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Ru(II) complexes imparting N_2O_2 donor bis chelating ligand N,N'-bis(salicylidine)-hydrazine in unusual coordination mode

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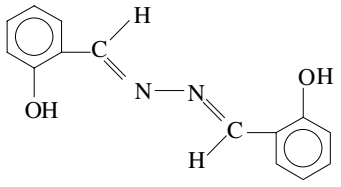
Abstract

The synthesis and characterization of binuclear ruthenium complexes [{(η^6-C_6H_6)Ru}$_2$(μ-bsh)$_2$] (**1**), [{(η^6-$C_{10}H_{14}$)Ru}$_2$(μ-bsh)$_2$] (**2**), [{(η^6-C_6Me_6)Ru}$_2$(μ-bsh)$_2$] (**3**), and rhodium complex [{(η^5-C_5Me_5)RhCl}$_2$(μ-bsh)] (**4**) (bsh = N,N'-bis(salicylidine)-hydrazine dianion) are reported. The complexes have been fully characterized by analytical and spectral techniques and unusual coordination mode of the ligand H_2bsh has been confirmed by single crystal X-ray analysis of the complex **2**. Structural data revealed extensive inter- and intra-molecular C–H···O and C–H···π interactions and involvement of methyl and isopropyl hydrogen from the *p*-cymene in hydrogen bonding.

Keywords: Ruthenium; Arene; N,N'-bis(salicylidine)-hydrazine; X-ray; Interaction

1. Introduction

Considerable recent attention has been paid towards synthesis and characterization of half-sandwich η^6-arene ruthenium(II) complexes owing to their potential use in various fields [1]. Reaction of the dimers [{(η^6-arene)Ru(μ-Cl)Cl}$_2$] (η^6-arene = benzene and its derivatives) with Lewis bases, a variety of other ligands and N,N' and N,O Schiff's base ligands derived from 2-formyl pyridine or salicylaldehyde have extensively been studied in this regard [2]. Literature survey further revealed that reactions of the arene ruthenium complexes with closely related N_2O_2 donor Schiff's base ligands, N,N'-bis(salicylidine)-hydrazine (H_2bsh), N,N'-bis(salicylidine)-*p*-phenylenediamine (H_2bsp) and N,N'-bis-(salicylidine)-*p*-biphenylenediamine (H_2bsb) possessing two dissociable protons have yet to be explored. Among these, H_2bsh (Fig. 1) is expected to form some unusual and rather interesting coordination compounds due to flexibility of the ligand about N–N single bond. At the same time, structurally characterized complexes of H_2bsh are rare and in the known complexes it adopts *trans* configuration [3].



N,N'-bis(salicylidine)-hydrazine(H_2bsh)

During past few years we have been interested in the synthesis of polynuclear complexes involving new type of bridging ligands, which can mediate electronic coupling through its π-type of orbital [4]. In this direction, reactivity of the ruthenium complexes [{(η^6-arene)Ru(μ-Cl)Cl}$_2$] and analogous rhodium complex [{(η^5-C_5Me_5)Rh(μ-Cl)Cl}$_2$] was examined with H_2bsh. Surprisingly, it was observed that reactions of arene ruthenium complexes with H_2bsh led in the formation of [{(η^6-arene)Ru}$_2$(μ-bsh)$_2$] involving the dianion bsh^{2-} in an unusual coordination mode. On the other hand, rhodium complex gave the expected binuclear complex [{(η^5-C_5Me_5)RhCl}$_2$(μ-bsh)]. In this paper we report the first structurally characterized complex [{(η^6-$C_{10}H_{14}$)-Ru}$_2$(μ-bsh)$_2$] in which the bsh^{2-} acts simultaneously as a bidentate ligand to one metal centre and mono dentate to the other one. Further, the role of hydrogen bonding in crystal engineering and supramolecular structures is

