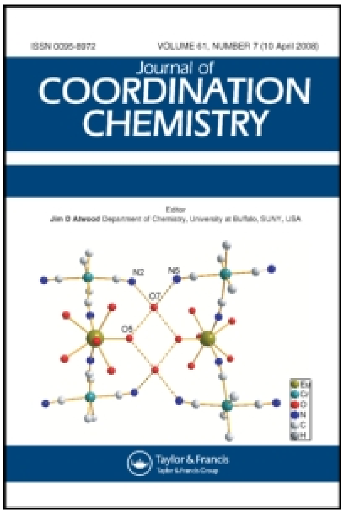

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Synthesis and spectral studies on heterobimetallic complexes of manganese and ruthenium derived from N-(2-hydroxynaphthalen-1-yl)methylenebenzoylhydrazide

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Synthesis and spectral studies on heterobimetallic complexes of manganese and ruthenium derived from N-(2-hydroxynaphthalen-1-yl)methylenebenzoylhydrazide

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The complex $[Mn^{IV}(napbh)_2]$ ($napbhH_2 =$ N-(2-hydroxynaphthalen-1-yl)methylenebenzoylhydrazide) reacts with activated ruthenium(III) chloride in methanol in 1 : 1.2 molar ratio under reflux, giving heterobimetallic complexes, $[Mn^{IV}(napbh)_2Ru^{III}Cl_3(H_2O)] \cdot [Ru^{III}(napbhH)Cl_2(H_2O)]$ reacts with $Mn(OAc)_2{\cdot}4H_2O$ in methanol in 1 : 1.2 molar ratio under reflux to give $[Ru^{III}(napbhH)Cl_2(H_2O)Mn^{II}(OAc)_2]$. Replacement of aquo in these heterobimetallic complexes has been observed when the reactions are carried out in the presence of pyridine (py), 3-picoline (3-pic), or 4-picoline (4-pic). The molar conductances for these complexes in DMF indicates 1 : 1 electrolytes. Magnetic moment values suggest that these heterobimetallic complexes contain Mn^{IV} and Ru^{III} or Ru^{III} and Mn^{II} in the same structural unit. Electronic spectral studies suggest six coordinate metal ions. IR spectra reveal that the $napbhH_2$ ligand coordinates in its enol form to Mn^{IV} and bridges to Ru^{III} and in the keto form to Ru^{III} and bridging to Mn^{II}.

Keywords: Heterobimetallic complexes; Manganese; Ruthenium; N-(2-hydroxynaphthalen-1-yl)methylenebenzoylhydrazide

1. Introduction

Metal complexes with Schiff bases [1–5] have applications in fields such as biological activity [6], oxidation catalysis [7], electrochemistry [8], and potential inhibitors for many enzymes [9]. A tetramanganese complex present in photosystem-II (PS-II) activates CO_2 and H_2O in such a way that light energy is transformed into fuel by reduction of CO_2 and simultaneously water is oxidized to molecular oxygen. Oxygen evolution continues even when some of the manganese atoms are replaced with other divalent metal ions that restore electron transport in PS-II [10]. A way to develop an efficient system for this conversion is to mimic natural photosynthesis in green plants.

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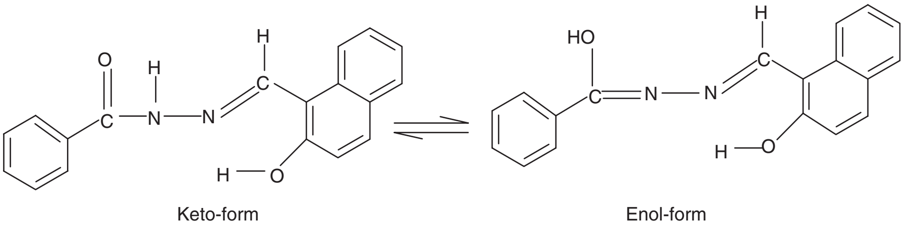

Figure 1. Keto- and enol-forms of N-(2-hydroxynaphthalen-1-yl)methylenebenzoylhydrazide.

