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Novel tris-*o*-semiquinonato cobalt complexes, where quinonato fragments are modified by cyclic substituents

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ABSTRACT

Octacarbonyldicobalt reacts with tricyclic 5,8-di(*tert*-butyl)-2,3-dihydro-1,4-ethanoquinoxaline-6,7-dione and 5,8-di-*tert*-butyl-2,3-dihydrobenzo[b][1,4]dioxine-6,7-dione to give tris-*o*-semiquinonato complexes (**1** and **2**, respectively). X-ray structural study indicate exact trigonal prismatic environment of cobalt in **1** and slightly twisted one in **2**. Rigid and flexible steric configurations of *N*,*N*′-piperazino- and *O*,*O*′-ethane-1,2-diolato-cyclic fragments of ligands are responsible for trigonal prismatic molecular geometry of **1** and twisted one for **2**. Magnetic moment temperature dependences have very close shapes for **1** and **2** and correspond to $S = 1/2$ ground state. High temperature limits exceed spin-only value calculated for three noninteracting spins on three semiquinones. Precision calorimetric study of temperature dependence of heat capacity of **1** does not detect significant anomalies.

1. Introduction

Homoleptic tris-*o*-semiquinonato complexes attract attention as good models for studding of charge distribution between metal and ligands and creating magneto-structural correlations [1]. Asymmetrically substituted 3,5-di-*tert*-butyl-*o*-benzoquinone (3,5-DBQ) coupled with cobalt forms tetrameric coordination unite of formula $[Co(3,5\text{-}DBSQ)_2]_4$ [2]. Binding of $Co(3,5\text{-}DBSQ)_2$ fragments occurs through oxygen atom which has not *tert*-butyl group in *ortho*-position. Structural study and magnetic measurements indicate divalent high spin cobalt. Symmetrical 3,6-di-*tert*-butyl-*o*-benzoquinone (3,6-DBQ) forms monomeric complex $Co(3,6\text{-}DBSQ)_3$ which geometry is close to octahedral [3]. Magnetic measurements indicate low spin trivalent cobalt connected to three *o*-semiquinones. *o*-Semiquinonato ligands in $Co(3,6\text{-}DBSQ)_3$ are coupled weakly antiferromagnetically through metal d-orbitals in contrast to similar $Ga(3,6\text{-}DBSQ)_3$ and $Al(3,6\text{-}DBSQ)_3$ species [3]. The most recent publication [4] indicate homoleptic indium complex $In(3,6\text{-}DBSQ)_3$ to have trigonal prismatic geometry with strong antiferromagnetic ligand–ligand interaction.

Here we report structural, EPR and magnetic studies of analogous homoleptic tris-*o*-semiquinonato cobalt complexes with 3,6-di-*tert*-butyl-*o*-benzoquinone having cyclic *N*,*N*′-piperasino- and *O*,*O*′-ethane-1,2-diolato-fragments in 4,5-back positions.

2. Results and discussion

Complexes **1** and **2** were obtained by the reaction of octacarbonyldicobalt with three moles of corresponding *o*-quinone (Scheme 1). Both complexes were isolated and characterized by IR-NIR, EPR, magnetic measurements and structurally. Precision calorimetric measurement was performed for **1**.

Structural study indicated the complex **1** molecule to have exact trigonal prismatic geometry (point group D_{3h}) (Fig. 1). The most close analogue $Co(3,6\text{-}DBSQ)_3$ has geometry close to octahedral. Only one homoleptic complex $In(3,6\text{-}DBSQ)_3$ – the derivative of 3,6-di-*tert*-butyl-*o*-semiquinone which has trigonal prismatic configuration is known till current moment [4]. Chelate and aromatic rings of each semiquinone in **1** are exactly planar. C–O bonds lengths (Table 1) which are responsible for charge distribution between metal and quinonato ligand are very short (1.256(2) Å). This value is intermediate between distances typical for C–O double (1.23–1.25 Å) and sesquialteral (1.27–1.31 Å) bonds [1,5]. It should

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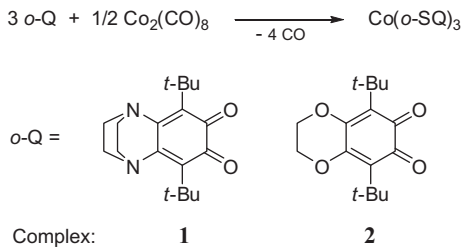

Scheme 1. Synthesis of complexes **1** and **2**.

be mentioned that slight shortening of C–O bonds in *o*-semiquinones being connected to cobalt in trigonal prismatic coordination mode have been already observed [6,7]. As a consequence of short C–O bond length the angle O–Co–O (75.78(9)°) is too small for coordinated derivatives of 3,6-di-*tert*-butyl-*o*-semiquinone [8]. Distances Co–O (1.995(2) Å) also are intermediate between values typical for Co(III) low spin 1.86–1.91 Å and Co(II) high spin 1.98–2.08 Å [8] coupled with semiquinonato fragments. Another peculiarity of the **1** structure is the position of methyl groups in *tert*-butyl substituents. Methyl group which is directed towards metallic centre lies in the plane of semiquinone (Fig. 1, left). In other words this methyl and adjacent carbonyl are in eclipsing conformation.