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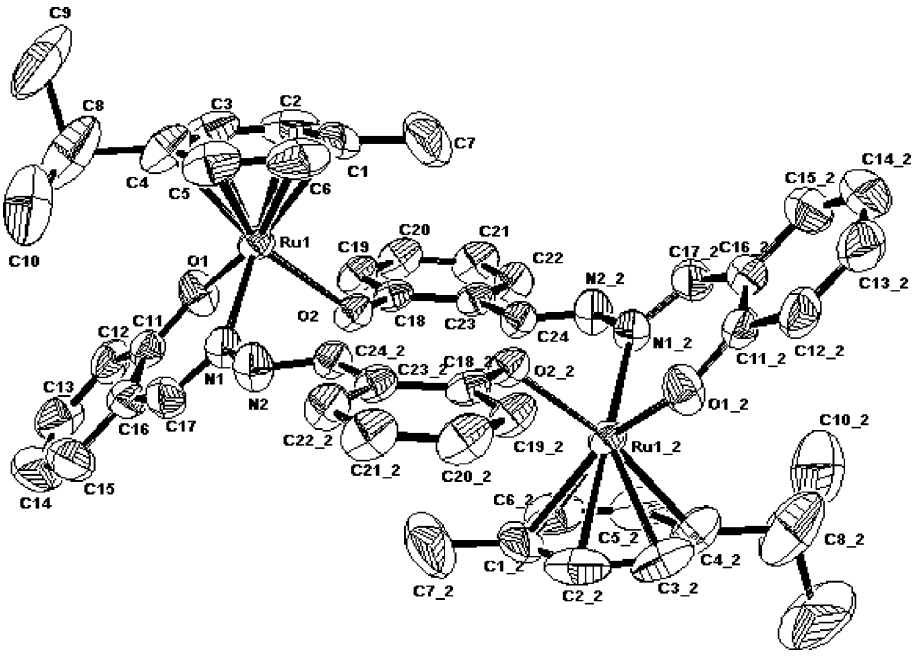


Fig. 1. Molecular presentation of complex **2**, hydrogen atoms has been omitted for clarity.

well documented [5]. Special attention is being paid towards organometallic systems, which can provide new type of hydrogen bonding donor and acceptor groups [6]. Crystal structure of the *p*-cymene containing Ru(II) complex $[\{(\eta^6\text{-}C_{10}H_{14})Ru\}_2(\mu\text{-bsh})_2]$ **2** further revealed that inter and intra molecular C–H···O and C–H···π interactions results in a resting chair motif. Although, various groups have reported C–H···O and C–H···π type of interactions in arene ruthenium complexes, involvement of methyl and isopropyl hydrogen in such interactions are rare [7]. We, also report herein the involvement of methyl and isopropyl groups of *p*-cymene ring in hydrogen bonding.

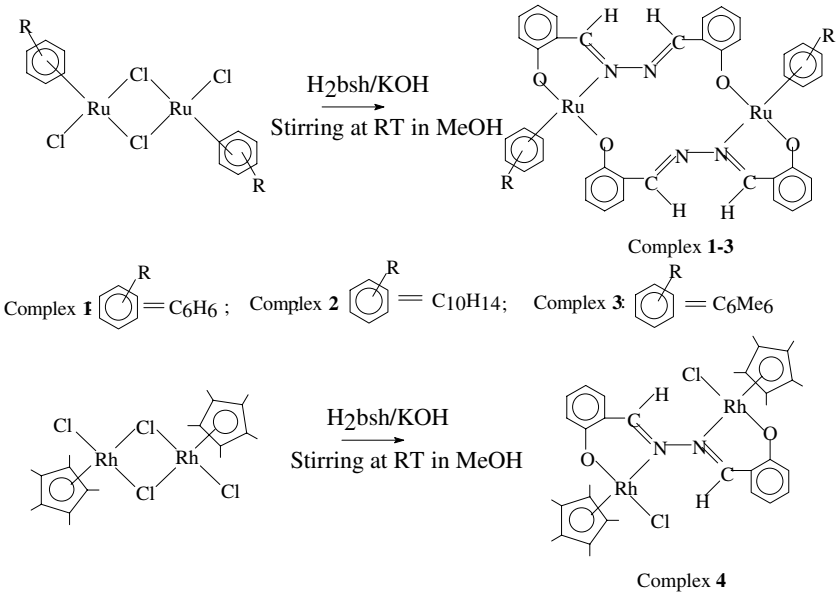
2. Results and discussion

Reaction of the dimers $[\{(\eta^6\text{-arene})Ru(\mu\text{-Cl})Cl\}_2]$ or $[\{(\eta^5\text{-}C_5Me_5)Rh(\mu\text{-Cl})Cl\}_2]$ with a potassium derivative of bsh^{2-} (obtained from H_2bsh and KOH in MeOH) at room temperature under stirring gives the complexes **1**–**4** in good yields (Scheme 1).

