Novel Synthesis of $[Ru(phen)_2Br_2]X$ ($X =$ Br, ClO_4 or BPh_4) and Convenient Synthesis of Bis(2,2′-bipyridine) Complexes of Ruthenium(III) and Tris(2,2′-bipyridine) or (1,10-Phenanthroline) Complexes of Ruthenium(II)

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Abstract

Synthesis of the new ruthenium complexes $[Ru(phen)_2Br_2]X$ ($X =$ Br, ClO_4 or BPh_4) and convenient synthesis of $[Ru(bipy)_2Cl_2]X$, ($X =$ Cl or ClO_4) are reported using $[RuBr_3(Me_2SO)_3]$ and *fac*- and *mer*-$[RuCl_3(Me_2SO)_3]$. Syntheses of ruthenium(II) complexes $[Ru(bipy)_3]X_2$ ($X =$ Cl, Br, ClO_4 or BPh_4) and $[Ru(phen)_3]X_2$, ($X = ClO_4$ or BPh_4) are reported using $[RuBr_3(Me_2SO)_3]$, *fac*- and *mer*-$[RuCl_3(Me_2SO)_3]$, $[RuBr_2(Me_2SO)_3]$ and $(RuCl_2(Me_2SO)_4]$. The compounds are characterised using various physical methods.

Introduction

Reports on the syntheses of Ru(III) complexes containing (mono or bis) 2,2′-bipyridine or 1,10-phenanthroline and bromide ligands are few. $[RuBr_2(py)_2(bipy)][ClO_4]$ and $[RuBr(py)_3(bipy)][ClO_4)_2$ were made by the oxidation of their Ru(II) analogues with cerium(IV) ammonium sulfate [1]. $NH_4[RuBr_4(bipy)]2H_2O$ and $[phenH][RuBr_4(phen)]\cdot H_2O$ were made by the metathesis of chloro compounds by bromide [1]. In the present report the synthesis of dibromo bis(1,10-phenanthroline) ruthenium(III) is described for the first time. The synthesis is achieved by simple substitution of Me_2SO groups and a Br with 1,10-phenanthroline in $[RuBr_3(Me_2SO)_3]$. Synthesis of Ru(III) complexes containing mono, bis or tris diimine is generally achieved by the oxidation of their Ru(II) analogues with (i) chlorine [1–4], (ii) a cerium(IV) compound [5–9], (iii) lead(IV) oxide [10, 11] or (iv) silver nitrate [5]. The synthesis of $[Ru(bipy)_2Cl_2]Cl\cdot 2H_2O$ was first described by Liu *et al.* [3] by the oxidation of $[Ru(bipy)_2(C_2O_4)]^-$ with chlorine and later by Fergusson and Harris [4] by the oxidation of $[Ru(bipy)_2Cl_2]$ with chlorine. Recently Bottomley and Mukaida [12] reported a one-pot synthesis of this compound using a blue solution of ruthenium generated by the action of formic acid on $RuCl_3$. We report here its synthesis by the substitution of Me_2SO groups in easily synthesisable Ru(III) compounds, viz. *fac*- or *mer*-$[RuCl_3(Me_2SO)_3$ [13]. Syntheses of tris diimine complexes of Ru(II) are also reported here from *fac*- or *mer*-$[RuCl_3(Me_2SO)_3]$, *cis*-$[RuCl_2(Me_2SO)_4]$, $[RuBr_3(Me_2SO)_3]$ and $[RuBr_2(Me_2SO)_3]$.

Experimental

Ruthenium trichloride trihydrate was obtained from Aurora Matthey Ltd., Calcutta. *fac*- and *mer*-$[RuCl_3(Me_2SO)_3]$, $[RuBr_3(Me_2SO)_3]$, $[RuBr_2(Me_2SO)_3]$ and *cis*-$[RuCl_2(Me_2SO)_4]$ were prepared according to reported methods [13–15]. The analyses for chloride and bromide were carried out by a standard method [16]. Carbon, hydrogen and nitrogen analyses were obtained from the Regional Sophisticated Instrumentation Centre, C.D.R.I., Lucknow. Physical measurements, viz. IR, UV–Vis and ESR spectra, magnetic and conductivity measurements were carried out as reported earlier [13].

