# Kinetics and Mechanism of Elimination of Chloride from *cis*-Chlorobis(ethylenediamine)(glycinato-*N*)cobalt(III) Ion: a Study of Copper(II)-ion Catalysis

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The rate of elimination of chloride from the *cis*-chlorobis(ethylenediamine)(glycinato-*N*-)cobalt(III) ion has been studied under varying conditions of pH and copper(II) concentration in a medium of constant ionic strength of 0·3M. Copper(II) has been found to catalyse the reaction *via* formation of the binuclear species $[(en)_2CoCl(NH_2CH_2CO_2)Cu]^{3+}$. The product of the reaction in the presence and absence of $Cu^{II}$ has been identified as the *cis*-bis(ethylenediamine)(glycinato-*ON*)cobalt(III) chelate. At 50 °C the rate constant, activation enthalpy, and entropy for loss of chloride ion from $[(en)_2CoCl(NH_2CH_2CO_2)]^+$, $[(en)_2CoCl(NH_2CH_2CO_2H)]^{2+}$, and $[(en)CoCl(NH_2CH_2CO_2)Cu]^{3+}$ species are: $(2{\cdot}65 \pm 0{\cdot}03) \times 10^{-5}\ s^{-1}$, $90{\cdot}4 \pm 1{\cdot}7$ kJ $mol^{-1}$, $-54{\cdot}1 \pm 5{\cdot}4$ J $K^{-1}$ $mol^{-1}$; $(1{\cdot}27 \pm 0{\cdot}01) \times 10^{-5}\ s^{-1}$, $92{\cdot}5 \pm 1{\cdot}3$ kJ $mol^{-1}$, $-53{\cdot}1 \pm 3{\cdot}3$ J $K^{-1}$ $mol^{-1}$; and $(2{\cdot}74 \pm 0{\cdot}10) \times 10^{-4}\ s^{-1}$, $88{\cdot}3 \pm 2{\cdot}9$ kJ $mol^{-1}$, $-41{\cdot}0 \pm 9{\cdot}2$ J $K^{-1}$ $mol^{-1}$, respectively. Co–Cl Bond breaking is tentatively suggested to be rate limiting for the loss of chloride ion from all the three species mentioned above.

SEVERAL metal ions have been found to catalyse aquation of penta-amminecarboxylatocobalt(III) complexes derived from oxalic,[1] malonic,[2] and salicylic [3] acids. It was shown that binuclear complexes of the catalysts with these cobalt(III) substrates are involved as reactive intermediates. Catalysis by metal ions has also been observed in the elimination of chloride ion from chloro(ethylenediaminetetra-acetato)cobalt(III).[4,5] The metal ions are presumed to associate with $[(edta)CoCl]^{2-}$ through the free carboxylate group and then assist the elimination of chloride ion from the cobalt(III) centre. These results prompted us to extend the study of the metal-ion catalysis to aquation reactions of some suitable aminehalogenocobalt(III) complexes. This paper describes the kinetics of elimination of chloride ion from *cis*-chlorobis(ethylenediamine)(glycinato-*N*)cobalt(III) in the presence and absence of copper(II). The aim of the present work was to (*i*) examine the complexing ability of $[(en)_2CoCl(NH_2CH_2CO_2)]^+$ towards $Cu^{II}$, (*ii*) assess and compare the reactivity of the binuclear complex $[(en)_2CoCl(NH_2CH_2CO_2)Cu]^{3+}$ with that of $[(en)_2CoCl(NH_2CH_2CO_2H)]^{2+}$ and its deprotonated form, and (*iii*) elucidate the mechanism of elimination of the chloride ion from the cobalt(III) centre in the presence and absence of $Cu^{II}$. Recently Comley and Higginson [6] studied the reaction under investigation in the presence and absence of $Pb^{II}$ at 45 °C and $I = 1{\cdot}0$M.* It is of interest to compare their results with ours.

