

Ruthenium Carbonyl Complexes with 4-R-Benzaldehyde Thiosemicarbazone as an Ancillary Ligand: Synthesis and, Structural, Spectral and Electrochemical Properties

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Abstract Reaction of 4-R-benzaldehyde thiosemicarbazone (denoted as HL-R; where H stands for the dissociable acidic proton and R (R = OCH₃, CH₃, H, Cl and NO₂) for the substituents) with [Ru(CO)₂Cl₂]_n in toluene in the presence of triethylamine affords a group of yellow complexes of the type [Ru(CO)₂(L-R)₂]. Structure of [Ru(CO)₂(L-NO₂)] has been determined by X-ray crystallography. In [Ru(CO)₂(L-R)₂] complexes, the thiosemicarbazone ligands are bound to the metal center as monoanionic bidentate N,S-donor forming four-membered chelate ring. All the complexes are diamagnetic, and show characteristic ¹H NMR signals. The [Ru(CO)₂(L-R)₂] complexes show intense absorptions in the visible and ultraviolet regions, which have been analyzed by DFT calculations. Cyclic voltammetry on the complexes shows two irreversible oxidations near 0.87 and 1.28 V versus SCE, and an irreversible reduction around -1.24 V versus SCE.

Keywords Ruthenium carbonyl complex · Benzaldehyde thiosemicarbazone · Crystal structure · Spectral and electrochemical properties

1 Introduction

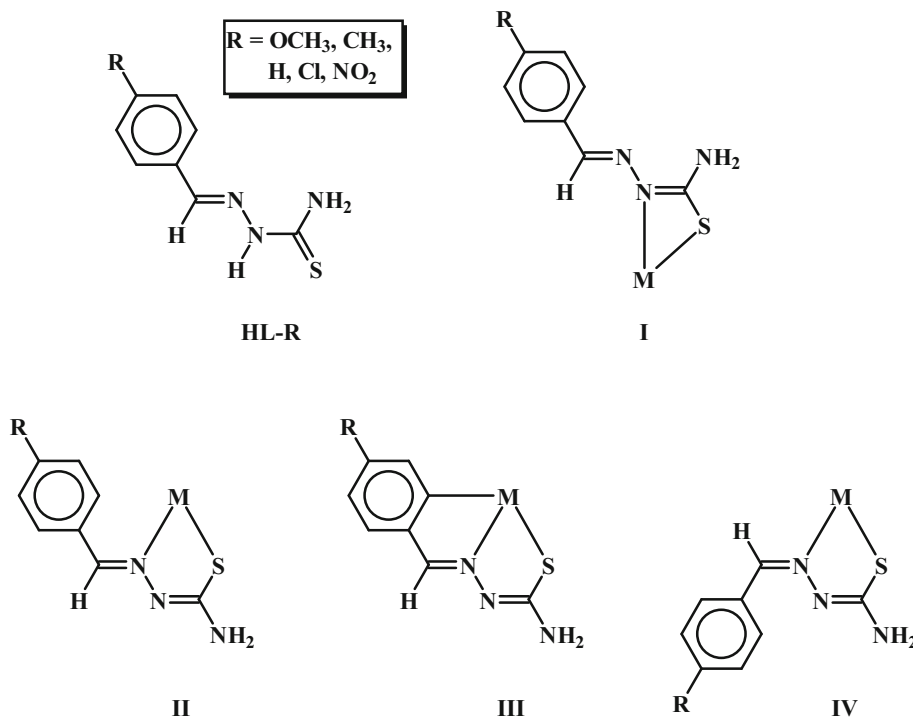
Mixed-ligand ruthenium carbonyl complexes have been receiving considerable current attention, mainly because of their catalytic and biological applications [1–15]. Reactivity of such complexes is dictated by both the carbonyl and the other ancillary ligands. Binding of ligands of selected types to the metal center in the Ru(CO)_n fragment is of significant importance for modulation of the properties of such mixed-ligand complexes. For the present study, which has originated from our interest in the chemistry of mixed-ligand ruthenium carbonyl complexes [16–20], we have selected a group of five 4-R-benzaldehyde thiosemicarbazones, abbreviated in general as HL-R, where H stands for the dissociable acidic proton and R for the substituent in the phenyl ring. Though the thiosemicarbazone complexes are cultivated usually for their bioinorganic relevance [21–23], we have been exploring the chemistry of transition metal complexes of the thiosemicarbazones mainly because of the variable binding mode displayed by these ligands in their complexes [16, 24–34]. For example, from our earlier studies we have found that the chosen thiosemicarbazones can bind to a metal center as N,S-donor forming four-membered chelate ring (I), as N,S-donor forming five-membered chelate ring (II), as C,N,S-donor forming (III), and as N,S-donor forming five-membered chelate ring with a change in geometry around the pre-existing C=N bond (IV) [24–34]. We were interested to examine the mode of binding of the selected thiosemicarbazones to ruthenium with carbonyl as the co-ligand. As the source of ruthenium, we chose [Ru(CO)₂Cl₂]_n, as it can readily provide the Ru(CO)₂ fragment and also because of its demonstrated ability to undergo facile reaction with organic ligands of different types [19]. Herein, we wish to report our findings on the formation of a

