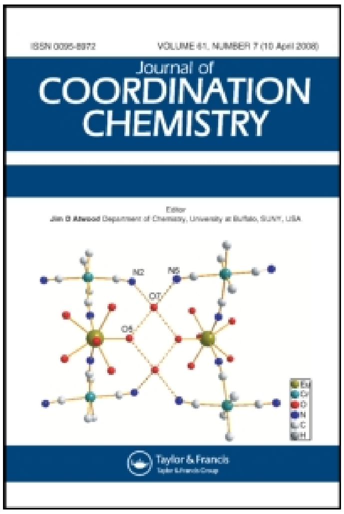

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# Synthesis and structural characterization of manganese(III, IV) and ruthenium(III) complexes derived from 2-hydroxy-1-naphthaldehydebenzoylhydrazone

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Reaction of 2-hydroxy-1-naphthaldehydebenzoylhydrazone(napbh$H_2$) with manganese(II) acetate tetrahydrate and manganese(III) acetate dihydrate in methanol followed by addition of methanolic KOH in molar ratio (2 : 1 : 10) results in [Mn(IV)(napbh)$_2$] and [Mn(III)(napbh)(OH)($H_2O$)], respectively. Activated ruthenium(III) chloride reacts with napbh$H_2$ in methanolic medium yielding [Ru(III)(napbhH)Cl($H_2O$)]Cl. Replacement of aquo ligand by heterocyclic nitrogen donor in this complex has been observed when the reaction is carried out in presence of pyridine(py), 3-picoline(3-pic) or 4-picoline(4-pic). The molar conductance values in DMF (N,N-dimethyl formamide) of these complexes suggest non-electrolytic and 1 : 1 electrolytic nature for manganese and ruthenium complexes, respectively. Magnetic moment values of manganese complexes suggest Mn(III) and Mn(IV), however, ruthenium complexes are paramagnetic with one unpaired electron suggesting Ru(III). Electronic spectral studies suggest six coordinate metal ions in these complexes. IR spectra reveal that napbh$H_2$ coordinates in enol-form and keto-form to manganese and ruthenium metal ions in its complexes, respectively. ESR studies of the complexes are also reported.

*Keywords*: Manganese(III); Manganese(IV); Ruthenium(III); 2-Hydroxy-1-naphthaldehydebenzoylhydrazone; Pyridine bases

## 1. Introduction

Metal complexes of Schiff bases represent an important class of coordination compounds [1–7]. Schiff bases containing polyfunctional groups produce stable complexes of transition, non-transition, inner-transition and actinide metal ions. Manganese is an important trace element needed for normal physiological functions. It is also a cofactor or required metal for enzymes such as superoxide dismutase (SOD), glutamine synthetase and azide insensitive catalase [8–11]. Manganese complexes in high-oxidation state are potentially used as oxidizing agents, catalysts [12] and electro-catalysts [13] for oxidation of alcohols, ethers, and water. Manganese in photosystem-II is of particular interest where manganese in higher

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oxidation state functions as a catalyst for oxidizing two molecules of water to molecular oxygen [14, 15].

Ruthenium has received considerable attention [16], primarily because of the fascinating redox, photophysical, and photochemical properties exhibited by complexes. Ruthenium complexes have been investigated as photovoltaic devices [17–20], as catalysts in oxidation [21], reduction [22], and as organic conductors [23, 24]. The versatility of ruthenium complexes is due to redox properties, intense electronic absorption bands, and stability, which can be manipulated by subtle changes to the axial ligands [25]. Ruthenium complexes have shown satisfactory DNA-cleavage ability [9, 26, 27].

Complexes of transition metal ions with 2-hydroxy-1-naphthaldehydebenzoylhydrazone have been reported [28–30], but there is no report on complexes with manganese(III, IV) and ruthenium(III) metal ions. That is why manganese and ruthenium ions have been selected for the present study.

## 2. Experimental

### 2.1. *Materials*

Manganese(II) acetate tetrahydrate, ruthenium(III) chloride trihydrate, potassium hydroxide, ethylbenzoate, hydrazine hydrate, and 2-hydroxy-1-naphthaldehyde were of GR (E-Merck) or equivalent grade reagents. Reagent grade organic solvents were purified and dried by recommended procedures [31]. Manganese(III) acetate dehydrate [32] and benzoylhydrazine [33] have been obtained by literature procedures. Commercial grade ruthenium trichloride was activated by dissolving in concentrated hydrochloric acid and then evaporating to dryness over a steam bath before use.

### 2.2. *Analysis of the complexes*

Estimation of manganese, ruthenium, and chlorine was done by following the standard literature procedures [34, 35]. Carbon, hydrogen, and nitrogen were determined microanalytically.

### 2.3. *Physical measurements*

Molar conductances of the complexes at $10^{-3}$ M dilution in DMF were measured on a Systronics Direct Reading Conductivity meter-304 with a dip-type conductivity cell at room temperature. Magnetic susceptibility measurements were carried out on a Vibrating Sample Magnetometer. Electronic spectra were recorded on a Spectroscan 2600, Double beam UV–Vis spectrophotometer (Chemito), and on a Perkin Elmer Lambda 25 UV–Vis spectrophotometer. Infrared spectra were recorded on a Perkin Elmer Model BX-II IR spectrophotometer from 4000 to 450 $cm^{-1}$ as KBr pellets and in the range 600–50 $cm^{-1}$ in CsI discs. 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.

