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Solid-state valence tautomeric octahedral {Co^II[(BQ-N-Cat)]_2}^0 complex formation via ligand-centered phenolic C−O bond breaking and Co−O bond making†

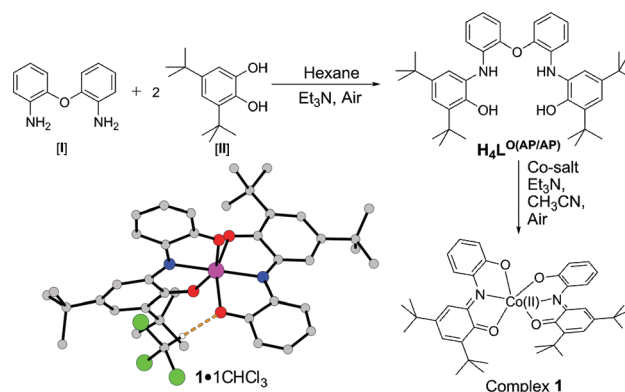Manas Kumar Mondal,[a] Archana Tiwari[b] and Chandan Mukherjee*[a]

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

Transition metal complexes, which are coordinated to redox-active ligands, have achieved great importance in the fields of biomimetic catalysis, C−H bond activation, C−C cross coupling, C−N bond activation, bistable as well as valence tautomeric complex formation, *etc.*[1–3] The redox-active ligands, which are coordinated to a metal ion, may exist in 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 and Co(II)-quinone electronic isomers is under progressive investigation because of the demand for the development of logic gates and bistable and spin-switch materials.[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 the general formula [Co^IIIE([SQ]^{•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 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 the square planar [Co^III([AP]^{2−})_2]^− complex the two coordinating-ligands orient in a *trans*-fashion. Thus, oxidative addition of both alkyl and halide units was not possible in the system.

As the foremost step to impose a non-coplanar arrangement between two radical-generation units, two H_2AP ligands were combined by a bridging O atom that connects the two ligands *via* the *ortho*-carbon atom of the two aniline moieties. The thus formed new ligand will be designated here as H_4L^{O(AP/AP)} (Scheme 1; Fig. S8, ESI†). 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*-alignments of the radical-generating 3,5-di-*tert*-butyl

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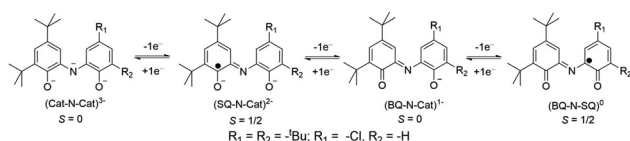
Scheme 1 Schematic representation of ligand H_4L^{O(AP/AP)} and complex **1** formation. X-ray molecular structure of complex **1**·1CHCl_3.

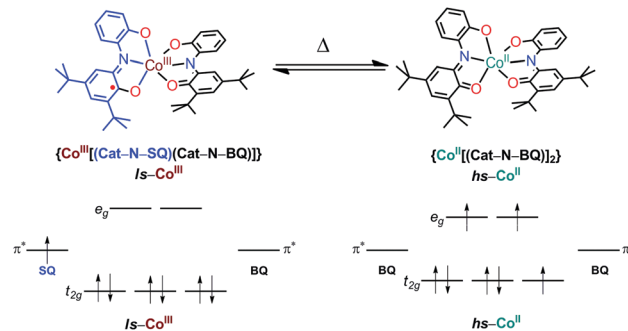amidophenolate units could be restricted and the required vacant site for *cis*-coordination might be availed.

Ligand $H_4L^{O(AP/AP)}$ was synthesized in 64% yield by reacting 1:2 2,2′-oxodianiline (**I**) with 3,5-di-*tert*-butyl catechol (**II**) in hexane in air in the presence of triethyl amine (Et$_3$N) [Scheme 1]. The ligand reacted with an equivalent amount of Co(ClO$_4$)$_2$·6H$_2$O or CoCl$_2$·6H$_2$O in CH$_3$CN in air for 7 hours in the presence of Et$_3$N and provided a blue-green solid (complex **1**). The solid upon recrystallization from a 5:2 CHCl$_3$:CH$_3$CN solvent mixture appeared as rectangular-shaped crystals (**1**·1CHCl$_3$). However, the crystals were not stable during X-ray diffraction measurement (Table S2, ESI†) even at 100 K. Hence, the molecular structure analysis of the formed complex **1**·1CHCl$_3$ [Scheme 1; Fig. S8; Tables S1 and S2, ESI†] was not worthy enough for the definite assignment of the oxidation state of the central metal ion as well as the coordinated ligands. Nevertheless, from the crystal-lographic 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.*, a new tridentate ligand was formed during the reaction *via* ligand-centered phenolic C–O bond cleavage.

