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Sn(IV) complexes with bi- and tridentate phenoxazin-1-one ligands: Synthesis, structure and magnetic properties

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ABSTRACT

Two six-coordinate Sn(IV) complexes, *bis*-[2,4,6,8-tetra-(*tert*-butyl)-9-oxyphenoxazinyl-1-onolate]Sn(IV) **4** and *bis*-[2,4,6,8-tetra-(*tert*-butyl)-phenoxazinyl-1-onolate]Sn(IV) dichloride **5** with redox-active tridentate 2,4,6,8-tetra(*tert*-butyl)-9-hydroxyphenoxazin-1-one **2** and bidentate 1-*H*-1-oxo-2,4,6,8-tetra(*tert*-butyl) phenoxazine-1-one **3** ligands were synthesized and their molecular structures determined with the use of X-ray crystallography. Electronic structures of the complexes were investigated with DFT B3LYP*/6-311++G(d,p) calculations, SQUID magnetometry and EPR spectroscopy and assigned to the biradical Sn(IV)$(CatNSQ)_2$ and Sn(IV)$(ISQ)_2Cl_2$ electromeric forms, where $(CatNSQ)^{2-}$ and $(ISQ)^{-}$ are radical-anions formed by the ligands **2** and **3**, correspondingly. Weak ferromagnetic coupling of the two paramagnetic centers was established in complex Sn(IV)$(CatNSQ)_2$ with ligands **2**, whereas in the same type complex formed by ligands **3** the coupling of the paramagnetic centers bears weak antiferromagnetic character. The calculated exchange coupling constants J for **4** and **5** (5 cm^{-1} and -8 cm^{-1}, respectively) are in sufficiently good agreement with the values obtained from analysis of $\mu_{eff}(T)$ dependences (3.5 cm^{-1} and -1 cm^{-1}).

1. Introduction

The considerable interest in the study of metal coordination compounds with redox-active (non-innocent) ligands is primarily determined by the unusual magnetic properties of these compounds containing several paramagnetic centers within a molecule [1–4]. The extensively developed chemistry of such type complexes is almost entirely focused on transition metals, while the non-transition-metal analogues have attracted attention of researchers only in the recent 15–20 years [5–14]. The molecules of non-transition-metal complexes with redox-active ligands have one or more unpaired electrons localized on the ligands that under certain spatial conditions can be ferromagnetically coupled to form species with a potential for magnetic molecular memories [15,16]. Another important property of these complexes is the ability of their redox-active ligands bonded to a non-transition-metal ion to reduce or oxidize substrates coordinated to the metal and thus emulate specific reactivity and catalytic properties of transition-metal complexes [11,6–22]. Tin(IV) complexes based on the bidentate *o*-quinone [9,13,23–25] and *o*-iminoquinone [11,26–28] ligands are among the most intensely studied non-transition-metal complexes. Less studied are tin(IV) complexes with redox-active tridentate ligands [6,29] which are represented by a complex formed by the semiquinonate radical-anion of (3,5-di-*tert*-butyl)-phenyl-1-one-(2-hydroxy-3,5-di-*tert*-butyl-phenyl)imine **1**. The data on temperature dependence of magnetic susceptibility of the complex [6] supported by the DFT calculations [30] of a model structure stripped of four bulky *tert*-butyl groups point to its triplet ground state structure characterized by a ferromagnetic coupling between the unpaired electrons localized on the ligands and stabilized by about 50 cm^{-1} with respect to the singlet form.

