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Synthesis, EPR, electrochemistry and EXAFS studies of ruthenium(III) complexes with a symmetrical tetradentate N_2O_2 Schiff base

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Abstract

A series of new hexa-coordinated ruthenium(III) complexes of the type $[RuX(Nap-o-phd)(EPh_3)]$ (where, H₂-Nap-o-phd = N,N'bis(2-hydroxy-1-naphthaldehyde) o-phenylene diamine; X = Cl or Br; E = P or As) have been prepared by reacting $[RuX_3(EPh_3)_3]$ and $[RuBr_3(PPh_3)_2(MeOH)]$ (where X = Cl or Br; E = P or As) with tetradentate Schiff base ligand (H₂-Nap-o-phd) in 1:1 molar ratio. The complexes have been characterized by elemental analyses, infra red, electronic, electron paramagnetic resonance spectroscopy and cyclic voltammetry. The coordination geometry and structure of the complexes have been investigated by extended X-ray absorption fine structure (EXAFS) spectroscopy and an octahedral structure has been proposed.

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1. Introduction

Organometallic complexes containing Schiff bases have played an important role in coordination chemistry of transition metals, mainly due to their stability, ease of preparation, structural variability and variety of applications [1]. Ligands containing two bidentate components separated by a spacer group have been extensively used in self assembly recently [2–5]. Schiff base ligands have been extensively investigated with regard to their numerous applications in organic synthesis as well as in pharmacology. Indeed, such ligands are of interest not only in the field of optical sensors [6] and liquid crystals [7] but also as transition metal chelating agents for applications in nuclear medicine [8–13] and asymmetric catalysis [14,15]. Several N_2S_2 and N_2O_2 ligands have already been synthesized and used as chelating

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agents [16–21]. The planarity of the Schiff base ligand provides a means of creating a large vacant site, where coordination of a transition metal could be carried out [22–24].

Transition metal complexes of ruthenium have proved to be useful catalysts in many reactions, such as oxidation, hydrogenation, carbonylation and hydroformylation, by virtue of the accessibility of ruthenium in different oxidation states and ease of coordination with different ligands [25–27]. In connection with our ongoing interest in this field of research we have already investigated several ruthenium(II) and ruthenium(III) complexes [28–32].

In view of the diverse chemistry possessed by the Schiff base ligands and transition metal like ruthenium, we undertook the synthesis of a series of novel N₂O₂ chromophore containing ruthenium(III) complexes. These complexes are structurally characterized by extended X-ray absorption fine structure (EXAFS), spectral techniques and electrochemistry. The structure of the Schiff base ligand used in the present work is shown in Fig. 1.

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Fig. 1. Structure of the Schiff base ligand.

2. Experimental

2.1. Materials

All the reagents used were of Analar grade. Solvents were purified and dried according to the standard procedure [33]. The starting complexes [RuCl₃(PPh₃)₃] [34], [RuCl₃(Ash₃)₃] [35], [RuBr₃(AsPh₃)₃] [36] and [RuBr₃(PPh₃)₃(MeOH)] [37] and ligand [38–40] were prepared and characterized according to the literature procedures.

2.2. Preparation of ruthenium(III) complexes

All the ruthenium(III) complexes were prepared by the following general procedure. To a benzene solution (20 cm^3) of $[\text{RuX}_3(\text{EPh}_3)_3]$ (E = P or As; X = Cl or Br) or $[\text{RuBr}_3(\text{PPh}_3)_2(\text{MeOH})]$ (0.1 mmol, 0.89–1.259 g) the appropriate Schiff base (0.1 mmol, 0.0416 g) was added in 1:1 molar ratio. The mixture was refluxed for 5 h and the solution was concentrated to ca. 3 cm³. The product was separated by the addition of small quantity of petroleum ether (60–80 °C) and recrystallised from CH₂Cl₂/petroleum ether (60–80 °C). The individual synthesis is given below.

[RuCl(PPh₃)(Nap-*o*-phd)] (1) was prepared from [RuCl₃(PPh₃)₃] (0.0994 g; 0.1 mmol) and H₂-Nap-*o*-phd (0.0416 g; 0.1 mmol). Yield (80%). *Anal.* Calc. for [RuCl(PPh₃)(Nap-*o*-phd)]: C, 67.94; H, 4.09; N, 3.44. Found: C, 68.12; H, 4.87; N, 3.08%. IR: ν (C=N) 1604 s cm⁻¹, ν (C–O) m 1357 cm⁻¹. λ_{max} 260, 320, 371, 465 nm. M.p. 283 °C.

