# Reactions of Co-ordinated Nitriles. Part I. Reactions of *cis*-(Aminoacetonitrile)bis(ethylenediamine)halogenocobalt(III) Complexes in Aqueous Solution

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In near neutral or basic solution, the ions $[Co(en)_2X(NH_2CH_2CN)]^{2+}$ ($X = Cl$ or Br; en = ethylenediamine) undergo rapid base-catalysed ring closure to give purple $[Co(en)\{NH_2{\cdot}CH_2{\cdot}C(NH_2){:}N{\cdot}CH_2{\cdot}CH_2{\cdot}NH_2\}X]^{2+}$, (I), containing a tridentate amidine ligand. The kinetics of this process have been studied spectrophotometrically at 25 °C and $I = 0{\cdot}1$M in the pH range 5·9—7·0 ($X = Cl$, $k_{OH} = 2{\cdot}57 \times 10^4$ l mol$^{-1}$ s$^{-1}$; $X = Br$, $k_{OH} = 4{\cdot}50 \times 10^4$ l mol$^{-1}$ s$^{-1}$). Condensation in the ring-closed product (I) occurs at the nitrogen centre *trans* to the halide ion. Base hydrolysis of the halogeno-ligands in (I; $X = Cl$ or Br) has been studied, both spectrophotometrically and by pH-stat at 25 °C and $I = 0{\cdot}1$M. The two methods give rate constants in excellent agreement, $k^{Cl}{}_{OH} = 2{\cdot}44$, $k^{Br}{}_{OH} = 1{\cdot}18 \times 10^1$ l mol$^{-1}$ s$^{-1}$. The $Hg^{II}$ catalysed aquation of (I; $X = Cl$ or Br) has also been investigated. Both base hydrolysis and mercury(II)-catalysed aquation appear to occur with essentially complete retention of configuration. The mercury(II)-catalysed reactions of the chloro- and bromo-complexes $[Co(en)_2X(NH_2CH_2CN)]^{2+}$ in 0·537M-$HClO_4$ have been investigated. The product of these reactions is the chelated glycine amide complex $[Co(en)_2(NH_2{\cdot}CH_2{\cdot}CO{\cdot}NH_2)]^{3+}$, and the mechanism of this reaction is discussed.

In recent years there has been considerable interest in hydrolysis of nitriles in the co-ordination sphere of metal ions. Breslow *et al.*[1] first reported that hydrolysis of 2-cyano-1,10-phenanthroline was catalysed by metal ions. Base hydrolysis of the 1 : 1 nickel complex is $10^7$ times faster than that of the uncomplexed substrate. A similar catalytic effect has recently been observed in nickel(II)-catalysed hydrolysis of 2-cyano-8-hydroxyquinoline.[2] Pinnell *et al.* have reported [3] that aromatic nitriles co-ordinated to penta-amminecobalt(III) complexes are rapidly hydrolysed by base to give nitrogen-bonded carboxamido-complexes. Rate enhancements of $2 \times 10^6$ were observed in these reactions.

*cis*-(Aminoacetonitrile)chlorobis(ethylenediamine)-cobalt(III) chloride, $[Co(en)_2Cl(NH_2CH_2CN)]Cl_2$, was first prepared by Chan and Chan.[4] These authors observed that in near neutral solution the red *cis*-complex rapidly became violet and that ν(CN) at 2 260 cm$^{-1}$ disappeared to be replaced by a band at 1 680 cm$^{-1}$; this was attributed to a *cis–trans*-isomerisation. Buckingham *et al.*[5] have determined the crystal structure of the violet product, (I), and the same group [6] have also observed that addition of mercury(II) to acidic solutions of the ions $[Co(en)_2X(NH_2CH_2CN)]^{2+}$ ($X = Cl$ or Br) rapidly gave the chelated *O*-bonded glycine amide species $[Co(en)_2(NH_2{\cdot}CH_2{\cdot}CO{\cdot}NH_2)]^{3+}$. In the present paper we describe detailed kinetic studies of these reactions.

