

Mechanistic Studies on the Reaction of *cis*-Diaquobisbiguanidecobalt(III) Ion & Phenylbiguanide in Aqueous Acidic Solution: Formation of Mixed Chelate of Cobalt(III)

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The formation of mixed chelate complex, bis-biguanidemonophenylbiguanidecobalt(III) from diaquobisbiguanidecobalt(III) and its deprotonated form hydroxoquoobisbiguanidecobalt(III) with different protonated forms of phenylbiguanide has been studied spectrophotometrically in the pH range 1.5 to 6.0. Only one form of the ligand, the monoprotonated phenylbiguanide, takes part in the formation reaction. The rate constants, k_{corr} and k'_{corr} for diaquo- and hydroxoquo-forms respectively of the complex cation, are derived from k_{obs} and fractions of complex and ligand (nucleophile) species. Second order rate constants, k_1 and k_2 , have been derived from the equations $k_{\text{corr}} = k_1[\text{PhBigH}]_{\text{total}}$ and $k'_{\text{corr}} = k_2[\text{PhBigH}]_{\text{total}}$. The hydroxoquo-form of the complex is 4-5 times more reactive than the diaquo-form and the reaction is entropy-controlled as the enthalpies of the reactions with both forms are almost equal. Ion-pair formation is completely absent and multiple hydrogen bonding seems to be responsible for the associations of the reactants. Significant bond formation takes place before bond breakage is complete in the transition state.

REACTIONS involving replacement of aquo ligands in cobalt(III) complexes by various anions have been reported by different authors^{1-9,17}. Such reactions usually proceed through ion-pair formation. With neutral species (e.g. oxalic acid) formation of ion-pair is untenable and some sort of hydrogen bonding is responsible for the reaction¹. In the present investigation, because of like charges on the reacting species, ion-pair formation is doubtful and it is interesting to study which factors are responsible for the process. The present study was made over a wide range of pH (1.5 to 6.5) to distinguish between the reactions of various complex and ligand species. Below pH ca 1.5 aquation and above pH ca 8 base hydrolysis of the mixed chelate complex become appreciable and studies in these ranges were left out in this investigation.

Materials and Methods

cis-Diaquobisbiguanidecobalt(III) perchlorate was prepared as follows: Hydroxoquoobisbiguanidecobalt(III) sulphate was prepared following Ray and Ghosh¹⁰. It crystallized out with two and half molecules of water (Found: Co, 13.64; N, 31.21. Required: Co, 13.50; N, 32.03%).

The perchlorate salt was prepared in solution, whenever required by the metathesis of the complex sulphate with barium perchlorate in solution. Below pH 4.0 the complex ion (pK 6.0) exists almost entirely in the diaquo-form.

Bis-biguanidemonophenylbiguanidecobalt(III) perchlorate was prepared in solution by the metathesis of complex sulphate with barium perchlorate. The complex sulphate was prepared following Dutta and Sarkar¹¹ (Found: Co, 7.94; N, 34.81. Required: Co, 8.01; N, 36.20%).

Phenylbiguanide hydrochloride was prepared as described by Smolka and Friedrich¹². It was twice recrystallized before use.

All other reagents were either of reagent grade or else were purified by suitable methods. Conductivity water was used throughout for making the solutions.

Determination of the pK of the complex equilibria — It was determined graphically from the pH titration of a 0.025M hydroxoquo complex (this complex ion is very little soluble in water and almost a saturated solution was used) with 0.1M perchloric acid. The pH at the half-neutralization point is the required pK value.

Absorbance measurements — A Beckman DU-2 spectrophotometer was used for absorbance measurements. The absorption spectra of the diaquobisbiguanide complex ion, in its protonated or deprotonated forms, are identical. It exhibited absorption maxima at 490 nm (E_M 125) and the product complex ion at 480 nm (E_M 178). The spectra of a $1 \times 10^{-3}M$ solution of the complex ion in the presence of an excess of the chelating agent at different pH, in the range 1.5 to 6.5, changes with time at various rates and ultimately becomes identical with the spectra of bis-biguanidemonophenylbiguanide complex ion. (Actually a small difference was always observed, E_M^{480} being 175.) Kinetic runs were carried out in stoppered silica cells placed in a thermostated chamber where the temperature was maintained to within $\pm 0.1^\circ$ of the desired value. Ionic strengths (μ) of the solutions were maintained by adding sodium perchlorate.