Two analogous tridentate ligands, as present in complex **1**·1CHCl$_3$, are already available in the literature[5] and it has been demonstrated that the ligands may exist in their three different stable oxidation states in their 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-N-Cat)$^{1-}$ ligands, *i.e.*, {Co^{II}[(BQ-N-Cat)]$_2$}^{0} or (b) a Co(III) ($S_{Co(III)}$ = 0, low-spin) ion with coordinated paramagnetic (SQ-N-Cat)$^{2-}$ [S_L = 1/2] and (BQ-N-Cat)$^{1-}$ ($S_{L'}$ = 0) ligands, *i.e.*, {Co^{III}[(SQ-N-Cat)(BQ-N-Cat)]}^{0} (Scheme 3).

In order to distinguish between the two possible compositions, X-band EPR measurement on **1**·0.3CHCl$_3$[6] was performed at 77 K in a CH$_2$Cl$_2$/toluene solvent mixture (Fig. 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) × 10^{-4} cm^{-1}. Interestingly, it was observed that the signal vanished at 295 K. The temperature-dependent signal also held true for solid-state X-band EPR measurements of the complex (Fig. 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 the solid state the complex underwent valence tautomerization; at low temperature
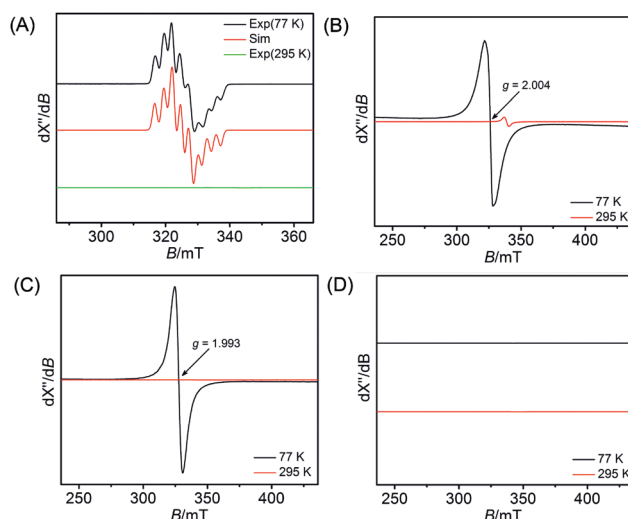

Scheme 3 Valence tautomeric species.

Fig. 1 X-band EPR spectra measured at 77 and 295 K; (A) complex **1**·0.3CHCl$_3$ in a CH$_2$Cl$_2$/toluene (2:1) solvent mixture; microwave frequency (GHz): 9.444; modulation frequency (kHz): 100; amplitude = 1.0; (B) complex **1**·0.3CHCl$_3$ in the solid state; microwave frequency (GHz): 9.142; modulation frequency (kHz): 100; amplitude (G) = 0.3; (C) complex **1**·0.8CH$_3$CN 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.

(77 K) the composition of the complex was Co(III), (SQ-N-Cat)$^{2-}$ and (BQ-N-Cat)$^{1-}$, while at 295 K both the coordinated ligands were in the (BQ-N-Cat)$^{1-}$ form and the central metal was Co(II). Vanishing of the X-band EPR signal at 295 K was due to zero-field splitting (>0.3 cm^{-1}) that resulted upon high spin–orbit coupling at Co(II). Herein, it is noteworthy that valence tauto-merization between octahedral {Co^{III}[(SQ-N-Cat)(BQ-N-Cat)]}^{0} and {Co^{II}[(BQ-N-Cat)]$_2$}^{0} is well known in solution; however, the phenomenon is absent in the solid state within the 2–295 K temperature range.[7]

