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Inter-ligand azo (N=N) unit formation and stabilization of a Co(II)-diradical complex via metal-to-ligand dπ–pπ* back donation: synthesis, characterization, and theoretical study†

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An azide (−N₃) group attached at the -ortho carbon atom to the aniline moiety of 2-anilino-4,6-di-tert-butylphenol formed a diradical-containing Co(II) complex via inter-ligand azo (N=N) bond formation. Metal-to-ligand (azo), dπ-to-pπ* back donation stabilized the metal in its lower oxidation state.

Radical-containing transition metal complexes have attracted great interest because of the discovery of radical involvement in various metalloenzymatic activities.[1] Several redox-active organic compounds, known as non-innocent ligands, and their corresponding radical-containing Cu–, Ni–, Co–, Fe–, Mn–, V– complexes have been synthesized[2] as structural and/or functional enzyme models. The complexes have been studied by X-ray crystallography and various other spectroscopic techniques, with the aim of a better understanding of metal–radical interaction and, consequently, the metalloenzymatic activities.

2-Anilino-4,6-di-tert-butylphenol {H₂[AP^H]} behaves as a non-innocent ligand. Recently, we observed that attaching an -ortho substituent (–CN, –OMe), having weak coordinating property, to the aniline moiety of H₂[AP^H] ligand can activate the central metal ion, and, thereafter, ligand centre C–N bond breaking and C–O formation can occur in the corresponding radical-containing vanadium complex formation process.[2i] To continue our study for improved understanding of the effect of -ortho substitution, where the substituent is residing at a position (aniline moiety) far from the radical occupying centre, we

synthesized ligand H₂Rich^(AP)N3 (Scheme 1). We choose an azide group at the -ortho position because (i) it might interact with metal ions and provide stable metal–imido/nitrene complexes, in which the metal ions would be in a higher state and coordinated to π-radical, and/or (ii) the generated imido/nitrene species might couple with another imido/nitrene unit to form an azo functional unit. The azo (N=N) functional unit can act as a π-accepter and, therefore, could stabilize the metal ion in its lower oxidation state. Hence, this provides a potential route to synthesis of π-radical coordinated low-valent metal complexes, which are known to be good oxidation and oxygenation catalysts.

Herein, we present synthesis of H₂Rich^(AP)N3 ligand, and corresponding Co complex found to be a Co(II)-diradical and formed by ligand centre –N₃ to azo (N=N) bond formation.

The organic moiety H₂Rich^(AP)N3 was synthesized by reacting 1:1 2-azidoaniline and 3,5-di-tert-butylcatechol in hexane in the presence of Et₃N under air (Scheme 1). When a CH₃CN solution of 1:1 H₂Rich^(AP)N3 and CoCl₂·6H₂O was stirred at room temperature (30 °C) under air in the presence of Et₃N, complex 1 was isolated as a dark brown solid. Recrystallization of the solid from a 3:1 CH₂Cl₂–CH₃CN solvent mixture provided a crystalline solid that was suitable for single crystal X-ray diffraction study.
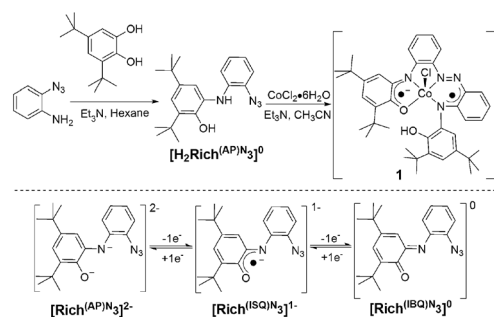
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Scheme 1

In the infrared (IR) spectrum of $H_2Rich^{(AP)N}3$, $\nu(OH)$, $\nu(NH)$ stretching bands appeared at 3424 and 3348 cm^{-1}, respectively. The asymmetric, symmetric and overtone vibration frequencies for the methyl $\nu(C-H)$ of *tert*-butyl groups appeared at 2955, 2867, and 2900 cm^{-1}, respectively.[2i] The bands at 2131 and 2093 cm^{-1} confirmed the presence of $-N_3$ group in $H_2Rich^{(AP)N}3$. In complex **1**, a slightly broad and medium band appeared at 3243 cm^{-1} because of hydrogen bonded $\nu(OH)$ stretching. Interestingly, no stretching band representing the $-N_3$ group was present, rather, a medium band appeared at 1384 cm^{-1}. This band indicated the presence of azo (N=N) unit[3] in **1**.

Electrospray ionization mass spectra (ESI-MS) for both $H_2Rich^{(AP)N}3$ and complex **1** were recorded in CH_3CN in positive mode. A 100% molecular ion peak at m/z = 339.22 was observed for $H_2Rich^{(AP)N}3$. The isotope distribution pattern showed $[C_{20}H_{26}N_4O + H]^+$ as the composition of the molecular mass and confirmed the formation of $H_2Rich^{(AP)N}3$. The ESI-MS for **1** showed a 100% mass peak at m/z = 676.32 that corresponded to $[M - Cl]^+$; M = molecular mass of **1**, and confirmed $C_{40}H_{49}CoN_4O_2$ as the composition of $[M - Cl]$ moiety.

