Synthetic Aspects of Rhodium(III) Chemistry. I. A High Yield Route to *cis*-Bis(1,2-diaminoethane)rhodium(III) Complexes

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Dedicated to Jannik Bjerrum on the occasion of his 70th birthday

A crude, approx. 1:1 mixture of *trans*- and *cis*-[RhCl$_2$(en)$_2$]ClO$_4$ (en = 1,2-diaminoethane) is obtained in *ca.* 80 % yield following the pH-controlled reaction of RhCl$_3$.3H$_2$O with en (as en.2HCl) and a subsequent heat-treatment of the evaporated reaction mixture. The crude mixture is converted to [Rh(ox)(en)$_2$]$^+$ (ox = oxalate) by the borohydride-promoted reaction of the former with oxalate ion in boiling aqueous solution, and the oxalato complex can be isolated as the pure perchlorate or bromide salts in *ca.* 80 % yield. The *cis*-dihalo complexes, *cis*-[RhX$_2$(en)$_2$]X.*n*H$_2$O (X = Cl, *n* = 1½; X = Br, *n* = 1) are obtained in almost quantitative yield following the reaction of [Rh(ox)(en)$_2$]$^+$ (as the perchlorate) with boiling 6 M HX, so that the entire reaction sequence described above permits the synthesis of the *cis*-dihalo complexes in ≥ 60 % overall yield based on RhCl$_3$.3H$_2$O.

The first reliable route to bis(diamine)rhodium(III) complexes was provided in 1960 by Anderson and Basolo with their synthesis of the two geometric isomers of the dichlorobis(1,2-diaminoethane)-rhodium(III) cation[1] and was elaborated on in a subsequent paper.[2] For the latter complexes their method involves the gradual addition of base to a boiling aqueous solution containing RhCl$_3$.3H$_2$O and the stoichiometric quantity of half-neutralized diamine dihydrochloride, the *trans* and *cis* isomers then being isolated as the nitrate salts in *ca.* 33 and *ca.* 11 % yield, respectively. Other workers[3−6] have subsequently employed minor variations of the original procedure in an attempt to improve the total yield and/or modify the ratio of *trans* to *cis*

isomer, but with only limited success. Gillard *et al.*[7] reported the isolation of *trans*-[RhCl$_2$(en)$_2$]-NO$_3$ (en = 1,2-diaminoethane) in 50 % yield following the reaction between *trans*-[RhCl$_2$(py)$_4$]$^+$ (py = pyridine) and en in aqueous solution, and Dvurechenskaya *et al.*[6] using the reaction of [Rh(NO$_2$)$_6$]$^{3−}$ with en obtained a 40 % overall yield of a mixture of the two isomers of [RhCl$_2$-(en)$_2$]NO$_3$, the *cis* isomer comprising 70 % of the total.

The rather low overall yields obtained using these methods, combined with difficulties encountered in separating pure *cis*-[RhCl$_2$(en)$_2$]$^+$ from *cis/trans* mixtures in satisfactory yield,[2,6] have undoubtedly had an inhibitory effect on work on *cis*-bis(1,2-diaminoethane)rhodium(III) systems, although the observation by Addison *et al.*[4] that *trans*-[RhCl$_2$-(en)$_2$]$^+$ can be converted in high yield to the chelate oxalato complex [Rh(ox)(en)$_2$]$^+$, which in turn reacts stereoretentively with, *e.g.*, aqueous HX (X = Cl or Br) to give *cis*-[RhX$_2$(en)$_2$]$^+$, has improved matters. In the present paper I describe a synthetic procedure, based upon that of Basolo *et al.*,[1,2] which gives a *ca.* 80 % yield of an approx. 1:1 mixture of *trans*- and *cis*-[RhCl$_2$(en)$_2$]ClO$_4$. The pure perchlorate or bromide salts of [Rh(ox)-(en)$_2$]$^+$ can be prepared from the latter mixture in *ca.* 65 % overall yield based on RhCl$_3$.3H$_2$O (which is the most commonly available starting material), and complexes such as *cis*-[RhX$_2$(en)$_2$]$^+$ (X = Cl or Br) can thus be synthesized in considerably higher yield than has previously been possible.

