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Yttrium Complexes with 3,6-Bis(*tert*-Butylcatecholate)

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Abstract—Heterometallic complex $[K_3Y(Cat^{36})_3(Dme)_4]$ (**I**) or binuclear complex $[Y_2(Cat^{36})_3(Dme)_3] \cdot Dme$ (**II · Dme**) is synthesized, depending on the reactant ratio, by the reaction of YCl_3 with 3,6-bis(*tert*-butylcatecholate) potassium salt (K_2Cat^{36}) in 1,2-dimethoxyethane (Dme). Both complexes are characterized by single-crystal X-ray diffraction analysis (CIF files CCDC nos. 1527929 (**I**) and 1527930 (**II**)) and ^1H and ^{13}C NMR spectroscopy.

Keywords: rare-earth elements, yttrium, quinones, X-ray diffraction analysis

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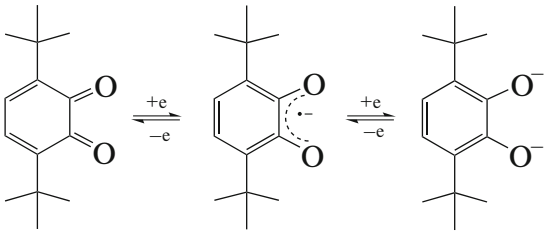
INTRODUCTION

The recent decades are marked with significant progress in the chemistry of complexes with so-called redox-active ligands capable of existing in metal complexes in several oxidation states [1–3]. 1,2-Benzoquinone derivatives capable of stepwise reducing to the *o*-semiquinolate radical anion and catecholate dianion (Scheme 1) represent a classical example of these ligands. The redox activity of both the metal and ligand can result in the manifestation of redox isomerism: thermo- or photoinduced reversible intramolecular electron transfer between the metal and ligand [4–8]. Interest in the redox isomerism phenomenon is caused by the possibility of using similar systems for the construction of molecular sensors and nanosized devices for information recording and storage.



Q^{36} $(SQ^{36})^-$ $(Cat^{36})^{2-}$

Scheme 1.

In spite of numerous examples of transition metal complexes with 1,2-benzoquinone derivatives, their complexes with rare-earth metals are fairly poorly studied [9–18]. This is additionally due to the affinity of the catecholate rare-earth metal complexes to oxidation in air. Although the homoleptic catecholate rare-earth metal complexes are known [9–12], high coordination numbers characteristic of these metals more frequently result in the formation of polynuclear and/or heteroleptic complexes (for example, with solvent molecules). This often leads to a complicated stoichiometry of the synthesized complexes. At the same time, the lanthanide complexes with the benzoquinone derivatives can exhibit interesting magnetic and optical properties or their combinations, and the modification of an organic benzoquinone derivative allows one to directly change these properties [19, 20].

The purpose of this work is to synthesize yttrium complexes with 3,6-bis(*tert*-butylcatecholate).

EXPERIMENTAL

All procedures on the synthesis, purification, and characterization of the complexes were carried out in an inert atmosphere using the standard Schlenk technique. Solvents for the syntheses were dehydrated and degassed by reflux and distillation in an inert gas atmosphere using the corresponding drying agents [21]. The starting 3,6-bis(*tert*-butyl-*o*-benzoquinone) was synthesized using a known procedure [22]. IR spectra in KBr pellets were recorded on a SCIMITAR FTS 2000 instrument.

Synthesis of complex I. 3,6-Bis(*tert*-butyl-*o*-benzoquinone) (255 mg, 1.16 mmol) was placed in the Schlenk vessel, dissolved in ~25 mL of anhydrous degassed 1,2-dimethoxyethane (Dme), and stirred with an excess potassium (~150 mg, 3.85 mmol) at room temperature to obtain a yellowish solution. The remaining potassium was removed, and solid YCl_3

(75 mg, 0.384 mmol) was added to the solution. The vessel was evacuated, heated at 60°C for 20 h, and cooled. A fine white precipitate of KCl was filtered off through a glass filter (G4), and the residue was hermetically sealed in an L-shaped tube. The slow evaporation of the yellowish solution resulted in the formation of colorless crystals of complex **I** suitable for X-ray diffraction analysis. The yield of complex **I** was 275 mg (59%).

For $C_{58}H_{100}K_3O_{14}Y$		
anal. calcd., %:	C, 56.75;	H, 8.21.
Found, %:	C, 56.15;	H, 8.55.

