One-pot and selective synthesis of a series of $[RuCl_{6-2n}L_n]$ (L = bidentate ligand, $n = 0$–3) types of complexes with polypyridyl ligands; another example of the synthetic utility of 'ruthenium-blue' solution

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(Received November 8, 1991; revised February 14, 1992)

Abstract

Convenient (one-pot) and selective syntheses of a series of ruthenium complexes with polypyridyl ligands, $[RuL_3]^{2+}$, *cis*-$[RuCl_2L_2]^+$ and $[RuCl_4L]^-$ (L = bpy, phen or Hdpa (di-2,2-dipyridylamine)), including $[RuCl_6]^{3-}$, have been reported as further examples of the synthetic utility of 'ruthenium-blue' solution. The methods developed here are also useful for synthesizing selectively such pair complexes as $[Ru^{III}Cl_3(terpy)]$–$[Ru^{II}(terpy)_2]^{2+}$ and $[Ru^{III}Cl_4py_2]^-$–$[Ru^{II}Cl_2py_4]$.

Introduction

Interest in ruthenium complexes with polypyridyl ligands has been growing recently, especially because they can participate in photocatalytic or electron transfer reactions [1–7]. These complexes have generally been synthesized using a commercial hydrated ruthenium chloride, '$RuCl_3 \cdot nH_2O$', as the starting material [8–13]. Several reports about preparations of ruthenium complexes using 'ruthenium-blue' solution, an activated species generated from hydrated ruthenium chloride, have appeared over the past years [14–20]. Although the constitution of the 'ruthenium-blue' solution is still not settled [21, 22], the solution appears to be useful for the syntheses. Actually, we have performed syntheses of a series of tetrakis(pyridine)ruthenium(II, III or IV) complexes with chloro, aqua, hydroxo, nitrosyl, nitro, nitrito, methoxo or monooxygen ligands [23–25]. Syntheses of numerous β-diketonato complexes of Ru(II and III) have also been reported [20]. The present paper reports one-pot and selective syntheses of a series of ruthenium complexes with polypyridyl ligands (bpy, phen, Hdpa (di-2,2-dipyridylamine)), $[RuL_3]^{2+}$, *cis*-$[RuCl_2L_2]^+$ and $[RuCl_4L]^-$, along with $[RuCl_6]^{3-}$, as further examples of the synthetic utility of 'ruthenium-blue' solution. The methods developed here are also useful for synthesizing selectively such pair complexes as $[Ru^{III}Cl_3(terpy)]$–$[Ru^{II}(terpy)_2]^{2+}$ and $[Ru^{III}Cl_4py_2]^-$–$[Ru^{II}Cl_2py_4]$.

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Results and discussion

Although most of the complexes prepared here are not new, the following advantages are emphasized, in comparison to previous methods for the corresponding polypyridyl complexes which have been prepared without the use of 'ruthenium-blue' solution: (i) procedure is simple and reproducible results are obtained with less skill, (ii) four species ($[RuL_3]^{2+}$, *cis*-$[RuCl_2L_2]^+$, and $[RuCl_4L]^-$, including $[RuCl_6]^{3-}$ which has no coordinated polypyridyl ligand), are available selectively in good yields. We believe that the present method is useful for syntheses of other Ru complexes with polypyridyl ligands. The following are the main factors which affect the present selective syntheses: (a) the amount-of-substance ratio of polypyridyl ligand to Ru ion, (b) existence (or absence) of HCl, (c) reaction temperature. Typical conditions for the syntheses of 2,2′-bipyridine complexes are summarized in Table 1.

0020-1693/92/$5.00

TABLE 1. Typical experimental conditions for the selective syntheses of 2,2′-bpy complexes[a]

	bpy/Ru	en/Ru	HCl	Temperature
$[Ru(bpy)_3]^{2+}$	4/1		not added	reflux
$[RuCl_2(bpy)_2]^+$	2.3/1		added	reflux
$[RuCl_4(bpy)]^-$	2.3/1		added	room temperature
$[RuCl_6]^{3-}$		3/1	added	reflux

[a]Details are described in 'experimental'.

