

## Short Communications

### Synthesis and Characterisation of *cis*-Tetraammine Rhodium(III) Complexes

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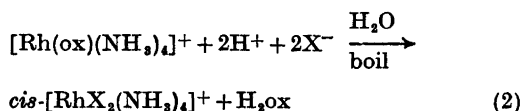
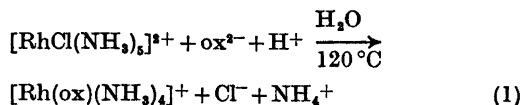
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Although the *trans*-isomer of the tetraammine-dichlororhodium(III) cation was first prepared many years ago<sup>1</sup> and increasingly efficient methods for the synthesis of *trans*-[RhX<sub>2</sub>(NH<sub>3</sub>)<sub>4</sub>]<sup>+</sup> (X = Cl, Br or I) have subsequently been devised,<sup>2,3</sup> there appears to have been no report in the literature of the synthesis of any rhodium(III) complexes containing the *cis*-tetraammine moiety. This is rather surprising in view of the fact that cobalt(III) complexes of both the *trans*- and *cis*-tetraammine series have been known since the time of Werner.<sup>4</sup> This communication reports the synthesis and characterisation of the tetraammineoxalato-rhodium(III) cation, [Rh(ox)(NH<sub>3</sub>)<sub>4</sub>]<sup>+</sup>, and the ready conversion of the latter to the *cis*-tetraamminedichloro and dibromo complexes in high yield.

The synthesis of [Rh(ox)(NH<sub>3</sub>)<sub>4</sub>]<sup>+</sup> involves the reaction of the easily-prepared<sup>5,6</sup> complex [RhCl(NH<sub>3</sub>)<sub>5</sub>]<sup>2+</sup> (as the chloride salt) with oxalate ion, in the presence of one proton per complex ion, in water at 120 °C for 24 h in an autoclave. Addition of perchloric acid to the resulting, cooled solution results in the rapid crystallisation of the sparingly soluble crude perchlorate salt of the desired complex. Pure [Rh(ox)(NH<sub>3</sub>)<sub>4</sub>]ClO<sub>4</sub>·H<sub>2</sub>O is then obtained in ca. 55 % yield on recrystallisation.

The *cis*-dihalo complexes, *cis*-[RhX<sub>2</sub>(NH<sub>3</sub>)<sub>4</sub>]X·½H<sub>2</sub>O (X = Cl or Br), may be isolated in high yield from the solutions obtained by boiling the oxalato complex in the appropriate strong aqueous hydrohalic acid. Further purification is readily achieved by recrystallisation from hot aqueous hydrohalic acid. No evidence was obtained for any *cis*→*trans* isomerisation during the above procedures. The sparingly soluble, pure crystalline dithionate salts of *cis*-[RhX<sub>2</sub>(NH<sub>3</sub>)<sub>4</sub>]<sup>+</sup> (X = Cl or Br) are readily obtained by addition of sodium dithionate to concentrated aqueous solutions of the halide salts.

The reactions involved in the synthesis of the new *cis*-tetraammine complexes are summarized in Scheme 1.



Scheme 1. ox<sup>2-</sup> = oxalate dianion, C<sub>2</sub>O<sub>4</sub><sup>2-</sup>; X = Cl or Br.

Oxalato complexes of the type formed in reaction (1) are established for bis(diamine)rhodium(III) systems<sup>7-9</sup> and are known to undergo conversion to the corresponding *cis*-dichloro and dibromo species, under the same conditions as employed in reaction (2) here, with retention of geometric configuration.<sup>8,9</sup>

A comparison of the Guinier powder photographs of *cis*-[MCl<sub>2</sub>(NH<sub>3</sub>)<sub>4</sub>]Cl·½H<sub>2</sub>O (M = Co or Rh) showed the two complexes to be isomorphous, thereby demonstrating the *cis*-configuration of the rhodium(III) complex. The IR spectra (4000–400 cm<sup>-1</sup>) of the two compounds are extremely similar to one another. The IR spectra of [M(ox)(NH<sub>3</sub>)<sub>4</sub>]ClO<sub>4</sub>·H<sub>2</sub>O (M = Co or Rh) are also very similar, although the Guinier powder photographs indicate these congeners to be non-isomorphous. Further evidence concerning the nature of the new rhodium(III) complexes is provided by their ligand-field spectra, which are very similar to those of the well-characterised<sup>3,7,8</sup> bis(ethylenediamine)rhodium(III) analogues (Table 1). Data for the *trans*-dichloro and *trans*-dibromo isomers of the tetraammine and bis(ethylenediamine)rhodium(III) complexes are also included in Table 1 for comparison purposes. It can be seen that the longer-wavelength absorption maxima for the *cis*-tetraammine complexes occur at somewhat lower energy than those for the *cis*-bis(ethylenediamine) analogues, as is also the case for the *trans*-dihalo complexes of the two systems.

