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Binuclear ruthenium(III) bis(thiosemicarbazone) complexes: synthesis, spectral, electrochemical studies and catalytic oxidation of alcohol

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Abstract

A new series of binuclear ruthenium(III) thiosemicarbazone complexes of general formula $[(EPh_3)_2(X)_2Ru-L-Ru(X)_2(EPh_3)_2]$ (where E = P or As; X = CI or Br; L = NS chelating bis(thiosemicarbazone ligands) has been synthesized and characterized by analytical and spectral (FT-IR, UV-Vis and EPR). IR spectra show that the thiosemicarbazones behave as monoanionic bidentate ligands coordinating through the azomethine nitrogen and thiolate sulphur. The electronic spectra of the complexes indicate that the presence of d–d and intense LMCT transitions in the visible region. The complexes are paramagnetic (low spin d⁵) in nature and all the complexes show rhombic distortion around the ruthenium ion with three different 'g' values ($g_x \neq g_y \neq g_z$) at 77K. All the complexes are redox active and exhibit an irreversible metal centered redox processes ($Ru^{III}-Ru^{II}/Ru^{IV}-Ru^{IV}$; $Ru^{III}-Ru^{II}/Ru^{II}-Ru^{II}$) within the potential range of 0.38 to 0.86 V and -0.39 to -0.66 V respectively, versus Ag/AgCl. Further, the catalytic efficiency of one of the complexes [$Ru_2Cl_2(AsPh_3)_4(L1)$] (4) has been investigated in the case of oxidation of primary and secondary alcohols into their corresponding aldehydes and ketones in the presence of N- methylmorpholine-N-oxide(NMO) as co-oxidant. The formation of high valent $Ru^V=O$ species is proposed as catalytic intermediate for the catalytic cycle.

Keywords: Binucleating thiosemicarbazone ligands; Ruthenium(III) complexes; Synthesis; spectra; Redox property and Oxidation of alcohol.

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1. Introduction

The synthesis and structural investigation of thiosemicarbazones and their transition metal complexes are considerable centre of attention because of their potentially beneficial variation in their bonding modes [1-3]. Recently coordination chemistry of mixed hard-soft N and S donor ligands received much attention due to a most important factor in this objective probably for designing of ligands with an appropriate structural backbone. They are versatile ligands and exhibit a wide range of coordination modes in their metal complexes (Scheme 1). They usually bind to a metal ion, either in the neutral thione form (1a) or in the anionic thiolate form (1b), as bidentate N, S donor ligands forming five membered chelate ring. The ligand can also bind to the metal ion via the hydrazinic nitrogen and the thiolate sulphur as monoanionic bidentate N, S donors forming a four membered chelate ring (1c). However, the binding capacity of thiosemicarbazones is further increased by condensation of the thiosemicarbazide with an aldehyde or ketone containing an additional donor atom in a suitable position for chelation [4-6]. In recent years, ruthenium(III) complexes have been proved to be extremely useful catalysts in organic synthesis such as epoxidation [7, 8], oxidation [9, 10], reduction [11], hydrolysis [12, 13], transfer hydrogenation [14] and other transformation of organic compounds [15].

Transition metal based catalytic conversion of primary or secondary alcohols into their corresponding aldehydes or ketones are essential reaction in organic synthesis [16-18]. The development of effective, green catalytic system that uses clean and inexpensive oxidants such as molecular oxygen or hydrogen peroxide for converting alcohols on an industrial scale remains an important challenge [19]. Ruthenium complexes containing triphenylphosphine or triphenylarsine ligands have been extensively investigated and well established [20] as catalyst for alcohol oxidation in combination with various oxidants such as dioxygen [21, 22], iodosobenzene [23], t-BuOOH [24], H₂O₂ [25], NaIO₄ [26] and NMO [27, 28]. Ruthenium based oxidation catalysis is a powerful and extremely versatile synthetic tool to afford selectively oxygenated products both in homogeneous and in heterogeneous conversions [29].