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group of new complexes through interaction of the selected thiosemicarbazones with $[\text{Ru}(\text{CO})_2\text{Cl}_2]_n$, their structures, and their spectral and electrochemical properties.



2 Experimental

2.1 Materials and methods

Ruthenium trichloride was purchased from Arora Matthey, Kolkata, India. $[\text{Ru}(\text{CO})_2\text{Cl}_2]_n$ was prepared by following a reported procedure [35]. Thiosemicarbazide was procured from Spectrochem, Mumbai, India. The 4-R-benzaldehyde thiosemicarbazones (HL-R; $\text{R} = \text{OCH}_3, \text{CH}_3, \text{H}, \text{Cl}$ and NO_2) were prepared by reacting equimolar amounts of thiosemicarbazide and the respective 4-R-benzaldehyde in 1:1 ethanol–water mixture. All other chemicals and solvents were reagent grade commercial materials and were used as received. Tetrabutylammonium hexafluorophosphate (TBHP), obtained from Aldrich, and AR grade acetonitrile, procured from Merck, India, were used for electrochemical work.

2.2 Physical Measurements

Microanalyses (C, H, N) were performed using a Heraeus Carlo Erba 1108 elemental analyzer. Magnetic susceptibilities were measured using a Sherwood MK-1 balance.

^1H NMR spectra recorded in CDCl_3 solution on a Bruker Avance DPX 300 NMR spectrometer using TMS as the internal standard. IR spectra were obtained on a Perkin Elmer Spectrum Two spectrometer with samples prepared as KBr pellets. Electronic spectra were recorded on a JASCO V-630 spectrophotometer. 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 structure and energy calculation were carried out by density functional theory (DFT) method using the Gaussian 03 (B3LYP/SDD-6-31G) package [36].

2.3 Synthesis of Complexes

All the five $[\text{Ru}(\text{CO})_2(\text{L-R})_2]$ complexes were prepared by following a general procedure. Specific details are given below for a particular complex.

[Ru(CO)₂(L-OCH₃)₂] To a solution of 4-methoxy-benzaldehyde thiosemicarbazone (101 mg, 0.48 mmol) in warm toluene (40 ml), triethylamine (49 mg, 0.48 mmol) was added. To this solution [Ru(CO)₂Cl₂]_n (50 mg, 0.22 mmol) was added.¹ The mixture was refluxed for 3 h to yield an orangish-yellow solution. The solvent was evaporated and the solid mass thus obtained was subjected to purification by thin layer chromatography on a silica plate. With acetonitrile:benzene (1:2) as the eluant, a yellow band separated, which was extracted with acetonitrile. Evaporation of the acetonitrile extract gave [Ru(CO)₂(L-OCH₃)₂] as a yellow crystalline solid. Yield: 61 %. Anal. calcd. for C₂₀H₂₀N₆O₄S₂Ru: C, 41.88; H, 3.49; N, 14.66. Found: C, 41.96; H, 3.44; N, 14.68 %. ¹H NMR (300 MHz, CDCl₃)² δ: 3.84 (OCH₃), 5.74 (s, NH₂), 6.97 (d, *J* = 7.0, 2H), 7.58 (d, *J* = 8.0, 2H), 8.78 (s, azomethine). IR (cm⁻¹): 3443, 3332, 2045, 1978, 1602, 1585, 1507, 1462, 1441, 1420, 1369, 1324, 1306, 1206, 1170, 1112, 1096, 1054, 1028, 953, 931, 873, 856, 831, 812, 775, 735, 722, 657, 583, 572, 526.

