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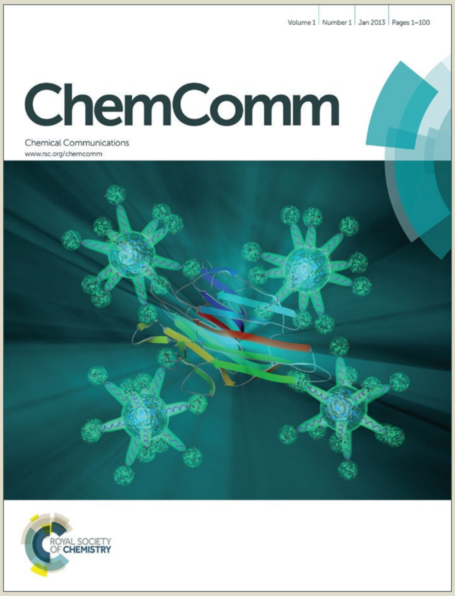

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A Solid-State Valence Tautomeric Octahedral $\{Co^{II}[(BQ\text{-}N\text{-}Cat)]_2\}^0$ Complex Formation *via* Ligand-Centered Phenolic C-O Bond breaking and Co-O Bond making

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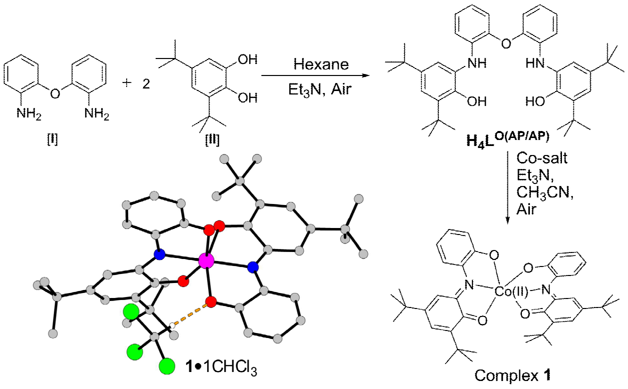
Ligand $H_4L^{O(AP/AP)}$ underwent ligand-centered C-O bond cleavage during complexation reaction with Co(II)-salt. Thus formed octahedral $\{Co^{II}[(BQ\text{-}N\text{-}Cat)]_2\}^0$ complex showed valence tautomerization in solid state. While, the process was triggered by the presence of lattice solvent, the nature of the solvent molecule has less effect to the process.

Transition metal complexes, which are coordinated to redox-active ligands, have achieved great importance in the field of biomimetic catalysis, C-H bond activation, C-C cross coupling, C-N bond activation, bistable as well as valence tautometic complex formation, etc.[1-3] The redox-active ligands, which are coordinated to a metal ion, may exist in their various oxidation states. Furthermore, a redox-active ligand coordinated to a metal ion in multiple numbers can exist in different oxidation states. Soper *et al.* have reported that the electrophilic and nucleophilic behaviours of square planar Co(III) complexes depend on the redox state of the coordinated redox-active ligands.[2] Redox-active ligand-coordinated cobalt complexes have recently been reported as catalysts for C-C coupling reactions.[1g,2] Apart from the catalytic reactivity, valence tautomerization between Co(III)-semiquinone to Co(II)-quinone electronic isomers are under progressive investigation for the demand of logic gates, bistable, and spin-switch materials developments.[3] Thus, the study of cobalt complexes that are coordinated to redox-active ligands has drawn special attention.

