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Monoradical-Containing Four-Coordinate Co(III) Complexes: Homolytic S-S, Se-Se Bond Cleavage and Catalytic Isocyanate to Urea Conversion Under Sunlight

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Ganesh Chandra Paul,^{a†} Samir Ghorai^{a†} and Chandan Mukherjee^a*

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Four-coordinate, monoradical-containing Co(III) complexes participated in non-innocent ligand driven homolytic cleavage of S-S and Se-Se bonds and catalyzed the conversion of RNCO (R =phenyl and naphthyl) to the corresponding urea derivatives (TON 480) in dry CH₂Cl₂ under sunlight stimulus.

Since last two decades, metal-coordinated redox active organic ligands, known as non-innocent ligands, are under continuous investigation as electron acceptor and/or electron donor for catalytic oxidation and reduction reactions.^{1,2} For instances: Chaudhuri, Wieghardt, and coworkers have studied Cu(II)bis(iminosemiquinone) complexes extensively as functional models of Galactose Oxidase for the two-electron oxidation of primary alcohols to their corresponding aldehydes^{1h}; a four-coordinate Co(III)-bis(amidophenolate) complex has been successfully employed as a catalyst for C-C bond formation reactions by Soper and coworkers.^{1a} Recently, Sarkar and coworkers have described an electrocatalytic C-C bond formation reaction employing electrochemically in situ generated a four-coordinate Co(II)-bis(1,2diamide) complex as the catalyst and benzylbromide as the substrate.^{1e} In 2015, van der Vlugt and coworkers have utilized the redox active nature of a coordinated-2-amidophenoate derivative in a four-coordinate Pd(II) complex for the one-electron homolytic S-S bond cleavage of diphenyl disulfide.¹ⁱ Recently, we have demonstrated that H₂ gas can be generated employing Cu(II)bis(iminoquinone) complex and NaBH₄ in dry acetonitrile.^{1g}

To continue our study on the development of ligand-radicalcontaining transition metal complexes for diatomic (homo and/or hetero) bond scission/formation reactions, we have investigated on few Co(III) complexes based on the non-innocent ligands $H_2L^{AP(R)}$ (R = -Me and -Ph), shown in Scheme 1. The ligand scaffolds were primarily based on bidentate 2-anilino-3,5-di-*tert*-butylphenol (H_2L^{AP}) backbone with methyl and phenyl substituents at the *ortho*- position of the aniline part. We envisaged that the presence of an *ortho*- substituent would exert steric crowding and consequently, the possibility of four-coordinate cobalt complex formation over six-coordinate would be favorable. Noteworthy, cobalt complexes with unsaturated-coordination environment are essential for the substrate activation and catalysis.



Scheme 1. (A) Cartoons of the ligands employed in this study. (B) Three possible oxidation states of the ligands. Subscriptions AP, ISQ and IBQ stand for amidophenol, iminosemiquinone, and iminobenzoquinone forms of the ligands, respectively.

Herein, we report on two four coordinate, monoradicalcontaining Co(III) complexes (**1** and **2**; $[Co^{III}(L^{AP(R)})(L^{ISQ(R)})]^0$), which were synthesized by reacting the ligands with Co(CIO₄)₂•6H₂O under air. Thus formed complexes reduced diphenyl disulfide and diphenyl diselenide by an electron and provided the corresponding five-coordinate, diradical-containing complexes where the axial position was occupied by a –XPh group (X = S(**1a/2a**) and Se(**2b**); parenthesis indicates the complex; $[Co^{III}(L^{ISQ(R)})_2XPh]^0)$. Hence, less explored one-electron reduction of S-S and Se-Se bond has been investigated. Interestingly, the four- and five-coordinate complexes under sunlight in a close-vessel in dry CH₂Cl₂ catalyzed the conversion of phenyl isocyanate and naphthyl isocyanate to the

^{a.} Department of Chemistry, Indian Institute of Technology Guwahati, Guwahati, 781039, Assam, India

⁺ GCP and SG contributed equally.

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corresponding urea derivatives. A maximum TON 480 in 6 hours has been achieved.



Scheme 2: Schematic representation for the syntheses.