[Ru(CO)₂(L-CH₃)₂] Yield: 65 %. Anal. calcd. for C₂₀H₂₀N₆O₂S₂Ru: C, 44.36; H, 3.69; N, 15.52. Found: C, 44.25; H, 3.71; N, 15.49 %. ¹H NMR (300 MHz, CDCl₃) δ: 2.35 (CH₃), 5.77 (s, NH₂), 7.19 (d, *J* = 6.6, 2H), 7.54 (d, *J* = 8.1, 2H), 8.79 (s, azomethine). IR (cm⁻¹): 3441, 3335, 2044, 1974, 1603, 1584, 1507, 1411, 1367, 1325, 1310, 1291, 1227, 1211, 1178, 1111, 1098, 1054, 1018, 958, 935, 873, 854, 814, 774, 735, 711, 657, 583, 574, 513.

[Ru(CO)₂(L-H)₂] Yield: 62 %. Anal. calcd. for C₁₈H₁₆N₆O₂S₂Ru: C, 42.09; H, 3.12; N, 16.37. Found: C, 42.17; H, 3.15; N, 16.41 %. ¹H NMR (300 MHz, CDCl₃) δ: 5.78 (s, NH₂), 7.35 (d, *J* = 8.0, 2H), 7.41 (d, *J* = 8.1, 2H), 7.67 (t, *J* = 7.0, H), 8.82 (s, azomethine). IR (cm⁻¹): 3445, 3330, 2045, 1975, 1602, 1583, 1509, 1487, 1416, 1369, 1325, 1306, 1287, 1223, 1198, 1180, 1156, 1106, 1096, 1052, 1026, 950, 936, 869, 845, 808, 779, 755, 722, 691, 660, 626, 583, 574, 508.

[Ru(CO)₂(L-Cl)₂] Yield: 61 %. Anal. calcd. for C₁₈H₁₄N₆O₂S₂Cl₂Ru: C, 37.11; H, 2.41; N, 14.43. Found: C, 37.20; H, 2.39; N, 14.46 %. ¹H NMR (300 MHz, CDCl₃) δ: 5.81 (s, NH₂), 7.34 (d, *J* = 7.8, 2H), 7.59 (d, *J* = 8.1, 2H), 8.78 (s, azomethine). IR (cm⁻¹): 3443, 3331, 2046, 1978, 1596, 1583, 1511, 1488, 1416, 1403, 1384, 1330, 1300, 1281, 1248, 1217, 1200, 1175, 1147, 1090, 1057,

1012, 956, 935, 866, 851, 824, 810, 741, 729, 710, 685, 667, 625, 592, 580, 511.

[Ru(CO)₂(L-NO₂)₂] Yield: 59 %. Anal. calcd. for C₁₈H₁₄N₈O₆S₂Ru: C, 35.82; H, 2.32; N, 18.57. Found: C, 35.73; H, 2.29; N, 18.53 %. ¹H NMR (300 MHz, CDCl₃) δ: 5.92 (s, NH₂), 7.79 (d, *J* = 8.7, 2H), 8.23 (d, *J* = 8.7, 2H), 8.88 (s, azomethine). IR (cm⁻¹): 3444, 3332, 2042, 1974, 1600, 1590, 1513, 1489, 1409, 1384, 1331, 1298, 1256, 1225, 1197, 1173, 1149, 1104, 1055, 1011, 963, 934, 876, 853, 839, 804, 750, 690, 658, 626, 592, 579, 502.

2.3.1 X-Ray Crystallography

Single crystals of the [Ru(CO)₂(L-NO₂)₂] complex were grown by slow evaporation of solvent from a solution of the complex in acetonitrile. Selected crystal data and data collection parameters are given in Table 1. Data were collected on a Bruker SMART CCD diffractometer using graphite monochromated MoK α radiation (λ = 0.71073 Å). X-ray data reduction and structure solution and refinement were done using SHELXS-97 and SHELXL-97 programs [37]. The structure was solved by the direct methods.