Absence of hydrochloric acid and presence of excess amounts of 2,2′-bpy ligand are essential for a high yield synthesis of $[Ru(bpy)_3]^{2+}$ (see Table 1); otherwise the product is contaminated by *cis*-$[RuCl_2(bpy)_2]Cl$. When the procedure for *cis*-$[RuCl_2(bpy)_2]Cl$ is carried out without HCl, it also gives a mixture of *cis*-$[Ru(bpy)_3]^{2+}$ and *cis*-$[RuCl_2(bpy)_2]^+$. The preparation of $[RuCl_4(bpy)]^-$ should be run at room temperature.

In addition to these complexes with the polypyridyl ligand(s), hexachlororuthenate(III), $[RuCl_6]^{3-}$, formulated as $(enH_2)_2[RuCl_6]Cl \cdot H_2O$, can be isolated by almost the same procedure as that adopted for the preparation of *cis*-$[RuCl_2(bpy)_2]Cl$, by using en ligand instead of 2,2′-bpy ligand. The procedure which gives the $[RuCl_6]^{3-}$ complex ion was followed in an attempt to obtain *cis*-$[RuCl_2(en)_2]^+$, but we could not isolate it under our experimental conditions.

The mono- and bis-types of chelate complexes, $[RuCl_4(bpy)]^-$ and *cis*-$[RuCl_2(bpy)_2]^+$, are useful starting materials for the preparation of mixed ligand complexes of ruthenium(II) and (III). In particular, the $[RuCl_2(bpy)_2]^+$ complex is worth using for such preparations, compared to the corresponding ruthenium(II) complex, $[RuCl_2(bpy)_2]$, because the former complex is pretty soluble in various solvents, especially in water, and can liberate its chloride ligands easily. Preparative methods reported so far for *cis*-$[RuCl_2(bpy)_2]Cl$ are limited to those of Bailer and co-workers [13], where a two-stage procedure is necessary: ($[RuCl_2(bpy)_2]$ is prepared first and, then it is oxidized by Cl_2 to give $[RuCl_2(bpy)_2]Cl$). Since $[RuCl_2(bpy)_2]Cl$ can easily be reduced quantitatively to $[RuCl_2(bpy)_2]$ when an acidic solution of the Ru(III) complex is warmed while adding a small amount of $SnCl_2 \cdot 2HCl$, the present method which gives $[RuCl_2(bpy)_2]Cl$ is useful as a convenient and high yield synthesis of $[RuCl_2(bpy)_2]$*. Another preparative method for the latter complex, $[RuCl_2(bpy)_2]$, has recently been reported by Sullivan *et al.* [26].

'Ruthenium-blue' solution can react with 2,2′:6′2″-terpyridine to give two type of complexes, $[RuCl_3(terpy)]$ and $[Ru(terpy)_2]^{2+}$, by the same experimental conditions as those adopted for $[RuCl_2(bpy)_2]^+$ and $[Ru(bpy)_3]^{2+}$, respectively.

The present method is also applicable to the selective synthesis of two types of complexes with pyridine ligands: $[RuCl_2py_4]$ and $[RuCl_4py_2]^-$. When 'ruthenium-blue' solution was mixed with pyridine, it gave the former complex, while adding HCl to the mixed solution afforded the latter. More complexes with pyridine analogue ligands are available: when 'ruthenium-blue' solution was treated by the same procedure as that described for $[RuCl_2(py)_4]$, using 4-methylpyridine, 3-methylpyridine, 4-ethylpyridine or 3-ethylpyridine, the complexes with a composition of $[Ru^{II}Cl_2L_4]$ were obtained while the complexes with that of $[Ru^{III}Cl_4L_2]^-$ could be isolated when 4-cyanopyridine or 4-chloropyridine was used**. This result which gives two types of pyridine analogue complexes, in which the oxidation number of the ruthenium atom differs, is very similar to the previous observation that two type of complexes of ruthenium(II) and (III) with various β-diketonato ligands, ($[Ru^{II}(\beta\text{-diketonato})_3]^-$ and $[Ru^{III}(\beta\text{-diketonato})_3]$), have been obtained depending on the nature of the β-diketonato ligands used (i.e. p*K* or Hammet constant of the ligands) [20]; both 4-cyanopyridine and 4-chloropyridine are ligands that have a positive Hammet constant of the substituent on the ligand, whereas alkylpyridines have a negative one. No hexakis(pyridine) type of complex, $[Ru(py)_6]^{2+}$, could be obtained by the present method.