### 2.4. *Preparation of ligand*

The ligand, 2-hydroxy-1-naphthaldehydebenzoylhydrazone(napbh$H_2$) was prepared in two steps. In the first step, benzoylhydrazine(BH) was prepared by reaction of ethylbenzoate (48.0 mL) and hydrazine hydrate (16.3 mL) in 1 : 1 molar ratio under reflux for 4 h. The product thus isolated was recrystallized from hot benzene [33], [Yield: 78%]. In the second step, benzoylhydrazine (2.0 g) in ethanol (30 mL) solution reacted with 2-hydroxy-1-naphthaldehyde (2.50 g) in 1 : 1 molar ratio at 70°C with constant gentle stirring for 30–45 min. The cream polycrystalline precipitate thus obtained was purified by repeated washing with hot ethanol and dried over anhydrous $CaCl_2$ [28, 36], [Yield: ~82%]. (m.p. 198°C) [Found: C, 74.92; H, 4.70; N, 9.56; Calcd for $C_{18}H_{14}N_2O_2$: C, 74.48; H, 4.82; N, 9.65 (%). $\lambda_{max}$ (nm), 297(7742 $dm^3\,mol^{-1}\,cm^{-1}$), 327(5149 $dm^3\,mol^{-1}\,cm^{-1}$) and 363(4714 $dm^3\,mol^{-1}\,cm^{-1}$); $\nu$ ($cm^{-1}$) 3550–3300(sbr), 3448(s), 3185(sbr), (OH + NH); 1654(s), 1642(s)(C = O); 1625(m), 1604(m)(C = N); 1561(m), 1547(m) [amide II(CO + NH) + (C–O)(naphtholic)]; 1291(s), 1284(s) [$\beta$(C–O)]].

### 2.5. *Preparation of [Mn(III)(napbh)(OH)($H_2O$)] (1)*

To a 50 mL methanolic solution of $Mn(OAc)_3{\cdot}2H_2O$ (0.460 g, 1.742 mM), 1.0 g, 3.448 mM of napbh$H_2$ was added and magnetically stirred at 70°C for half an hour. To the resulting light brown suspension, 10 mL methanolic solution of KOH (0.384 g, 10.66 mM) was added drop wise with constant stirring and stirred for 45 min, resulting in a dark green solution. The solution was filtered and the filtrate was kept for crystallization, which yielded dark green precipitate after 3 days. The precipitate was washed several times with methanol and dried over anhydrous $CaCl_2$ [Yield: 68.42%].

### 2.6. *Preparation of [Mn(IV)(napbh)$_2$] (2)*

To a 25 mL methanolic suspension of napbh$H_2$ (2.0 g, 6.89 mM), 40 mL methanolic solution of $Mn(OAc)_2 \cdot 4H_2O$ (0.844 g, 3.44 mM) was added with stirring at 70°C and further stirred for 45 min. The suspension was made soluble by adding dropwise 10 mL methanolic solution of KOH (0.771 g, 21.41 mM) maintaining the temperature at 70°C and finally stirred for an additional 30 min. The dark brown solution obtained was filtered and the filtrate was kept for crystallization, which yielded dark brown precipitate after 3 days. The precipitate was suction filtered and washed several times with methanol dried over anhydrous $CaCl_2$ [Yield: 65.20%].

### 2.7. *Preparation of [Ru(III)(napbhH)Cl($H_2O$)]Cl (3)*

To a 20 mL methanolic suspension of 2-hydroxy-1-naphthaldehydebenzoyl hydrazone(napbh$H_2$) (1.12 g, 3.862 mM), 20 mL methanolic solution of $RuCl_3{\cdot}3H_2O$ (1.0 g, 3.824 mM) was added slowly with stirring and further refluxed for 1.5 h. The color of the reaction mixture changed from reddish to brown and was filtered hot. The undissolved material was rejected and the filtrate was kept for crystallization which yielded dark brown precipitate after 3 days. The precipitate was suction filtered, washed with methanol and ether and dried over anhydrous $CaCl_2$ [Yield: 76%].

### 2.8. *Preparation of [Ru(III)(napbhH)Cl(A)]Cl [A = py(4), 3-pic(5) or 4-pic(6)]*

The complexes were obtained essentially by the same procedure as used for synthesis of [Ru(III)(napbhH)Cl($H_2O$)]Cl only by adding pyridine, 3-picoline or 4-picoline to the reaction mixture obtained after refluxing of napbh$H_2$ and $RuCl_3 \cdot 3H_2O$ mixture. The reaction mixture containing pyridine was further refluxed for 1 h and filtered hot. The filtrate yielded green precipitate after 3 days, which was collected [Yield: 66.2%(**4**), 64.9%(**5**), 65%(**6**)].

## 3. Results and discussion

The complexes isolated in the present study, together with their color, decomposition temperature, analytical data, magnetic moment, electronic spectral bands, and molar conductance data are presented in table 1. The analytical data and stoichiometry of the complexes reveal complexes of compositions [Mn(III)(napbh)(OH)($H_2O$)] (**1**), [Mn(IV)(napbh)$_2$] (**2**), [Ru(III)(napbhH)Cl(A)]Cl [A = $H_2O$(**3**), py(**4**), 3-pic(**5**), 4-pic(**6**)]. The complexes are air stable, insoluble in water and common organic solvents such as EtOH, MeOH, $CH_3COCH_3$, $CCl_4$, $CHCl_3$, $Et_2O$, $C_6H_6$, $CH_2Cl_2$, and $CH_3CN$ but soluble only in coordinating solvents like DMF and DMSO. Manganese complexes do not decompose up to 300°C, while the ruthenium complexes decompose in the temperature range 225–258°C. Weight loss experiments for the complexes were carried out by heating a small amount of sample in a glass tube for 4 h in an electric oven maintained at 110, 180 and 220°C. None of the complexes show weight loss at 110°C, ruling out the presence of lattice water. Complexes **1** and **3** show weight loss corresponding to one water at 180°C, suggesting the presence of coordinated water. Complexes **4**–**6** show weight loss at about 220°C corresponding to one molecule of pyridine, 3-picoline or 4-picoline. Expulsion of these molecules at such a high temperature indicates they are coordinated to the metal.