Table 1 Crystallographic data for [Ru(CO)₂(L-NO₂)₂]

Empirical formula	C ₁₈ H ₁₄ N ₈ O ₆ S ₂ Ru·CH ₃ CN
Formula weight	644.64
Crystal system	Monoclinic
Space group	C2/c
<i>a</i> (Å)	20.5784 (13)
<i>b</i> (Å)	8.9429 (5)
<i>c</i> (Å)	29.1579 (3)
β (°)	90.268 (7)
<i>V</i> (Å ³)	5365.9 (6)
<i>Z</i>	8
<i>D</i> _{calcd} (mg m ⁻³)	1.596
<i>F</i> (000)	2592
Crystal size (mm)	0.07 × 0.11 × 0.26
<i>T</i> (K)	296
μ (mm ⁻¹)	0.793
Collected reflections	40,585
<i>R</i> _{int}	0.109
Independent reflections	6171
<i>R</i> ₁ ^a	0.0668
<i>wR</i> ₂ ^b	0.2763
GOF ^c	0.84

¹ The mmol calculation was done based on the mass of the repeating Ru(CO)₂Cl₂ fragment.

² Chemical shifts are given in ppm and multiplicity of the signals along with the associated coupling constants (*J* in Hz) are given in parentheses. Overlapping signals are marked with an asterisk.

$$^a R_1 = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}$$

$$^b wR_2 = \left[\frac{\sum [w(F_o^2 - F_c^2)]^2}{\sum [w(F_o^2)]^2} \right]^{1/2}$$

$$^c GOF = \left[\frac{\sum [w(F_o^2 - F_c^2)]^2}{(M - N)} \right]^{1/2}, \text{ where } M \text{ is the number of reflections and } N \text{ is the number of parameters refined}$$

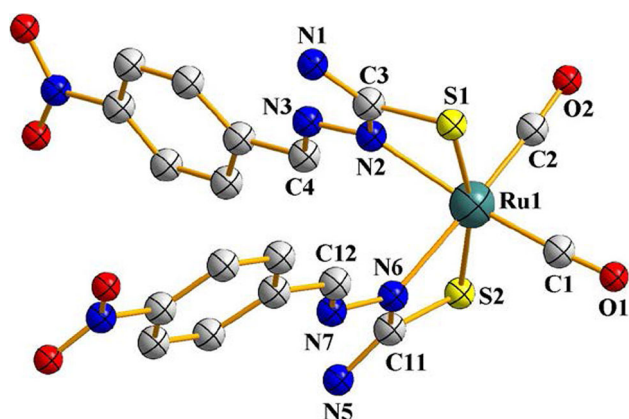


Fig. 1 Structure of $[\text{Ru}(\text{CO})_2(\text{L-NO}_2)_2]$ (hydrogen atoms are omitted for clarity)

3 Results and Discussion

3.1 Synthesis and Characterization

As delineated in the introduction, the initial aim of the present study was to study the interaction of the selected 4-R-benzaldehyde thiosemicarbazones (HL-R) with $[\text{Ru}(\text{CO})_2\text{Cl}_2]_n$ and see how they bind to the metal center. Five different substituents in the thiosemicarbazone ligands, with different electron withdrawing properties, were chosen to study their influence, if any, on the redox properties of the resulting complexes. Reactions of the selected thiosemicarbazones (HL-R) with $[\text{Ru}(\text{CO})_2\text{Cl}_2]_n$ proceeded smoothly in refluxing toluene to afford a group of yellow complexes of the type, viz. $[\text{Ru}(\text{CO})_2(\text{L-R})_2]$, in decent yields. Preliminary characterization data (micro-analysis, IR, NMR, etc.) of the complexes were found to be consistent with their compositions. In order to find out the stereochemistry of the complexes, as well as to ascertain coordination mode of the thiosemicarbazone ligands, structure of a representative member of this series, viz. $[\text{Ru}(\text{CO})_2(\text{L-NO}_2)_2]$, was determined by X-ray crystallography. The structure is shown in Fig. 1 and some relevant bond distances and bond angles are listed in Table 2. The structure shows that both the thiosemicarbazones are coordinated to ruthenium, as N,S-donors in a bidentate fashion and forming four-membered chelate ring (I). Two carbonyls are also coordinated to the metal center. Ruthenium is thus having a distorted octahedral $\text{N}_2\text{S}_2\text{C}_2$ coordination environment, where both nitrogen atoms are *cis*, both sulfur atoms are *trans*, and both carbon atoms are *cis*. The Ru–N, Ru–S and Ru–C distances are quite normal and are within the accepted values for a chelated thiosemicarbazone [24–34], and coordinated carbonyls [16–20]. The presence of an acetonitrile as solvent of crystallization per molecule of $[\text{Ru}(\text{CO})_2(\text{L-NO}_2)_2]$ in the crystal lattice indicates existence of non-covalent interactions between