(a) $[Ru(phen)_2Br_2]Br$

To a solution of $[RuBr_3(Me_2SO)_3]$ (0.2 g) in toluene (10 cm^3), 1,10-phenanthroline (0.1 g) (molar ratio 2:3) was added and the mixture warmed on a water-bath for 10 min. A compound separated, which was centrifuged, washed with ethanol and then with ether and dried *in vacuo*. Yield 0.16 g, (66%).

(b) $[Ru(phen)_2Br_2]X$, ($X = ClO_4$, BPh_4)

$[Ru(phen)_2Br_2]Br$ (0.2 g) was dissolved in methanol (20 cm^3) and a methanolic solution of NH_4ClO_4 or $NaBPh_4$ (molar ratio of the complex: X = 2:3) was added to it. In the case of $NaBPh_4$, an orange compound separated on mixing at room temperature, whereas in the case of NH_4ClO_4 refluxing of the mixture for 30 min and cooling to room temperature yielded a brown crystalline com-

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pound. The compounds were centrifuged, washed with ether and dried *in vacuo.*

(c) $[Ru(bipy)_2Cl_2]Cl\cdot 2H_2O$

To a solution of *fac*- or *mer*-$[RuCl_3(Me_2SO)_3]$ (0.2 g) in methanol (10 cm^3), 2,2′-bipyridine (0.11 g) (molar ratio, 2:3) was added and the mixture refluxed on a water-bath for 30 min. In the case of *mer*-$[RuCl_3(Me_2SO)_3]$, the product separated out on cooling, whereas in the case of *fac*-$[RuCl_3(Me_2SO)_3]$, diethyl ether was added to precipitate the orange coloured compound. It was centrifuged, washed with ether and dried *in vacuo*. Yield 0.18 g (75%).

(d) $[Ru(bipy)_2Cl_2]ClO_4$

To a solution of $[Ru(bipy)_2Cl_2]\cdot Cl\cdot 2H_2O$ (0.2 g) in methanol (10 cm^3), a solution of NH_4ClO_4 (0.05 g) in methanol (5 cm^3) was added and the mixture was refluxed on a water-bath for 15 min, concentrated and cooled to room temperature. A brown crystalline compound separated out. It was centrifuged, washed with ether and dried *in vacuo*.

(e) $[Ru(bipy)_3]Cl_2\cdot H_2O$

To a solution of *fac*- or *mer*-$[RuCl_3(Me_2SO)_3]$ (0.2 g) in ethanol (20 cm^3), 2,2′-bipyridine (0.22 g) (molar ratio 1:3) was added and the mixture was refluxed for 2 h, when a dark orange solution was obtained. The solution was concentrated to 5 cm^3, cooled to room temperature and diethyl ether was added to precipitate the compound. The compound was centrifuged, washed with ether and dried *in vacuo*. Yield 0.2 g (65%).

The compound could also be obtained by the reaction of $[RuCl_2(Me_2SO)_4]$ and 2,2′-bipyridine (molar ratio 1:4) under the conditions mentioned above.

(f) $[Ru(bipy)_3]Br_2$

$[RuBr_3(Me_2SO)_3]$ (0.2 g) was dissolved in ethanol (20 cm^3) and a solution of 2,2′-bipyridine (0.2 g) (molar ratio 1:4) in ethanol was added to it. The mixture was refluxed for 2 h when an orange solution was obtained. The solution was concentrated, cooled, and diethyl ether was added to precipitate a yellow–orange compound. It was centrifuged, washed with ether and dried *in vacuo*. Yield 0.18 g (72%).

The compound could also be obtained by the reaction of $[RuBr_2(Me_2SO)_3]$ and 2,2′-bipyridine under the conditions mentioned above.

(g) $[Ru(bipy)_3]X_2\cdot H_2O$ ($X = ClO_4$, BPh_4)

To the orange coloured solution obtained in reaction (e) or in reaction (f) above, an ethanolic solution of NH_4ClO_4 or $NaBPh_4$ (molar ratio of the complex: X = 1:3) was added. In the case of $NaBPh_4$, the mixture on stirring at room temperature for 5 min yielded an orange coloured compound, whereas in the case of NH_4ClO_4, refluxing of the mixture for 15 min and cooling to room temperature yielded the red crystalline compound. The compounds were separated as in (e) above.