Though the oxidation of alcohol has been extensively studied using various ruthenium complexes, there is no report in the literature where binuclear ruthenium(III) bis(thiosemicarbazone) complexes was used as a catalyst for this reaction. In continuation of our research on the synthesis, characterization and catalytic applications of ruthenium and palladium thiosemicarbazone complexes [30], we herein describe the synthesis and characterization of

binuclear ruthenium(III) complexes of the type $[(EPh_3)_2(X)_2Ru-L-Ru(X)_2(EPh_3)_2]$. Further, the catalytic activity of the synthesized complexes was investigated in the case of oxidation of alcohol in the presence of NMO.

2. Experimental

2.1. Reagents and material

Commercially available RuCl₃.3H₂O was used as supplied from Loba Chemie Pvt. Ltd. Triphenylphosphine, triphenylarsine, terepthaldehyde, thiosemicarbazide and Nmethylmorpholine–N-Oxide (NMO) derivatives were purchased from Sigma–Aldrich and were used as received. All the reagents used were chemically pure and analytical grade. The solvents were freshly distilled prior to use following the standard procedures and degassed before use [**31**]. The supporting electrolyte, tetra butyl ammonium perchlorate (n-Bu₄NClO₄), was dried in vacuum prior to use. The starting precursor ruthenium(III) complexes [RuCl₃(PPh₃)₃], [RuCl₃(AsPh₃)₃] and [RuBr₃(AsPh₃)₃] [**32-34**] and terepthaldehyde thiosemicarbazone ligands [**35**] were prepared according to the literature procedures.

2.2. Physical measurements

Melting points are uncorrected and were determined in capillary tubes on a Boetius micro heating apparatus. The analysis of carbon, hydrogen, nitrogen and sulphur was performed at Sophisticated Test and Instrumentation Centre (STIC), Cochin University of Science And Technology, Kochi. Infrared spectra of complexes were recorded in KBr pellets with a Perkin–Elmer 597 spectrophotometer in the range 4000–400 cm⁻¹. Electronic spectra of the complexes were recorded in DMSO solution with a Cary 300 Bio UV–Vis Varian spectrophotometer in the range 800–200 nm using cuvettes of 1 cm path length. Magnetic susceptibility measurements of the complexes in the solid state were determined by using EG and G model 155 vibrating sample magnetometer. The X-band EPR spectra of the powdered samples were recorded on JEOL JES-FA200 EPR spectrometer. Electrochemical studies were performed using a Princeton EG and G-PARC model potentiostat in degassed 0.001M acetonitrile solutions of TBAP as supporting electrolyte. A three electrode cell was employed with carbon working electrode, a platinum wire auxiliary electrode and an Ag/AgCl reference electrode. Capillary gas chromatography was

performed on a Bruker GC-436 scion gas chromatography with a BR-1ms FS column (15m * 0.25mm * 0.25um).

2.3. Synthesis of binuclear ruthenium(III) bis(thiosemicarbazone) complexes

A degassed benzene solution (20 mL) $[RuX_3(EPh_3)_3]$ was taken in a clean 100 ml round bottom flask. The bis(thiosemicarbazone) ligands (1 mmol) were added to the above solution. The mixture was heated at reflux for 9 h. The initial dark brown color of the solution gradually changed to dark green. The solvent was then evaporated under high vacuum at low temperature, followed by petroleum ether (60–80°C) work up gave a green colored solid. The solid mass thus obtained was purified using a silica column (60-120 mesh) chromatography. Evaporation of the afforded 65-70% solvent under reduced pressure of new ruthenium(III) bis(thiosemicarbazone) complexes.