*To a hydrochloric acid solution (2 mol dm^{-3}, 30 cm^3) containing *cis*-$[RuCl_2(bpy)_2]Cl \cdot 2H_2O$ (100 mg) $SnCl_2 \cdot 2HCl$ (solid, 20 mg) was added. The brown solution darkened; then it was concentrated on a hot plate to precipitate a black solid. The solid material was collected by filtration, washed with water, and air dried. Yield 90%.

**$[RuCl_2(py\text{-}X)_4]$ (X = 3-Me, 3-Et, 4-Et): the complexes were prepared by a procedure similar to that for $[RuCl_2(4Me\text{-}py)_4]$ [25]. To the blue solution (0.33 g of '$RuCl_3 \cdot 3H_2O$') was added each alkylpyridine (25 cm^3). The mixed solution was refluxed for 1 h, and then the volume of the solution was reduced on a rotary evaporator until yellow crystals deposited. The crystals were collected by filtration and washed with water, ethanol, and finally ether. *Anal.* Calc. for $[RuCl_2(3Me\text{-}py)_4]$: N, 10.28; C, 52.94; H, 5.18. Found: N, 10.35; C, 52.91; H, 5.30%. Calc. for $[RuCl_2(3Et\text{-}py)_4]$: N, 9.32; C, 56.70; H, 6.41. Found: N, 9.61; C, 56.70; H, 6.41%. Calc. for $[RuCl_2(4Et\text{-}py)_4]$: N, 9.32; C, 56.70; H, 6.41. Found: N, 9.61; C, 56.50; H, 6.41%. {(X-py)H}$[RuCl_4(py\text{-}X)_2]$ (X = 4-CN, 4-Cl): the complexes were prepared by the same procedures, adding of large amount of the ligands (the amount-of-substance ratio of ligand to Ru was 20–30/1), to that of $[RuCl_2(py)_4]$ reported previously [25]. *Anal.* Calc. for {(4Cl-py)H}$[RuCl_4(4Cl\text{-}py)_2] \cdot 4H_2O$: C, 27.43; H, 3.22; N, 6.39. Found: C, 27.20; H, 2.80; N, 6.73%. Calc. for {(4CN-py)H}$[RuCl_4(4CN\text{-}py)_2] \cdot H_2O$: C, 37.64; H, 2.63; N, 14.63. Found: C, 37.85; H, 2.73; N, 14.68%.

Experimental

'Ruthenium-blue' solution was first prepared according to the procedure reported previously [25]. Hydrated ruthenium trichloride, '$RuCl_3 \cdot 3H_2O$' (Nihon Engelhardt, 0.5 g) was dissolved in a mixed solution of EtOH (15 cm^3) and H_2O (10 cm^3), and the solution was refluxed gently with continuous bubbling. The color of the solution changes gradually from a dark brown to deep blue, via dark green, within approximately 4 h, which is a necessary refluxing time for a good yield of the products described below. At times, the coloration may stop at the stage where a dark green solution is generated, without giving the deep blue solution. However, the dark green solution, obtained by 4 h refluxing, is still useful for the present syntheses when the solution is refluxed further (15–30 min) by adding more fresh EtOH (5 cm^3). A prolonged refluxing may result in the deposition of a black solid material on the walls of the glassware (this is a good indication of completion of the procedure to give the blue solution). The black material appears to be either ruthenium oxide or some cluster compound. (Formation of the black material can be avoided if the procedure is carried out under argon. In this case, however, some modifications will be needed for the following procedures, especially in the mole ratio of polypyridyl ligand to Ru ion.)

