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Synthesis, structure and electrochemical properties of some thiosemicarbazone complexes of ruthenium

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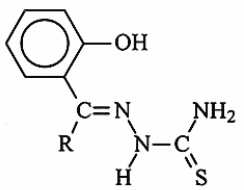
Reaction of salicylaldehyde thiosemicarbazone (L^1), 2-hydroxyacetophenone thiosemicarbazone (L^2) and 2-hydroxynapthaldehyde thiosemicarbazone (L^3) with $[Ru(dmso)_4Cl_2]$ affords a family of three dimeric complexes (**1**), (**2**) and (**3**) respectively. Crystal structure of the complex (**3**) has been determined. In these complexes, each monomeric unit consists of one ruthenium center and two thiosemicarbazone ligands, one of which is coordinated to ruthenium as O,N,S-donor and the other as N,S-donor forming a five-membered chelate ring. Two such monomeric units remain bridged by the sulfur atoms of the O,N,S-coordinated thiosemicarbazones. Due to this sulfur bridging, the two ruthenium centers become so close to each other, that a ruthenium-ruthenium single bond is also formed. All the complexes are diamagnetic in the solid state and in dimethylsulfoxide solution show intense absorptions in the visible and ultraviolet region. Origin of these spectral transitions has been established from DFT calculations. Cyclic voltammetry on the complexes shows two irreversible ligand oxidations on the positive side of SCE and two irreversible ligand reductions on the negative side.

Keywords: Coordination chemistry**,** Coordination modes, Thiosemicarbazones, Ruthenium

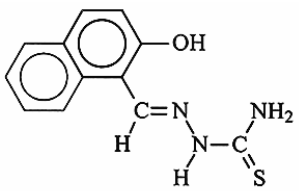
The chemistry of thiosemicarbazone complexes of the transition metal ions has been receiving significant attention currently, largely because of the bioinorganic relevance of these complexes[1-8]. A large majority of the thiosemicarbazone complexes have found wide medicinal applications owing to their potentially beneficial biological (viz, antibacterial, antimalarial, antiviral and antitumor) activities[9-17]. Systematic studies on the binding of thiosemicarbazones to different transition metal ions are of considerable importance in this respect. We have been exploring the chemistry of platinum metal complexes of thiosemicarbazones[18-28], with the primary objective of gaining a chemical control over the variable binding mode of these ligands, and the present work has emerged out of this exploration.

Herein we have chosen three potentially tridentate thiosemicarbazones, viz., thiosemicarbazones of salicylaldehyde (**L^1**), 2-hydroxyacetophenone (**L^2**) and 2-hydroxynaphthaldehyde (**L^3**), and to interact with these thiosemicarbazones, ruthenium has been selected as the metal center.

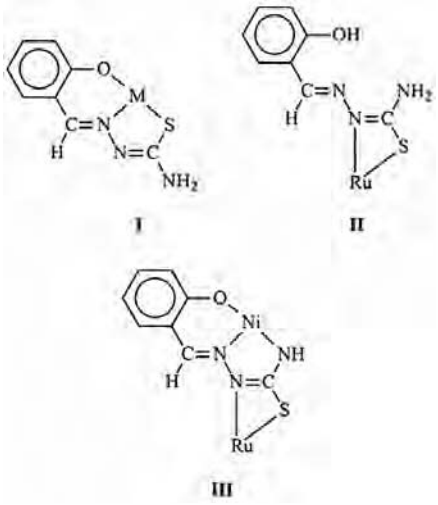
Salicylaldehyde thiosemicarbazone (as well as each of the other two ligands) is usually expected to bind to a metal center, via dissociation of two acidic protons, as a dianionic tridentate O,N,S-donor forming stable chelate (**I**), and this mode of binding has been truly observed by us in its complexes of rhodium[24], iridium[22], palladium[20] and platinum[21]. However, upon reaction with $[Ru(PPh_3)_3Cl_2]$, it displayed a rather unusual coordination mode (**II**), where, in spite of having the phenolic oxygen as a potential third donor site, it binds to ruthenium as a bidentate N,S-donor forming a four-membered chelate ring[28]. The ruthenium-bound thiosemicarbazone in (**II**) has been utilized further for the construction of an interesting ruthenium-nickel heterometallic assembly (**III**), where all the five available donor atoms in the thiosemicarbazone ligand are engaged in coordination along with bridging mode of binding from the sulfur to nickel[25]. The fact that a simple O,N,S-chelate for ruthenium (**I**, M = Ru) could not be obtained so far, has led us to look for possible ways to achieve this goal.