Thus, the heterobimetallic complexes of manganese and ruthenium have potential to develop special characteristics by cooperative interaction, which may find applications in the conversion of solar energy to fuel and electricity. A bimetallic Ru(III) complex undergoes oxidation by either chemical or electrochemical means to produce O_2 from two coordinated water molecules [11].

Homobimetallic systems are more efficient in activation than corresponding monometallic analogues, so the heterobimetallic complexes derived from widely varying transition metal ions may have potential in this field [12]. Although monometallic and homobimetallic complexes of manganese and ruthenium have been investigated in some detail to mimic natural photosynthesis in green plants, studies using manganese and ruthenium in the same complexes are quite meager. The synthesis of bimetallic products is accessible by strategies developed by Lintvedt *et al.* [13] *via* monometallic complex intermediates with polydentate ligands or Davies *et al.* [14] *via* transmetalation beginning with a complex of discrete molecularity as target and another metal salt or complex as a transmetalator.

A polydentate ligand N-(2-hydroxynaphthalen-1-yl)methylenebenzoylhydrazide (napbhH_2) is a potential ligand for synthesizing heterobimetallic complexes. Monometallic complexes of N-(2-hydroxynaphthalen-1-yl)methylenebenzoylhydrazide with a variety of transition metals have been reported [15–21], but there is no report of heterobimetallic complexes of this ligand containing manganese and ruthenium. Thus, keeping in view the importance of manganese and ruthenium complexes, an attempt has been made to synthesize and characterize the heterobimetallic complexes of manganese and ruthenium derived from N-(2-hydroxynaphthalen-1-yl)methylenebenzoylhydrazide. The keto–enol forms of the ligand are shown in figure 1.

2. Experimental

2.1. *Materials*

The materials used are same as discussed in our earlier report [22].

2.2. *Analysis of the complexes*

Estimation of manganese, chlorine, and ruthenium was done by following standard procedures [23, 24]. C, H, and N were determined microanalytically.

2.3. *Physical measurements*

The methods and instruments used for physical measurements are discussed in our earlier report [25].

2.4. *Preparation of ligand and the precursor complexes*

The ligand N-(2-hydroxynaphthalen-1-yl)methylenebenzoylhydrazide (napbhH$_2$) and precursor complexes [Mn^{IV}(napbh)$_2$] and [Ru^{III}(napbhH)Cl$_2$(H$_2$O)] were prepared by our earlier reported method [22].

2.5. *Preparation of [Ru^{III}(napbhH)Cl$_2$(H$_2$O)Mn^{II}(OAc)$_2$] (1)*

To a methanolic (40 mL) suspension of [Ru^{III}(napbhH)Cl$_2$(H$_2$O)] (0.5 g, 1 mM), 20 mL of a methanol solution of Mn^{II}(OAc)$_2 \cdot 4H_2O$ (0.216 g, 1.25 mM) was added dropwise with constant stirring within 15 min. The reaction mixture thus obtained was stirred for another 30 min at 60–70°C followed by reflux for 2 h, which yielded a light green compound of composition [Ru^{III}(napbhH)Cl$_2$(H$_2$O)Mn^{II}(OAc)$_2$]. The compound was purified by repeated washing with methanol and ether and drying over anhydrous CaCl$_2$; yield: 64.8%.

2.6. *Preparation of [Ru^{III}(napbhH)Cl$_2$(A)Mn^{II}(OAc)$_2$] [A = py (2), 3-pic (3), or 4-pic (4)]*

Complexes **2**–**4** were isolated by the same method used for preparation of **1** by adding, for example, pyridine (5 mM) to the reaction mixture containing the precursor complex (1 mM) and Mn^{II}(OAc)$_2 \cdot 4H_2O$ (1.2 mM) and refluxing for another 2 h. Yields were 66.2, 68.3, and 68.5% for **2**, **3**, and **4**, respectively.

