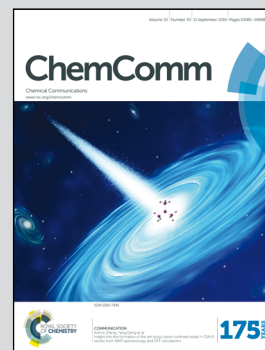


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An elusive vinyl radical isolated as an appended unit in a five-coordinate Co(III)–bis(iminobenzosemiquinone) complex formed *via* ligand-centered C–S bond cleavage

Ligand-centred C–S bond cleavage leads to an elusive vinyl radical formation. X-Ray single crystal, X-band EPR spectrum, variable-temperature magnetic susceptibility measurements and DFT calculations confirm that the radical is being stabilized as an appended unit in the corresponding five-coordinate Co(III)–bis(iminosemiquinone) complex.

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An elusive vinyl radical isolated as an appended unit in a five-coordinate Co(III)–bis(iminobenzo-semiquinone) complex formed *via* ligand-centered C–S bond cleavage†

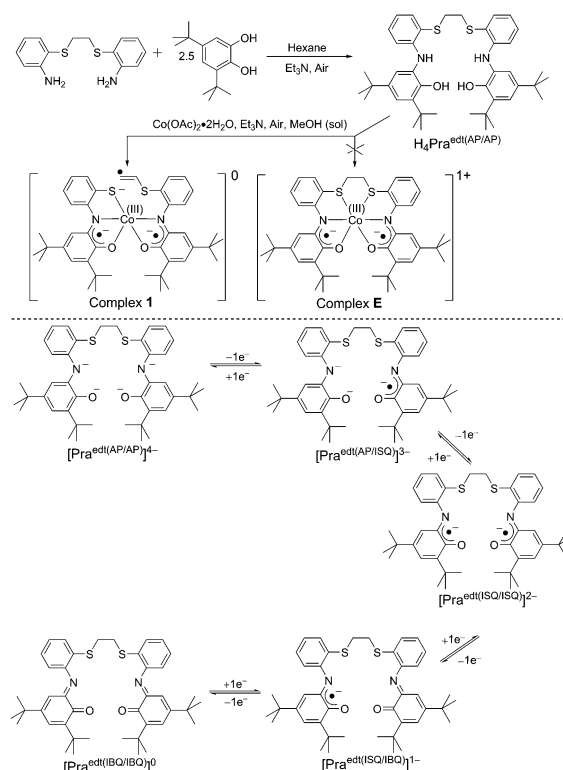
Prasenjit Sarkar,^a Archana Tiwari,^b Amrit Sarmah,^c Subhrajyoti Bhandary,^d Ram Kinkar Roy^c and Chandan Mukherjee^{*a}

Redox-active ligand $H_4Pra^{edt(AP/AP)}$ experienced C–S bond cleavage during complexation reaction with $Co(OAc)_2 \cdot 2H_2O$ in the presence of Et_3N in CH_3OH in air. Thus, formed complex 1 was composed of two iminobenzo-semiquinone radicals in its coordination sphere and an unprecedented stable tethered-vinyl radical. The complex has been characterized by mass, X-ray single crystal, X-band EPR, variable-temperature magnetic moment measurements and DFT based computational study.

Since the last decade transition metal complexes with redox-active (non-innocent) ligands have received special attention for the homolytic cleavage of homodiatom or heterodiatom bonds.¹ In the process, an electron transfer takes place favorably from the coordinated non-innocent ligand to the bond without any change in the metal oxidation state. Hence the oxidation state of the ligand increases by one unit. An electron transfer from a metal complex to a bond generates a radical species, which generally being very reactive combines with another radical centre to proceed finally to a non-radical-containing stable species. Hence, such stable radical-containing species are very scarce and demand special attention.