## EXPERIMENTAL

The complex *cis*-$[(en)_2CoCl(NH_2CH_2CO_2H)]Cl_2$ was prepared by the method of Alexander and Busch.[7] Repeated crystallization of the chloride salt from sodium nitrate solution yielded the nitrate salt which was washed successively with ice-cold water, ethanol, and diethyl ether and finally stored over fused calcium chloride {Found: Cl, 8·75; Co, 14·4. Calc. for $[(en)_2CoCl(NH_2CH_2CO_2H)][NO_3]_2$: Cl, 8·60; Co, 14·25%}. Sodium perchlorate (Riedel) and perchloric acid (Baker analysed) were used to adjust the ionic strength and acidity of the reaction medium respectively. Acetic acid and sodium hydroxide were B.D.H. (AnalaR) quality. Copper(II) perchlorate was prepared from copper(II) carbonate (E. Merck, extra pure). The free acid and copper(II) contents of the stock copper(II) perchlorate solution were estimated by ion-exchange and iodometric methods respectively. Dowex 50W-X8 resin in the acid form was used in all ion-exchange experiments. Optical-density measurements were made with a Beckmann DU 2 spectrophotometer using 10 mm matched silica cells.

*Kinetics.*—Rate measurements were made under varying conditions of pH, $[Cu^{II}]$, and temperature. The ionic strength of the reaction medium was adjusted to 0·3M with sodium perchlorate. Solutions of the desired composition were prepared in 50 $cm^3$ volumetric flasks and thermostatted. After thermal equilibrium had been reached a known weight of *cis*-$[(en)_2CoCl(NH_2CH_2CO_2H)][NO_3]_2$ was transferred to the reaction flask. The complex dissolved quickly on rapid shaking and the volume was then made up with distilled water which had been previously equilibrated at the reaction temperature. Aliquot portions (5 $cm^3$) of the reaction mixture were withdrawn at convenient time intervals and run into a beaker containing ice-cold distilled water (5 $cm^3$) and a few grams of Dowex 50W-X8 resin in the acid form. On rapid agitation the coloured ions exchanged into the resin phase. The colourless supernatant solution was filtered through a well packed bed of glass wool. The resin was washed quantitatively with cold distilled water. The chloride-ion content of the combined filtrate and resin washings was estimated potentiometrically using 0·02M-$AgNO_3$ as titrant. Pseudo-first-order rate constants were obtained from gradients of least-squares plots of ln $(V_\infty - V_t)$ against time where $V_t$ and $V_\infty$ are titre values at time $t$ and complete release of chloride respectively.

The rate of formation of the chelated bis(ethylenediamine)(glycinato-*ON*)cobalt(III) complex was followed spectrophotometrically. Aliquot portions (5 $cm^3$) of the reaction mixture were withdrawn at convenient time intervals, cooled to room temperature, and the optical density measured immediately at 350 nm. Rate constants were computed from least-squares gradients of ln $(D_\infty - D_t)$ against time plots. All calculations of rate constants were

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* 1M = 1 mol $dm^{-3}$.

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made using a least-squares computer program adapted to an IBM 1130 computer

## RESULTS

*Effect of pH.*—Table 1 presents the observed pseudo-first-order rate constants ($k_{obs.}$) for chloride release in the absence of $Cu^{II}$. It is to be noted that $k_{obs.}$ increased with decreasing hydrogen-ion concentration, limiting values being attained above pH 4·7 and below pH 1; $k_{obs.}$ was virtually independent of the concentration of acetate ion in the range studied. The pH–rate profile is in keeping with the rate law (1) where $c_t$ is the total concentration of the chloro-

$$-\mathrm{d}\ln c_t/\mathrm{d}t = k_{obs.} = \frac{(k_0K_1/[H^+]) + k_1}{1 + (K_1/[H^+])} \qquad (1)$$

complex at time $t$, $k_0$ and $k_1$ are rate constants for $[(en)_2CoCl(NH_2CH_2CO_2)]^+$ and its acid form respectively, and $K_1$ is the dissociation constant of the glycine complex as defined in equation (2). p$K$ For $[(en)_2CoCl(NH_2CH_2CO_2H)]^{2+}$ has

$$[(en)_2CoCl(NH_2CH_2CO_2H)]^{2+} \overset{K_1}{\rightleftharpoons} [(en)_2CoCl(NH_2CH_2CO_2)]^+ + H^+ \qquad (2)$$