Single crystal X-ray structural measurement for **1** was performed at 296 K. Complex **1** crystallized in the triclinic space group $P\bar{1}$. The molecular structure is presented in Fig. 1. Selected bond distances and bond angles are provided in Table 1 (S5†).

In the neutral complex **1**, the symmetrical organic moiety (L^X; the generated ligand coordinated to the Co atom in the complex) provided an asymmetrical coordination environment around the central Co atom, which was caused by coordination of the N2 atom from the azo unit and non-coordination of the phenolic O2 atom. The hydrogen atom attached to the non-coordinating phenolic O2 atom formed a relatively strong hydrogen bond with Cl1 atom [H–Cl1 = 2.293(4) Å], as shown in Fig. 1.[4]

The central Co1 atom in **1** was five-coordinate, where the basal plane was composed of N_3O donor set and the apical position, *i.e.* the fifth position, was occupied by Cl1 atom. Co1 atom was situated ~0.26 Å above the basal plane and the geometry around the Co centre could be described as an almost perfect square pyramidal (τ = 0.04). The Co–N, and Co–O bond distances were not very informative with regards to assigning

the formal oxidation state of Co1 atom. The Co1–N1 = 1.861(2), and Co1–N4 = 1.862(2) Å bond distances were in accord with previously reported square pyramidal Co complexes, where the Co atom was claimed to have +III formal oxidation state,[5] while a long Co1–O1 = 1.890(2) Å bond distance was indicative of a lower oxidation state of Co1 atom than that of +III. The short Co1–N2 = 1.849(2) Å bond distance compared with the other Co–N bond distances, indicated metal(dπ)-to-azo(pπ^*) back donation. The azo bond distance [N2–N3 = 1.282(3) Å] was found to be ~0.04 Å long compared to normal N=N bond distance, and ~0.07 Å short compared to one-electron reduced azo π-radical anion,[6] and, therefore, supported only back-donation.[7]

The organic moiety (L^X) was composed of four C_6 phenyl rings. Of these, two contained two *tert*-butyl groups each, at the 3,5-positions, and the other two rings did not. The C_6 phenyl rings composed of C1-to-C6, C7-to-C12, C13-to-C18, and C19-to-C24 atoms will be represented here as ring A, ring B, ring C, and ring D, respectively (Fig. 1). The C–C bond distances of ring A were not all within the 1.39 ± 0.01 Å range,[2f–h] as expected for the fully reduced 3,5-di-*tert*-butylamidopheno-late form $[(AP)^{2-}]$.[8] Rather, alternating short and long C–C bond distances were found [C3–C4 = 1.378(4), C4–C5 = 1.421(4), C5–C6 = 1.357(4)], as previously observed for one-electron oxidized iminosemiquinone $[(ISQ^{1-})]$ π-radical form of the moiety.[2a,5,8] Additionally, the observed $C_{Ph}-O_{Ph}$ and $C_{Ph}-N_{Ph}$ (O_{Ph} and N_{Ph} stand for the oxygen and nitrogen atoms attached to a phenyl ring, respectively) bond distances [C2–O1 = 1.302(3) Å and C1–N1 = 1.355(4)], which were found in between their single bond and double bond range, emphasized the presence of π-radical and its delocalization between phenolic O1 and amide N1 atoms.[2a,5,8] Rings B and D showed no quinoid-type distortion and the phenyl C–C bond distances were within the 1.372–1.402 Å range (Table 1, S5†). Furthermore, single bond character emphasizing C7–N1 = 1.401(4), C12–N2 = 1.434(4), C19–N4 = 1.449(4), and C24–O2 = 1.364(4) Å bond distances consolidated the fully reduced form of the phenyl rings.[8e,f] The short C13–N3 = 1.365(4) and C18–N4 = 1.361(4) Å bond distances,[5a] along with quinoid-type distortion (Table 1, S5†) in ring C, invoked the presence of delocalized π-radical in the ring. Therefore, from the X-ray crystallographic analysis, it was found that the central Co1 atom in the square pyramidal complex **1** was coordinated to two π-radicals. In order to maintain neutrality, the Co1 then would be in the +II formal oxidation state.

