



## Communication

# Synthesis and characterization of a tetrametallic coordination complex of tetrahydroxy-*p*-benzoquinone



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## ABSTRACT

A new tetrametallic coordination complex of tetrahydroxy-*p*-benzoquinone (THBQ = C<sub>6</sub>O<sub>2</sub>(OH)<sub>4</sub>) has been synthesized by a single step reaction of THBQ with Re<sub>2</sub>(CO)<sub>10</sub> in the absence of an ancillary ligand. This is only the second report on the synthesis of a discrete, planar, tetrametallic coordination complex containing THBQ<sup>4-</sup> anion and its crystal structure.

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## 1. Introduction

The design and synthesis of compounds (organic and inorganic) possessing a hydroxyquinone unit or its derivatives have got immense interest owing to the non-innocent nature, photo and redox activities of the quinone ring [1]. Among the various quinone derivatives, tetrahydroxy-*p*-benzoquinone (THBQ) has the ability to form stable complexes with various metal ions in a variety of coordination modes using its four hydroxyl and two ketonic oxygen donor atoms, out of which the bis-bidentate bridging mode of THBQ<sup>2-</sup> has been commonly observed (Fig. S1) [1]. Though, THBQ offers a wide variety of coordination modes and oxidation states, metal complexes containing oxocarbon tetra-anion THBQ<sup>4-</sup> (C<sub>6</sub>O<sub>6</sub><sup>4-</sup>) unit are scarce in particular (Fig. S1). The countable metal salts and complexes bearing the THBQ<sup>4-</sup> unit are M<sub>4</sub>-THBQ<sup>4-</sup> (M = Li(I) or K(I)) [2], [(tBu<sub>4</sub>PcTi)<sub>2</sub>(C<sub>6</sub>O<sub>6</sub>)] [3], [Pd<sub>7</sub>(C<sub>6</sub>O<sub>6</sub>)<sub>2</sub>(t-ben)<sub>6</sub>](PF<sub>6</sub>)<sub>4</sub> [4], and [(*n*-C<sub>4</sub>H<sub>9</sub>)<sub>4</sub>N]<sub>3</sub>[Mo<sub>6</sub>O<sub>15</sub>(C<sub>6</sub>O<sub>6</sub>)<sub>2</sub>] [5]. In particular, the Li<sup>+</sup> and K<sup>+</sup> salts of THBQ<sup>4-</sup> have been proved to be potential materials for metal ion-based battery [2]. Moreover, it has

always been a challenge to establish synthetic methodologies for multi-nuclear metal complexes [6]. As a result; efforts are still being expanded towards synthesis of multi-nuclear metal complexes containing THBQ<sup>4-</sup> unit. Our ongoing work on the synthesis of functional rhenium based complexes possessing quinone derivatives provided motivation towards the reaction of THBQ with Re<sub>2</sub>(CO)<sub>10</sub> in the absence of ancillary ligands *e.g.* nitrogen/phosphorus/phosphine-oxide donors [7]. Herein we report on a planar tetrametallic coordination complex containing THBQ<sup>4-</sup> anion. The complex was characterized by elemental analysis, FT-IR, Raman and <sup>13</sup>C NMR spectroscopic techniques. The structural features were established by a single crystal X-ray diffraction analysis.

## 2. Results and discussion

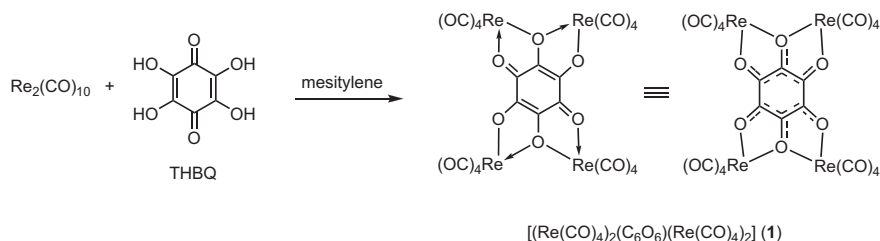
The neutral, tetranuclear complex **1** was prepared in a one step reaction between Re<sub>2</sub>(CO)<sub>10</sub> and THBQ under solvothermal conditions using non-coordinating solvents *e.g.* mesitylene in 60% yield (Scheme 1). The dark brown product was air and moisture stable and moderately soluble in polar organic solvents such as methanol, acetone, acetonitrile and dimethylsulfoxide.