$[Ru(bpy)_3](ClO_4)_2 \cdot 0.5H_2O$ [27]

To the hot blue solution (containing 0.5 g of '$RuCl_3 \cdot 3H_2O$') was added 2,2'-bipyridine (bpy) (1.2 g) in EtOH (10 cm^3). The mixture was refluxed for 0.5–1 h, during which time the solution color changed from blue to deep red. The solution was evaporated to dryness using a rotary evaporator. The solid materials was dissolved in acetone (30 cm^3) to give a red solution. If any insoluble matter remained (it is mostly *cis*-$[RuCl_2(bpy)_2]Cl$), it was separated by filtration. $[Ru(bpy)_3](ClO_4)_2 \cdot 0.5H_2O$ was isolated, as red crystals, by adding $NaClO_4$ (0.5 g/H_2O 10 cm^3) to the red solution. The crystals collected were washed by acetone, and then ether, and were recrystallized with diluted HCl (3 mol dm^{-3}) solution. Yield 80%. *Anal.* Found: C, 46.32; H, 3.03; N, 10.80. Calc. for $RuC_{30}H_{25}N_6Cl_2O_{8.5}$: C, 46.34; H, 3.24; N, 10.80%. UV–Vis spectral data, λ_{max} (nm) (ϵ mol^{-1} dm^3 cm^{-1})) in H_2O: 454 (1.33×10^4), 428 (1.17×10^4). ($[Ru(bpy)_3]Cl_2 \cdot 6H_2O$ was deposited from the red solution when the volume of the solution was reduced. Yield 60%. *Anal.* Found: C, 48.47; H, 4.25; N, 11.85. Calc. for $RuC_{30}H_{36}N_6Cl_2O_6$: C, 48.13; H, 4.84; N, 11.22%.)

cis-$[RuCl_2(bpy)_2]Cl \cdot 2H_2O$ [8, 13]

To the hot blue solution (0.5 g of '$RuCl_3 \cdot 3H_2O$') was added bpy (0.7 g) in EtOH (10 cm^3), along with hydrochloric acid (2 cm^3). The mixture was refluxed for 0.5 h, during which time the solution color changed from blue to dark brown. The volume of the solution was reduced by using a rotary evaporator (or by heating on a hot plate). The deep brown crystalline materials deposited were collected by filtration, washed with acetone and then ether. The crude product was recrystallized with hot diluted HCl (3 mol dm^3). Yield 90%. *Anal. Found*: *C*, 43.42; *H*, 3.60; *N*, 10.18; *Cl*, 19.0. *Calc.* for $RuC_{20}H_{20}N_4Cl_3O_2$: C, 43.21; H, 3.62; N, 10.07; Cl, 19.1%. μ_{eff}: 1.96 BM (291 K). UV–Vis spectral data, λ_{max} (nm) (ϵ(mol^{-1} dm^3 cm^{-1})) in H_2O: 370 (5.51×10^4), 315 (2.78×10^4).

{(bpy)H}[$RuCl_4$(bpy)]$\cdot H_2O$ [10]

To the blue solution (0.33 g of '$RuCl_3 \cdot 3H_2O$'), which was cooled down by ice water was added bpy (0.5 g) in EtOH (10 cm^3), along with hydrochloric acid (2 cm^3). The mixed solution was stirred for 2 h at room temperature. The resultant solution was kept standing overnight, without a glass cover, to reduce the solution volume spontaneously. Reddish-brown crystals which deposited were collected by filtration, washed with EtOH, and then ether. Yield 50%. *Anal.* Found: C, 41.57; H, 3.12; N, 9.60. *Calc.* for $RuC_{20}H_{19}N_4Cl_4O$: C, 41.82; H, 3.33; N, 9.75%. μ_{eff}: 2.01 BM (293 K). UV–Vis spectral data, λ_{max} (nm) (ϵ(mol^{-1} dm^3 cm^{-1})) in HCl (6 mol dm^{-3}): 400(sh), 365 (5.3×10^3), 294 (3.2×10^4), 254 (1.8×10^4).