Table 2 Selected bond distances and bond angles for $[\text{Ru}(\text{CO})_2(\text{L-NO}_2)_2]$

Bond distances (Å)			
Ru(1)–S(1)	2.407(2)	N(2)–N(3)	1.317(12)
Ru(1)–S(2)	2.421(3)	N(3)–C(4)	1.365(12)
Ru(1)–N(2)	2.151(8)	S(2)–C(11)	1.733(10)
Ru(1)–N(6)	2.171(8)	N(6)–C(11)	1.337(11)
Ru(1)–C(1)	1.849(9)	N(5)–C(11)	1.324(13)
Ru(1)–C(2)	1.834(12)	N(6)–N(7)	1.372(10)
S(1)–C(3)	1.688(9)	N(7)–C(12)	1.278(12)
N(2)–C(3)	1.359(12)	O(1)–C(1)	1.133(11)
N(1)–C(3)	1.325(11)	O(2)–C(2)	1.153(15)
Bond angles (°)			
S(1)–Ru(1)–N(2)	65.2(2)	S(1)–Ru(1)–S(2)	165.61(9)
S(2)–Ru(1)–N(6)	66.79(17)	N(2)–Ru(1)–C(1)	161.8(4)
Ru(1)–C(1)–O(1)	176.7(7)	N(6)–Ru(1)–C(2)	168.2(3)
Ru(1)–C(2)–O(2)	177.1(7)		

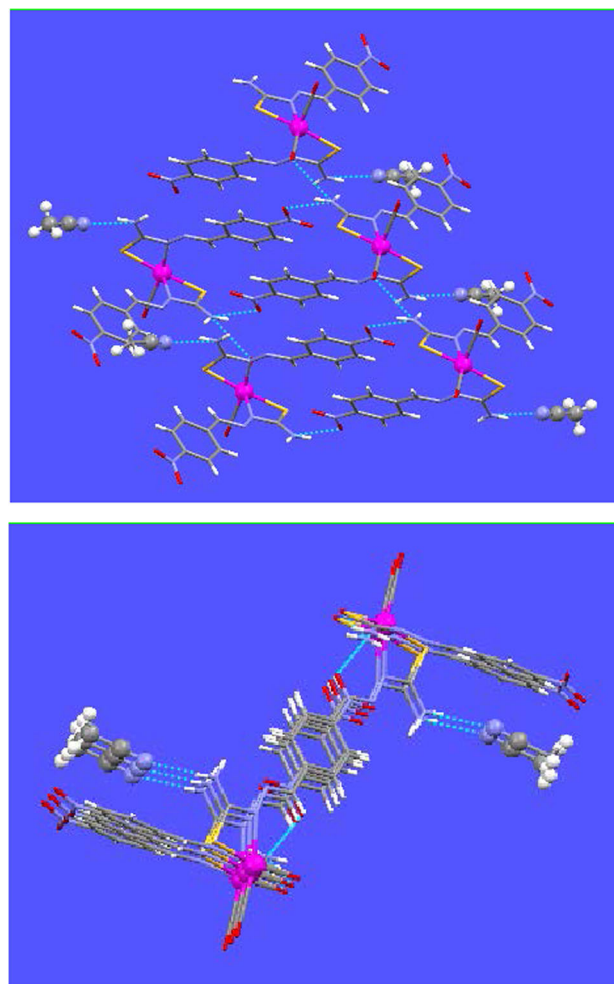


Fig. 2 Intermolecular N–H...N(CH_3CN), N–H...O(NO_2) and N–H...O(CO) interactions (top) and π ... π interactions (bottom) in the lattice of $[\text{Ru}(\text{CO})_2(\text{L-NO}_2)_2]$