2.4. Catalytic oxidation

Catalytic oxidation of primary alcohols to the corresponding aldehydes and secondary alcohols to ketones by binuclear ruthenium(III) complexes was studied in the presence of NMO as co-oxidant. A typical reaction using the complex $[Ru_2Cl_2(AsPh_3)_4(L1)]$ (4) as a catalyst and primary or secondary alcohol as substrates at a 1:100 molar ratio is described as follows. A solution of ruthenium complex (4) (0.01 mmol) in 20 cm³ CH₂Cl₂ was added to the solution of substrate (1 mmol) and NMO (3 mmol). The solution mixture was refluxed for 3 to 8h. The filtrate obtained was evaporated under reduced pressure and the residual mass was dissolved in a mixture of ethyl acetate/hexane (1:4) and then passed through a short column of silica gel using hexane/ethyl acetate (4:1) as eluent. Removal of solvent and usual workup gave the corresponding aldehydes or ketones, which were identified by GC and ¹H-NMR.

3. Result and Discussion

The thiosemicarbazone ligand derivatives were conveniently prepared in an excellent yield by the condensation of substituted terepthaldehyde with thiosemicarbazone in 2:1M ratio respectively. These ligands are react with ruthenium(III) precursors [RuX₃(EPh₃)₃] (where E = P, X = Cl; E = As, X = Cl or Br) in 1:2 molar ratio respectively in benzene in the presence of triethylamine as base. The reaction mixture was heated to reflux for 9 h afforded new binuclear

Ru(III) complexes of the general formula $[(EPh_3)_2(X)_2Ru-L-Ru(X)_2(EPh_3)_2]$ (Scheme 2). All the complexes have been obtained in good yields . The ligands behave as mono anionic bidentate, replacing one triphenylphosphine/triphenylarsine and one chlorine/bromine from the ruthenium(III) precursors and the oxidation state of ruthenium remain unchanged during the formation of the complex. All the complexes are dark green in colour, air stable and are non-hygroscopic in nature. The synthesized ruthenium(III) complexes are soluble in organic solvents such as CH_2Cl_2 , DMF, DMSO and CH_3CN . Attempts made to grow single crystal were unsuccessful. The analytical data (C, H, N and S) are listed in (**Table 1**) are in good agreement with the calculated values confirming the general molecular formula proposed for all the complexes.

4. Characterization

4.1. IR Spectra

The coordination mode of the thiosemicarbazone ligand to the ruthenium(III) centre in complex was investigated using by FT-IR spectroscopy (Table 2). The FT-IR spectra of the free ligands display a strong band 1602-1620 cm⁻¹ is attributed to the $v_{C=N}$ stretch of the ligand. The coordination of the ligand to the Ru(III) ion through azomethine nitrogen is expected to reduce the electron density in the azomethine nitrogen the $v_{C=N}$ absorption and has been observed at a lower frequency in the complexes (1584-1606 cm⁻¹) [36], which confirms the coordination of azomethine nitrogen. A sharp band appeared for the ligand at 826-847 cm⁻¹ corresponding to $v_{C=S}$ vibration is disappeared completely in the complexes and a new band is appeared at 1299– 1324 cm⁻¹ corresponding to a possible v_{C-S} vibration, indicating coordination of a thiolate sulphur after enolisation [37]. The free ligands displayed absorptions due to $v_{C=S}$ and v_{N-H} of N-NH-C=S group in the region 842-854 cm⁻¹ and 3394-3388 cm⁻¹ respectively and are absent in all the complexes. In addition, characteristic bands for PPh₃ and AsPh₃ were also observed in the regions 1440-1448 cm⁻¹ and 1096-1106 cm⁻¹ in all the complexes. The IR spectra of the all complexes therefore confirm the coordination mode of the ligands to ruthenium(III) ion via the azomethine nitrogen and the thiolate sulphur along with the presence of coordinated triphenylphosphine / arsine ligands [38].