The complexes were isolated as dark red to orange red solids and were fully characterized by elemental analyses, FAB MS, ^{1}H NMR, electronic spectral. In the ^{1}H NMR spectra of the complexes **1**–**3,** resonances corresponding to –C(H)=N– protons were observed at two different positions (recorded in Section 3). It is only possible if, there are two chemically inequivalent –C(H)=N– moieties about the ruthenium centre. While the complex **4** exhibited only one resonance corresponding to –C(H)=N– protons. Nature of the complexes **1**–**3** were not immediately obvious as the analyses and mass spectral and ^{1}H NMR data did not accord with the expected mono or binuclear formulation $[(\eta^6\text{-arene})RuCl(bsh)]$ and $[\{(\eta^6\text{-arene})RuCl\}_2(\mu\text{-bsh})]$. Rather it accorded well to the formulation $[\{(\eta^6\text{-arene})Ru\}_2(\mu\text{-bsh})_2]$. On the other hand, the analytical and spectral data of the complex **4** corroborated well to the expected binuclear formulation $[\{(\eta^5\text{-}C_5Me_5)RhCl\}_2(\mu\text{-bsh})]$ in which, two $[(\eta^5\text{-}C_5Me_5)RhCl]^+$ moieties are *trans* disposed and are bridged by bsh^{2-}.

Provided with four donor sites, two oxygen and nitrogen donor atoms, the ligand H_2bsh is fundamentally able to act as mono, bi, tri or tetradentately. Usually, it interacts with the metal centre through both the bischelating O, N donor sites leading to the formation of binuclear complexes. The analytical and spectral data of the complexes **1**–**3** suggested unusual coordination of the bsh^{2-}. Its authentication was further achieved by single crystal X-ray diffraction analysis on the representative *p*-cymene complex $[\{(\eta^6\text{-}C_{10}H_{14})Ru\}_2(\mu\text{-bsh})_2]$ **2**. Molecular structure of the complex **2** is shown in Fig. 1 and selected bond lengths and angles are recorded in Table 2. Crystal structure of the complex **2** shows that two equivalent but independent molecules are present in the asymmetric unit and in each of them the $[(\eta^6\text{-}C_{10}H_{14})Ru]^{2+}$ moieties are bridged by two bsh^{2-} anions, which simultaneously binds both the metal centres through two of its phenolate-O and one immine-N donor atoms. It occupies special position and therefore, only half of its atoms are numbered (Fig. 1).

The metal centre Ru(1) is coordinated with phenolato oxygen O(1), immine nitrogen N(1) from bsh^{2-}, phenolato oxygen O(2) from the other bsh^{2-} and *p*-cymene



Scheme 1. Showing two different coordination modes of the ligand H_2bsh.

Table 1
Crystallographic data for the complex **2**

Empirical Formula	$C_{48}H_{48}N_4O_4Ru_2$
Molecular weight	947.04
Color and habit	Dark red, needles
Crystal size (mm)	$0.2 \times 0.5 \times 0.5$
Space group	P-1
System	Triclinic
Unit cell dimensions	
a (Å)	12.282(5)
b (Å)	13.124(2)
c (Å)	14.189(8)
α (°)	103.42(4)
β (°)	110.19(5)
γ (°)	91.26(3)
V (Å^3)	2074.9(15)
Z	2
d_{calc} (g cm^{-3})	1.516
μ (mm^{-1})	6.290
Temperature (K)	293 (2)
No. of reflections	7870
No. of refined parameters	530
R_1 factor all	0.0383
R_1 factor $[I > 2\sigma(I)]$	0.0360
wR_2	0.1425
$wR_2[I > 2\sigma(I)]$	0.1399
Goodness-of-fit	1.273

ring. Considering the coordination of the *p*-cymene ring as a single coordination site bonded in η^6-manner through its centroid, coordination geometry about the metal centre Ru(1) might be regarded as typical ''piano-stool'' geometry. Analogous arrangement of different atoms is observed about the other metal centre too. The *p*-cymene ring is planar and the Ru–C distances are almost equal with an average bond distance of 2.182 Å [range 2.14(4)–2.20(4) Å]. The metal centre Ru(1) and Ru(2) is displaced by 1.674 Å and 1.672 Å respectively from centroid of the *p*-cymene ring and is consistent with those reported for other ruthenium complexes [8].