IR (KBr), ν, cm^{-1}: 3070, 2988, 2953, 1506, 1489, 1472, 1457, 1448, 1366, 1345, 1286, 1243, 1202, 1149, 1116, 1094, 1075, 1026, 972, 938, 853, 806, 783, 769, 679, 653. ^{1}H NMR (C_4D_8O), δ, ppm: 6.84 (s, 6H, CH_{cat}), 3.43 (s, 16H, CH_2), 3.27 (s, 24H, OCH_3), 1.65 (s, 54H, $C(CH_3)_3$). ^{13}C NMR (C_4D_8O), δ, ppm: 160.77 (C–O), 131.18 (C_{cat}), 110.54 (C_{cat}), 72.59 (CH_2), 58.72 (OCH_3), 34.45 ($\underline{C}(CH_3)_3$), 30.18 ($C(\underline{C}H_3)_3$).

Synthesis of complex II was carried out using a procedure similar to that of the synthesis of complex **I** from 3,6-bis(*tert*-butyl-*o*-benzoquinone) (172 mg, 0.78 mmol) and YCl_3 (102 mg, 0.52 mmol). The slow evaporation of the yellowish solution resulted in the formation of colorless needles of complex **II · Dme** suitable for X-ray diffraction analysis. The yield was 155 mg (50%).

For $C_{58}H_{100}O_{14}Y_2$		
anal. calcd., %:	C, 58.09;	H, 8.40.
Found, %:	C, 58.05;	H, 8.70.

IR (KBr), ν, cm^{-1}: 3060, 2956, 2872, 1502, 1469, 1439, 1388, 1362, 1356, 1345, 1275, 1202, 1179, 1063, 1025, 966, 950, 868, 825, 805, 673, 653. ^{1}H NMR (C_6D_6), δ, ppm: 6.84 (s, 6H, CH_{cat}), 3.14 (s, 40H, CH_2 + OCH_3), 1.65 (s, 54H, $C(CH_3)_3$). ^{13}C NMR (C_6D_6), δ, ppm: 156.57 (C–O), 132.50 (C_{cat}), 114.20 (C_{cat}), 71.64 (CH_2), 59.81 (OCH_3), 34.37 ($\underline{C}(CH_3)_3$), 31.78 ($C(\underline{C}H_3)_3$).

X-ray diffraction analysis. Diffraction data for a single crystal of complex **I** were obtained on an Agilent Xcalibur automated diffractometer (AtlasS2 two-coordinate detector, graphite monochromator, $\lambda(MoK_\alpha) = 0.71073$ Å, ω scan mode). Integration was performed, an absorption correction was applied, and unit cell parameters were determined using the CrysAlisPro program package [23]. Diffraction data for a single crystal of complex **II · Dme** were obtained on a Bruker Duo automated diffractometer (CCD detector, graphite monochromator, $\lambda(MoK_\alpha) = 0.71073$ Å, ω scan mode). The primary data including the unit cell parameters, Miller indices, and intensities of measured reflections were processed using the software supplied together with the diffractometer [24]. An absorption correction was applied semiempirically using the SADABS program [24]. The crystal structures of complexes **I** and **II · Dme** were solved by a direct method and refined by full-matrix least squares in the anisotropic (except for hydrogen atoms) approximation using the SHELX-2014 program package [25]. The positions of the hydrogen atoms of the organic ligands were geometrically calculated and refined by the riding model. The crystallographic data and details of diffraction experiments are given in the Table 1.

The full tables of interatomic distances, bond angles, atomic coordinates, and atomic shift parameters were deposited with the Cambridge Crystallographic Data Centre (CCDC nos. 1527929 (**I**) and 1527930 (**II**); deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk/data_request/cif) and can be available from the authors.

RESULTS AND DISCUSSION

The reaction of potassium 3,6-bis(*tert*-butylcatecholate) (K_2Cat^{36}) (obtained in situ from K and the corresponding quinone in Dme) with YCl_3 in a ratio of 3 : 1 affords a yellow solution from which large colorless crystals of catecholate complex **I** were isolated. The same reaction with a reactant ratio of 3 : 2 affords colorless needles of complex **II · Dme**. The crystals of both complexes are very sensitive to oxygen and gradually become dark blue even on keeping in a dry box filled with argon, indicating the easiness of the oxidation of the coordinated catecholate ligands to the corresponding semiquinolates.