2.7. *Preparation of [Mn^{IV}(napbh)$_2$Ru^{III}Cl$_3$(H$_2$O)] (5)*

To a suspension of [Mn^{IV}(napbh)$_2$] (0.5 g, 0.8 mM) in 50 mL methanol, 30 mL of RuCl$_3 \cdot 3H_2O$ (0.248 g, 0.948 mM) in methanol was added dropwise with constant stirring within 10 min. The reaction mixture thus obtained was stirred for another 30 min at 60–70°C followed by reflux for 3 h, which yielded a reddish-brown compound [Mn^{IV}(napbh)$_2$Ru^{III}Cl$_3$(H$_2$O)], which was purified by repeated washing with methanol and ether and drying over anhydrous CaCl$_2$; yield: 67%.

2.8. *Preparation of [Mn^{IV}(napbh)$_2$Ru^{III}Cl$_3$(A)] [A = py (6), 3-pic (7) or 4-pic (8)]*

Complexes **6**–**8** were isolated by the method used for synthesis of **5** by adding pyridine, 3-picoline, or 4-picoline in molar ratio [Mn^{IV}(napbh)$_2$]: RuCl$_3 \cdot 3H_2O$: pyridine base: 1 : 1.2 : 5 and refluxing for about 3 h. Yields were 66.4, 65.0, and 65.8% for **6**, **7**, and **8**, respectively.

3. Results and discussion

The complexes isolated in the present study, together with their color, decomposition temperature, analytical data, magnetic moment, molar conductance, and electronic spectral data are presented in table 1. The analytical data and stoichiometries of the complexes reveal compositions $[Ru^{III}(napbhH)Cl_2(A)Mn^{II}(OAc)_2]$ [A = H_2O (**1**), py (**2**), 3-pic (**3**), or 4-pic (**4**)] and $[Mn^{IV}(napbh)_2Ru^{III}Cl_3(A)]$ [A = H_2O (**5**), py (**6**), 3-pic (**7**), or 4-pic (**8**)]. All are air stable, insoluble in water and common organic solvents except DMF and DMSO and do not decompose up to 300°C. The weight loss experiments for the complexes were carried out by heating a small amount of sample in glass tube for 4 h in an electric oven maintained at 110, 180, and 220–240°C. None of the complexes show weight loss at 110°C, ruling out the presence of lattice water in their structure; complexes **1** and **5** show weight loss corresponding to one water molecule at 180°C, suggesting the presence of coordinated water. The water molecules were identified by passing the issuing vapors through a trap containing anhydrous $CuSO_4$, which turned blue. Further, complexes **2**–**4** and **6**–**8** show weight loss in the temperature range 220–240°C corresponding to one molecule of pyridine, 3-picoline, or 4-picoline, respectively. The vapors evolved in this temperature range turned a solution of $CHCl_3$ containing a drop of 5 M NaOH solution red, confirming pyridine bases [26].

3.1. *Molar conductances*

The complexes have molar conductance values in the range of 52.70–62.10 $\Omega^{-1}\,cm^2\,mol^{-1}$ at 10^{-3} M in DMF, slightly lower than the reported values for 1 : 1 electrolytes [27], perhaps due to a large cation with low mobility.