L^1 (R = H)
L^2 (R = CH_3)



L^3



Herein we have selected $[Ru(dmso)_4Cl_2]$ as the source of ruthenium. This particular complex has been selected as the ruthenium starting material for the present study because of its demonstrated ability to serve as an efficient synthon towards preparation of homoleptic complexes by providing six donor sites on the metal center via facile elimination of all the four dimethylsufoxides and two chlorides[29,30]. Reaction of the selected thiosemicarbazones with $[Ru(dmso)_4Cl_2]$ has indeed afforded a group of three homoleptic complexes of ruthenium. The chemistry of these complexes is reported in this paper with special reference to their formation, structure and, spectral and electrochemical properties.

Materials and Methods

Commercial ruthenium trichloride was purchased from Arora Matthey, Kolkata, India, and converted to $[Ru(dmso)_4Cl_2]$ by an earlier reported method[31]. Salicylaldehyde, 2-hydroxyacetophenone and 2-hydroxynaphthaldehyde were obtained from SD Fine Chem, Mumbai, India. Thiosemicarbazide was procured from Loba Chemie, Mumbai, India. The thiosemicarbazone ligands ($\mathbf{L^1}$, $\mathbf{L^2}$ and $\mathbf{L^3}$) were prepared by condensing equimolar amounts of the respective aldehyde or ketone with thiosemicarbazide in hot ethanol. Tetrabutylammonium hexafluorophosphate (TBHP) procured from Aldrich, and AR grade acetonitrile procured from Merck (India) were used in electrochemical studies. All other chemicals and solvents were reagent grade commercial materials and were used as received.

Microanalyses (C, H, N) were performed using a Heraeus Carlo Erba 1108 elemental analyzer. Mass spectra were recorded with a Micromass LCT electrospray (Qtof Micro YA263) mass spectrometer by electrospray ionization method. IR spectra were obtained on a Perkin-Elmer 783 spectrometer with samples prepared as KBr pellets. ^{1}H NMR spectra were recorded in $CDCl_3$ and DMSO-d_6 solutions on a Bruker Avance DPX 300 NMR spectrometer using TMS as the internal standard. Electronic spectra were recorded on a Jasco V-570 spectrophotometer. Magnetic susceptibilities were measured using a Sherwood MK-1 balance. Electrochemical measurements were made using a CH Instruments (model 600A) electrochemical analyzer. A platinum disc working electrode, a platinum wire auxiliary electrode and an aqueous saturated calomel reference electrode (SCE) were used in the cyclic voltammetry experiments. All electrochemical experiments were performed under a dinitrogen atmosphere. All electrochemical data were collected at 298 K and are uncorrected for junction potentials. Optimization of ground state structures and energy calculations of the ruthenium complexes were carried out by density functional theory (DFT) method using the GAUSSIAN 03 (B3LYP/SDD-6-31G) package[32,33].

Synthesis of the complexes

To a solution of the ligand ($\mathbf{L^1}$, $\mathbf{L^2}$ or $\mathbf{L^3}$) (60 mg, 0.30 mmol), in hot ethanol (30 mL), triethylamine (62 mg, 0.60 mmol) was added followed by $[Ru(dmso)_4Cl_2]$ (50 mg, 0.10 mmol). The mixture was heated at reflux for 6 h to yield a brown solution. Evaporation of this solution gave a brown solid, which was subjected to purification by thin layer chromatography on a silica plate. With 1:1 acetonitrile-benzene as the eluant, a brown band separated, which was extracted with acetonitrile. Upon evaporation of the acetonitrile extract, the complex was obtained as a crystalline brown solid.