4.2. Electronic Spectra

Electronic spectra of all the binuclear Ru(III) complexes showed intense absorptions in the ultraviolet and visible region. The electronic spectra of all the complexes have been recorded in DMSO and display four intense absorptions in the region 800–200 nm. The electronic spectral data of 1–6 are listed in (**Table 3**) and selected spectrum is shown in **Fig. 1**. The absorption in the visible region at 648-660 nm is due to d-d transition and the bands observed in the region 413–425 nm have been assigned to LMCT transitions. The bands in the regions 352–368 nm are due to n– π^* transition of non-bonding electrons present on the nitrogen of the azomethine group in the ruthenium(III) complexes. The band observed around 251–260 nm is assigned to $\pi - \pi^*$ transitions of the ligand. The pattern of the electronic spectra of all the complexes indicate the presence of an octahedral environment around ruthenium(III) similar to that of other ruthenium(III) octahedral complexes [**39-41**].

4.3. Magnetic moment and EPR Spectra

The room temperature magnetic susceptibility measurements for two of the binuclear ruthenium(III) bis(thiosemicarbazone) complexes, viz. $[Ru_2Cl_2(AsPh_3)_4L1]$ (1) and $[Ru_2Cl_2(PPh_3)_4L1]$ (4) were measured. The room temperature μ_{eff} values per ruthenium ion for the complexes are 1.79 and 1.84 BM respectively. It has been observed that the μ_{eff} values indicate a single unpaired electron present in each ruthenium ion and is consistent with non-interacting d⁵ metal centers or the absence of any strong magnetic interactions between the two-ruthenium centres of the molecule [42].

EPR spectra of all the complexes were recorded at X-band frequencies at room temperature and LNT. The low spin d⁵ configuration is a good probe of molecular structure and bonding since the observed 'g' values are very sensitive to small changes in structure and to the metal–ligand covalency. The EPR spectra of all the complexes in the solid state exhibit well defined single isotropic lines with 'g' values in the range 2.40–2.45 at room temperature. Such isotropic lines are usually the results of either intermolecular spin exchange, which can broaden the lines or occupancy of the unpaired electron in a degenerate orbital. However, the EPR spectra of the complexes recorded in toluene solution at 77 K show rhombic spectra with three distinct g values ($g_x \neq g_y \neq g_z$) are ($g_x = 2.39-2.59$, $g_y = 2.02-2.23$, $g_z = 1.71-1.93$) respectively. The EPR data

are summarized in (**Table 4**) and a representative spectrum is shown in **Fig. 2**. The rhombicity of the spectra reflect the asymmetry of electronic environments around ruthenium in the complexes **[43, 44]**. The EPR spectra of the present binuclear ruthenium(III) thiosemicarbazone complexes are similar nature to these of the mononuclear complexes and this indicate that two paramagnetic centers are equivalent and there is no super exchange interaction between the two metal centers **[45]**. However, these new complexes are one unpaired electron each ruthenium(III) atom leading S-value of 1. The pairing of electron is prevented by the greater distance between two ruthenium(III) atoms provide by the bidentate thiosemicarbazone ligands **[46]**. That is a spin-forbidden transition, characteristic of dinuclear complexes with one unpaired electron on each ruthenium(III) atom (S = $\frac{1}{2}$). Overall the position of the lines and the nature of the EPR spectra of the complexes are characteristics of low-spin ruthenium(III) octahedral complexes. Hence, the results from the EPR spectral analysis indicate that these binuclear ruthenium(III) complexes are significantly distorted from an octahedral geometry.

4.5. Electrochemical Study

The electrochemical properties of the binuclear ruthenium(III) complexes were studied in an oxygen free acetonitrile solution by cyclic voltammetry using a glassy carbon electrode and the potentials are expressed with reference to Ag/AgCl. All the binuclear complexes $(1\times10^{-3}M)$ are electro active and exhibit two successive irreversible oxidations and two reductions waves. The potentials are summarized in (**Table 5**) and a representative voltammogram is shown in **Fig. 3**. The first reduction process takes place in the potential range -0.39 to -0.51 V and the second reduction response observed at -0.55 to -0.66 V. Similarly, the irreversibility of first oxidation process takes place in the potential range +0.38 to +0.51 V and the second oxidation response observed at +0.76 to +0.86 V. The first oxidation or reduction was attributed to the oxidation or reduction of one of the ruthenium(III) centres to the corresponding mixed valence complex and the second to the ruthenium(IV) or ruthenium(II) **[14]**.