The rates of formation of the mixed chelate complex were conveniently followed in self-buffered solutions (pH adjusted with sodium hydroxide or perchloric acid) containing excess of the reagent

(phenylbiguanide) by measuring the change in absorbance of the solutions with time at 480 nm. The pseudo first-order rate constants were evaluated graphically by the usual method of plotting $\log(A_{t_2}-A)/t_2(A_{t_1}-A_{t_2})$ vs (t_2-t_1) , A_{t_1} , A_{t_2} and A_{t_2} being absorbance at time t_1 , t_2 and after attainment of equilibrium.

Results and Discussion

The pK value for the reaction (1) was determined at various temperatures (28-35°) and μ (0.025-0.5M) and found to be 5.93 ± 0.07 . It was almost independent of temperature and ionic strength. Below pH 4, the complex ion exists almost entirely as the diaquo species (I) and between pH 4 and 6 both the protonated (I) and the deprotonated (II) forms exist simultaneously.

The ionization constants of the diprotonated and the monoprotated ligands (phenylbiguanide) were determined according to Ray *et al.*¹³ at 32° as $pK_{a_1}=10.7$ and $pK_{a_2}=2.2$. Our determination of pK_{a_1} at 28° and 22° gives the values as 2.25 and 2.30 respectively.

In the experimental pH range, only two forms of the substituting reagent, the monoprotated and the diprotonated species were present, with complete absence of any deprotonated form.

Considering all the forms of the complex and ligand species which exist between pH 1.5 and pH 6.5, the overall reaction may be represented as shown in Scheme 1.

The pH ranges in which diprotonated ligand and deprotonated complex exist are far apart, thereby ruling out the possibility of their interreaction. Ion-pair formation is also eliminated because of like charges on each reacting species. It was later verified by the plots of k_{obs} vs total [ligand] under different conditions, all of which were linear indicating no ion-pair formation.

k_{obs} values were derived from the initial slopes of the conventional first-order plots to avoid the complications of any pH drift. The plots of rate constant (k_{obs}) versus [nucleophile] at a given pH , μ and temperature were linear with zero intercept. Consequently there is no reagent independent path or at least it should be extremely slow. Moreover, it also eliminates the possibility of any ion-pair formation, where a non-linear relationship between the rate and [nucleophile] exists. Rate law which holds good up to $pH \sim 4$, where both the

protonated forms of the ligand are present, may be derived as

$$\text{Rate} = k_1[\text{Co}(\text{BigH})_2(\text{H}_2\text{O})_2^{3+}][\text{PhBigH}_2^+] + k_2[\text{Co}(\text{BigH})_2(\text{H}_2\text{O})_2^{3+}][\text{PhBigH}_3^{2+}]$$

$$\text{Hence } k_{obs} = k_1[\text{PhBigH}_2^+] + k_2[\text{PhBigH}_3^{2+}] \quad \dots(5)$$

Table 1 records the observed rates at constant μ and [nucleophile] up to pH 3.82 at two different temperatures. In this pH range the complex exists entirely as the diaquo species. If ' f ' be the fraction of the ligand which exists in the mono-protonated form at any specified pH , then $k_{obs}/f = k_{corr}$ denotes the corrected first-order rate constant for the species involved in reaction (3). The relative constancy of k_{corr} indicates that only monoprotated species is reactive enough to be observable under this condition. The diprotonated form is present as a non-reactive species due to strong electrostatic repulsive forces between the like charges on the reacting species. Eq. (5), after replacing the non-reacting term and k_{obs} by k_{corr} , simplifies to

$$k_{corr} = k_1 [\text{nucleophile}]_{total} \quad \dots(6)$$

k_1 being the second-order rate constant for the complex formation with the diaquo species. k_1 values at various temperatures are given in Table 2. k_1 values have also been derived in another way. Dependence of rate constant, k_{obs} on the fraction of nucleophile in monoprotated form in the pH range 1 to 3.8 is shown in Fig. 1 at various temperatures. The second-order rate constants have been derived by extrapolating the plots to 1M nucleophile