been reported to be 2·1 (25 °C, $I$ = 0M) [7] and 2·5 (45 °C, $I$ = 1·0M).[6] These data predict that more than 99% of the complex will exist in the deprotonated and protonated forms at pH 4·7 and in 0·3M-$HClO_4$ respectively. This was in fact found to be true as $k_{obs.}$ levelled off under these extreme conditions of pH. Since $k_{obs.}$ was insensitive to the variation of acetate-ion concentration in the range studied, $k_0$ was taken to be the weighted-average value of the observed rate constants measured in acetate buffer. The weighted-average value of $k_1$ was obtained from values of $k_{obs.}$ at $[HClO_4]$ = 0·1, 0·2, and 0·3M; $k_0$ and $k_1$ being known, $K_1$ was calculated by a weighted least-squares procedure from values of $k_{obs.}$ at $[H^+] < 0{\cdot}1$M utilizing relation (3) where

$$K_1 = \{[HClO_4] + c(k_{obs.} - k_1)/(k_0 - k_1)\}(k_{obs.} - k_1)/(k_0 - k_{obs.}) \qquad (3)$$

$c$ is the total concentration of the chloro-complex at zero reaction time (the complex was added in the acid form) and all other terms have their usual meaning. Equation (3) is derived from (1) and the mole-balance relation for $H^+$ ion at zero time. Values of the parameters $k_0$, $k_1$, and $K_1$ at 45, 50, and 60 °C are given in Table 1.

TABLE 1

Effect of pH on the rate of chloride elimination from *cis*-$[(en)_2CoCl(NH_2CH_2CO_2H)]^{2+}$ with $I$ = 0·3 and [complex] = (3·9 ± 0·3) × $10^{-3}$M

| | | $10^5k_{obs.}/s^{-1}$ | | |
|---|---|---|---|---|
| $[HClO_4]$/M | | 45·0 ± 0·1 | 50·0 ± 0·1 | 60·0 ± 0·1 °C |
| 0·000 | | 1·29 ± 0·07 | 2·24 ± 0·09 | 6·10 ± 0·10 |
| 0·005 | | 1·09 ± 0·06 | 1·86 ± 0·10 | 5·52 ± 0·21 |
| 0·010 | | 0·98 ± 0·04 | 1·65 ± 0·08 | 4·88 ± 0·15 |
| 0·020 | | 0·89 ± 0·04 | 1·56 ± 0·08 | 4·40 ± 0·09 |
| 0·050 | | 0·80 ± 0·04 | 1·36 ± 0·12 | 4·00 ± 0·19 |
| 0·100 | | 0·77 ± 0·04 | 1·26 ± 0·05 | 3·80 ± 0·04 |
| 0·200 | | 0·75 ± 0·03 | 1·25 ± 0·04 | 3·60 ± 0·08 |
| 0·300 | | 0·76 ± 0·03 | 1·28 ± 0·02 | 3·70 ± 0·07 |
| Acetate buffer | | | | |
| $[NaO_2CMe]$ M | $[MeCO_2H]$ M | | | |
| 0·010 | 0·010 | 1·57 ± 0·08 | | |
| 0·020 | 0·020 | 1·47 ± 0·10 | 2·60 ± 0·12 | |
| 0·040 | 0·040 | | 2·53 ± 0·16 | |
| 0·020 | 0·040 | | 2·64 ± 0·15 | |
| 0·010 | 0·020 | | 2·70 ± 0·07 | 7·32 ± 0·19 |
| 0·040 | 0·020 | | 2·83 ± 0·21 | |
| 0·020 | 0·010 | | 2·55 ± 0·16 | 7·62 ± 0·19 |
| $10^5k_0/s^{-1}$ | | 1·53 ± 0·05 | 2·65 ± 0·03 | 7·47 ± 0·15 |
| $10^5k_1/s^{-1}$ | | 0·76 ± 0·01 | 1·27 ± 0·01 | 3·75 ± 0·05 |
| $10^3K_1$/mol l$^{-1}$ | | 4·60 ± 0·30 | 4·90 ± 0·40 | 4·70 ± 0·40 |