(h) $[Ru(phen)_3]X_2\cdot nH_2O$ ($X = ClO_4$, $n = 2$; $X = BPh_4$, $n = 6$)

fac- or *mer*-$[RuCl_3(Me_2SO)_3]$ (0.2 g) was dissolved in ethanol (5 cm^3) and 1,10-phenanthroline (0.28 g) (molar ratio 1:3) was added to the solution. To the above reaction mixture, toluene (10 cm^3) was added and the mixture heated on a water-bath for 2 h. The solution of NH_4ClO_4 or $NaBPh_4$ (molar ratio of the complex:X = 1:3) was added. The complexes separated in a way similar to that in reaction (g) above.

The compounds were obtained also when $[RuCl_2(Me_2SO)_4]$ or $[RuBr_2(Me_2SO)_3]$ was used instead of $[RuCl_3(Me_2SO)_3]$.

Results and Discussion

Reported syntheses of ruthenium(III) complexes containing 2,2′-bipyridine or 1,10-phenanthroline were generally by the oxidation of their ruthenium(II) analogues [1–11]. Only in the case of the mono diimine complexes have direct reactions of commercially available $RuCl_3\cdot xH_2O$ with the diimines been reported [17–19]. We have been able to achieve the synthesis of bis diimine ruthenium(III) complexes using easily synthesisable compounds, viz. *fac*- or *mer*-$[RuCl_3(Me_2SO)_3]$ and $[RuBr_3(Me_2SO)_3]$. Reaction between the Me_2SO complexes and the diimine resulted, under suitable conditions, in complete substitution of Me_2SO and the formation of bis diimine ruthenium(III) complexes.

The reaction of $[RuBr_3(Me_2SO)_3]$ with 1,10-phenanthroline yielded a brown compound of the composition $[Ru(phen)_2Br_2]Br$. Reactions of $[Ru(phen)_2Br_2]Br$ with NH_4ClO_4 or $NaBPh_4$ in methanolic solution yielded $[Ru(phen)_2Br_2]X$, ($X = ClO_4$, BPh_4). The composition of these compounds, viz. $[Ru(phen)_2Br_2]X$ (X = Br, ClO_4 or BPh_4) was confirmed by the elemental analyses (Table 1). They showed molar conductance values in acetonitrile in the range 100–110 Ω^{-1} cm^2 mol^{-1} (Table 1), confirming that these are 1:1 electrolytes [20]. The IR spectra of these compounds showed bands at 1600, 1575, 1425, 1145, 845 and 725 cm^{-1} which are characteristic of 1,10-phenanthroline [21]. No band of appreciable intensity was observed in the region 1100–900 cm^{-1} (except for ClO_4^-), which confirmed the absence of any Me_2SO groups present. In the case of complexes containing ClO_4^- and BPh_4^- anions, IR absorptions at 1085 and 1580

TABLE 1. Analytical and physical data of ruthenium(III) and ruthenium(II) complexes containing 2,2'-bipyridyl or 1,10-phenanthroline

Compounds	Colour	Λ_M in CH_3CN (Ω^{-1} cm^2 mol^{-1})	Analytical data^a (%)		
			C	H	N
$[Ru(phen)_2Br_2]Br$	brown	118	41.0(41.1)	2.6(2.3)	7.7(8.0)
$[Ru(phen)_2Br_2]ClO_4$	reddish brown	120	39.6(39.9)	2.0(2.2)	7.6(7.8)
$[Ru(phen)_2Br_2]BPh_4$	orange	120	61.0(61.2)	3.6(3.8)	5.6(5.9)
$[Ru(bipy)_2Cl_2]Cl·2H_2O$	orange	120	43.1(43.2)	3.8(3.6)	9.9(10.1)
$[Ru(bipy)_2Cl_2]ClO_4$	brown	130	41.0(41.1)	2.9(2.7)	9.4(9.6)
$[Ru(bipy)_3]Cl_2·H_2O$	orange	220	54.3(54.7)	3.6(3.9)	12.5(12.8)
$[Ru(bipy)_3]Br_2·2H_2O$	yellow–orange	260	42.4(42.6)	3.8(3.3)	9.7(9.9)
$[Ru(bipy)_3](ClO_4)_2H_2O$	red	230	45.9(45.8)	3.2(3.3)	10.6(10.7)
$[Ru(bipy)_3](BPh_4)_2H_2O$	orange	220	76.0(76.3)	5.6(5.5)	6.7(6.9)
$[Ru(phen)_3](ClO_4)_2·2H_2O$	brown	210	46.2(46.4)	3.0(3.0)	8.8(9.0)
$[Ru(phen)_3](BPh_4)_26H_2O$	yellow–orange	220	72.3(72.6)	5.1(5.4)	6.0(6.1)

^{a}Calculated values are in parentheses

cm^{-1}, respectively were also observed which are characteristic of the ionic nature of the respective anionic groups [22, 23].