Variable-temperature magnetic susceptibility measurements performed in the temperature range 15–300 K at 0.1 T are shown in Fig. 2. The μ_{eff} = 1.99μ_B at 15 K indicated an S = 1/2 ground state with $g > 2.0$ for **1**. This $g > 2.0$ value indicated a metal (Co)-centered unpaired electron. Increasing temperature caused the μ_{eff} value to increase, reaching 3.65μ_B at 300 K. The nature of the curve indicated the presence of multi-paramagnetic centers in **1**, and they were coupled to each other antiferromagnetically to provide an S = 1/2 ground state. The experimental result was reproduced quite well using the following parameters; $g_{Co(II, S=3/2)}$ = 2.19, $g_{R(S=1/2)}$ = 2.00, $J_{12} = J_{23}$ =
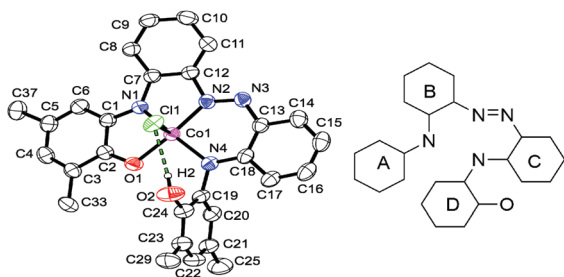

Fig. 1 Molecular structure of **1**; thermal ellipsoids are drawn at the 50% probability level. The methyl groups attached at C25, C29, C33, and C37, together with hydrogen atoms, are omitted for clarity.

Fig. 2 Left: variable-temperature μ_{eff} vs. T plot for **1**; $B = 0.1$ T. Right: X-band EPR spectrum for **1**. Conditions: temperature 77 K, X-band microwave frequency (GHz), 9.142; modulation frequency (kHz), 100; and microwave power, 0.998 [μW].

−73, and $J_{13} = −10$ cm^{-1}, where J_{12} and J_{23} are the coupling constants between Co(II) and the radicals, and J_{13} is the coupling constant between the two radicals.

In order to find the exact location of the unpaired electron, X-band EPR measurement was performed in a 1 : 1 CH$_2$Cl$_2$–toluene solvent mixture at 77 K, as depicted in Fig. 2. An anisotropic EPR signal was found. The best fit to the experimental data provided the parameters; $g_1 = 1.995$, $g_2 = 2.140$, $g_3 = 2.150$, $g_{av} = 2.095$, $^{Co}(A_1, A_2, A_3) = (1, 20, 63) \times 10^{-4}$ cm^{-1}. These parameters clearly indicated the presence of an unpaired electron on the Co(II) centre. Therefore, from the magnetic susceptibility measurements as well as X-band EPR studies, it was evidenced that two π-radicals ($S_R = 1/2$) were antiferromagnetically coupled with high-spin at the Co(II) centers ($S_{Co} = 3/2$).

Density functional theory (DFT)-based molecular modeling was carried out to support the single crystal X-ray structural measurement study. The computations were performed at UB3PW91 (hybrid Becke three-parameter exchange density functional combined with the gradient-corrected Perdew-Wang 91 correlation functional)[9] with customized basis sets, i.e. 6-31G+(d,p) for all the atoms except Co. An effective core potential (ECP) based[10] LanL2DZ basis set was used for Co atom, as implemented in the Gaussian09 package.[11] Fig. 3

Fig. 3 The optimized geometry of **1** with selected bond distances (in Å unit).

represents the optimized structure of the complex, which shows reasonable agreement with the experimental molecular structure obtained from X-ray crystallographic data (Table 3, S6†).

Conclusions

To conclude, we synthesized a new non-innocent ligand H$_2$Rich$^{(AP)N}$3 by placing a –N$_3$ group at the -ortho position to the aniline moiety of the parent 2-anilino-4,6-di-tert-butyl-phenol ligand. The ligand reacted with CoCl$_2$·6H$_2$O and provided a diradical-containing paramagnetic Co(II) square pyramidal complex through ligand centre azo (N=N) unit formation between two coordinating ligands. The complex was stable under air and even on continuous purging of O$_2$ through a dichloromethane solution of the complex for 8 hours; no appreciable change was seen in the UV-vis/NIR spectrum. Metal dπ-to-ligand (azo) pπ* back donation potentially was the main factor behind stabilization of the metal ion in its lower formal oxidation state. To the best of our knowledge, this is the first complex to show the existence of stable π-radical proximate to the azo group. In addition, in **1** the metal ion was stabilized at its lower oxidation state. Note also that **1** can be synthesized by employing a –NH$_2$ group in place of the azide group in the ligand. Although the mechanism for this is not yet understood, it seems that formation of the azo unit and, consequently, **1**, was propagated through a nitrene radical anion formation pathway (S10†).[12] The experimental structural parameters are strongly supported by relevant computational studies. In future, we shall concentrate on finding the possible role of the π-radical in the complex formation process, and the detailed mechanism behind the azo moiety formation from azide and/or amine groups. Also, several transition metal complexes in which the central metal ions will be stable in their lower oxidation state, will be synthesized, having potential as oxidizing and/or oxygenating catalysts.

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