent in the ^{1}H NMR spectra of the platinum and cobalt complexes, signifying the dissociation of the N–H proton upon complexation. The resonance of the methylene protons appeared in the platinum complexes as a singlet (δ 5.29–5.48 ppm), in contrast to the doublet of the ligands (δ 4.68–4.69 ppm), indicating the lack of vicinal coupling due to the absence of the N–H proton [17]. The resonances of the pair of methylene protons in the $[(L)_2Co]^+$ ion appeared as two doublets signifying the substantial difference in chemical shielding within the pair. Resonances for the other aromatic protons are consistent with the structure as determined by X-ray studies (see below). The ^{1}H NMR data are collected in Section 3.

2.3. X-ray structure of $(L^3)PtCl$

Suitable crystals of $(L^3)PtCl$ were grown by the slow evaporation of a dichloromethane–methanol mixed solution. The X-ray structure of $(L^3)PtCl$ was determined and the perspective view of the molecule along with the atom numbering scheme is shown in Fig. 2. Selected bond distances and angles are collected in Table 1. The geometry about platinum is distorted square planar where the $(L^3)^-$ binds in a tridentate (*N*,*N*,*N*) fashion. A chloride ligand satisfies the tetracoordination. The three nitrogen

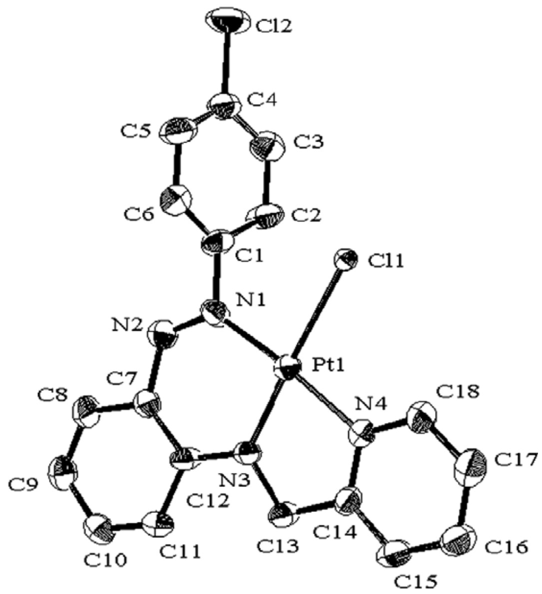


Fig. 2. Perspective view of $(L^3)PtCl$ with the atom numbering scheme. Hydrogen atoms are omitted.

Table 1
Selected bond distances (Å) and angles (°) for $(L^3)PtCl$

Bond distances			
Pt(1)–N(1)	2.004(13)	C(7)–C(12)	1.40(2)
Pt(1)–N(3)	1.957(11)	C(11)–C(12)	1.49(2)
Pt(1)–N(4)	2.054(12)	N(3)–C(13)	1.44(2)
N(1)–N(2)	1.265(19)	C(10)–C(11)	1.37(2)
N(2)–C(7)	1.44(2)	C(9)–C(10)	1.39(3)
N(1)–C(1)	1.38(2)	C(8)–C(9)	1.37(2)
N(3)–C(12)	1.345(19)	C(7)–C(8)	1.43(2)
C(13)–C(14)	1.50(2)	N(4)–C(14)	1.352(19)
Pt(1)–Cl(1)	2.540(3)		
Bond angles			
Cl(1)–Pt(1)–N(1)	92.6(4)	Cl(1)–Pt(1)–N(3)	173.5(4)
Cl(1)–Pt(1)–N(4)	93.0(3)	N(1)–Pt(1)–N(3)	92.5(5)
N(1)–Pt(1)–N(4)	174.2(5)	N(1)–C(1)–C(2)	117.3(14)
N(3)–Pt(1)–N(4)	82.0(5)	Pt(1)–N(1)–N(2)	127.7(11)
N(2)–C(7)–C(12)	127.4(13)	N(1)–N(2)–C(7)	122.5(14)
C(12)–N(3)–C(13)	117.7(12)	Pt(1)–N(3)–C(12)	125.0(10)
Pt(1)–N(4)–C(14)	113.0(9)	N(3)–C(13)–C(14)	110.1(12)

