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Synthesis and redox properties of dinuclear rhodium(II) carboxylates with 2,6-di-*tert*-butylphenol moieties

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ABSTRACT

By exploiting the peculiar reactivity of $[Rh_2(\mu\text{-}O_2CBu^t)_4(H_2O)_2]$ (**1**) the examples of dinuclear rhodium(II) carboxylates containing N-donor axial ligands (**2**, **3**) $[Rh_2(\mu\text{-}O_2CBu^t)_4L_2]$ [where *L* = benzonitrile (**2**), 3,5-di-*tert*-butyl-4-hydroxybenzonitrile (**3**)] were synthesized and characterized by elemental analysis, IR, multinuclear NMR spectroscopy, MALDI-TOF mass spectrometry. It was found by X-ray diffraction that pairs of **3** in crystals are associated through H atoms of phenol groups to produce a dimer of dimers. The chemical oxidation of dirhodium complexes with 2,6-di-*tert*-butyl-4-cyanophenol pendants studied by means of ESR method in solutions leads to the formation of phenoxyl radicals **3**′ in dirhodium system. The ESR data show the interaction of the unpaired electron with ligand nuclei (^1H, ^{14}N) and ^{103}Rh. The stability of radical complexes with phenoxyl fragments in axial position is influenced by the temperature. The enthalpy of the **3**′ decomposition followed by the formation of cyanophenoxyl radical as 20 ± 1 kJ/mol was estimated. Redox transformations in dirhodium system including both metal and axial ligands were investigated by electrochemistry. CV experiments confirm the assumption of the metal oxidation ($Rh^{II} \rightarrow Rh^{III}$) as the first step following by the oxidation of the ligand.

1. Introduction

Dirhodium tetracarboxylates, $Rh_2(\mu\text{-}O_2CR)_4L_2$ with various axial ligands containing a variety of strong N, O, P bases L have long been known [1], and their paddlewheel structure, bonding, and reactivity have been extensively investigated [2–5]. Dirhodium complexes are of interest because of their applications in the field of material science and nanotechnology [6,7]. The use of dirhodium salts as catalysts for C–C bond formation in cycloaddition reactions of olefins [8], acetylenes [9] or in ring-forming C–H insertion reactions [10] has become such powerful synthetic tool as the development of highly enantioselective chiral Rh(II) catalysts [11].

Additionally, recent results achieved in the molecular design and focused synthesis of metal-based drugs suggest that transition metal complexes are promising anti-tumor agents [12]. Studies of the biological activity of dirhodium complexes support the assumption that dirhodium tetracarboxylates act as antibacterial agents, exhibit cytostatic activity against tumors [13] and a significant in vivo antitumor activity [14].

Although the precise anti-tumor mechanism of dirhodium carboxylate compounds has not been elucidated, it is known that they bind to DNA nucleobases and exhibit a strong preference for axial binding of guanine due to the hydrogen bonding interactions between the exocyclic amine group and a carboxylate oxygen atom [15–18]. A systematic variation of the axial and equatorial ligands has shed light on the structure-activity relationship in this family of compounds. It has been shown, for instance, that the anti-tumor activity increases in the series $Rh_2(\mu\text{-}O_2CR)_4$ (R = Me, Et, Pr) with the increase of lipophilicity of the R group [19]. Moreover, since there is the increasing evidence that the oxidative stress plays a critical role in certain pathological states including cancer the application of antioxidants in cancer therapy is strongly needed [20].

The metal complexes containing antioxidative groups of 2,6-di-*tert*-butylphenols have shown the activity as antioxidants, inflammatory agents, scavengers for reactive oxygen species [21–25] which makes them promising agents in complex cancer therapy.

We believe that a systematic research is needed in order to get more insight into complexation of lipophilic phenolic pendants by dirhodium(II) carboxylate molecules, as these interactions play an important role in design of new polytopic redox systems.

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Previously we demonstrated that the introduction of 2,6-di-*tert*-butulphenols into the ligand environment of transition metal increases the stability of corresponding phenoxyl radicals due to the interaction of the unpaired electron with the metal center [26].