We have previously synthesized and studied molecular and electronic structures of a series of *pseudo*-octahedral metal (M = Mn, Fe, Co, Ni, Cu, Zn) complexes of a new redox-active ligand, 2,4,6,8-tetra(*tert*-butyl)-9-hydroxyphenoxazin-1-one **2**, which is a heterocyclic analogue of **1** [31]. In the present study aimed at extending the series of Sn-centered complexes with redox-active ligands we have synthesized tin(IV) complexes containing radical-anion derivatives of the tridentate ligand **2** and bidentate 1-*H*-1-oxo-2,4,6,8-tetra(*tert*-butyl) phenoxazine-1-one ligand **3**,

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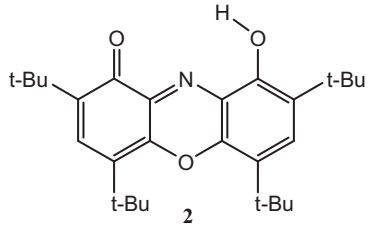
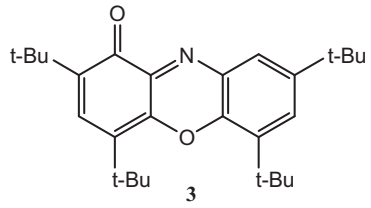
determined their molecular structure with the use of X-ray crystallography, studied magnetic and EPR spectral properties and examined the electronic structures with the use of DFT B3LYP*/6-311++G(d,p) calculations.



2

2,4,6,8-tetra-(*tert*-butyl)-9-hydroxyphenoxazin-1-one



3

1-H-1-oxo-2,4,6,8-tetra(*tert*-butyl)phenoxazine-1-one

2. Experimental

2.1. Synthesis

All the materials used, including $SnCl_2{\cdot}2H_2O$, were of reagent grade purchased from Aldrich and used without further purification. The ligands, 2,4,6,8-tetra-(*tert*-butyl)-9-hydroxyphenoxazin-1-one **2** and 1-*H*-1-oxo-2,4,6,8-tetra(*tert*-butyl)phenoxazine **3**, were prepared following the literature procedures [32,33].

2.1.1. Bis-[2,4,6,8-tetra-(tert-butyl)-9-oxyphenoxazinyl-1-onolate] Sn(IV) *4*

$Sn(CatNSQ)_2$ was prepared by mixing methanol solutions of 0.219 g (0.500 mmol) of 2,4,6,8-tetra-(*tert*-butyl)-9-hydroxyphenoxazin-1-one **2** (20 mL) and 0.056 g (0.250 mmol) of $SnCl_2{\cdot}2H_2O$ (10 mL) under aerobic conditions. The solution was heated at reflux for 2 h, then cooled to room temperature and the precipitated crystals of complex **4** were filtered off, vacuum-dried and recrystallized from benzene and hexane.

Brown crystals (yield 0.16 g, 65%). M.p. 350 °C. *Anal.* Calc. for $C_{56}H_{76}N_2O_6Sn$: C, 67.81; H, 7.72; N, 2.82; Sn, 11.96. Found: C, 67.78; H, 7.65; N, 2.80; Sn, 11.93%. IR(cm^{-1}): 1603(s), 1570(m), 1481(m), 1416(w), 1390(s), 1283(m), 1246(m), 1203(m), 1177(m), 1065(w), 1046(m), 1031(s), 907(m), 876(m), 746(m), 711(m), 633(m), 599(s). The ^1H NMR spectrum of **4** measured in $CDCl_3$ contains two broadened signals of *tert*-butyl groups at 0.86 and −0.34 ppm with the same intensity. The electronic absorption spectrum of **4** is characterized by the intense bands with λ_{max}(toluene)/nm 384 (ε/dm^3 mol^{-1} cm^{-1} 20800), 405 (42000), 490 (6400), 523 (20300), 790 (6000).

2.1.2. Bis-[2,4,6,8-tetra-(tert-butyl)-phenoxazinyl-1-onolate]dichloride Sn(IV) *5*

A solution of 0.422 g (1.00 mmol) of 1-*H*-1-oxo-2,4,6,8-tetra(*tert*-bytyl)phenoxazine-1-one **3** in 25 mL of methanol was added dropwise to a solution of 0.113 g (0.500 mmol) $SnCl_2{\cdot}2H_2O$ in 8.00 mL of methanol. The reaction mixture was allowed to stand for 10–12 h and precipitated crystals of complex **5** were filtered off, vacuum-dried and recrystallized from benzene and diethyl ether.