donors are azo (*N*(azo)), pyridyl (*N*(py)) and deprotonated amino (*N*(am)) nitrogens. The Pt–N(azo), Pt–N(py) and Pt–Cl lengths (2.004(13), 2.054(12) and 2.540(3) Å, respectively) are within the normal range [15,19,20]. The geometry about platinum is planar (mean deviation 0.067 Å) consistent with a dipositive oxidation state of platinum and the uninegative ligand, since the complex is non-electrolyte.

The C(12)–N(3) length (1.345(19) Å) is shorter compared to a C–N single bond (N(1)–C(1) 1.38(2) Å) in the same molecule and is similar to the imine (C=N) distance [14–17]. The effect of imine formation due to delocalisation has been reflected in the adjacent phenyl ring (C(7)–C(12)) which is distorted with two short (∼1.37 Å) and four long (∼1.43 Å) bonds [14–17]. Thus, the formation of a diazoketiminato chelate could be inferred from the X-ray results and the structural formula of $(L^3)PtCl$ has been drawn accordingly in **6** of Scheme 2 (*vide supra*). All the non-hydrogen atoms of $(L^3)PtCl$, excluding the pendant phenyl ring (C(1)–C(6)), make a good plane (mean deviation 0.220 Å).

2.4. X-ray structure of $[(L^3)_2Co]ClO_4$

Table 2
Selected bond distances (Å) and angles (°) of $[(L^3)_2Co]ClO_4$

Bond distances			
Co–N(1)	1.919(3)	N(4)–C(18)	1.346(4)
Co–N(3)	1.910(3)	N(4)–C(14)	1.344(4)
Co–N(4)	1.980(3)	N(1)–N(2)	1.277(4)
Co–N(5)	1.924(3)	N(5)–N(6)	1.292(3)
Co–N(7)	1.915(3)	C(25)–C(26)	1.431(5)
Co–N(8)	1.977(3)	C(26)–C(27)	1.345(6)
C(7)–C(8)	1.413(5)	C(27)–C(28)	1.381(8)
C(8)–C(9)	1.347(6)	C(28)–C(29)	1.374(5)
C(9)–C(10)	1.410(6)	C(29)–C(30)	1.424(5)
C(10)–C(11)	1.355(6)	C(25)–C(30)	1.421(6)
C(11)–C(12)	1.420(5)	N(7)–C(31)	1.451(5)
C(7)–C(12)	1.452(5)	N(7)–C(30)	1.343(4)
N(3)–C(13)	1.468(4)	N(8)–C(32)	1.342(5)
N(3)–C(12)	1.329(4)	N(8)–C(36)	1.358(4)
N(1)–C(1)	1.449(4)	N(5)–C(19)	1.444(5)
Bond angles			
N(1)–Co–N(3)	91.67(11)	N(1)–N(2)–C(7)	123.7(3)
N(1)–Co–N(5)	88.09(12)	N(5)–Co–N(3)	93.19(12)
N(3)–Co–N(4)	83.37(11)	Co–N(1)–N(2)	128.30(19)
N(2)–C(7)–C(12)	126.3(3)	N(8)–Co–N(7)	83.32(12)
N(1)–Co–N(4)	175.04(11)	N(7)–Co–N(1)	93.82(11)
N(5)–N(6)–C(25)	122.5(3)	C(14)–N(4)–C(18)	118.7(3)
Co–N(3)–C(12)	127.7(2)	Co–N(4)–C(14)	114.0(2)
N(3)–Co–N(7)	172.68(14)	N(5)–Co–N(7)	91.83(12)