[RuCl(AsPh₃)(Nap-*o*-phd)] (**2**) was prepared from [RuCl₃(AsPh₃)₃] (0.1126 g; 0.1 mmol) and H₂-Nap-*o*-phd (0.0416 g; 0.1 mmol). Yield (85%). *Anal.* Calc. for [RuCl(AsPh₃)(Nap-*o*-phd)]: C, 64.45; H, 3.88; N, 3.73. Found: C, 64.62; H, 4.48; N, 3.84%. IR: ν (C=N) 1604 s cm⁻¹, ν (C–O) m 1355 cm⁻¹. λ_{max} 225, 272, 302, 478 nm. M.p. 224 °C.

[RuBr(AsPh₃)(Nap-*o*-phd)] (**3**) was prepared from [RuBr₃(AsPh₃)₃] (0.1259 g; 0.1 mmol) and H₂-Nap-*o*-phd (0.0416 g; 0.1 mmol). Yield (73%). *Anal.* Calc. for [RuBr(AsPh₃)(Nap-*o*-phd)]: C, 61.28; H, 3.69; N, 3.10. Found: C, 60.94; H, 3.42; N, 3.04%. IR: ν (C=N) 1604 s cm⁻¹, ν (C–O) m 1353 cm⁻¹. λ_{max} 281, 337, 478 nm. M.p. 197 °C.

 $[RuBr(PPh_3)(Nap-o-phd)]$ (4) was prepared from $[RuBr_3(PPh_3)_2(MeOH)]$ (0.0897 g; 0.1 mmol) and H₂-Nap-o-phd (0.0416 g; 0.1 mmol). Yield (75%). *Anal.* Calc. for $[RuBr(PPh_3)(Nap-o-phd)]$: C, 64.41; H, 3.87; N, 3.26.

Found: C, 64.84; H, 4.18; N, 3.76%. IR: v (C=N) 1602 s cm⁻¹, v (C–O) m 1357 cm⁻¹. λ_{max} 260, 320, 371, 465 nm. M.p. 212 °C.

2.3. Measurements

Elemental analyses of the complexes were performed with Vario EL III CHNS at Department of Chemistry, Bharathiar University, Coimbatore, India. IR spectra of the ligand and complexes have been recorded in KBr pellets with a Shimadzu/Nicolet instrument in the 400- 4000 cm^{-1} range. The electronic spectra of the complexes have been recorded in methanol using a Systronics 119 spectrophotometer in the 800-200 nm range. Electron paramagnetic resonance (EPR) spectra of the powder samples were recorded with a Jeol Tel-100 instrument at Xband frequencies at room and liquid nitrogen temperatures (77 K) using 2,2'-diphenyl-1-picrylhydrazine hydrate (DPPH) as internal standard. The cyclic voltammetric studies were carried out on EG&G Princeton Applied Research Electrochemical Analyzer in dichloromethane using a glassy-carbon electrode and all potentials were referenced to standard Ag/AgCl electrode.

The transmission mode EXAFS measurements were performed (Ru K-edge at 22117 eV, As K-edge at 11867 eV and Br K-edge at 13474 eV) at the beamline X1.1 of the Hamburger Synchrotron Radiation Laboratory (HASYLAB) at DESY, Hamburg, and at the XAS beamline at the Angstroemquelle Karlsruhe (ANKA) at FZK, Karlsruhe, Germany. The complexes were measured with Si(311) double crystal monochromator at the Ru

Table 1 EPR spectral data of Ru(III) Schiff base complexes

Complex	Temperature (K)	g_x	g_y	g_z	$\langle g \rangle^*$
1	77	2.28	2.04	1.88	2.073
1	298	2.87	2.38	2.10	2.47
2	298	2.46	2.18	2.11	2.28
3	298	2.56	2.28	2.14	2.33
4	298	2.37	2.18	2.08	2.21

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



Fig. 2. EPR spectrum of 1.



Fig. 3. Cyclic voltammogram of 2.

Table 2 Cyclic voltammetric data^a of Ru(III) Schiff base complexes

			-	
Complex	$E_{\rm pc}$ (V)	$E_{\mathrm{pa}}\left(\mathbf{V}\right)$	$E_{\rm f}\left({ m V} ight)$	$\Delta E_p \ (\mathrm{mV})$
1	-0.80	-1.05	0.925	250
2	-0.82	-1.08	0.95	260
3	-0.80	-1.00	0.90	200
4	-0.86	-1.08	0.97	220

^a Supporting electrolyte: [NBu₄]BF₄ (0.1 M); concentration of the complex: 0.001 M; scan rate: 100 mV s⁻¹. All the potentials are referenced to Ag/AgCl; $E_{\rm f} = 0.5$ ($E_{\rm pa} + E_{\rm pc}$), where $E_{\rm pa}$ and $E_{\rm pc}$ are anodic and cathodic potentials, respectively.