Further work on the *cis*-tetraammine rhodium(III) system will be described in a subsequent publication.<sup>9</sup>

Table 1. Ligand-field spectra.

Complex	$\lambda_{\max}$	$\epsilon_{\max}$	Ref.
[Rh(ox)(NH <sub>3</sub> ) <sub>4</sub> ] <sup>+</sup>	333	167	This work
[Rh(ox)(en) <sub>2</sub> ] <sup>+</sup>	325	260	7
<i>cis</i> -[RhCl <sub>2</sub> (NH <sub>3</sub> ) <sub>4</sub> ] <sup>+</sup>	360, 295	126, 108	This work
<i>cis</i> -[RhCl <sub>2</sub> (en) <sub>2</sub> ] <sup>+</sup>	352, 295	155, 180	2
<i>cis</i> -[RhBr <sub>2</sub> (NH <sub>3</sub> ) <sub>4</sub> ] <sup>+</sup>	377, <i>ca.</i> 275(sh)	170, <i>ca.</i> 940	This work
<i>cis</i> -[RhBr <sub>2</sub> (en) <sub>2</sub> ] <sup>+</sup>	362, 276(sh)	210, 900	2
<i>trans</i> -[RhCl <sub>2</sub> (NH <sub>3</sub> ) <sub>4</sub> ] <sup>+</sup>	412, —	66, —	2
	415, 293	74, 85	3
<i>trans</i> -[RhCl <sub>2</sub> (en) <sub>2</sub> ] <sup>+</sup>	406, 286	75, 130	2
<i>trans</i> -[RhBr <sub>2</sub> (NH <sub>3</sub> ) <sub>4</sub> ] <sup>+</sup>	441, <i>ca.</i> 280(sh)	111, <i>ca.</i> 2700	3
<i>trans</i> -[RhBr <sub>2</sub> (en) <sub>2</sub> ] <sup>+</sup>	425, 276	100, 1800	2

**Experimental. Materials.** [RhCl(NH<sub>3</sub>)<sub>5</sub>]Cl<sub>2</sub> and [CoCO<sub>3</sub>(NH<sub>3</sub>)<sub>4</sub>]ClO<sub>4</sub> were kindly provided by Dr. Erik Pedersen and Dr. Claus Schäffer, respectively, of this department. The *cis*-[CoCl<sub>2</sub>(NH<sub>3</sub>)<sub>4</sub>]<sup>+</sup> ion was prepared essentially as in Ref. 10, starting from [CoCO<sub>3</sub>(NH<sub>3</sub>)<sub>4</sub>]ClO<sub>4</sub>, and purified as the dithionate salt according to Ref. 4. The pure chloride salt was then prepared from the dithionate by a modification of Werner's original method,<sup>4</sup> involving the use of ice-cold conc. hydrochloric acid in place of an ammonium chloride solution. The fine blue-violet crystals were washed with ice-cold conc. hydrochloric acid and then 96 % ethanol, and air-dried. (Found: N 22.57; H 5.34; Cl 44.25. Calc. for *cis*-[CoCl<sub>2</sub>(NH<sub>3</sub>)<sub>4</sub>]Cl· $\frac{1}{2}$ H<sub>2</sub>O: N 23.08; H 5.40; Cl 43.90). [Co(ox)(NH<sub>3</sub>)<sub>4</sub>]ClO<sub>4</sub>·H<sub>2</sub>O was prepared by boiling an aqueous solution containing *cis*-[CoCl<sub>2</sub>(NH<sub>3</sub>)<sub>4</sub>]Cl· $\frac{1}{2}$ H<sub>2</sub>O and a slight excess of oxalic acid, treating the carmine-red solution with lithium perchlorate and cooling it in ice. The crimson-red crystals were then recrystallised from hot water by addition of lithium perchlorate, washed with 96 % ethanol and air-dried. (Found: C 7.24; N 16.98; H 4.32; Cl 10.61. Calc. for [Co(ox)(NH<sub>3</sub>)<sub>4</sub>]ClO<sub>4</sub>·H<sub>2</sub>O: C 7.22; N 16.84; H 4.24; Cl 10.67). The visible absorption spectrum agreed with that published previously.<sup>11</sup>

All other chemicals were of reagent grade and were used without further purification.