Table 1. Ligand-field absorption spectra of *cis*-bis(1,2-diaminoethane)rhodium(III) complexes.

Complex	Medium	λ_{max}	λ_{min}	ε_{max}	ε_{min}	Ref.
$[Rh(ox)(en)_2]^+$	H_2O	325.5	304	253	196	This work [a]
	H_2O	325		270		4
	H_2O	325		260		5
cis-$[RhCl_2(en)_2]^+$	0.1 M HCl	352, 295	322, 272.5	194, 189	129 118	This work
	H_2O	352, 295		155, 180		2
	H_2O	352, 296		195, 185		4
		352, 294		190, 190		14
cis-$[RhBr_2(en)_2]^+$	H_2O	366, *ca.*280(sh)	334	255, *ca.*980	174	This work
	H_2O	362, 276(sh)		210, 900		2
	H_2O	363, 280(sh)		260, 900		4

[a] Bromide monohydrate.

EXPERIMENTAL

Materials. $RhCl_3.3H_2O$ was supplied by Johnson-Matthey Ltd. and 1,2-diaminoethane dihydrochloride ("*puriss*") by Fluka. All other chemicals were of analytical or reagent grade and were used without further purification.

Analyses. Microanalyses were performed as described previously.[8]

Spectra. Absorption spectra in the wavelength region 600 – 250 nm were recorded on a Cary Model 14 or a Carl Zeiss DMR 21 recording spectrophotometer. Characterizing 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 $l \ mol^{-1} \ cm^{-1}$.

Synthetic procedures. *1.* trans + cis-*Dichlorobis-(1,2-diaminoethane)rhodium(III)* *perchlorate mixture,trans + cis*-$[RhCl_2(en)_2]ClO_4$. $RhCl_3.3H_2O$ (5.0 g, 19 mmol) and 1,2-diaminoethane dihydrochloride (5.05 g, 38 mmol) were dissolved in water (30 ml) with gentle heating, and 2 M NaOH (19 ml, 38 mmol) was then added to the deep red solution. The brick-red suspension was then heated under reflux with magnetic stirring, giving a clear cherry-red solution. After the solution had boiled for *ca.* 1 min, 2 M NaOH (*ca.* 19 ml) was added dropwise, through the reflux condenser, over a period of 5 – 10 min until the pH of the boiling solution became steady at 6.5 – 7 (narrow-range indicator paper). The orange-red solution was then evaporated to dryness carefully on a rotary evaporator, and the flask and solid residue were heated at 170 °C for 24 h. The orange-yellow solid was dissolved by boiling with 0.1 M HCl (50 ml) and to the hot, filtered solution was added a hot solution of $NaClO_4.H_2O$ (10 g) in water (10 ml). On cooling slightly a copious yellow precipitate was rapidly

formed, and after keeping the mixture in a refrigerator for 2 d with occasional agitation the product was isolated by filtration, washed with a little ice-cold water, 96 % ethanol and finally ether, and air-dried. Yield 5.83 g (*ca.* 79 %).

Comparison of the electronic absorption spectrum of the product mixture with the spectra of *trans*-[1,2] and *cis*-$[RhCl_2(en)_2]^+$ (Table 1) indicated the mixture to contain both isomers in *ca.* 1:1 molar ratio, although this ratio appears to be somewhat variable.

2. *Bis(1,2-diaminoethane)oxalatorhodium(III)* *perchlorate*, $[Rh(ox)(en)_2]ClO_4$. A portion of crude *trans*- + *cis*-$[RhCl_2(en)_2]ClO_4$ mixture obtained as in prep. 1 above (8.0 g, *ca.* 20.3 mmol) and sodium oxalate (5.2 g, 38.8 mmol) were boiled in water (240 ml) in a 500 ml round bottom flask until all the solid had dissolved. After a further 2 min a small speck of sodium borohydride was placed in the boiling solution with a glass spatula. This was repeated twice more at 5 min intervals and the solution was finally allowed to boil for a further 10 min. The hot solution was then quickly filtered by suction through a fine porosity sintered glass funnel, the flask and funnel were rinsed with boiling water (2×20 ml) and the washings were filtered into the bulk filtrate. A solution of $NaClO_4.H_2O$ (15 g) in water (15 ml) was added to the filtrate and the mixture was then left to stand in a refrigerator (*ca.* 5 °C) for 24 h. The grey-tinged pale yellow crystals were isolated by filtration, washed with ice-cold water and then redissolved in water (450 ml) by boiling. After adding activated charcoal (*ca.* 1 g) and boiling for *ca.* 1 min the mixture was filtered by suction through a fine porosity sintered glass funnel, the flask and funnel were rinsed with boiling water (2×25 ml), and to the combined filtrate was added a boiling, filtered solution of $NaClO_4.H_2O$ (15 g)

