

Short communication

## Slow diffusion in situ ruthenium/ligand reaction: Crystal structures, fluorescence and biological properties

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## ABSTRACT

Promoted by  $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$  coordination in the mixed solvent DMF/ $\text{H}_2\text{O}$ , diverse *in situ* S–S bond reactions such as S–S bond scission and S-oxidation occurred in the disulfide ligand of 2,2'-dithiodibenzoic acid (dtdb) to yield the new sulfinato-benzoate ligand (sb). The X-ray analysis of complexes of  $[\text{Ru}(\text{phen})_2(\text{sb})]$  (**1**) and  $[\text{Ru}(\text{bipy})_2(\text{sb}) \cdot \text{H}_2\text{O}]$  (**2**) revealed that in both complexes, the ruthenium ion was found to be in an octahedral geometry, coordinating to the sulfur atom, rather than the oxygen of sulfinate. The complexes were found to be active against the bacterial strains tested with MIC ranging from 14.3–261  $\mu\text{M}$ . In addition, the metal complexes present strong DNA binding affinity constants in the major or minor grooves at the order of magnitude  $10^5$ – $10^6 \text{ M}^{-1}$ . The antioxidant activities of the ligand and its metal complexes were investigated through scavenging effects for DPPH *in vitro*, indicating that the compounds show stronger activities than some standard antioxidants, such as ascorbic and vitamin C.

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*In situ* metal/disulfide reactions under slow diffusion conditions undergo S–S mediated bond reactions, such as S-oxidation, S–S and C–S bond scission. This is a very important research field in coordination chemistry as it leads to structurally novel coordination architectures with interesting physical properties [1–3]. In this respect, the use of organosulfur compounds containing carboxylate groups can be attractive due to their flexibility and versatile coordinating modes of both sulfur and oxygen atoms and, generating unprecedented coordination frameworks which can act as linkers between inorganic moieties [4–8]. Up to now, a series of transition metal complexes have been found to react with 2,2'-dithiodibenzoic acid (dtdb), giving rise to 1D chains, 2D sheets or 3D network whereby the carboxylate act as monodentate or bidentate donor with or without cleavage of the S–S bond [9]. Recently, we have isolated new copper(II) coordination polymers, whereby dtdb underwent simultaneous S–S and C–S scission under slow diffusion conditions, leading to the formation of 1D coordination polymers [10]. In the presence of 1,10 phenanthroline (phen) and 2,2'-bipyridine (bipy), in addition to extrusion of the sulfur atom, the oxidation of sulfur to a sulfate ion was observed. These observations, coupled with the fact that there are no reports of ruthenium complexes derived from dtdb, stimulated our interest to investigate its coordination behavior. Hence, in this work we report for the first time new coordination polymers obtained from  $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$  and dtdb in the presence of phen and bipy,

which exhibit sulfinato-benzoate units. The fluorescent, antioxidant and antibacterial properties of the complexes have also been studied, since ruthenium complexes are considered as an attractive alternative to platinum in anticancer drug design and biological applications [11–13] due to their lower toxicity towards healthy tissues [14,15].

The mononuclear ruthenium(II) complexes  $[\text{Ru}(\text{phen})_2(\text{sb})]$  (**1**) and  $[\text{Ru}(\text{bipy})_2(\text{sb}) \cdot \text{H}_2\text{O}]$  (**2**) were characterized by IR,  $^1\text{H}$  and  $^{13}\text{C}$ -NMR, X-ray, UV, and elemental analysis. The complexes were found to be stable at room temperature, non-electrolyte and insoluble in most organic solvents except DMSO.

