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ORIGINAL ARTICLE

Synthesis and spectral studies on heterobimetallic complexes of manganese and ruthenium derived from *bis[N-(2-hydroxynaphthalen-1-yl)methylene]oxaloyldihydrazide*

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Abstract The complex $[Mn(L)(H_2O)_2]$ [H_4L = *bis[N-(2-hydroxynaphthalen-1-yl)methylene]-oxaloyldihydrazide]* reacts with activated ruthenium(III) chloride in methanol in 1:1.2 M ratio under reflux resulting in heterobimetallic complex of the composition $[Mn(L)(H_2O)_4RuCl_2]Cl$. The complexes of the composition $[Mn(L)(A)_4RuCl_2]Cl$ were obtained when the above reaction was carried out in presence of heterocyclic nitrogen bases(A) such as pyridine(py), 3-picoline(3-pic) and 4-picoline(4-pic). The molar conductance values for these complexes in DMF(*N*,*N*-dimethyl formamide) solution indicate their 1:1 electrolytic nature. Magnetic moment values suggest that these heterobimetallic complexes contain Mn(IV) and Ru(III) in the same structural unit. Electronic spectral studies suggest six coordinated metal ions in these complexes. IR spectra reveal that the H_4L ligand coordinates in its keto-form to Mn(IV) and Ru(III).

1. Introduction

Metal complexes of Schiff bases containing nitrogen and other donor sites are well documented (Lal et al., 2008; Maxim et al., 2008; Singh et al., 2008; Singh et al., 2009; Abdallah et al., 2010; Xishi et al., 2003) by virtue of their stability, biological activity (Khalil et al., 2005) and potential applications in many fields such as oxidation catalysis (Djebbar-Sid et al., 1997) and electrochemistry (Hamada, 1997). H_4L is also an important Schiff base derived from the condensation of oxaloyldihydrazide and 2-hydroxy-1-naphthaldehyde (Singh et al., 2008). The high affinity for the complexation of the Schiff bases towards the transition metal ions is utilized in preparing their solid complexes. Monometallic complexes of H_4L with a variety of transition metals have been reported (Bhattacharyya et al.,

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1998; Singh et al., 2008; Lal et al., 1998) but there is no report on heterobimetallic complexes of Mn and Ru metal ions. The main target of the present article is to study the coordination behaviour of H_4L Schiff base that incorporates several binding sites towards Mn(IV) and Ru(III) ions. The choice for Mn(IV) and Ru(III) metal ions for heterobimetallic complex synthesis has been received from the applications of manganese complexes in converting light energy into fuel in PS-II (Mukhopadhyay et al., 2004) and ruthenium complexes to produce O_2 from its coordinated water molecules (Kaizer et al., 2007), respectively. The results of our investigations are presented in this communication.

2. Experimental

2.1. Materials and reagents

Manganese(II) acetate tetrahydrate, ruthenium(III) chloride trihydrate, potassium hydroxide, diethyloxalate, hydrazine hydrate and 2-hydroxy-1-naphthaldehyde were GR (E-Merck) or equivalent grade reagents. Commercial grade ruthenium trichloride was activated by dissolving in concentrated hydrochloric acid and then evaporating to dryness over steam bath before using it for synthesis of complexes. Organic solvents used included absolute ethylalcohol, diethylether, methanol, dimethylsulphoxide (DMSO) and dimethylformamide (DMF). Reagent grade organic solvents were purified and dried by recommended procedures (Chan et al., 1995). Hydrochloric and nitric acids (E-Merck) were used. De-ionized water collected from all glass equipments was usually used in all preparations.