Table 3 Electronic spectral and cyclic voltammetric data

Complex	Electronic spectral data ^a	Cyclic voltammetric data ^b E/V versus SCE
	λ_{\max} , nm (ϵ , M ⁻¹ cm ⁻¹)	
[Ru(CO) ₂ (L-OCH ₃) ₂]	508 (4710), 344 (20,100)	1.29 ^c , 0.88 ^c , -1.25 ^d
[Ru(CO) ₂ (L-CH ₃) ₂]	512 (3770), 345 (19,060)	1.24 ^c , 0.86 ^c , -1.23 ^d
[Ru(CO) ₂ (L-H) ₂]	516 (3960), 343 (18,100)	1.28 ^c , 0.87 ^c , -1.24 ^d
[Ru(CO) ₂ (L-Cl) ₂]	511 (3610), 345 (21,200)	1.27 ^c , 0.87 ^c , -1.23 ^d
[Ru(CO) ₂ (L-NO ₂) ₂]	510 (4090), 343 (22,920)	1.31 ^c , 0.89 ^c , -1.22 ^d

^a In dichloromethane^b Solvent, acetonitrile; supporting electrolyte, TBHP; scan rate, 50 mV s⁻¹^c E_{pa} (anodic peak-potential) value^d E_{pc} (cathodic peak-potential) value**Table 4** Composition of selected molecular orbitals

Complex	Contributing fragments ^a	% Contribution to	
		HOMO	LUMO
[Ru(CO) ₂ (L-OCH ₃) ₂]	Ru	11.1	7.3
	{L-OCH ₃ } ¹	83.5	44.4
	{L-OCH ₃ } ²	0.1	47.5
	CO	5.3	0.8
[Ru(CO) ₂ (L-CH ₃) ₂]	Ru	11.4	7.8
	{L-CH ₃ } ¹	82.4	43.7
	{L-CH ₃ } ²	0.6	47.6
	CO	5.6	0.9
[Ru(CO) ₂ (L-H) ₂]	Ru	11.6	8.7
	{L-H} ¹	81.9	43.4
	{L-H} ²	0.3	47.1
	CO	6.2	0.8
[Ru(CO) ₂ (L-Cl) ₂]	Ru	10.8	6.9
	{L-Cl} ¹	82.3	44.8
	{L-Cl} ²	1.0	47.6
	CO	5.9	0.7
[Ru(CO) ₂ (L-NO ₂) ₂]	Ru	8.0	7.1
	{L-NO ₂ } ¹	81.9	0.00
	{L-NO ₂ } ²	3.4	92.9
	CO	6.7	0.00

^a {L-R}¹ and {L-R}² depict the two chelated thiosemicarbazone ligands

the solvent and complex molecule, in addition to those between the complex molecules. A closer look at the packing pattern in the crystal lattice (Fig. 2) reveals that intermolecular interactions of four different types, viz. N-H...N(CH₃CN), N-H...O(NO₂), N-H...O(CO) and π ... π interactions, are active in the lattice. Each complex molecule is thus linked with the surrounding complex molecules through such non-covalent interactions, and these extended intermolecular interactions seem to be responsible for holding the crystal together. As all the [Ru(CO)₂(L-R)₂]

complexes were synthesized similarly and they show similar properties (vide infra), the other four [Ru(CO)₂(L-R)₂] complexes (with R \neq NO₂) are assumed to have similar structures as the [Ru(CO)₂(L-NO₂)₂] complex.

3.2 Spectral Studies

Magnetic susceptibility measurements show that all the ruthenium complexes are diamagnetic, which corresponds to the +2 oxidation state of ruthenium (low-spin d⁶,

