Synthetic Aspects of Rhodium(III) Chemistry. II. Binuclear Di-\(\mu\)-hydroxo Complexes of Rhodium(III)

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The dithionate salts of the new diol cations \([\text{LL})_2\text{Rh(OH)}_2\text{Rh(LL)}_2]^{4+}\) (LL = 2NH\(_3\) or en) have been synthesised by thermal deaquation of cis-\([\text{Rh(OH)}_2\text{H}_2\text{O})(\text{LL})_2]_2\text{S}_2\text{O}_6\) at 120 °C and purified as the bromide salts. Guinier X-ray powder photographs indicate \([\text{NH}_3)_2\text{Rh(OH)}_2\text{Rh(NH}_3)_2\text{Br}_4\cdot 4\text{H}_2\text{O}\) and \([\text{en})_2\text{Rh(OH)}_2\text{Rh(en)}_2\text{]}_2\text{S}_2\text{O}_6\_2\) to be isomorphous with their well-characterised cobalt(III) and chromium(III) analogues, whereby it may be concluded that the rhodium(III) en diol cation possesses the meso (\(\Delta,\Delta\)) configuration.

Considerable interest has been shown recently in the chemistry and the structural and spectroscopic properties of so-called diol complexes of chromium(III) and cobalt(III), i.e., binuclear complexes of the type

\[
\begin{array}{c}
\text{H} \\
\text{O} \\
\text{M(LL)}_2 \\
\text{H}
\end{array}
\]

\(\text{M} = \text{Cr}: \text{LL} = 2\text{NH}_3, 1\)

1,2-diaminoethane(en),\(^{1,5}\) 2-picolyamine,\(^6\) 1,10-phenanthroline\(^7-10\) or 2,2'-bipyridine,\(^9,10\) or \((\text{LL})_2 = 1,6\text{-bis(2'-pyridyl)}-2,5\text{-diazahexane}\), \(\text{M} = \text{Co: LL} = 2\text{NH}_3\)\(^1\) or en\(^1,12\). The heteronuclear species \((-)(3s97\Delta\Delta\text{-[en})_2\text{Cr(OH)}_2\text{Co(en)}_2\text{]}^{4+}\) has also been prepared and its equilibria with mononuclear bridged systems examined.\(^13\)

With the exception of the cation \([\text{H}_2\text{O})_4\text{Rh(OH)}_2\text{Rh(H}_2\text{O)}_4\text{]}^{4+}\), whose formation was tentatively suggested to rationalise data obtained in the potentiometric titration of the hexaaquarhodium(III) cation,\(^14\) no bi- or polynuclear hydroxo-bridged complexes have been reported for rhodium(III), and in this connection the availability of cis-tetraammine- and cis-bis(1,2-diaminoethane)rhodium(III) complexes from previous work\(^15,16\) made it of interest to try to synthesise the corresponding octaaammine- and tetrakis-(1,2-diaminoethane) diol systems. This paper describes the synthesis of the latter via the intermediary of the isolated and purified cis-aquahydroxy mononuclear complexes, and their characterisation by chemical and spectroscopic means.

A brief account of this work has been presented previously.\(^17\)

EXPERIMENTAL

Materials. cis-\([\text{RhCl}_2(\text{NH}_3)_2]\text{Cl}_4\text{H}_2\text{O}\) and cis-\([\text{RhCl}_2(\text{en})_2]\text{Cl}_4\text{H}_2\text{O}\) were prepared as described previously.\(^15,16\) Samples of \([\text{NH}_3)_3\text{M(OH)}_2\text{M- (NH}_3)_2\text{]Br}_4\cdot 4\text{H}_2\text{O}\) and meso-\([\text{en})_3\text{M(OH)}_2\text{M(en)}_2\text{]}_2\text{S}_2\text{O}_6\ (\text{M} = \text{Cr or Co})\) were kindly provided by Johan Springborg of this department. All other chemicals were of analytical or reagent grade and were used without further purification.

Analyses. Microanalyses for C, H, N, S and Br were performed as described previously.\(^18\)

Spectra. Absorption spectra in the wavelength region 500 – 250 nm were recorded on a Carl Zeiss DMR 21 spectrophotometer at 25 °C. Characterising data for absorption maxima, minima or shoulders (sh) in Table I are given with the wavelength \(\lambda\) in nm and the molar absorbance \(e\) in 1 mol\(^{-1}\) cm\(^{-1}\). Infrared spectra (4000–400 cm\(^{-1}\)) of powdered samples dispersed in KBr discs were recorded on a Perkin-Elmer 457 instrument.

X-Ray powder photographs were taken with CuK\(\alpha\) radiation using a focussing camera of the Guinier type. Silicon was added to the powdered samples as internal standard.