TABLE 1 — RATE OF FORMATION OF $\text{Co}(\text{BigH})_2(\text{PhBigH})^{3+}$ BY THE REACTION OF $\text{Co}(\text{BigH})_2(\text{H}_2\text{O})_2^{3+}$ AND PhBigH_2^+ AT VARIOUS ACIDITIES AND TEMPERATURES

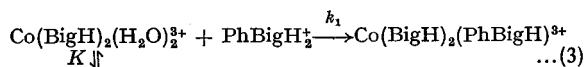
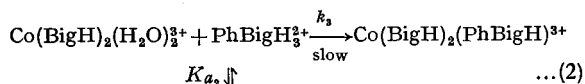
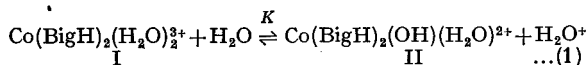
$\{\mu=0.5; [\text{complex}]=0.001M; [\text{PhBigH}]=0.020M\}$

pH	$10^2 k_{obs}$ min ⁻¹	f	$10^2 k_{corr}$ min ⁻¹
TEMP. 28°			
1.50	0.36	0.15	2.40
2.20	1.1	0.53	2.08
2.87	1.9	0.80	2.47
3.00	2.03	0.85	2.39
3.64	2.43	0.98	2.49
TEMP. 32°			
2.0	1.2	0.38	3.15
2.2	1.3	0.5	2.60
3.0	2.4	0.86	2.78
3.82	3.50	0.98	3.51

TABLE 2 — SECOND-ORDER RATE CONSTANTS FOR THE FORMATION REACTIONS

$(\mu=0.5M)$

Temp. °C	$10^3 k_1$ sec ⁻¹	$10^3 k_2$ sec ⁻¹
22	1.38	5.60
27	1.85	1.93
28	(2.50)	8.83
32	2.00	—
35	2.59	—
	3.20	11.75



(BigH = biguanide, PhBigH = phenylbiguanide)

Scheme 1

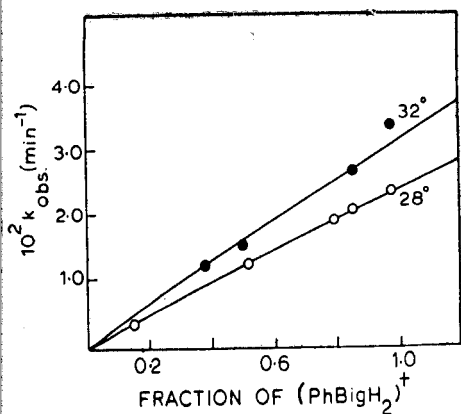


Fig. 1 — Dependence of k_{obs} on the fraction of the nucleophile in the monoprotonated form

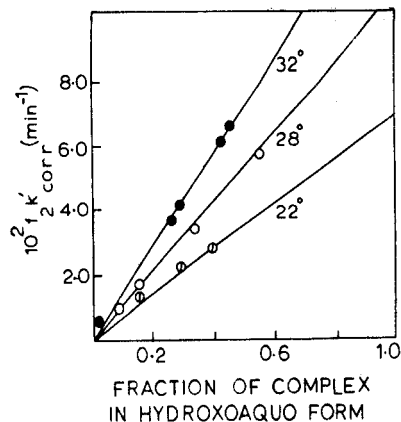


Fig. 2 — Dependence of rate observed for hydroxoquo species on the fraction of the complex in the deprotonated form