K-edge and with Si(111) double crystal monochromator at the As and Br K-edges. The measurements were carried out at ambient conditions and, ion chambers filled with inert gases (nitrogen and argon) were used to measure the incident and transmitted intensities. Energy calibration was monitored by measuring the absorption through a reference simultaneously with the absorption through the complexes, by means of a third ion chamber. For Ru K-edge measurements, ruthenium metal foil was used as the reference. A 20-µm thick gold metal foil having L_{III}-edge at 11919 eV was used as reference for As K-edge measurements and the same foil having L_{II}-edge at 13734 eV was used as reference for Br K-edge measurements. The complexes in solid state were embedded in a polyethylene matrix and pressed into pellet. The concentration was adjusted to yield an extinction of 1.5. The data were analysed with a program package especially developed for the requirements of amorphous samples [41]. The program AUTOBK [42] was used for the removal of background and the program EXCURV98 [43] was used for the evaluation of EXAFS function. Curved wave theory using XAL-PHA phase and amplitude functions was used for the data analysis in k space and the resulting EXAFS function was weighted with k^3 . The mean free path of the scattered electrons was calculated from the imaginary part of the potential (VPI set to -4.00), the amplitude reduction factor AFAC was fixed at 0.8 and Fermi energy shift $E_{\rm F}$ was introduced to give a best fit to the data.

3. Results and discussion

3.1. EPR studies

The solid state EPR spectra of powdered samples were recorded at room temperature and the 'g' values are listed



Fig. 4. Experimental (solid line) and calculated (dotted line) EXAFS functions (a) and their corresponding Fourier transform plots (b) for the different ruthenium(III) Schiff base complexes with triphenylphosphine/arsine measured at the Ru K-edge.

in Table 1. All the complexes showed three lines with three different 'g' values indicating magnetic anisotropy in these systems. The average 'g' value is in the range 2.21–2.47 and these values agree very well with the values obtained for other similar ruthenium(III) complexes [44,45]. The EPR spectrum recorded for [RuCl(PPh₃)(Nap-*o*-phd)] at liquid nitrogen temperature (77 K) showed very little variation from that observed at room temperature (Fig. 2) indicating rhombic distortion in these complexes.

3.2. Electrochemical studies

Cyclic voltammetric studies were performed for all the complexes at a glassy-carbon working electrode at a scan rate of 100 mV s^{-1} . The supporting electrolyte used was 0.1 M [NBu₄]BF₄ in dichloromethane solution. The concentration of the complex was 0.001 M. The solution was degassed with a continuous flow of N₂ gas before scanning. All the complexes showed only a reversible reduction wave

Table 3 EXAFS determined structural parameters at Ru, As and Br K-edges

in the -0.8 to -1.08 V range (Fig. 3). The voltammetric data are given in Table 2. As the ligand used in this work is not reversibly reduced within the potential limit (0.00 to -2.00 V), we believe that the reduction processes observed for these complexes are metal-centered only. The peak-to-peak separation (ΔE_p value) ranging from 200 to 260 mV reveals that the reduction process is quasireversible [46]. It has been observed that there is no variation in the redox potential of the complexes due to the replacement of triphenylphosphine by triphenylarsine. Similar behaviour has been reported for β -diketonato ruthenium(III) complexes [30] and complexes with N₂S₂ chromophore [28].

3.3. EXAFS studies

In spite of several attempts, single crystals suitable for X-ray structure determination were not obtained. Hence, the local structure and the coordination geometry of the

