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# Mechanistic Studies on Six-membered Chelate Complexes. Aquation of Some Dichlorobis(Substituted Biguanide)Rhodium(III) Nitrates

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*Studies on the aquation of dichlorobis(substituted biguanide)rhodium(III) complexes were carried out in aqueous and aqueous methanol media by conductometric method. The release of chlorides in all the complexes takes place in a stepwise manner and rates of each step were determined by a graphical method. Rates of aquation decrease with any substituent and remain nearly equal for all the substituents for both steps. Inductive effect does not seem to be responsible as it changes very little with substitution. In aqueous methanol, rates decrease with increased percentage of methanol for the unsubstituted biguanide complex, but the reverse is true for the phenyl substituted complex. This is due to the greater solvation of phenyl complex in the organic enriched solvent. From various factors it was indicated that the probability of bond formation in the transition state is greater with substituted complexes.*

## Introduction

Aquation of octahedral metal complexes, shown by equation 1, where M = cobalt(III), rhodium(III) *etc.* and AA = bidentate chelate, primarily proceeds by a dissociative mechanism [1]. This is supported by the enhanced rate of aquation with increased size and number of substituted groups on the chelate [2]. But the substitution of two methyl groups on a six-membered chelate, 1,3-propanediamine, indicates a decrease in rate [2] and it is likely that the substitution on a six-membered chelate introduces some change in the chelate structure so that the mechanistic path of the complex changes completely. A literature survey could not present any more information in this regard. So, we have undertaken the present study to clarify the mechanism of aquation of substituted six-membered chelate complexes. The study has been made with the dichloro-complexes of methyl, ethyl and phenyl substituted bis-biguanide complexes of rhodium(III). As the dichlorobisbiguanide complexes of cobalt(III) are unstable in aqueous solution [3], they are not suitable for the present study. Apart from the mechanistic details, this study will help in the general understanding on the effect of increased size of the non-labile ligand on the rate of aquation of rhodium(III) complexes.

$$[M(AA)_2Cl_2]^+ + 2H_2O \longrightarrow [M(AA)_2(H_2O)_2]^{3+} + 2Cl^- \qquad (1)$$

## Experimental

### *Preparation of the Complexes*

Materials

(i) Rhodium trichloride$\cdot$x$H_2O$ (Johnson-Mathey, U.K.). (ii) Substituted biguanide chlorides – the

Analysis*

| | % | Rh | C | H | N |
|---|---|---|---|---|---|
| $[Rh(MeBigH)_2Cl_2]NO_3\cdot4H_2O$ | found | 19.00 | 13.52 | 5.03 | 27.82 |
| | calcd. | 19.14 | 13.38 | 4.83 | 28.62 |
| $[Rh(EtbigH)_2Cl_2]NO_3\cdot4H_2O$ | found | | 17.58 | 5.49 | 27.70 |
| | calcd. | | 16.96 | 5.30 | 27.20 |
| $[Rh(PhBigH)_2Cl_2]NO_3\cdot4H_2O$ | found | | 28.70 | 5.21 | 24.00 |
| | calcd. | | 29.00 | 4.83 | 23.26 |

(MeBigH = Methylbiguanide; EtBigH = Ethylbiguanide; PhBigH = Phenylbiguanide)

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*Analyses of C, H and N for all the complexes were made by Prof. H. Malissa, G. Reuter, Analytical Laboratory, D-5250 Engelskirchen, West Germany.

TABLE I. Rate Constants for the First ($k_1$) and Second ($k_2$) Stages of Aquation at Different Temperatures.