{(en)H_2}$_2$[$RuCl_6$]$Cl \cdot H_2O$ [28, 29]

To the hot blue solution (0.5 g of '$RuCl_3 \cdot 3H_2O$') was added ethylenediamine hydrochloric acid salt (en·2HCl, 0.8 g) solution. The mixed solution was refluxed at 120 °C for 1 h, while the color of the mixed solution changed slowly to brown. The solution was transferred to a beaker to reduce its volume by heating, and then it was kept overnight at room temperature. Brown crystals appeared. These were collected by filtration, washed with water, EtOH and then ether. Yield 60%. *Anal.* Found: C, 9.71; H, 4.54; N, 11.34; Cl, 50.55. Calc. for $RuC_4H_{24}N_4Cl_7O$: C, 9.77; H, 4.51; N, 11.39; Cl, 50.49%. μ_{eff}: 2.13 BM (298 K). UV–Vis spectral data, λ_{max} (nm) (ϵ(mol^{-1} dm^3 cm^{-1})) in HCl (12 mol dm^{-3}): 348 (3.0×10^3), 310 (2.2×10^3).

$[Ru(phen)_3](ClO_4)_2 \cdot H_2O$ [27]

This was prepared by the same procedure as that for the corresponding $[Ru(bpy)_3]Cl_2 \cdot 2H_2O$. Yield 60%. *Anal.* Found: C, 50.25; H, 2.77; N, 9.80. Calc. for $RuC_{36}H_{26}N_6Cl_2O_9$: C, 50.35; H, 3.05; N, 9.78%. UV–Vis spectral data in H_2O, λ_{max} (nm) (ϵ(mol^{-1} dm^3 cm^{-1})): 448 (1.73×10^4), 262 (1.23×10^5).

cis-[$RuCl_2(phen)_2$]$Cl \cdot 2H_2O$ [12]

This was prepared by the same procedure as that for *cis*-[$RuCl_2(bpy)_2$]$Cl \cdot 2H_2O$. Yield 90%. *Anal.* Found: C, 47.70; H, 3.12; N, 9.30. Calc. for $RuC_{24}H_{20}N_4Cl_3O_2$: C, 47.73; H, 3.33; N, 9.27%. UV–Vis spectral data, λ_{max} (nm) (ϵ(mol^{-1} dm^3 cm^{-1})) in CH_3CN: 372 (7.1×10^3), 265 (5.5×10^4). Paramagnetic.

{(phen)H}[$RuCl_4$(phen)]$\cdot H_2O$ [10]

This complex was prepared by the same procedure as that for bpyH[$RuCl_4$(bpy)]$\cdot H_2O$. Yield 40%. *Anal.* Found: C, 46.55; H, 2.81; N, 9.00. Calc. for $RuC_{24}H_{19}N_4Cl_4O$: C, 46.32; H, 3.07; N, 9.00%. UV–Vis spectral data, λ_{max} (nm) (ϵ(mol^{-1} dm^3 cm^{-1})) in HCl (6 mol dm^{-3}): 400(sh), 363 (7.8×10^3). Paramagnetic.

[Ru(Hdpa)$_3$](PF$_6$)$_2$ [29, 31]

Preparative conditions for the Hdpa complexes are almost the same as those of the corresponding 2,2'-bipyridine complexes, except that a higher mole ratio of ligand/Ru is required in this synthesis. A mixed solution of the hot blue solution (containing 1 g '$RuCl_3 \cdot 3H_2O$') and Hdpa (4 g) was refluxed for 3 h, while the solution color changed from blue to green. To the green solution, NH_4PF_6 (2 g) was added as a precipitant. The yellow–green crystalline product obtained was collected by filtration and washed with water and EtOH, then dried *in vacuo*. The crude product was recrystallized with acetone–EtOH solvent to give yellow crystals. Yield 80%. *Anal. Found*: *C*, 39.80; *H*, 2.95; *N*, 13.80. *Calc. for* $RuC_{30}H_{27}N_9P_2F_{12}$: C, 39.83; H, 3.00; N, 13.93%. UV–Vis spectral data in CH_3CN, λ_{max} (nm) (ϵ(mol^{-1} dm^3 cm^{-1})): 286 (5.0×10^4), 249 (3.3×10^4). Diamagnetic.

cis-[$RuCl_2$(Hdpa)$_2$]$Cl \cdot H_2O$ [32]

A mixed solution of the hot blue solution (containing 1 g of '$RuCl_3 \cdot 3H_2O$'), di-2,2'-dipyridylamine (1.7 g) and hydrochloric acid (5 cm^3) was refluxed for 1 h, while the solution color changed from blue to dark green. The dark green solution was kept at room temperature overnight, during which time green crystals deposited. The product was collected by filtration, washed with water and acetone, and air dried. *Anal.* Found: C, 42.45; H, 3.44; N, 14.83. Calc. for $RuC_{20}H_{20}N_6Cl_3O$: C, 42.30; H, 3.55; N, 14.79%. UV–Vis spectral data in CH_3CN, λ_{max} (nm) (ϵ(mol^{-1} dm^3 cm^{-1})): 626 (1.1×10^3), 422 (1.40×10^4), 296 (2.00×10^4). Yield 80%.