3.2. *Magnetic moments*

Complexes **1**–**4** and **5**–**8** have μ_{eff} values in the ranges 6.30–6.50 and 4.40–4.60 B.M., respectively. Complexes **1**–**4** derived from reaction of $[Ru^{III}(napbhH)Cl_2(H_2O)]$ and $Mn(OAc)_2 \cdot 4H_2O$ are expected to possess six unpaired electrons but their magnetic moments are higher than the expected value for five unpaired electrons for Mn^{II} [$\mu_B = 5.9$ B.M. for $S = 5/2$] and Ru^{III} systems containing one unpaired electron [$\mu_B = 1.73$ B.M. for $S = 1/2$] [22, 28], but μ_B is slightly lower than expected for six unpaired electrons resulting from the presence of Mn^{II} and Ru^{III} in the same structural unit. The value of μ_B is slightly lower than the theoretical one for a system containing six unpaired electrons, which suggests that there may be a weak interaction between Mn^{II} and Ru^{III} centers in the complexes. Complexes **5**–**8** derived from the reaction of $[Mn^{IV}(napbh)_2]$ with $RuCl_3 \cdot 3H_2O$ are expected to possess four unpaired electrons in the heterobimetallic complexes. The μ_B values for these complexes are slightly lower than the theoretical value for a system containing four unpaired electrons [$\mu_B = 4.90$ B.M., $S = 2$] [29] but higher than the μ_B value for Mn^{III} complexes which usually occur in the range 3.80–4.20 B.M. The experimental μ_B values suggest that the heterobimetallic complexes contain Mn^{IV} and Ru^{III} ions in the same structural unit with superexchange among metal ions *via* the bridging oxygens.

Table 1. Analytical data, magnetic moment, molar conductance, and electronic spectral data for **1**–**8** complexes of manganese and ruthenium with N-(2-hydroxynaphthalen-1-yl)methylenebenzoylhydrazide (napbhH_2).

Complex (Color)	% Yield (Dec. Temp. °C)	Elemental analysis – found (Calcd) (%) Mn	Ru	C	H	N	Cl	μ_B^{a,b}(BM)	$\Lambda_M(\Omega^{-1}\,cm^2\,mol^{-1})$	Electronic spectral bands Λ_{max} (nm) (ε_{max} $dm^3\,mol^{-1}\,cm^{-1}$)
1	64.8	8.41	15.42	40.50	3.26	4.30	11.00	6.30	52.70	302(4590), 621(3830), 366(4630), 705(3700), 478(8450)
(Light green)	(>300)	(8.43)	(15.49)	(40.49)	(3.22)	(4.29)	(10.88)			
2	66.2	7.50	14.11	46.00	3.34	6.10	10.20	6.38	58.90	307(3760), 625(3980, 364(4800), 697(376), 483(8770)
(Dark green)	(>300)	(7.71)	(14.16)	(45.44)	(3.36)	(5.89)	(9.95)			
3	68.3	7.50	13.96	47.01	3.55	5.82	10.50	6.42	53.60	296(6470), 701(4410), 361(6470), 785(2640), 487(11710),
(Dark green)	(>300)	(7.56	(13.89)	(46.21)	(3.57)	(5.77)	(9.76)			
4	68.5	7.66	14.00	46.88	3.60	5.89	10.80	6.50	62.10	298(6420), 705(4490), 362(6420), 785(2620), 489(11580)
(Dark green)	(>300)	(7.56)	(13.89)	(46.21)	(3.57)	(5.77)	(9.76)			
5	67.0	6.40	11.88	52.22	3.01	6.61	12.46	4.40	60.00	298(6530), 458(9530), 366(8250), 645(1230)
(Reddish brown)	(>300)	(6.42)	(11.79)	(50.43)	(3.03)	(6.53)	(12.43)			
6	66.4	6.00	11.14	54.27	3.18	7.70	11.55	4.42	58.00	294(7155), 458(8880), 362(7195), 641(855)
(Dark brown)	(>300)	(5.99)	(11.08)	(53.62)	(3.16)	(7.62)	(11.60)			
7	65.0	5.88	10.80	55.53	3.33	7.56	11.96	4.51	55.00	302(7265), 485(9780), 362(7155), 661(1195)
(Dark brown)	(>300)	(5.90)	(10.84)	(54.10)	(3.32)	(7.51)	(11.43)			
8	65.8	5.85	10.82	55.44	3.30	7.48	11.66	4.60	57.00	298(5700), 458(5790), 505(11110), 645(6750)
(Dark brown)	(>300)	(5.90)	(10.84)	(54.10)	(3.32)	(7.51)	(11.43)			

[a] μ_B for $[Ru^{III}(napbhH)Cl_2(H_2O)]$ is 1.65; [b] μ_B for $[Mn^{IV}(napbh)_2]$ is 4.05.