| Complex | | Temperature, °C | | | | | | Ref. |
|---|---|---|---|---|---|---|---|---|
| | | 32° | 40° | 45° | 50° | 55° | 60° | |
| $Rh(BigH)_2Cl_2^+$ | $10^3$ $k_1$, $sec^{-1}$ | 2.40 | 5.10 | | 9.23 | | | 6 |
| $Rh(MeBigH)_2Cl_2^+$ | " | | | 3.31 | 5.14 | 6.30 | 8.57 | |
| $Rh(EtBigH)_2Cl_2^+$ | " | | | 3.21 | 4.67 | 6.30 | 8.39 | |
| $Rh(PhBigH)_2Cl_2^+$ | " | | | 2.60 | 3.85 | 6.16 | 7.97 | |
| $Rh(BigH)_2(H_2O)Cl^{2+}$ | $10^4$ $k_2$ $sec^{-1}$ | 3.65 | 5.29 | | 10.10 | | | 6 |
| $Rh(MeBigH)_2(H_2O)Cl^{2+}$ | " | | | 7.96 | 9.05 | 10.20 | 14.20 | |
| $Rh(EtBigH)_2(H_2O)Cl^{2+}$ | " | | | 6.20 | 8.00 | 10.20 | 13.99 | |
| $Rh(PhBigH)_2(H_2O)Cl^{2+}$ | " | | | 3.22 | 5.27 | 7.28 | 8.76 | |

respective biguanide sulphates were prepared by the method given in the literature [4]. Corresponding chlorides were obtained *in situ* with barium chloride from aqueous solutions.

All the three dichlorobis(substituted biguanide)-rhodium(III) chlorides were obtained by digesting rhodium trichloride with twice the equivalent amount of substituted biguanide chloride in the presence of a few drops of concentrated hydrochloric acid for about thirty minutes as in the case of dichlorobis-biguaniderhodium(III) complex [5]. All of these were crystallized from hot aqueous solutions. Respective nitrates were obtained by metathesis of the complex chlorides with silver nitrate in aqueous solution. The products were obtained as fine yellow crystals by the concentration of the filtrates. These nitrates crystallise with four molecules of water.

Conductivity water and methanol (G. R. E. Merck) were used as such for making all the solutions. All the complexes, like the dichlorobisbiguaniderhodium-(III) complex ion, aquate in water and also in methyl alcohol–water mixed solvent medium by successive release of chloride ions and the course of aquation was determined by measuring the change in conductance, which is the reciprocal of measured resistance, of the experimental solution. Measurements of resistance were made with a Philips conductivity bridge (Philips PR 9500/90) at the desired time interval with a dip-type cell which was thermostatted at the desired temperature. Kinetic runs were made in the same way as described earlier [6].

## Results and Discussion

The amount of chloride ion released during the aquation, obtained by eluting the experimental solution through a cation exchanger (Amberlite 120, 100–150 mesh), and measured as AgCl indicates that the aquation reaction with all the complexes proceeds almost completely in the forward direction forming $Rh(S\text{-}BigH)_2(H_2O)_2^{3+}$ (S = methyl, ethyl or phenyl substitution). The reactions do not follow simple first order kinetics and so it was assumed that these reactions occur in steps as shown in equation (2),

$$[Rh(S\text{-}BigH)_2Cl_2]NO_3 + H_2O \xrightarrow{k_1} [Rh(S\text{-}BigH)_2(H_2O)Cl]NO_3\cdot Cl \qquad (2a)$$

and

$$[Rh(S\text{-}BigH)_2(H_2O)Cl]NO_3\cdot Cl\cdot + H_2O \xrightarrow{k_2} [Rh(S\text{-}BigH)_2(H_2O)_2]NO_3\cdot 2Cl \qquad (2b)$$

The values of $k_1$ and $k_2$ for each complex ion were derived graphically in a similar manner as the dichlorobisbiguaniderhodium(III) complex [6]. Triplicate runs were made for each rate plot. Average values of the rate constants thus obtained at various temperatures are listed in Table I. The rates showed a reproducibility of ±3%.