Complex	A-Bs ^a	N^{b}	r^{c} (Å)	$\sigma^{\rm d}$ (Å)	$E_{\rm F}^{\rm e}~({\rm eV})$	k-range (Å ⁻¹)	R-factor
1	Ru–N/O	4	2.01 ± 0.02	0.050 ± 0.005	6.514	3.59-16.08	25.00
	Ru–Cl/P	2	2.36 ± 0.03	0.077 ± 0.009			
	Ru–C	2	2.92 ± 0.03	0.050 ± 0.006			
2	Ru–N/O	4	2.01 ± 0.02	0.077 ± 0.008	8.064	3.46-16.05	26.57
	Ru–Cl	1	2.35 ± 0.03	0.050 ± 0.006			
	Ru–As	1	2.48 ± 0.03	0.063 ± 0.008			
	Ru–C	2	2.82 ± 0.03	0.081 ± 0.010			
3	Ru–N/O	4	2.01 ± 0.02	0.074 ± 0.007	8.619	3.59-16.00	24.67
	Ru–As/Br	2	2.50 ± 0.03	0.063 ± 0.007			
	Ru–C	2	2.90 ± 0.03	0.050 ± 0.007			
4	Ru–N/O	4	2.00 ± 0.02	0.059 ± 0.006	5.586	3.44-16.03	28.85
	Ru–P	1	2.34 ± 0.03	0.067 ± 0.008			
	Ru–Br	1	2.52 ± 0.03	0.071 ± 0.008			
	Ru–C	2	2.91 ± 0.03	0.050 ± 0.008			
2^{f}	As–C	3	1.93 ± 0.02	0.055 ± 0.006	-4.516	3.05-16.03	47.62
	As–Ru	1	2.49 ± 0.03	0.071 ± 0.008			
	As–C	6	2.90 ± 0.03	0.077 ± 0.009			
3 ^f	As–C	3	1.94 ± 0.02	0.055 ± 0.006	-7.526	2.82-16.00	40.80
	As–Ru	1	2.49 ± 0.03	0.077 ± 0.008			
	As–C	6	2.91 ± 0.03	0.077 ± 0.009			
2 ^g	As–C	3	1.92 ± 0.02	0.055 ± 0.006	-1.668	3.15-16.05	34.05
	As–Ru	1	2.48 ± 0.03	0.071 ± 0.008			
	As–C	6	2.91 ± 0.03	0.077 ± 0.009			
3 ^g	As–C	3	1.93 ± 0.02	0.055 ± 0.006	-5.238	3.00-16.00	29.52
	As–Ru	1	2.48 ± 0.03	0.077 ± 0.008			
	As–C	6	2.91 ± 0.03	0.077 ± 0.009			
3	Br–Ru	1	2.52 ± 0.03	0.074 ± 0.008	-0.665	2.93–14.04	29.75
4	Br–Ru	1	2.54 ± 0.03	0.087 ± 0.009	-2.375	2.93-13.53	28.23

^a Absorber (A)-backscatterers (Bs).

^b Coordination number N.

^c Interatomic distance r.

 $^{\rm d}$ Debye-Waller factor σ with its calculated deviation.

^e Fermi energy $E_{\rm F}$.

^f Evaluated using multiple scattering formalism.

^g Evaluated using Fourier filter analysis (1.0-3.0 Å range).

complexes were determined by EXAFS spectroscopy, which provides information on the coordination number, the nature of the scattering atoms surrounding the absorbing atom, the interatomic distance between the absorbing atom and the backscattering atoms and the Debye–Waller factor, which accounts for the disorders due to the static displacements and thermal vibrations [47]. For all the complexes in the fitting procedure, the coordination numbers were fixed to known values for different backscatterers surrounding the excited atom, and the other parameters including interatomic distances, Debye–Waller factor and Fermi energy value were varied by iterations.

3.3.1. Ru K-edge

The experimentally determined and theoretically calculated EXAFS functions in k space and their Fourier transforms in real space for the different ruthenium(III) Schiff base complexes with triphenylphosphine/arsine measured at the Ru K-edge are shown in Fig. 4 and the corresponding structural parameters are summarized in Table 3. In the analysis of the complexes 1–4, the first shell was found at about 2.01 Å consisting of two nitrogen and two oxygen backscatterers from the coordinating ligand. Due to the similar backscattering behaviour of the near neighbours, i.e., nitrogen and oxygen, occurring nearly at the same distance, they could not be fitted separately and thus were fitted as one shell with a coordination number four, with nitrogen amplitude- and phase-functions. The determined ruthenium-nitrogen and ruthenium-oxygen distances are in agreement with those found for similar organo-ruthenium complexes [48]. In complex 1, the second shell was determined at about 2.36 Å having one phosphorus and one chlorine backscatterer. For the same reason stated earlier, a single shell was fitted with a combined coordination

number of two with chlorine amplitude- and phase-functions. The Ru-P and Ru-Cl distances found for the new complexes match very well with those found in cis-[Ru(dppm)₂(MeCN)₂]-(BF₄)₂ (Ru–P distance ranges from 2.34 Å to 2.37 Å) [49] and mer-[RuCl₃(AsMe₂Ph)₃] (Ru-Cl distance ranges from 2.35 Å to 2.39 Å) [50]. In the case of complexes 2 and 4, a well-defined second shell with either chlorine or phosphorus backscatterer with a coordination number of one could be fitted at about 2.35 Å distance. Further, in complex 2, a single arsenic backscatterer was determined at about 2.48 Å distance. Due to the similar backscattering behaviour of arsenic and bromine backscatterers, they were fitted together with a combined coordination number of two, with arsenic amplitude- and phase-functions at a distance of about 2.50 Å in complex 3, whereas in the case of complex 4, the single bromine backscatterer was determined at about 2.52 Å distance. The determined ruthenium-arsenic and ruthenium-bromine distances were in good agreement with those reported for mer-[RuBr₃(AsMe₂Ph)₃] [50]. Further, in all the complexes an additional shell consisting of two carbon backscatterers, possibly originating from the proximal carbon atoms of the ligand, could be determined at about 2.90 Å distance (slightly shortened in the case of complex 2). The obtained EXAFS results indicate sixfold coordination geometry around the ruthenium atom.