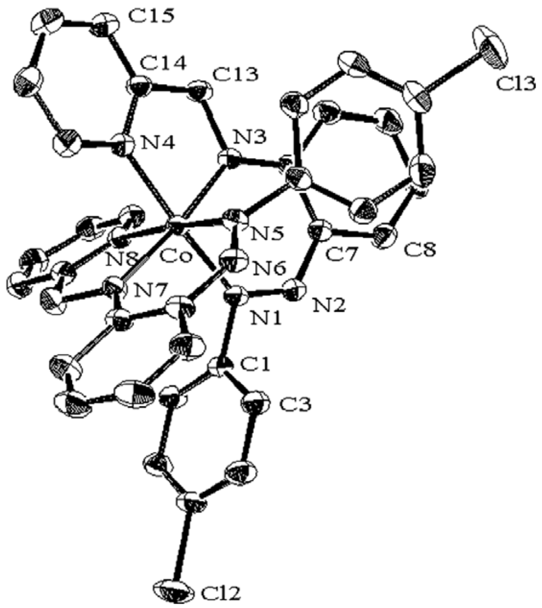


Fig. 3. Perspective view of $[(L^3)_2Co]^+$ with the atom numbering scheme. Hydrogen atoms and the perchlorate ion are omitted.

Suitable crystals of $[(L^3)_2Co]ClO_4$ were obtained from the methanolic mother liquor. The X-ray structure of $[(L^3)_2Co]ClO_4$ was determined and the perspective view of the $[(L^3)_2Co]^+$ cation along with the atom numbering scheme is shown in Fig. 3. Selected bond distances and angles are collected in Table 2. The geometry about the Co(III) centre is distorted octahedral, where the two anionic ligands, $[L^3]^-$, coordinated meridionally give rise to a CoN_6 coordination sphere. A perchlorate (ClO_4^-) ion satisfies the unipositive charge of the complex cation, $[(L^3)_2Co]^+$. The relative orientations of *N*(py), *N*(azo) and *N*(am) pairs are *cis*, *cis* and *trans*, respectively. Extensive electron delocalisation along the ligand backbone is also observed in this case. As a result, the C(12)–N(3) length (1.329(4) Å) and C(30)–N(7) length (1.343(4) Å) are shorter compared to the C–N single bonds (N(1)–C(1) 1.449(4) Å; N(5)–C(19) 1.444(5) Å) in the same molecule and are similar to the imine (C=N) distance [19–22]. The effect of imine formation due to delocalisation has also been reflected in the adjacent phenyl ring (C(7)–C(12)) which is distorted with two short (∼1.35 Å) and four long (∼1.42 Å) bonds, consistent with the formation of a diazoketiminato chelate [14–17,23]. The structural formula of $[(L^3)_2Co]ClO_4$ has been drawn accordingly in **7** of Scheme 2 (*vide supra*).

2.5. Redox processes and nature of redox orbitals

$(L^3)PtCl$ and $[(L^3)_2Co]ClO_4$ displayed one and two irreversible oxidative responses, respectively, in their cyclic voltammograms (0.924 V versus SCE for the Pt(II) complex and 0.78, 1.14 V versus SCE for the Co(III) complex). To have an insight into the nature of the redox orbitals, the EHMO results have been taken into account (Supplementary material). The HOMO of (L)PtCl and $[(L)_2Co]ClO_4$ (Figs. S20 and S22) were found to be primarily ligand orbitals. Thus, the oxidative responses have been attributed to ligand oxidations as given in

$$[(L)Pt^{II}Cl] \xrightarrow{-e} [(L^{\cdot})PtCl]^{+} \qquad (1)$$

$$[(L)_2Co^{III}]^{+} \xrightarrow{-e} [(L^{-})(L^{\cdot})CO]^{2+} \xrightarrow{-e} [(L^{\cdot})(L^{\cdot})Co]^{3+} \qquad (2)$$

3. Experimental

3.1. Materials

The solvents used in the reactions were of reagent grade obtained from E. Merck, Kolkata, India, and were purified and dried by reported procedures [23,24]. 2-(Arylazo) anilines and 1*N*-(2-pyridyl-2-methyl)-2-arylazoaniline were prepared according to reported procedures [14,15,17]. Chloroplatinic acid, cobalt carbonate, potassium carbonate, perchloric acid and potassium chloride were purchased from E. Merck, Kolkata, India. 2-(Chloromethyl) pyridine hydrochloride was purchased from Lancaster, England. Potassium tetrachloroplatinate was prepared by reported procedures [25]. Cobalt(III) perchlorate was prepared by oxidation of Co(II) perchlorate with H_2O_2 [26].