## EXPERIMENTAL

Aminoacetonitrile was obtained from Koch–Light as the hydrogen sulphate salt $NCCH_2\overset{+}{N}H_3,HSO_4^-$, molecular weight, by titration with standard base, 154·1 (calc. 154·15). *trans*-Dichlorobis(ethylenediamine)cobalt(III) chloride was prepared as described by Krishnamurty,[7] and *trans*-dibromobis(ethylenediamine)cobalt(III) bromide as described by Werner.[8]

*Preparations.*— cis-(*Aminoacetonitrile*)*chlorobis*(*ethylenediamine*)*cobalt*(III). *trans*-Dichlorobis(ethylenediamine)-cobalt(III) chloride (17·13 g) and the hydrogen sulphate salt of aminoacetonitrile (9·24 g) were ground together in a mortar, and water (5 cm$^3$) added to give a paste. Triethylamine (12 cm$^3$) was then added dropwise, with stirring, and the resulting purple-red product was treated with methanol–acetone (10 : 1; 60 cm$^3$) and filtered. The solid complex was washed successively with ethanol and ether, and recrystallised from the minimum volume of hot water to which a few drops of concentrated hydrochloric acid had been added. The complex was dried *in vacuo* over $P_2O_5$ (Found: C, 20·9; H, 6·1; N, 24·2. Calc. for $C_6H_{20}Cl_3CoN_6$: C, 21·1; H, 5·9; N, 24·6%). *cis*-(Aminoacetonitrile)-bromobis(ethylenediamine)cobalt(III) bromide was prepared similarly using the hydrogen sulphate salt of aminoacetonitrile (9·24 g) and *trans*-$[Co(en)_2Br_2]Br$ (25·1 g) (Found: C, 14·9; H, 4·4; N, 17·4. Calc. for $C_6H_{20}Br_3CoN_6$: C, 15·2; H, 4·2; N, 17·7%).

Both the above complexes have a band at 2 250 cm$^{-1}$ in the i.r. spectrum assigned to ν(CN) of the $NH_2$-co-ordinated nitrile. In addition $CH_2$ rocking vibrations occur at 870 and 885 cm$^{-1}$ (chloro-complex) and 860 and 875 cm$^{-1}$ (bromo-complex). In this region *cis*-bis(ethylenediamine)-cobalt(III) complexes normally give two bands and the *trans*-isomer only one.[9] The splitting is due to the lower symmetry of the *cis*-derivatives. The chloro-complex has $\lambda_{max.}$ 525 (ε 81) and 368 nm (ε 85 l mol$^{-1}$ cm$^{-1}$), while the bromo-complex has $\lambda_{max.}$ 545 (ε 84) and a shoulder at *ca.* 370 nm (ε 168 l mol$^{-1}$ cm$^{-1}$) in water. The electronic spectra are consistent with a *cis*-configuration.[10,11]

*Amidine complexes*, $[Co(en)\{NH_2{\cdot}CH_2{\cdot}C(NH_2){:}N{\cdot}CH_2{\cdot}CH_2{\cdot}NH_2\}X]^{2+}$ ($X = Cl$ *or* Br). *cis*-(Aminoacetonitrile)-chlorobis(ethylenediamine)cobalt(III) chloride (2 g), or the analogous bromo-complex, was dissolved in water (25 cm$^3$) and the pH of the solution adjusted to 7·3 by addition of sodium hydroxide. The absorbance at 552 (Cl complex) or 566 nm (Br complex) was monitored as a function of time. When no further increase in absorbance occurred (*ca.* 0·5 h), the solution was acidified to pH 4 with the appropriate

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[1] R. Breslow, R. Fairweather, and J. Keana, *J. Amer. Chem. Soc.*, 1967, **89**, 2135.

[2] R. W. Hay and C. R. Clark, unpublished work.

[3] D. Pinnell, G. B. Wright, and R. B. Jordan, *J. Amer. Chem. Soc.*, 1972, **94**, 6104.

[4] S. C. Chan and F. K. Chan, *Austral. J. Chem.*, 1970, **23**, 1175.

[5] D. A. Buckingham, B. M. Foxman, A. M. Sargeson, and A. Zannella, *J. Amer. Chem. Soc.*, 1972, **94**, 1007.

[6] D. A. Buckingham, A. M. Sargeson, and A. Zanella, *J. Amer. Chem. Soc.*, 1972, **94**, 8246.

[7] M. Krishnamurty, *J. Inorg. Nuclear Chem.*, 1972, **34**, 3915.

[8] A. Werner, *Annalen*, 1912, **386**, 118.

[9] M. E. Baldwin, *J. Chem. Soc.*, 1960, 4369.

[10] R. S. Nyholm and M. L. Tobe, *J. Chem. Soc.*, 1956, 1707.