2-Anilino-4,6-di-*tert*-butylphenol (H_2AP) is an established bidentate non-innocent ligand.[4] The square planar Co(III) complex that formed by the coordination of two equivalents of $[AP]^{2-}$ ligand, $[Co^{III}([AP]^{2-})_2]^-$, is known to behave as a strong nucleophile and undergoes $2e^-$ oxidative addition with alkyl halides. In this process, each $[AP]^{2-}$ ligand undergoes one-electron oxidation and consequently, alkyl-coordinated square pyramidal complexes having general formula of $[Co^{III}E([SQ]^{\bullet 1-})_2]$ (where E = CH_2Cl, alkyl) form. To initiate an oxidative C-C cross coupling reaction *via* the oxidative addition of both alkyl and halide units to the Co center in a Co complex requires *cis*- orientation between the alkyl and the halide units. Therefore, *cis*- orientation is necessary between the two coordinated non-innocent ligands to create a vacant site for *cis*-coordination of alkyl halide. In square planar $[Co^{III}([AP]^{2-})_2]^-$ complex the two coordinating-ligands orient in *trans*- fashion. Thus, oxidative addition of both alkyl and halide units was not possible in the system.



Scheme 1. Schematic representation of ligand $H_4L^{O(AP/AP)}$ and complex 1 formation. X-ray molecular structure of complex **1**•1CHCl$_3$.

As a foremost step to impose non-coplanar arrangement between two radical-generation units, two H_2AP ligands were combined by a bridging O atom that connects two ligands *via* the *ortho*- carbon atom of the two aniline moieties. Thus formed new ligand will be designated here as $H_4L^{O(AP/AP)}$ (Scheme 1; Figure S8, S12). Because of the O-bridge the angle around the O atom would be ~ 105 °, hence, two aniline rings of the two H_2AP units in ligand $H_4L^{O(AP/AP)}$ could not situate parallel to each other in coordination complexes. Hence, coplanar and *trans*- alignment of the radical-generating 3,5-di-*tert*-butyl amidophenolate units could be restricted and the required vacant site for *cis*- coordination might be availed.

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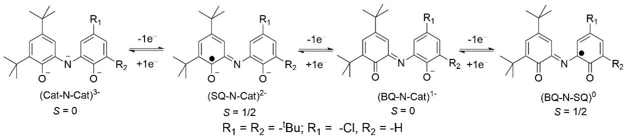
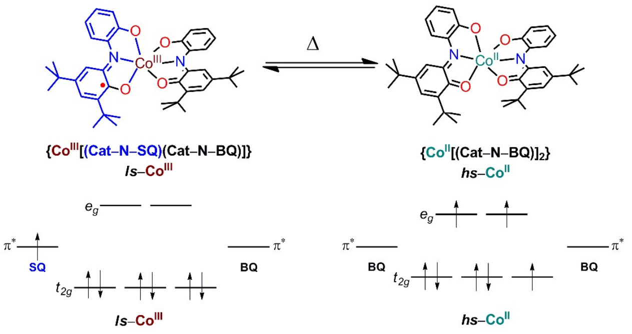
Ligand $H_4L^{O(AP/AP)}$ was synthesized in 64% yield by reacting 1:2 2,2′-oxodianiline (**I**) and 3,5-di-*tert*-butyl catechol (**II**) in hexane under air in the presence of triethyl amine (Et_3N) [Scheme 1]. The ligand reacted with equivalent amount of $Co(ClO_4)_2•6H_2O$ or $CoCl_2•6H_2O$ in CH_3CN under air for 7 hours in the presence of Et_3N and provided blue-green solid (complex **1**). The solid upon recrystallization from a 5:2 $CHCl_3$:CH_3CN solvent mixture appeared as rectangular-shaped crystals (**1**•1$CHCl_3$). However, the crystals were not stable during X-ray diffraction measurement (Table S2, S16) even at 100 K. Hence, the molecular structure analysis of the formed complex **1**•1$CHCl_3$ [Scheme 1; Figure S8, S12; Table S1-S2, S15-S16] was not worthy enough for the definite assignment of oxidation state of the central metal ion as well as the coordinated ligands. Nevertheless, from the crystallographic analysis it was evident that the complex was neutral, mononuclear-octahedral (*mer*), and the ligand backbone was different from that of the initially employed ligand for the complexation reaction, *i.e.*, new tridentate ligand was formed during the reaction *via* ligand-centered phenolic C-O bond cleavage.



Scheme 2. Various possible oxidation states of $(Cat\text{-}N\text{-}Cat)^{3-}$ species.