2.2. Instruments

The molar conductance values of the complexes at 10^{-3} M in DMF solution were measured on a Systronics Direct Reading Conductivity meter-303 with a dip type conductivity cell at room temperature. Magnetic susceptibility measurements were carried out on a Vibrating Sample Magnetometer. UV–Vis Spectra of the complexes were recorded in DMF solution (10^{-3} M) on a Perkin–Elmer Lambda 25 UV–Vis spectrophotometer. Infrared spectra were recorded on a Perkin–Elmer Model spectrum BX-II IR spectrophotometer in the range 4000–450 cm^{-1} in KBr discs and in the range 600–50 cm^{-1} in CsI discs. The ESR spectra of the complexes were recorded at X-band frequency on a Varian E-112E-line century series ESR spectrometer using TCNE ($g = 2.00277$) as an internal field marker. Microanalytical (C, H and N) data were obtained with an Elementar Vario EL 1108 at SAIF, Central Drug Research Institute, Lucknow, India. For determining Mn and Ru, the complexes were decomposed with aqua regia till all the organic moieties were oxidized. The solution was evaporated to dryness and treated with concentrated HCl. The concentrated HCl solution was also evaporated to dryness and finally the solution was made in distilled water. After adjusting the concentration of H^+ (0.2–0.5 M) H_2S was passed which gave the precipitation of Ru, leaving Mn metal in solution (Busev et al., 1981) which was filtered and washed. The precipitate was dissolved in concentrated HCl and the solution was used for the estimation of Ru by spectrophotometric method (Snell and Snell, 1959). After the separation of Ru, filtrate containing Mn was used for the estimation of manganese gravimetrically following the standard literature procedure (Vogel, 1961).

2.3. Synthesis of the ligand (H_4L)

The ligand (H_4L) was prepared in two steps. In the first step oxaloyldihydrazide was prepared by refluxing for 45 min the reaction mixture of diethyloxalate (5 mL) and hydrazine hydrate (4.1 mL) in 1:2 M ratio. The product thus isolated was recrystallized from dilute ethanol. In the second step, oxaloyldihydrazide (1.0 g, 8.47 mmol) in ethanol (150 mL) solution was allowed to react with 2-hydroxy-1-naphthaldehyde (3.205 g, 18.63 mmol) in ethanol (250 mL) over a hot plate at 70 °C with constant gentle stirring for about 30 min and the reaction mixture was refluxed for 2 h. The yellow precipitate so obtained was purified by repeated washing with hot ethanol and finally with ether and dried over anhydrous $CaCl_2$. [Yield: 72%] (m.p. > 300 °C). Anal. Calcd for $C_{24}H_{18}N_4O_4$ (%): C, 67.60; H, 4.22; N, 13.14. Found: C, 68.00; H, 4.30; N, 13.20. The electronic spectral data of the ligand are presented in Table 2 while the IR spectral data in Table 3.

2.4. Synthesis of the precursor complex, $[Mn(L)(H_2O)_2]$

To a suspension of *bis[N-(2-hydroxynaphthalen-1-yl)methylene]oxaloyldihydrazide* (1.0 g, 2.347 mmol in 30 mL methanol) a 30 mL methanolic solution containing $Mn(OAc)_2 \cdot 4H_2O$ (0.556 g, 2.269 mmol) was added with vigorous stirring for 45 min which resulted in a dark yellow mixture. To this,

Table 1 Analytical data and physical properties of the complexes.

Complex (Colour)	% Yield (melting temp. °C)	Elemental analysis found calcd%						μ_B (B.M.)	Λ_M (Ω^{-1} cm^2 mol^{-1}) (25 °C)
		Mn	Ru	C	H	N	Cl		
$[Mn(L)(H_2O)_4RuCl_2]Cl$ (1)	70.20	7.30	13.30	38.25	2.91	7.38	14.38	4.88	69.00
(Black)	(> 300 °C)	(7.27)	(13.35)	(38.07)	(2.90)	(7.40)	(14.07)		
$[Mn(L)(py)_4RuCl_2]Cl$ (2)	68.00	5.77	10.22	52.35	3.40	10.99	11.12	4.90	70.00
(Black)	(> 300 °C)	(5.49)	(10.09)	(52.77)	(3.39)	(11.19)	(10.64)		
$[Mn(L)(3\text{-pic})_4RuCl_2]Cl$ (3)	68.10	5.00	9.58	53.90	3.87	10.56	9.92	4.90	62.00
(Black)	(> 300 °C)	(5.20)	(9.55)	(54.51)	(3.97)	(10.60)	(10.08)		
$[Mn(L)(4\text{-pic})_4RuCl_2]Cl$ (4)	71.00	5.10	9.50	54.46	3.97	10.70	10.00	4.92	65.00
(Black)	(> 300 °C)	(5.20)	(9.55)	(54.51)	(3.97)	(10.60)	(10.08)		

Table 2 UV–Visible spectral data of the complexes.