{(Hdpa)H}[$RuCl_4$(Hdpa)]$\cdot H_2O$

After the blue solution (1 g of '$RuCl_3 \cdot 3H_2O$') was cooled down to room temperature, Hdpa ligand (0.75 g) and HCl (6 cm^3) were added. The solution was stirred for 3 h and then it was kept overnight, during which time a gray–green crystalline material was deposited. The product was collected by filtration, washed with water and then acetone, and dried *in vacuo*. *Anal.* Found: C, 39.93; H, 3.27; N, 13.89. Calc. for $RuC_{20}H_{21}N_6Cl_4O$: C, 39.75; H, 3.50; N, 13.90%. Paramagnetic. Yield 40%.

[$RuCl_2py_4$] [15, 33]

The preparation of the complex using 'ruthenium-blue' solution has already been reported [25]. To the 'ruthenium-blue' solution, generated in the round bottomed flask, was added pyridine (30 cm^3). Then the mixed solution was heated for 0.5–1 h, while the solution color changed from the original blue–green to a deep brown. The volume of the brown solution was reduced on a rotary evaporator until a orange crystalline product was deposited. The product was collected using a glass filter, then washed with water, EtOH, and finally ether.

pyH[$RuCl_4py_2$] [34]

To the blue solution (0.5 g of '$RuCl_3 \cdot 3H_2O$'), which was cooled down by ice water, pyridine (10 cm^3) was added along with hydrochloric acid (2 cm^3). The mixed solution was stirred for 12 h at room temperature. Brown powdered material was deposited when the volume of the reaction solution was reduced. The product was collected by filtration, washed with EtOH, and then with ether. *Anal.* Found: C, 37.1; H, 3.4; N, 8.4. Calc. for $RuCl_{15}H_{16}N_3Cl_4$: C, 37.4; H, 3.3; N, 8.7%. Paramagnetic. Yield 60%.

[Ru(terpy)$_2$](PF$_6$)$_2$ [35]

To the hot blue solution (0.13 g of '$RuCl_3 \cdot 3H_2O$') was added terpyridine (0.25 g) in EtOH (20 cm^3). The mixture was refluxed for 30–60 min; during this time the solution color changed to reddish brown. The solution was evaporated to dryness using a rotary evaporator. The solid material which deposited was dissolved in hot water (20 cm^3), and the red solution obtained was filtered through paper. [Ru(terpy)$_2$](PF$_6$)$_2$ was precipitated by adding a precipitant minimum amount of NH_4PF_6. The red product material was collected by filtration, then washed with ethanol and ether. The crude product was recrystallized from an acetone–methanol solution. *Anal.* Found: C, 41.95; H, 2.49; N, 9.80. Calc. for $RuC_{30}H_{22}N_6P_2F_{12}$: C, 42.02; H, 2.59; N, 9.80%. Diamagnetic. Yield 60%.

[$RuCl_3$(terpy)]0.5H_2O [10, 36, 37]

To the hot blue solution (0.33 g of '$RuCl_3 \cdot 3H_2O$'), terpyridine (0.36 g) in EtOH (10 cm^3) was added. The mixture was warmed gently (50–60 °C) for 5 min and then the solution was acidified by adding hydrochloric acid (1 cm^3). The solution was refluxed for 30 min to give a red colored solution, from which a brown material

was precipitated. The product was collected by filtration, washed with EtOH and then acetone. *Anal.* Found: C, 40.13; H, 2.89; N, 9.30. Calc. for $RuC_{15}H_{12}N_3Cl_3O_{0.5}$: C, 40.00; H, 2.67; N, 9.33%. Yield 50%.

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