The FT-IR spectrum of **1** in KBr shows strong bands at 2120, 2027, 1993, 1949 and 1924 cm<sup>-1</sup> characteristic of carbonyl groups bonded to rhenium ions (Fig. S2) [7]. The band at 2120 cm<sup>-1</sup> clearly explained the presence of a Re(CO)<sub>4</sub> moiety [8]. The absence of

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**Scheme 1.** Synthesis of tetranuclear complex **1**.

absorption bands at 1629 (C=O, THBQ), 1319 and 1234  $\text{cm}^{-1}$  (OH bending, THBQ) and the presence of the band at 1470  $\text{cm}^{-1}$  confirmed the coordination of the THBQ<sup>4-</sup> unit to the metal ions. A similar vibrational stretching pattern for the quinone ring was observed for M<sub>4</sub>C<sub>6</sub>O<sub>6</sub> salts (M = Li or K) [2a].

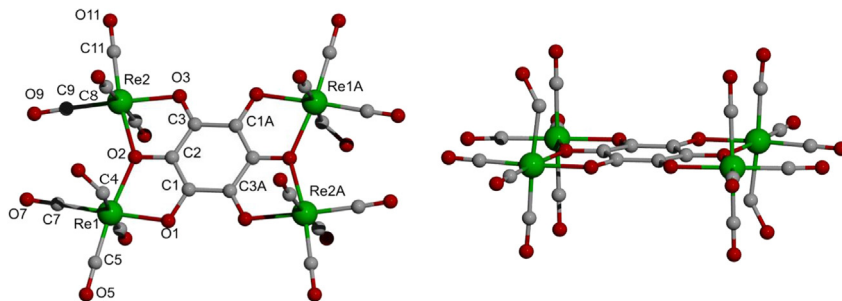
The <sup>13</sup>C NMR spectrum of **1** revealed two chemical resonances at 137 and 124 ppm ascribed to the quinonoid carbon and the hydroxyl carbon whereas the chemical shift values for the corresponding carbon atoms in THBQ are 181 and 134 ppm respectively. The large upfield shift and close proximity of the two peaks ( $\delta = 13$  ppm) in **1** confirm the bonding of rhenium ions with ligand oxygens and indicate towards an unsymmetrical charge delocalization in the THBQ<sup>4-</sup> ring. A symmetrical charge delocalization in the THBQ<sup>4-</sup> ring has resulted in a single broad resonance [2a].

Raman spectrum of **1** in solid state shows two broad humps between 1050 and 1700  $\text{cm}^{-1}$  whereas the ligand THBQ shows sharp peaks at 1707, 1647, 1516 and 1308  $\text{cm}^{-1}$ . This broadening of Raman bands in **1** is a consequence of the coupling of stretching modes of C=O and C=C bonds due to electron delocalization in the C<sub>6</sub>O<sub>6</sub><sup>4-</sup> ring after metal coordination. A small peak belonging to the stretching frequency of carbonyl groups of Re(CO)<sub>4</sub> unit was observed at 2028  $\text{cm}^{-1}$ .

A single crystal X-ray diffraction analysis at 150(2) K revealed that **1** adopts a M<sub>4</sub>L-type composition consisting of one C<sub>6</sub>O<sub>6</sub><sup>4-</sup> anion and four Re(CO)<sub>4</sub><sup>+</sup> cores (Fig. 1). Each Re(I) ion in **1** adopts a distorted octahedral arrangement with a C<sub>4</sub>O<sub>2</sub>-donor environment in the form of four carbonyl carbons and two oxygens from THBQ<sup>4-</sup> unit. The tetranionic C<sub>6</sub>O<sub>6</sub><sup>4-</sup> unit is planar in **1** and acts as a hexadentate twelve electron donor utilizing its two *p*-quinone oxygen atoms and four hydroxyl oxygen atoms. The C–C bond distances of THBQ<sup>4-</sup> unit in **1** are C1–C2: 1.37(3) Å, C2–C3: 1.43(3) Å and C3–C1: 1.49(3) Å whereas the corresponding bond distances for the THBQ are 1.34 Å, 1.48 Å and 1.47 Å respectively which indicate that the  $\pi$ -electrons are not completely delocalized over the quinone ring and it is asymmetric [9]. It is important to note that the delocalization of the  $\pi$ -electrons is confined in the chelating unit