concentration, and dividing the rate thus obtained by the fraction of PhBigH which is in the monoprotonated form at the particular $p\text{H}$. The values thus obtained are also included in Table 2. The second-order rate constants, k_1 arrived by either method are similar. At $p\text{H}$ 4 and above, both forms of the complex cation, I and II, are present together. k_{obs} values above $p\text{H}$ 4 are made of two terms due to two reacting complex species. Their contributions being proportional to their fractions present at the specified $p\text{H}$. If f_1 and f_2 are the fractions of diaquo- (I) and hydroxoquo- (II) species at any time, then $k_{obs} = k_{corr} \times f_1 + k'_{corr} f_2$, where k'_{corr} is the corrected first-order rate for the reaction of the species (II). f_1, f_2 were determined from the pK value of reaction (1). $f_2 k'_{corr}$ values were obtained by subtracting $f_1 k_{corr}$ from k_{obs} and are recorded in Table 3. A plot of rate due to hydroxoquo species versus f_2 (Fig. 2) gives k'_{corr} at $f_2 = 1$. The second-order rate constant, k_2 , for the reaction of hydroxoquo complex is given by Eq. (7)

$$k'_{corr} = k_2 [\text{PhBigH}]_{total} \quad \dots(7)$$

k_2 values at various temperatures are also given in Table 2. The hydroxoquo complex is much

more (4-5) times reactive than the diaquo complex, owing to the well-known labilizing influence of OH^- adjacent to H_2O .

In reactions (3) and (4), no intermediate with monodentate phenylbiguanide and with one aquo or hydroxyl ligand could be detected on an ion-exchange column or by spectral method. This intermediate species must be sufficiently reactive to ring closure to avoid its detection by any means. Similar fast ring closing steps have been observed in the anation of $\text{Co}(\text{en})_2(\text{H}_2\text{O})_2^{3+}$ ($\text{en} = \text{ethylenediamine}$) and oxalic acid or oxalate ion in acidic aqueous solution¹. This may be correlated with the fact that monodentate biguanide or substituted biguanide complexes are unknown. Any attempt at their preparation, leads to ring closure. In reaction (4), H_2O is replaced before OH^- is based on the reactivity of these two ligands on cobalt(III) pentammines and also on the fact that while few complexes of the type $[\text{Co}(\text{BigH})_2(\text{OH})\text{X}]^{n+}$ are known¹³, $[\text{Co}(\text{BigH})_2(\text{H}_2\text{O})\text{X}]^{(n+1)+}$ complex ion would have been so unstable that not a single one of the later type could be isolated.

The activation parameters corresponding to second-order reaction rates, k_1 and k_2 , were evaluated by the usual Eyring plot. The ΔH^\ddagger and ΔS^\ddagger values for these and few other similar reactions are

TABLE 3 — RATE OF FORMATION OF $\text{Co}(\text{BigH})_2(\text{PhBigH})_3^{3+}$ BY THE REACTION OF $\text{Co}(\text{BigH})_2(\text{OH})(\text{H}_2\text{O})_2^{2+}$ AND $(\text{PhBigH})_3^+$ AT VARIOUS ACIDITIES AND TEMPERATURES

{Complex} = $1 \times 10^{-3} M$; [PhBigH] $2 \times 10^{-2} M$; $\mu = 0.5 M$

Temp. C.	pH	$10^2 k_{obs}$ min ⁻¹	f_1	$10^2 f_1 k_{corr}$ min ⁻¹	f_2	$10^2 f_2 k'_{corr}$ min ⁻¹
32	3.82	3.50	0.99	2.92	0.010	0.58
32	4.20	3.60	0.98	2.90	0.018	0.70
32	5.50	6.0	0.729	2.15	0.271	3.85
32	5.55	6.26	0.706	2.07	0.294	4.19
32	5.75	8.06	0.59	2.00	0.43	6.10
32	5.86	8.10	0.54	1.53	0.46	6.57
28	4.88	3.34	0.924	2.25	0.076	1.1
28	5.10	4.26	0.871	2.15	0.13	2.11
28	5.20	3.90	0.843	2.08	0.157	1.82
28	5.65	4.83	0.655	1.60	0.345	3.23
28	6.12	6.6	0.44	1.10	0.56	5.50
22	5.20	3.3	0.843	1.7	0.157	1.6
22	5.55	3.65	0.706	1.4	0.294	2.25
22	5.75	3.8	0.60	1.2	0.40	2.6