in water (10 ml). Fine pale yellow crystals were rapidly formed, and after leaving the mixture to stand at room temperature for 24 h and then at *ca.* 5 °C for a further 24 h, the product was isolated by filtration, washed with cold water, 96 % ethanol and finally ether, and air-dried. Yield 7.04 g (*ca.* 84 %, or 66 % based on RhCl$_3$.3H$_2$O). Anal. [Rh(C$_2$O$_4$)(C$_2$H$_8$N$_2$)$_2$]ClO$_4$: C, H, N, Cl.

3. Bis(1,2-diaminoethane)oxalatorhodium(III) bromide monohydrate, [Rh(ox)(en)$_2$]Br.H$_2$O. Crude *trans-* + *cis*-[RhCl$_2$(en)$_2$]ClO$_4$ mixture (5.83 g, *ca.* 14.8 mmol) was converted to the chloride salts by stirring with Amberlite IRA-400 resin (Cl$^-$ form; 50 ml of wet resin) in water (100 ml) at 25 °C for 1 h. The resin was removed by filtration, washed with water (3 × 20 ml), and to the combined filtrate plus washings was added sodium oxalate (4 g, 29.8 mmol). The mixture was boiled, treated with sodium borohydride and filtered as described in prep. 2. To the hot filtrate was added a hot solution of NaBr (12 g) in water (20 ml), and the mixture was then kept in a refrigerator for 2 d. The resulting pale yellow crystals were filtered off on a fine porosity sintered glass funnel, washed with methanol and air-dried. The product was recrystallized by dissolving it on the filter in boiling water (total *ca.* 100 ml) and adding a boiling solution of NaBr (5 g) in water (10 ml) to the filtered solution which had been reheated to boiling. The mixture was left to cool to ambient temperature and then kept in a refrigerator for 2 d. The crystals were isolated by filtration, washed several times with ice-cold 2 M HBr, then 96 % ethanol and air-dried. Yield 4.85 g (*ca.* 80 %, or 62 % based on RhCl$_3$.3H$_2$O). Anal. [Rh(C$_2$O$_4$)(C$_2$H$_8$N$_2$)$_2$]Br.H$_2$O: C, H, N, Br.

4. cis-Dichlorobis(1,2-diaminoethane)rhodium- (III) chloride 1½ hydrate, cis-[RhCl$_2$(en)$_2$]Cl.1½-H$_2$O. [Rh(ox)(en)$_2$]ClO$_4$ (5.0 g, 12.2 mmol) was boiled for 2 min with 6 M HCl (70 ml). The resulting bright lemon-yellow solution was allowed to cool to ambient temperature and then kept in a refrigerator (*ca.* 3 °C) for 24 h. The large bright yellow crystals were filtered off, washed liberally with 96 % ethanol and air-dried. Yield 4.13 g (95 %, or 63 % based on RhCl$_3$.3H$_2$O). The unrecrystallized product is sufficiently pure for most purposes. Electronic absorption spectrum (*cf.* Table 1) (λ,ε)$_{max}$: (352,193), (295,191). (λ,ε)$_{min}$: (322,129), (272.5,124). A portion of this "crude" product (4.0 g) was recrystallized from boiling 6 M HCl (total 60 ml) by allowing the filtered solution to cool to ambient temperature and then keeping the mixture in a refrigerator for 2 d. The crystals were filtered off and washed and dried as before. Recrystallization yield 3.68 g (92 %). Anal. [RhCl$_2$(C$_2$H$_8$N$_2$)$_2$]Cl.1½-H$_2$O: C, H, N, Cl. The electronic absorption spectrum of the product (Table 1) did not change on further recrystallization.