Inspired by X-band EPR results, variable-temperature magnetic susceptibility measurement was carried out on a solid sample of complex **1**·0.3CHCl$_3$[6] at 1 T external magnetic field to reinforce the solid-state valence tautomeric nature of the complex. The $\chi_M T$ *vs.* T plot is depicted in Fig. 2. At 10 K, $\chi_M T$ = 0.44 emu K mol^{-1} was observed. This value was closely commensurate with the
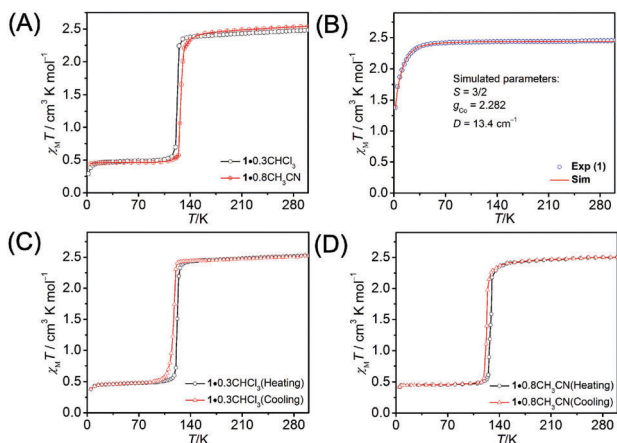

Scheme 2 Various possible oxidation states of (Cat-N-Cat)$^{3-}$ species.

Fig. 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$_3$ and (D) hysteresis measurement of **1**·0.8CHCl$_3$.

system having one-unpaired electron (an $S = 1/2$ spin). The value remained almost unchanged up to 118 K. Interestingly, in the 118 to 125 K temperature range a sharp transition in the 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 the ligand-centric SQ unit that then transformed to its one-electron oxidized BQ form (Scheme 3). Therefore, it can be argued that till 118 K the complex was existing in the $\{Co^{III}[(SQ\text{-}N\text{-}Cat)(BQ\text{-}N\text{-}Cat)]\}^0$ form, while above 125 K the complex continued to exist in the $\{Co^{II}[(BQ\text{-}N\text{-}Cat)]_2\}^0$ 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]

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, 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 was obtained from the 3 : 1 Et$_2$O : CH$_3$CN solvent mixture (Fig. S8D, ESI†). The nonexistence of solvent molecule was confirmed in the crystal (complex **1**) that was obtained from toluene (Fig. S8C, ESI†). Noteworthily, the quality of crystals was not good enough for the assignment of acute and appropriate oxidation states of ligands as well as the metal center (Tables S1 and S2, ESI†).

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 Fig. 2. The temperature-dependent change in $\chi_M T$ for **1**·0.8CH$_3$CN was very similar to that of **1**·0.3CHCl$_3$. However, T_c of **1**·0.8CH$_3$CN was slightly higher ($\sim$4.4 K) compared to that of **1**·0.3CHCl$_3$. Unlike solvated crystals, in the case of complex **1**, the $\chi_M T = 2.46$ emu K mol^{-1} value remained

almost constant in the temperature range 50–300 K. Upon further lowering the temperature, the $\chi_M T$ value decreased and reached 1.71 emu K mol^{-1} at 5 K. Herein, the decrease in the $\chi_M T$ value was due to zero-field splitting ($D = 13.4$ cm^{-1}, Fig. 2B) that arose because of strong spin–orbit coupling at the Co(II) center. Thus, it was apparently evident that in the absence of lattice solvent the complex remained in the $\{Co^{II}[(BQ\text{-}N\text{-}Cat)]_2\}^0$ form and no valence tautomerization took place.

