Inorganic Chemistry Communications 159 (2024) 111704

Contents lists available at ScienceDirect

Inorganic Chemistry Communications

journal homepage: www.elsevier.com/locate/inoche

Short communication

Cobalt(III) complex with a redox non-innocent bis (o-aminophenol)

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ARTICLE INFO

Keywords:
Cobalt complex
Redox non-innocent ligand
Crystal structure
Oxidation states

ABSTRACT

The redox non-innocent ligand bis(*o*-aminophenol) N,N′-bis(3,5-di-tertbutyl-2-hydroxy-phenyl)-1,2-phenylenediamine, H_4L, reacts with $CoCl_2{\cdot}6H_2O$ in a methanol solution under aerobic conditions to form $[Co(HL)_2]$. Both bis(*o*-aminophenol) ligands coordinate as tridentate and the ligand set can be described as a resonance structure of two partially oxidized ligands, while the formal oxidation state of the metal centre appears as + III. In this resonance structure, one ligand carries an odd electron, which makes the Co(III) complex paramagnetic.

Made known to almost six decades ago, coordination compounds with redox non-innocent ligands have been extensively studied for their fascinating and unusual behaviour.[1] By definition, a ligand is called as 'redox non-innocent' if it reacts with metal precursors to form complexes where the oxidation states of the ligand and the metal atom cannot be unquestionably defined.[2,3] The motivation for this research has predominantly been in the development of new homogenous catalysts, which could use these ligands as electron reservoirs during the catalytic cycles. Such redox non-innocent ligands can be, for example, simple molecules, e.g. O_2, NO, CO, synthetic non-saturated molecules, e.g. catechols or o-aminophenols, or large biomolecules.[4,5] Certainly, o-aminophenols and their derivatives are archetypical examples on chelating non-innocent ligands that can coordinate to the metal centres to form five-membered rings.[6,7] For instance, N,N′-bis(3,5-di-tertbutyl-2-hydroxy-phenyl)-1,2-phenylenediamine, H_4L, which was first published by Wieghardt at the turn of the millennium, combines two o-aminophenol moieties to offer a potentially tetradentate coordination mode, whereas the electrochemical behaviour of H_4L allows five possible oxidation states as illustrated in Scheme 1 [8].

The rich redox-chemistry as well as the ability to coordinate to different transition metals have motivated researchers to utilize H_4L for the syntheses of several metal complexes in 1:1 and 2:1 stoichiometries, sometimes supported with other ligands. [9–17] Besides the redox processes and the formation of stable radical species, H_4L can undergo other structural reorganisations upon coordination. Particularly, Lesh et al. demonstrated in 2012 that an intra-ligand cyclisation occurs when H_4L is allowed react to with anhydrous $CoCl_2$ under open atmosphere in the presence of a base. Instead to the formation of Co species with coordinated ligands L, the reaction yielded $[Co(L')_2]$, a low-spin Co(III) complex of phenoxide/phenoxazine radical ligand species (Scheme 2a).[14] This reactivity of $CoCl_2$ with H_4L was reported to differ from that of $MnCl_2$ or $FeCl_3$,which did not result in such ligand rearrangement under identical conditions, but the isolated products were $[Mn(HL)_2]$ and [Fe(L)Cl], respectively.[14] Similarly, the use of Ni(II) precursor leads to formation of $[Ni(HL)_2]$, which has closely similar bonding parameters and molecular geometry to $[Mn(HL)_2]$.[17] Recently, we prepared an Fe(III) complex $[Fe(HL)_2]$ using the reaction of anhydrous $FeCl_3$ with two equivalents of H_4L and further converted the product to $[Fe(L')_2]$ by allowing it to react with atmospheric oxygen in basic acetonitrile solution.[16] The overall molecular structure of $[Fe(L')_2]$ is closely similar to $[Co(L')_2]$, although the electronic states of the ligands were not exactly identical.