Molecular C_3 axes of all molecules are parallel to *c*-dimension of unit sell. Planes of two semiquinones are parallel to *ac* and *bc* edges of unit sell (Fig. 2, left). Molecules form layers where cobalt atoms lie in one plane (Fig. 2 right). Separation between two adjacent planes 10.321 Å – one half of *c* unit sell dimension.

In a layer of **1** the intermolecular interactions between C1 atom of SQ ligand and hydrogen atom of piperazine were found (Fig. 3). Distances C1(SQ)...H(piperazine) are 2.77 Å which correspond to shortened Van der Waals C...H interactions (2.52–2.82) [9]. In such a way each molecule interacts with three adjacent ones via 12 equivalent C...H contacts (4 contacts per each pair interaction). Apparently these intermolecular C...H contacts in crystal lattice are responsible for trigonal prismatic configuration of molecules of **1**.

Molecule of complex **2** is less symmetrical (Fig. 4). Two ligands are equivalent to each other and differ from the third one so that the whole molecule has symmetry axis C_2 which is parallel to *b*-dimention of unit sell. In general the geometry of **2** molecule is close to trigonal prismatic but it is slightly twisted towards antiprism. Pseudo axis C_3 is parallel to *c*-dimension of unit sell and orthogonal to C_2 molecular axis (Fig. 5). The angle between the plane *ab* and chelate cycle of one ligand (mean plane Co1–O5–C17–C17′–O5′) is 78.96° and between the plane *ab* and the plane of the other chelate cycle (mean plane Co1–O1–C1–C6–O2) is 77.43°. In exact trigonal prism both angles should be 90°. In other words the ligands are twisted about 11–13° from trigonal prism configuration.

Bonds lengths and angle (Table 2) which reflect charge distribution between metal and quinonic fragment are in the range typical for semiquinonic coordination mode (C–O 1.270(2)–1.273(2) Å; O–Co–O 76.65(6)–77.19(4)°). Co–O distances are characteristic for high spin metal (Co–O 2.020(1)–2.030(2) Å). In contrast to complex **1**, the molecule of **2** has usual orientation of *tert*-butyl groups which are slightly twisted in accordance with ligand bend (Fig. 4, left).

As in the case of **1** the complex **2** molecules form layers where cobalt atoms lie in one plane and molecular pseudo axes C_3 are parallel (Fig. 5, right). Separation between adjacent planes is 10.416 Å which is one half of *c*-dimension of unit sell.

Analysis of crystal packing of **2** has revealed that the SQ ligands of adjacent molecules in a layer are involved in intermolecular interactions as well as in **1** (Fig. 6). In contrast to **1** the intermolecular contacts in crystal of **2** occur in different ways. Two oxygen atoms (O(2A) and O(2AA) of SQ ligands of central complex molecule Co(1A)) interact with *O,O′*-ethane-1,2-diolato-substituent of complex Co(1B) via atoms H(24G) and H(24E), respectively. Distances of O(2A)...H(24G) and O(2AA)...H(24E) contacts are 2.63 Å which is close to the sum of Van der Waals radii of O and H (2.7 Å [10]). The third SQ ligand of complex Co(1A) have contacts with H atoms of *O,O′*-ethane-1,2-diolato-fragments in complexes Co(1C) and Co(1D). Distances of C(17A)...H(16I), C(17B)...H(16O) and C(17A)...H(16P), C(17B)...H(16J) contacts are 2.88 and 2.85 Å, respectively. These values are close to the sum of Van der Waals radii of C and H (2.9 Å [10]). Obviously the participation of

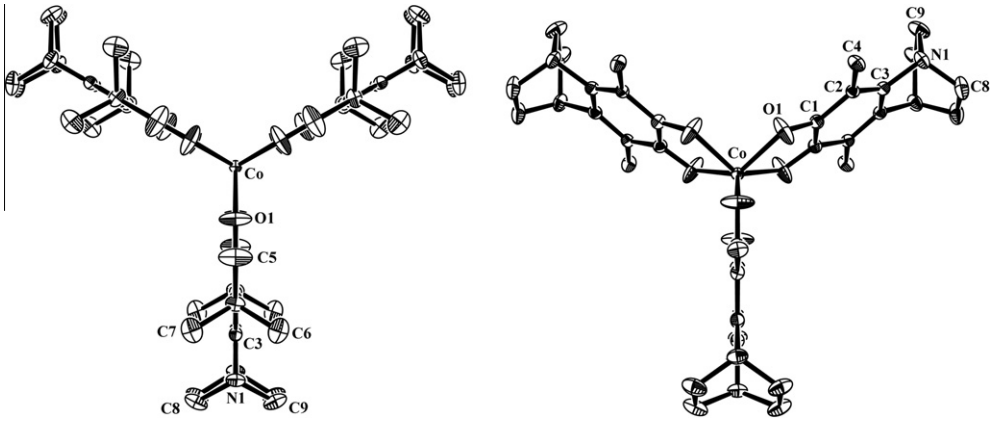

Fig. 1. General view of complex **1** molecule (30% ellipsoid probability). View along C_3 axis (left) and slightly twisted one without methyl groups of *tert*-butyl substituents (right).

Table 1
Selected bonds lengths in **1** molecule.

Bond	Co–O1	O1–C1	C1–C2	C2–C3	C3–N1	N1–C8	N1–C9	C1–C1′	C3–C3′
Length (Å)	1.995(2)	1.256(2)	1.437(3)	1.374(3)	1.443(2)	1.482(3)	1.479(3)	1.493(4)	1.448(4)