3.2. Syntheses of the Pt(II) complexes

The complexes $(L^1)PtCl$, $(L^2)PtCl$ and $(L^3)PtCl$ were prepared by a similar procedure. A representative example for $(L^1)PtCl$, is given below.

3.2.1. $(L^1)PtCl$

A solution of HL^1 (0.1 g, 0.35 mmol) in 10 cm^3 methanol was added to a solution of K_2PtCl_4 (0.145 g, 0.35 mmol) in 5 cm^3 water. The mixture was stirred for 15 h. The dark solid precipitate that formed was purified by washing with benzene–petroleum ether (80:20) mixed solvent. The pure solid was then dissolved in dichloromethane with a few drops of methanol and kept for crystallisation. Pure crystalline solid of $(L^1)PtCl$ was obtained. Yield: 50%. *Anal.* Calc. for $C_{18}H_{15}N_4PtCl$, $(L^1)PtCl$: C, 41.75; H, 2.92; N, 10.82. Found: C, 41.73; H, 2.90; N, 10.85%. Electronic spectrum (λ_{max}/nm (ε/$dm^2\ mol^{-1}$), dichloromethane): 578 (2200), 359 (5000), 259 (14260). IR (KBr pellets, cm^{-1}): $\nu_{N=N}$ 1405, ν_{Pt-Cl} 326. ^1H NMR ($CDCl_3$, ppm): δ 9.67 (d, 1H); 7.99 (d, 1H); 7.88–7.83 (m, 2H); 7.66–7.62 (m, 1H); 7.59 (d, 1H); 7.42–7.39 (m, 3H); 7.36–7.27 (m, 2H); 7.03 (d, 1H); 6.65 (t, 1H); 5.48 (s, 2H).

3.2.2. $(L^2)PtCl$ and $(L^3)PtCl$

Complexes $(L^2)PtCl$ and $(L^3)PtCl$ were prepared using the ligands HL^2 and HL^3 in place of HL^1. Yield: $(L^2)PtCl$, 50% and $(L^3)PtCl$, 55%, respectively.

Anal. Calc. for $C_{19}H_{17}N_4PtCl$, $(L^2)PtCl$: C, 42.89; H, 3.19; N, 10.53. Found: C, 42.92; H, 3.23; N, 10.50%. Electronic spectrum (λ_{max}/nm (ϵ/$dm^2\ mol^{-1}$), dichloromethane): 579 (1230), 358 (2750), 259 (7483). IR (KBr pellets, cm^{-1}): $\nu_{N=N}$ 1402, ν_{Pt-Cl} 325. ^1H NMR ($CDCl_3$, ppm): δ 9.61 (d, 1H); 8.13 (d, 1H); 7.97–7.96 (m, 2H); 7.35–7.29 (m, 3H); 7.26–7.21 (m, 3H); 7.17–7.23 (m, 1H); 6.62 (m, 1H); 5.29 (s, 2H); 2.40 (s, 3H).

Anal. Calc. for $C_{18}H_{14}N_4PtCl_2$, $(L^3)PtCl$: C, 39.14; H, 2.56; N, 10.14. Found: C, 39.10; H, 2.60; N, 10.20%. Electronic spectrum (λ_{max}/nm (ϵ/$dm^2\ mol^{-1}$), dichloromethane): 581 (3200), 359 (7050), 258 (18380). IR (KBr pellets, cm^{-1}): $\nu_{N=N}$ 1400, ν_{Pt-Cl} 324. ^1H NMR ($CDCl_3$, ppm): δ 9.72 (d, 1H); 7.97 (m, 2H); 7.90 (t, 1H); 7.67 (m, 2H); 7.60 (d, 1H); 7.37–7.29 (m, 3H); 7.04 (d, 1H); 6.67 (t, 1H); 5.47 (s, 2H).

