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Metal ion promoted tautomerization and C-N bond cleavage: conversion of catechol to a p-benzoquinone derivative†

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Catechols and p-benzoquinones are redox active agents which participate in several biological electron transfer reactions.1,2 Although the transformations of catechols to o-benzoquinones and p-hydroquinones to p-benzoquinones and vice versa are common in chemistry, the interconversion of catechol to p-benzoquinone is not achieved so far. In this communication, we report the conversion of catechol to a p-quinone derivative by two-step reactions which involve the transformation of catechol to 2,5-bis(p-tolylamino)-4-p-tolyliminobenzoquinone (Qp,NO) followed by a metal promoted tautomerization and a C-N bond cleavage leading to the formation of a p-benzoquinone derivative. The metal promoted conversion/interconversion of redox noninnocent quinone ligands is relevant to predict the structures of the quinoproteins3 and the area is a subject of topical interest to model tautomeric molecular switches4 and new coordination complexes.5 Metal promoted tautomerization was reported first by Kaim et al6 in an azophenine ligand having ground electronic state similar to Qp,NO. Recently, the coordination chemistry of azophenine,7 2,5-diamino-1,4-benzoquinonedimine,8 1,2,4,5-tetra(alkylamine)benzene9 and zwitterionic N-substituted benzoquinone monomine10 as bridging ligands in different aspects was reported. The coordination chemistry of Qp,NO11 is not explored so far.

In this investigation, palladium(II) ion promoted tautomerization of Qp,NO to 3-hydroxy-4-(p-tolylamino)-o-bis(p-tolyliminobenzoquinone) (Qp,NN) affording [PdII(Qp,NN)Cl2] (1) in good yields was authenticated. The similar reaction of Qp,NO with RhCl3 in presence of PPh3 as co-ligands in moist MeCN/EtOH progresses further surprisingly with a C-N bond cleavage affording [RhIII(PPh3)(p-toluidine)(MeCN)Cl] (2) and 2,5-bis(p-tolylamino)-p-benzoquinone (Qp,OO)12 as products as shown in Scheme 1. Details of all the synthetic reactions are outlined in the experimental section (ESI†). The probable paths of formation of Qp,NO from catechol are depicted in Scheme 2.

The tautomerization and the cleavage reaction of Qp,NO as illustrated in Scheme 1 were established by the isolations of the related products which were characterized by the analytical data. IR, mass, 1H and 13C NMR, UV-vis absorption spectra including the single crystal X-ray structure determinations of Qp,NO, 1 and 2. Energies of the tautomers of Qp,NO and Qp,NN are analyzed by the density functional theory (DFT) calculations at
the B3LYP level of the theory \textit{(vide infra)}.

The coordination of palladium(II) ion to Q3-NO promotes a proton transfer generating Q3-NO complex of palladium(II) ion. On the contrary, the reaction of Q3-NO with RhCl3 and PPh3 as cosoligands in moist MeCN/EtOH mixture promotes the tautomerization and a hydrolytic cleavage of the coordinated \textit{=}N-p-tol group trans to keto group producing \textit{p}-benzoquinone (Q4-NO) and \textit{p}-toluidine which coordinates to rhodium(III) ion affording orange 2. The reaction progresses with a diminobenzenemiquinone anion radical13 intermediate of rhodium (III) ion (Chart 1(a)) detected by the EPR spectrum of the frozen reaction mixture at 150 K with the g parameter at 1.996 as shown in Fig. 1(a). The probable paths of the cleavage reaction are depicted in Scheme 3. It is noteworthy that under this experimental condition (1:1 acetonitrile and ethanol and without rhodium precursor), Q3-NO does not undergo any hydrolysis reaction. In dry solvents and in absence of moisture, 2 was not obtained. It is observed that the reaction of RhCl3 with PPh3 and \textit{p}-toluidine affords 2, similarly the reaction of H2[PtCl4] with \textit{p}-toluidine produces trans-[PtCl4(\textit{p}-toluidine)]2,14 However, boiling of 1 in MeCN/EtOH mixture does not undergo any cleavage reaction inferring that the hydrolytic cleavage reaction is rhodium ion selective.

The Q3-NO exhibits the mass peak (m/z) at 317.96 and 316.95 (Fig. S1, ESI1); the calculated mass of Q3-NO is 318.14. The absorption bands due to stretching vibrations of C=O and N-H of

\begin{figure}[h]
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\includegraphics[width=\textwidth]{chart1.png}
\caption{Chart 1}
\end{figure}