Complex (1): Yield: 60 mg (65 %). Anal. (%): Calcd for $C_{32}H_{30}N_{12}O_4S_4Ru_2$: C, 39.34; H, 3.07; N, 17.21. Found: C, 39.45; H, 3.11; N, 17.18. Mass: 977, $[M+H]^+$; 489, $[M/2 + H]^+$.

Complex (2): Yield: 65 mg (71 %). Anal. (%): Calcd for $C_{36}H_{38}N_{12}O_4S_4Ru_2$: C, 41.86; H, 3.68; N, 16.28. Found: C, 41.95; H, 3.64; N, 16.23. Mass: 1033, $[M+H]^+$; 846, $[M-L^2+Na]^+$.

Complex (3): Yield: 58 mg (63 %). Anal. (%): Calcd for $C_{48}H_{38}N_{12}O_4S_4Ru_2$: C, 48.98; H, 3.23; N, 14.28. Found: C, 48.76; H, 3.29; N, 14.34. Mass: 1177, $[M+H]^+$; 593, $[M/2 +2H_2 + H]^+$.

Crystallographic studies

Single crystals of complex (**3**) were obtained by slow evaporation of an acetonitrile solution of the

complex. Selected crystal data and data collection parameters are given in Table 1. Data on the crystal were collected on a Marresearch Image Plate system using graphite monochromated Mo-K_α radiation (λ = 0.71073 Å). X-ray data reduction and, structure solution and refinement were done using SHELXS-97 and SHELXL-97 programs[34]. The structure was solved by direct methods.

Results and Discussion

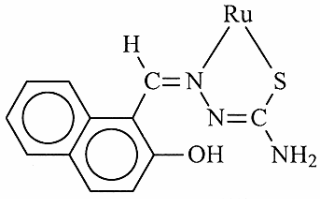
Synthesis and structure

Reactions of the selected thiosemicarbazones ($\mathbf{L^1}$, $\mathbf{L^2}$ and $\mathbf{L^3}$) have been carried out with $[Ru(dmso)_4Cl_2]$ in refluxing ethanol in the presence of triethylamine, which have afforded three brown complexes, referred to respectively as complex (**1**), (**2**) and (**3**). Mass spectra of these complexes point to a dinuclear formulation, consisting of two ruthenium and four thiosemicarbazone ligands. Though the chosen thiosemicarbazones are all potentially tridentate, the dinuclear composition indicates that all four thiosemicarbazones present in each of the complexes are not serving as tridentate ligands. In order to find out the coordination mode(s) of the thiosemicarbazones in these complexes, the structure of one i.e., complex (**3**), has been determined by X-ray crystallography. The structure is shown in Fig. 1 and selected bond parameters are given in Table 2. The structure reveals that the complex is indeed dimeric in nature, where each monomeric unit consists of a bis-thiosemicarbazone-ruthenium moiety with one thiosemicarbazone coordinated to ruthenium as a dianionic O,N,S-donor (as in **I**) forming adjacent six- and five-membered chelate rings, while the other thiosemicarbazone is bound to ruthenium as a monoanionic N,S-donor forming a five-membered chelate ring (**IV**). Though the O,N,S-mode of binding (as in **I**) to ruthenium, which was our main target, is exhibited by two of the four thiosemicarbazone ligands, the N,S-mode of coordination (**IV**) displayed by the other two thiosemicarbazone ligands has been quite intriguing. In comparison with the structure of the uncoordinated ligand[35], it is quite apparent that this five-membered chelate ring formation has been associated with a rather unusual conformational change around the imine C=N bond. This mode of binding by salicylaldehyde thiosemicarbazone, and related ligands, appears to be unprecedented. The sulfur atoms of the O,N,S-coordinated thiosemicarbazone ligands bridge the two monomeric units to form the dimeric complex. As a consequence of this sulfur-bridging, the two ruthenium centers come close to each-other resulting in the formation of a ruthenium-ruthenium bond (Ru-Ru distance is 2.812(2) Å). While examples of sulfur-bridging