To complete our studies on the transition metal complexes of this fascinating non-innocent ligand, we re-examined the reaction of H_4L with $CoCl_2$ by making slight modifications on the initial experimental conditions.[14] Namely, Et_3N in acetonitrile was used in the original reaction to deprotonate the ligand precursor to produce $[Co(L')_2]$ (Scheme 2a), but when we carried out the reaction of $CoCl_2{\cdot}6H_2O$ with H_4L in a methanol solution in the absence of any additional base, complex $[Co(HL)_2]$ was formed as a only isolable product (Scheme 2b, see Supplementary material for details).

Single-crystal X-ray studies revealed that in solid state, the molecular complex $[Co(HL)_2]$ (Fig. 1) is isomorphous with $[Mn(HL)_2]$ and it is practically isostructural with above-mentioned Mn, Fe and Ni complexes (Table 1) (see Tables S1 and S2 in the supplementary material).

The two Co-O distances (1.928, 1.939 Å) as well as all four Co-N distances (1.862–1.946 Å) are rather short, indicating a low-spin Co(III) central ion.[18,19] The oxidation state of the metal centre in redox

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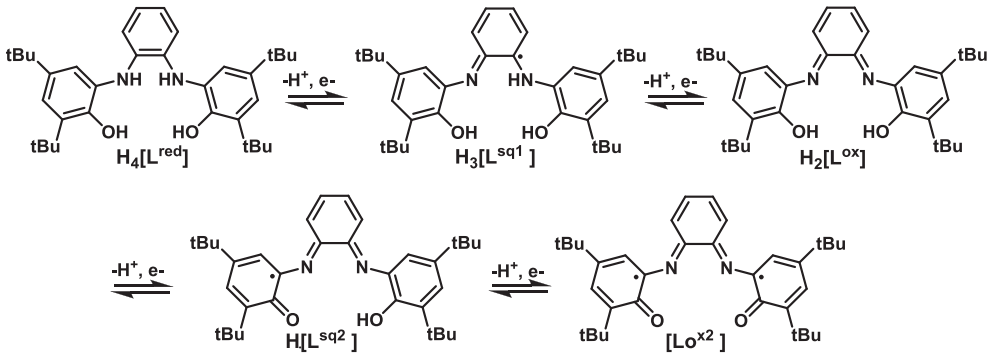
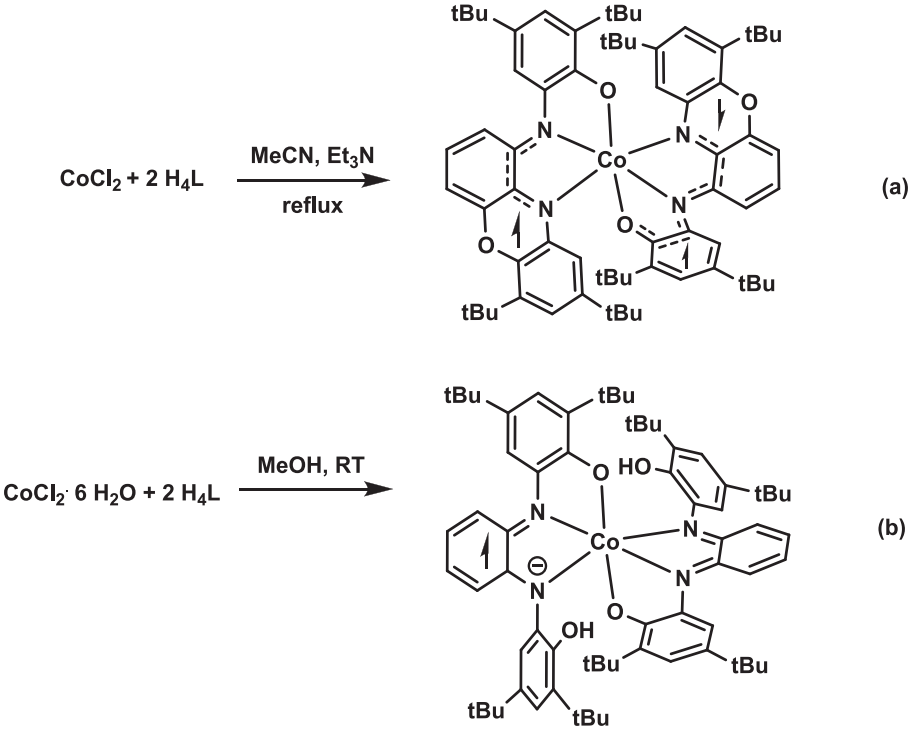
https://doi.org/10.1016/j.inoche.2023.111704
Received 30 June 2023; Received in revised form 13 October 2023; Accepted 7 November 2023
Available online 10 November 2023