[11] R. W. Hay and P. L. Cropp, *J. Chem. Soc.* (*A*), 1969, 42.

mineral acid. Acetone (50 cm$^3$) was then added and the solution cooled in ice. The crystalline amidine complex was removed by filtration and washed successively with acetone and ether. The complex was recrystallised from the minimum volume of hot water to which a few drops of the appropriate concentrated mineral acid had been added, and dried *in vacuo* (Found: C, 21·4; H, 5·7; N, 24·8. Calc. for $C_6H_{20}Cl_3CoN_6$: C, 21·1; H, 5·9; N, 24·6. Found: C, 15·4; H, 4·0; N, 17·9. Calc. for $C_6H_{20}Br_3CoN_6$: C, 15·2; H, 4·2; N, 17·7%). The i.r. band at 2 250 cm$^{-1}$ due to ν(C≡N) is now absent and a new band at *ca.* 1 670 cm$^{-1}$ occurs which can be assigned to ν(C=N) of the amidine. The $CH_2$ rocking band of the cobalt–ethylenediamine ring is no longer split (885 cm$^{-1}$). The chloro-complex has $\lambda_{max.}$ 552 nm (ε 206 l mol$^{-1}$ cm$^{-1}$) in water, while the bromo-complex has $\lambda_{max.}$ 566 nm (ε 250 l mol$^{-1}$ cm$^{-1}$).

For kinetic studies, solutions of the amidine complexes were prepared as follows. Aqueous solutions of the halogeno-complexes $[Co(en)_2X(NH_2CH_2CN)]^{2+}$ (X = Cl or Br) (*ca.* 5 × 10$^{-3}$M) were adjusted to pH 7·3 and maintained at this value until the amidine complexes were completely formed (no further increase in absorbance at 552 nm for the chloro-complex and 566 nm for the bromo-complex). The resulting solutions were then acidified to *ca.* pH 4, diluted to the requisite volume, and the concentrations determined spectrophotometrically. These solutions (A) were used as stock solutions for the following experiments.

(i) *Mercury*(II)-*catalysed aquation.* Aliquot portions of solution (A), to which sodium perchlorate had been added, were diluted to a definite volume with dilute perchloric acid solution. Requisite volumes of the resulting solutions were added to solutions of known mercury(II) concentration containing the same concentrations of perchloric acid and sodium perchlorate. For the chloro-complex the kinetics were monitored by following the decrease in absorbance at 552 nm using a Gilford 2400s instrument. Hydrolysis of the bromo-complex was very rapid and in this case the decrease in absorbance at 568 nm was monitored on a Durrum–Gibson stopped-flow instrument. Plots of log $(A_t - A_\infty)$ against time were linear in each case and observed pseudo-first-order rate constants were obtained from the gradients of such plots. [Mercury(II) was present in large excess in all runs.] Values of $k_{Hg}$, the second-order rate constant, were obtained using the relation $k_{Hg} = k_{obs}/[Hg^{II}]$.

(ii) *Mercury*(II)-*catalysed aquation followed by treatment with the appropriate hydrogen halide.* Requisite volumes of stock solutions (A) were aquated as in (i). The solutions were then adjusted to *ca.* pH 3 and precipitated mercury(II) removed by filtration. The filtrates were evaporated to dryness and the residues treated with concentrated HBr or HCl. The resulting solutions were evaporated to dryness on a steam-bath. Two further hydrogen-halide treatments were carried out. Absorption spectra of the resulting halogeno-complexes were determined in aqueous solution [chloro-complex, $\lambda_{max.}$ 552 (ε *ca.* 200); bromo-complex, $\lambda_{max.}$ 566 nm (ε *ca.* 250 l mol$^{-1}$ cm$^{-1}$)]. The spectral data agreed, within experimental error, with those previously obtained for authentic samples of complexes (I; X = Cl or Br).

(iii) *Base hydrolysis followed by treatment with the appropriate hydrogen halide.* Aliquot portions of solutions (A) were subjected to base hydrolysis. The hydroxo-complex so obtained was treated with concentrated HBr or HCl, and the resulting solutions evaporated to dryness. The residues were again treated with the appropriate halogen acid and the resulting solution, evaporated to dryness. The crystalline complexes obtained were dissolved in water and the visible spectrum determined: chloro-complex, $\lambda_{max.}$ 552 (ε *ca.* 200); bromo-complex, $\lambda_{max.}$ 566 nm (ε *ca.* 250 l mol$^{-1}$ cm$^{-1}$).