 $Ru^{II}-Ru^{II} \longrightarrow Ru^{III}-Ru^{II} \longrightarrow Ru^{III}-Ru^{III} \longrightarrow Ru^{IV}-Ru^{III} \longrightarrow Ru^{IV}-Ru^{IV}$ Irreversible Reduction Irreversible oxidation

The observed electro chemical behavior supports for the binuclear nature of the complexes. It has been observed that there is not much variation in the redox potentials due to the replacement of PPh₃ by AsPh₃ and nature of bridging ligand present in the complexes **[47, 48]**.

5. Catalytic oxidation of alcohols

Ruthenium mediated oxidations are finding increasing application due to the unique properties of this extremely versatile transition metal, whose oxidation states can vary from -2 to +8 and this prompted us to carry out this type of reaction. The present work describes the catalytic oxidation of primary and secondary alcohols by the synthesized ruthenium(III) complex [Ru₂Cl₂(AsPh₃)₄(L1)] (4) in CH₂Cl₂ in the presence of NMO and the byproduct water was removed by using about 0.25 g of molecular sieves (Scheme 3). In no case was there any detectable oxidation of alcohols in the presence of NMO alone or the Ru(III) complexes.

In order to optimize the reaction conditions, various substrate: catalyst ratios in presence of various co-oxidant were carried out and the results are summarized in (**Table 6**). For these initial experiments pentan-2-ol was selected as a test-substrate for oxidation with catalytic quantity of ruthenium(III) complex (4) in the presence of various co-oxidants. When increasing the C:S ratio 1:100 and up to 1:500 in dichloromethane, the reaction still proceeds smoothly accompanied by a moderate drop in conversions. Thus, it was concluded that catalyst: substrate ratio is 1:100 and co-oxidant NMO is the best compromise between optimal reaction rate in dichloromethane.

Complex(4) oxidizes primary alcohols to corresponding aldehydes and secondary alcohols to ketones with moderate to high conversion and the results are listed in (**Table 7**) (entries 1–10). The aldehydes or ketones formed after 3 or 8 h of refluxing were determined by GC (Figure S1–S7, Supplementary data). The results of the present investigation suggest that the complexes efficiently react with NMO to yield high valent $Ru^{V}=O$ species [49], capable of oxygen atom transfer to alcohols. This was supported by spectral changes that occur on the addition of NMO to a CH₂Cl₂ solution of the Ru(III) complexes. The appearance of a peak at 390 nm is attributed to the formation of Ru^V=O, which is in conformity with other Ru(V) complexes [49, 50] (Scheme 4).

In the present study of oxidation, the catalytic oxidation of benzylalcohol to benzaldehyde results in 74% conversion in 3 h and the maximum conversion 89% was obtained after 8 h. The complex catalyzes the oxidation of 1-phenyl ethanol into corresponding ketones in 94% conversion. In the case of diphenylmethanol the oxidation product benzophenone is 96%. Interestingly, the complex efficiently catalyzes the oxidation of five, six, seven and eightmembered cyclic alcohols to the corresponding ketones with conversions >86%. Further, the complex effectively catalyze the aliphatic alcohols like butan-2-ol, pentan-2-ol and pentan-3-ol to the corresponding ketones with moderate conversions in 3 h and the conversions were improved to 82%, 99% and 89% respectively after 8 h. It has been observed that the present catalyst (4) has better catalytic efficiency in the oxidation of alcohols than the previous report on similar ruthenium complexes [9].

