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

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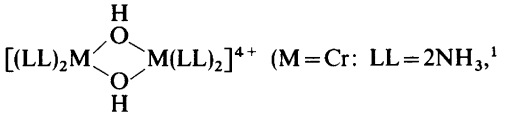
The dithionate salts of the new *diol* cations $[(LL)_2Rh(OH)_2Rh(LL)_2]^{4+}$ (LL = $2NH_3$ or en) have been synthesised by thermal deaquation of *cis*-$[Rh(OH)(H_2O)(LL)_2]S_2O_6$ at 120 °C and purified as the bromide salts. Guinier X-ray powder photographs indicate $[(NH_3)_4Rh(OH)_2Rh(NH_3)_4]Br_4.4H_2O$ and $[(en)_2Rh(OH)_2Rh(en)_2](S_2O_6)_2$ 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* (Δ,Λ) 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



$[(LL)_2M(OH)_2M(LL)_2]^{4+}$ (M = Cr: LL = $2NH_3$,[1] 1,2-diaminoethane(en),[1-5] 2-picolylamine,[6] 1,10-phenanthroline[7-10] or 2,2'-bipyridine,[9,10] or $(LL)_2$ = 1,6-bis(2'-pyridyl)-2,5-diazahexane.[11] M = Co: LL = $2NH_3$[1] or en[1,12]). The heterobinuclear species $(-)_{589}$-Λ,Δ-$[(en)_2Cr(OH)_2Co(en)_2]^{4+}$ has also been prepared and its equilibria with mono-bridged systems examined.[13]

With the exception of the cation $[(H_2O)_4Rh(OH)_2Rh(H_2O)_4]^{4+}$, 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 octaammine- and tetrakis-(1,2-diaminoethane) *diol* systems. This paper describes the synthesis of the latter *via* the intermediacy of the isolated and purified *cis*-aquahydroxo mononuclear complexes, and their characterisation by chemical and spectroscopic means.

A brief account of this work has been presented previously.[17]

EXPERIMENTAL

Materials. *cis*-$[RhCl_2(NH_3)_4]Cl.\frac{1}{2}H_2O$ and *cis*-$[RhCl_2(en)_2]Cl.1\frac{1}{2}H_2O$ were prepared as described previously.[15,16] Samples of $[(NH_3)_4M(OH)_2M(NH_3)_4]Br_4.4H_2O$ and *meso*-$[(en)_2M(OH)_2M(en)_2](S_2O_6)_2$ (M = 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 1 are given with the wavelength λ in nm and the molar absorbance ε 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 Cu$K\alpha$ 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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Table 1. Ligand-field absorption spectra.

Complex	Medium	λ_{max}	λ_{min}	ε_{max}	ε_{min}	Ref.
cis-$[Rh(H_2O)_2(NH_3)_4]^{3+}$	0.12 M $HClO_4$	326,268	294	107,91	63	This work
cis-$[Rh(OH)_2(NH_3)_4]^{+}$	0.1 M NaOH	335,281	308	122,118	95	This work
cis-$[Rh(H_2O)_2(en)_2]^{3+}$	0.12 M $HClO_4$	318.5,270	289.5	171,135	115	This work
$(+)_{589}$-*cis*-$[Rh(H_2O)_2(en)_2]^{3+}$	*a*	314		184		20
cis-$[Rh(OH)_2(en)_2]^{+}$	0.1 M NaOH	329,278.5	303	179,171	138	This work
	a	332,284		170,164		21 [b]
$(+)_{589}$-*cis*-$[Rh(OH)_2(en)_2]^{+}$	*a*	330		189		20
$[(NH_3)_4Rh(OH)_2Rh(NH_3)_4]^{4+}$	0.012 M $HClO_4$	336	304.5	305	204	This work
	H_2O	336	304.5	308	203	This work
meso-$[(en)_2Rh(OH)_2Rh(en)_2]^{4+}$	0.012 M $HClO_4$	331.5	307	523	443	This work
	H_2O	331.5	307	513	435	This work

[a] Not specified clearly. [b] Calculated spectrum.

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

Syntheses. 1. cis-*Tetraammineaquahydroxorhodium(III) dithionate·0.2 hydrate*, *cis*-$[Rh(OH)(H_2O)(NH_3)_4]S_2O_6 \cdot 0.2H_2O$. A mixture of *cis*-$[RhCl_2(NH_3)_4]Cl.\frac{1}{2}H_2O$ [15] (1.0 g; 3.49 mmol) and $AgNO_3$ (1.77 g; 10.46 mmol) in water (30 ml) was heated under reflux for 3½ 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 $Na_2S_2O_6.2H_2O$ (1.80 g) was added to the combined filtrate plus washings 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 $Na_2S_2O_6.2H_2O$ 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. $[Rh(OH)(H_2O)(NH_3)_4]S_2O_6.0.2H_2O$: H, N, S.