The X-ray crystallographic data of **1** and **2** are given in Table 1 while selected bond lengths and bond angles are listed in Table S1. The structures of complexes **1** and **2** crystallize in triclinic and monoclinic systems respectively. Their configuration is based on the *in situ* reaction of the disulfide ligand cleavage to form the new sulfinato-benzoate ligand,  $(\text{C}_6\text{H}_4)(\text{SO}_2)(\text{COO})^-$  (sb). The Ru(II) ion in both complexes is six-coordinated and resides in a distorted octahedral  $[\text{ON}_4\text{S}]$  coordination geometry (Fig. 1), where the metal ion is coordinated to four nitrogens of the phen/bipy moieties, one oxygen and one sulfur of sb. The oxidation of sulfur to sulfinates has been reported [16,17], however this is a rare example where the metal ion is coordinated to the sulfur atom, rather than the oxygen of sulfinate. The overlay of the structures of both molecular species match each other closely, however their packing arrangements differ (Figs 2 and 3). This is due not only to the symmetry of the different space groups, but also to the fact that the structure of **1** is composed of two chemically identical but crystallographically

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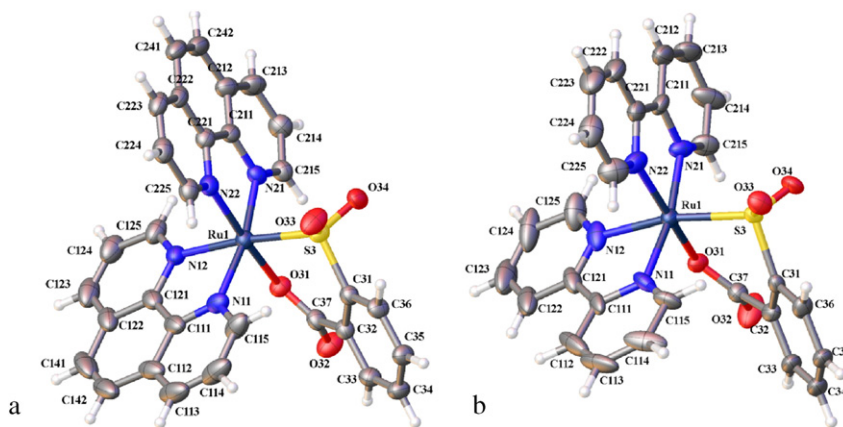
**Table 1**  
Data collection and refinement parameters for the crystal structures of **1** and **2**.

Identification code	<b>1</b>	<b>2</b>
Empirical formula	C <sub>31</sub> H <sub>20</sub> N <sub>4</sub> O <sub>4</sub> RuS	C <sub>27</sub> H <sub>20</sub> N <sub>4</sub> O <sub>4</sub> RuS·O
Formula weight	645.64	613.60
Temperature (K)	100(2) K	200 K
Wavelength (Å)	0.71075 Å	0.71073 Å
Crystal system	Triclinic	Monoclinic
Space group	P-1	C2/c
<i>Unit cell dimensions</i>		
a (Å)	13.4610(9)	31.7361(19)
b (Å)	15.0930(11)	8.5039(5)
c (Å)	15.4114(11)	19.4112(12)
α (°)	103.697(5)°	90
β (°)	93.562(5)°	102.919(3)
γ (°)	113.626(6)°	90
Volume/Å <sup>3</sup>	2743.4(4)	5106.1(5)
Z	4	8
ρ <sub>calc</sub> (mg/mm <sup>3</sup> )	1.563	1.596
Absorption coefficient (mm <sup>-1</sup> )	0.692	1.050
F(000)	1304	2480
Crystal	Block; red	Plate; yellow
Crystal size (mm <sup>3</sup> )	0.28 × 0.09 × 0.05	0.04 × 0.14 × 0.35
θ range for data collection (°)	2.3–27.5°	1.3–28.4°
Reflections collected	37,678	6365
Independent reflections	12,502	6365
Completeness to θ max	99.6%	99.9%
Max and min transmission	1.000 and 0.522	1.000 and 0.8664
Data/restraints/parameters	12,502/0/739	6365/1/384
Goodness-of-fit on F <sup>2</sup>	0.991	1.186
Final R indexes [I ≥ 2σ (I)]	R1 = 0.0528, wR2 = 0.1371	R1 = 0.0865, wR2 = 0.2344
Final R indexes [all data]	R1 = 0.0678, wR2 = 0.1462	R1 = 0.1101, wR2 = 0.2448
Largest diff. peak/hole (e Å <sup>-3</sup> )	0.94/−1.08	1.54/−1.58
CCDC deposition number/ref. code	1417781	1417780

