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# Syntheses, structures, spectroscopic properties and DFT calculations of Re(V)-benzothiazole and 2-(2-aminophenyl)benzothiazole complexes

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ABSTRACT

The paper presents a combined experimental and computational study of novel oxorhenium(V) complexes of benzothiazole (bt) and 2-(2-aminophenyl)benzothiazole (apbt). The complexes $[Re_2O_3Cl_4(bt)_4]\cdot H_2O$ (**1**$\cdot H_2O$), $[ReO(OEt)Cl_2(bt)(PPh_3)]\cdot Me_2CO$ (**2**$\cdot Me_2CO$), $[ReO(OPr^i)Cl_2(bt)(PPh_3)]$ (**3**), $[ReOCl_2(apbt)(OPPh_3)]$ (**4**) and $[ReOCl_2(apbt)(OAsPh_3)]\cdot 0.5CHCl_3$ (**5**$\cdot 0.5CHCl_3$) have been characterized structurally (by single-crystal X-ray diffraction) and spectroscopically (by IR, NMR, UV–Vis). For compounds **1**, **2** and **4**, DFT and TD-DFT calculations have been performed to obtain their IR and UV–Vis absorption spectra, and satisfactory theoretical–experimental agreement was achieved. Additional information about binding between the rhenium atom and oxo ligand in the complexes **1**, **2** and **4** has been obtained by NBO analysis.

## 1. Introduction

The widespread contemporary interest in the coordination chemistry of rhenium arises mainly from the introduction of $\beta^-$ emitting isotopes $^{188}$Re and $^{186}$Re in radiotherapy and its similarity with technetium, whose metastable $\gamma$-emitting isotope $^{99m}$Tc plays important role in diagnostic nuclear medicine [1–5]. The success of the $^{186}$Re(Sn)HEDP (HEDP = hydroxyethylenediphosphonic acid) radiopharmaceutical as a palliative of bone pain has particularly reawakened interest in the coordination chemistry of rhenium in order to develop new $^{186/188}$Re radiopharmaceuticals which could be used for the treatment of cancer [6]. Although kit preparations for the imaging of almost all main organs and organ systems exist and there is some experience in the labeling of biomolecules, there is still a need for new approaches and new labeling procedures. It is obvious that promising contributions are expected from the coordination chemistry and organometallic chemistry which plays an important role in the development of novel rhenium and technetium radiopharmaceuticals. It is a challenge for synthetic chemists to supply novel methods and compound for the radiopharmaceutical community. In this context, the design, synthesis and reactivity of the rhenium complexes, especially oxocompounds, has become the aim of several laboratories, including ours [7–9].

On the other hand, compounds containing a benzothiazole moiety constantly attract the interest of chemists and pharmacists on account of their versatile biological activity and industrial applications. Most of them exhibit anticancer [10], antitumor [11], antimicrobial [12], antifungal [13], anti-inflammatory [14] and antiallergic [15] activity and play important role in design and synthesis of organic luminescent materials [16]. Furthermore, possessing two endocyclic heteroatoms with pronounced donor abilities, e.g. S and N, they are of significant interest in coordination chemistry binding to metal centers in a monodentate way or forming supramolecular arrangements [17,18].

Surprisingly, studies on rhenium complexes incorporating such ligands have been relatively rare [19–22]. Recently, we have reported results of our studies on the tricarbonyl rhenium(I) complex of 2-(2-aminophenyl)benzothiazole (apbt) [23]. Here, we present the synthesis, spectroscopic characterization, crystal and molecular structure of three novel rhenium compounds of benzothiazole $[Re_2O_3Cl_4(bt)_4]\cdot H_2O$ (**1**$\cdot H_2O$), $[ReO(OEt)Cl_2(bt)(PPh_3)]$ (**2**$\cdot Me_2CO$) and $[ReO(OPr^i)Cl_2(bt)(PPh_3)]$ (**3**) and two oxocompounds $[ReOCl_2(apbt)(OPPh_3)]$ (**4**) and $[ReOCl_2(apbt)(OAsPh_3)]\cdot 0.5CHCl_3$ (**5**$\cdot 0.5CHCl_3$) incorporating 2-(2-aminophenyl)benzothiazole (apbt, Scheme 1).

The experimental studies have been accompanied computationally by the density functional theory (DFT) calculations. Currently density functional theory (DFT) is commonly used to examine the electronic structure of transition metal complexes. It meets with the requirements of being accurate, easy to use and fast enough to allow the study of relatively large molecules of transition metal complexes. Gancheff et al. [24,25] have performed extended tests of the ability of different DFT methods, including B3LYP with LANL2DZ basis set, for rhenium compounds in a geometry optimization and calculation of spectral properties. Although

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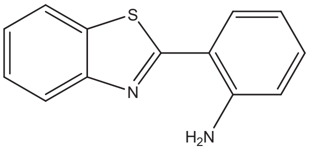

**Scheme 1.** Structure of 2-(2-aminophenyl)benzothiazole (apbt) ligand.

LANL2DZ is not a very extended basis set, its use with B3LYP has shown to be sufficient for the geometry optimization and calculation of spectral properties. It gives good agreement with the experimental data and its use is justified in the case of large molecules.