In the present paper we report on the synthesis, characterization and redox properties of dirhodium complexes with 2,6-di-*tert*-butulphenol moiety in the ligand $[Rh_2(\mu\text{-}O_2CBu^t)_4L_2]$, where L = 3,5-di-*tert*-butyl-4-hydroxybenzonitrile (**3**) and its analogue $[Rh_2(\mu\text{-}O_2CBu^t)_4L_2]$, where L = benzonitrile (**2**).

The X-ray crystal structure of phenol containing complex (**3**) is described as well. We found by ESR that the chemical oxidation of **3** leads to phenoxyl radicals, the stability of which depends on temperature. We also studied electrochemical properties of dirhodium complexes.

2. Experimental

2.1. Materials and equipment

The starting complex $[Rh_2(\mu\text{-}O_2CCBu^t)_4(H_2O)_2]$ (**1**) [27] and 3,5-di-*tert*-butyl-4-hydroxybenzonitrile [28] were prepared according to literature procedures. All other chemicals are commercially available and used as supplied. $CDCl_3$ (Merck) was used without further purification; other solvents were routinely distilled and dried prior to use. Elemental analysis was performed in the Laboratory of Microanalysis at the Moscow State Lomonosov University (Moscow), Russia.

Infrared spectra were recorded on KBr pellets or in CH_2Cl_2 solution with a "IR200 (Thermo Nicolet)" spectrometer. Electronic absorption spectra were measured on a Cari 219 Varian spectrophotometer.

The ^1H, ^{13}C NMR measurements were performed with a Bruker Avance-400 spectrometer operating on 400 or 100 MHz, respectively in $CDCl_3$.

The MALDI-TOF spectra were acquired using a Autoflex II (Bruker daltonics) mass spectrometer. The samples were dissolved in $CHCl_3$ with 2,5-dihydroxybenzoic acid (DHB) as matrix and put at target.

ESR spectra were recorded on the Bruker EMX spectrometer at X-band frequency (9.8 GHz). The measurements were carried out after pre-evacuation 10^{-2} Torr) of tubes with solutions of samples (concentration $1\cdot10^{-4}$ Mol L^{-1}). The oxidant PbO_2 (Aldrich) was taken in a tenfold excess.

Cyclic voltammetry experiments were performed in CH_3CN solution with 0.05 M Bu_4NBF_4 as supporting electrolyte using a model IPC-Win potentiostat in a conventional one - compartment three-electrode cell (10 ml of solution). A platinum working electrode, platinum wire auxiliary electrode and aqueous Ag/AgCl/KCl reference electrode were used. The electrode was thoroughly polished and rinsed before measurements. The measurements were performed at scan rate equal to 100 mV s^{-1}. The formal potential of the ferrocene Fc/Fc^+ couple versus RE in the dichloromethane solution is equal to 550 mV. All solutions were thoroughly deaerated before and during the CV experiments using argon gas.

2.2. Syntheses

2.2.1. $[Rh_2(\text{-}O_2CBu^t)_4(PhCN)_2]$ (**2**)

To a suspension of **1** (0.200 g, 0.310 mmol) in 10 ml toluene benzonitrile (0.070 g, 0.679 mmol) was added. The solid phase immediately dissolved after addition of benzonitrile. The color of solution immediately changed from pale green to purple. The solution was left for 1 h. The solvent was slowly removed in vacuum, the resulting brown-red crystals were washed with hexane and dried in the air. Yield 0.197 g (85%). *Anal.* Calc. for $C_{34}H_{46}N_2O_8Rh_2$: C, 50.01; H, 5.68; N, 3.43. Found: C, 50.07; H, 5.39; N, 3.64%.

IR (KBr pellet, cm^{-1}): 1583 (vs), 1483 (m), 1414 (s), 1223 (s), ν(CN) 2249 (w), ν(CH) 2871–2962 (s). MS (MALDI-TOF), *m/z*: 610 $[C_{20}H_{36}O_8Rh_2]^+$.