3.3.2. As K-edge

The EXAFS evaluation at the As K-edge was performed using the multiple scattering formalism, as there could be considerable interference effects due to the neighbouring backscatterers. The multiple scattering calculations were done considering all the different pathways surrounding the central arsenic atom. The maximum order of scattering



Fig. 5. Experimental (solid line) and calculated (dotted line) EXAFS functions (a) and their corresponding Fourier transform plots (b) for the different ruthenium(III) Schiff base complexes with triphenylarsine measured at the As K-edge evaluated using multiple scattering formalism.



Fig. 6. Experimental (solid line) and calculated (dotted line) EXAFS functions (a) and their corresponding Fourier transform plots (b) for the different ruthenium(III) Schiff base complexes with triphenylphosphine/arsine measured at the Br K-edge.

and the maximum atoms in one path were set to three and the maximum path length was set to ten during the calculations. The experimentally determined and theoretically calculated EXAFS functions in k space and their Fourier transforms in real space for the different ruthenium(III) Schiff base complexes with triphenylarsine measured at the As K-edge evaluated using the multiple scattering formalism are shown in Fig. 5. The EXAFS determined structural parameters are given in Table 3. In both the complexes 2 and 3, the k^3 -weighted EXAFS function could be best described by a three-shell model. The first shell at about 1.93 Å was fitted with three carbon backscatterers originating from the three proximal carbon atoms of the coordinating triphenyl group. The reported arsenic-carbon distances range from 1.90 Å to 1.97 Å in mer-[RuCl₃(As-Me₂Ph)₃] and mer-[RuBr₃(AsMe₂Ph)₃] [50]. The second shell consisting of a single ruthenium backscatterer was determined at about 2.49 Å and the third shell comprising of six carbon backscatterers stemming from the second near-neighbour carbon atoms of the phenyl ring was determined at about 2.91 Å distance. In both the complexes 2 and 3, the arsenic-ruthenium distances determined at the As K-edge were in good agreement with those determined at the Ru K-edge. In both the cases, the fitting of the EXAFS function to the experimental spectra resulted in very high R-factor values. This could be attributed to the ambiguous coordination geometry around the arsenic atom and apart from the first three shells, the other shells could not be fitted unequivocally. Further, to confirm this supposition, Fourier filter analysis was performed in the range 1.0–3.0 Å, in order that the contributions from only the first three shells are considered. The results of the Fourier filter analysis are summarised in Table 3 and it could be noted that the *R*-factor value improved considerably by

about 29% in the case of complex 2 and about 28% in the case of complex 3.

3.3.3. Br K-edge

The experimentally determined and theoretically calculated EXAFS functions in k space and their Fourier transforms in real space for the different ruthenium(III) Schiff base complexes with triphenylphosphine/arsine measured at the Br K-edge are shown in Fig. 6 and the EXAFS determined structural parameters are summarized in Table 3. The Br K-edge EXAFS spectra of the complexes 3 and 4 were almost similar to each other. Both of them show a single huge peak in Fourier transform plot at about 2.52 Å (for 3) or 2.54 Å (for 4), which could be unequivocally fitted with a single ruthenium backscatterer. The obtained bromine-ruthenium distances were in agreement with those in similar bromo-ruthenium complexes [50]. Further, the values were also in accordance with distances determined from the Ru K-edge measurements.



Fig. 7. General structure of ruthenium(III) complexes.

The EXAFS investigations allowed us to determine only the local structure, however the exact geometry of the coordinated ligands could not be determined. Based on the analytical, spectral, cyclic voltammetry and EXAFS studies, the following octahedral structure has been proposed for the new ruthenium(III) complexes (Fig. 7).

4. Conclusion

Mononuclear complexes of the type $[RuX(EPh_3)(Nap$ o-phd)] (where X = Cl or Br; E = P or As; H₂-Nap-ophd = tetradentate Schiff base ligand) were synthesised. Based on spectral and the EXAFS studies, an octahedral geometry has been confirmed for all the complexes.

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