### 3.1. *Molar conductance*

Molar conductance values for **1** and **2** are 10.70 and 7.0 $\Omega^{-1}\,cm^2\,mol^{-1}$ in DMF at $10^{-3}$ M, respectively, while those for ruthenium complexes **3**–**6** fall in the range 65.80–72.30 $\Omega^{-1}\,cm^2\,mol^{-1}$. A comparison of the molar conductance data with literature values indicates that manganese complexes are non-electrolytes [37], while ruthenium complexes have 1 : 1 electrolytic nature in DMF. The high molar conductance values for ruthenium complexes may be attributed to the fact that these complexes undergo solvolysis in the highly coordinating DMF; the possibility of one chloride out of the coordination sphere cannot be ruled out.

### 3.2. *Magnetic moment*

Manganese complexes **1** and **2** have $\mu_{eff}$ values of 4.33 and 4.05 B.M., respectively. The $\mu_{eff}$ values for the Mn(IV) complexes are reported to lie in the range 3.83–4.12 B.M. with $d^3$ configuration ($S = 3/2$) [38, 39], while Mn(III) complexes have $\mu_{eff}$ values in the

Table 1. Analytical data, magnetic moment, molar conductance and electronic spectral data for 2-hydroxy-1-naphthaldehydebenzoylhydrazone(napbh$H_2$) and its manganese(III, IV) and ruthenium(III) complexes.

| Complex (color) | % Yield (Dec. Temp.°C) | Elemental analysis found (Calcd) (%) Mn/Ru | C | H | N | Cl | $\mu_B$ (B.M) | $\Lambda_M$ ($\Omega^{-1}\,cm^2\,mol^{-1}$) | Electronic spectral bands $\Lambda_{max}$ (nm) ($\varepsilon_{max}\,dm^3\,mol^{-1}\,cm^{-1}$) |
|---|---|---|---|---|---|---|---|---|---|
| [$Mn^{III}$(napbh)(OH)($H_2O$)] (**1**) (Dark green) | 68.42(> 300°C) | 14.36(14.55) | 57.10(57.14) | 3.94(3.96) | 7.33(7.40) | – | 4.33 | 10.70 | 279(6800), 426(2650)<br>314(4000), 452(2740)<br>340(4300), 480(2400) |
| [$Mn^{IV}$(napbh)$_2$] (**2**) (Black-brown) | 65.20(> 300°C) | 8.5(8.71) | 68.58(68.46) | 3.38(3.80) | 8.85(8.87) | – | 4.50 | 7.00 | 305(6150), 362(6200),<br>528(12540) |
| [$Ru^{III}$(napbhH)Cl($H_2O$)]Cl (**3**) (Dark brown) | 76.00(225°C) | 20.67(21.08) | 45.20(45.09) | 3.20(3.13) | 5.80(5.84) | 14.85(14.82) | 1.63 | 72.30 | 305(6945), 451(8535)<br>364(6910) 652(4000) |
| [$Ru^{III}$ (napbhH)Cl(py)]Cl (**4**) (Dark brown) | 66.20(248°C) | 18.50(18.70) | 50.80(51.11) | 3.31(3.33) | 7.80(7.77) | 13.20(13.14) | 1.65 | 69.70 | 294(6070), 493(1111)<br>354(6020), 689(4120) |
| [$Ru^{III}$(napbhH)Cl(3-pic)]Cl (**5**) (Light green) | 64.90(252°C) | 18.20(18.23) | 52.00(51.98) | 3.60(3.61) | 7.58(7.58) | 12.85(12.81) | 1.69 | 65.80 | 301(5960), 697(4190)<br>362(5920), 761(1850)<br>489(1108) |
| [$Ru^{III}$(napbhH)Cl(4-pic)]Cl (**6**) (Light green) | 67.30(258°C) | 18.15 (18.23) | 52.00(51.98) | 3.62(3.61) | 7.60(7.58) | 12.88(12.81) | 1.70 | 70.30 | 298(5584), 699(8040)<br>362(5476), 797(6200)<br>481(7552) |

range 4.80–5.20 B.M. with $d^4$ configuration ($S=2$) [40, 41]. The $\mu_{\text{eff}}$ value of 4.33 B.M. for **1** is higher than the values for Mn(IV), ruling out the presence of manganese(IV), however, this value is slightly lower than $\mu_{\text{B}}$ values for manganese(III) complexes. Such $\mu_{\text{B}}$ value suggests that the complex contains manganese in +3 oxidation state with the possibility of metal–metal interaction. The $\mu_{\text{eff}}$ value of 4.05 B.M. for **2** suggests manganese in the +4 oxidation state.

All of the ruthenium complexes have $\mu_{\text{B}}$ value in the range 1.63–1.70 B.M., suggesting one unpaired electron. Thus, the $\mu_{\text{eff}}$ values for the complexes are in accord with the +3 oxidation of ruthenium (low-spin, $d^5$, $S=1/2$) [42].

### 3.3. *Electronic spectra*

Mn(III) having $d^4$ electronic configuration with $^5D$ ground state is expected to show only one spin-allowed absorption ($^5E_g \rightarrow {}^5T_{2g}$) in the visible region. Mn(III) octahedral complexes generally show a broad band around 20000 cm$^{-1}$ (500 nm) [43]. In the present study the ligand shows three absorption bands at 297(7742), 327(5149) and 363 nm (4714 dm$^3$ mol$^{-1}$ cm$^{-1}$) due to carbonyl and imino chromophores in conjugation with phenyl or naphthyl group. Complex **1** shows absorption bands at 426, 452 and 480 nm in addition to other ligand bands. The bands at 426 and 452 nm with molar extinction coefficient values 2650 and 2740 dm$^3$ mol$^{-1}$ cm$^{-1}$, respectively, may be assigned to charge-transfer bands arising from transfer of charge from naphtholate oxygen to Mn(III). The additional band at 480 nm may be assigned to d–d transition in octahedral stereochemistry around Mn(III). The molar extinction coefficient of this band is higher than expected for d–d transitions, which may be caused by the presence of near by charge transfer band. Spectra of six-coordinate Mn(III) complexes are not so simple and are difficult to interpret, presumably because both static and dynamic Jahn–Teller effects perturb the $O_h$ symmetry. Complex **2** shows two bands at 305 (6150) and 362 nm (6200 dm$^3$ mol$^{-1}$ cm$^{-1}$) in the UV region assigned to intraligand transitions. In addition, the complex shows a very strong band at 528 nm (12540 dm$^3$ mol$^{-1}$ cm$^{-1}$), which may have its origin from charge-transfer from naphtholate oxygen to Mn(IV) [38, 43a, 44–46]. Complexes **3**–**6** show two to three bands in the region 450–797 nm in addition to intra-ligand bands with high molar extinction coefficients. In view of the molar extinction coefficients, these bands may be assigned to ligand to metal charge transfer (LMCT) transitions. The splitting of the bands in the visible region of the electronic spectrum suggests the ligand field around the central metal ion is of very low symmetry. Most probably, the d–d bands arising out of the transitions $^2T_{2g} \rightarrow {}^4T_{1g}$, $^2T_{2g} \rightarrow {}^4T_{2g}$ and $^2T_{2g} \rightarrow {}^2T_{1g}$ are masked by strong LMCT bands [43a, 47].