6. Conclusion

Binuclear ruthenium(III) complexes containing bidentate thiosemicarbazone, halides and triphenylphosphine or triphenylarsine have been synthesized. Analytical and spectral results confirm the coordination of azomethine nitrogen and thiolate sulphur of the ligand to ruthenium. The rhombic EPR spectral pattern indicates ruthenium ions are in a distorted octahedral environment. Further, these complexes were tested as catalyst for the oxidation of variety of alcohols in the presence of N-methylmorpholine-N-oxide (NMO) and the maximum conversion was obtained upto 99%.

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Scheme 2. Synthesis of new binuclear Ru(III) bis(thiosemicarbazone) complexes



Scheme 4. Proposed catalytic cycle for the oxidation of alcohols by complex (4)



Fig. 1. Absorption spectrum of $[Ru_2Cl_2(PPh_3)_4(L2)]$ (1) in DMSO



Fig. 2. EPR spectrum of the complex [Ru₂Cl₂(PPh₂)₂(L1)] (3) at 77 K



Fig. 3. Cyclic voltammogram of complex $[Ru_2Cl_2(AsPh_3)_2(L1)]$ (2)

Table 1

Analytical data of binuclear Ru(III) (bis)thiosemicarbazone complexes.

* decomposition temperature

S.No.	Complexes	M.P*		Calculated (found) %	
		(°C)	С	Н	N	S
1	$[\operatorname{Ru}_2\operatorname{Cl}_2(\operatorname{PPh}_3)_4(L1)]$	289-291	58.84 (58.81)	4.13 (4.22)	4.91 (4.87)	3.68 (3.64)
2	$[Ru_2Cl_2(PPh_3)_4(L2)]$	294-296	59.28 (59.36)	4.30 (4.24)	4.81 (4.76)	3.61 (3.77)
3	$[Ru_2Cl_2(PPh_3)_4(L3)]$	295-297	61.83 (61.79)	4.23 (4.18)	4.52 (4.61)	3.43 (3.38)
4	$[\operatorname{Ru}_2\operatorname{Cl}_2(\operatorname{AsPh}_3)_4(L1)]$	283-285	58.92 (58.87)	4.22 (4.29)	5.03 (4.96)	3.84 (3.78)
5	$[Ru_2Cl_2(AsPh_3)_4(L2)]$	281-284	56.47 (56.40)	3.93 (3.85)	4.20 (4.14)	3.21 (3.32)
6	$[Ru_2Cl_2(AsPh_3)_4(L3)]$	298-300	59.36 (59.41)	4.39 (4.46)	4.94 (4.87)	3.77 (3.69)
7	$[\operatorname{Ru}_2\operatorname{Br}_2(\operatorname{AsPh}_3)_4(L1)]$	273-275	53.16 (53.09)	3.74 (3.67)	4.38 (4.54)	3.34 (3.47)
8	$[\operatorname{Ru}_2\operatorname{Br}_2(\operatorname{AsPh}_3)_4(\operatorname{L2})]$	280-283	53.68 (53.58)	3.83 (3.76)	4.35 (4.48)	3.28 (3.21)
9	$[\operatorname{Ru}_2\operatorname{Br}_2(\operatorname{AsPh}_3)_4(\operatorname{L3})]$	298-300	56.32 (56.26)	3.81 (3.93)	4.09 (4.03)	3.06 (3.11)

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Table 2

IR data of binuclear Ru(III) bis(thiosemicarbazone) complexes.

		IR frequencies (ν/cm^{-1})			
Complexes	NHR	C=N	PPh ₃	C-S	
1	3385	1586	1438	1318	
2	3378	1584	1442	1312	
3	3381	1595	1440	1317	
4	3383	1594	1442	1310	
5	3386	1587	1441	1309	
6	3388	1596	1445	1299	
7	3394	1606	1448	1303	
8	3372	1572	1438	1314	
9	3374	1586	1443	1324	

Table 3

Complexes λ max (nm) ϵ (dm³/mol⁻¹cm⁻¹) 425(3290)^b $647(2420)^{a}$ 354(6168)^c $258(13240)^{d}$ 1 251(9260)^d 416(2410)^b 357(4200)^c 651(1861)^a 2 361(6167)^c 254(14192)^d 648(2642)^a 417(3670)^b 3 260(16085)^d 652(3165)^a 415(4330)^b 352(7545)^c 4 259(11711)^d 653(3285)^a 414(4587)^b 359(7812)^c 5 660(3055)^a 413(4440)^b 368(6270)^c 258(15250)^d 6

Absorption data of binuclear Ru(III) bis(thiosemicarbazone) complexes.