In continuation of our ongoing research in understanding homolytic bond cleavage and stabilization of transient radical-containing species in the presence of non-innocent ligands, we have combined two non-innocent 2-anilino-4,6-di-*tert*-butylphenol

$\{H_2[AP^{H}]\}^2$ ligands with a 1,2-ethanedithiolate unit. Each S atom of the dithiolate unit was attached at the *ortho*-position to each aniline moiety from the two $H_2[AP^{H}]$ ligands. Thus the designed ligand will be designated here as $H_4Pra^{edt(AP/AP)}$ (Scheme 1).³ The hexadentate ligand should be capable of undergoing six-coordination with a central metal ion, and we envisaged that in the formed complex the ligand might exist in its radical form (Scheme 1). Under the circumstances, the 1,2-phenylthioethane unit of the ligand backbone could behave as a substrate and might experience homolytic C–S and/or C–C bond cleavage in the thioethane unit by accepting an electron



Scheme 1

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† Electronic supplementary information (ESI) available: Synthesis and characterization of the ligand, and complex 1; DFT based computational study; a table providing bond distances and bond angles for the complex; crystallographic data and structure refinement parameters; and the proposed mechanism for the formation of complex 1. CCDC 1468751. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c6cc02751b

from the non-innocent coordinating ligand part. The formed radical in the scission could then be stabilized *via* a conjugation effect. Therefore, the isolated final product (complex) could be a transient radical-containing species.

In this report we discuss the synthesis and characterization of ligand $\text{H}_4\text{Pra}^{\text{edt}(\text{AP}/\text{AP})}$ and its corresponding Co complex (complex **1**). X-ray single crystal analysis confirmed the cleavage of a C–S bond and the existence of both coordinated amido-phenolate C_6 rings in their one-electron oxidized iminobenzosemiquinone (ISQ^{1-}) state. Interestingly, it has been observed that the vinyl unit, which formed as a result of the C–S bond cleavage, actually existed as a vinyl radical. The room temperature X-band EPR spectrum as well as solid state magnetic moment measurements confirmed the paramagnetic nature of complex **1**. To the best of our knowledge this is the first report that demonstrates the isolation, characterization, and stabilization of a transient vinyl radical.

Ligand $\text{H}_4\text{Pra}^{\text{edt}(\text{AP}/\text{AP})}$ was synthesized in 71% yield by reacting one equivalent of 1,2-bis(aminophenylthio)ethane with 2 equivalents of 3,5-di-*tert*-butyl-catechol in air in the presence of triethylamine (Et_3N) in hexane (Scheme 1). The ligand upon reacting with an equivalent amount of $\text{Co}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ in the presence of Et_3N in air in methanol provided complex **1** as a violet color solid in good yield (Scheme 1). Single crystals suitable for X-ray diffraction analysis were grown by slow evaporation of a 4 : 1 CHCl_3 : CH_3OH solvent mixture. Interestingly, the skeleton of the coordinated ligands in the complex was different than that of the initially employed ligand $\text{H}_4\text{Pra}^{\text{edt}(\text{AP}/\text{AP})}$ (*vide infra*) and a C–S bond cleavage in the ligand backbone during the complex formation was warranted.

The composition and confirmation of formation of the ligand as well as complex **1** were examined by the electrospray ionization (ESI) mass spectrometric method in a positive mode in CH_3CN solution. The mass spectrum of the ligand showed a 100% molecular ion peak at $m/z = 685.39$ amu, which corresponded to the composition $\text{C}_{42}\text{H}_{57}\text{N}_2\text{O}_2\text{S}_2$ as evident from isotope pattern distribution analysis (Fig. S2 and S5, ESI†). The composition confirmed the formation of the expected ligand $\text{H}_4\text{Pra}^{\text{edt}(\text{AP}/\text{AP})} = \text{C}_{42}\text{H}_{56}\text{N}_2\text{O}_2\text{S}_2$ and the observed peak corresponded to the expected $[\text{H}_4\text{Pra}^{\text{edt}(\text{AP}/\text{AP})} + \text{H}]^+$ species. A 100% molecular ion peak at $m/z = 738.14$ amu appeared for complex **1**. Isotope pattern distribution indicated that the peak corresponded to the $\text{C}_{42}\text{H}_{51}\text{N}_2\text{O}_2\text{S}_2\text{Co}$ composition and $z = 1$ (Fig. S6 and S7, ESI†). Noteworthy, complex **1** was neutral in charge (*vide infra*). Therefore, the composition of the complex would be $\text{C}_{42}\text{H}_{50}\text{N}_2\text{O}_2\text{S}_2\text{Co} = \text{C}_{42}\text{H}_{51}\text{N}_2\text{O}_2\text{S}_2\text{Co}-\text{H}$, *i.e.*, one hydrogen atom less than the found $\text{C}_{42}\text{H}_{51}\text{N}_2\text{O}_2\text{S}_2\text{Co}$ composition. This clearly confirmed that the employed ligand ($\text{C}_{42}\text{H}_{56}\text{N}_2\text{O}_2\text{S}_2$) lost six hydrogen atoms after the complex formation. It was expected that the ligand would lose four hydrogen atoms in the form of protons from two aminophenol units to generate two amido-phenolate units. Therefore, the loss of other two hydrogen atoms was definitely from the other part of the ligand backbone. It has been found by molecular structure analysis that the loss of two protons was from the ethane moiety (*vide infra*). Thus, the ESI mass spectrum of complex **1** supported the composition