Ligand/complex	Wave length ($\lambda_{max,nm}$) (ε_{max} L mol^{-1} cm^{-1})
$H_4L(C_{24}H_{18}N_4O_2)$	259(14,586), 327(10,216), 382(8462), 435(1200)
$[Mn(L)(H_2O)_2]$ (precursor)	298(1429), 366(1402), 501(2005)
$[Mn(L)(H_2O)_4RuCl_2]Cl$ (1)	260(14,272), 323(5000), 398(9244), 472(2600), 658(1600)
$[Mn(L)(py)_4RuCl_2]Cl$ (2)	244(11,131), 328(9920), 382(14,716), 456(5300), 660(1300)
$[Mn(L)(3\text{-pic})_4RuCl_2]Cl$ (3)	263(16,625), 315(10,600), 364(9700), 440(4375), 693(5100)
$[Mn(L)(4\text{-pic})_4RuCl_2]Cl$ (4)	261(1380), 326(1600), 364(8600), 444(3920), 696(4600)

Table 3 FT-IR spectral data of the ligand and the complexes.

Ligand/complex	ν(OH) + ν(NH)	ν(C=O)	ν(C=N)	AmideII + ν (C–O) (naphtholic)	β(C–O)	ν(M–O)	ν(N–N)	ν(M–O) carbonyl	ν(M–Cl)
$H_4L(C_{24}H_{18}N_4O_2)$	3530–3300 (sbr), 3251(s), 3442(s), 3171(s)	1699(s) 1690(s)	1629(s) 1607(s)	1534(s)	1272(m)	–	1031(w)	–	–
$[Mn(L)(H_2O)_2]$ (precursor)	3600–3000 (vsbr), 3400(s)	–	1617(s) 1598(s)	1534(vs)	1298(m)	558 msh	1033(w)	–	–
$[Mn(L)(H_2O)_4RuCl_2]Cl$ (1)	3552–3000 (sbr)	1670(s)	1620(s) 1600(s)	1537(s)	1295(m)	562 msh	1035(w)	455(s)	335(s) 320(s)
$[Mn(L)(py)_4RuCl_2]Cl$ (2)	3552–3000 (sbr)	1659(m) 1641(s)	1626(s) 1605(s)	1530(m)	1276(w)	526(w)	1043(m)	470(s)	340(s) 318(m)
$[Mn(L)(3\text{-pic})_4RuCl_2]Cl$ (3)	3550–3000 (sbr)	1649(m) 1643(m)	1620(s) 1600(s)	1532(m)	1287(w)	542(w)	1035(w)	429(s)	330(s) 319(s)
$[Mn(L)(4\text{-pic})_4RuCl_2]Cl$ (4)	3600–3200 (sbr)	1658(s)	1620(s)	1530(m)	1287(m)	542(m)	1034(m)	480(m)	334(m) 323(m)

KOH (1.018 g, dissolved in 20 mL methanol) was added accompanied by gentle stirring which gave a clear brown solution and any undissolved material was removed by filtration. The solution was stirred for another half an hour which yielded a brown amorphous compound which was filtered, washed with methanol and dried over anhydrous $CaCl_2$. [Yield: 56.3%] (m.p. > 300 °C). Anal. Calcd for $[Mn(L)(H_2O)_2]$(%): Mn, 10.72, C, 56.14; H, 3.50; N, 10.91. Found: Mn, 10.66, C, 55.22; H, 3.41; N, 10.86. μ_B (BM), 4.12; Λ_M (Ω^{-1} cm^{-1} mol^{-1}), 10.60. The electronic spectral data of the precursor complex are presented in Table 2 while the IR spectral data in Table 3.

2.5. Synthesis of heterobimetallic complexes

$[Mn(L)(H_2O)_4RuCl_2]Cl$(1): To a 50 mL methanolic suspension of the precursor complex, $[Mn(L)(H_2O)_2]$ (0.5 g, 0.975 mmol), 30 mL methanolic solution of $RuCl_3{\cdot}3H_2O$ (0.305 g, 1.166 mmol) was added drop by drop with constant stirring within a duration of 10 min. The reaction mixture thus obtained was stirred for another 30 min at 60–70 °C and the mixture was refluxed for 3 h which yielded a black micro-crystalline compound of the composition $[Mn(L)(H_2O)_4RuCl_2]Cl$. The compound was suction filtered and washed with methanol and ether and dried over anhydrous $CaCl_2$.