Table 1 — Crystallographic data for the complex (**3**)

Sample	(**3**) $4H_2O$
Empirical formula	$C_{48}H_{46}N_{12}O_8S_4Ru_2$
Formula weight	1248.33
Crystal system	Orthorhombic
Space group	*Pbcn*
a (Å)	37.5560(6)
b (Å)	9.894(2)
c (Å)	26.532(3)
V (Å^3)	9859(2)
Z	8
λ (Å)	0.71073
Crystal size (mm^3)	0.05 × 0.05 × 0.30
T (K)	150
μ (mm^{-1})	0.850
*R*1[a]	0.1430
w*R*2[b]	0.3406
GOF[c]	0.90

[a]$R1 = \Sigma \, || F_o | - | F_c || / \Sigma \, | F_o |$.
[b]$wR2 = [\Sigma \{ w(F_o^2 - F_c^2)^2 \} / \Sigma \{ w(F_o^2) \}]^{1/2}$.
[c]$GOF = [\Sigma(w(F_o^2 - F_c^2)^2)/(M-N)]^{1/2}$, where *M* is the number of reflections and *N* is the number of parameters refined.



IV

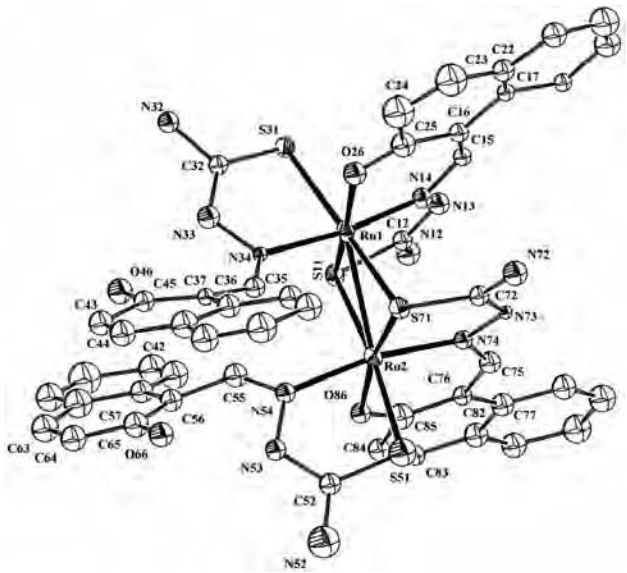


Fig. 1 — View of the complex (**3**).

coordination mode of thiosemicarbazone ligands are available in the literature[19,25,36-39], such sulfur-bridging leading to Ru-Ru bond formation seems to be unknown so far. The Ru-Ru, Ru-O, Ru-N and Ru-S distances in this dinuclear complex are all quite usual, and so are the bond parameters in the coordinated ligands[20-22,24-28,40,41]. Each ruthenium in this dinuclear complex is nested in a $N_2O_1S_3$ coordination environment, which is significantly distorted from ideal octahedral geometry as reflected in the bond parameters around the metal centers.

In the crystal lattice of complex (**3**) there are four molecules of water per complex molecule. In order to find out the nature of interaction between these water molecules and the complex molecule, the packing pattern in the lattice has been scrutinized (Fig. 2), which shows that the water molecules are hydrogen-bonded with the phenolate and NH_2 fragments of the thiosemicarbazone ligands, and also hydrogen-bonded among themselves. Besides, there exists C-H---π interaction between the naphthalene rings belonging to a pair of adjacent complex molecules. These extended hydrogen-bonding interactions seem to be responsible for holding the crystal together. As all the three complexes (**1**, **2** and **3**) were obtained similarly, and they show similar properties (*vide infra*), the complexes (**1**) and (**2**) are assumed to have similar structure as complex (**3**).