Thermogravimetry was performed on the recording thermobalance described by Pedersen.\(^19\)

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using 10–15 mg samples. The temperature was normally raised at a rate of 2 °C min⁻¹.

**Syntheses.** 1. *cis*-Tetraammineaquahydroxoro-
dium(III) dithionate 0.2 hydrate. *cis*-Rh(OH)₃-
(H₂O)(NH₃)₃SO₄·0.2H₂O. A mixture of *cis-
[RhCl₃(NH₃)₃]Cl₃H₂O¹⁵ (1.0 g; 3.49 mmol) and
AgNO₃ (1.77 g; 10.46 mmol) in water (30 ml) was
heated under reflux for 3 ½ h in a 100 ml RB flask
wrapped in aluminium foil to exclude light. The
cooled solution was filtered through a fine porosity
sintered glass funnel by suction and the AgCl was
washed with water (2×3 ml). Solid Na₂S₂O₅·2H₂O (1.80 g) was added to the combined filtrate plus
washes and the pale yellow solution stirred to
dissolve the crystals. Pyridine (2 ml) was then
added dropwise under vigorous magnetic stirring and
cooling in an ice-bath. After further stirring and
cooling for 2 h, the pale yellow crystalline product
was isolated by filtration, washed with ice-cold
water, 96% ethanol and finally ether, and air-dried.
Yield 0.76 g (59%).

The crude product was purified by dissolution in
a slight excess of cold 0.5 M HCl containing
Na₂S₂O₅·2H₂O and reprecipitation by dropwise
addition of the stoichiometric amount of 1 M NaOH
to the filtered solution with stirring and cooling as
before. The product was filtered off and washed and
dried as previously. Anal. [Rh(OH)(H₂O)₃-
(NH₃)₃]SO₄·0.2H₂O: H, N, S.

2. *cis*-Aquabis(1,2-diaminoethane)hydroxoro-
dium(III) dithionate, *cis*-Rh(OH)(H₂O)(en)₂-
SO₄·2H₂O. Anal. [RhCl(en)₂Cl]ClH₂O¹⁶ (6.0 g; 16.83 mmol) and
AgNO₃ (8.57 g; 50.45 mmol) were heated under reflux for 3 h in water (50 ml) as in prep. 1,
and the pale yellow product isolated as before from
the filtered solution plus washings (total volume
of 80 ml) following the addition of Na₂S₂O₅·2H₂O
(6.0 g) and then pyridine (5 ml) under stirring and
cooling. The impure product was purified by re-
precipitation as described in prep. 1. Yield 3.63 g
(52%). Anal. [Rh(OH)₂(H₂O)(en)₂]SO₄·2H₂O: C, H, N, S.
The characterising spectral data for the complex in acidic and basic solution are given in
Table 1.

3. Di-µ-hydroxobis[tetraamminerhodium(III)] brom-
id tetrahydrate, [(NH₃)₃Rh(OH)₂Rh(NH₃)₃]-
Br₄·4H₂O. *cis*-Rh(OH)(H₂O)(NH₃)₃SO₄·0.2
H₂O (0.50 g) was spread on a watch glass and heated
in an oven at 120 °C for 15 h. The crude diol
dithionate was then allowed to cool to room
temperature and a sample (0.38 g) was suspended
in saturated NH₄Br solution (5 ml). The mixture
was stirred vigorously and cooled in an ice-bath
for 1 h. The pale-yellow precipitate was isolated
by filtration, washed with ice-cold 1:1 aqueous
ethanol, then 96% ethanol and air-dried. For re-
crystallisation the product was dissolved on the
filter in water (ca. 15 ml), and to the filtered solution
was added saturated NH₄Br solution (5 ml). The
mixture was then kept in an ice-bath for 2 h and
the yellow crystals were isolated as before and air-
dried. Yield 0.25 g (60%). Anal. [(NH₃)₃Rh(OH)₂-
Rh(NH₃)₃]Br₄·4H₂O: H, N, Br.

4. meso-Di-µ-hydroxobis[bis(1,2-diaminoethane)-
rhodium(III)] dithionate, meso-[en]₂Rh(OH)₂-
Rh(en)₂SO₄·2H₂O. *cis*-Rh(OH)(H₂O)(en)₂-
SO₄·0.80 g) was heated at 120 °C for 10 h as described in
prep. 3. The product appears to be practically pure,
as judged by the identity of its IR spectrum with
that of the pure dithionate (vide infra), and by
microanalysis. Anal. [(C₂H₈N₂)₂Rh(OH)₂-
(C₂H₈N₂)₂][SO₄]·2H₂O: C, H, N, S.
The pure dithionate was obtained from the pure
bromide dihydrate (prep. 5) by metathesis with
sodium dithionate. It was filtered off, washed with
ice-cold water and 96% ethanol, and air-dried.

*Not specified clearly. *b Calculated spectrum.