\begin{figure}[h]
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\includegraphics[width=\textwidth]{scheme3.png}
\caption{Scheme 3}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig2.png}
\caption{UV-vis absorption spectra of Q3-NO (black), 1 (red) and 2 (green) in CH2Cl2 at 298 K.}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig3.png}
\caption{Molecular geometries of (a) Q3-NO-MeCN (b) 1.0EtOH (Pd(1)) \& (N1)(2), 2.010(2); Pd(1)(N8)(2), 2.017(2); Pd(1)-C(1)(2), 2.278(2); Pd(1)(C)(2) \& (2), 2.280(2); and (c) 2 (Rh(N20)(2), 2.1624(2); Rh-N10(2), 2.017(4); Rh-N10(2), 2.397(2); Rh-C(2) (2), 2.314(2); Rh-C(3)(2), 2.371(2)) in crystals (H atoms and solvents are omitted for clarity) (d) comparison of significant bond lengths of Q3-NO-MeCN and 1.0EtOH.}
\end{figure}
depicted in Fig. 3(a). Significant bond parameters are summarized in the panel (d) of Fig. 3. The bond length trend with the quinoidal distortion of the central phenyl ring corroborates well with the p-iminobenzoquinone state of the ligand. C(7)-N(8) and C(4)-O(29) lengths are 1.287(2) and 1.236(2) Å. The C(2)-C(3) and C(5)-C(6) bond lengths are relatively shorter than those observed in an aromatic ring. However, the C(4)-C(5) and C(2)-C(7) lengths are longer than average aromatic C-C lengths. In comparison to those expected in an aromatic amine compound, C(2)-N(1) and C(5)-N(21) bonds in Q_{p,NO} crystallize in \P1 space group. The molecular geometry and the atom labelling scheme are shown in Fig. 3(b).

The significant bond parameters are listed in panel (d) and under the caption of Fig. 3. PdN_2Cl_2 sites including the central phenyl ring are planar. Significant changes of the C(4)-O(29) and C(2)-N(1) bond lengths in going from Q_{p,NO} to 1. EtOH are recorded. In 1.EtOH, C(4)-O(29) lengthens to 1.321(2) from 1.237(2) Å, while the C(2)-N(1) length shortens to 1.309(3) from 1.335(2) Å that is observed in Q_{p,NO}. The C-N and C-O bond length features in 1.EtOH do not correlate with the Q_{p,NO} tautomer. C(4)-O(29) length is much longer than a C=O length, while the C(5)-N(21) length, 1.350(3) Å, does not change notably. The C(7)-N(8) bond length is 1.322(2) Å. Further, the shortening of C(3)-C(4) length is consistent with the existence of Q_{NN} state of the ligand in 1.EtOH.метрический параметр анализ подтвердил таутомерию Q_{p,NO} в Q_{NN} in 1.EtOH. In 1.EtOH, the two halves five-centered 6π delocalization units which correlate to the Q_{p,NO} state in 1.EtOH. In the MeCN to 1.EtOH crystallization, the molecular coordinates almost linearly with a Rh-N-C angle of 170.1° while the p-toluidine molecules coordinates angularly with a Rh-N-C angle of 119.2° (Table S4, ESI). The significant bond parameters of the coordination sphere are listed under the caption of Fig. 3. The MeCN ligand coordinates almost linearly with a Rh-N-C angle of 170.1° while the p-toluene molecules coordinates angularly with a Rh-N-C angle of 119.2° (Table S4, ESI).

The redox activities of Q_{p,NO} and 1 were investigated by cyclic voltammetry. The redox potential data referenced to the ferrocenium/ferrocene, Fe^*/Fc, couple are summarized in Table 1 and the voltammograms are shown in Fig. S2. The anodic waves of both the molecules are irreversible, while the cathodic wave of 1 at -1.33 V is quasi reversible. EPR spectrum of [1] at 298 K (Fig. 1(b)) corresponding to the g value at 1.992 authenticated that the cathodic peak is because of the Q_{NN} p, NO/NN couple. Q_{NN} is a diminozenosemiquinone anion radical as shown in Chart 1(b) and [1] is defined as [Pd(Q_{p, NO}^2-Cl)_2].

Ground state energies of the four tautomers, Q_{p,NO}, Q_{p,NN}, Q_{p,NN} and Q_{p,NO} as illustrated in Chart 2(a) are calculated at the B3LYP/DFT level (Tables S5-S12, ESI). The calculations reveal the minimum ground state energy of the Q_{p,NO} tautomer while upon coordination to a zinc(II) ion having crystal field stabilization energy zero, Q_{p,NN} tautomer has the least energy as shown in Chart 2(b). The observations correlate well with the isolation of Q_{p,NO} as the only quinone derivative that turns to Q_{p,NN} tautomer in 1 (Chart 2(a)). Molecular orbital analyses have detected the two halves five-centered delocalization units in Q_{p,NO} and 1, which are illustrated in Fig. 4. The features are consistent with the bond parameters obtained from the single crystal X-ray determinations of Q_{p,NO} and 1.EtOH as listed in Tables S2-S3 (ESI). TD DFT calculations elucidated that the lower energy absorption band of 1 which is absent in Q_{p,NO}, is because of the palladium (II) ion to Q_{p,NN} charge transfer (Tables S13-S14 and Fig. S3-S4, ESI).

### Conclusion

In conclusion, a path of conversion of catechol to p-quinone derivatives is authenticated.

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### Notes and references
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