Though structural characterization of complexes (**1**) and (**2**) by X-ray crystallography was not possible since single crystals of these species could not be grown, structures of both the complexes were geometrically optimized through DFT calculations[32,33]. The optimized structures of complexes (**1**) and (**2**), and some selected bond parameters have been shown in Supplementary Data (Fig. S1, Fig. S2, Table S1 and Table S2). The computed bond parameters are found to be comparable with those observed for complex (**3**). As two di-anionic and two mono-anionic thiosemicarbazones are present in each complex, the formal oxidation state of each ruthenium is +3 (low-spin d^5, S=1/2). Hence, both the metal centers in these diruthenium complexes should be one-electron paramagnetic. However, magnetic susceptibility measurements show that these complexes are diamagnetic, and this observed diamagnetism is attributable to strong anti-ferromagnetic interaction between the two proximal paramagnetic metal centers[40,41]. It may be noted here that in the starting complex, $[Ru(dmso)_4Cl_2]$, ruthenium was in +2 oxidation state and in the diruthenium complexes each ruthenium is in +3 state. Hence, the metal center has undergone a one-electron oxidation, and aerial oxygen probably has served as the oxidant.

Table 2 — Selected bond lengths (Å) and bond angles (°) for the complex (**3**)

Bond lengths (Å)

Ru1 - Ru2	2.812(2)	Ru2 – O86	2.052(12)
Ru1 – O26	2.082(15)	Ru2 – N74	2.020(15)
Ru1 – N14	1.962(15)	Ru2 – S71	2.262(6)
Ru1 – S11	2.250(5)	Ru2 – N54	2.062(15)
Ru1 – N34	2.109(11)	Ru2 – S51	2.333(7)
Ru1 – S31	2.363(5)	Ru2 – S11	2.337(5)
Ru1 – S71	2.338(6)	C72 – S71	1.77(2)
C12 – S11	1.815(19)	C72 – N72	1.37(2)
C12 – N12	1.37(3)	C72 – N73	1.26(2)
C12 – N13	1.29(3)	N73 – N74	1.46(2)
N13 – N14	1.42(2)	C75 – N74	1.29(3)
C15 – N14	1.34(2)	C85 – O86	1.29(3)
C25 – O26	1.23(3)	C52 – S51	1.71(2)
C32 – S31	1.710(19)	C52 – N52	1.33(3)
C32 – N32	1.42(3)	C52 – N53	1.39(3)
C32 – N33	1.34(3)	N53 – N54	1.39(2)
N33 – N34	1.37(2)	C55 – N54	1.28(3)
C35 – N34	1.30(2)	C65 – O66	1.32(2)
C45 – O46	1.35(2)		

Bond angles (°)

O26 – Ru1 – S11	168.1(4)	O86 – Ru2 – S71	170.2(4)
N14 – Ru1 – N34	171.8(6)	N54 – Ru2 – N74	168.6(6)
S31 – Ru1 – S71	168.7(2)	S11 – Ru2 – S51	168.4(2)
S11 – Ru1 – N14	82.4(5)	S71 – Ru2 – N74	83.5(4)
N14 – Ru1 – O26	91.9(6)	N74 – Ru2 – O86	92.0(6)
N34 – Ru1 – S31	81.4(4)	N54 – Ru2 – S51	81.3(5)

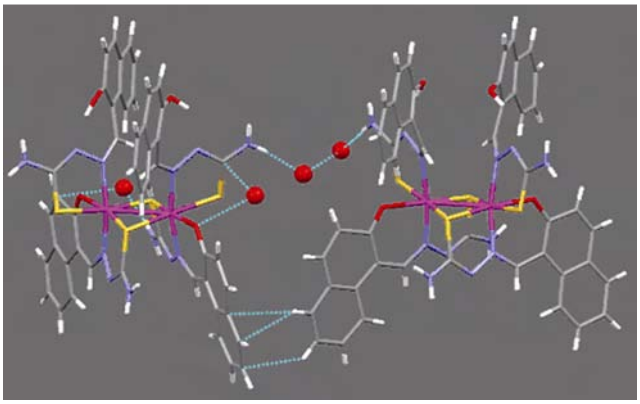


Fig. 2 — Hydrogen-bonding interactions in the lattice of complex (**3**).