In a molecule of complex **I** (Fig. 1), the environment of the Y atom is formed by six oxygen atoms of the catecholate anions. The Y–O bond lengths range from 2.2229(8) to 2.2605(8) Å. The coordination polyhedron is an almost undistorted trigonal prism. The dihedral angle between its triangular faces is 0.1°, and the dihedral angles between these faces and the planes of the central OCCO fragments of the catecholate ligands are 85.5°–88.2°. The Y atom lies almost in the plane of all catecholate ligands, and its deviation from the planes of their central OCCO fragments is 0.20–0.35 Å. One $\{K(Dme)\}^+$ fragment is additionally coordinated to the oxygen atoms at the edges of the prism to form a unique clathrochelate with the $K–O_{cat}$ distances in a range of 2.6847(9)–2.8401(9) Å. The Y(1)···K(1) and Y(1)···K(2) distances are 3.4357(3) and 3.3950(3) Å, respectively (the K(1)Y(1)K(2) angle is 176.03°). In addition, $\{K(Dme)_2\}^+$ fragment is coordinated to the arene ring of one of the catecholate ligands via the η^6 mode (K–C 3.0875(13)–3.2870(12), $K–C_{center}$ 2.845 Å).

Table 1. Crystallographic data and refinement parameters for the structures of complexes **I** and **II · Dme**

Parameter	Value	
	I	**II · Dme**
FW	1227.58	1199.19
Crystal system, space group	Monoclinic, $P2_1/c$	Trigonal, $R3c$
Temperature, K	130	150
a, Å	18.91797(17)	36.7243(9)
b, Å	14.91562(13)	36.7243(9)
c, Å	23.6314(2)	23.4937(16)
β, deg	100.4314(9)	90
V, Å^3	6557.93(11)	27440(2)
Z	4	18
F(000)	2624	11 484
μ, mm^{-1}	1.137	1.954
Crystal size, mm	0.35 × 0.25 × 0.20	0.40 × 0.40 × 0.15
T_{min}, T_{max}	0.937, 1.000	0.602, 0.745
Range of data collection θ, deg	3.246–29.683	1.848–26.483
Range of indices *h*, *k*, *l*	$-21 \le h \le 26$, $-16 \le k \le 20$, $-32 \le l \le 32$	$-43 \le h \le 46$, $-46 \le k \le 40$, $-29 \le l \le 22$
Number of measured, independent, and observed ($I > 2\sigma(I)$) reflections	63655 16549 14557	60869 11991 10610
R_{int}	0.0192	0.0541
R_1, wR_2 ($I > 2\sigma(I)$)	0.0274, 0.0645	0.0319, 0.0739
R_1, wR_2 (all reflections)	0.0351, 0.0677	0.0403, 0.0764
GOOF	1.022	1.003
Number of refined parameters	711	724
Number of restraints	0	37
$\Delta\rho_{max}$, $\Delta\rho_{min}$, *e* Å^{-3}	0.88, –0.49	0.51, –0.38

Complex **II** crystallizes as a solvate with Dme and represents a dimer (Y(1)···Y(2) 3.3701(6) Å) in which two yttrium atoms have different coordination numbers (6 and 8). Three catecholate anions are also coordinated via different modes: terminal and two different bidentate bridging modes (μ-κ^{2}O,O':κ^{2}O,O' and μ-κ^{2}O,O':κ^{1}O) (Fig. 2). The chelate angle of the terminal catecholate ligand is 73.05(10)°, and the chelate angles in the bidentate bridging catecholates are substantially smaller (O(201)Y(1)O(202) 65.02(9)°, O(201)Y(2)O(202) 65.39(9)°).

The Y(1) atom is coordinated by the oxygen atoms of the catecholate anions and the oxygen atom of the Dme molecule coordinated via rather rare κ^1 mode. According to the Cambridge Structural Database (release 2016 [26]), a similar coordination of Dme is met in 62 cases (most frequently in the complexes of *s*-metals and rare-earth elements). For comparison, the most typical κ^2 coordination mode is met in almost 1600 cases. The Y(2) atom is coordinated by eight O atoms of two Dme molecules and two catecholate anions. The coordination polyhedron of Y(2) is a distorted tetragonal antiprism with the bases formed by the O(201), O(202), O(501), O(502) and O(301), O(302), O(601), O(602) atoms, and the dihedral angle between their planes is 2.7°.