3.3. Syntheses of the Co(III) complexes

The complexes $[(L^1)_2Co]ClO_4$, $[(L^2)_2Co]ClO_4$ and $[(L^3)_2Co]ClO_4$ were prepared by a similar procedure. A representative example for $[(L^1)_2Co]ClO_4$, is given below.

3.3.1. $[(L^1)_2Co]ClO_4$

A solution of HL^1 (0.2 g, 0.70 mmol) in 10 cm^3 methanol was added to a 5 cm^3 methanolic solution of $Co(ClO_4)_3 \cdot 6H_2O$ (0.150 g, 0.35 mmol). The mixture was refluxed for 1 h. The colour of the solution became blue-violet. It was kept for five days. Pure crystalline solid of $[(L^1)_2Co]ClO_4$ was obtained. Yield: 65%. *Anal.* Calc. for $C_{36}H_{30}N_8CoClO_4$, $[(L^1)_2Co]ClO_4$: C, 58.98; H, 4.12; N, 15.28. Found: C, 59.00; H, 4.17; N, 15.25%. Electronic spectrum (λ_{max}/nm (ϵ/$dm^2\ mol^{-1}$), dichloromethane): 552 (5000), 368 (7300), 300 (21900). IR (KBr pellets, cm^{-1}): $\nu_{N=N}$ 1409, ν_{Cl-O} 1102. ^1H NMR ($CDCl_3$, ppm): δ 7.76 (t, 1H); 7.67 (d, 1H); 7.52–7.48 (m, 2H); 7.29–7.26 (m, 1H); 7.21–7.17 (m, 2H); 7.05 (t, 2H); 6.88 (d, 1H); 6.57 (t, 1H); 6.33 (d, 2H); 5.28 (d, 1H); 4.42 (d, 1H).

3.3.2. $[(L^2)_2Co]ClO_4$ and $[(L^3)_2Co]ClO_4$

Complexes $[(L^2)_2Co]ClO_4$ and $[(L^3)_2Co]ClO_4$ were prepared using the ligands HL^2 and HL^3 in place of HL^1, respectively. Yield: $[(L^2)_2Co]ClO_4$, 70% and $[(L^3)_2Co]ClO_4$, 60%.

Anal. Calc. for $C_{38}H_{34}N_8CoClO_4$, $[(L^2)_2Co]ClO_4$: C, 59.96; H, 4.50; N, 14.72. Found: C, 59.90; H, 4.53; N, 14.70%. Electronic spectrum (λ_{max}/nm (ϵ/$dm^2\ mol^{-1}$), dichloromethane): 569 (6340), 368 (11000), 310 (22750). IR (KBr pellets, cm^{-1}): $\nu_{N=N}$ 1410, ν_{Cl-O} 1085. ^1H NMR ($CDCl_3$, ppm): δ 7.88 (t, 1H); 7.64 (d, 1H); 7.53–7.50 (m, 2H); 7.33–7.26 (m, 2H); 6.83 (d, 3H); 6.61 (t, 1H); 6.19 (d, 2H); 5.15 (d, 1H); 4.44 (d, 1H); 2.25 (s, CH_3).

Anal. Calc. for $C_{36}H_{28}N_8CoCl_2ClO_4$, $[(L^3)_2Co]ClO_4$: C, 53.91; H, 3.52; N, 13.97. Found: C, 53.88; H, 3.55; N, 13.95%. Electronic spectrum (λ_{max}/nm (ϵ/$dm^2\ mol^{-1}$), dichloromethane): 570 (5560), 363 (10120), 304 (21660). IR (KBr pellets, cm^{-1}): $\nu_{N=N}$ 1408, ν_{Cl-O} 1089. ^1H NMR ($CDCl_3$, ppm): δ 7.78 (t, 1H); 7.67 (d, 1H); 7.53 (d, 1H); 7.45 (d, 1H); 7.35 (t, 1H); 7.24 (d, 1H); 7.01 (d, 2H); 6.94 (d, 1H); 6.61 (t, 1H); 6.27 (d, 2H); 5.37 (d, 1H); 4.47 (d, 1H).