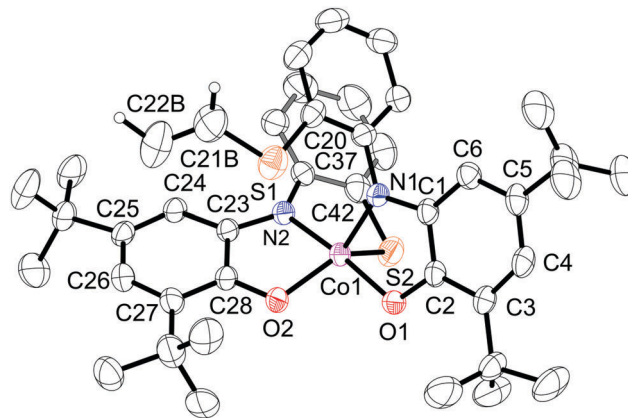


Fig. 1 ORTEP representation of **1**; thermal ellipsoids were drawn at the 50% probability level. H atoms, except for two H atoms attached in the S1–C21A–C22A unit, and the solvent molecule CHCl_3 were omitted for clarity.

$\text{C}_{42}\text{H}_{50}\text{N}_2\text{O}_2\text{S}_2\text{Co}$ and a difference of six hydrogen atoms between the employed ligand and the ligand backbones present in complex **1**.

X-ray single crystal diffraction measurement for complex **1**· CHCl_3 was performed at 293(2) K. The complex crystallized in the monoclinic space group $P2_1/c$. The molecular structure with the numbering scheme is shown in Fig. 1. Selected bond distances and bond angles are listed in Tables S1 and S10 (ESI†).

In neutral complex **1**, the central Co atom was five-coordinate. $\tau_5^4 = 0.72$ indicated distorted trigonal bipyramidal geometry around the Co atom. The largest angle around the Co atom was $\text{O1}-\text{Co1}-\text{N2} = 174.63(11)^\circ$. Therefore, $\text{Co1}-\text{O1}$ and $\text{Co1}-\text{N2}$ have been assigned as the two axes and thus, N1 , O2 , and S2 atoms constructed the basal plane. The $\text{Co1}-\text{N1} = 1.858(3)$, $\text{Co1}-\text{N2} = 1.874(3)$, $\text{Co1}-\text{O1} = 1.887(2)$, $\text{Co1}-\text{O2} = 1.858(2)$, and $\text{Co1}-\text{S2} = 2.2069(12)$ Å bond distances were in accord with the previously reported low-spin $\text{Co}(\text{III})-\text{N}$, $\text{Co}(\text{III})-\text{O}$, and $\text{Co}(\text{III})-\text{S}$ bonds.^{5,6} Hence, the oxidation state of the central Co1 atom has been assigned as III.

All the C–C bond distances of the two *tert*-butyl group-containing C_6 aryl rings were not the same and within 1.39 ± 0.01 Å (Table S1 and S10, ESI†). Rather, alternating short–long–short bonds followed by three long bonds have been observed. This type of bond arrangement in a C_6 ring is known as quinoid-type distortion and found in one-electron as well as two-electron oxidized aryl ring systems. The $\text{C1}-\text{N1} = 1.354(4)$, $\text{C2}-\text{O1} = 1.297(4)$, $\text{C23}-\text{N2} = 1.357(4)$, and $\text{C28}-\text{O2} = 1.305(4)$ Å bond distances were between their corresponding single bond (C–N = 1.46, C–O = 1.38 Å) and double bond (C = N = 1.30, C=O = 1.22 Å) values. These bond distances were in accord with the previously reported iminobenzosemiquinone systems⁷ and thus, confirmed the one-electron oxidized iminobenzosemiquinone form (ISQ^{1-}) for both *tert*-butyl group-containing aryl moieties.