Two analogous tridentate ligands, as present in complex **1**•1$CHCl_3$, are already available in literatures[5] and it has been demonstrated that the ligands may exist in their three different stable oxidation states in its corresponding transition metal complexes (Scheme 2). Therefore, the composition of the neutral complex **1** can be either, (a) a Co(II) ($S_{Co(II)}$ = 3/2, high-spin) ion with two coordinated diamagnetic $(BQ\text{-}N\text{-}Cat)^{1-}$ ligands, *i.e.*, $\{Co^{II}[(BQ\text{-}N\text{-}Cat)]_2\}^0$ or (b) a Co(III) ($S_{Co(III)}$ = 0, low-spin) with coordinated paramagnetic $(SQ\text{-}N\text{-}Cat)^{2-}$ [S_L = 1/2] and $(BQ\text{-}N\text{-}Cat)^{1-}$ ($S_{L'}$ = 0) ligands, *i.e.*, $\{Co^{III}[(SQ\text{-}N\text{-}Cat)(BQ\text{-}N\text{-}Cat)]\}^0$ (Scheme 3).

In order to distinguish between the two possible compositions, X-band EPR measurement on **1**•0.3$CHCl_3$[6] was performed at 77 K in a CH_2Cl_2/toluene solvent mixture (Figure 1A). A ligand-centered S = 1/2 signal with a reasonable ^{59}Co (I = 7/2) super-hyperfine interaction was established by the simulation of the experimental spectrum. The parameters obtained by the simulation were; g_1 = 2.007, g_2 = 2.007, and g_3 = 1.998; g_{iso} = 2.004; $^{59}Co(A_1, A_2, A_3) = (7, 7, 27) \times 10^{-4}$ cm^{-1}. Interestingly, it was observed that the signal vanished at 295 K. The temperature-dependent signal was also hold true for solid-state X-band EPR measurements of the complex (Figure 1B). The intensity of the signal decreases drastically at 295 K. In fact, the nature of the observed EPR signal was different than that of ligand-centered S =1/2 and indeed, very weak in intensity, *i.e.*, almost X-band EPR silent. Therefore, it can be argued that in solution as well as in solid-state the complex underwent valence tautomerization; at low temperature (77 K) the composition of the complex was a Co(III), a $(SQ\text{-}N\text{-}Cat)^{2-}$ and a $(BQ\text{-}N\text{-}Cat)^{1-}$, while, at 295 K both the coordinated ligands were in $(BQ\text{-}N\text{-}Cat)^{1-}$ form and the central metal was Co(II). Vanishing of X-band EPR signal at 295 K was due to zero-field splitting (> 0.3 cm^{-1}) that resulted by high spin-orbit coupling at Co(II). Herein, it is noteworthy that valence tautomerization between octahedral $\{Co^{III}[(SQ\text{-}N\text{-}Cat)(BQ\text{-}N\text{-}Cat)]\}^0$ and $\{Co^{II}[(BQ\text{-}N\text{-}Cat)]_2\}^0$ is well known in solution, however, the phenomenon is absent in solid state within 2-295 K temperature range.[7]



Scheme 3. Valence tautomeric species.