**Spectra.** Absorption spectra in the region 600–250 nm were recorded using a Cary Model 14 spectrophotometer. Data for absorption maxima or shoulders (sh) in Table 1 are given as  $\lambda_{\max}$  and  $\epsilon_{\max}$  with the wavelength  $\lambda$  in nm and the molar absorbance  $\epsilon$  in l mol<sup>-1</sup> cm<sup>-1</sup>. Medium: water.

**Preparation of new complexes. 1. Tetraammine-oxalatorrhodium(III) perchlorate monohydrate.** [Rh(ox)(NH<sub>3</sub>)<sub>4</sub>]ClO<sub>4</sub>·H<sub>2</sub>O. A mixture of [RhCl(NH<sub>3</sub>)<sub>5</sub>]Cl<sub>2</sub> (2.0 g, 6.8 mmol), disodium oxalate (0.91 g, 6.8 mmol), oxalic acid (0.43 g, 3.4 mmol) and water (70 ml) was placed in a stainless-steel autoclave (volume *ca.* 300 ml). The auto-

clave was tightly closed and heated in an oven at 120 °C for 24 h, after which it was allowed to cool to about 50 °C and opened. The contents were filtered and the autoclave rinsed with water (10 ml). The washings were filtered and added to the bulk solution which was then allowed to cool to room temperature. 70 % perchloric acid (2.5 ml) was added to the pale-yellow solution, whereupon crystals of the crude product began to form. After cooling and agitating the mixture in an ice-bath for 20 min the crystals were isolated by filtration, washed with a little ice-cold 2 M perchloric acid and then methanol, and air-dried. Yield 1.6 g. The crude product was purified by dissolving in the minimum volume of hot (90 °C) water, and adding activated charcoal (0.1 g) to the solution. The solution was then filtered through a fine sintered glass funnel, treated with a hot solution of lithium perchlorate (2.0 g) in water (10 ml) and cooled in ice. The pale-yellow crystals were recrystallised once more from hot water by adding lithium perchlorate as before and allowing the solution to cool overnight. They were isolated by filtration, washed with methanol and air-dried. Yield 1.4 g (55 %). (Found: C 6.24; N 14.87; H 3.98; Cl 9.44. Calc. for [Rh(ox)(NH<sub>3</sub>)<sub>4</sub>]ClO<sub>4</sub>·H<sub>2</sub>O: C 6.37; N 14.87; H 3.74; Cl 9.43).

**2. *cis*-Tetraamminedichlororhodium(III) chloride hemihydrate.** *cis*-[RhCl<sub>2</sub>(NH<sub>3</sub>)<sub>4</sub>]Cl· $\frac{1}{2}$ H<sub>2</sub>O. [Rh(ox)(NH<sub>3</sub>)<sub>4</sub>]ClO<sub>4</sub>·H<sub>2</sub>O (1.32 g, 3.5 mmol) was boiled for 1 min with 6 M hydrochloric acid (40 ml). The clear, bright-yellow solution was then cooled in ice for 10 min, when a good yield of bright-yellow crystals was obtained. Precipitation was completed by addition of methanol (40 ml) and further cooling. The crystals were isolated by filtration, washed with methanol and air-dried. Yield 0.98 g. The product was then recrystallised by dissolving in hot (95 °C) 3 M hydrochloric acid (25 ml), filtering the solution and allowing it to cool to room temperature. After further cooling at 0 °C overnight the bright-yellow needles were filtered off,

washed well with methanol and air-dried. Yield 0.89 g (91 %). (Found: N 19.34; H 4.60; Cl 36.62. Calc. for *cis*-[RhCl<sub>2</sub>(NH<sub>3</sub>)<sub>4</sub>]Cl<sub>2</sub>·½H<sub>2</sub>O: N 19.54; H 4.57; Cl 37.16).

3. *cis*-Tetraamminedibromorhodium(III) bromide hemihydrate, *cis*-[RhBr<sub>2</sub>(NH<sub>3</sub>)<sub>4</sub>]Br<sub>2</sub>·½H<sub>2</sub>O. [Rh(ox)(NH<sub>3</sub>)<sub>4</sub>]ClO<sub>4</sub>·H<sub>2</sub>O (0.70 g, 1.86 mmol) was boiled with 5 M hydrobromic acid (30 ml) until all the complex had dissolved (*ca.* 2–3 min). The resulting orange solution was allowed to cool to room temperature and then kept in a freezer at –15 °C overnight. The product was isolated by filtration, washed with 96 % ethanol and air-dried. Yield 0.68 g. Recrystallisation was performed as for the *cis*-dichloro chloride (prep. 2), using 3 M hydrobromic acid (30 ml) in place of hydrochloric acid. The orange crystals were filtered off, washed with 96 % ethanol and air-dried. Yield 0.60 g (77 %). (Found: N 13.48; H 3.08; Br 57.25. Calc. for *cis*-[RhBr<sub>2</sub>(NH<sub>3</sub>)<sub>4</sub>]Br<sub>2</sub>·½H<sub>2</sub>O: N 13.33; H 3.12; Br 57.10).