### 3.4. *Infrared spectra*

2-Hydroxy-1-naphthaldehydebenzoylhydrazone(napbhH$_2$) has four potential donor sites, carbonyl oxygen, phenolic oxygen, secondary amine and azine nitrogen. The IR spectrum of the ligand is very complicated due to overlapping regions for several group viz. –OH, –NH–, >C=O, >C=N–, –N–C=O, C–O (naphtholic), phenyl, etc. The structurally significant IR bands for free hydrazone and its complexes have been set out

Table 2. Characteristic IR bands ($cm^{-1}$) for 2-hydroxy-1-naphthaldehydebenzoylhydrazone(napbh$H_2$) and its manganese(III, IV) and ruthenium(III) complexes.

| Complex | $\nu$(OH) + $\nu$(NH) | $\nu$(C=O) | $\nu$(C=N) | AmideII + $\nu$(C–O) (naphtholic) | $\nu$(NCO) | $\beta$(C–O) | $\nu$(M–O) |
|---|---|---|---|---|---|---|---|
| [$Mn^{III}$(napbh)(OH)($H_2O$)] (**1**) (Dark green) | 3550–3200(sbr) 3435(s) | – | 1616(s) 1596(s) | 1537(vs) | 1537(vs) | 1300(m) | 588(w) |
| [$Mn^{IV}$(napbh)$_2$] (**2**) (Black-brown) | 3550–3200(sbr) 3435(s) | – | 1616(s) 1597(s) | 1537(vs) | 1537(vs) | 1292(s) | 586(w) |
| [$Ru^{III}$(napbhH)Cl($H_2O$)]Cl (**3**) (Dark brown) | 3550–3200(sbr) 3436(s) | 1641(s) | 1620(s) 1599(s) | 1562(s) 1527(s) | – | 1285(m) | 546(w) 488(m) |
| [$Ru^{III}$(napbhH)Cl(py)]Cl (**4**) (Dark brown) | 3550–3200(sbr) 3472(s) | 1643(s) | 1621(s) 1590(s) | 1560(m) 1537(m) | – | 1284(w) | 574(w) 468(w) |
| [$Ru^{III}$(napbhH)Cl(3-pic)]Cl (**5**) (Light green) | 3550–3200(sbr) 3234(s) | 1642(s) | 1620(s) 1600(s) | 1574(m) | – | 1284(m) | 540(w) 480(w) |
| [$Ru^{III}$(napbhH)Cl(4-pic)]Cl (**6**) (Light green) | 3550–3200(sbr) 3468(s) | 1640(s) | 1620(s) 1597(s) | 1574(s) 1537(s) | – | 1284m | 581(s) 4476(w) |

in table 2. A comparison of the IR spectra of the complexes with that of the free ligand, napbh$H_2$, suggests that hydrazone is coordinated to the metal center in enol-form in the manganese complexes and keto-form in ruthenium complexes.

The uncoordinated napbh$H_2$ shows two strong bands at 3448 and 3185 $cm^{-1}$ assigned to stretching vibrations due to –NH– and –OH [48]. These bands are replaced by a strong broad band in the region 3550–3000 $cm^{-1}$ in all of its complexes which may be assigned to either $\nu$(O–H) or $\nu$(N–H). The amide–I bands for napbh$H_2$ observed at 1654 and 1642 $cm^{-1}$ [49, 50] shifted to lower frequency by 5–7 $cm^{-1}$ accompanied by reduction of intensity in the ruthenium complexes suggest bonding of carbonyl oxygen. These bands disappear in manganese complexes suggesting collapse of amide structure, probably due to enolization of ligand resulting in coordination through the carbonyl oxygen in enol form, further supported by the appearance of an intense band at 1537 $cm^{-1}$ assigned to newly generated $\nu$(NCO) group [51]. The amide-II band in napbh$H_2$ is observed at 1561 $cm^{-1}$ undergoing negative shift in ruthenium complexes suggesting coordination of $>$C=O to the metal. The $\nu$(C–O)(naphtholic) observed at 1547 $cm^{-1}$ in the ligand suffers negative shift in the complexes, indicating its bonding to the metal [52]. Coordination of ligand to manganese in enol form probably arises due to the basic condition of the reaction. Acetic acid produced by reaction of manganese(II) acetate and ligand reacts with KOH promoting enolization of the ligand. Reaction of ruthenium(III) chloride with ligand liberates HCl reducing its pH, which suppresses enolization allowing coordination in keto-form to ruthenium(III).