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**Table 1. Ligand-field absorption spectra.**

<table>
<thead>
<tr>
<th>Complex</th>
<th>Medium</th>
<th>λ&lt;sub&gt;max&lt;/sub&gt;</th>
<th>λ&lt;sub&gt;min&lt;/sub&gt;</th>
<th>ε&lt;sub&gt;max&lt;/sub&gt;</th>
<th>ε&lt;sub&gt;min&lt;/sub&gt;</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>cis-[Rh(H₂O)₆(NH₃)₃]⁺⁺</td>
<td>0.12 M HClO₄</td>
<td>326,268</td>
<td>294</td>
<td>107,91</td>
<td>63</td>
<td>This work</td>
</tr>
<tr>
<td>cis-[Rh(OH)₂(H₂O)(NH₃)₂]⁺⁺</td>
<td>0.1 M NaOH</td>
<td>335,281</td>
<td>308</td>
<td>122,118</td>
<td>95</td>
<td>This work</td>
</tr>
<tr>
<td>cis-[Rh(H₂O)₆Cl]⁺⁺</td>
<td>0.12 M HClO₄</td>
<td>318,527</td>
<td>289.5</td>
<td>171,135</td>
<td>115</td>
<td>This work</td>
</tr>
<tr>
<td>(⁺)₃₉₀cis-[Rh(H₂O)₂(en)₂]⁺⁺</td>
<td>a</td>
<td>314</td>
<td>184</td>
<td>20</td>
<td></td>
<td></td>
</tr>
<tr>
<td>cis-[Rh(OH)₂(H₂O)(en)₂]⁺⁺</td>
<td>0.1 M NaOH</td>
<td>329,278.5</td>
<td>303</td>
<td>179,171</td>
<td>138</td>
<td>This work</td>
</tr>
<tr>
<td>(⁺)₃₉₀cis-[Rh(OH)(H₂O)(en)₂]⁺⁺</td>
<td>a</td>
<td>332,284</td>
<td>170,164</td>
<td>21</td>
<td></td>
<td></td>
</tr>
<tr>
<td>[(NH₃)₃Rh(OH)₂Rh(NH₃)₂]⁺⁺</td>
<td>0.012 M HClO₄</td>
<td>336</td>
<td>304.5</td>
<td>305</td>
<td>204</td>
<td>This work</td>
</tr>
<tr>
<td>H₂O</td>
<td>336</td>
<td>304.5</td>
<td>308</td>
<td>203</td>
<td>This work</td>
<td></td>
</tr>
<tr>
<td>meso-[en]₂Rh(OH)₂Rh(en)₂]⁺⁺</td>
<td>0.012 M HClO₄</td>
<td>331.5</td>
<td>307</td>
<td>523</td>
<td>443</td>
<td>This work</td>
</tr>
<tr>
<td>H₂O</td>
<td>331.5</td>
<td>307</td>
<td>513</td>
<td>435</td>
<td>This work</td>
<td></td>
</tr>
</tbody>
</table>
Anal. \([\text{C}_2\text{H}_8\text{N}_2\text{S}_2\text{Rh(OH)}_2\text{Rh(C}_2\text{H}_8\text{N}_2\text{S}_2\text{)}_2\text{]}\text{S}_2\text{O}_6\cdot \text{C, H, N, S.}\)

5. meso-Di-μ-hydroxobis[bis(1,2-diaminoethane)-rhodium(III)] bromide dihydrate, meso-[\(\text{en}_2\text{Rh(OH)}_2\text{Rh(en)}_2\text{]}\text{Br}_2\cdot 2\text{H}_2\text{O}\). Crude diol dithionate (prep. 4: 0.38 g) was stirred rapidly with saturated \(\text{NH}_4\text{Br}\) solution (5 ml) at room temperature for 1 h. The pale-yellow precipitate of crude bromide salt was then isolated and recrystallised from water (ca. 15 ml) by addition of saturated \(\text{NH}_4\text{Br}\) solution (8 ml) as in prep. 3. Yield 0.26 g (65%). Anal. \([\text{C}_2\text{H}_8\text{N}_2\text{S}_2\text{Rh(OH)}_2\text{Rh(C}_2\text{H}_8\text{N}_2\text{S}_2\text{)}_2\text{]}\text{Br}_4\cdot 2\text{H}_2\text{O}: \text{C, H, N, Br.}\)

RESULTS AND DISCUSSION

The new diol cations \([\text{LL}_2\text{Rh(OH)}_2\text{Rh(LL)}_2\] \(\text{^4+}\) (LL = 2NH\(_3\) or en) have been synthesised according to the scheme, eqns. (1)–(3).