The magnetic moment (μ_{eff}) values at room temperature for $[Ru(phen)_2Br_2]Br$ and $[Ru(phen)_2Br_2]ClO_4$ were 2.2 and 1.8 BM, respectively, which is characteristic of a low-spin d^5, ruthenium(III) complex. A room temperature EPR spectrum of $[Ru(phen)_2Br_2]Br$ showed a broad signal at g = 2.18 which further confirms the low-spin d^5 configuration for this complex [14]. The electronic absorption spectrum of the complex (Table 2) in CH_3CN showed absorptions at 560, 490, 395 and 360 nm having ϵ in the order of 10^3. These bands may be assigned to the charge-transfer from Br^- to the empty orbital on the metal viz. ($e_g{}^*$). Similar observations were reported for $[Ru(bipy)_2Cl_2]Cl·2H_2O$ [4]. Electronic absorptions in the UV region were observed at 292 and 265 nm with ϵ in the order of 10^4. These bands may be assigned to the π–π^* type of transition in 1,10-phenanthroline [4, 24].

TABLE 2. Electronic absorption spectral data of the complexes

Compounds	λ_{max} (nm) (ϵ) in CH_3CN
$[Ru(phen)_2Br_2]Br$	560(1.36 × 10^3); 490(4.30 × 10^3); 395(3.25 × 10^3); 360(2.93 × 10^3); 292sh; 267(4.2 × 10^4)
$[Ru(bipy)_2Cl_2]Cl·2H_2O$	420sh; 380(6.3 × 10^3); 310sh; 295(2.4 × 10^4)
$[Ru(bipy)_2Cl_2]ClO_4$	425sh; 382(6.5 × 10^3); 310sh; 295(2.7 × 10^4)
$[Ru(bipy)_3]Cl_2·2H_2O$	450(1.15 × 10^4); 420sh; 390sh; 350sh; 288(6.76 × 10^4); 254sh; 242(2.07 × 10^4)
$[Ru(bipy)_3][ClO_4]_2·H_2O$	450(1.12 × 10^4); 430sh; 392sh; 325sh; 284(7.5 × 10^4); 255sh; 240sh
$[Ru(bipy)_3][BPh_4]_2·H_2O$	450(1.32 × 10^4); 430sh; 395sh; 323sh; 286(7.8 × 10^4); 255sh; 240sh
$[Ru(phen)_3][BPh_4]_2·6H_2O$	442(1.64 × 10^4); 418(1.62 × 10^4); 315sh; 285sh; 262 (10.2 × 10^4)

$[Ru(bipy)_2Cl_2]Cl·2H_2O$, synthesised by the substitution of Me_2SO molecules from *fac*- or *mer*-$[RuCl_3(Me_2SO)_3]$, was characterised by elemental analysis (Table 1) and various physical methods. Similarly, $[Ru(bipy)_2Cl_2]ClO_4$ synthesised by the metathesis of the chloro compound, was also characterised. The electronic absorption spectra of these compounds in acetonitrile were similar to those reported earlier [3–5, 12]. In the complexes, bands at 1605, 1570, 1460, 1440, 1420, 1315, 1242, 1160 and 770 cm^{-1} were observed, which are characteristic of 2,2'-bipyridine [21] and no bands due to Me_2SO (*vide supra*) were observed. Far IR spectra showed two bands at 340 and 320 cm^{-1} which may be due to ν(Ru–Cl), similar to those reported earlier [3]. The presence of two bands due to ν(Ru–Cl) conforms to the *cis* geometry of the complex in the solid state [3]. In the case of $[Ru(bipy)_2Cl_2]ClO_4$ a very strong band at 1090 cm^{-1} was also observed, which is characterisitic of the $ClO_4{}^-$ group present as an anion [22]. An EPR spectrum of $[Ru(bipy)_2Cl_2]Cl·2H_2O$ in the powder form at room temperature showed only one broad signal around g = 2.15. However, a frozen solution EPR spectrum in chloroform at liquid nitrogen temperature gave three g values, g_1 = 2.62, g_2 = 2.43, g_3 = 1.64. *cis*-$[Ru(bipy)_2Cl_2]^+$, belonging to a C_2 point group, is expected to have a rhombic distortion, thereby giving three g values [25]. Thus the *cis* geometry proposed [3] for [Ru(bipy)$_2$Cl$_2$]Cl·2H$_2$O, is further confirmed by the EPR results. Similar results were reported for a low-spin Fe(III) complex, viz. [Fe(bipy)$_2$(CN)$_2$]$^+$ [25].