The $\nu$(C=N) occurs in the range 1630–1610 $cm^{-1}$ for Schiff bases derived from condensation of hydrazine with aromatic aldehydes or ketones [53]. The present hydrazone (napbh$H_2$) shows bands at 1625 and 1604 $cm^{-1}$ which shift to lower position by 5–10 $cm^{-1}$ in all the complexes, suggesting coordination of azomethine nitrogen [54–57].The aromatic ring vibrations at 1600 $cm^{-1}$ cannot be distinguished as it overlaps with $\nu$(C=N), amide-II or $\nu$(C–O)(naphtholate). The bending vibration bands for coordinated water found in the region 1640–1600 $cm^{-1}$ also overlapped.

The C–H in-plane and out-of-plane deformation bands in napbh$H_2$ at 1243, 1198, 1160, 1140, and 794, 739 $cm^{-1}$, respectively, remain either unaffected or slightly shifted in the complexes. Ruthenium complexes **4**–**6** show a new weak band at 1064–1067 $cm^{-1}$ probably arising from ring breathing suggesting the presence of pyridine, 3-picoline or 4-picoline in the complexes. Coordination to the metal has been inferred from positive shifts observed in bands due to in-plane and out-of-plane ring deformation. Two strong bands at 1291 and 1284 $cm^{-1}$ [$\beta$(C–O) in the IR spectrum of napbh$H_2$ due to bending vibration of naphtholic(C–O) group] [58, 59] merge into a single band in **1** and **2** and appear at 1300 and 1292 $cm^{-1}$, respectively. The positive shifts in these bands suggest that the naphthyl electron density flows to the metal center through naphtholate C–O. Negative shifts in these bands in complexes of ruthenium suggest the flow of naphthyl ring electron density to the ruthenium through azomethine nitrogen. The IR spectra of the complexes and dehydrated form were recorded under identical conditions to evaluate whether bridging –OH is present in the complexes. The IR spectra of **1** show a medium broad band centered at 3443 $cm^{-1}$ due to coordinated water, while dehydrated sample (heated at ~200°C for 4 h) shows a weak broad band at 3300–3550 $cm^{-1}$, very similar to that observed in hydroxo complexes [60–63]. Hence, this weak broad band is assigned to stretching vibration of –OH group. It appears that in hydrated **1**, the band due to stretching of –OH group is masked by coordinated water. Complex **1** in its hydrated and dehydrated forms shows a medium intensity band at 970 $\mathrm{cm}^{-1}$ assigned to bridging –OH bending. Similar results have been reported for $[Cu_2(OH)_2(bipy)_2]\cdot SO_4\cdot 5H_2O$ and others [61–63]. This medium intensity band at 970 $\mathrm{cm}^{-1}$ in **1** is not observed in IR spectra of free ligand or other complexes. Hence, this band is assigned to bending vibration of $M(\mu\text{-}OH)_2M$, further supported by anomalously low $\mu_B$ for **1** indicating metal–metal interaction through bridging.

From stereochemical consideration of napbh$H_2$, three metal–ligand vibrations arise due to $\nu$(M–O)(naphtholic), $\nu(\text{M–O–}\underset{|}{\text{C}}\text{=})$ or $\nu$(M–O=C<) and $\nu$(M–N) in its complexes. Non-ligand bands observed in the regions 588–540 $\mathrm{cm}^{-1}$ and 500–400 $\mathrm{cm}^{-1}$ have been assigned [64–66] to $\nu$(M–O)(naphtholate) and $\nu$(M–O)(carbonyl), respectively, in these complexes. Bands observed in the range 420–350 $\mathrm{cm}^{-1}$ have been assigned to $\nu$(M–N) [67–70] due to azomethine nitrogen and/or heterocyclic nitrogen. The bands at 344 and 335 $\mathrm{cm}^{-1}$ are assigned to $\nu$(Ru–Cl) [64, 71] suggesting *cis*-Ru–$Cl_2$ configuration [72].

### 3.5. *ESR spectra*

Manganese complex **1** was ESR silent consistent with the presence of Mn(III). Ruthenium complex **4** has featureless spectra. Complex **2** shows two ESR signals at RT and LNT in polycrystalline state, one strong near $g = 2.031$ and the other weak at $g = 4.334$. The same $g$ values at both temperatures indicate that the structure does not change on lowering the temperature. The $^{55}$Mn hyperfine structure is well resolved for the resonance near $g = 2.0$ in DMSO but not in DMF. Depending on the nature and extent of distortion of $O_h$ symmetry, the ESR spectra of a $d^3$ ion can assume different forms [73, 74]. The form observed here (strong $g = 2.031$ and weak $g = 4.334$ resonances) is characteristic of small axial distortion, $2D \ll h\upsilon$, where $D$ is the axial zero field splitting parameter and $h\upsilon$ is the microwave quantum (0.31 $\mathrm{cm}^{-1}$ at X-band). When $D$ is small, rhombic splitting is necessarily very small, since $D/E \geq 3$, where $E$ is the rhombic splitting parameter. Large distortion, $2D \gg h\upsilon$, occurs in a number of complexes [65, 75–80] and the $2D \ll h\upsilon$ situation for Mn(IV) has also been documented in few cases [72, 81, 82]. Interestingly, the $^{55}$Mn hyperfine coupling constant for the $g = 2.031$ signal lies close to 100 G for known $2D \ll h\upsilon$ species, suggesting small axial distortion in $O_h$ symmetry around Mn(IV) ion.