Scheme 1. Different oxidation states of an o-aminophenol N,N′-bis(3,5-di-tertbutyl-2-hydroxy-phenyl)-1,2-phenylenediamine (H_4L). From hereon, H_4L corresponds the ligand in any oxidation state.[8].



Scheme 2. Formation of $[Co(\acute{L})_2]$ (a)[14] and $[Co(L)_2]$ (b).

non-innocent *o*-aminophenolate complexes can be estimated by calculating the metrical oxidation states (MOS) of the ligands from the respective C–O, C–N and C–C bond distances.[20,21] In $[Co(HL)_2]$, the both ligands have a tridentate coordination mode with an ONN donor set, which can be seen as a combination of one bidentate *o*-aminophenolate moiety and one nitrogen donor. For two structurally closely identical ligands in $[Co(HL)_2]$, the MOS calculations gave values of −1.174 and −1.389, which - to some extent - supports the Co(III) oxidation state. Whereas the MOS calculations do not precisely describe the oxidation state of H_4L, which formally consists of two redox-active parts, it is worth noting that for e.g. $[Co(L')_2]$, the MOS calculation gives values of −1.325 and −1.531, which are close to the expected parameters for a Co(III) complex. Similarly, the MOS values for isostructural complexes $[Fe(HL)_2]$ (−1.525 and −1.595) and $[Ni(HL)_2]$ (−1.146 and −0.885), match well with the formal oxidation states of Fe (III) and Ni(II), respectively. Similarly, bond valence sum (BVS) analyses can be used to examine the oxidation states of the metals in coordination compounds, although it is more often used for the purely inorganic solids.[22–24] For $[Co(HL)_2]$, the BVS calculation gave the value + 3.15, which is close to the expected formal oxidation state. The overall structure of the ligands in $[Co(HL)_2]$ resembles that of $[HL^{ox}]^{1-}$/$[HL^{sq1}]^{2-}$ resonance structure found in $[Fe(HL)_2]$, *i.e.* one ligand ($[HL^{ox}]^{1-}$) is oxidized by one electron and the other ligand ($[HL^{sq1}]^{2-}$) by two electrons, respectively, while the unpaired electron on the radical ligand is antiferromagnetically coupled with the Fe(III) centre. In $[Co(HL)_2]$, the LS Co(III) centre carries an even number of electrons, therefore the net magnetic moment should equal to one electron situated on the ligand radical. Indeed, measuring the effective magnetic moment at 298 K in a $CDCl_3$ solution by Evans NMR method gave $\mu_{eff} = 1.532$ μB, which is close to the value of 1.7 μB for one unpaired electron in first-row metal complexes.