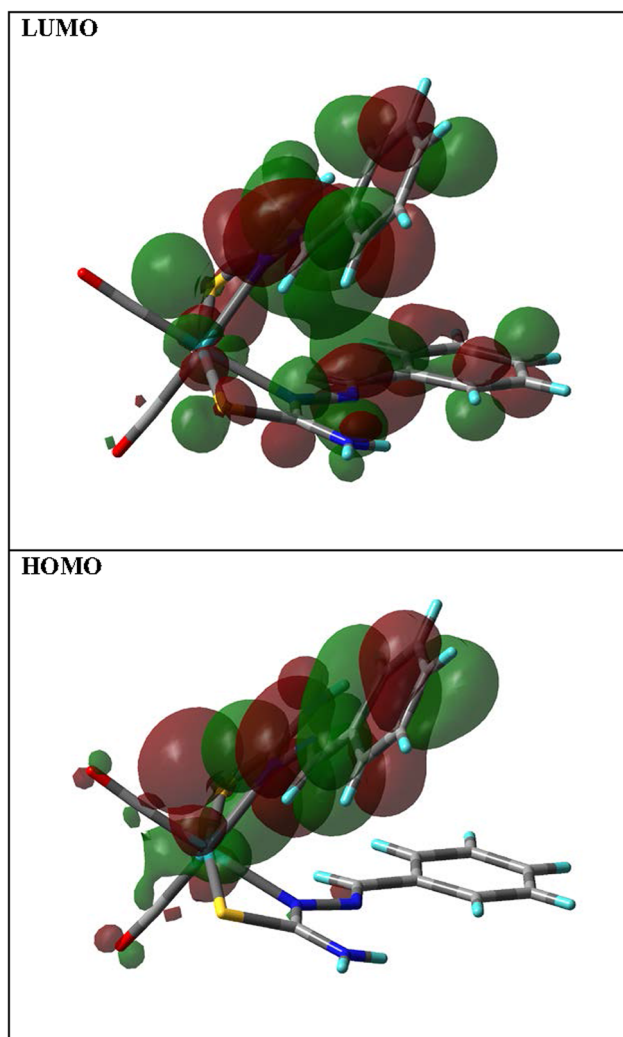


Fig. 3 Contour plots of selected molecular orbitals of $[\text{Ru}(\text{CO})_2(\text{L}-\text{H})_2]$

$S = 0$). ^1H NMR spectra of all $[\text{Ru}(\text{CO})_2(\text{L}-\text{R})_2]$ complexes are found to be consistent with the C_2 symmetry present in the molecule. The $[\text{Ru}(\text{CO})_2(\text{L}-\text{OCH}_3)_2]$ and $[\text{Ru}(\text{CO})_2(\text{L}-\text{CH}_3)_2]$ complexes show a sharp signal at 3.78 and 2.35 ppm respectively, for the methoxy and the methyl groups. From the coordinated thiosemicarbazone, signal for the NH_2 group is observed near 5.7 ppm, signal for the azomethine proton is observed around 8.8 ppm, and the aromatic proton signals are observed in the expected region.

Infrared spectrum of each $[\text{Ru}(\text{CO})_2(\text{L}-\text{R})_2]$ complex shows many bands of different intensities in the $400\text{--}4000\text{ cm}^{-1}$ region. Attempt has not been made to assign each band to a specific vibration. However, the N–H stretch, observed near 3290 cm^{-1} in the uncoordinated ligand, is found to be absent in the complexes, confirming de-protonation of the thiosemicarbazone ligand. Two weak bands have been found in all the spectra around 3443 and 3332 cm^{-1} , which are attributable to the $-\text{NH}_2$ fragment. Two strong bands have been observed near 2045 and 1975 cm^{-1} in all the $[\text{Ru}(\text{CO})_2(\text{L}-\text{R})_2]$ complexes, indicating the presence of two coordinated carbonyl ligands. Several sharp bands (e.g. near 1602 , 1583 , 1509 , 1416 , 1369 , 1325 , 1306 , 1287 , 1180 , 1096 , 1052 , 950 , 869 , 845 , 808 , 779 , 722 , 660 , 583 and 508 cm^{-1}) are also observed in the $[\text{Ru}(\text{CO})_2(\text{L}-\text{R})_2]$ complexes, which are attributable to the coordinated thiosemicarbazone ligands. The ^1H NMR and infrared spectral data are therefore found to be consistent with the composition and stereochemistry of the $[\text{Ru}(\text{CO})_2(\text{L}-\text{R})_2]$ complexes.

The $[\text{Ru}(\text{CO})_2(\text{L}-\text{R})_2]$ complexes are found to be readily soluble in dichloromethane, methanol, ethanol, chloroform, acetonitrile, etc., producing bright yellow solutions.