Appreciable twisting about the N–N bond takes place in both the bsh^{2-} to accommodate two metal ions, which is evident from the dihedral angle between the planes formed by salicylidine moieties of the same ligand [torsion angle: C(24#)–N(2)–N(1)–C(17) = 141.7(3)° and C(41)–N(3)–N(4)–C(42) = 129.9(3)°]. The ring formed by azo methine group, phenolic oxygen and ruthenium is planar. The Ru–O bond distances Ru(1)–O(1), Ru(1)–O(2), Ru(2)–O(3) and Ru(2)–O(4) are 2.05(3), 2.10(2), 2.05(2) and 2.09(2) Å respectively and are comparable with those in other Ru(II) complexes [9]. The Ru–N bond distances for Ru(1)–N(1) and Ru(2)–N(3) are 2.09(3) and 2.079(3) Å respectively and is comparable with Ru–N distances in other Ru(II) polypyridyl complexes [10]. The N–N and C=N distances are slightly higher than that in the ligand itself [11].

Resting chair like structure, results from the intra and intermolecular C–H···O and C–H···π bonds (Fig. 2). The interaction distances, angles along with their symmetry are summarized in Table 3. Intra molecular hydrogen bonds result by the interaction between the hydrogen present on phenyl carbons C(19), C(48) and phenolato oxygen O(1), O(3), salicylidine carbon atoms C(24), C(42) and phenolato oxygen O(2) and O(4). The isopropyl carbon C(32) is also involved in intramolecular hydrogen bonding through phenolato oxygen O(3). The hydrogen bond distances involving salicylidine carbon are slightly longer as compared to those involving phenyl carbon, suggesting that the latter interactions are strong and phenyl carbons are stronger donor in comparison to salicylidine carbons. Further, hydrogen bond distances involving isopropyl C(32) and methyl C(31) carbons of

Table 2
Selected bond length (Å), bond angles (°) and torsion angles (°) in the complex **2**

Ru(1)–O(1)	2.050(3)
Ru(1)–N(1)	2.090(3)
Ru(1)–O(2)	2.101(2)
Ru(2)–O(3)	2.051(2)
Ru(2)–N(3)	2.079(3)
Ru(2)–O(4)	2.093(2)
N(1)–N(2)	1.424(4)
N(2)–C(24)#1	1.263(4)
N(3)–C(41)	1.296(4)
N(3)–N(4)	1.429(4)
N(4)–C(42)	1.278(4)
O(1)–C(11)	1.298(4)
O(2)–C(18)	1.318(4)
O(3)–C(35)	1.299(5)
O(1)–Ru(1)–N(1)	86.89(12)
O(1)–Ru(1)–O(2)	86.19(11)
N(1)–Ru(1)–O(2)	84.07(10)
O(3)–Ru(2)–N(3)	87.85(11)
O(3)–Ru(2)–O(4)	86.57(10)
N(3)–Ru(2)–O(4)	82.33(11)
C(24#)–N(2)–N(1)–C(17)	141.7(3)
C(41)–N(3)–N(4)–C(42)	129.9(3)

the arene ring are slightly longer than those involving phenyl or salicylidine carbons, it may be due to sp^3 hybridization of C(31) and C(32) [12].

Intermolecular hydrogen bonding is resulting by interaction of methyl hydrogen C(31)–H(31) of the arene ring with the phenolato oxygen O(2) of another unit at the same time the methyl carbon C(7), from another molecule is involved in weak C–H $\cdots$ π intramolecular interaction (2.49A, 140°) with C(18)═C(23) of the phenyl ring [C(18)–C(23)] [13,14]. In the C–H $\cdots$ π bond, the distance of C(7)–H(7b) with the centroid of phenyl ring [C(18)–C(23)] is 2.99 Å is less than the vander wall radii [ΣvdW radii (1.2 + 1.7 = 3.0 Å)] [14]. The anomalous behavior of methyl carbons C(7) and C(31) may be attributed to the greater distortion of ring represented by C(43)–C(48) than C(18)–C(23) as the phenyl ring [C(18)–C(23)] located below C(7) is stabilized by the C–H $\cdots$ π interaction. All the phenolato oxygen atoms O(1), O(2), O(3) and O(4) are engaged in intra molecular hydrogen bonding except O(2) which is engaged in both the inter and intra molecular hydrogen bonding. It is also supported by related bond order calculations [15].