2. cis-*Aquabis(1,2-diaminoethane)hydroxorhodium(III) dithionate*, *cis*-$[Rh(OH)(H_2O)(en)_2]S_2O_6$, *cis*-$[RhCl_2(en)_2]Cl.1\frac{1}{2}H_2O$ [16] (6.0 g; 16.83 mmol) and $AgNO_3$ (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 *ca.* 80 ml) following the addition of $Na_2S_2O_6.2H_2O$ (6.0 g) and then pyridine (5 ml) under stirring and cooling. The impure product was purified by reprecipitation as described in prep. 1. Yield 3.63 g (52 %). Anal. $[Rh(OH)(H_2O)(C_2H_8N_2)_2]S_2O_6$: 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)] bromide tetrahydrate, $[(NH_3)_4Rh(OH)_2Rh(NH_3)_4]Br_4.4H_2O$. *cis*-$[Rh(OH)(H_2O)(NH_3)_4]S_2O_6 \cdot 0.2H_2O$ (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 NH_4Br solution (5 ml). The mixture was stirred vigorously and cooled in an ice-bath for 1½ h. The pale-yellow precipitate was isolated by filtration, washed with ice-cold 1:1 aqueous ethanol, then 96 % ethanol and air-dried. For recrystallisation the product was dissolved on the filter in water (*ca.* 15 ml), and to the filtered solution was added saturated NH_4Br solution (5 ml). The mixture was then kept in an ice-bath for *ca.* 2 h and the yellow crystals were isolated as before and air-dried. Yield 0.25 g (60 %). Anal. $[(NH_3)_4Rh(OH)_2Rh(NH_3)_4]Br_4.4H_2O$: H, N, Br.

4. meso-*Di-μ-hydroxobis[bis(1,2-diaminoethane)rhodium(III)]dithionate*, *meso*-$[(en)_2Rh(OH)_2Rh(en)_2](S_2O_6)_2$. *cis*-$[Rh(OH)(H_2O)(en)_2]S_2O_6$ (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. $[(C_2H_8N_2)_2Rh(OH)_2Rh(C_2H_8N_2)_2](S_2O_6)_2$: 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.

Anal. $[(C_2H_8N_2)_2Rh(OH)_2Rh(C_2H_8N_2)_2](S_2O_6)_2$: C, H, N, S.

5. meso-*Di-μ-hydroxobis[bis(1,2-diaminoethane)-rhodium(III)] bromide dihydrate, meso*-$[(en)_2Rh(OH)_2Rh(en)_2]Br_4.2H_2O$. Crude *diol* dithionate (prep. 4; 0.38 g) was stirred rapidly with saturated NH_4Br 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 NH_4Br solution (8 ml) as in prep. 3. Yield 0.26 g (65 %). Anal. $[(C_2H_8N_2)_2Rh(OH)_2Rh(C_2H_8N_2)_2]Br_4.2H_2O$: C, H, N, Br.

RESULTS AND DISCUSSION

The new *diol* cations $[(LL)_2Rh(OH)_2Rh(LL)_2]^{4+}$ (LL = $2NH_3$ or en) have been synthesised according to the scheme, eqns. (1)–(3).

$$cis\text{-}[RhCl_2(LL)_2]^+ + 2Ag^+ + 2H_2O \xrightarrow{\text{Reflux}} cis\text{-}[Rh(H_2O)_2(LL)_2]^{3+} + 2AgCl \quad (1)$$

$$cis\text{-}[Rh(H_2O)_2(LL)_2]^{3+} + OH^- \xrightarrow{Na_2S_2O_6} cis\text{-}[Rh(OH)(H_2O)(LL)_2]S_2O_6 \quad (2)$$

$$2cis\text{-}[Rh(OH)(H_2O)(LL)_2]S_2O_6 \xrightarrow{120\ ^\circ C} [(LL)_2Rh(OH)_2Rh(LL)_2](S_2O_6)_2 + 2H_2O \quad (3)$$

The formulation of the aquahydroxo 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 *cis*-$[Rh(H_2O)_2(en)_2]^{3+}$ [20] and *cis*-$[Rh(OH)_2(en)_2]^+$,[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 aquahydroxo 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 H_2O per mol Rh, microanalytical data being in satisfactory agreement with the composition $[Rh(OH)(H_2O)(NH_3)_4]S_2O_6 \cdot 0.2H_2O$; 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 $[Rh(OH)(H_2O)(en)_2]S_2O_6$, 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 H_2O per mol Rh.

Thermal deaquation of the aquahydroxo 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 $[(NH_3)_4Rh(OH)_2Rh(NH_3)_4]Br_4.4H_2O$ and $[(en)_2Rh(OH)_2Rh(en)_2](S_2O_6)_2$ 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[4] of $[(en)_2Cr(OH)_2Cr(en)_2]^{4+}$, and of the nitrate salt[12] of $[(en)_2Co(OH)_2Co(en)^2]^{4+}$ have demonstrated the *meso* (Δ,Λ) configuration of the cations. On the basis of the present Guinier powder photography results, indicating isomorphism of $[(en)_2M(OH)_2M(en)_2](S_2O_6)_2$ (M = Cr, Co or Rh), it may therefore be concluded that the cation $[(en)_2Rh(OH)_2Rh(en)_2]^{4+}$ also possesses the *meso* configuration.

Further work on binuclear di-μ-hydroxo 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 hydroxo bridge in the rhodium(III) *diols* to give monohydroxo-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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