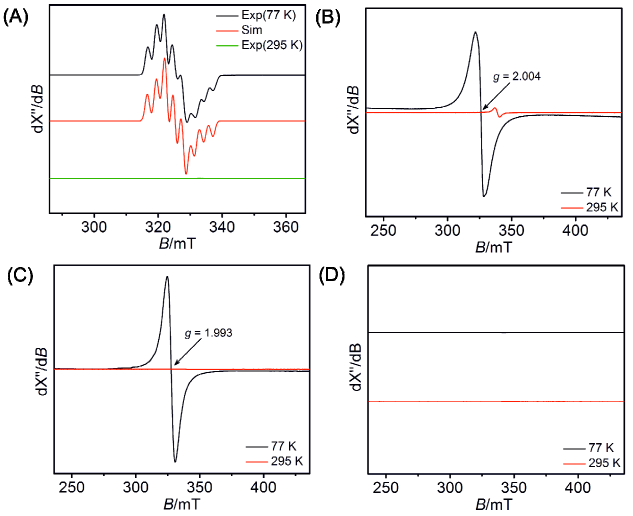


Figure 1. X–band EPR spectra measured at 77 and 295 K; (A) Complex **1**•0.3$CHCl_3$ in a CH_2Cl_2/toluene (2:1) solvent mixture: microwave frequency (GHz): 9.444; modulation frequency (KHz): 100; amplitude = 1.0. (B) Complex **1**•0.3$CHCl_3$ in solid state: microwave frequency (GHz): 9.142; modulation frequency (KHz): 100; amplitude (G) = 0.3; (C) Complex **1**•0.8CH_3CN in solid state, microwave frequency (GHz): 9.138; modulation frequency (KHz): 100; amplitude (G) = 1.0, and (D) Complex **1** in solid state: X–band microwave frequency (GHz): 9.143; modulation frequency (KHz): 100; amplitude (G) = 1.0.

Inspired by X-band EPR results, variable-temperature magnetic susceptibility measurement was carried out on solid sample of complex **1**•0.3$CHCl_3$[6] at 1 T external magnetic field to reinforce solid-state valence tautomeric nature of the complex. The $\chi_M T$ vs T plot is depicted in Figure 2. At 10 K, the $\chi_M T$ = 0.44 emu K mol^{-1} was observed. This value was closely commensurate with the system having one-unpaired electron

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(an *S* = 1/2 spin). The value remained almost unchanged up to 118 K. Interestingly, in between 118 to 125 K temperature range a sharp transition in magnetic moment to $\chi_M T$ = 2.34 emu K mol^{-1} was observed. The magnetic moment attained at 125 K remained almost constant up to 300 K. This feature supported a valence tautomeric phenomenon in the system, where, low-spin diamagnetic Co(III) was reduced to high-spin Co(II) by ligand-centric SQ unit that underwent then to its one-electron oxidized BQ form (Scheme 3). Therefore, it can be argued that till 118 K the complex was existing in $\{Co^{III}[(SQ\text{-}N\text{-}Cat)(BQ\text{-}N\text{-}Cat)]\}^0$ form, while, above the 125 K the complex was continued to exist in $\{Co^{II}[(BQ\text{-}N\text{-}Cat)]_2\}^0$ form. The critical temperature (T_c), which is defined as the temperature at which the free energy difference (ΔG) between the two inter-convertible species is nil, was 122 K.[8]

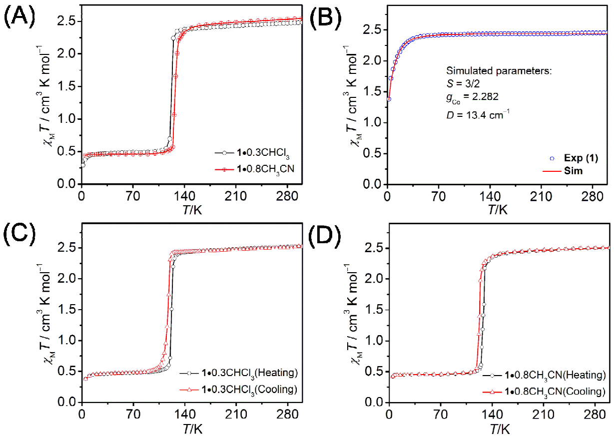

Figure 2. $\chi_M T$ vs *T* plots: (A) **1**•0.3CHCl$_3$ and **1**•0.8CH$_3$CN, (B) **1**, (C) hysteresis measurement of **1**•0.3CHCl$_3$ (D) hysteresis measurement of **1**•0.8CHCl$_3$.