The complexes obtained in (ii) and (iii) above were subjected to base hydrolysis. At constant pH, pseudo-first-order kinetics obtained and values of $k_{obs}/[OH^-]$ were 2·47 (chloro-complex) and 1·17 × 10$^1$ l mol$^{-1}$ s$^{-1}$ (bromo-complex) at $I$ = 0·1M and 25 °C. These constants agreed well with those previously determined for complexes (I; X = Cl or Br).

*Kinetics and Measurements.*—Some kinetic measurements were carried out with a Radiometer TTT2 automatic titrator used as a pH-stat. A high-alkalinity glass electrode, type G202B, was used as indicator and a saturated-calomel electrode with diffusion filter, type K401, as reference. The electrode system was standardised at 25·0 °C with 0·05M-potassium hydrogenphthalate (pH 4·005) and disodium tetraborate (pH 9·185) buffers. The general technique employed in the kinetic measurements has been outlined.[12] All pH-stat studies were carried out at $I$ = 0·1M (KCl) and 25 °C. Values of the hydroxide-ion concentrations were obtained from the pH, by use of a molar-activity coefficient of 0·772,[13] and a value of $pK_w$ = 13·9965 at 25 °C.[14]

Visible spectral measurements were made with Perkin-Elmer 402 and Unicam SP 800 spectrophotometers. Spectrophotometric kinetics were carried out using a Gilford 2400S spectrophotometer. The buffer solutions employed were 2,6-lutidine–, n-butylamine–, and Tris–hydrogen-chloride, and carbonate–hydrogencarbonate. The ionic strength was adjusted to 0·1M with $NaClO_4$ where appropriate. Cyclisation reactions were studied at 550 (chloro-complex) and 565 nm (bromo-complex). Reactions were followed to 75—80% completion and infinity absorbances determined after ten half-lives. Plots of log $(A_\infty - A_t)$ against time yielded straight lines, from the gradients of which the rate constants were evaluated. Hydrolysis of the halogeno-ligands was also monitored at the above wavelengths. Plots of log $(A_t - A_\infty)$ against time were linear. Mercury(II)-catalysed reactions were studied using $[HClO_4]$ = 0·537M and $I$ = 2·037M. The reactions were followed at 489 nm. Rate constants were obtained from plots of log $(A_\infty - A_t)$ against time.

## RESULTS AND DISCUSSION

In near neutral or basic solution, the ions *cis*-$[Co(en)_2(NH_2CH_2CN)X]^{2+}$ (X = Cl or Br) undergo rapid ring-closure reactions to give a tridentate amidine species, (I). Electronic absorption spectra of the various complexes are summarised in Table 1. One end of a bidentate ethylenediamine ligand reacts with the *N*-co-ordinated $NH_2CH_2CN$ group as shown below. The crystal structure of (I; X = Cl) has been reported.[5] Nucleophilic attack occurs *via* the nitrogen atom ***trans*** to the Cl$^-$, resulting in a *facial*-configuration for the tridentate ligand. In penta-ammine complexes similar to the reactant it is well established that NH protons ***trans***

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[12] R. W. Hay, L. J. Porter, and P. J. Morris, *Austral. J. Chem.*, 1966, **19**, 1197.

[13] C. W. Davies, *J. Chem. Soc.*, 1938, 2093.

[14] R. A. Robinson and R. H. Stokes, ' Electrolyte Solutions,' 2nd edn., Butterworths, London, 1965.