ESR spectra of the ruthenium complexes **3**, **5** and **6** were studied at RT and LNT in polycrystalline state as well as at LNT in DMF glass. The ESR spectrum of **3** in solid state consists of a single isotropic resonance with unresolved hyperfine structure at RT due to ruthenium with $g$-value equal to 2.051(Ruthenium has magnetic nuclei $^{99}$Ru and $^{101}$Ru with natural abundances of 12.89 and 16.98% and nuclear moments of 0.63 and 0.69 nm, respectively. Both isotopes have a nuclear spin of 5/2) [83]. When the sample was cooled to LNT, lines slightly narrowed and a slight change in the $g$-parameter (2.048) with no g anisotropy was observed. Isotropic lines are usually observed for intermolecular spin exchange, which can broaden the lines and/or occupancy of the unpaired electron in a degenerate orbital. Complex **3** shows well-resolved spectral features ($g_1 = 2.258, g_2 = 2.084, g_3 = 1.868, g_{av} = 2.07$) at LNT in DMF glass. In **5** and **6**, resolved $g$ features were observed in the polycrystalline phase at LNT while the spectra were featureless at RT. Hence, in **3**, the spin exchange may not be the main reason for isotropy. In this case the effective electronic environment may be such that the unpaired electron is in a low spin state with a degenerate or nearly degenerate ground state, prone

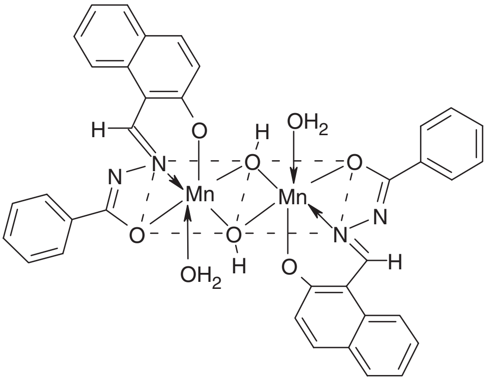

Figure 1. Suggested structure of $[Mn^{III}(napbh)(OH)(H_2O)]$.

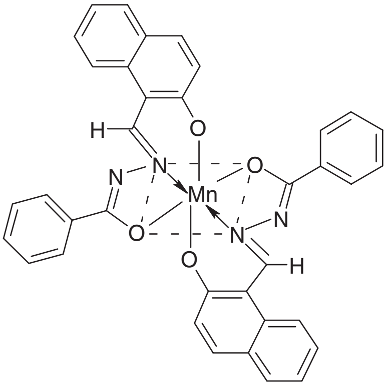

Figure 2. Suggested structure of $[Mn^{IV}(napbh)_2]$.

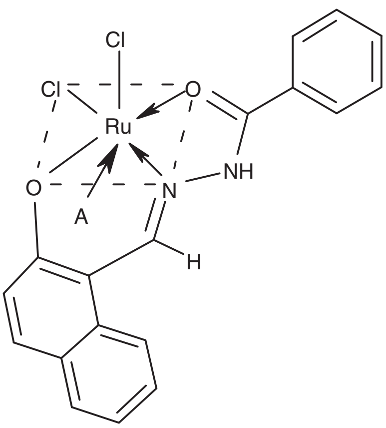

Figure 3. Suggested structure of $[Ru^{III}(napbhH)Cl(A)]Cl$ [where $A = H_2O$(**3**), py(**4**), 3-picoline(**5**) and 4-picoline(**6**)].

to Jahn–Teller instability [84]. If the instability is dynamic, one observes only an averaged *g*-value ($g_{av}$). It is, therefore, tentatively proposed that **3** exhibits a dynamic Jahn–Teller effect.

ESR spectra of **5** and **6** show poorly resolved features, ($g_1 = 2.995$, $g_2 = 2.408$, $g_3 = 1.970$, $g_{av} = 2.444$) and ($g_1 = 2.778$, $g_2 = 2.481$, $g_3 = 1.912$, $g_{av} = 2.390$), respectively, at LNT in solid state but are featureless at RT. Complexes **5** and **6** show well-resolved ESR spectral features, ($g_1 = 2.520$, $g_2 = 2.057$, $g_3 = 1.737$, $g_{av} = 2.10$) and ($g_1 = 2.196$, $g_2 = 2.077$, $g_3 = 1.862$, $g_{av} = 2.04$), in DMF solution at LNT. The $g_{av}$ values vary with temperature and with the axial ligand. The nature of the spectra is consistent with non-degenerate $t_{2g}$ orbital. The spectra are in general characterized by a rhombic *g* tensor with narrow lines at 77 K. Hyperfine coupling due to ruthenium was resolved on $g_1$ components in DMF solution at LNT which is equal to ~70 G.

ESR spectral results indicate that the complexes belong to a low spin $4d^5$ configuration and the symmetry at ruthenium is as low as $C_s$. This is in agreement with the proposed structure. The *g*-values at LNT, slightly different from those at RT, indicate that the geometry of the ruthenium changes with temperature. Also, the axial ligands have a significant effect on the *g* components. $g_{av}$ of **3** in DMF is very near to the $g_{av}$ in the solid state at LNT, while it is significantly different for **5** and **6** in DMF compared to RT. Such a large difference in $g_{av}$ values may be related to the complexes undergoing solvolysis in DMF and that in all complexes the axial position is occupied by DMF.

## 4. Conclusions

Based on stoichiometries and physico-chemical studies, the ligand behaves in enol-form and keto-form in its complexes of manganese and ruthenium, respectively. Octahedral stereochemistry around the metal ions have been proposed as shown in figures 1–3.

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## References

[1] J.R. Dilworth. *Coord. Chem. Rev.*, **21**, 29 (1976).
[2] P. Guerriero, S. Tamburini, P.A. Vigato. *Coord. Chem. Rev.*, **139**, 17 (1995).
[3] T.A.K. Al-Allaf, A.Z.M. Sheet. *Polyhedron*, **14**, 239 (1995).
[4] S.B. Halligudl, B.M. Devassy, N.K.K.R.M.P. Degaonkar, S. Gopinathan. *React. Kinet. Catal. Lett.*, **71**, 289 (2000).

[5] T. Xishi, Y. Xianhong, C. Qiang, T. Minyu. *Molecules*, **8**, 439 (2003).

[6] R.J.P. Corriu, E. Lancelle-Beltran, A. Mehdi, C. Reye, S. Brandes, R. Guilard. *Chem. Mater.*, **15**, 3152 (2003).

[7] B. Clarke. *J. Organomet. Chem.*, **559**, 55 (2003).

[8] G.D. Lawrence, D.T. Sawyer. *Coord. Chem. Rev.*, **27**, 173 (1978).

