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Convenient Syntheses of Bis(2,2′-bipyridine) Complexes of Ruthenium(III)

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Meyer *et al.* have described the interesting oxo-bridged complexes $[(\mathrm{RuX(bipy)_2})_2(\mu\text{-O})]^{2+}$ (X = Cl, Br, NO_2, bipy = 2, 2′-bipyridine) [1–3]. These were obtained by treating $[\mathrm{RuX(bipy)_2(NO)}]^{2+}$ (which was obtained in turn from $[\mathrm{Ru(NO_2)_2(bipy)_2}]$ [4]) with N_3^- and oxidising the resultant $[\mathrm{RuX(bipy)_2S}]^+$ (S = solvent) with O_2 [1]. We describe here the one-pot synthesis of $[\mathrm{RuCl_2(bipy)_2}]^+$ (previously obtained in a two-stage synthesis by Bailar *et al.* [5]) and the singly step conversion of this into $[(\mathrm{RuX(bipy)_2})_2(\mu\text{-O})]^{2+}$. The preparations are further examples of the synthetic utility of the blue solutions of ruthenium [6, 7].

Experimental

Ruthenium trichloride (Engelhardt Industries) (1 g) was activated by refluxing in a mixture of water (20 cm^3) and ethanol (20 cm^3) for 1 h.

$[\mathrm{RuCl_2(bipy)_2}]\mathrm{Cl}\cdot 2H_2O$

The above activated solution was evaporated to dryness in a porcelain dish on a steam bath. The residue was dissolved in a mixture of hydrochloric acid (1 M, 1 cm^3) and water (10 cm^3), transferred to a small beaker and a mixture of water (5 cm^3) and formic acid (5 cm^3) was added. The resultant solution was heated (uncovered) at 80–85 °C until the solution became green (approx. 1 h). The beaker was then covered and heating continued at 90–95 °C until the solution became deep blue (approx. 15 min). To the still hot deep blue solution was added a solution of 2,2′-bipyridine (1.5 g) in a mixture of acetone (2 cm^3) and water (20 cm^3). The resultant solution was heated on a water bath for 15 min, HCl (1 M, 5 cm^3) added, and the volume reduced to approx. 15 cm^3. On standing overnight at room temperature brown crystals formed. These were collected by filtration, washed with acetone and ether and air dried. The crude product was recrystallised from hydrochloric acid (3 M) as red crystals. Yield 1.2 g, 55% (based on $\mathrm{RuCl_3(H_2O)_3}$). *Anal.* Found: C, 43.4; H, 3.6; Cl, 19.0; N, 10.1; Ru, 18.4; H_2O (Karl Fischer method) 6.5%. Calcd. for $C_{20}H_{20}Cl_3N_4O_2Ru$: C, 43.2; H, 3.6; Cl, 19.2; N, 10.1; Ru, 18.1; H_2O, 6.5%. Effective magnetic moment 1.96 BM (291 K); lit. [8]. 2.02 BM (297 K). Electronic spectrum (CH_3OH): λ_{max} 378 nm ($\epsilon = 5.4 \times 10^3$); lit. 379 nm ($\epsilon = 5.9 \times 10^3$) in CH_3OH [5]; 379 nm ($\epsilon = 5.1 \times 10^3$) in CH_2Cl_2 [9].