The $\text{C20}-\text{S1} = 1.770(4)$ and $\text{C42}-\text{S2} = 1.743(4)$ Å bond distances corresponded to the previously reported thiophenolate bonds.⁶ Therefore, both the bonds exhibited single bond character and S2 that attached to the central Co1 atom was in S^{1-} form. $\text{C21B}-\text{S1} = 1.743(8)$ was found to be slightly shorter compared to aliphatic

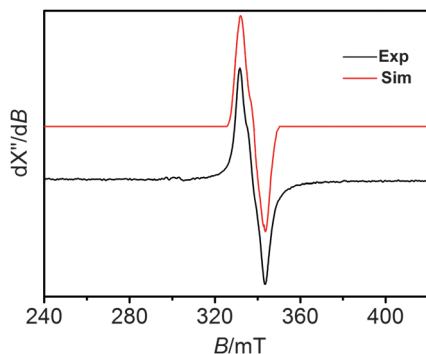


Fig. 2 Experimental (Exp) and simulated (Sim) X-band EPR spectra of complex **1**. Experimental conditions: microwave frequency (GHz): 9.443; modulation frequency (kHz): 100; power (mW) = 0.995; amplitude (G) = 100.0.

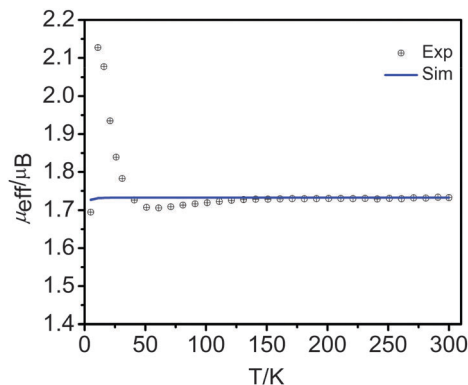


Fig. 3 μ_{eff} vs. T plot of complex **1**: CHCl_3 . Simulation was performed by using: $S = 1/2$ and $g = 2.00$.

C–S = 1.82 Å and C21B–C22B = 1.358(15) Å bond distances were slightly longer compared to C = C = 1.34 Å bond distances. The C21 and C22 atoms were disordered and thus very precise C21–C22 and C21–S1 bond distance values could not be obtained. The complex was neutral in charge; hence, the locus of the unpaired electron has been assigned to the C22 atom.

The X-band EPR spectrum of complex **1** was measured at room temperature in CHCl_3 solution (Fig. 2). The EPR spectrum was computer-simulated using the following parameters: $S = 1/2$, $g_1 = 1.967$, $g_2 = 1.990$, $g_3 = 2.035$; $^1\text{H}(A_1, A_2, A_3) = (12, 30, 16) \times 10^{-4} \text{ cm}^{-1}$. $g_{\text{iso}} = 1.997$ confirmed that the signal appeared because of an organic radical. The hyperfine coupling constant indicated the interaction of the unpaired electron, *i.e.* vinyl radical, with H atoms that were attached at C21A and C22A (Fig. 1).

Room temperature magnetic moment measurement in CDCl_3 using Evan's method (Fig. S8, ESI[†]) showed an effective magnetic moment (μ_{eff}) of $1.62 \mu_{\text{B}}$. This indicated that there was a single unpaired electron, which was most possibly an organic radical in nature.

Variable-temperature magnetic susceptibility measurement on solid **1**: CHCl_3 was carried out at 1 T external magnetic field (Fig. 3). Throughout the temperature range 300–110 K, $\mu_{\text{eff}} = 1.733 \mu_{\text{B}}$ remained almost unchanged and indicated that the magnetic moment appeared due to only one unpaired electron, which was an organic radical in nature ($S = 1/2$, and $g \sim 2.003$). Interestingly, a subtle decrease ($0.02 \mu_{\text{B}}$) followed by a step increase ($0.41 \mu_{\text{B}}$) in the magnetic moment in the temperature range 50–10 K was observed. Indeed, three unpaired electrons were present in the complex. The unpaired electrons would provide at the ground state either an $S = 3/2$ or an $S = 1/2$ *via* ferromagnetic coupling amongst the spins or antiferromagnetic coupling amongst the two $S = 1/2$ spins, respectively. The magnetic moment values (1.733 – $1.712 \mu_{\text{B}}$) in the 300–50 K temperature range emphasized that a very strong antiferromagnetic coupling prevailed between the two unpaired electrons. We concluded that two iminobenzosemiquinone π -radicals that were coordinated to the central low-spin Co(III) centre coupled antiferromagnetically through the filled metal-centred π -symmetric t_{2g} set of orbitals. Thus, the magnetic moment in the temperature

range arose due to the presence of an unpaired electron as the stable vinyl radical ($S = 1/2$) in complex **1**. The sharp transition in the magnetic moment below 50 K was possibly due to a ferromagnetic phase transition that transferred the system to the higher $S = 3/2$ spin state from the $S = 1/2$ spin state. Further magnetic studies are ongoing and will be reported elsewhere.