The condensation between 1:1 2-R-aniline (R = -Me and -Ph) and 3,5-di-*tert*-butylcatechol in the presence of Et₃N and air generated $H_2L^{AP(R)}$ ligands in good yields [Scheme 2(A)]. Under aerial atmosphere $H_2L^{AP(Me)}$, and $H_2L^{AP(Ph)}$ ligands were reacted individually with 0.5 equivalent of Co(ClO₄)₂•6H₂O in acetonitrile in the presence of Et₃N for an hour to synthesize the corresponding fourcoordinate, monoradical-containing Co(III) complexes (1; 83% yield and **2**; 53% yield). Noteworthy, the employment of CoCl₂•6H₂O during the complex synthesis should be restricted as the salt assists the formation of five-coordinate diradical-containing Co(III) complexes by the one-electron oxidation of the initially formed four-coordinate, monoradical-containing Co(III) complexes through putative inner sphere electron transfer mechanism (Scheme S2).

The addition of either diphenyl disulfide (Ph₂S₂) or diphenyl diselenide (Ph₂Se₂) during the synthesis of **1** and **2** provided the corresponding five-coordinate diradical-containing **1a/2a** and **2b** complexes. The complexes could also be synthesized by reacting Ph₂S₂ or Ph₂Se₂ to the isolated complexes **1** and **2** (Scheme 2B). X-band EPR measurements during the conversions showed an instantaneous disappearance of X-band EPR signal of complexes **1** and **2** (*vide infra*) with concomitant generation of an isotropic signal at g ~ 2.00 (Figure S33). This feature implied the formation of PhX[•] (X = S and Se) species along with diamagnetic **1a/2a** and **2b**.

Single crystal suitable for X-ray diffraction analysis for complex ${\bf 1}$ was obtained by slow evaporation of a 10:1 Et_2O:CH_3CN solvent

mixture. Noteworthy, complex **2** could not be obtained as single crystal due to solubility limitation. Furthermore, the complex abstract chlorine atom from chlorinated solvents (*e.g.* CH₂Cl₂, CHCl₃) and provided the corresponding five-coordinated, diradical-containing Co(III) complex **2c** (Figure S22). Similar reaction has also been observed for complex **1**, which provided complex **1b** (Figure S21). Nevertheless, X-band EPR and UV-vis-NIR spectral pattern analyses (*vide infra*) consolidated that **1** and **2** have similar-type of geometry and coordination environment.

Complex **1** acquired square planar geometry ($\tau^3 = 0.0$). The coordination sphere was comprised of two nitrogen atoms and two oxygen atoms form two ligands (Figure 1A). The Co-O = 1.830(3) and Co-N = 1.832(4) (Table S2) bonds were in accord with the previously reported Co(III) square planar complexes.⁴ Hence, the formal oxidation state of the Co atom in the complex was assigned to +III. It is to note that complex 1 was neutral in charge. Therefore, in order to maintain the neutrality, the two coordinated noninnocent ligands must be present in the complex in two different oxidation states, i.e. one-electron oxidized iminosemiguinone and fully reduced amidophenolate states.^{4,5} However, $C_{Ph}-O_{Ph} = 1.323(5)$ and C_{Ph} – N_{Ph} = 1.371(5) Å (C_{Ph} , N_{Ph} , and O_{Ph} stand for the C, N, and O atoms attached or belong to phenyl ring, respectively) bond distances (Table S2) in the two coordinated-ligands were same and corresponded to neither iminosemiquinone (C-N = 1.35 Å; C-O = 1.30 Å) form nor amidophenolate (C–N = 1.38 Å; C–O = 1.35 Å) form (Scheme 1). These features, as previously reported by Wieghardt, Chaudhuri and coworkers,⁴ implied the delocalization of the negative charge and the radical (hole) over the two coordinated-ligand units.



Figure 1. ORTEP plots of: (A) 1, (B) 1a, (C) 2a and (D) 2b. Thermal ellipsoids were drawn at 50% probability level. H atoms and methyl groups of the *tert*-butyl groups (for 1a, 2a and 2b) were omitted for the sake of clarity. In 1, C13 atom is disordered in 65:35 ratio between C13A and C13B atoms.

