Rhodium(III) Complexes of the *trans*- and *cis*-Bis(1,3-diaminopropane) Series

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Dedicated to Professor K. A. Jensen on his 70th birthday

The complexes *trans*- and *cis*-[RhX$_2$(tn)$_2$]$^+$ (X = Cl or Br; tn = 1,3-diaminopropane) have been prepared from RhCl$_3$.3H$_2$O by a controlled-pH method. In the presence of small amounts of sodium borohydride the dominant product, the *trans* isomer, undergoes a rapid reaction with oxalate ion in boiling aqueous solution to give the chelated oxalato species [Rh(ox)(tn)$_2$]$^+$ in high yield, and the latter reacts cleanly and stereoretentively with boiling aqueous HX (X = Cl or Br) to give the *cis*-dihalo complexes *cis*-[RhX$_2$(tn)$_2$]$^+$. The latter reaction sequence constitutes a more satisfactory synthesis of *cis*-[RhCl$_2$(tn)$_2$]$^+$ than the direct preparation from RhCl$_3$.3H$_2$O. The *trans* isomer of [RhBr$_2$(tn)$_2$]$^+$ is obtained in good yield from the reaction between *trans*-[RhCl$_2$(tn)$_2$]$^+$ and bromide ion in aqueous solution under reflux.

The new complexes have been isolated and purified as the perchlorate salts and their geometry established from a comparison of their ligand-field absorption spectra with those of the bis(1,2-diaminoethane) and tetraammine analogues.

Five-membered chelate ring bis(diamine) complexes of rhodium(III) with 1,2-diaminoethane (ethylenediamine, en)[1] and various *C*- or *N*-methyl substituted 1,2-diaminoethanes [1-4] have been known for some time and a number of them have been of key importance in studies of the substitutional behaviour of rhodium(III) complexes in solution.[5,6] No attention appears to have been paid, however, to analogous complexes containing six-membered diamine chelate rings. The present paper describes the synthesis, characterisation and interconversion of some *trans*- and *cis*-bis(diamine)rhodium(III) complexes of the latter type with the ligand 1,3-diaminopropane (trimethylenediamine, tn).

EXPERIMENTAL

Materials. RhCl$_3$.3H$_2$O was supplied by Johnson-Matthey Ltd. and 1,3-diaminopropane by Fluka. 1,3-Diaminopropane dihydrochloride was prepared by slow addition of a slight excess of a 1:1 (v/v) solution of conc. hydrochloric acid in ethanol to a 1:1 (v/v) ethanolic solution of 1,3-diaminopropane. The diamine solution was cooled in an ice-bath during the addition of the acid. After leaving the mixture to stand for 30 min at 0 °C, the white crystals were filtered off, washed with 96 % ethanol and dried by air suction. The product was recrystallised by dissolving it in conc. hydrochloric acid and slowly adding an excess of 96 % ethanol to the stirred, filtered solution. The crystals were then filtered off and washed and dried as before. Anal. C$_3$H$_{12}$N$_2$Cl$_2$: C, H, N.

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

Analyses. Microanalyses for carbon, hydrogen, nitrogen and halogen were performed by the microanalytical laboratory of this department, using standard methods.

Spectra. Absorption spectra in the wavelength region 600 – 250 nm were recorded using a Cary Model 14 spectrophotometer. 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 l mol^{-1} cm^{-1}. Water was used as solvent in all cases.

Synthesis of new complexes. 1. trans-*Dichlorobis(1,3-diaminopropane)rhodium(III) perchlorate,* trans-[RhCl$_2$(tn)$_2$]ClO$_4$.RhCl$_3$.3H$_2$O (5.26 g, 20 mmol) and 1,3-diaminopropane dihydro-

