



Research paper

Synthesis and redox activity of the ruthenium complexes based on 9-hydroxy-2,4,6,8-tetra-(*tert.*-butyl)phenoxazin-1-one ligands



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ABSTRACT

The redox-active bis-chelate hexacoordinate ruthenium complex **2** Ru(ONO)₂ comprising two redox-active 2,4,6,8-tetrakis(*tert.*-butyl)-9-hydroxyphenoxazin-1-one ligands **1** was synthesized by coupling ruthenium trichloride with **1** or its thallium salt. Reduction of **2** with zinc amalgam produces its radical-anion **2a**, which readily reacts with pyridine in aerobic conditions resulting in substitution of one of the tridentate hydroxyphenoxazinone ligand by three pyridine molecules and the formation of a salt of tris(pyridine)(tetra-(*tert.*-butyl)oxyphenoxazin-1-onate) Ru(II) cation **5**. The structure of this salt was established by X-ray crystallography and its redox activity investigated using cyclic voltammetry. The mechanism of the Ru^{III}/Ru^{II} conversion observed in this reaction was suggested based on the data of ESR, UV-Vis spectra and DFT B3LYP/6-311++G(d,p)/SDD calculations.

1. Introduction

In the recent years significant attention has been given to ruthenium complexes with redox-active (non-innocent) ligands known to exhibit highly variable electronic properties which are in demand of promotion of many redox-addressable catalytic reactions [1–6] and next generation antitumor metallotherapeutics [7,8]. It is in ruthenium complexes that the energy levels of the vacant π^* orbitals of redox-active ligands lie most closely to those of the metal $d\pi$ orbitals resulting in their extensive mixing and highly delocalized electron distribution within the coordination site [2,9–11], thus providing for the peculiar reactivity exhibited by these complexes. Studied in most detail are the complexes of ruthenium ions with the bidentate redox-active ligands, *o*-quinones [1,2,11–13] and their mono- and diimines [7,12–16]. We have previously described the synthesis of a versatile tridentate redox-active 2,4,6,8-tetrakis(*tert.*-butyl)-9-hydroxyphenoxazin-1-one ligand **1** containing a pincer-like ONO chelating triad [17,18]. The ligand has been successfully employed for the preparation of a series of hexacoordinated transition [19,20] and main group [20,21] metal complexes **2** M^{II}(ONO)₂ and also nonacoordinated tris-chelate lanthanide (III) complexes **3** M^{III}(ONO)₃ [22] (Scheme 1). While the synthesis of complexes **2** (M = Mn, Fe, Co, Ni, Cu, Zn) follows to the facile procedure

comprising short-term reflux of methanol solution of **1** and the appropriate metal(II) acetate, the attempts to use this approach for the preparation of the similar ruthenium complex **2** (M = Ru) failed. Unsuccessful were also our attempts to employ the method based on coupling Ru(II) acetate or chloride with the highly reactive reduced form of ligand **1** that was applied for the preparation of the lanthanide complexes **3**. The first synthesis of complex **2** (M = Ru) has been performed via substitution of the Pb(II) center in **2** (M = Pb) with ruthenium under treating the lead complex with [(*p*-cymene)RuCl₂]₂ as the divalent metal precursor [20,23].

The goals of the present work were the attempts to find an additional facile approach to preparation of Ru^{II} complex **2**, to explore its ability to ligand substitution reaction and to study the structure and electrochemical behavior of the product of this reaction.

2. Experimental

2.1. Synthesis

All chemicals were purchased from commercial sources and used without purification except 9-hydroxy-2,4,6,8-tetra-(*tert.*-butyl)phenoxazin-1-one **1** that was prepared according to the previously described procedure [18].

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2.1.1. Thallium(I) 2,4,6,8-tetra-(tert.-butyl)-1-oxo-1H-phenoxazin-9-olate **1a**