At any particular temperature for both stages, the rates of aquation of substituted complexes are smaller than the rates of aquation of the unsubstituted complex. The rates of aquation of substituted complexes are nearly equal for all the complexes even though the size of the substituent on the biguanide increases from methyl to ethyl and phenyl substitution. This observation is somewhat unusual and interesting as it goes against a bond-breaking process, as observed with ethylenediamine and substituted ethylenediamine rhodium(III) complexes [7]. Inductive effect is not responsible for this behaviour as, except phenylbiguanide, the basicities of all other biguanides are nearly equal. $pK_1$ Values of the biguanides at 32 °C (given within brackets) are as follows [4]:

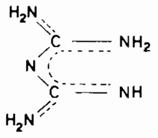
$$BigH(11.49) \sim MeBigH(11.4) \sim$$
$$EtBigH(11.5) > PhBigH(10.7)$$

The relative rates of aquation for the first and second steps indicate that, whereas for the first step the rate decreases with substitution, it is somewhat insensitive towards substitution for the second step, except for the phenylbiguanide complex.

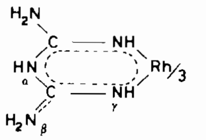
Relative rates of aquation:

| | BigH | MeBigH | EtBigH | PhBigH |
|---|---|---|---|---|
| First step | 1 | 0.56 | 0.50 | 0.42 |
| Second step | 1 | 0.90 | 0.90 | 0.51 |

The pseudo-aromaticity of the six-membered biguanide chelate ring [8 i, ii], is one of the factor that may be responsible for this behaviour. Biguanide and its metal chelates contain delocalized π-electron system over the whole molecule as shown below:



Biguanide



Metal Chelate

The positions of substitution have been predicted to be at the nitrogen atoms of the chelate ring coordinated to the metal ion, that is at the 'γ' positions only [8 ii]. Substitution of electron withdrawing groups, such as halogens, on the biguanide chelate ring decreases the stability of metal complex with greater rate of reaction through the interaction of $p_z$ orbital with the ring π system [8 ii]. In the experimental complexes, the free 'p' orbital electron of methyl and ethyl radicals will interact with ring π system (hyperconjugation), but this will hardly affect the stability of the complex, and substitution effects, if any, will be small. π–π interaction of the phenyl group with the biguanide chelate ring increases the stability of the complex by resonance and it will give a lower rate of chloride release. At the same time the strain involved with the bigger size of this complex will show an opposite effect. The combined effect of these two factors explains the insensitivity of rate on substitution of a phenyl group.

Table II records the $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ values for the aquation for both stages of chloride release as obtained with the Eyring equation [9]. The heat of activation, $\Delta H^{\ddagger}$ values for both steps of chloride release differs very little with substitution (*ca.* 0.5 kcal, except for the PhBigH complex in its second stage of aquation). The small variation of $\Delta H^{\ddagger}$ values with substitution indicates insensitivity of substitution effect towards metal–halide bond strengths. Nearly equal $\Delta H^{\ddagger}$ values in all the complexes indicate a nearly equal Rh–Cl bond strength. The observed lower rate of aquation for the phenylbiguanide complex seems to be due to an antropy effect. $\Delta S^{\ddagger}$ values for the release of the first chloride ion for all three complexes are very near the entropy of hydration of chloride ion ($\Delta S = -23.1$ e.u.) [10]. It seems that complete rupture of the Rh–Cl bond takes place in the transition state for all the complexes, consistent with the mechanism proposed earlier for unsubstituted biguanide complex [6]. But for the release of the second chloride ion in all the complexes, the more negative entropy value than the entropy of hydration of hydrogen chloride [11] ($\Delta S = -31.1$ e.u.) indicates that along with the release of one hydrogen chloride, bond formation by incoming aquo ligand in the transition state takes place. This is consistent with the bond formation tendency by the incoming water in the transition state observed with chloroamine complexes of Rh(III) [12]. These two factors, the release of one molecule of hydrogen chloride and fixation of one aquo ligand in the transition state [13], together give an entropy change of –34.1 e.u. There may

TABLE II. Activation Parameters for the Aquation of Rh(III)–BigH Complexes in Water.