chloride (5.88 g, 40 mmol) were dissolved in water (100 ml) and 2 M NaOH (20 ml, 40 mmol) was then added to the deep red solution. The resulting brick-red suspension was heated under reflux with vigorous magnetic stirring, giving a clear cherry-red solution. 2 M NaOH (ca. 20 ml) was then added, via the reflux condenser, in small aliquots (ca. 1 ml) over a period of about 10 min. The pH of the boiling solution was tested at intervals (universal indicator paper) and addition of NaOH was ceased when the pH was steady at ca. 7. The resulting dirty orange-yellow solution was suction filtered while still hot through a fine porosity sintered glass funnel (to remove some rhodium metal) and the clear, golden-yellow filtrate was treated with 70 % HClO₄ (30 ml), at which point orange-yellow crystals rapidly began to form. After leaving the mixture to stand overnight at room temperature the crystals were isolated by suction filtration on a fine porosity sinter, washed with ice-cold 25 % HClO₄ and then 96 % ethanol (CAUTION!*), and dried by air suction. The product was recrystallised by dissolving it on the filter in the minimum volume of boiling water, filtering the solution and adding 70 % HClO₄ (10 ml) to the filtrate which had been reheated to boiling point. The solution was then left to stand overnight, and the long orange-yellow needles were filtered off and washed and dried as before. Yield 3.15 g (37 %). Anal. [Rh(C₃H₁₀N₂)₂Cl₂]ClO₄: C, H, N, Cl.

2. *cis*-Dichlorobis(1,3-diaminopropane)rhodium(III) perchlorate dihydrate, *cis*-[RhCl₂-(tn)₂]ClO₄.2H₂O. *Isolation from the mother-liquor remaining after removal of the* trans *isomer.* The mother-liquor from prep. 1 (above) was treated with a further quantity of 70 % HClO₄ (20 ml) and then kept in a deep-freezer at ca. − 15 °C for 4 d, during which time a pale yellow precipitate of the crude cis isomer was deposited. The latter was removed by suction filtration and washed and dried as in prep. 1. The product was recrystallised twice from the m nimum volume of boiling water containing a few drops of 4 M HCl by adding a hot solution of LiClO₄.3H₂O (1 g) in water (5 ml) and then keeping the solution in a refrigerator (ca. 5°C) for several days. The lemon-yellow crystals were filtered off, washed with 96 % ethanol and dried by air suction. Yield 0.65 g (7 %). Anal. [Rh(C₃H₁₀N₂)₂Cl₂]ClO₄.2H₂O: C, H, N, Cl.

A more satisfactory synthesis of this isomer is provided by the reaction of [Rh(ox)(tn)₂]⁺ with HCl (prep. 5, below).

3. trans-*Dibromobis(1,3-diaminopropane)-rhodium(III) perchlorate,* trans-[RhBr₂(tn)₂]-ClO₄. A solution of *trans*-[RhCl₂(tn)₂]ClO₄ (1.15 g, 2.73 mmol) and NaBr (5.0 g, 48.6 mmol)

in water (50 ml) was heated under reflux for 3 h. The resulting orange-red solution was treated while hot with a hot solution of LiClO₄.3H₂O (3 g) in water (5 ml) and was then kept in a refrigerator overnight. The orange crystals were filtered off, washed with 96 % ethanol and dried by air suction. The crude product was then again heated under reflux with NaBr (5 g) in water (35 ml) for 2 h and the hot solution treated with 70 % HClO₄ (12 ml) and kept overnight in a refrigerator. The orange crystals were isolated by filtration and recrystallised, washed and dried as for the *trans*-dichloro perchlorate (prep. 1). Yield 0.80 g (57 %). Anal. [Rh(C₃H₁₀N₂)₂Br₂]ClO₄ C, H, N.

4. *Bis(1,3-diaminopropane)oxalatorhodium-(III) perchlorate* 2½ *hydrate,* [Rh(ox)(tn)₂]-ClO₄.2½H₂O. A mixture of *trans*-[RhCl₂(tn)₂]-ClO₄ (0.60 g, 1.42 mmol) and sodium oxalate (0.40 g, 2.98 mmol) in water (50 ml) was heated to boiling. After the solution had boiled for ca. 2 min a small speck of sodium borohydride was added, whereupon an immediate reaction occurred, the mixture darkening owing to the formation of a small amount of rhodium metal. Two further specks of sodium borohydride were added at 1 min intervals and the solution was then heated under reflux for 5 min. The hot solution was filtered through a fine porosity sintered glass funnel and the pale yellow filtrate was cooled to ca. 35 °C. Addition of 70 % HClO₄ (3 ml) and subsequent cooling in a refrigerator for 2 d resulted in the formation of long, pale yellow needles which were isolated by filtration, washed with a little ice-cold water and then 96 % ethanol, and dried by air suction. The product was recrystallised from boiling water (40 ml) by adding a hot solution of LiClO₄.3H₂O (4 g) in water (10 ml) and then keeping the solution in a refrigerator for 24 h. The crystals were filtered off and washed and dried as before. Yield 0.46 g (67 %). Anal. [Rh(C₃H₁₀N₂)₂(C₂O₄)]ClO₄.2½H₂O: C, H, N, Cl.