$[Mn(L)(A)_4RuCl_2]Cl$ [where A = py(2), 3-pic(3) or 4-pic(4)]: The complexes 2–4 were isolated by essentially following the same procedure used for the preparation of complex 1 by adding pyridine bases to the reaction mixture containing precursor complex, $RuCl_3{\cdot}3H_2O$ and pyridine base maintaining the molar ratio at 1:1.2:5 and refluxing for 3 h.

3. Results and discussion

3.1. Schiff base characterization

The Schiff base H_4L is subjected to elemental analyses. The result of elemental analyses(C, H and N) with molecular formula and the melting points are presented in the preparation section of the ligand. The results obtained are in good agreement with

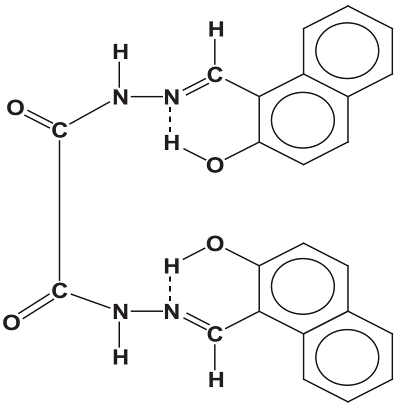
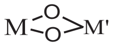


Figure 1 Structure of ligand, H_4L = *bis[N-(2-hydroxynaphthalen-1-yl)methylene]oxaloyldihydrazide*.

those calculated for the suggested formula. The structure of this Schiff base is also confirmed by IR. It takes the following structural formula (Fig. 1) and IUPAC name.



3.2. Composition and structures of heterobimetallic complexes

All the complexes are insoluble in common organic solvents but soluble in DMF and DMSO and do not melt or decompose up to 300 °C. The complex 1 shows weight loss corresponding to four water molecules at 180 °C suggesting the presence of coordinated water molecule to the metal centres. The complexes 2–4 show weight loss in the temperature range 220–240 °C corresponding to four molecules of pyridine, 3-picoline or 4-picoline, respectively. The vapours evolved in this temperature range turned a solution of $CHCl_3$ containing a drop of 5 M NaOH solution red confirming the presence of pyridine bases in the coordination sphere of metal ions (Feizel et al., 1975).

The isolated complexes comprising Mn(IV) and Ru(III) which were obtained from $[Mn(L)(H_2O)_2]$ and Ru(III) ions were subjected to elemental analyses (C, H, N and metal content), molar conductance, magnetic studies, IR, electronic and ESR to identify their tentative formulae in a trial to elucidate their molecular structures. The results of elemental analyses listed in Table 1 suggest the formulae $[M_1(L)(A)_4M_2Cl_2]Cl$ (where M_1 = Mn(IV) and M_2 = Ru(III), A = H_2O(1), pyridine(py)(2), 3-picoline (3-pic)(3) or 4-picoline(4-pic)(4)). The analytical data and stoichiometries of the heterobimetallic complexes are summarized in Table 1.

3.3. Molar conductivity measurements

The complexes were dissolved in DMF and the molar conductivities of 10^{-3} M of their solutions at 25 °C were measured. Table 1 shows the molar conductance values of the complexes. The molar conductivity values of the complexes fall in the range 62.0–70.0 Ω^{-1} cm^2 mol^{-1} indicating that these complexes are 1:1 electrolytes (Singh et al., 2009).

3.4. Magnetic susceptibility measurements

The μ_{eff} values for the Mn(IV) complexes are reported to lie in the range 3.83–4.12 B.M. with d^3 configuration (S = 3/2) (Chandra et al., 1990; Singh et al., 2008) while Ru(III), being a metal of second transition series, will always give a low-spin complex with μ_{eff} around 1.80 BM (Das et al., 2000). However, a combination of Mn(IV) [d^3, S = 3/2] and low-spin Ru(III) [d^5, S = ½] [Mn(IV)–Ru(III) system] in a complex will always be a four-electron system and its μ_{eff} values will be around 4.90 B.M. The μ_{eff} values for the synthesized complexes lie in the range 4.88–4.92 B.M. which suggest that the heterobimetallic complexes contain Mn(IV) and Ru(III) ions in the same structural unit.