Solution of 0.132 g (0.5 mmol) of thallium acetate in 15 mL of methanol were added to solution of 0.219 g (0.5 mmol) of 2,4,6,8-tetra-(tert.-butyl)-9-hydroxyphenoxazin-1-one **1** in 10 mL of benzene, the reaction mixture was evaporated to 5 mL and cooled. The precipitated salt was filtered off, and washed off with benzene to give 0.297 g (yield 93%) of the product. M.p. > 250 °C. *Anal. calc.* for **1a** C₂₈H₃₈NO₃Tl, %: C, 52.47; H, 5.98; N, 2.19; found %: C, 52.45; H, 5.95; N, 2.21. IR (ν , cm⁻¹): 2950 (w), 2908 (w), 2869 (w), 1801 (w), 1611 (w), 1587 (w), 1562 (w), 1502 (m), 1487 (m), 1464 (m), 1446 (m), 1429 (m), 1390 (w), 1348 (s), 1324 (m), 1274 (m), 1246 (m), 1225 (m), 1193 (m), 1167 (m), 1070 (m), 1031 (m), 996 (s), 977 (m), 926 (w), 903 (w), 894 (w), 877 (m), 822 (w), 804 (w), 793 (w), 774 (w), 740 (m), 727 (w), 709 (w), 690 (m), 654 (w), 610 (m), 571 (w), 555 (w). ¹H NMR (CDCl₃, ppm): tert-Bu 1.106 (s), 1.655 (s), aromatics 7.390 (s).

2.1.2. Bis(2,4,6,8-tetra-(tert.-butyl)-1,9-dioxophenoxazinate)ruthenium **2** (M = Ru)

Method a) 0.207 g (1.0 mmol) of RuCl₃ were added to a solution of 0.219 g (0.5 mmol) 2,4,6,8-tetra-(tert.-butyl)-9-hydroxyphenoxazin-1-one **1** in 5 mL of DMF (dimethylformamide). The reaction mixture was refluxed for 30 min until the solution acquired intense blue color, then cooled to room temperature and allowed to stand at this temperature for two days. The precipitated blue crystals were filtered off, dried and crystallized from benzene to give 0.182 g (yield 75%) of the product. M.p. > 250 °C. IR (ν , cm⁻¹): 2956 (w), 2917 (w), 2868 (w), 2851 (w), 2710 (w), 2660 (w), 2065 (w), 2019 (w), 1789 (w), 1740 (w), 1605 (m), 1591 (w), 1574 (m), 1558 (w), 1527 (m), 1499 (s), 1481 (m), 1459 (m), 1447 (m), 1421 (s), 1394 (w), 1359 (m), 1329 (s), 1281 (m), 1248 (s), 1238 (s), 1198 (m), 1168 (m), 1096 (m), 1060 (s), 1033 (w), 1016 (w), 933 (w), 897 (w), 878 (w), 830 (m), 786 (m), 742 (w), 715 (s), 641 (w), 618 (m), 582 (w), 554 (w). *Anal. calc.* for C₅₆H₇₆N₂O₆Ru, %: C, 69.04; H, 7.86; N, 2.88; found, %: C, 69.06; H, 7.82; N, 2.89. ¹H NMR (C₆D₆CD₃, ppm): tert-Bu 1.295 (s), 1.490 (s), aromatics 7.535 (s).

Method b) 0.320 g (0.5 mmol) of thallium(I) 2,4,6,8-tetra-(tert.-butyl)-1-oxo-1H-phenoxazin-9-olate **1a** and 0.104 g (0.5 mmol) of RuCl₃ were dissolved in 15 mL of methanol, the solution was refluxed for an hour, the formed precipitate filtered off and then solved in hot benzene. Remains of TlCl deposited under cooling of the solution were filtered off and the solvent evaporated to give 0.151 g (yield 62%) of **2** (M = Ru).

2.1.3. 2,4,6,8-tetra-(tert.-butyl)-9-hydroxyphenoxazin-1-onium perchlorate **1·HClO₄**

Two drops of concentrated (72%) perchloric acid were added to solution of 0.487 g (0.5 mmol) of ruthenium bis-(2,4,6,8-tetra-(tert.-butyl)-1,9-dioxophenoxazinate) **2** (M = Ru) in 3 mL of benzene and the solution was allowed to stand for two days. The deposited red crystals of salt **1·HClO₄** were collected, filtered off and crystallized from benzene. The yield is 0.318 g (yield 73%). M.p. is 214 °C (decomp). *Anal. calc.* for **1·HClO₄** C₂₈H₄₀ClNO₇, %: C, 62.50; H, 7.49; N, 2.60; found %: C, 62.48; H, 7.49; N, 2.59. IR (ν , cm⁻¹): 3370 (w), 2959 (m), 2910 (m), 2873 (m), 1618 (w), 1572 (m), 1523 (w), 1476 (s), 1455 (s), 1391 (s), 1364 (s), 1347 (s), 1299 (w), 1275 (w), 1251 (m), 1190 (m), 1163 (m), 1129 (s), 1089 (s), 1036 (s), 1008 (m), 915 (m), 887 (m), 840 (m), 810 (w), 761 (w), 736 (w), 683 (m), 668 (s), 647 (m), 623 (s), 559 (w). ¹H NMR (C₆D₆CD₃, ppm): tert-Bu 1.522 (s), 1.632 (s), aromatics 8.515 (s), OH 7.461 (s).