5. *cis*-[RhCl₂(tn)₂]ClO₄.2H₂O. *Preparation from* [Rh(ox)(tn)₂]ClO₄.2½H₂O. [Rh(ox)(tn)₂]-ClO₄.2½H₂O (0.50 g, 1.03 mmol) was boiled for 1 min with 4 M HCl (15 ml). The hot lemon-yellow solution was treated with 70 % HClO₄ (2 ml) and then kept in a refrigerator for 3 d. The crystals were isolated by filtration, washed with 96 % ethanol (CAUTION!*) and dried by air suction.

The product was recrystallised from boiling water (25 ml) as described in prep. 2. Yield 0.38 g (80 %).

Anal. [Rh(C₃H₁₀N₂)₂Cl₂]ClO₄.2H₂O: C, H, N, Cl.

The electronic absorption spectrum of the complex (Table 1) was identical with that of the product from prep. 2.

6. *cis*-*Dibromobis(1,3-diaminopropane)rho-dium(III) perchlorate* 1½ *hydrate,* *cis*-

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* To obviate any risk of explosion the suction flask should be emptied of perchloric acid washings and rinsed with water before the ethanol washing is performed.

* See footnote to prep. 1.

[RhBr₂(tn)₂]ClO₄.1½H₂O. This complex was prepared in the same way as the *cis*-dichloro analogue (prep. 5), using [Rh(ox)(tn)₂]ClO₄.2½-H₂O (0.50 g) and 5 M HBr (15 ml). After adding 70 % HClO₄ (5 ml) and allowing the solution to cool it was then kept in a deep-freezer at *ca.* −20 °C for several days. The resulting orange crystals were filtered off, washed with 96 % ethanol (CAUTION!*) and dried by air suction. The product was then recrystallised, washed and dried as in prep. 5. Yield 0.37 g (67 %).

Anal. [Rh(C₃H₁₀N₂)₂Br₂]ClO₄.1½H₂O: C, H, N.

RESULTS AND DISCUSSION

The complexes *trans*- and *cis*-[RhCl₂(tn)₂]⁺, the former of which is an excellent starting material for the synthesis of the other bis(tn) complexes described here, were prepared by an extension of the method of Johnson and Basolo[1] for the synthesis of the *trans* and *cis* isomers of [RhCl₂(en)₂]⁺, involving the gradual addition of base to a boiling aqueous solution containing rhodium trichloride trihydrate and the stoichiometric quantity of half-neutralised diamine dihydrochloride until the pH of the reaction mixture is steady at *ca.* 7. Both isomers were isolated as the perchlorate salts after addition of concentrated perchloric acid. The perchlorate salt of the *trans* isomer crystallises rapidly from the hot reaction mixture, whereas that of the *cis* isomer is only obtained, in low yield, after prolonged cooling of the mother-liquor. The yields of the two isomers prepared by this method are comparable to those of the analogous bis(en) complexes (isolated as their nitrate salts),[1] even though the formation of a certain amount of rhodium metal is observed during the synthesis of the 1,3-propanediamine complexes.

The low yield of *cis* isomer obtained as described above, together with the fact that several recrystallisations are necessary to ensure that the product is free from traces of the *trans* isomer, made it desirable to devise a better procedure for the synthesis of the former. In keeping with results obtained in earlier work with the bis(1,2-diaminoethane)-rhodium(III) system[7] it was found that sodium borohydride promotes the rapid reaction of *trans*-[RhCl₂-(tn)₂]⁺ with oxalate ion in boiling aqueous solution to give the chelated oxalato complex [Rh(ox)(tn)₂]⁺. The latter can be isolated
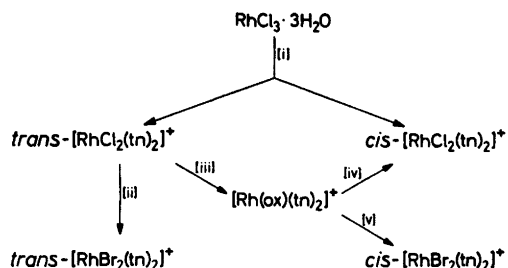