3.5. Electronic spectral measurements

UV–Vis spectra of the ligand, precursor complex and the heterobimetallic complexes were recorded in DMF solution (10^{-3} M) and the relevant data are given in Table 2. The electronic spectra of heterobimetallic complexes were compared with those of the precursor complex and the ligand. The ligand bands observed for heterobimetallic complexes in the region 200–400 nm are more or less the same as found in the ligand (Singh et al., 2008). Heterobimetallic complexes 1–4 show two bands in the regions 440–472 and 658–696 nm in addition to ligand bands. The electronic spectra of (1–4) show the intra ligand and d–d transition bands. For octahedral manganese(IV) complexes three spin-allowed d–d transitions $^4A_{2g} \rightarrow {}^4T_{2g}$, $^4A_{2g} \rightarrow {}^4T_{1g}(F)$ and $^4A_{2g} \rightarrow {}^4T_{1g}(p)$ are expected. The manganese(IV) complex, $[MnF6]^{2-}$, shows two absorption bands at 360 and 450 nm assignable to $^4A_{2g} \rightarrow {}^4T_{1g}(F)$ and $^4A_{2g} \rightarrow {}^4T_{2g}$, respectively (Pei et al., 1988; Balch et al., 1989), while the third band arising due to $^4A_{2g} \rightarrow {}^4T_{1g}(p)$ is obscured by either charge transfer or ligand bands. The d–d absorption bands in the heterobimetallic complexes 1–4 cannot be identified with certainty as they are obscured by charge transfer or ligand bands. The bands observed for heterobimetallic complexes 1–4 in the region 440–472 nm cannot be assigned to a spin-allowed d–d transition because their absorption co-efficient lies in the range of charge transfer bands. So, these bands are assigned to charge transfer bands, probably arising from the naphtholate (oxygen) to the d-orbital of the Mn(IV). Ru(III) octahedral coordination cannot be distinguished due to masking by strong LMCT bands (Lever, 1984) except the band in the region 658–696 nm. This band has been assigned to the spin-allowed $^1A_{1g} \rightarrow {}^1T_{1g}$ transition (Dharamraj and Natarajan, 1994) with intensity borrowed from an adjacent charge transfer bands.

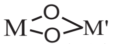
3.6. IR spectral studies

FT-IR spectral data of the ligand, precursor complex and the heterobimetallic complexes are given in Table 3. The most crucial feature of the IR spectra for the complexes is the development of a couple of strong bands in the region 1641–1670 cm^{-1} which are absent in the IR spectrum of the precursor complex, $[Mn(L)(H_2O)_2]$, but are similar in nature to those of the ligand at 1699 and 1690 cm^{-1}. The presence of these bands indicates the development of >C=O groups in the heterobimetallic complexes in the coordinated form which originated probably from the conversion of –N=C–O$^-$ group present in the precursor complex(Singh et al., 2008) into the –NH–C = O in the heterobimetallic complexes. This dismisses the possibility of existence of the ligand in the enol form in these complexes. However strong absorption bands due to ν(N–H) in the region 3000–3500 cm^{-1} could not be identified due to strong broad band in this region in the IR spectra of heterobimetallic complexes. The negative shift by 20–49 cm^{-1} in the ν(C=O) band with respect to free ligand in these complexes suggests the coordination of >C=O group to the metal centre.

These complexes show a medium to strong intensity band in the region 1532–1537 cm^{-1} which arises due to amide-II + ν(C–O) (naphtholate). The ν(N–N) band in the heterobimetallic complexes appears in the region 1034–1043 cm^{-1} as a weak to medium band which appeared at 1031 and 1033 cm^{-1} for free ligand and precursor complex, respectively. This indicates coordination of only one hydrazine nitrogen atom to the metal centre similar to that in the precursor complex. The present complexes do not show any new bands in the region 750–850 cm^{-1} which appears due to tetra-atomic (Hendawy et al.,

Table 4 ESR parameters of heterobimetallic complexes.