In order to understand the origin of the tautomerization, and such a rare and abrupt transition, initially we have tried to understand the solvent effect. Hence, the complex **1** was recrystallized from; (a) a 3:1 Et$_2$O:CH$_3$CN solvent mixture, and (b) toluene. Crystals, which were obtained from the two crystallization processes, were measured by X-ray single crystal diffraction methods. Indeed, 1 equivalent of CH$_3$CN was found to exist in the crystal lattice of the crystal (**1**•1CH$_3$CN) that obtained from the 3:1 Et$_2$O:CH$_3$CN solvent mixture (Figure S8D, S12). Existence of no solvent molecule was confirmed in the crystal (complex **1**) that obtained from toluene (Figure S8C, S12). Noteworthy, the quality of crystals were not good enough for the assignment of acute and appropriate oxidation state of ligands as well as metal center (Table S1-S2, S15-S16).

Nevertheless, variable-temperature magnetic susceptibility measurements for **1**•0.8CH$_3$CN[6] and **1**[6] were carried out on solid samples at 1 T external magnetic field. The $\chi_M T$ vs *T* plots are depicted in Figure 2. The temperature-dependent change in $\chi_M T$ for **1**•0.8CH$_3$CN was very similar as that of **1**•0.3CHCl$_3$. However, the T_c for **1**•0.8CH$_3$CN was slightly higher (~ 4.4 K) compared to **1**•0.3CHCl$_3$. Unlike solvated crystals, in case of complex **1**, $\chi_M T$ = 0.25 emu K mol^{-1} value remained almost constant in the temperature range 50-300 K. Upon further lowering in temperature, $\chi_M T$ value decreased and reached at 1.71 emu K mol^{-1} at 5 K. Herein, the decrease in $\chi_M T$ value was due to zero-field splitting (*D* = 13.4 cm^{-1}, Figure 2B) that arose because of strong spin-orbit coupling at Co(II) center. Thus, it was apparently evident that in the absence of lattice solvent the complex remained in $\{Co^{II}[(BQ\text{-}N\text{-}Cat)]_2\}^0$ form and no valence tautomerization took place.

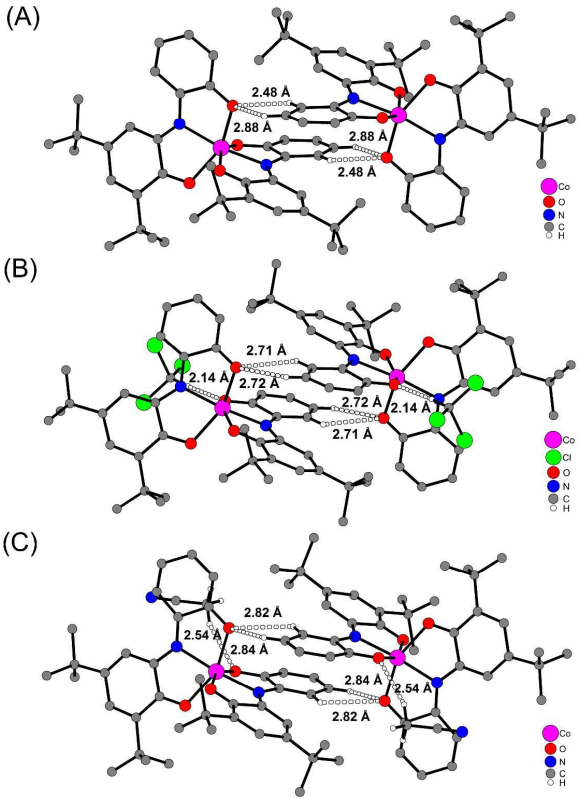

Figure 3. H-honds between the two adjacent molecules: (A) complex **1**, (B) complex **1**•1CHCl$_3$, and (C) complex **1**•1CH$_3$CN.