Fig. 1. Reaction scheme for synthesis and interconversion of bis(tn) rhodium(III) complexes. [i], 2 mol tn.2HCl + gradual addition of NaOH to boiling solution; [ii], excess Br⁻ + reflux; [iii], oxalate ion + trace NaBH₄ + boiling; [iv] + [v], aqueous HX (X = Cl or Br) + boiling.

and purified in high yield as the perchlorate salt and is a convenient precursor for the synthesis of other *cis*-bis(1,3-diaminopropane) rhodium(III) complexes since, by analogy with [Rh(ox)(en)₂]⁺ [7] and [Rh(ox)(NH₃)₄]⁺,[8] it reacts rapidly and stereoretentively with boiling aqueous hydrohalic acid HX (X = Cl or Br) to give *cis*-[RhX₂(tn)₂]⁺.

The *trans* isomer of [RhBr₂(tn)₂]⁺ may be prepared by the reaction of *trans*-[RhCl₂(tn)₂]⁺ with bromide ion (excess) in aqueous solution under reflux and isolated in high yield as the perchlorate.

The initial synthetic- and subsequent interconversion reactions employed in the present work are summarised in Fig. 1.

The geometric configuration of *trans*- and *cis*-[RhX₂(tn)₂]⁺ (X = Cl or Br) is assigned on the basis of a comparison of their ligand-field absorption spectra with those of the known bis(1,2-diaminoethane) and tetraammine analogues (Table 1). The spectrum of [Rh(ox)(tn)₂]⁺ (which necessarily has the *cis* configuration) is, as expected, very similar to those of [Rh(ox)(en)₂]⁺ and [Rh(ox)(NH₃)₄]⁺ (Table 1).

Recent work [12,13] on the kinetics and the steric course of base hydrolysis of *trans*-[RhCl₂(en)₂]⁺ has revealed a rate-law of the form: $k_{obs} = k_1 + k_2[OH^-]$. Appreciable *trans* → *cis* isomerisation, which is otherwise very rare in rhodium(III) systems of this type, occurs at moderately high pH and is apparently associated with the second-order pathway.[12] With this in mind a kinetic study of the base hydrolysis behaviour of *trans*-[RhCl₂(tn)₂]⁺ is currently in progress.[14]

Table 1. Ligand-field spectra of *trans*- and *cis*-bis(1,3-diaminopropane)rhodium(III) complexes and some related chromophores.

Complex	λ_{max}	λ_{min}	ε_{max}	ε_{min}	Ref.
trans-$[RhCl_2(tn)_2]^+$	418, ca.315(sh), 289	363, 281	80, ca. 85, 136	10.7, 132	This work
trans-$[RhCl_2(en)_2]^+$	406, 286		75, 130		1
	406, 286		84, 130		9
	415, 293		74, 85		10
trans-$[RhCl_2(NH_3)_4]^+$	ca.387(sh), 293	321, 278	ca. 89, 125	71, 105	This work
cis-$[RhCl_2(tn)_2]^+$	353, 295		123, 180		1
cis-$[RhCl_2(en)_2]^+$	352, 296		155, 185		7
	352, 295		195, 108		8
cis-$[RhCl_2(NH_3)_4]^+$	360, ca.342(sh), 281	379, 268	119, ca. 58, 3170	11.8, 2590	This work
trans-$[RhBr_2(tn)_2]^+$	441, 276		100, 1800		1
trans-$[RhBr_2(en)_2]^+$	425, 276		107, 2720		9
	428, ca.280(sh)		111, ca.2700		10
trans-$[RhBr_2(NH_3)_4]^+$	441, ca.405(sh), ca.278(sh)	339	ca.125, ca.1140	114	This work
cis-$[RhBr_2(tn)_2]^+$	368, 276(sh)		158, 900		1
cis-$[RhBr_2(en)_2]^+$	362, 280(sh)		210, 900		7
	363, ca.275(sh)		260, ca. 940		8
cis-$[RhBr_2(NH_3)_4]^+$	377	307	170	142	This work
$[Rh(ox)(tn)_2]^+$	329		172		11
$[Rh(ox)(en)_2]^+$	325		260		7
	325		270		
$[Rh(ox)(NH_3)_4]^+$	333		167		8

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