3.3. *Electronic spectra*

Electronic spectra of heterobimetallic complexes were compared with those of their precursor complexes. Ligand bands observed for heterobimetallic complexes in the region 200–400 nm are more or less the same as found in precursor complexes with wavelength differences of ± 10 nm.

Heterobimetallic complexes **1–4** also show two bands in the regions 478–489 and 621–785 nm while the precursor Ru(III) complex shows bands at 451 and 652 nm [22]. The band at 451 nm for the Ru(III) precursor red shifts in the heterobimetallic complexes. This band cannot be assigned to d–d transitions as intensities in the range 8450–11,580 $dm^3 mol^{-1} cm^{-1}$ suggest a charge transfer band. The band in the region 621–785 nm is split probably due to d–d transition in either Mn(II) or Ru(III) or both, with low symmetry around the metal ions. Probably, the d–d bands arising from $^2T_{2g} \rightarrow {}^4T_{1g}$, $^2T_{2g} \rightarrow {}^4T_{2g}$ and $^2T_{2g} \rightarrow {}^2T_{1g}$ in Ru(III) are masked by strong LMCT bands [30, 31].

Heterobimetallic complexes **5–8** show two bands in addition to ligand bands in the regions 458–505 and 641–661 nm. The first is blue shifted in comparison to the Mn(IV) precursor complex and could be assigned to d–d transition corresponding to Mn(IV), but its high intensity suggests charge transfer probably arising from charge transfer from the naphtholate oxygen to the Mn(IV) overshadowing the d–d transition [30,32–35]. The band in the range 641–661 nm appears to arise from d–d transitions due to Ru(III) center with intensity borrowed from an adjacent charge transfer band.

3.4. *Infrared spectra*

Characteristic IR bands [15–18] of $napbhH_2$, $[Mn^{IV}(napbh)_2]$, and $[Ru^{III}(napbhH)Cl_2(H_2O)]$ are included in table 2. IR spectra of **1–4** show spectral features similar to $[Ru^{III}(napbhH)Cl_2(H_2O)]$, suggesting a similar mode of bonding of the $napbhH_2$ to Ru(III) ion in its heterobimetallic complexes. The positions of bands due to ν(C–O)(naphtholic) and β(C–O) in these complexes suggest that naphtholate oxygen bridges two metal centers. The precursor complex $[Mn^{IV}(napbh)_2]$ shows a broad band in the region 3200–3550 cm^{-1} due to either ν(O–H) from water or ν(N–H) from the secondary amine. The amide-I bands mainly due to ν(C=O) appearing in $napbhH_2$ at 1654 and 1642 cm^{-1} are absent in the Mn(IV) complex, suggesting collapse of the amide structure and coordination of hydrazone through carbonyl oxygen in the enol form. The ν(C–O)(naphtholic) band at 1547 cm^{-1} in $napbhH_2$ suffers a negative shift of 10 cm^{-1} in the Mn(IV) precursor complex, indicating bonding of naphtholate through the oxygen [36]. The ν(C=N) band occurs in the range 1630–1610 cm^{-1} for Schiff bases derived from hydrazine and aromatic aldehydes or ketones [37]. The hydrazone ligand $napbhH_2$ shows two bands at 1625 and 1604 cm^{-1}, assigned to stretching vibration of the >C=N– group; corresponding bands in the Mn(IV) precursor complex appear at 1616 and 1599 cm^{-1}, suggesting coordination of the azomethine nitrogen. From IR spectra the ligand $napbhH_2$ is a dianionic tridentate ligand towards Mn(IV).

IR spectra of **5–8** show IR features similar to those of $[Mn^{IV}(napbh)_2]$, suggesting a similar mode of bonding of $napbhH_2$ to Mn(IV). The positions of ν(C–O) (naphtholic + enolic) and β(C–O) bands in these heterobimetallic complexes suggest metal centers are bridged through the naphtholate oxygen and the enolate oxygen [37],

Table 2. Characteristic IR bands (cm^{-1}) for complexes **1**–**8**.