\[
\begin{align*}
\text{cis-[RhCl}_3\text{(LL)}_2\] & + 2\text{Ag}^+ + 2\text{H}_2\text{O} \xrightarrow{\text{Reflux}} \text{cis-[Rh(H}_2\text{O)}_2\text{(LL)}_2\] 3+ + 2\text{AgCl}^+ \tag{1} \\
\text{cis-[Rh(OH)}_2\text{(LL)}_2\] 3+ + \text{OH}^- & \xrightarrow{\text{Na}_2\text{S}_2\text{O}_6} \text{cis-[Rh(OH)}_2\text{(H}_2\text{O)}\text{(LL)}_2\] \text{S}_2\text{O}_6 \tag{2} \\
2\text{cis-[Rh(OH)}_2\text{(H}_2\text{O)}\text{(LL)}_2\] \text{S}_2\text{O}_6 & \xrightarrow{120 \degree \text{C}} \text{[LL}_2\text{Rh(OH)}_2\text{Rh(LL)}_2\] \text{S}_2\text{O}_6\cdot 2\text{H}_2\text{O} \tag{3}
\end{align*}
\]

The formulation of the aquahydroxido complexes obtained in (2), which have not previously been isolated in pure form, is confirmed by (i) the pH-dependence of the ligand-field absorption spectra, (ii) the reasonable agreement between the spectral data for the bis(en) complex in acidic and basic medium and limited data reported previously for \(\text{cis-[Rh(H}_2\text{O)}_2\text{(en)}_2\] 3+ \(20\) and \(\text{cis-[Rh(OH)}_2\text{(en)}_2\] \(19,20,21\) respectively, and (iii) the close resemblance of the spectrum of the tetraammine complex to that of the bis(en) complex in a given medium (see Table 1).

The thermal deaquation of the aquahydroxido dithionates (reaction (3)) was monitored by thermogravimetry. In the case of the tetraammine complex the thermogravimetric curves for two separately prepared samples revealed a weight loss between ca. 30 °C and 120 °C corresponding to loss of ca. 1.2 mol \(\text{H}_2\text{O}\) per mol Rh, microanalytical data being in satisfactory agreement with the composition \([\text{Rh(OH)}_2\text{(H}_2\text{O)}\text{(NH}_3\text{)}_4\] \text{S}_2\text{O}_6\cdot 0.2\text{H}_2\text{O}; however, it was not possible to distinguish clearly between loss of crystal water and loss of coordinated water. The microanalytical data for the bis(en) complex were consistent with the composition \([\text{Rh(OH)}_2\text{(H}_2\text{O)}\text{(en)}_2\] \text{S}_2\text{O}_6\), and thermogravimetry revealed a weight loss beginning at ca. 70 °C which was complete at 120 °C and which corresponded to loss of 1.0 mol \(\text{H}_2\text{O}\) per mol Rh.

Thermal deaquation of the aquahydroxido complexes on a preparative scale was performed at 120 °C, this temperature corresponding closely to the midpoint of the plateau at the top of the weight-loss step on the thermogravimetric curves. The resulting crude diol dithionates were then purified as the more soluble bromides. Compelling evidence for the diol structure is provided by the extreme similarity of the Guinier X-ray powder photographs and IR spectra of \([\text{NH}_3\text{Rh(OH)}_2\text{Rh(NH}_3\text{)}_4\] \text{Br}_4\cdot 4\text{H}_2\text{O}\) and \([\text{en}_2\text{Rh(OH)}_2\text{Rh(en)}_2\] \text{S}_2\text{O}_6\) to those of the well-characterised \(^1\) cobalt(III) and chromium(III) analogues. Single crystal X-ray diffraction studies of the dichloride diperchlorate dihydrate and the dithionate salts\(^6\) of \([\text{en}_2\text{Cr(OH)}_2\text{Cr(en)}_2\] \(14\) \(14\) and of the nitrate salt\(^12\) of \([\text{en}_2\text{Co(OH)}_2\text{Co(en)}_2\] \(14\) \(14\) have demonstrated the meso (\(\Delta,\Delta\)) configuration of the cations. On the basis of the present Guinier powder photography results, indicating isomorphism of \([\text{en}_2\text{M(OH)}_2\text{M(en)}_2\] \text{S}_2\text{O}_6\)\(_2\) (\(\text{M} = \text{Cr, Co or Rh}\)) it may therefore be concluded that the cation \([\text{en}_2\text{Rh(OH)}_2\text{Rh(en)}_2\] \(14\) \(14\) also possesses the meso configuration.

Further work on binuclear di-μ-hydroxido rhodium(III) systems is in progress and will be reported later.

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Note added in proof. Preliminary results\(^22\) indicate that opening of one hydroxido bridge in the rhodium(III) diols to give monohydroxy-bridged species (monools) occurs rapidly in aqueous medium at 25 °C, and that the characterising spectral data for the diols given in Table 1 represent those for equilibrium mixtures containing small proportions of monool species.

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