4. *cis*-Tetraamminedichlororhodium(III) dithionate, *cis*-[RhCl<sub>2</sub>(NH<sub>3</sub>)<sub>4</sub>]<sub>2</sub>S<sub>2</sub>O<sub>6</sub>. [RhCl<sub>2</sub>(NH<sub>3</sub>)<sub>4</sub>]Cl<sub>2</sub>·½H<sub>2</sub>O (0.25 g, 0.87 mmol) was dissolved in water (20 ml) at room temperature and the solution filtered. A solution of sodium dithionate dihydrate (0.5 g, 2.1 mmol) in water (10 ml) was added, whereupon crystals of the desired product began to form immediately. After cooling the solution overnight at 0 °C the fine pale-yellow crystals were isolated by filtration, washed well with ice-cold water and then 96 % ethanol, and air-dried. Yield 0.21 g (75 %). (Found: N 17.58; H 3.45; S 9.88. Calc. for *cis*-[RhCl<sub>2</sub>(NH<sub>3</sub>)<sub>4</sub>]<sub>2</sub>S<sub>2</sub>O<sub>6</sub>: N 17.39; H 3.76; S 9.93).

5. *cis*-Tetraamminedibromorhodium(III) dithionate, *cis*-[RhBr<sub>2</sub>(NH<sub>3</sub>)<sub>4</sub>]<sub>2</sub>S<sub>2</sub>O<sub>6</sub>. This complex was prepared in the same way as the *cis*-dichloro dithionate (prep. 4), using *cis*-[RhBr<sub>2</sub>(NH<sub>3</sub>)<sub>4</sub>]Br<sub>2</sub>·½H<sub>2</sub>O (0.30 g, 0.71 mmol) dissolved in water (25 ml). The shiny orange crystals were filtered off, washed with ice-cold water and 96 % ethanol, and air-dried. Yield 0.23 g (78 %). (Found: N 13.78; H 2.83; S 7.89. Calc. for *cis*-[RhBr<sub>2</sub>(NH<sub>3</sub>)<sub>4</sub>]<sub>2</sub>S<sub>2</sub>O<sub>6</sub>: N 13.63; H 2.94; S 7.80).

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## On the Structure of Deuterated Squaric Acid, C<sub>4</sub>D<sub>2</sub>O<sub>4</sub>, at Room Temperature

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The crystal structure of 3,4-dihydroxy-3-cyclobutene-1,2-dione (Squaric acid, hereafter denoted H<sub>2</sub>SQ) as determined by X-ray diffraction has been reported previously.<sup>1</sup> Interest in this compound developed recently due to the discovery of a continuous phase transition in both H<sub>2</sub>SQ (*T*<sub>C</sub> = 97 °C) and D<sub>2</sub>SQ (*T*<sub>C</sub> = 243 °C).<sup>2</sup> The magnitude of the isotope effect in the transition temperatures of these compounds suggests that the hydrogen bonds are essential to the dynamics of the transition. Since the length of the hydrogen bonds in H<sub>2</sub>SQ lie in the range where isotope effects in these bonds are to be expected, it was considered of importance to acquire exact information of the crystal structure of D<sub>2</sub>SQ.

Squaric acid (H<sub>2</sub>SQ) has also been independently examined by X-ray and neutron diffraction.<sup>3</sup> However, there are some points of disagreement between that work and our X-ray study.<sup>2</sup> In our X-ray study squaric acid crystals were found almost invariably to be twinned, and it was only after considerable effort that an untwinned sample could be found. Such difficulties were apparently not encountered in the combined X and N study.<sup>3</sup> A high degree of consistency was obtained between chemically equivalent but crystallographically independent bonds in our X-ray study,<sup>1</sup> but not in the combined study.<sup>3</sup> In the latter study poor agreement was also obtained for certain bond distances between the X-ray and neutron results. The X-ray structure determination of D<sub>2</sub>SQ was therefore also undertaken in order to establish the validity of our previous X-ray work.<sup>1</sup>