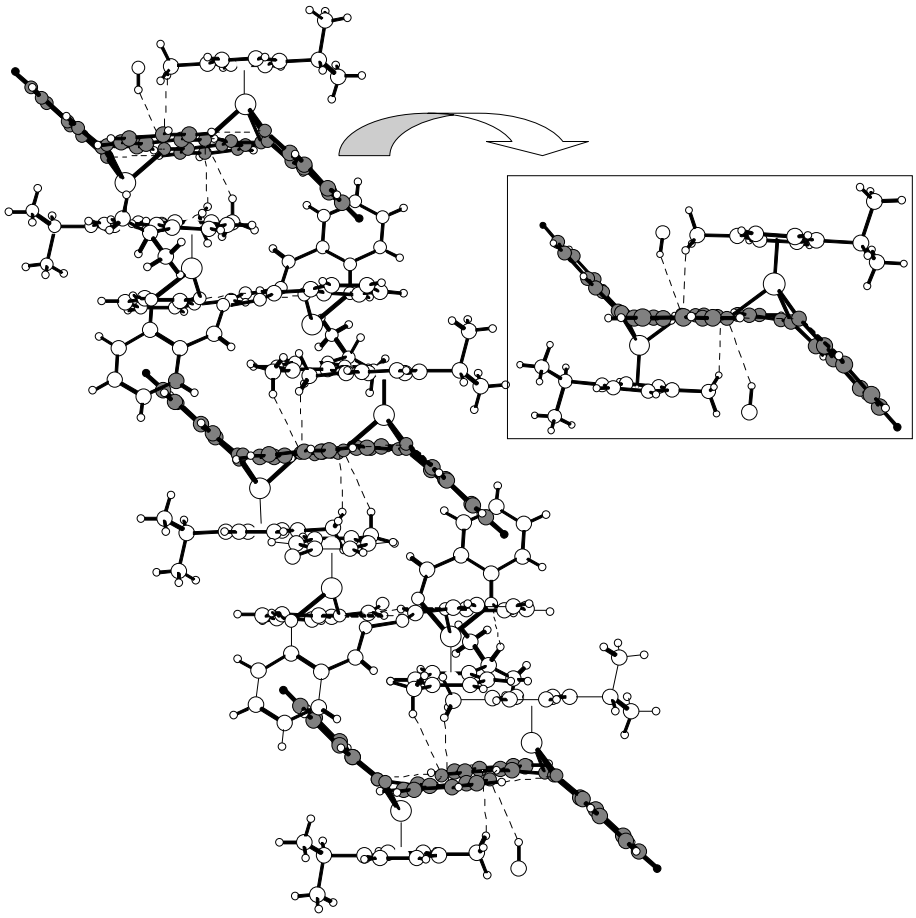


Fig. 2. A resting chair network assembled through inter and intra C–H $\cdots$ O and C–H $\cdots$ π interactions. Inset shows a single unit of chair form.

Table 3
Significant hydrogen bonds (Å and °) for complex **2**

D–H···A	*d*(D–H)	*d*(H···A)	*d*(D···A)	∠(DHA)
C–sp^3(31)–H(31A)···O(2)[a]	0.96	2.58	3.434(6)	148.4
C–sp^2(19)–H(19)···O(1)[b]	0.93	2.35	3.098(4)	136.7
C–sp^2(24)–H(24)···O(2)[c]	0.93	2.45	3.238(4)	142.2
C–sp^2(42)–H(42)···O(4)[b]	0.93	2.50	3.282(4)	142.1
C–sp^2(48)–H(48)···O(3)[b]	0.93	2.37	3.095(5)	134.6
C– sp^3(32)–H(32)···O(3)[b]	0.98	2.58	3.388(8)	139.4
C–sp^3(7)–H(7b)···π [C(18) = C(23)]	0.96	2.49	3.293	140.5

[a] $x, y-1, z-1$.
[b] $-x, -y, -z-1$.
[c] $-x, -y+2, -z$.