Ligand/Complex	ν(OH) + ν(NH)	ν(C = O)	ν(C = N)	Amide II + ν(C–O) (naphtholic)	Acetato vibration	β(C–O)	ν(N–N)	ν(M–O) (phenolate)	ν(M–O) (carbonyl)	ν(Ru–Cl)
napbhH_2	3550–3300sbr 3448s 3185sbr	1654s 1642s	1625m 1604m	1561m 1547m	–	1291s 1284s	911w	–	–	–
$[Ru^{III}(napbhH)Cl_2(H_2O)]$	3500–3200sbr 3436s	1641s	1620s 1599s	1562s 1527s	–	1285m	930w	546w	470w	344s 334s
$[Mn^{IV}(napbh)_2]$	3550–3200sbr 3435s	–	1616s 1597s	1537s	–	1296s	920w 912w	586w	465w	–
1	3600–3250sbr 3400s	1635s	1616s 1599s	1560s 1537s	1545s 1407w	1284m	913w	577m	463w	310m 235w
2	3600–3250sbr 3436s	1641s	1620s 1599s	1560s 1527s	1510s 1393s	1283s	913w	581s	471s	302m 228w
3	3600–3250sbr 3430s	1635s	1615s 1605s	1560s 1530s	1520s 1405s	1282s	912w	575s	465m	305m 230w
4	3600–3250sbr 3440s	1640s	1618s 1602s	1562s 1525s	1535s 1390s	1284s	914w	580m	470m	308m 235w
5	3600–3250sbr	–	1620s 1600s	1560s 1540s	–	1310s	911w	575m	475m	310m 290m
6	3600–3250sbr	–	1600s	1559s 1535s	–	1313m	912w	587m	461s	315m 295m
7	3600–3250sbr 3426s	–	1620s 1600s	1562m 1532m	–	1312m	911w	583m	475m	315m 290m
8	3600–3250sbr 3400s	–	1620s 1598s	1560s 1535s	–	1315m	913w	580s	470m	320m 295m

Note: s = strong, m = medium, w = weak, br = broad.

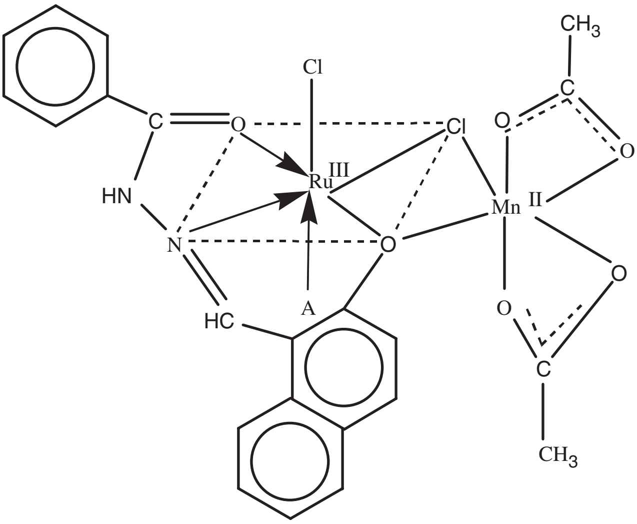

Figure 2. Suggested structure of $[Ru^{III}(napbhH)Cl_2(A)Mn^{II}(OAc)_2]$ [$A = H_2O$ (**1**), py (**2**), 3-picoline (**3**), or 4-picoline (**4**)].

further supported by appearance of a new weak band (existing neither in the ligand nor in the precursor complexes) in these complexes at $\sim 860\,\text{cm}^{-1}$ which is a characteristic of oxo-bridged Ru–O–Mn [18, 37, 38].

The ν(N–N) appears as a weak band in the IR spectra of the complexes almost at the same position as in free ligand, indicating bonding of only one hydrazinic nitrogen to the metal.