All the five-coordinate neutral complexes were almost square pyramidal ($\tau^3 = 0.07$ [1a], 0.08[2a], and 0.0[2b]). In the complexes, the central cobalt atom (Co1) was situated above the N2O2 basal plane, and towards the apical –XPh group (Figure 1). The Co–O = 1.858-to-1.881 Å, and Co–N = 1.845-to-1.871 Å bond distances (Table S2-S3, S5-S6) in the complexes corresponded to previously reported square pyramidal cobalt complexes having +III oxidation state.⁴ Thus, herein, the oxidation state of the central cobalt atom

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has been assigned as +III. All the C–C bonds of the *tert*-butyl-groups containing C_6 phenyl rings were not within 1.39±0.01 Å, rather, an alternating short-long-short, *i.e.*, a quinoid-type distortion, has been observed (Table S2-S5). Furthermore, average $C_{Ph}-O_{Ph} = 1.311(4)$ [**1a**], 1.307(3)[**3a**] 1.298(8)[**2b**] Å and $C_{Ph}-N_{Ph} = 1.349(4)$ [**1a**], 1.351(4)[**2a**], 1.362(9)[**2b**] Å bond distances were in between of their single bond and double bond values and emphasized the one-electron oxidized iminosemiquinone form^{4,5} of the coordinated ligands in the complexes. Hence, X-ray single crystal analyses suggested that four-coordinate complexe **1** was monoradical-containing, while, the five-coordinate complexes (**1a**, **2a**, and **1b**) were diradical-containing. Noteworthy, better quality crystal data would have been more convincing, however, diffraction measurements even at 100 K could not improve the staructural quality, which is due to the nature of the crystals.



The five-coordinate diradical-containing square pyramidal Co(III) [low-spin; $S_{co} = 0$] complexes (1a, 2a, and 2b) were diamagnetic owing a strong antiferromagnetic coupling between the two ligand-centered π -radicals ($S_{R} = 1/2$). The diamagnetic character of the complexes was further supported by ¹H NMR analysis (Figure S18-S20). In the monoradical-containing fourcoordinate square planar Co(III) complexes (1, and 2), the metal center possesses two unpaired electrons, which were residing at d_1^2 and d_{xy} magnetic orbitals [$S_{Co} = 1.0$]. An antiferromagnetic coupling among the Co(III) d_z^2 magnetic orbital, and ligand center p_z orbital led to an S_{total} = 1/2 ground state and paramagnetism in the complexes, where the unpaired electron resided at the d_{xy} magnetic orbital. Hence, cobalt (III)-centered X-band EPR spectra for 1 and 2 were observed. Experimental as well as simulated EPR spectra for 1 and 2 complexes were shown in Figure 2. For both the complexes, the signals were anisotropic in nature. Simulation to the experimental spectra provided the following parameters: g_1 = 1.992[1], 1.980[2]; $g_2 = 2.220[1]$, 2.020[2]; $g_3 = 2.750[1]$, 3.215[2]; $^{Co}(A_1, A_2, A_3) = (5, 42, 93) \times 10^{-4} \text{ cm}^{-1}$, for complex 1; $^{Co}(A_1, A_2, A_3) =$ (2, 1, 110) \times 10⁻⁴ cm⁻¹ for complex **2**. The average q value for the complexes 1 and 2 were 2.342 and 2.405, respectively, and supported metal-centered unpaired electron.

UV-vis-NIR spectra of **1** and **2** showed an absorption manifold centered at around 1600 nm (Figure S23, S26). It has previously been established that the band appeared due to an intervalence ligand(amidophenolate) to ligand(iminosemiquinone) charge transfer.⁴ This experimental fact further consolidated that both the complexes have same electronic structure. In the UV-vis-NIR spectra of five-coordinate, diradical-containing complexes (**1a**, **2a** and **2b**), the band at around 1600 nm was absent and a

ligand(iminosemiquinone) to ligand(iminosemiquinone) charge transfer band was present at around 830 nm (Figure S24, S27-S28). Thus, the conversion of four-coordinate $[Co^{III}(L^{AP(R)})(L^{ISQ(R)})]^0$ to five-coordinate $[Co^{III}(L^{ISQ(R)})_2XPh]^0$ or *vice versa* could be monitored by analyzing the band at 1600 nm.