Computational study: The computational details are given in the ESI.[†] The optimized structure of the complex along with geometrical parameters (selected bond distances) is reported in Fig. S9 (ESI[†]). It is noteworthy that the optimized geometrical parameters correlate well with the experimental X-ray data.

We have thoroughly examined the distribution of the radical electron cloud on complex **1**. The presence of unpaired electrons (radicals) over both the five-membered rings containing Co, N and O atoms and the pendent vinyl unit was well established from the experimental results. The findings of high level DFT calculations were also unambiguous to the experimental facts. Apparently, the SOMO (singly occupied molecular orbital) plot (Fig. 4) provided strong evidence for the presence of delocalized radical electron density on the appended vinyl carbon unit adjacent to the sulfur atom (S1), and expectedly, on the two five-membered rings. The computed spin density plot (Fig. 4) provided further evidence for the existence of a significantly large amount of unpaired electron density at the C22 atom of the vinyl fragment. The natural bond orbital (NBO) analysis provided vital information to elucidate the hybridization and bond order of the appended S1–C21–C22 unit. The S1 atom was in the sp^3 hybridized state (electronic charge 0.307) and the S1–C21 bond

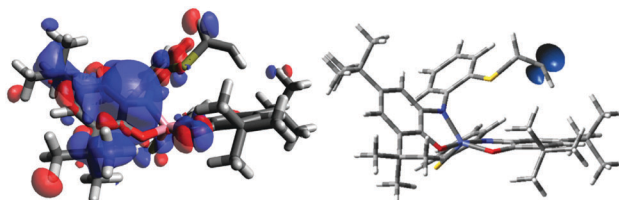


Fig. 4 Left: singly occupied molecular orbital (SOMO) computed at the PBEPBE/def2-TZVP level (iso-value = 0.03). Probability decreases from blue to red. Right: Spin density plot computed at the PBEPBE/def2-TZVP level (iso-value = 0.03). Blue color indicates the location of unpaired electrons.

order was one. The NBO analysis showed that C21 was sp^2 hybridized (electronic charge -0.514) and the C21–C22 bond order was 2. The adjacent C22 atom was sp^2 hybridized and accommodated a less negative charge (-0.053) on it. Complementary evidence was obtained by analyzing the electrostatic potential map (Fig. S10 and S9, ESI†). All the above inferences clearly showed the existence of a radical in the appended S1–C21–C22 unit.

To summarize, herein we have demonstrated the formation of a mononuclear five-coordinate Co(III) complex *via* ligand centered C–S bond cleavage. X-ray single crystal molecular structure analysis confirms that in the complex the central Co(III) ion is coordinated to two iminobenzosemiquinone radical anions and a thiophenolate unit. In the complex, a stable vinyl radical is present in the appended S1–C21B–C22B moiety. DFT analysis further confirms the presence of a vinyl radical in complex **1**. The paramagnetic nature ($S = 1/2$) of complex **1** with a radical-centered unpaired electron is evinced by both X-band EPR spectrum analysis and variable-temperature magnetic moment measurements.

To date, no stable vinyl radical has been reported. Herein, the stability of the vinyl radical possibly arises due to the interaction of the unpaired electron with the antibonding σ^* orbital of the C21–S1 bond and weak stacking interaction of the radical with the 3,5-di-*tert*-butyl-iminosemiquinonato unit that lies beneath the vinyl unit. Although further studies are required for a better understanding of the mechanism behind the formation of complex **1**, it seems that the reaction proceeds *via* the hemolytic cleavage of an aliphatic C–S bond that leads to the formation of a sulfanyl radical and thioethyl radical ($-S-CH_2-CH_2^\bullet$) [Fig. S11 and S10, ESI†]. The ethyl radical unit releases a hydrogen atom and becomes vinyl. Meanwhile, the formed sulfanyl radical abstracts a hydrogen atom from the vinyl unit and generates the vinyl radical. The resulting thiophenol unit releases a proton and then undergoes coordination to the central Co(III) ion (Fig. S11 and S10, ESI†).

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