(C1–C2–C3) and the C1–C3A represents a true single bond (1.49 Å) (Scheme 1). The C–O bond distances in THBQ<sup>4-</sup> unit clearly distinguish between the carbonyl and hydroxyl groups and confirm that the C3 carbon belongs to a carbonyl group whereas the C1 and C2 are the hydroxyl containing carbons. The Re1–O2 (2.179(17) Å) and Re2–O2 (2.183(18) Å) bond distances in **1** are closer to those observed in Re(I) based metallacycles containing alkoxy bridging binding mode ( $\mu_2$ - $\eta^2$ O) [10]. The two axial Re–C(O)<sub>ax</sub> bonds (Re1–C4 and Re2–C8) showed marked differences in their bond lengths. Re2–C8 bond length (1.99 Å) is relatively shorter than that of Re1–C4 bond length (2.13 Å) suggesting that the Re2 is bonded with the  $\pi$ -accepting quinone–hydroxy chelating fragment (O3–C3–C2–O2) of the THBQ<sup>4-</sup> ligand. This observation along with the C–O bond lengths validates two types of chelating units in the THBQ<sup>4-</sup> ligand in **1** namely the C1–C2 and C2–C3 units. In the chelating units, the quinonoid oxygen (O3) and the hydroxyl oxygen (O1) act as a neutral two electron donor and anionic one electron donor respectively with monodentate ( $\eta^1$ O) bonding mode whereas the middle hydroxyl oxygen (O2) act as a three electron donor in the form of a bidentate bridging ( $\mu_2$ - $\eta^2$ ) bonding mode. Thus, the tetranionic THBQ<sup>4-</sup> unit in **1** is behaving as a twelve electron donor using its two *p*-quinone oxygen and four hydroxyl oxygen atoms.

The packing diagram of **1** demonstrates two important intermolecular non-covalent interactions. The molecules of **1** stack in a head-to-tail fashion through unusual, intermolecular carbonyl⋯carbonyl interactions between the axial carbonyls of one molecule and the equatorial carbonyl of the other with closest O⋯C contact at 3.065 Å (van der Waals radii = 3.12 Å). This stacking extends along the 'b' directions and the parallel chains are interlinked by an additional pair of carbonyl⋯carbonyl contacts between the molecules of **1** (Fig. S3) [11]. The molecules of **1** also display a weak intermolecular interaction between a THBQ<sup>4-</sup> ring oxygen (O1) and axial rheniumcarbonyl carbon (C4) of the other molecule with a separation of 2.76 Å (Fig. S4). This interaction can be rationalized by a weak donation of charge from oxygen (*via* lone pair) to the carbonyl carbon of the other causing a slight bending of



**Fig. 1.** Ball and stick view of the crystal structure of **1**. Atomic labels with "A" represents equivalent atoms generated from the symmetry code  $-x + 1, -y + 2, -z + 1$ . Relevant bond distance (Å) and angles ( $^\circ$ ): for **1**, C1–C2 1.37(3), C2–C3 1.43(3), C3–C1A 1.49(3), C1–O1 1.32(3), C2–O2 1.35(3), C3–O3 1.23(3), Re1–O1 2.159(16), Re1–O2 2.179(17), Re2–O2 2.183(18), Re2–O3 2.135(15), Re1–C(4) 2.13(2), Re1–C5 1.88(3), Re1–C6 1.89(3), Re1–C7 1.93(3), Re2–C(8) 1.99(3), Re2–C9 1.92(2), Re2–C10 1.99(3), Re2–C11 1.91(2), O(1)–Re(1)–O(2) 77.9(6), C(7)–Re(1)–O(2) 100.9(8), C(5)–Re(1)–C(7) 87.6(11), C(5)–Re(1)–O(1) 93.6(10), O(2)–Re(1)–O(3) 76.4(6), C(11)–Re(2)–O(3) 96.1(9), C(11)–Re(2)–C(9) 86.2(11), C(9)–Re(2)–C(2) 101.3(9).

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