| Complex | $\Delta H^{\ddagger}$ (kcal/mol) | $\Delta S^{\ddagger}$ (e.u.) | Ref. |
|---|---|---|---|
| $Rh(BigH)_2Cl_2^+$ | 14 ± 0.2 | –25 ± 0.8 | 6 |
| $Rh(MeBigH)_2Cl_2^+$ | 14.8 ± 0.4 | –23.8 ± 1.8 | |
| $Rh(EtBigH)_2Cl_2^+$ | 14.4 ± 0.4 | –24 ± 1.7 | |
| $Rh(PhBigH)_2Cl_2^+$ | 14.4 ± 0.3 | –25.5 ± 1 | |
| $Rh(BigH)_2(H_2O)Cl^{2+}$ | 12.3 ± 0.2 | –34.4 ± 0.9 | 6 |
| $Rh(MeBigH)_2(H_2O)Cl^{2+}$ | 11.5 ± 0.6 | –36,8 ± 2.7 | |
| $Rh(EtBigH)_2(H_2O)Cl^{2+}$ | 11.7 ± 0.6 | –36 ± 2.6 | |
| $Rh(PhBigH)_2(H_2O)Cl^{2+}$ | 10.6 ± 0.5 | –40 ± 2 | |

TABLE III. Rate Constants for First and Second Steps of Aquation of $[Rh(BigH)_2Cl_2]^+$ and $[Rh(PhBigH)_2Cl_2]^+$ in Methanol–Water Mixed Solvents at 35 °C.

| Solvent (%Methanol v/v) | $10^3$ $k_1$, $s^{-1}$ | $[Rh(BigH)_2Cl_2]^+$<br>3 + log$k_1$ | $10^4$ $k_2$, $s^{-1}$ | 4 + log$k_2$ | Y |
|---|---|---|---|---|---|
| 0 | [3.14][a] | 0.50 | [4.54][a] | 0.66 | 3.49 |
| 10 | 3.12 | 0.49 | 2.55 | 0.41 | 3.28 |
| 25 | 3.00 | 0.48 | 1.96 | 0.29 | 2.90 |
| 40 | 2.81 | 0.45 | 1.71 | 0.23 | 2.39 |
| 50 | 2.47 | 0.39 | 1.50 | 0.18 | 1.97 |

| Solvent (%Methanol v/v) | $10^3$ $k_1$, $s^{-1}$ | $[Rh(PhBigH)_2Cl_2]$<br>3 + log$k_1$ | $10^4$ $k_2$, $s^{-1}$ | 4 + log$k_2$ | Y |
|---|---|---|---|---|---|
| 0 | 1.98 | 0.30 | 1.20 | 0.08 | 3.49 |
| 10 | 2.03 | 0.31 | 1.45 | 0.16 | 3.28 |
| 25 | 2.32 | 0.37 | 1.44 | 0.16 | 2.90 |
| 40 | 3.45 | 0.54 | 1.48 | 0.17 | 2.39 |
| 50 | 3.45 | 0.54 | 1.60 | 0.20 | 1.97 |

[a] Calculated values from ref. 6. Y values for methanol–water mixed solvents are taken from ref. 20.

also be other factors such as electrostriction effect. The entropy change for the second step of aquation for all the complexes is very near to this value. Release of HCl was confirmed by the observed decrease in pH of the experimental solution during aquation. Fixation of aquo ligand in the transition state indicates that bond formation by the incoming ligand is as important as the dissociation of a chloride ion.

A further clarification of the mechanism was sought by employing a water–methanol mixed solvent system in the kinetic study. The study was made with the dichlorobisbiguanide- and dichlorobisphenylbiguanide complexes. During kinetic investigations, no spectral evidence for methylation was observed with these complexes, as the nature of absorption curves changes in the same manner with the same isosbestic points in water and also in methyl alcohol–water mixed solvents containing up to 50 percent methyl alcohol. In these mixed solvents, the aquation reaction proceeds in a stepwise manner as in aqueous medium [6] forming at least 97% $Rh(S\text{-}BigH)_2(H_2O)_2^{3+}$ as observed by the estimation of released chloride ion with a cation exchanger. The reverse reaction must be small, if not negligible, in comparison with the forward reaction. The rates were calculated from the initial points of the plots. Good first-order kinetics were observed with all the solvent systems. The rates thus obtained are reported in Table III.