*Copper*(II) *Catalysis.*—The effect of $Cu^{II}$ ion on the rate of chloride release was studied as a function of $[Cu^{II}]$ at a fixed hydrogen-ion concentration. Pseudo-first-order rate constants are collected in Table 2. Catalysis by $Cu^{II}$ is evident from such data. Furthermore, values of $(k_{obs.} - k_{obs.}')/[Cu^{II}]$ (where $k_{obs.}' = k_{obs.}$ at $[Cu^{II}] = 0$) at all three temperatures are not constant and decrease with increasing $[Cu^{II}]$. This is in keeping with the fact that copper(II) associates with the substrate and the resulting binuclear complex catalyses the rate of chloride release from the cobalt(III) centre. Consistent with our observations the rate law for chloride elimination in the presence of $Cu^{II}$ is given by equation (4) where $k_2$ is the rate constant for the

$$-\mathrm{d}\ln c_t/\mathrm{d}t = k_{obs.} = \frac{(k_0K_1/[H^+]) + k_1 + (k_2K_2K_1[Cu^{2+}]/[H^+])}{1 + (K_1/[H^+]) + (K_2K_1[Cu^{2+}]/[H^+])} \qquad (4)$$

binuclear complex $[(en)_2CoCl(NH_2CH_2CO_2)Cu]^{3+}$ and $K_2$ its formation constant as defined by $[(en)_2CoCl(NH_2CH_2CO_2)]^+ + Cu^{2+} \overset{K_2}{\rightleftharpoons} [(en)_2CoCl(NH_2CH_2CO_2)Cu]^{3+}$. With the best values of $k_0$, $k_1$, and $K_1$ the observed rate constants were fitted to equation (4) by means of a least-squares computer program which varied the parameters $(k_2K_2K_1)$ and $(K_1K_2)$ and minimized the sum of the weighted residuals $\Sigma[(k_{calc.} - k_{obs.})/\sigma(k_{obs.})]^2$. Calculated values of $(k_2K_2K_1)$, $(K_1K_2)$, $k_2$, and $K_2$ at different temperatures are in Table 2.

TABLE 2

Effect of copper(II) on the rate of chloride elimination from *cis*-$[(en)_2CoCl(NH_2CH_2CO_2H)]^{2+}$ with $I$ = 0·3, [complex] = (3·7 ± 0·2) × $10^{-3}$, and $[HClO_4]$ = 0·02M

| $[Cu^{2+}]$/M | $10^5k_{obs.}/s^{-1}$ | | |
|---|---|---|---|
| | 45·0 ± 0·1 | 50·0 ± 0·1 | 60·0 ± 0·1 °C |
| 0·000 | 0·89 ± 0·04 | 1·56 ± 0·08 | 4·40 ± 0·09 |
| 0·005 | | | 4·75 ± 0·05 |
| 0·010 | 1·03 ± 0·02 | 1·75 ± 0·05 | 5·03 ± 0·08 |
| 0·020 | 1·12 ± 0·08 | 1·95 ± 0·07 | 5·90 ± 0·10 |
| 0·030 | 1·20 ± 0·08 | 2·25 ± 0·05 | 6·30 ± 0·12 |
| 0·040 | 1·31 ± 0·06 | 2·38 ± 0·07 | 6·92 ± 0·15 |
| 0·050 | 1·41 ± 0·08 | 2·78 ± 0·10 | 7·35 ± 0·15 |
| 0·060 | | 2·99 ± 0·10 | 8·02 ± 0·18 |
| $10^6k_2K_2K_1/s^{-1}$ | 2·91 ± 0·22 | 6·32 ± 0·21 | 16·7 ± 0·4 |
| $10^2K_2K_1$ | 2·31 ± 0·01 | 2·30 ± 0·01 | 2·41 ± 0·01 |
| $10^4k_2/s^{-1}$ | 1·26 ± 0·10 | 2·74 ± 0·10 | 6·93 ± 0·17 |
| $K_2$/l mol$^{-1}$ | 5·02 ± 0·33 | 4·70 ± 0·38 | 5·13 ± 0·32 |

TABLE 3

Rates of formation of $[(en)_2Co(NH_2CH_2CO_2)]^{+}$ at $I$ = 0·3M, 45·0 ± 0·1 °C, and [complex] = (5·0 ± 0·3) × $10^{-3}$M

| $[HClO_4]$/M | $[Cu^{II}]$/M | $10^5k_{obs.}/s^{-1}$ |
|---|---|---|
| 0·000 | | 1·30 ± 0·03 |
| 0·005 | | 1·11 ± 0·04 |
| 0·100 | | 0·99 ± 0·02 |
| 0·020 | 0·010 | 1·05 ± 0·03 |
| 0·020 | 0·030 | 1·15 ± 0·02 |
| 0·020 | 0·050 | 1·32 ± 0·02 |