^ad-d Transition

^b LMCT

 $^{c}n-\pi^{*}$

 d π - π^{*}

Table4

Complexes	g _x	gy	gz	<g*></g*>
1	2.50	2.15	1.93	2.11
2	2.46	2.18	1.83	2.06
3	2.55	2.23	1.89	2.22
4	2.54	2.17	1.85	2.20
5	2.59	2.02	1.74	2.14
6	2.39	2.06	1.71	2.15

EPR data of binuclear Ru(III) bis(thiosemicarbazone) complexes at LNT.

 $\langle g^* \rangle = [1/3 g_x^2 + 1/3 g_y^2 + 1/3 g_z^2]^{1/2}$

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Table 5

Complexes	Ru ^(III) -Ru ^(III) /Ru ^(II) -Ru ^(II)		Ru ^(III) -Ru ^(III) /Ru ^(IV) -Ru ^(IV)		
	$E_{\rm Pc}({ m V})$	$E_{\rm Pc}({ m V})$	$E_{\rm Pa}({ m V})$	$E_{\mathrm{Pa}}(\mathrm{V})$	
1	-0.49	-0.61	0.42	0.80	
2	-0.52	-0.66	0.47	0.83	
3	-0.43	-0.56	0.38	0.76	
4	-0.51	-0.66	0.51	0.86	
5	-0.45	-0.58	0.40	0.79	
6	-0.39	-0.55	0.46	0.84	

Electrochemical data of binuclear ruthenium(III) bis(thiosemicarbazone) complexes

Supporting electrolyte: $[(NBu_4)ClO_4]$ (0.001 M); complex: 0.001 M; solvent: acetonitrile; scan rate: 100 mV s⁻¹. All the potential referenced to Ag/AgCl.

Table 6

Optimization of oxidation of alcohol by pentan-2-ol with $[Ru_2Cl_2(AsPh_3)_4(L1)]$ (4).

Entry	C:S ratio ^a	Conversion ^b	Co-oxidant
1	1:100	80	PhIO
2	1:100	74	^t BuOOH
3	1:100	71	NaIO ₄
4	1:100	91	NMO
5	1:300	78	NMO
6	1:500	52	NMO

^a Substrate (1mmol); complex (0.01mmol); solvent dichloromethane; Temp. 40 ^oC;Time 3 h.
^b Conversion is determined by GC with area normalization; GC conditions: BR-1ms FS column, 60 (15m * 0.25mm * 0.25um), 250 °C; FID detector, 280 °C; injector, 250 °C; carrier gas: N2; rate: 25 mL/min.

Table 7:	Catalytic oxidation of a	alcoholsby [Ru2Cl2(AsPh	n ₃) ₄ (L1)] (4).	CRIPS
Entry	Substrate ^a	Products	Time (h)	Conversion ^b (%)
1	ОН	СНО	3/8	74/88
2 3	OH OH OH		3	92
			3	96
4	ОН		3/8	87/96
5	ОН		3/8	85/99



^a Substrate (1 mmol); NMO (3 mmol); complex (0.01 mmol); solvent dichloromethane; Temp. 40 ^oC;

^b Conversion is determined by GC with area normalization.

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Graphical Abstract



Research Highlights

- New binuclear Ru(III) complexes containing (bis)thiosemicarbazones were reported.
- Characterisation of complexes were accomplished by analytical and spectral methods.
- Electrochemical study supports for the binuclear nature of the complexes.
- Reported as effective catalyst for the oxidation of alcohols.

Accepter