3. Experimental

3.1. Materials

All the synthetic manipulations were performed under oxygen free nitrogen atmosphere. The solvents were dried and distilled before use following the standard procedures. α-phellandrene (Fluka), hydrated ruthenium(III) chloride, cyclohexa-1,3-diene, hexamethylbenzene (all Aldrich), salicylaldehyde and hydrazine (s.d.fine chem.) were used as received. The ligand *N*, *N*′-bis(salicylidine)-hydrazine (H_2bsh) and the precursor complexes [{(η^6-C_6H_6)Ru(μ-Cl)Cl}$_2$], [{(η^6-$C_{10}H_{14}$)-Ru(μ-Cl)Cl}$_2$] and [{(η^6-C_6Me_6)Ru(μ-Cl)Cl}$_2$] and [{(η^5-C_5Me_5)Rh(μ-Cl)Cl}$_2$] were prepared and purified following the literature procedures [3,16].

3.2. Instrumentation

Elemental analyses of the complexes were performed at Sophisticated Analytical Instrument Facility, Central Drug Research Institute, Lucknow. Infrared spectra were recorded on a Perkin–Elmer-577 spectrophotometer. NMR spectra were taken on Bruker-DRX300 MHz spectrometers with tetramethylsilane as an internal standard. Electronic spectra of the complexes were obtained on a Shimadzu UV-1601. The FAB mass spectra were recorded on a JEOL SX 102/DA 6000 mass spectrometer using Xenon (6 kV, 10 mA) as the FAB gas. The accelerating voltage was 10 kV and the spectra were recorded at room temperature with *m*-nitrobenzyl alcohol as the matrix.

3.3. Preparation of the complexes

3.3.1. [{(η^6-arene)Ru}$_2$(μ-bsh)$_2$] (**1–3**)

In a typical reaction, to a solution of potassium derivative of bsh [prepared from H_2bsh (1.0 mmol) and KOH (2.0 mmol) in methanol (25 cm^3)], dimers [{(η^6-arene)Ru(μ-Cl)Cl}$_2$](**1**–**3**) or [{(η^5-C_5Me_5)Rh(μ-Cl)Cl}$_2$] (**4**) (1.0 mmol) were added and the resulting suspension was stirred for 4 hrs at room temperature. Slowly, the dimeric complexes dissolved and gave dark red to orange red complexes, which, were separated by filtration and recrystallized from CH_2Cl_2-diethylether. Selected data of the complexes are recorded below.

3.3.2. [{(η^6-C_6H_6)Ru}$_2$(μ-bsh)$_2$] (**1**)

Yield: (701 mg, 84%). (Found: C, 57.57; H, 4.17; N, 6.39. M 834 requires $C_{40}H_{32}N_4O_4Ru_2$: C, 57.55; H, 3.83; N, 6.71%. M 834). λ_{max}/nm, dmso; (ε/dm^3 mol^{-1} cm^{-1}) 404 (38003), 298 (56600), 256 (89033). ^{1}H NMR (300 MHz; $CDCl_3$; $SiMe_4$, *J* Hz): δ 10.28 (s), 8.44 (s), 7.99 (d, 6.9 Hz), 7.70 (d, 8.4 Hz), 7.30 (m), 7.14 (d, 8.4 Hz), 6.75 (t, 7.35 Hz), 6.56 (t, 7.5 Hz), 5.29 (s). *m*/*z*; 418 (417) (M$^+$ − [(η^6-C_6H_6)Ru(bsh)]).

3.3.3. [{(η^6-$C_{10}H_{14}$)RuCl}$_2$(μ-bsh)$_2$] (**2**)

Yield: (804 mg, 85%). (Found: C, 60.84; H, 5.12; N, 5.96. M 946 requires $C_{48}H_{48}N_4O_4Ru_2$: C, 60.88; H, 5.07; N, 5.91%. M 946). λ_{max}/nm, dmso; (ε/dm^3 mol^{-1} cm^{-1}) 410 (36900), 303 (49100), 268 (80300). ^{1}H NMR (300 MHz; $CDCl_3$; $SiMe_4$, *J* Hz): δ 10.12 (s), 8.31 (s), 7.91 (d, 7.8 Hz), 7.72 (d, 8.7 Hz), 7.25 (m), 7.06 (d, 8.4 Hz), 6.63 (t, 7.35 Hz), 6.49 (t, 7.36 Hz), 5.20–5.12 (dd, 6.0 Hz), 2.58 (sep., 6.9 Hz), 1.80 (s), 1.12–0.99 (dd, 6.9 Hz). *m*/*z*; 475 (473) (M$^+$ − [(η^6-$C_{10}H_{14}$)Ru(bsh)]).