$[(\mathrm{RuBr(bipy)_2})_2(\mu\text{-O})]\mathrm{Br_2}\cdot 5H_2O$

A mixture of $[\mathrm{RuCl_2(bipy)_2}]\mathrm{Cl}\cdot 2H_2O$ (0.45 g, 0.8 mM) and sodium acetate (3 g, 22 mM) was dissolved in an aqueous (50 cm^3) solution of acetic acid (2 cm^3) and heated at 80 °C for 1 h. The solution changed colour from red to green. To the solution was added NaBr (1.5 g, 14.5 mM) and the solution was concentrated by heating until black-green crystals appeared. After cooling overnight the crystals were collected by filtration, washed with cold water, methanol and ether and air dried. Yield 0.4 g, 40%. Recrystallisation from water containing NaBr was possible, but due to the high solubility of $[(\mathrm{RuBr(bipy)_2})_2(\mu\text{-O})]\mathrm{Br_2}$ in water yields were very low. *Anal.* Found: C, 38.0; H, 3.4; Br, 25.7; N, 8.9; Ru, 16.2%. Calcd. for $C_{40}H_{42}Br_4N_8O_6Ru_2$: C, 38.3; H, 3.35; Br 25.6; N, 8.9; Ru, 16.1%. Effective magnetic moment 1.97 BM. Electronic spectrum (CH_3CN solution): λ_{max} 663 ($\epsilon = 2.3 \times 10^4$), 289 ($6.1 \times 10^4$), 242 ($5.8 \times 10^4$) nm.

$[(\mathrm{RuCl(bipy)_2})_2(\mu\text{-O})](\mathrm{PF_6})_2\cdot 3H_2O$

This complex was prepared by the same procedure as for $[(\mathrm{RuBr(bipy)_2})_2(\mu\text{-O})]\mathrm{Br_2}\cdot 5H_2O$ except that NaCl (1.0 g, 17.0 mM) was added in place of NaBr. After concentrating the solution to 30 cm^3 by heating on a steam bath, NH_4PF_6 (0.2 g, 1.23 mM) was added to precipitate the product. This was collected by filtration, washed with small amounts of water, methanol and ether and air dried. Yield 0.5 g, 50%. *Anal.* Found: C, 38.4; H, 2.75; N, 8.6%. Calcd. for $C_{40}H_{38}Cl_2F_{12}N_8O_4P_2Ru_2$: C, 38.2; H, 3.0; N, 8.9%.

$[(\mathrm{Ru(NO_2)(bipy)_2})_2(\mu\text{-O})](\mathrm{NO_2})_2\cdot 3H_2O$

This complex was prepared by an analogous method to that for $[(\mathrm{RuBr(bipy)_2})_2(\mu\text{-O})]\mathrm{Br_2}\cdot 5H_2O$ except that $NaNO_2$ (5.0 g) was used instead of NaBr. The solution was concentrated until crystals appeared. The yield (0.15 g, 17%) was low because the nitro complex was very soluble in water. *Anal.* Found: C, 43.9; H, 3.9; N, 15.6; Ru, 18.5%. Calcd. for $C_{40}H_{38}N_{12}O_{12}Ru_2$: C, 44.4; H, 3.8; N, 15.6; Ru, 18.7%. Electronic spectrum (CH_3CN

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solution): λ_{max} 632 ($\epsilon = 2.6 \times 10^4$); 286 ($4.6 \times 10^4$); 242 ($4.9 \times 10^4$) nm; lit. 632 ($2.57 \times 10^4$); 284 ($4.89 \times 10^4$); 244 ($3.84 \times 10^4$) nm [1].

Microanalyses for C, H and N were performed by the Institute of Chemical and Physical Research, Wako, Saitama, Japan 354; Ru, halogen and H_2O were determined in these laboratories; electronic spectra were measured on a Hitachi 624 spectrophotometer and magnetic moments were by the Guoy method.

Discussion

All of the complexes obtained by the new synthetic route have chemical and physical properties similar to those described previously.

The syntheses make use of a blue solution of ruthenium generated by the action of formic acid/hydrochloric acid on Ru(III). Several such blue solutions have been described previously and the blue colour has been ascribed to a variety of different species [10–14]. We do not wish to speculate on the species responsible for the blue colour of our solution. Indeed, the reactive complex(es) which make(s) these solutions such attractive synthetic reagents may not be blue at all. The blue solution is not stable for long periods in air.

It seems most likely that $[(RuX(bipy)_2)_2(\mu\text{-}O)]^{2+}$ is formed from $[RuCl_2(bipy)_2]^+$ by initial loss of one or both chloride ligands. Subsequent mono-deprotonation of $[RuCl(bipy)_2(H_2O)]^{2+}$ or $[Ru(bipy)_2(H_2O)_2]^{3+}$ would be facile [15] and dimerisation of the resultant hydroxo complex would provide the bridging oxygen atom.

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