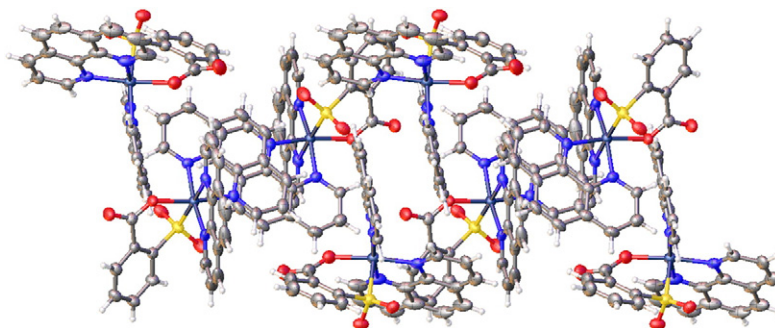
unique molecules in the asymmetric unit, whereas **2** has only one. In structure **2** the ligand sb shows rotational disorder in a 0.70:0.30 ratio. The dihedral angles between the two least square planes formed by the disordered sb ligand and the phenanthroline ligand trans to the Ru–S bond are 63.8(2) and 61.8(4)°.

The Ru–N, Ru–O and Ru–S bond lengths in complexes **1** and **2** were found to be in the range of 2.046(3)–2.130(3), 2.075(2)–2.103(10) and 2.217(1)–2.232(1) Å and agree well with previous reports [18,19]. The S–O bond lengths are in the range of 1.465(3)–1.489(3) Å, typical of the S=O bond [20]. The carboxylate groups in both complexes adopt the μ<sub>1</sub>:<sub>1</sub>1:1° monodentate coordination mode [21]. The N–Ru–O bond angles in the axial plane in **1** and **2** are 171.9(1) and 166.4(3), deviating from the perfect octahedral geometry. The angles in the equatorial plane are in the range of 78.3(3)–97.3(1)°. In addition, the structure of **1** contains interchain π–π stacking interactions between the pyridyl rings of the phen moiety, with centroid–centroid separation ranging from 3.592–3.835 Å. There are additional π–π stacking interactions between the sb ligands from one of the unique molecules within **1** (3.820 Å). The π–π stacking interactions which are present within **2** differ to **1** as they occur between the benzoate ring and one half of the bipy moiety (C221–C225). Several weak hydrogen bonds (C–H...O) exist within both crystal structures which help stabilize each molecular packing arrangement. The donor to acceptor hydrogen bond distances and D–H...A angles range from 2.83(5)–3.48(14) Å and 106–170° respectively (Table S2).

The infrared spectral bands that are most useful in determining the coordination modes of the ligand towards the ruthenium metal are ν(C=O), ν(C–S) and ν(Ru–N). The ν(C=O) band in the free ligand shifted from 1674 cm<sup>-1</sup> to 1648 and 1654 cm<sup>-1</sup> in **1** and **2** respectively, a clear indication of monodentate type of coordination [22]. The characteristic band of ν(C–S) at 896 cm<sup>-1</sup> in dtdb is shifted to lower frequency (857 cm<sup>-1</sup>), due to coordination of the sulfur atom [23]. The new peaks



**Fig. 1.** a) X-ray crystal structure of **1** (Ru(phen)<sub>2</sub>(sb)). Only one of the chemically identical pair of molecules in the asymmetric unit is shown for clarity. b) X-ray crystal structure of **2** (Ru(bipy)<sub>2</sub>(sb)·H<sub>2</sub>O) with labels provided. A solvent water molecule has been omitted for clarity. Thermal ellipsoids are drawn at 50% probability level.



**Fig. 2.** The X-ray crystal structure packing of **1** viewed down crystallographic axis A (Ru(phen)<sub>2</sub>(sb)). Thermal ellipsoids are drawn at 50% probability level.

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