3.3.4. [{(η^6-C_6Me_6)Ru}$_2$(μ-bsh)$_2$] (**3**)

Yield: (822 mg, 82%). (Found: C, 62.14; H, 5.69; N, 5.19, M 1002 requires $C_{52}H_{56}N_4O_4Ru_2$: C, 62.27; H, 5.58; N, 5.58%. M 1002). λ_{max}/nm, dmso; (ε/dm^3 mol^{-1} cm^{-1}) 429 (37128), 304 (52130), 269 (81540). ^{1}H NMR (300 MHz; $CDCl_3$; $SiMe_4$, *J* Hz): δ 8.38 (s), 7.90 (d, 7.8 Hz), 7.72 (d, 8.7 Hz), 7.26 (m), 7.08 (d, 7.4 Hz), 6.59 (t, 7.2 Hz), 6.55 (t, 7.2 Hz), 2.29 (s). *m*/*z*; 503 (501) (M$^+$ − [(η^6-C_6Me_6)Ru(bsh)]).

3.3.5. [{(η^5-C_5Me_5)Rh}$_2$(μ-bsh)] (**4**)

Yield: (644 mg, 82%). (Found: C, 51.53; H, 5.25; N, 3.51. M 785 requires $C_{32}Cl_2H_{40}N_2O_2Rh_2$: C, 51.25; H, 5.43; N, 3.71%. M 785). ^{1}H NMR (300 MHz; $CDCl_3$;$SiMe_4$, *J* Hz): δ 8.39 (s), 8.01 (d, 7.8 Hz), 7.77 (d, 8.7 Hz), 7.31 (m), 7.11 (d, 7.4 Hz), 6.69 (t, 7.2 Hz), 6.46

(t, 7.2 Hz), 1.54 (s). m/z; 785 (785) (M^+); 749 (749) ($M^+ - Cl$); 712 (714) ($M^+ - 2Cl$).

3.4. Crystal structure determination

Cell dimensions and intensity data for [{(η^6-$C_{10}H_{14}$)Ru}$_2$(μ-bsh)$_2$] **2** was obtained on Enraf–Nonius CAD-4 four-Circle automatic diffractometer employing graphite monochromated Cu Kα radiation ($\lambda = 1.54180$ Å) at 293(2) K. Diffracted intensities were collected with $\omega/2\theta$ scanning technique (2θ range 3.87–75.14°). All the pertinent data for complex **2** are given in Table 1. The structure was solved by direct methods (SHELXS 97) and refined by full-matrix least squares calculations on F^2 (SHELX 97) [17]. In the final cycles of refinement all the non-H atoms were treated anisotropically. The H-atoms attached to carbon atoms were included as fixed contribution and were geometrically calculated and refined using the SHELX riding model. The function minimized was $\sum w(F_0 - F_e)^2$, where $w^{-1} = \sigma^{-2}(F) + 0.0012F^2$, resulting in $R = 0.0383$; $\omega R_2 = 0.1425$; GOF = 1.273. Complex **2** occupies some special position and therefore only half of it is labeled. The computer program PLATON was used for analyzing the interaction [17].

Crystal data for complex **2** has been deposited to CCDC and deposition code is CCDC 210341.

4. Conclusions

The results reported here are very promising with regard to the synthesis of complexes involving different coordination modes of the ligand H_2bsh. At this stage, it has not been possible for us to find a way to control, which way the ligand reacts with each metal complex, leading to the formation of entirely different products. Further, inter and intra molecular C–H$\cdots$O and C–H$\cdots\pi$ interactions leads to resting chair like motif of the complex [{(η^6-$C_{10}H_{14}$)Ru}$_2$(μ-bsh)$_2$]. It presents first example wherein, methyl and isopropyl groups from *p*-cymene are involved in the intermolecular hydrogen bonding. Follow up is in progress to synthesize new complexes, to optimize conditions and to look into the reactivity of the complexes resulting from interaction of *N*,*N*′-bis(salicylidine)-hydrazine and closely related ligands *N*,*N*′-bis(salicylidine)-*p*-phenylenediamine and *N*,*N*′-bis(salicylidine)-*p*-biphenylenediamine with metal complexes under varying conditions.

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