Table 1. Optimization of urea derivatives formation.[⊥]

#	Substrate	Product	Cat (mol %)			Isolated yield (%)		
			1	2	2a	1	2	2a
1	III	IV	2.5	2.5	2.5	72	78	76
2	Ш	NR	0	0	0	0	0	0
3	1	Ш	2.5	2.5	2.5	80	86	82
4	1	NR	0	0	0	0	0	0
5	III+Ph ₂ S ₂ ^a	IV	2.5	2.5	-	68	75	-
6	Ш	IV	_	1.0	-	-	72	_
7	Ш	IV	-	0.1	-	-	48	_
		At	sence o	f sunlig	ht			
8	III	IV	2.5	2.5	2.5	10	12	15
9	III+Ph ₂ S ₂ ^a	IV	2.5	2.5	-	9	12	-
10	I	Ш	2.5	2.5	2.5	10	11	10

¹ NR stands for no reaction. The temperature of the reaction bath was 36 °C. All the reactions were carried out for 6 hours in a closed tube. ^a 1:1 mixture.

When CH₂Cl₂ solutions of 1a and 2a were subjected to sunlight irradiation, the 1600 nm band was started appearing with the concomitant shifting of ~570 nm band to 660 nm (Figure S30-S31). This phenomenon indicated homolytic Co-SPh bond cleavage and consequent generation of 1 and 2. Similar phenomenon had also been observed for 2b (Figure S32A), where 2 was generated by the cleavage of Co-SePh bond. The appearance of Co-centered EPR signal (Figure S30-S32) in the processes further supported the formation of 1 and 2. As five-coordinate, diradical-containing complexes could be converted to the corresponding fourcoordinate, monoradical-containing complexes under the sunlight stimulus, and four-coordinate complexes have already been found as one-electron transferring agent, we have investigated the catalytic ability of four-coordinate as well as five-coordinate complexes (1, 2 and 2a) for the conversion of RNCO (R = phenyl and naphthyl) to the corresponding C-N coupled urea derivatives. Noteworthy, 1,3-diaryl urea derivatives are in agricultural and medicinal uses.⁶ Table 1 contains the reaction details. In the catalysis, maximum turnover number (TON) 480 has been achieved by employing 0.1 mol% complex 2. To note, the bulkiness of the substrates and ortho- substituents did not pronouncedly affect the product yield. This emphasized that substrates approached the Co(III) centre along the axial position. The essentiality of both the catalysts as well as sunlight was further established by performing blank reactions (Table 1). No products formation in the absence of catalyst refuted the conversion RNCO compounds to the corresponding amines and photo-driven [2+2] cycloaddition

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reaction (Table 1, #2 and #4). The low TON (4-6) in the absence of sunlight (Table 1, #8 and #10) supported the possibility that during the catalysis a substrate-bound five-coordinate intermediate was formed (Figure 3) and a photo stimulus was then essential for the regeneration of four-coordinate catalysts by the cleavage of Cosubstrate bond in the intermediate. The formation of 1,1,2,2,tetrachloroethane was being established by GC and GC-MS (Figure SX) analyses during the catalysis of III to IV in the presence of catalyst 2. The compound was formed by the C-C coupling of two CH₂Cl₂ molecules and thus, implied the abstraction of hydrogen atom from the solvent molecule during the formation of urea derivatives. Although further investigation is essential for the better understanding of the catalysis, depending on the above stated results a mechanistic proposal for the C-N coupling between two isocyanate molecules for the formation of urea derivative is given in Figure 3.



Figure 3. Proposed mechanism for the formation of urea derivative form an isocyanate compound.

Conclusions

In summary, four-coordinate, monoradical-containing Co(III) complexes have been successfully synthesized and employed for the S-S/Se-Se bond activation and scission by an electron transfer to the bonds. The solo example is known in the literature for the ligand-induced S-S bond cleavage reaction is based on air sensitive Pd(II)-amidophenolate complex. Thus, less explored phenomena has been studied employing air stable Co(III) complexes. The resulted diradical-containing square pyramidal Co(III) complexes with axial -XPh (X = S and Se) ligands experienced homolytic Co-XPh bond cleavage under the influence of sunlight and produced the corresponding four-coordinate, monoradical Co(III) complexes (Figure S30-S32). Both four- and five-coordinate Co(III) complexes catalysed the conversion of aromatic isocyanates to the corresponding urea derivatives. Thus, we have presented, to the best of our knowledge, the first examples for the synthesis of urea from the solo use of isocyanate compounds. Presently, in our laboratory sunlight-driven PhX* radical addition reactions to various organic units are ongoing.

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