## 2. Experimental

### 2.1. General procedure

All chemicals were purchased from commercial sources and used without further purification. The $[ReOCl_3(PPh_3)_2]$, $[ReOCl_3(AsPh_3)_2]$ and $[ReOCl_3(OPPh_3)(SMe_2)]$ complexes were prepared according to the published methods [26–29].

### 2.2. Physical measurements

Infrared spectra were recorded on a Perkin–Elmer 1600 FTIR spectrophotometer in the spectral range 4000–400 $cm^{-1}$ with the samples in the form of KBr pellets. Electronic spectra were measured on a spectrophotometer Lab Alliance UV–Vis 8500 in the range 1100–180 nm in $CH_3OH$ solution. The $^1H$ NMR spectra were obtained DMSO-$d_6$ at room temperature on a Bruker AM 400 spectrometer. Chemical shifts ($\delta$, ppm) are relative to internal TMS.

### 2.3. Preparation of $[Re_2O_3Cl_4(bt)_4]\cdot H_2O$ (**1**$\cdot H_2O$)

$[ReOCl_3(OPPh_3)(SMe_2)]$ (0.50 g, 0.70 mmol) was suspended in methanol (60 ml) and benzothiazole (0.21 g, 1.40 mmol) was added. The mixture was stirred at ambient temperature for 48 h and filtered, yielding a bluish-green solid, which was washed with ethanol and then recrystallized from acetonitrile. Yield: 78%. IR (KBr, $cm^{-1}$): 1617(w), 1589(w), 1564(w) $\nu$(C=N) and $\nu$(C=C); 932(s) $\nu$(Re=O); 673(vs) $\nu_{as}$(Re–O–Re). $^1H$ NMR (400 MHz, DMSO-$d_6$): 9.49 (s, 2H), 9.40 (s, 2H), 8.65–8.61 (m, 2H), 8.34–8.29 (m, 2H), 8.19 (d, 2H), 8.10 (d, 2H), 7.81–7.74 (m, 4H), 7.56 (t, 2H), 7.50 (t, 2H), 3.41 (2H, $H_2O$).

### 2.4. Preparation of $[ReO(OEt)(bt)(PPh_3)]\cdot Me_2CO$ (**2**$\cdot Me_2CO$)

A mixture of $[ReOCl_3(PPh_3)_2]$ (0.50 g, 0.60 mmol) and benzothiazole (0.16 g, 1.18 mmol) in ethanol (60 ml) was refluxed for 2 h and allowed to cool to ambient temperature. The resulting brown suspension was filtered. Purple microcrystalline precipitate was washed with ethanol and then recrystalized from a mixture ethanol/acetone. Yield: 72%. IR (KBr, $cm^{-1}$): 1708 $\nu$(C=O), 1587(w), 1572(w) $\nu$(C=N) and $\nu$(C=C), 1116(s) $\nu$(OEt), 951(s) $\nu$(Re=O), 511(s) $\nu$(Re–OEt). $^1H$ NMR (400 MHz, DMSO-$d_6$): 9.41 (s, 1H), 8.18 (d, 1H), 8.10 (d, 1H), 7.70–7.53 (m, 16H), 7.49 (t, 1H), 3.47–3.40 (qr, 2H), 2.19 (s, 6H), 1.05 (t, 3H).

### 2.5. Preparation of $[ReO(OPr^i)(bt)(PPh_3)]$ (**3**)

A procedure similar to that for **2** was used with benzothiazole (0.16 g, 1.18 mmol) and $[ReOCl_3(PPh_3)_2]$ (0.5 g, 0.60 mmol) in propan-2-ol (60 ml). The purple crystalline precipitate of **3** was collected in 74% yield. IR (KBr, $cm^{-1}$): 1590(w), 1562(w), 1542(w) $\nu$(C=N) and $\nu$(C=C); 1124(s) $\nu$(OiPr), 953(s) $\nu$(Re=O), 511(s) $\nu$(Re–OiPr). $^1H$ NMR (400 MHz, DMSO-$d_6$): 9.40 (s, 1H), 8.17 (d, 1H), 8.10 (d, 1H), 7.67–7.53 (m, 16H), 7.50 (td, 1H), 3.77 (sp, 1H), 1.04 (t, 6H); UV–Vis ($CH_3OH$; $\lambda_{max}$ (nm) ($\varepsilon$ ($dm^3 mol^{-1} cm^{-1}$))): 558.2 (510), 456.4 (2700), 292.0 (16380), 273.0 (28140), 254.0 (43210), 210.5 (129540).