5. cis-Dibromobis(1,2-diaminoethane)rhodium- (III) bromide monohydrate, cis-[RhBr$_2$(en)$_2$]Br.-H$_2$O. The latter complex was prepared in the same way as the *cis*-dichloro analogue (prep. 4), using [Rh(ox)(en)$_2$]ClO$_4$ (3.0 g) and 6 M HBr (65 ml). Yield of unrecrystallized, but almost pure product 3.41 g (97 %, or 64 % based on RhCl$_3$.3H$_2$O). Anal. [RhBr$_2$(C$_2$H$_8$N$_2$)$_2$]Br.H$_2$O: C, H, N, Br. Electronic absorption spectrum (*cf.* Table 1) (λ,ε)$_{max}$: (366,253), (*ca.* 280(sh), *ca.* 1020). (λ,ε)$_{min}$: (335,171). A portion of the "crude" product (2.0 g) was recrystallized as in prep. 4, using 6 M HBr (*ca.* 70 ml). Recrystallization yield 1.85 g (93 %). Anal. [RhBr$_2$(C$_2$H$_8$N$_2$)$_2$]Br.-H$_2$O: C, H, N, Br. The electronic absorption spectrum of the product did not change on further recrystallization.

RESULTS AND DISCUSSION

The widely-used method of Basolo *et al.*[1,2] for the synthesis of *trans-* and *cis*-[RhCl$_2$(en)$_2$]$^+$ gives a moderate yield of *trans* isomer together with a poor yield of *cis* isomer. The same type of approach has been employed in the synthesis of analogous rhodium(III) complexes with a variety of other diamines[2,8–10] or with linear tetraamines[11,12] but in no cases were total yields exceeding 50 % obtained. A possible explanation for the failure to isolate such a large proportion of the initial amount of Rh(III) employed is that highly soluble aqua species containing incompletely-coordinated amine ligands (*e.g.* monodentate en) are formed together with the desired complexes, and on this basis it seemed likely that the total yield of *e.g.*, *trans-* and *cis*-[RhCl$_2$(en)$_2$]$^+$ could be improved by thermal deaquation of such species in the solid state. This approach has proved successful and has enabled the preparation of a crude, approx. 1:1 mixture of *trans-* and *cis*-[RhCl$_2$(en)$_2$]ClO$_4$ in *ca.* 80 % total yield.

Although recent work[13] has shown that it is possible to separate the two isomers of [RhCl$_2$-(en)$_2$]$^+$ by ion-exchange chromatography such a procedure is tedious from the preparative point of view, and as far as isolation of the *trans*-isomer from the crude mixture obtained in the present work is concerned it constitutes no significant improvement over the method of Basolo *et al.*[1,2] for the direct isolation of pure *trans*-[RhCl$_2$(en)$_2$]-NO$_3$. However, by making use of previous observations on the formation of the chelate oxalato complex [Rh(ox)(en)$_2$]$^+$ in the reaction of the *trans*[4] and *cis*[5] isomers of [RhCl$_2$(en)$_2$]$^+$ with oxalate ion

in aqueous solution under various conditions, it has proved possible to synthesize the pure perchlorate or bromide salts of $[Rh(ox)(en)_2]^+$ in high yield from the crude *trans-* + *cis*-$[RhCl_2(en)_2]$-ClO_4 mixture. The oxalato complex reacts cleanly and stereoretentively[4] with aqueous HX (X = Cl or Br) to give the corresponding *cis*-dihalo complexes essentially quantitatively; thus the entire reaction sequence described here permits the synthesis of *cis*-$[RhX_2(en)_2]X.nH_2O$ (X = Cl, $n = 1\frac{1}{2}$; X = Br, $n = 1$) in *ca.* $60-65 \%$ overall yield based on the commonly used starting material $RhCl_3.3H_2O$.

It seems likely that the approach described in this paper may be of rather general applicability in improving the yield of rhodium(III) amine complexes whose synthesis entails the use of the procedure of Basolo *et al.*[1,2]

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