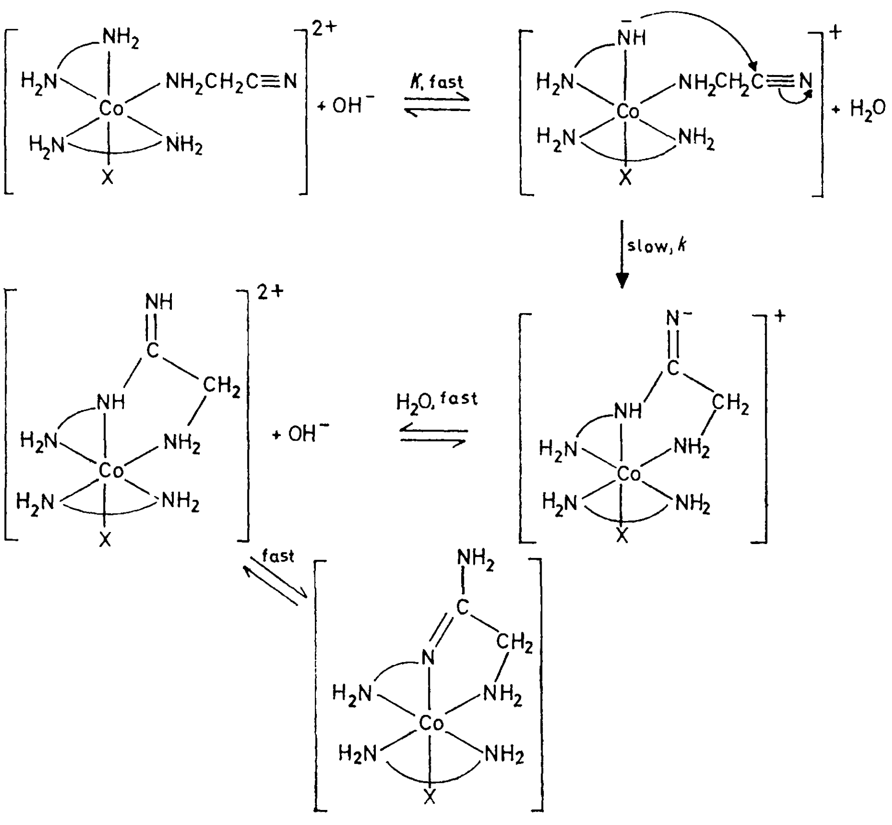
to an anionic substituent exchange much faster (>50 times) than those *cis*.[15] It has therefore been suggested that the observed stereospecificity arises because the NH centre *trans* to $Cl^-$ or $Br^-$ is by far the most available nucleophile. In addition to the stepwise mechanism, considered above, which involves the amido-conjugate base as intermediate, a synchronous mechanism can also be considered. A p.m.r. study has shown [5] that proton exchange is at least 40 times faster than ring closure thus excluding this mechanism and confirming that attack of the amido-group on the nitrile carbon atom is the rate-determining step.

TABLE 1

Absorption spectra of the complexes

| Ion | $\lambda_{max.}$/nm | $\varepsilon$/l mol$^{-1}$ cm$^{-1}$ | $\lambda_{max.}$/nm | $\varepsilon$/l mol$^{-1}$ cm$^{-1}$ |
|---|---|---|---|---|
| $[Co(en)_2(NH_2CH_2CN)Cl]^{2+}$ | 525 | 80·6 | 368 | 85 |
| $[Co(en)_2(NH_2CH_2CN)Br]^{2+}$ | 545 | 84 | 370 † | 168 |
| $[Co(en)\{NH_2{\cdot}CH_2{\cdot}CH_2{\cdot}C(NH_2){:}N{\cdot}CH_2{\cdot}CH_2{\cdot}NH_2\}Cl]^{2+}$ | 552 | 206 | 358 | 374 |
| $[Co(en)\{NH_2{\cdot}CH_2{\cdot}CH_2{\cdot}C(NH_2){:}N{\cdot}CH_2{\cdot}CH_2{\cdot}NH_2\}Br]^{2+}$ | 566 | 243 | 360 † | 405 |
| $[Co(en)\{NH_2{\cdot}CH_2{\cdot}CH_2{\cdot}C(NH_2){:}N{\cdot}CH_2{\cdot}CH_2{\cdot}NH_2\}OH]^{2+}$ | 498 | 148 | 343 | 233 |
| $[Co(en)\{NH_2{\cdot}CH_2{\cdot}CH_2{\cdot}C(NH_2){:}N{\cdot}CH_2{\cdot}CH_2{\cdot}NH_2\}OH_2]^{3+}$ | 500 | 130 | 349 | 244 |
| $[Co(en)_2(NH_2{\cdot}CH_2{\cdot}CO{\cdot}NH_2)]^{3+}$ | 487 | 100 | 343 | 109 |

† Shoulder.