[9] L.-N. Zhu, Y.-W. Jin, X.-Z. Li, J. Wang, D.-M. Kong, H.-F. Mi, D.-Z. Liao, H.-X. Shen. *Inorg. Chim. Acta*, **361**, 29 (2008).

[10] V.V. Dukhande, G.H. Malthankar–Phatak, J.J. Hugus, C.K. Daniels, J.C.K. Lal. *Neurochem. Res.*, **31**, 1349 (2006).

[11] W.F. Beyer, I. Fridovich. In *Manganese in Metabolism and Enzyme Function*, V.L. Schramm, F.C. Wedler (Eds), p. 193, Academic Press, New York (1986).

[12] M. Ray, S. Mukherjee, R.N. Mukherjee. *J. Chem. Soc., Dalton Trans.*, 3635 (1990).

[13] P.A. Goodson, A.R. Oki, J. Glerup, D.J. Hodgson. *J. Am. Chem. Soc.*, **112**, 6248 (1990).

[14] A.J. Bearden, R. Malkin. *Q. Rev. Biophys.*, **7**, 131 (1974).

[15] K.A. Sauer. *Acc. Chem. Res.*, **13**, 249 (1980).

[16] M. Dasgupta, S. Nag, G. Das, M. Netaji, S. Bhattacharya. *Polyhedron*, **27**, 139 (2008).

[17] T. Rawling, A.M. McDonagh, S.B. Colbran. *Inorg. Chim. Acta*, **361**, 49 (2008).

[18] M.K. Nazeeruddin, R. Humphy-Baker, M. Gratzel, B.A. Murrer. *Chem. Commun.*, 719 (1998).

[19] M. Yanagisawa, F. Korodi, J. He, L. Sun, V. Sundstron, B. Akermark. *J. Porphyrins Phthalocyanines*, **6**, 217 (2002).

[20] M. Yanagisawa, F. Korodi, J. Bergquist, A. Holmberg, A. Hagfeldt, B. Akermark, L. Sun. *J. Porphyrins Phthalocyanines*, **8**, 1228 (2004).

[21] M. Bressan, N. Celli, N. d'Alessandro, L. Liberatore, A. Morvillo, L. Tonucci. *J. Organomet. Chem.*, **593–594**, 416 (2000).

[22] M. Ebadh, C. Alexiou, A.B.P. Lever. *Can. J. Chem.*, **79**, 992 (2001).

[23] J. Pohmer, M. Hanack, J.O. Barcina. *J. Mater. Chem.*, **6**, 957 (1996).

[24] S. Knecht, R. Polley, M. Hanack. *Appl. Organomet. Chem.*, **10**, 649 (1996).

[25] T. Rawling, H. Xiao, S.-T. Lee, S.B. Colbran, A.M. McDonagh. *Inorg. Chem.*, **46**, 2805 (2007).

[26] R. Caspar, L. Musatklna, A. Tatosyan, H. Amouri, M. Gruselle, C.G. Duhayon, R. Duval, C. Cordler. *Inorg. Chem.*, **43**, 7986 (2004).

[27] A. Bouskila, E. Amouyal, C. Verchere-Beaur, I. Sasaki, A. Gaudemer. *J. Photochem. Photobiol.*, **B76**, 69 (2004).

[28] K.K. Narang, M.K. Singh. *Inorg. Chim. Acta*, **131**, 241 (1987).

[29] L. Sacconi. *J. Am. Chem. Soc.*, **76**, 3400 (1954).

[30] R.L. Datta, A.K. Pal. *Indian J. Chem.*, **22A**, 871 (1983).

[31] S.C. Chan, L.L. Koh, P.H. Leung, J.D. Ranford, K.Y. Sin. *Inorg. Chim. Acta*, **236**, 101 (1995).

[32] (a) O.T. Christeinsion, *Z. Anorg. Allg. Chem.*, **27**, 25 (1901); (b) R.F. Winland, G. Fisher, *Z. Anorg. Allg. Chem.*, **120**, 161 (1921).

[33] T. Curtius, H. Mesbash. *J. Prakt. Chemie*, **81**, 545 (1910).

[34] A.I. Vogel. *A Text Book of Quantitative Inorganic Analysis*, 3rd Edn, ELBS and Longmans, London (1961).

[35] (a) K.K. Narang, A. Aggarwal. *Inorg. Chim. Acta*, **9**, 137 (1974); (b) N.S. Biradar, S.D. Angali. *J. Inorg. Nucl. Chem.*, **38**, 1405 (1976).

[36] J.C. Decius, D.P. Pearson. *J. Am. Chem. Soc.*, **75**, 2436 (1953).

[37] W.J. Geary. *Coord. Chem. Rev.*, **7**, 81 (1971).

[38] D.P. Kessissoglou, X. Li, W.M. Butler, V.L. Pecoraro. *Inorg. Chem.*, **26**, 2487 (1987).

[39] K. Koikawa, H. Okawa. *J. Chem. Soc., Dalton Trans.*, 641 (1988).

[40] A. Garcia-Deibe, M.R. Bermejo, A. Sousa, C.A. McAuliffe, P. McGlynn, P.T. Ndifon, R.G. Pritchard. *J. Chem. Soc., Dalton Trans.*, 1605 (1993).

[41] M.K. Singh, S. Bhaumik, R.A. Lal. *J. Indian Chem. Soc.*, **84**, 419 (2007).

[42] A.K. Das, S.M. Poug, S. Bhattacharya. *J. Chem. Soc., Dalton Trans.*, 181 (2000).

[43] (a) A.B.P. Lever. *Inorganic Electronic Spectroscopy*, 2nd Edn, Elsevier, New York (1984); (b) F.A. Cotton, G. Wilkinson, C.A. Marillo, M. Bochmann. *Advanced Inorganic Chemistry*, 6th Edn, p. 764, John Wiley and Sons, Inc, New York (1999).