*Formation of* cis-$[(en)_2Co(NH_2CH_2CO_2)]^+$.—The product of chloride elimination from *cis*-$[(en)_2CoCl(NH_2CH_2CO_2H)]^{2+}$, in the presence and absence of $Cu^{II}$, had absorption maxima at 488 and 347 nm with the molar absorption coefficients of 98 ± 2 and 105 ± 2 l mol$^{-1}$ cm$^{-1}$ respectively. These data are in excellent agreement with the wavelength maxima and corresponding absorption coefficients for the chelated glycinato-complex reported by Alexander and Busch ($\varepsilon_{max.}$ 98 ± 2 at 487 ± 2, and 107 ± 2 l mol$^{-1}$ cm$^{-1}$ at 346 ± 2 nm).[7] The chloro-complex was subjected to base hydrolysis and the reaction mixture was then acidified to pH 1. The absorption spectrum of the resulting solution corresponded exactly to that of the $[(en)_2Co(NH_2CH_2CO_2)]^+$ chelate. The rate of formation of the *cis*-bis(ethylenediamine)(glycinato-*ON*)cobalt(III) chelate, followed at 350 nm, was also found to obey first-order kinetics with no induction period under varying conditions of pH and copper(II) concentration. Observed rate constants for the chelation reaction are collected in Table 3. It is interesting to note that $k_{obs.}$ for the chloride elimination is very nearly equal to the rate constant for the chelation process under comparable conditions of acidity and $Cu^{II}$ concentration (see Tables 1—3). These facts suggest that the chloro-complex is transformed to the *cis*-$[(en)_2Co(NH_2CH_2CO_2)]^+$ chelate, both in the presence and absence of $Cu^{II}$, without formation of the corresponding aqua-complex as intermediate.

## DISCUSSION

Comley and Higginson [6] have reported $k_0 = (1{\cdot}89 \pm 0{\cdot}02) \times 10^{-5}$ s$^{-1}$, $k_1 = (9{\cdot}00 \pm 0{\cdot}09) \times 10^{-6}$ s$^{-1}$, and $K_1 = (3{\cdot}25 \pm 0{\cdot}26) \times 10^{-3}$ mol l$^{-1}$ at 45 °C and 1·0M ionic strength. These data compare well with ours at 45 °C and 0·3M ionic strength. Both sets of data reveal that $[(en)_2CoCl(NH_2CH_2CO_2)]^+$ is twice as reactive as its conjugate-acid form. This difference in rate may be due to electrostatic interaction between the free carboxylate group of the glycinato-complex and the positive cobalt(III) centre as well as the leaving chloride ion. The activation parameters for the $k_0$ and $k_1$ paths are collected in Table 4 together with those for aquation of some aminechlorobis(ethylenediamine)cobalt(III) complexes. It is to be noted that $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ for the $k_0$ path are comparable to those for the $k_1$ path and for aquation of hydroxyalkylamine and cyclohexylamine complexes. Further, the activation parameters for the $k_0$ and $k_1$ paths of the glycine complex as well as those for aquation of several complexes of the type *cis*-$[(en)_2CoCl(NH_2R)]^{2+}$ {R = Me, Et, $Pr^i$, $Pr^n$, $CH_2{:}CH{\cdot}CH_2$, $CH{:}C{\cdot}CH_2$, $OH[CH_2]_2$, MeCH(OH), $OH[CH_2]_3$, and $C_6H_{11}$}[8–10] satisfy the isokinetic relation $\Delta H^{\ddagger} = \alpha + \beta\Delta S^{\ddagger}$, with $\alpha = 111 \pm 2$ and $\beta = 0{\cdot}370 \pm 0{\cdot}048$. This shows that the mechanism of elimination of chloride ion from the cobalt centre is virtually independent of the nature of the non-labile amine ligand. As Co–Cl bond fission has been invoked to be rate determining in aquation reactions of aminehalogenocobalt(III) complexes, it is justifiable to associate such a mechanism with the $k_0$ and $k_1$ paths of the chloroglycine complex under study. The lack of evidence in favour of formation of aqua-complexes as intermediates in the $k_0$ and $k_1$ paths may be attributed to intramolecular trapping of the five-co-ordinate intermediates {$[(en)_2Co(NH_2CH_2CO_2)]^{2+}$ and its conjugate acid} by the free carboxylate or carboxyl groups (the latter with loss of proton) respectively.