(I)

Formation of the complexes (I; X = Cl or Br) was followed spectrophotometrically at 25 °C and $I$ = 0·1M. The reaction is first order in [Complex] and $[OH^-]$ (Table 2). For the chloro- and bromo-derivatives $k_{OH} = (2{\cdot}57 \pm 0{\cdot}10) \times 10^4$ and $(4{\cdot}50 \pm 0{\cdot}13) \times 10^4$ l mol$^{-1}$ s$^{-1}$ respectively. pH-Stat measurements confirmed that no base is consumed in the cyclisation reaction, and no evidence for general base catalysis was noted with the buffer systems employed. Our results are in good agreement with the preliminary findings of Buckingham *et al.*,[5] who reported values of $k_{OH} = 1{\cdot}6 \times 10^4$ (chloro-complex) and $k_{OH}$ $2{\cdot}4 \times 10^4$ l mol$^{-1}$ s$^{-1}$ (bromo-complex) at 25 °C and $I$ = 1·0M (when suitable allowances are made for the differences in ionic strength). It is clear that the initial suggestion made by Chan and Chan,[4] that the reaction involved a change from $Co{-}NH_2CH_2CN$ to $Co{-}NCCH_2NH_2$ co-ordination with concomitant *cis–trans*-rearrangement, is incorrect.

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[15] D. A. Buckingham, P. A. Marzilli, and A. M. Sargeson, *Inorg. Chem.*, 1969, **8**, 1595.

*Base Hydrolysis of the Ring-closed Complexes.*—Base hydrolysis of the complexes (I; X = Cl or Br) was studied both spectrophotometrically and by pH-stat, close agreement being obtained between the rate constants therefrom (Table 3). The reactions are first order in [Complex] and [OH$^-$].

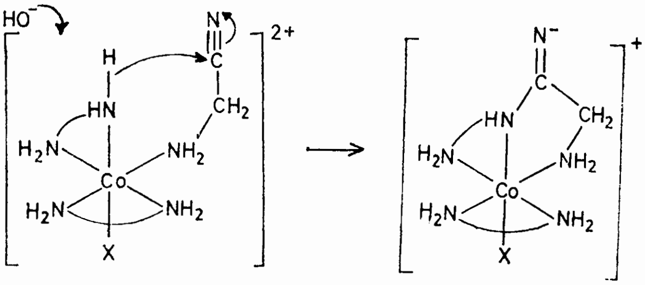


Table 2

Kinetics of the ring-closure reaction of the $[Co(en)_2X(NH_2CH_2CN)]^{2+}$ ions at $I$ = 0·1M and 25 °C

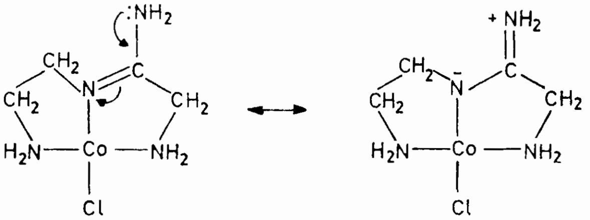
(*a*) $[Co(en)_2Cl(NH_2CH_2CN)]^{2+}$, reaction monitored at 550 nm, using 2,6-lutidine buffers.

| pH | $10^4k_{obs}/s^{-1}$ | $\frac{10^{-4}k_{obs}/[OH^-]}{l\ mol^{-1}\ s^{-1}}$ |
|---|---|---|
| 5·94 | 2·78 | 2·52 |
| 6·24 | 5·60 | 2·53 |
| 6·49 | 10·13 | 2·58 |
| 6·73 | 18·23 | 2·67 |
| 7·00 | 32·33 | 2·55 |

(*b*) $[Co(en)_2Br(NH_2CH_2CN)]^{2+}$, reaction monitored at 565 nm, using 2,6-lutidine buffers.

| | | |
|---|---|---|
| 5·90 | 4·57 | 4·52 |
| 6·19 | 8·78 | 4·47 |
| 6·43 | 14·97 | 4·37 |
| 6·61 | 23·77 | 4·57 |
| 6·85 | 41·18 | 4·57 |

Observed rate constants at constant pH, $k_{obs}$, were converted to second-order rate constants using the expression $k_{OH} = k_{obs}/[OH^-]$. For the chloro- and bromo-complexes $k_{OH} = 2·43 \pm 0·11$ and $(1·18 \pm 0·06) \times 10$ l mol$^{-1}$ s$^{-1}$ respectively at $I$ = 0·1M and 25 °C. As is usually the case, the bromo-complex hydrolyses some five times faster than the chloro-complex. It is noteworthy that the chloro-complex undergoes base hydrolysis at only 1/5 of the rate observed for chloropenta-amine complexes of the type $[Co(en)_2Cl(NH_2R)]^{2+}$, where for primary amines $k_{OH}$ is *ca.* $1·25 \times 10$ l mol$^{-1}$ s$^{-1}$ at 25 °C and $I$ = 0·1M.[11] Crystallographic evidence[5] suggests that there is considerable electron delocalisation in the amidine ligand of (I).