TABLE 4 — ACTIVATION PARAMETERS OF VARIOUS SUBSTITUTION REACTIONS OF COBALT(III) CHELATE COMPLEXES

Complex	Entering ligand	ΔH^\ddagger kcal/ mole	ΔS^\ddagger e.u.	Ref.
Co en ₂ (H ₂ O) ₃ ³⁺	H ₂ O	28.9	+15.1	15
Co en ₂ (H ₂ O) ₃ ³⁺	H ₂ C ₂ O ₄	24.8	1.5	1
Co(DMG) ₂ (NO ₂) (H ₂ O)	HC ₂ O ₄ ⁻	22.5	—	6
Co(DMG) ₂ I(H ₂ O)	Br ⁻	17.8	-14.0	6
Co(BigH) ₂ (H ₂ O) ₃ ³⁺	PhBigH ₂ ⁺	13.8	-20.8	This work
Co(BigH) ₂ (OH) ₂ ²⁺ (H ₂ O) ₂ ²⁺	PhBigH ₂ ⁺	14.0	-17.2	do
Co(DMG) ₂ (H ₂ O) ₃ ³⁺	Cl ⁻ , Br ⁻ , I ⁻	16.19	—	7

included in Table 4. ΔH^\ddagger and ΔS^\ddagger values for k_1 and k_2 are identical within experimental limitations, indicating similar mechanisms for the replacement of aquo ligands in each form of the complex ion. It is interesting to note that ΔH^\ddagger and ΔS^\ddagger values decrease as the π -back bonding tendency of the bisbidentate chelate on the aquo complex increases as en < DMG⁷ < BigH (DMG = dimethylglyoxime). BigH is an unsaturated ligand¹⁴, and the extra stability of the biguanide chelate ring is due to π -bonding phenomenon, introducing a quasi-aromatic character to the chelate ring¹⁶. The rate of substitution reaction is also in the same order as their basicity would warrant, i.e. en (1.0) < DMG (10.0) < BigH (10³). This suggests that bis-biguanide complex of Co(III) has some class (b) character. It is likely that the π -bonding of the bischelate ligand removes electron cloud around cobalt atom from t_{2g} orbitals, making these orbitals increased acceptor of the incoming ligand. This results in a faster reaction rate for biguanide complexes. In this case, significant bond formation takes place before any bond breakage in the transition state.

After the removal of the first aquo ligand, the replacement of second H₂O or OH⁻ ligand takes place immediately with ring closure, due to high ring formation tendency of the unsaturated biguanide ligand forming six-membered quasi-aromatic ring¹⁶.

The approach of the monoprotonated ligand to the complex ion takes place through the non-protonated end. Large tendency of ring formation, removes the attached proton from the ligand along with aquo ligand as H₃O⁺.

Because of the protonation on both ends, the approach of the diprotonated ligand towards the metal atom through either end is restricted due to electrostatic effects. The loss of unsaturation of the diprotonated form¹⁴ also loses its quasi-aromatic ring formation tendency. This is the reason for no reaction with this form of ligand.

The association of the reactants may greatly be facilitated by the multiple hydrogen bonding possibilities of the aquo ligand of the complex ion. Hydrogen bonding tendency of H₂O over OH⁻ facilitates the approach of the ligand through this end, with its removal. Because of its basic nature, phenylbiguanide forms stronger bonds than H₂O. Once the attachment at one end is formed, the ring closure takes place immediately with simultaneous removal of H₃O⁺ or H₂O.

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