Complex	For Mn(IV) fragment *g* values		For Ru(III) fragment *g* values	
	RT (powder)	LNT (powder)	RT (powder)	LNT (powder)
$[Mn(L)(H_2O)_4RuCl_2]Cl$ (1)	2.019, 4.332	2.019, 4.332	2.306	2.306
$[Mn(L)(py)_4RuCl_2]Cl$ (2)	2.019, 4.335	2.019, 4.335	2.665	2.665
$[Mn(L)(3\text{-pic})_4RuCl_2]Cl$ (3)	2.017, 4.321	2.017, 4.321	2.532	2.532
$[Mn(L)(4\text{-pic})_4RuCl_2]Cl$ (4)	2.032, 4.331	2.032, 4.331	2.643	2.643

1988) species,  $M\overset{O}{\underset{O}{<>}}M'$ dismissing the possibility of naphtholate oxygen atom in bridging. The complexes (2–4) show a new medium intensity band at 631, 649 and 667 cm^{-1} assigned to in-plane deformation mode of pyridine, 3-picoline and 4-picoline respectively, and suggest their coordination to the metal centre as co-ligand. The ν(C=N) band shows positive shifts in heterobimetallic complexes as compared to that in the precursor one which signifies an increase in $>$C=N bond order suggesting the flow of electron density to a decreased extent from azomethine nitrogen-to-metal centre giving weaker azomethine nitrogen-to-metal bond than that in the precursor monometallic complex. The nature of the ν(C=N) bands in these complexes suggests an inequivalency in $>$C=N groups which indicates the coordination of dihydrazone to the metal centre in *anti-cis*-configuration in such a manner that half hydrazone part is out-of-plane of the molecule while the other half remains in the plane (Rudolf et al., 1988). The β(C–O) band appearing in the range 1287–1295 cm^{-1} in heterobimetallic complexes suggests the bonding of naphtholate oxygen atom to metal centre. All of the complexes show non-ligand weak intensity bands in the regions 526–562 and 455–480 cm^{-1} assigned to ν(M–O) (naphtholate) (Singh et al., 2008) and ν(M–O) ($>$C=O) to the metal centre, respectively. The complexes also show a couple of medium to strong bands in the region 319–340 cm^{-1} which is assigned to Ru–Cl stretching vibrations (Singh et al., 2009).

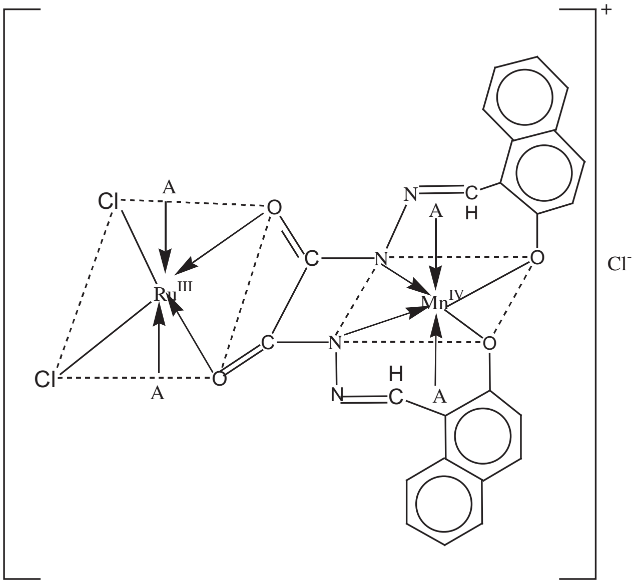


Figure 2 Suggested structure of the complex $[Mn^{IV}(L)(A)_4Ru^{III}Cl_2]Cl$ [where, A = H_2O(1); py(2); 3-pic(3) and 4-pic(4)].

3.7. Electron spin resonance spectra

The complexes show essentially similar ESR spectral features in the solid state at RT as well as at LNT in polycrystalline form. This shows that the structures of the complexes do not undergo change on lowering the temperature. ESR data of the complexes are presented in Table 4. The complexes show twinlar features. Two resonances are observed: a strong signal in the region g = 2.017–2.032 and weak one in the region g = 4.321–4.335 which are characteristic of small axial distortion in octahedral symmetry around Mn(IV) (Pal et al., 1985). Similar behaviour has been observed in monometallic Mn(IV) complexes of the ligand under study (Singh et al., 2008). All the complexes show an additional signal in the region 2.306–2.665 which is attributed to arise due to Ru(III) in octahedral symmetry (Singh et al., 2008).

4. Conclusion

The stoichiometries and physico-chemical studies reveal the formation of heterobimetallic complexes comprising Mn(IV) and Ru(III) metal ions. The complexes confirm 1:1 electrolytic nature on the molar conductance values. The ligand coordinates to the metal centres in keto-form. Octahedral stereochemistry around the metal ions has also been proposed on the basis of above-mentioned studies as shown in Fig. 2.

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