For the unsubstituted biguanide complex, for both steps, the rates of aquation decrease as the percentage of water decreases in the solvent system. This is in agreement with the normal trend observed with chloro-amine complexes of cobalt(III) [14, 15], chromium(III) [16] and iridium(III) [14]. But for the phenylbiguanide complex, rates of aquation increase as the percentage of methanol increases in the system. For the chloropentaminerhodium(III) complex, Burgess and Price have observed this sort of rate increase with increasing percentage of ethanol. They tried to explain this anomalous behaviour with possible redox catalysis of traces of rhodium(I) and/or rhodium(II) present in the system [14]. We do not think that this type of redox catalysis plays any role in the aquation of phenylbiguanide complex as there is no reason for the unsubstituted complex to behave in the opposite way. No such redox catalysis was observed in the aquation of dihalobisethylenediamine [17] and dihalobisphenanthrolinerhodium(III) [18] complexes. With these biguanide complexes, though rate variations indicate the opposite trend, an altogether different mechanism is very unlikely. Substitution of a phenyl group on the chelate ring favours solvation by the more organic methanol in the methanol enriched medium. Increased solvation gives an increased rate of aquation.

It is now fairly well established that Grunwald–Winstein solvent Y values correlate well with the logarithms of rate constants for aquation of Co(III)–Cl complexes [19]. Such correlations, however, have been reported for chloropentaminerhodium(III) complex [14] but are yet to be established. Y Values change very little with temperature [20] and the values of 25 °C have been used as such in the present case. Plots of log k *versus* Y for both steps of aquation of $[Rh(BigH)_2Cl_2]$ give nearly linear plots at 35 °C with slight curvature. The most probable straight lines drawn through these points have gradients 0.10 ± 0.02 and 0.22 ± 0.01. The curvature in these plots as well as the observed small gradients may be attributed to some associative character for the

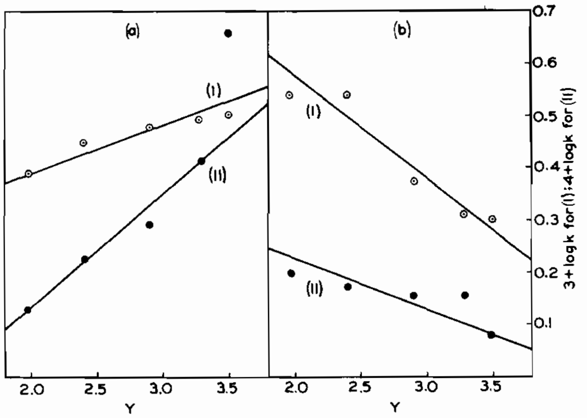


Figure 1. Grunwald–Winstein plot for methanol–water mixed solvents. (a) $Rh(BigH)_2Cl_2^+$: (i) first-step of aquation ($m_1$ = 0.10 ± 0.02); (ii) second-step of aquation ($m_2$ = 0.22 ± 0.01). (b) $Rh(PhBigH)_2Cl_2^+$ : (i) first-step of aquation ($m_1$ = –0.20 ± 0.02); (ii) second-step of aquation ($m_2$ = –0.095 ± 0.015).

aquation of the complex ion. Plots of log k *versus* Y for the phenylbiguanide complex also give nearly linear plots for both steps with negative slopes ($m_1$ = –0.2 ± 0.02 and $m_2$ = –0.095 ± 0.015; Figure 1). The opposite nature of the slopes of log k *versus* Y plots are again due to greater solvation of the phenyl substituted complex in the organic enriched medium. Small values of the gradients indicate some associative character for each step of aquation. An exact mechanism is difficult to assess with the present limited data but it can be said that significant solvent assistance takes place in the aquation of these six-membered pseudo-aromatic ring complexes.

## Conclusion

In conclusion, it may be said that the rates of replacement of the chlorides are remarkably insensitive to substituent effects of the sort studied in this work. The reason for this insensitivity is not known exactly, but the pseudo-aromatic biguanide ring seems to be responsible in some way at least.

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