Table 3 — Electronic spectral and cyclic voltammetric data of (**1**), (**2**) and (**3**)

Complex	λ_{max}, nm (ε, $M^{-1}cm^{-1}$)[a]	E (V) vs SCE[b]
(**1**)	433(2000)[c], 390(3000)[c], 340(4500), 308(6900)[c]	0.40[d], 0.86[d], -0.71[e], -1.24[e]
(**2**)	439(2000)[c], 397(3100), 344(4500)[c], 302(6900)[c]	0.50[d], 0.78[d], -0.80[e], -1.23[e]
(**3**)	546(1100)[c], 440(5200)[c], 405(6900)[c], 371(9000), 317(10500)[c]	0.79[d], 1.18[d], -0.40[e], -0.95[e]

[a]In dimethylsulfoxide.
[b]Solvent, acetonitrile; supporting electrolyte, TBAP; scan rate 50 mV s^{-1}.
[c]Shoulder.
[d]E_{pa} value.
[e]E_{pc} value.

Spectral properties

Infrared spectra of all the three complexes (**1**, **2** and **3**) show several vibrations of different intensities in the 1600–400 cm^{-1} region. Assignment of each individual band to a specific vibration has not been attempted. However, a broad band observed near 3440 cm^{-1} in all the three complexes is attributable to the phenolic OH fragment of the N,S-coordinated thiosemicarbazones. Several prominent bands (e.g. near 1267, 1283, 1368, 1492 and 1534 cm^{-1}) displayed by these complexes are obviously due to the coordinated thiosemicarbazone ligands. Though all these diruthenium complexes were found to be diamagnetic in the solid state, none of their ^1H NMR spectra in $CDCl_3$ solution showed any recognizable signal.

The diruthenium complexes are moderately soluble in acetonitrile, ethanol, acetone, etc., but are readily soluble in dimethylsulfoxide and dimethylformamide to produce intense brown solutions. Electronic spectra of all the complexes have been recorded in dimethylsulfoxide solution. The complexes showed several intense absorptions in the visible and ultraviolet region (Table 3). The absorptions in the ultraviolet region are attributable to transitions within the ligand orbitals. In complexes of trivalent ruthenium with imine-based ligands, intense absorptions in the visible region are usually believed to be due to ligand-to-metal charge-transfer transitions. However, to have an insight into the nature of the absorptions in the visible region in the present complexes, electronic structures of the complexes have been probed with the help of DFT calculations[32,33], and the composition of selected molecular orbitals is given in Table 4. Electron distributions in the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) for complex (**3**) are shown in Fig. 3. The same for complexes (**1**) and (**2**) are shown in Supplementary Data (Figs. S3 and S4). Though the two monomeric units in each of the three complexes are similar in composition and structural features, electron distributions over the two monomeric units are unsymmetrical. In all the three complexes both the HOMO and LUMO are distributed mostly over the thiosemicarbazone ligands, with much less contributions coming from the metal centers. Hence, the absorption in the visible region is assignable to a transition within the filled (HOMO) and vacant (LUMO) orbitals of the thiosemicarbazone ligands.

Table 4 — Composition of selected molecular orbitals

Complex	Contributing fragments[a]	Contribution (%) of fragments to HOMO	Contribution (%) of fragments to LUMO
(**1**)	Ru_1	7	16
	Ru_2	11	12
	ONS_1	34	30
	ONS_2	46	8
	NS_1	4	24
	NS_2	29	10
(**2**)	Ru_1	6	9
	Ru_2	12	12
	ONS_1	44	28
	ONS_2	4	29
	NS_1	8	11
	NS_2	26	11
(**3**)	Ru_1	17	12
	Ru_2	8	13
	ONS_1	55	34
	ONS_2	11	38
	NS_1	8	1
	NS_2	1	2

[a]The two Ru centers are denoted as Ru_1 and Ru_2 on arbitrary basis. ONS_1 and ONS_2 denote tri-coordinated thiosemicarbazone ligands bound to Ru_1 and Ru_2 respectively. NS_1 and NS_2 denote bi-coordinated thiosemicarbazone ligands bound to Ru_1 and Ru_2 respectively.