The single-crystal volume of **1** increased with incorporation of lattice solvent (Table S2, S16). Therefore, it was evident that the presence of lattice solvent molecules within the crystal lattice promoted flexibility or softness[3a,3n] in the systems (Figure S9-S10, S13-S14) and favored the required-structural changes in valence tautomeric transition. Crystal-structure packing analyses revealed that in complex **1** two adjacent molecules were firmly held by strong intermolecular H-bonds, while, in complex **1**•1CHCl$_3$ and complex **1**•1CH$_3$CN the intermolecular H-bonds were weak in nature (Figure 3). The strong H-bonds, which can be consider as stabilizing factor, presumably prevented complex **1** in undergoing any required structural change for valence tautomerization. The abrupt transition within very small (7 K) temperature range (Figure 2) in **1**•0.3CHCl$_3$ and **1**•0.8CH$_3$CN reinforced a strong cooperative effect[3a,3n] that was propagated through lattice solvent network (Figure S9-S10, S13-S14). Although, the crystallographic phases and the nature of the lattice solvent molecule were different

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for the different complexes (Figure 4), no consequence on the nature of transition, transition temperature, and hysteresis effect (Figure 2C, and 2D) were discerned. These experimental facts reinforced that no correlative inference can be formulated amongst T_c, solvent nature, and crystallographic phases.

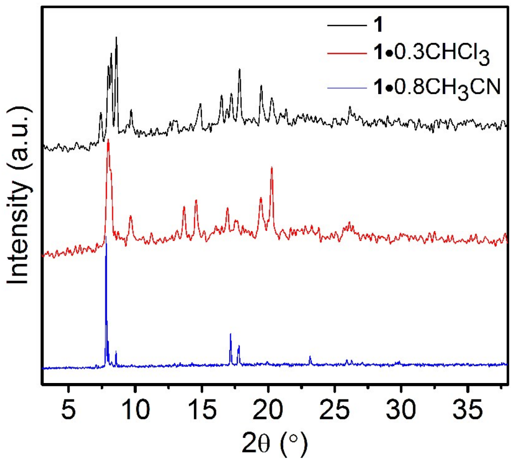

Figure 4. X-ray Powder diffractograms of crystalline samples of the complexes.

To conclude, herein we have presented a new tetradentate non-innocent ligand [$H_4L^{O(AP/AP)}$) that in the presence of Co(II)-salt, Et_3N and air forms $\{Co^{II}[(BQ\text{-}N\text{-}Cat)]_2\}^0$ complex. During the complex formation, a weak interaction between the Co center and the bridging O atom is postulated (Scheme S3, S10; Figure S7, S11). This interaction drives the formation of Co-O bond *via* homolytic phenolic C-O bond cleavage. The complex undergoes valence tautomerization in solution (Figure S11, S15) as well as in lattice solvent-containing solid phase. From the solid state X-band EPR measurements, it was confirmed that at room temperature (295 K), the complex exists as $\{Co^{II}[(BQ\text{-}N\text{-}Cat)]_2\}^0$, while, at low temperature (77 K) it exists as $\{Co^{III}[(SQ\text{-}N\text{-}Cat)(BQ\text{-}N\text{-}Cat)]\}^0$.

Variable-temperature magnetic susceptibility measurements on **1**, **1**•$0.3CHCl_3$ and **1**•$0.8CH_3CN$ again substantiate that the tautomerization is triggered by the presence of lattice solvent molecule. Interestingly, the process and the T_c value are almost independent to the nature of lattice-solvent and the corresponding crystallographic phase. Although, it appears that the valence tautomerization in the present system is governed by the change in temperature-dependent lattice packing-structure, a good quality crystal-structure would lead to confirmation. Therefore, in the near future a further study will be continued to have better quality crystals by using various others solvents for crystallization. Additionally, syntheses of other similar-type of ligands, where various different substituents would be attached at the main ligand-backbone, and their corresponding Co-complexes will also be continued to examine packing effect on valence tautomerization.

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8 Complex **1**•$0.3CHCl_3$: $\Delta H = 101\ kJ\ mol^{-1}$; $\Delta S = 825\ J\ K^{-1}\ mol^{-1}$; complex **1**•$0.8CH_3CN$: $\Delta H = 79\ kJ\ mol^{-1}$; $\Delta S = 618\ J\ K^{-1}\ mol^{-1}$; Calculations were performed based on the mole-fraction formula as described in reference 7c.