These findings are backed up by single point DFT calculations done at the PBE0/def2-TZVP (and def2-SVP) level using the coordinates from the crystal structure. Starting from either Co(II) or Co(III) LS systems using different fragment based initial guesses result in a minimum energy structure similar to described above where one of the two ligands is formally a paramagnetic $S = ½$ system while no significant spin is localized on the Co centre. This is also supported by EPR spectroscopy measurements (ESI, Figure S2) that give one signal with g = 1.997 (uncalibrated), which is within the typical range for organic radicals and

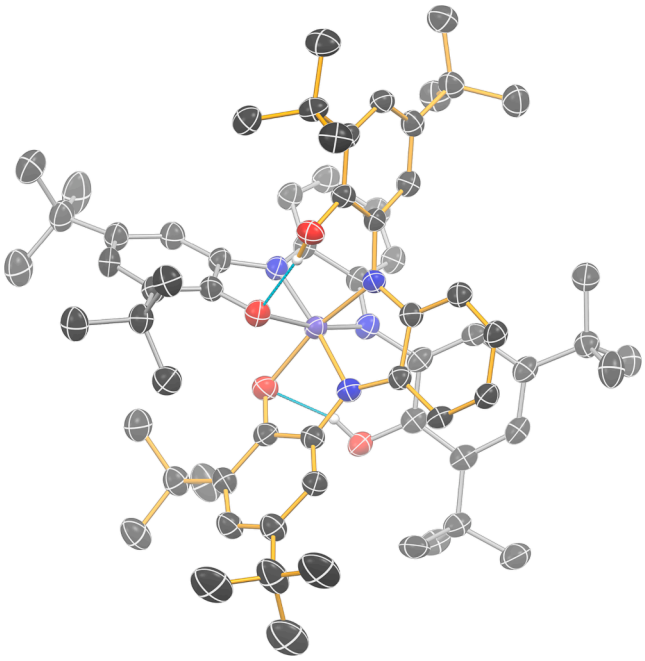


Fig. 1. The molecular structure of $[Co(HL)_2]$. Displacement ellipsoids are drawn at the 50% probability level. Disordered *tert*-butyl group and C–H H atoms are omitted from the figure.

Table 1
Selected bond lengths (Å) and angles (°) for $[Co(HL)_2]$.

Co1-O1	1.939(4)	O1-Co1-N2	167.24(15)
Co1-O3	1.928(3)	O3-Co1-N4	167.32(16)
Co1-N1	1.875(4)	N1-Co1-N3	175.09(17)
Co1-N2	1.929(4)	O1-Co1-N1	83.88(16)
Co1-N3	1.862(4)	N1-Co1-N2	83.36(17)
Co1-N4	1.946(4)	O1-Co1-O3	88.79(15)

outside the range expected for Co-centred radical species. The ligands in $[Co(HL)_2]$ can accommodate several oxidation states, therefore the redox behaviour of the complex was studied by running the cyclic voltammetry measurements in acetonitrile at room temperature. As a result, three reversible redox processes were observed at $E_{1/2}$ = -0.21, +0.03 and + 0.97 V, respectively (see Figure S1), whereas corresponding phenoxide/phenoxazine complex $[Co(L')_2]$ is reported to present five distinct processes[14]. In $[Co(L')_2]$, two redox couples at the most negative potentials are assigned to the reduction of phenoxazinylate groups, which are obviously not seen for $[Co(HL)_2]$. Accordingly, the redox events obtained for $[Co(HL)_2]$ likely originate from the oxidation of phenolate and amide moieties without any metal-based redox processes.

In conclusion, cobalt(II) chloride reacts with two molecules of N,N′-bis(3,5-di-tertbutyl-2-hydroxy-phenyl)-1,2-phenylenediamine in the absence of additional bases to form an octahedral Co(III) complex, where both ligands are coordinated as tridentate ONN donors. The ligand construction appears as a resonance structure, where one ligand is oxidized by one electron and the other ligand is oxidized by two electrons to form a radical. The paramagnetic complex carries an unpaired electron on the ligand.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

Acknowledgements

We wish to gratefully acknowledge the Turku Bioscience Protein Structure and Chemistry Core Facility, a member of Biocenter Finland and FINStruct, for their expertise and for providing access to single crystal X-ray diffraction instrument. We also acknowledge the Molecular Plant Biology unit in the University of Turku for their help in carrying out EPR experiments.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.inoche.2023.111704.

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