[Ru(bipy)$_3$]Cl$_2$ and [Ru(L–L)$_3$]X$_2$·nH$_2$O (X = ClO$_4$, BPh$_4$; L–L = bipy or phen) were obtained by the reaction of *fac*- or *mer*-[RuCl$_3$(Me$_3$SO)$_3$], *cis*-[RuCl$_2$(Me$_2$SO)$_4$] or [RuBr$_2$(Me$_2$SO)$_3$] with excess of the diimines and metathesis of the chloro/bromo analogue (obtained *in situ*) with ClO$_4^-$ or BPh$_4^-$, respectively [Ru(bipy)$_3$]Br$_2$·2H$_2$O was obtained by the reaction of [RuBr$_3$(Me$_2$SO)$_3$] or [RuBr$_2$(Me$_2$SO)$_3$] with excess of 2,2′-bipyridine. These complexes are diamagnetic in nature, thereby confirming that ruthenium is present in the 2+ oxidation state. The reduction of ruthenium(III) in [RuX$_3$(Me$_2$SO)$_3$] (X = Cl or Br) to ruthenium(II) compounds might have been achieved by the diimines, which could act both as the ligand and the reducing agents, in these reactions. In fact, most of the methods of preparation of these complexes make use of the reaction of ruthenium(III) or ruthenium(IV) compounds with excess of diimines [26]. [Ru(bipy)$_3$]Cl$_2$·H$_2$O, obtained either from [RuCl$_3$(Me$_2$SO)$_3$] or from *cis*-[RuCl$_2$(Me$_2$SO)$_4$] and [Ru(bipy)$_3$]X$_2$·H$_2$O (X = ClO$_4$ or BPh$_4$) obtained either from *fac*- or *mer*-[RuCl$_3$(Me$_2$SO)$_3$] or from [RuBr$_3$(Me$_2$SO)$_3$] are the same as evidenced from the overlapping IR and ^{1}H NMR spectra.

The characterization of these complexes was made with the help of analytical data (Table 1) and various physical methods. The UV–Vis spectra of these complexes (Table 2) were super-imposable with those of the reported ones [24, 27, 28]. The IR spectra of all these complexes did not show absorption bands due to Me$_2$SO groups (*vide supra*). All IR absorption bands due to 2,2′-bipyridine or 1,10-phenanthroline were present (*vide supra*). The IR spectra of these complexes in the region 350–200 cm^{-1} showed no absorption bands, thereby confirming the absence of any covalently bonded terminal chloro groups. The presence of ionic ClO$_4^-$ groups was confirmed by the appearance of a strong and broad band at 1085 cm^{-1} [22]. The presence of BPh$_4^-$ groups in the complexes was confirmed by the appearance of bands at 1575 and 1480 cm^{-1} [23]. Appearance of broad bands at 3450 and 1630 cm^{-1} may be attributed to the presence of lattice water in these complexes and may be assigned to ν(O–H) and δ(HOH), respectively [22].

The ^{1}H NMR spectra of [Ru(bipy)$_3$]X$_2$ (X = Cl, ClO$_4$) in (CD$_3$)$_2$SO showed a doublet at δ 8.9, a triplet at δ 8.2 and a quintet at δ 7.7. The signals were the same as reported for the [Ru(bipy)$_3$]$^{2+}$ systems [29]. The ^{1}H NMR spectrum of the compound [Ru(bipy)$_3$](BPh$_4$)$_2$·H$_2$O showed all the signals as mentioned above and more signals in the region δ 6.7 to 7.3 which could be assigned due to the phenyl protons of BPh$_4^-$ groups. The ^{1}H NMR spectrum of [Ru(phen)$_3$](ClO$_4$)$_2$ showed signals in the region δ 7.3–8.6. The signals are similar to the ones reported earlier [30].

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