2.1.4. Tris-pyridine-(2,4,6,8-tetra-(tert.-butyl)-1,9-dioxophenoxazinate)ruthenium)Py₃ZnCl₃ **5**

Metallic zinc (0.05 g) and HgCl₂ (0.01 g) were added to solution of 0.975 g (1 mmol) of bis-(2,4,6,8-tetra-(tert.-butyl)-1-oxo-1H-

phenoxazin-9-olate)ruthenium **2** (M = Ru) in 10 mL of pyridine. At the argon atmosphere, the reaction mixture was heated to the boiling point of the solvent and kept at this temperature for 15–20 min. The solution acquired deep green color was cooled, filtered off from powdered zinc and exposed to air. The color of the solution rapidly changes from green to red. The deposited crystals were washed with hexane, dissolved in chloroform and the solvent was slowly evaporated, the deposited solid crystallized from benzene to give 0.550 g (yield 71%) red crystals of **5**. M.p. > 250 °C. *Anal. calc.* for **5** C₆₆H₇₆Cl₃N₅O₃RuZn, %: C, 66.64; H, 6.89; N, 7.23; found %: C, 66.67; H, 6.92; N, 7.21. IR (ν , cm⁻¹): 3108 (w), 2956 (w), 2917 (w), 2867 (w), 1605 (w), 1573 (w), 1551 (w), 1524 (m), 1503 (w), 1482 (m), 1449 (m), 1416 (m), 1361 (w), 1327 (m), 1277 (w), 1246 (m), 1233 (m), 1214 (m), 1198 (w), 1170 (w), 1154 (w), 1097 (w), 1057 (m), 1015 (w), 957 (w), 930 (w), 904 (w), 877 (w), 838 (w), 790 (w), 765 (m), 745 (w), 735 (m), 694 (s), 650 (w), 635 (w), 619 (w), 575 (w). ¹H NMR (C₆D₆CD₃, ppm): tert-Bu 1.506 (s), 1.553 (s), aromatics 7.429–7.475 (m), 7.766–7.710 (m), 7.816–7.950 (m), 8.315–8.367 (m), 8.969–9.029 (m).

2.2. Electrochemistry

The cyclic voltammogram of complex **5** (Fig. 6) was measured in 5 mM solution with the use of three-electrode configuration (glassy-carbon working electrode, Pt counter electrode, Ag/Ag⁺ reference electrode (0.01 M AgNO₃ in CH₃CN)) and potentiostat – galvanostat Elins P-45X. The ferrocene/ferrocenium (Fc/Fc⁺) couple served as internal reference.

2.3. Physical methods

Electronic absorption spectra were recorded in hexane on an Agilent 8453 spectrophotometer. NMR spectra were measured on a Varian Unity-300 spectrometer and referenced to tetramethylsilane (TMS). IR spectra were recorded on Varian 3100 FTIR, Excalibur series instrument in Nujol. EPR measurements were carried out in X-band spectrometer Bruker EMX Plus. The theoretical spectrum was calculated using the Bruker WinEPR Simfonia v.1.25 program.

2.4. Computational details

DFT calculations were performed by means of the Gaussian 09 program package [24] using the B3LYP functional [25] with the standard 6-311 + G(d,p) basis set for all atoms with the exception of Ru, for which the effective core potential and SDD basis set were employed. No account was taken for the dispersion contribution, which is critically important for the correct description of intermolecular interactions of compounds bearing dissociable protons [26] and less significant in the analysis of tasks of intramolecular origin, such as molecular geometry optimization [27]. The stationary points on the potential energy surfaces were located by full geometry optimization and checked for the stabilities of the DFT wave function. The calculations were performed without symmetry constraints. Structural visualizations of the molecular structures were prepared using the ChemCraft software [28].

2.5. Crystallographic methods

Diffraction data for **1·HClO₄** and **5** were collected on Bruker SMART APEX II CCD diffractometer [λ (MoK α) = 0.71072 Å, ω -scans]. The substantial redundancy in data allows empirical absorption correction to be applied with SADABS program, using multiple measurements of equivalent reflections. The structures were solved by direct methods and refined by the full-matrix least-squares technique against F² in the anisotropic-isotropic approximation. The analysis of the Fourier density synthesis has revealed that ClO₄ anion in **1·HClO₄** is disordered by two

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