Red crystals (yield 0.44 g, 85%). M.p. >300 °C. *Anal.* Calc. for $C_{56}H_{78}N_2O_4SnCl_2$: C, 57.25; H, 6.97; N, 2.36; Sn, 10.10. Found: C, 57.10; H, 7.01; N, 2.40; Sn, 10.18%. IR(cm^{-1}): 1591(s), 1538(m), 1450(m), 1411(m), 1394(s), 1359(w), 1278(m), 1256(m), 1243(w), 1202(m), 1176(m), 1124(s), 1081(w), 1046(m), 1013(s), 991(s), 930(s), 887(m), 867(s), 764(s), 737(m), 646(m), 615(m), 583(s).

The ^1H NMR spectrum of **5** measured in $CDCl_3$ contains two groups of broadened signals of *tert*-butyl groups in the range of 6 ÷ 3 and 2 ÷ −1 ppm. The electronic absorption spectrum of **5** is characterized by the intense bands with λ_{max}(toluene)/nm 344 (ε/dm^3 mol^{-1} cm^{-1} 11100), 405 (24400), 530 (13900), 928 (2500).

2.2. Physical methods

IR spectra were recorded on Varian 3100 FT-IR, Excalibur Series instrument by means of Attenuated Total Reflectance (ATR) method. The electronic absorption spectra were recorded on an Agilent Technologies HP-8453 spectrophotometer, ^1H NMR spectra were measured using a Bruker 600 MHz instrument with Me_4Si as an internal standard. EPR measurements were carried out at X-band frequency in continuous-wave (CW) mode using a Bruker Elexsys E580 X/Q-band EPR spectrometer equipped with an Oxford Instruments temperature control system (*T* 4–300 K). EPR spectra of complexes dissolved in toluene at concentration of 1.7 mM were recorded; spectra were simulated using *Easyspin* toolbox for Matlab [34]. The magnetic susceptibility of the polycrystalline complexes was measured with a Quantum Design MPMS*XL* SQUID magnetometer in the temperature range 5–300 K with magnetic fields of up to 5 kOe. Diamagnetic corrections were made using the Pascal constants. The effective magnetic moment was calculated as $\mu_{eff}(T) = [(3k/N_A\mu_B^2)\chi T]^{1/2} \approx (8\chi T)^{1/2}$.

2.3. Crystallographic methods

Intensity data for single crystals of **4** and **5** were collected on a Smart Apex II (Bruker AXS) diffractometer at 240 K using graphite monochromatized Mo Kα radiation (λ = 0.71073 Å). Absorption correction included with the Bruker SADABS program, version 2.10. The structures were solved by direct methods (BRUKER-SHELXS) and refined by the full-matrix or full-matrix least-squares methods on F^2 (BRUKER-SHELXL).

The positions of the hydrogen atoms were calculated geometrically and refined isotropically using the riding model. Two heptane solvent molecules are definitely localized in the Δρ synthesis for **4** that corresponds to the composition **4**·$2C_7H_{14}$ and for **5** a single crystal contains a diethyl ether molecule (**5**·0.5 Et_2O). However, when we tried to refine atomic positions of these molecules, especially in an anisotropic approximation, the resulting atomic displacement parameters pointed to the need to separate each molecule of **2** or more items. For this reason, the solvate molecules were excluded at the last stage of refinement (SQUEEZE contribution of PLATON [35]). All structure solutions and refinement calculations were performed with Bruker SHELXTL Version 6.14 software.

2.4. Computational Details

DFT calculations were performed by means of the Gaussian 03 program package [36] using the modified B3LYP* functional [37] known to provide for more accurate data on the relative energies of the electronic states with different multiplicities [38,39]. The standard 6-311++G(d,p) basis set well reproducing energy parameters of a number of open electronic shell metal coordination compounds was used for all atoms with the exception of Sn, for which the effective core potential and SDD basis set were employed. The stabilities of Hartree–Fock solutions for all structures were checked.