The single-crystal volume of **1** increased with the incorporation of lattice solvent (Table S2, ESI†). Therefore, it was evident that the presence of lattice solvent molecules within the crystal lattice promoted flexibility or softness[3a,n] in the systems (Fig. S9 and S10, ESI†) and favored the required structural changes in the 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 (Fig. 3). The strong H-bonds, which can be considered as a stabilizing factor, presumably prevented complex **1** from undergoing any required structural change for valence tautomerization. The abrupt transition within a very small (7 K) temperature range (Fig. 2) in **1**·0.3CHCl$_3$ and **1**·0.8CH$_3$CN reinforced a strong cooperative effect[3a,n] that was propagated through the lattice solvent network (Fig. S9 and S10, ESI†). Although, the crystallographic phases and the nature of the lattice solvent molecule were different for the different complexes (Fig. 4), no consequence on the nature of transition, transition temperature, and hysteresis
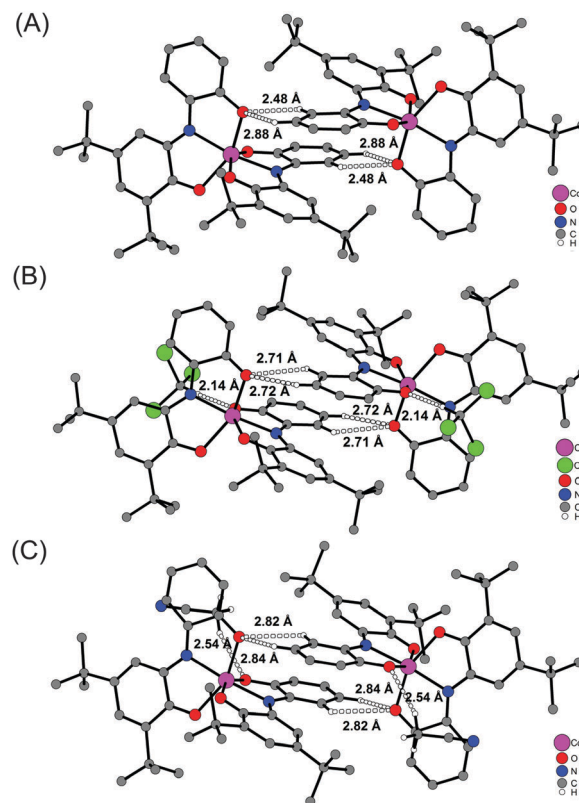

Fig. 3 H-bonds between the two adjacent molecules: (A) complex **1**, (B) complex **1**·1CHCl$_3$, and (C) complex **1**·1CH$_3$CN.
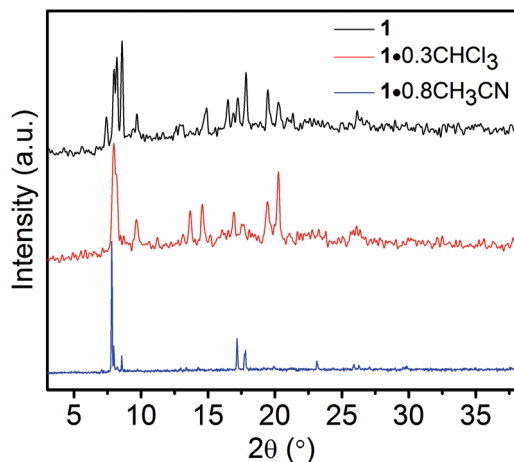
Fig. 4 X-ray powder diffractograms of crystalline samples of the complexes.

effect (Fig. 2C and D) was discerned. These experimental facts reinforced that no correlative inference can be formulated amongst T_c, solvent nature, and crystallographic phases.

To conclude, herein we have presented a new tetradentate non-innocent ligand $[H_4L^{O(AP/AP)}]$ which in the presence of Co(II)–salt, Et_3N and air forms a $\{Co^{II}[(BQ\text{-}N\text{-}Cat)]_2\}^0$ complex. During the complex formation, a weak interaction between the Co center and the bridging O atom is postulated (Scheme S3; Fig. S7, ESI†). This interaction drives the formation of Co–O bond *via* homolytic phenolic C–O bond cleavage. The complex undergoes valence tautomerization in solution (Fig. S11, ESI†) as well as in the 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 a 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**, **1·0.3CHCl₃** and **1·0.8CH₃CN** again substantiate that the tautomerization is triggered by the presence of the lattice solvent molecule. Interestingly, the process and the T_c value are almost independent of 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 the temperature-dependent lattice packing-structure, a good quality crystal-structure would lead to confirmation. Therefore, in the near future further studies will be conducted to have better quality crystals by using various other 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 conducted to examine the packing effect on valence tautomerization.

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8 Complex **1·0.3CHCl₃**: $\Delta H = 101$ kJ mol^{-1}; $\Delta S = 825$ J K^{-1} mol^{-1}; complex **1·0.8CH₃CN**: $\Delta H = 79$ kJ mol^{-1}; $\Delta S = 618$ J K^{-1} mol^{-1}; calculations were performed based on the mole-fraction formula as described in ref. 7c.