Electrochemical properties

Electrochemical properties of the complexes have been studied by cyclic voltammetry in acetonitrile solution (0.1 *M* TBAP). Voltammetric data are given in Table 3. All the complexes show two irreversible

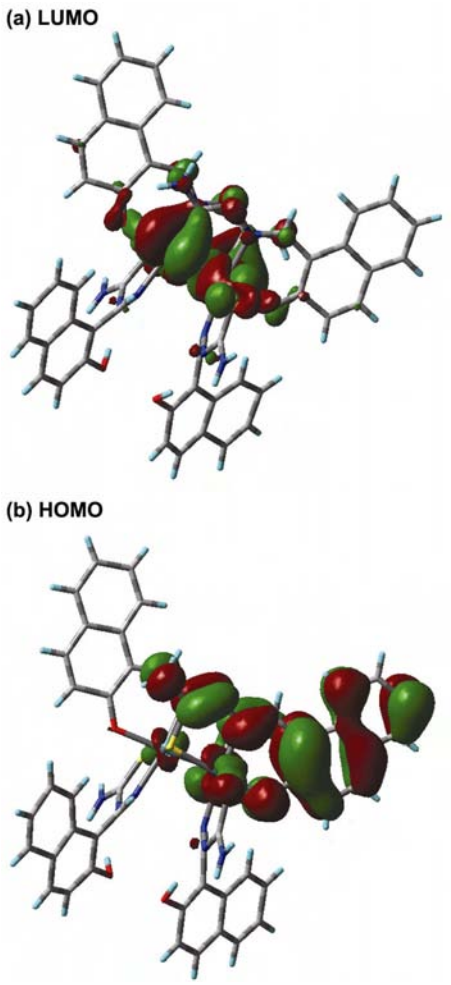


Fig. 3 — Contour plots of (a) HOMO and (b) LUMO of complex (**3**).

oxidative responses on the positive side of SCE and two irreversible reductive responses on the negative side. A selected voltammogram is shown in Supplementary Data (Fig. S5). In view of the composition of the HOMO, the first oxidative response is assigned to oxidation of the coordinated thiosemicarbazone. Similarly, in view of the composition of the LUMO, the first reductive response is assigned to reduction of the coordinated thiosemicarbazone. The second oxidation and the second reduction are tentatively assigned respectively to oxidation and reduction of the coordinated thiosemicarbazone ligands.

Conclusions

The present study shows that salicylaldehyde thiosemicarbazone (L^1), and two similar ligands (L^2 and L^3) readily react with $[Ru(dmso)_4Cl_2]$ affording a group of homoleptic diruthenium complexes (**1**, **2** and **3**), where these ligands display two interestingly different types of binding mode, viz., O,N,S-mode (**I**) with additional bridging from the sulfur-site and N,S-mode (**IV**) associated with conformational change across the imine (C=N) fragment. The sulfur-bridging leads to the formation of a Ru-Ru bond in each of these complexes and due to strong antiferromagnetic interaction between these two closely spaces ruthenium(III) centers these complexes exhibit diamagnetic character in the solid state.

Supplementary Data

CCDC 805680 contains the supplementary crystallographic data for complex (**3**). These data have been deposited at the Cambridge Crystallographic Data Centre (CCDC) and may be obtained free of charge from the Director, CCDC, 12 Union road, Cambridge, CB2 1EZ, UK, via www. ccdc.cam.ac.uk/data_request/cif. Other supplementary data, viz., DFT optimized structures of complex (**1**) (Fig. S1) and complex (**2**) (Fig. S2), selected bond parameters for DFT optimized structures of complex (**1**) (Table S1) and complex (**2**) (Table S2), contour plots of HOMO and LUMO of complex (**1**) (Fig. S3) and complex (**2**) (Fig. S4), and cyclic voltammogram of complex (**3**) (Fig. S5) may be obtained from the author on request.

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