3.4. Physical measurements

Microanalyses (C, H, N) were performed using a Perkin–Elmer 240C 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- 2401 PC

Table 3
Crystallographic data for $(L^3)PtCl$ and $[(L^3)_2Co]ClO_4$

Chemical formula	$(C_{18}H_{14}Cl_2N_4Pt) \cdot 0.5CH_2Cl_2$	$C_{36}H_{28}Cl_2CoN_8 \cdot ClO_4$
Formula weight	594.78	801.94
Crystal system	triclinic	triclinic
Space group	$P\bar{1}$ (no. 2)	$P\bar{1}$ (no. 2)
a (Å)	11.2488(4)	10.9360(7)
b (Å)	11.9115(4)	11.5597(7)
c (Å)	16.0851(5)	14.9478(14)
α (°)	89.647(2)	100.236(2)
β (°)	78.830(2)	99.415(2)
γ (°)	69.847(2)	106.886(2)
λ (Å)	0.71073	0.71073
V (Å^3)	1980.67(12)	1732.3(2)
Z	4	2
$F(000)$	1132	820
Temperature (K)	293	293
$\rho_{\text{calc.}}$ (Mg/m^3)	1.995	1.538
μ (mm^{-1})	7.499	0.781
R (all data)	0.0537	0.0493
wR_2 [$I > 2\sigma(I)$]	0.1882	0.1550
Goodness-of-fit	1.26	0.98

spectrophotometer. ^{1}H NMR spectra were obtained on Brucker Avance RPX 500 NMR spectrometers in $CDCl_3$ and in DMSO, using TMS as the internal standard. Electrochemical measurements were performed using a PAR Versastat II potentiostat, a platinum disk working electrode, a platinum wire auxiliary electrode and aqueous saturated calomel (SCE) as the reference, (0.1 M) Bu_4NClO_4 supporting electrolyte, and in acetonitrile solvent. Electrochemical measurements were carried out under a dinitrogen atmosphere at 298 K and were uncorrected for junction potentials.

3.5. Crystallography

Data for the crystals, $(L^3)PtCl$ and $[(L^3)_2Co]ClO_4$, were collected by the ω-scan technique on a Brucker smart CCD diffractometer with Mo Kα radiation monochromated by a graphite crystal. The structure solution was done by direct methods with the SHELXS-97 program. Full matrix least square refinements were performed using the SHELX-97 program (PC version). All non-hydrogen atoms were refined anisotropically using reflections $I > 2\sigma(I)$. Hydrogen atoms were included at calculated positions. The crystal data and data collection parameters are listed in Table 3. The asymmetric unit of $(L^3)PtCl$ consists of two independent molecules and a dichloromethane molecule as the solvent of crystallization. Although the bond parameters of the two molecules in the asymmetric unit were not identical, they are consistent with each other.

4. Conclusion

The general coordination mode of 1*N*-(2-pyridyl-2-methyl)-2-arylazoaniline, HL towards Pt(II) and Co(III) has been determined. Formation of diazoketiminato chelates of Co(III) have been reported for the first time. The hypothetical mechanism of reaction between HL and metal substrates has been further supported with the formation of diazoketiminato chelates of Pt(II) and Co(III). The redox properties of the complexes have been assumed to be due predominantly to ligand centered.

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Appendix A. Supplementary material

CCDC 652204 and 652203 contain the supplementary crystallographic data for $(L^3)PtCl$ and $[(L^3)_2Co]ClO_4$. These data can be obtained free of charge via http://www.ccdc.cam.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. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.poly.2007.08.029.

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