[44] M.E. Bodini, L.A. Willis, T.H. Richel, D.T. Sawyer. *Inorg. Chem.*, **15**, 1538 (1978).

[45] J.R. Hartman, B.M. Foxman, S.R. Cooper. *Inorg. Chem.*, **33**, 1381 (1984).

[46] H. Okawa, M. Nakamura, S. Kida. *Bull. Chem. Soc. Jpn.*, **55**, 466 (1982).

[47] S.K. Sengupta, S.K. Sahni, R.N. Kapoor. *Polyhedron*, **2**, 317 (1983).

[48] R.M. Silverstein, G.C. Bassler, I.C. Morrill. *Spectrometric Identification of Organic Compounds*, 4th Edn, John Wiley and Sons, New York (1931).

[49] M. Mashimo. *Bull. Chem. Soc. Jpn.*, **35**, 332, 338, 2020 (1962).

[50] K. Nagano, H. Kinoshita, A. Kirakawa. *Chem. Pharm. Bull.*, **12**, 1202 (1964).

[51] H. Yamada. *Bull. Chem. Soc. Jpn.*, **32**, 1051 (1959).

[52] N.S. Biradar, V.H. Kulkarni. *J. Inorg. Nucl. Chem.*, **33**, 2451 (1971).

[53] C.S. Marvell, S. Aspey Alan, E.A. Dodley. *J. Am. Chem. Soc.*, **82**, 6064 (1960).
[54] M.F. Iskander, A.M. Al-Aggau, L.S. Refaat, L. El-Sayed. *Inorg. Chim. Acta*, **14**, 167 (1975).
[55] M. Husain, S.S. Bhattacharjee, K.B. Singh, R.A. Lal. *Polyhedron*, **10**, 779 (1991).
[56] N.S. Birader, B.R. Havinale. *Inorg. Chim. Acta*, **17**, 157 (1976).
[57] P. Ponka, J. Borova, J. Neuwirt, O. Fuches, E. Necos. *Biochim. Biophys. Acta*, **586**, 278 (1979).
[58] C.P. Prabhakaran, B.G. Nair. *Transition Met. Chem.*, **8**, 368 (1983).
[59] D.K. Rastogi, S.K. Dua, V.B. Rana, S.K. Sahni. *J. Inorg. Nucl. Chem.*, **40**, 1323 (1978).
[60] J.R. Ferraro, W.R. Walker. *Inorg. Chem.*, **4**, 1382 (1965).
[61] J.R. Ferraro, R. Driver, W.R. Walker, W. Wozniak. *Inorg. Chem.*, **6**, 1586 (1967).
[62] G. Blyholder, N. Ford. *J. Phys. Chem.*, **68**, 1496 (1964).
[63] V.A. Marow, T.S. Spiro. *J. Am. Chem. Soc.*, **89**, 45 (1967).
[64] G.C. Percy. *J. Inorg. Nucl. Chem.*, **37**, 2071 (1975).
[65] M. Mikami, I. Nakagawa, T. Shimanouchi. *Spectrochim. Acta*, **23A**, 1037 (1967).
[66] (a) R.J.H. Clark. *J. Chem. Soc.*, 1377 (1962); (b) R.J.H. Clark, *C.S. Williams. Chem. Ind.*, 1317 (1864); (c) ibid, *Inorg. Chem.*, **4**, 350 (1965).
[67] L. Sacconi, A. Sabatini, P. Gaus. *Inorg. Chem.*, **3**, 771 (1964).
[68] G.C. Percy, D.A. Thornton. *J. Inorg. Nucl. Chem.*, **34**, 3369 (1972).
[69] D.M. Adams. *Metal–Ligand and Related Vibration*, Edward Ernold Press, London (1967).
[70] C.W. Frank, L.B. Rogers. *Inorg. Chem.*, **5**, 615 (1966).
[71] A.B.P. Lever, E. Mantovani. *Inorg. Chim. Acta*, **5**, 429 (1971).
[72] P.K. Santra, C. Sinha, W.-J. Sheen, F.-L. Liao, T.-H. Lu. *Polyhedron*, **20**, 599 (2001).
[73] (a) E. Pederson, H. Toftlund. *Inorg. Chem.*, **13**, 1603 (1974); (b) D.C. Bradley, R. Copperthwaite, S.A. Cotton, K.D. Sales, J.F. Gibson. *J. Chem. Soc. Dalton Trans.*, 191 (1973).
[74] S. Pal, P. Ghosh, A. Chakraborty. *Inorg. Chem.*, **24**, 3704 (1985).
[75] M.W. Lynch, D.N. Hendrickson, B.J. Fitzgerald, C.G. Pierpont. *J. Am. Chem. Soc.*, **106**, 2041 (1984).
[76] S.M. Saadeh, M.S. Lah, V.L. Pecoraro. *Inorg. Chem.*, **30**, 8 (1991).
[77] X. Li, M.S. Lah, V.L. Pecoraro. *Acta Crystallogr.*, **C45**, 1517 (1989).
[78] M.K. Chan, W.H. Armstrong. *Inorg. Chem.*, **28**, 3777 (1989).
[79] D.T. Richens, D.T. Sawyer. *J. Am. Chem. Soc.*, **101**, 3681 (1979).
[80] M. Koikawa, H. Okawa, S. Kida. *J. Chem. Soc., Dalton Trans.*, 641 (1998).
[81] S.K. Chandra, A. Chakraborty. *Inorg. Chem.*, **31**, 760 (1992).
[82] K.L. Brown, R.M. Golding, K.J. Healy Jessop, W.C. Tennant. *Aust. J. Chem.*, **27**, 2075 (1974).
[83] M.M. Taqui Khan, D. Srinivas, R.I. Kureshy, N.H. Khan. *Inorg. Chem.*, **29**, 2320 (1990).
[84] H.A. Jahn, E. Teller. *Proc. R. Soc. London, Sect. A*, **101**, 220 (1937).