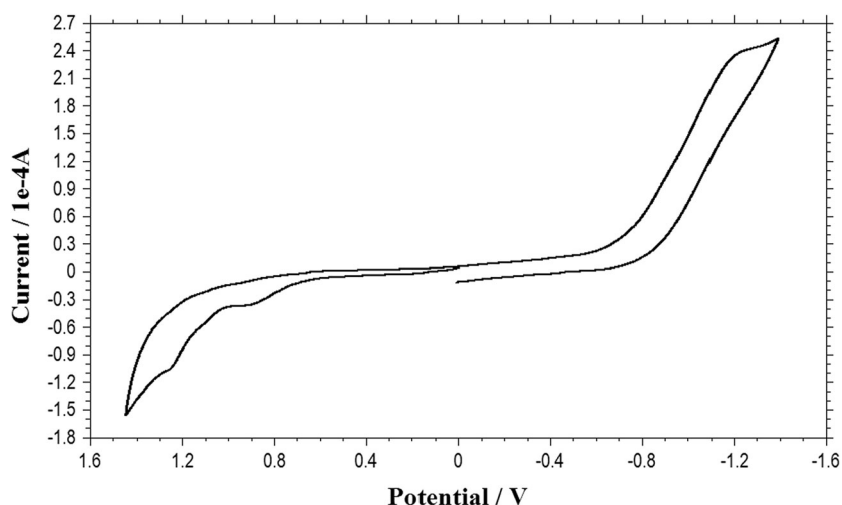


Fig. 4 Cyclic voltammogram of $[\text{Ru}(\text{CO})_2(\text{L}-\text{Cl})_2]$ in acetonitrile solution (0.1 M TBHP) at a scan rate of 50 mV s^{-1}

Electronic spectra of the complexes were recorded in dichloromethane solution. Each $[\text{Ru}(\text{CO})_2(\text{L-R})_2]$ complex shows two intense absorptions near 510 and 344 nm. Spectral data are presented in Table 3. The absorption in the ultraviolet region is attributable to a transition within the ligand orbitals. To have an insight into the nature of absorption in the visible region, DFT calculations were performed on the $[\text{Ru}(\text{CO})_2(\text{L-R})_2]$ complexes [36]. Compositions of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) are given in Table 4 and contour plots of these molecular orbitals for a representative complex is shown in Fig. 3. For all the five complexes, the HOMO is found to have maximum (>80 %) contribution from a coordinated thiosemicarbazone, while the LUMO is found to be delocalized mostly (>90 %) on the coordinated thiosemicarbazones.³ The lowest energy absorption displayed by the $[\text{Ru}(\text{CO})_2(\text{L-R})_2]$ complexes near 510 nm is therefore assignable to a transition from a filled orbital of a coordinated thiosemicarbazone to a vacant orbital spread almost equally over the coordinated thiosemicarbazones (see Footnote 3).

3.3 Electrochemical Properties

Electrochemical properties of the $[\text{Ru}(\text{CO})_2(\text{L-R})_2]$ complexes have been studied by cyclic voltammetry in acetonitrile solution (0.1 M TBHP). Voltammetric data are given in Table 3 and a selected voltammogram is shown in Fig. 4. Each complex shows two oxidative responses on the positive side of SCE and a reductive response on the negative side. All the responses are found to be irreversible in nature. In view of composition of the HOMO in all these complexes, the first oxidative response near 0.87 V versus SCE is assigned to oxidation of a coordinated thiosemicarbazone ligand. Similarly, based on the composition of the LUMO, the reduction near -1.24 V versus SCE is assigned to reduction of the second coordinated thiosemicarbazone ligand. The second oxidative response near 1.28 V versus SCE is tentatively assigned to ruthenium(II)–ruthenium(III) oxidation. Potential of the redox responses does not show any systematic variation with the nature of the substituent R in the thiosemicarbazone ligand.

4 Conclusion

The present study shows that the 4-R-benzaldehyde thiosemicarbazones (HL-R) can readily interact with $[\text{Ru}(\text{CO})_2\text{Cl}_2]_n$ to afford a group of ruthenium carbonyl

complexes of type $[\text{Ru}(\text{CO})_2(\text{L-R})_2]$, where the thiosemicarbazones display N,S-binding mode (I) forming a four-membered chelate ring. Presence of two mutually *cis* carbonyl ligands, together with the two anionic N,S-coordinated thiosemicarbazones, has made these complexes good candidates for application in catalysis, which is currently under exploration.

5 Supporting Information

Crystallographic data have been deposited with the Cambridge Crystallographic Data Center, CCDC 1486586.

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³ For $[\text{Ru}(\text{CO})_2(\text{L-NO}_2)_2]$ the LUMO is spread over mostly (~90%) on one of the two coordinated thiosemicarbazones.

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