The heterobimetallic complexes containing pyridine or substituted pyridine ligands show a new weak-to-medium intensity band in the region $1064–1087\,\text{cm}^{-1}$ due to ring breathing, indicating the presence of coordinated py/3-pic/4-pic [39].

IR spectra of **1**–**4** show new bands in the regions 1510–1545 and $1390–1405\,\text{cm}^{-1}$, present in neither the free ligand nor in the precursor complexes, identified as ν_{as}(OCO) and ν_s(OCO), respectively, due to coordinated acetate. The positions of ν_{as}(OCO) and ν_s(OCO) are consistent with chelating bidentate acetate [40, 41].

In addition to the complicated ligand bands in the low frequency region, the complexes also show new bands which may be assigned to metal–ligand vibrations. New medium to strong bands in the regions 577–587 and $463–475\,\text{cm}^{-1}$ are tentatively assigned to ν(M–O)(naphtholate) [42] and ν(M–O)(carbonyl oxygen) [43, 44], respectively, indicating hydrazone bonded to the metal center through the naphtholate oxygen and carbonyl oxygen.

All of the complexes show two weak to medium intensity non-ligand bands in the region $225–320\,\text{cm}^{-1}$ (strong bands at 344 and $334\,\text{cm}^{-1}$ in $[Ru(napbhH)Cl_2(H_2O)]$) corresponding to ν(Ru–Cl), showing the existence of *cis*-$RuCl_2$ [45]. The bands at 225–235 and $290–295\,\text{cm}^{-1}$ in the heterobimetallic complexes **1**–**4** and **5**–**8**, respectively, with the shift for **1**–**4** consistent with the bridging chloro is very similar to chloro-bridged complexes [40]. The slightly higher value of bridging ν(Ru–Cl) bands in **1**–**4** might be attributed to $+3$ oxidation state of ruthenium in the heterobimetallic complexes.

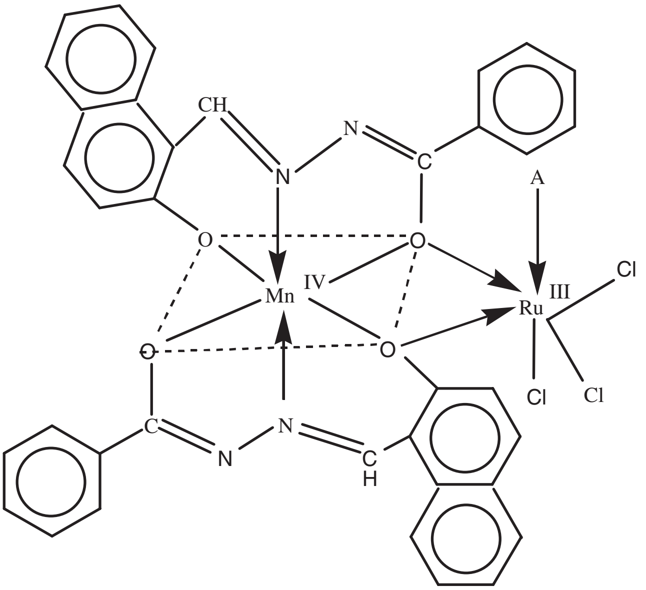

Figure 3. Suggested structure of [$Mn^{IV}(napbh)_2Ru^{III}Cl_3(A)$] [$A = H_2O$ (**5**), py (**6**), 3-picoline (**7**), or 4-picoline (**8**)].

4. Conclusions

Stoichiometries and physico-chemical studies reveal the formation of heterobimetallic complexes comprising (Ru^{III}, Mn^{II}) and (Mn^{IV}, Ru^{III}). The ligand behaves in keto- and enol-forms in complexes derived from (Ru^{III}, Mn^{II}) and (Mn^{IV}, Ru^{III}), respectively. Octahedral stereochemistry around the metal ions is proposed. The proposed tentative structures of the complexes are shown in figures 2 and 3.

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