TABLE 4

Activation parameters for chloride elimination from *cis*-$[(en)_2CoCl(am)]^{2+}$ complexes

| am | $\Delta H^{\ddagger}$/kJ mol$^{-1}$ | $\Delta S^{\ddagger}$/J K$^{-1}$ mol$^{-1}$ | Calc. from ref. |
|---|---|---|---|
| $^-O_2CCH_2NH_2$ | 90·4 ± 1·7 | −54·1 ± 5·4 | This work |
| $HO_2CCH_2NH_2$ | 92·5 ± 1·3 | −53·1 ± 3·3 | This work |
| $[Cu(O_2CCH_2NH_2)]^+$ | 88·3 ± 2·9 | −41·0 ± 9·2 | This work |
| $C_6H_{11}NH_2$ | 81·2 ± 2·1 | −77·0 ± 6·3 | 8 |
| $HOCH_2CH_2NH_2$ | 91·6 ± 0·4 | −47·3 ± 1·7 | 9 |
| $MeCH(OH)CH_2NH_2$ | 93·3 ± 0·4 | −45·2 ± 1·7 | 9 |
| $HOCH_2CH_2CH_2NH_2$ | 97·5 ± 0·4 | −41·0 ± 1·7 | 9 |

Copper(II) accelerates the rate of elimination of chloride ion from the glycinato-complex *via* formation of the reactive intermediate $[(en)_2CoCl(NH_2CH_2CO_2)Cu]^{3+}$. The rate and stability constants for formation of this binuclear complex at 45 °C and $I$ = 0·3M are $(1{\cdot}26 \pm 0{\cdot}10) \times 10^{-4}$ s$^{-1}$ and 5·02 ± 0·33 l mol$^{-1}$ respectively (see Table 2); those for the binuclear complex of $Pb^{II}$ reported by Comley and Higginson [6] are $(2{\cdot}75 \pm 0{\cdot}23) \times 10^{-4}$ s$^{-1}$ and 14·6 ± 4 l mol$^{-1}$ at 45 °C and $I$ = 1·0M respectively. Lead(II) appears to be a more efficient catalyst than $Cu^{II}$ in the reaction under investigation. The stability constants of monoacetato-complexes of $Cu^{II}$ and $Pb^{II}$ reported by Hutchinson and Higginson [11] are 47·8 ± 2·4 and 152 ± 9 l mol$^{-1}$ at 25 °C and $I$ = 1·0M respectively. Apparently the glycinato-complex acts as a weaker complexing agent towards $Cu^{II}$ and $Pb^{II}$ as compared to acetate ion. The observed reactivity sequence, $[(en)_2CoCl(NH_2CH_2CO_2)M]^{3+}$ (M = $Cu^{II}$ and $Pb^{II}$) > $[(en)_2CoCl(NH_2CH_2CO_2)]^+$ > $[(en)_2CoCl(NH_2CH_2CO_2H)]^{2+}$, however, can be accounted for if it is assumed that the catalyst metal ions in their binuclear complexes are bonded simultaneously to the carboxylate group and the chloride ion attached to the cobalt(III) centre. This type of double-bridging action of *cis*-$[(en)_2CoCl(NH_2CH_2CO_2)]^+$ towards $Pb^{II}$ and $Cu^{II}$ is reasonable as the observed reactivity of the binuclear complexes of these metal ions parallels the stability constants of their monochloro-complexes ($K_{PbCl^+} > K_{CuCl^+}$).[11] Activation parameters for the $Cu^{II}$-catalysed path are comparable to those for the $k_0$ and $k_1$ paths (see Table 4). This is consistent with rate-limiting Co–Cl bond-heterolysis mechanism for the metal-ion catalysed path.

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