^1H NMR ($CDCl_3$): 1.03 (s, 36 H, $C(CH_3)_3$); 7.56 (t, 4H, Ph), 7.70 (t, 2H, Ph), 7.85 (d, 4H, Ph).

^{13}C NMR: 27.74 ($OOCC(CH_3)_3$); 40.55 ($OOCC(CH_3)_3$); 112.46; 117.27; 129.18; 132.67; 133.13 (C-arom); 117.27 (CN), 198.48 (C=O).

UV–Vis spectrum (EtOH), lg ε (λ_{max}/nm): 4.32 (249); 2.63 (422); 2.62 (590).

2.2.2. $[Rh_2(\text{-}O_2CBu^t)_4L_2]$ (**3**)

To a solution of **1** (0.265 g, 0.410 mmol) in 3 ml toluene 3,5-di-*tert*-butyl-4-hydroxybenzonitrile (0.200 g, 0.865 mmol) was added. The color of solution immediately changed from pale green to dark blue. The solution was stirred for 15 min. The solvent was partially removed by evaporation, and then 2 ml of benzene were added and left for crystallization on the air. Purple crystals of **2** were collected after precipitation by filtration, washed with hexane and dried in the air. Yield 0.303 g (69%). *Anal.* Calc. for $C_{50}H_{78}N_2O_{10}Rh_2$: C, 55.97; H, 7.33; N, 2.61. Found: C, 56.27; H, 6.97; N, 2.40%.

IR (KBr pellet, cm^{-1}): 1585 (vs), 1482 (m), 1414 (s), 1223 (s), ν(CN) 2246 (w), ν(CH) 2873–2960 (s), ν(OH associated) 3546 (w), ν(OH non-associated) 3623 (w).

^1H NMR ($CDCl_3$): δ (ppm): 1.03 (s, 18 H, $C(CH_3)_3$); 1.48 (s, 18 H, $C(CH_3)_3$); 5.62 (s, 1 H, OH); 7.36 (s, 2H, C_6H_2).

^{13}C NMR: 27.69 ($OOCC(CH_3)_3$); 29.89 ($ArC(CH_3)_3$); 34.43 ($OOCC(CH_3)_3$); 40.41 ($ArC(CH_3)_3$); 103.01, 129.96, 136.98, 158.00 (C-arom.); 118.01 (CN), 198.48 (C=O).

Table 1
Crystallographic data and structure refinement for $[Rh_2(\mu\text{-}O_2CBu^t)_4L_2]\cdot4C_6H_6$. ($\mathbf{3}\cdot4C_6H_6$, L= 3,5-di-*tert*-butyl-4-hydroxybenzonitrile).

Formula	$C_{74}H_{102}N_2O_{10}Rh_2$
Formula weight	1385.40
T (K)	120(2)
λ (Å)	0.71073
Crystal system	triclinic
Space group	$P\bar{1}$
Unit cell dimensions	
a (Å)	12.755(6)
b (Å)	12.939(9)
c (Å)	13.725(6)
α (°)	66.93(4)
β (°)	67.18(3)
γ (°)	81.67(4)
V ($Å^3$)	1920.7(18)
D_{calc} (Mg/m3)	1.198
Absorption coefficient (mm^{-1})	0.482
F(0 0 0)	730
Crystal size (mm)	0.35 × 0.23 × 0.15
Theta range for data collection (°)	1.71–28.25
Limiting indices	$-8 \leqslant h \leqslant 12$, $-12 \leqslant k \leqslant 17$, $-18 \leqslant l \leqslant 16$
Reflections collected/unique	13 655/9421 [R_{int} = 0.0625]
Completeness to theta	28.25 93.5%
Maximum and minimum transmission	0.9312 and 0.8494
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	9421/0/424
Goodness-of-fit (GOF) on F^2	1.014
Final *R* indices [$I > 2\sigma(I)$]	R_1 = 0.0671, wR_2 = 0.1794
R indices (all data)	R_1 = 0.0724, wR_2 = 0.1827
Largest difference in peak and hole (e A^{-3})	1.352 and −1.640