### 2.6. Preparation of $[ReOCl_2(apbt)(OPPh_3)]$ (**4**)

#### 2.6.1. Method A

2-(2-aminophenyl)benzothiazole (0.35 g, 1.55 mmol) was added to $[ReOCl_3(OPPh_3)(SMe_2)]$ (0.50 g, 0.77 mmol) in a mixture of methanol/tetrahydrofuran (30/30 ml) and refluxed for 4 h. The resulting brown solution was reduced in volume to ~20 ml and allowed to cool to room temperature. Brown crystalline precipitate of $[ReOCl_2(apbt)(OPPh_3)]$ was filtered off and dried in the air. Single brown crystals, suitable for X-ray measurement were obtained by recrystallization from the mixture of methanol and chloroform. Yield: 68%.

#### 2.6.2. Method B

$[ReOCl_3(PPh_3)_2]$ (0.50 g, 0.6 mmol) was added to 2-(2-aminophenyl)benzothiazole (0.27 g, 1.2 mmol) in a mixture of methanol/tetrahydrofuran (30/30 ml) and refluxed for 4 h. The resulting brown solution was reduced in volume to ~20 ml and allowed to cool to room temperature. Brown crystalline precipitate of $[ReOCl_2(apbt)(OPPh_3)]$ was filtered off and dried in the air. Single crystals were obtained by recrystallization from the mixture of methanol and THF. Yield: 45%.

IR (KBr, $cm^{-1}$): 3293 (m) $\nu$(N–H); 1600(w) 1589(w), 1567(w) $\nu$(C=N) and $\nu$(C=C); 1134 (s) 1119 (sh) $\nu$(P=O); 970(s) $\nu$(Re=O). $^1H$ NMR (400 MHz, DMSO-$d_6$): $\delta$ = 9.26 (d, 1H), 8.24 (d, 1H), 8.11 (d, 1H), 8.03 (d, 1H), 7.93 (d, 1H), 7.66–7.52 (m, 15H), 7.28 (d, 1H), 6.96 (d, 1H), 6.75–6.69 (m, 1H).

### 2.7. Preparation of $[ReOCl_2(apbt)(OAsPh_3)]\cdot 0.5CHCl_3$ (**5**$\cdot 0.5CHCl_3$)

A procedure similar to that for $[ReOCl_2(apbt)(OPPh_3)]$ was used with $[ReOCl_3(AsPh_3)_2]$ (0.50 g, 0.54 mmol) and 2-(2-aminophenyl)benzothiazole (0.25 g, 1.10 mmol). Yield: 62%. IR (KBr, $cm^{-1}$): 3293 (m) $\nu$(N–H); 1598(w) 1565(w) $\nu$(C=N) and $\nu$(C=C); 962(s) $\nu$(Re=O); 857(s), 847(sh) $\nu$(As=O). $^1H$ NMR (400 MHz, DMSO-$d_6$): $\delta$ = 9.24 (d, 1H), 8.25 (d, 1H), 8.10 (d, 1H), 8.01 (d, 1H), 7.93 (d, 1H), 7.90–7.73 (m, 15H), 7.29–7.19 (m, 1H), 6.89 (d, 1H), 6.75–6.64 (m, 1H). UV–Vis ($CH_3OH$; $\lambda_{max}$ (nm) ($\varepsilon$ ($dm^3 mol^{-1} cm^{-1}$))): 445.0 (2580), 372.0 (8300), 362.0 (7775), 303.5 (11555), 290.0 (12435), 222.5 (43800), 211.5 (92995).

### 2.8. Crystal structure determination and refinement

The X-ray intensity data of the complexes were collected on a Gemini A Ultra diffractometer equipped with Atlas CCD detector and graphite monochromated Mo K$\alpha$ radiation ($\lambda$ = 0.71073 Å) at room temperature. Details concerning crystal data and refinement are given in Table 1. Lorentz, polarization and empirical absorption correction using spherical harmonics implemented in SCALE3 ABSPACK scaling algorithm [30] were applied. The structure was solved by the Patterson method and subsequently completed by the difference Fourier recycling. All the non-hydrogen atoms were refined anisotropically using full-matrix, least-squares technique. The hydrogen atoms were treated as "riding" on their parent carbon atoms and assigned isotropic temperature factors equal 1.2 (non-methyl) times the value of equivalent temperature factor of the parent atom. SHELXS97 and SHELXL97 [31,32] programs were used for all the calculations. After the final cycle of the refinement of the compounds **1**, **3** and **4**, the models of structures contain solvent