In the structure of complex **I**, the C–C (1.4352(18)–1.4397(17) Å) and C–O (1.3350(15)–1.3448(14) Å) distances in the YOCCO metallocycles correspond to the values expected for the coordinated catecholates [27] and thus confirm the dianionic redox state of these ligands. The signals of the carbon atoms at the O_{cat} atoms in the ^{13}C NMR spectra have the chemical shifts characteristic of catecholates. As could be expected, the C–O distances in the bidentate

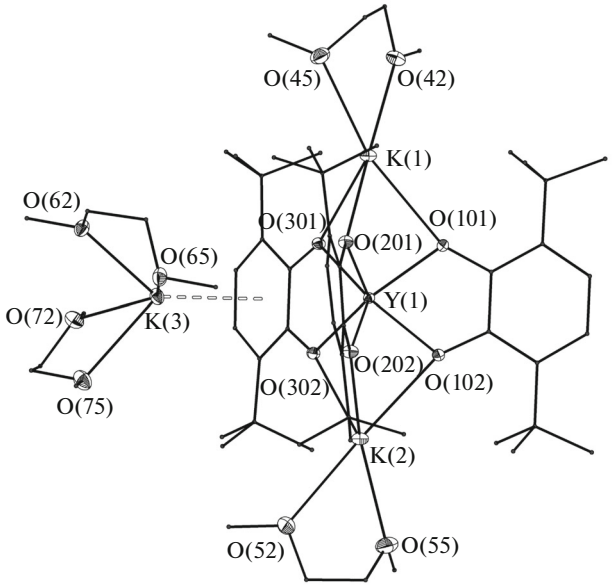


Fig. 1. Structure of complex **I**. Hydrogen atoms are omitted. Selected bond lengths (Å): Y(1)–O(101) 2.2229(8), Y(1)–O(102) 2.2306(9), Y(1)–O(201) 2.2433(8), Y(1)–O(202) 2.2295(9), Y(1)–O(301) 2.2394(9), and Y(1)–O(302) 2.2605(8).

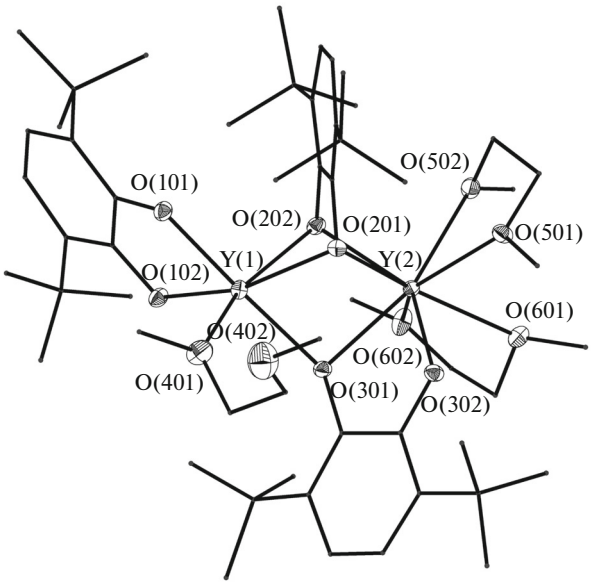


Fig. 2. Structure of complex **II** · **Dme**. Hydrogen atoms are omitted. Selected bond lengths (Å): Y(1)–O(101) 2.174(3), Y(1)–O(102) 2.162(3), Y(1)–O(201) 2.372(3), Y(1)–O(202) 2.326(3), Y(1)–O(301) 2.303(3), Y(1)–O(401) 2.364(3), Y(2)–O(201) 2.324(3), Y(2)–O(202) 2.351(3), Y(2)–O(301) 2.329(3), Y(2)–O(302) 2.169(3), Y(2)–O(501) 2.477(3), Y(2)–O(502) 2.493(3), Y(2)–O(601) 2.532(3), Y(2)–O(602) 2.488(3), Y(1)–C(201) 2.921(4), Y(1)–C(202) 2.901(4), Y(2)–C(201) 2.934(4), and Y(2)–C(202) 2.951(4).

bridging catecholates in structure **II** are somewhat elongated compared to those in the terminal groups.

To conclude, the following polynuclear catecholate complexes were isolated and characterized by single-crystal X-ray diffraction analysis and ^{1}H and ^{13}C NMR spectroscopy: heterometallic tetranuclear $[K_3Y(Cat^{36})_3(Dme)_4]$ and binuclear $[Y_2(Cat^{36})_3(Dme)_3]$. The different coordination numbers of the Y atoms (6 and 8) and three different coordination modes of the catecholate ligand are observed for $[Y_2(Cat^{36})_3(Dme)_3]$. In addition, the rare κ^1 coordination mode of the dimethoxyethane molecule is observed in this complex.

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