In the $S_{N}1$(CB) mechanism for base hydrolysis it is generally considered that the proton *trans* to the anionic substituent is removed to give the conjugate base. It is currently believed that the amido-group, with its electron pair, functions as a π-donor, stabilising the five-co-ordinate intermediate. The conjugate base produced with (I) possibly involves deprotonation of the amidine group.

Table 3

Base hydrolysis of the halogeno-ligands in the ring-closed complexes at 25 °C and $I$ = 0·1M

Chloro-complex

(*a*) Spectrophotometric kinetics at 550 nm using *n*-butylamine–hydrogen chloride buffers.

| pH | $10^3k_{obs}/s^{-1}$ | $\frac{k_{obs}/[OH^-]}{l\ mol^{-1}\ s^{-1}}$ |
|---|---|---|
| 9·60 | 0·12 | 2·35 |
| 9·90 | 0·26 | 2·57 |
| 10·32 | 0·67 | 2·50 |
| 10·51 | 1·03 | 2·50 |
| 10·79 | 1·78 | 2·32 |
| 11·09 | 3·79 | 2·42 |
| 11·39 | 7·28 | 2·33 |

(*b*) pH-Stat kinetics.

| | $10^4k_{obs}/s^{-1}$ | |
|---|---|---|
| 9·95 | 2·85 | 2·50 |
| 10·10 | 3·93 | 2·43 |
| 10·22 | 4·85 | 2·40 |
| 10·55 | 11·12 | 2·47 |
| 10·80 | 19·27 | 2·40 |

Bromo-complex

(*a*) Spectrophotometric kinetics at 565 nm.

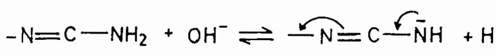
| | $10^4k_{obs}/s^{-1}$ | $\frac{10^{-1}k_{obs}/[OH^-]}{l\ mol^{-1}\ s^{-1}}$ |
|---|---|---|
| 8·60 * | 0·62 | 1·20 |
| 8·90 * | 1·22 | 1·20 |
| 9·60 † | 6·13 | 1·21 |
| 9·80 † | 9·35 | 1·16 |
| 10·04 † | 16·72 | 1·19 |
| 10·29 | 30·20 | 1·21 |
| 10·49 | 45·18 | 1·12 |
| 10·70 | 95·80 | 1·21 |
| 10·90 | 110·95 | 1·12 |

(*b*) pH-Stat kinetics.

| | | |
|---|---|---|
| 9·19 | 2·23 | 1·13 |
| 9·48 | 4·70 | 1·20 |
| 9·78 | 8·75 | 1·14 |
| 10·02 | 15·70 | 1·17 |

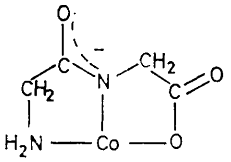
* Tris-hydrogen chloride buffer. † Carbonate–bicarbonate buffer, all other runs being in *n*-butylamine–hydrogen chloride buffers.

Such a conjugate base would be expected to be a poorer π-electron donor than a 'normal' amido-group, thus giving rise to lower rates of hydrolysis.



$$\text{-N=C-NH}_2 + \text{OH}^- \rightleftharpoons \text{-N=C-NH} + \text{H}_2\text{O}$$

The *X*-ray studies[5] have shown that there is considerable strain in the tridentate ligand as a result of adopting the *facial* configuration. Molecular models indicate that the least-strained arrangement would be the one in which the tridentate amidine ligand adopted a *meridional* configuration. A somewhat similar situation occurs with bis(dipeptide)cobalt(III) complexes, where the ligand has rather similar structural features to those found in the tridentate amidine. Dipeptide complexes such as bis-(glycylglycinato)cobalt(III) only occur in the meridional form.[16] The stereochemistry of the products of base hydrolysis were therefore investigated since a rearrangement may have occurred in the five-co-ordinate intermediate to give the least-strained meridional isomer.

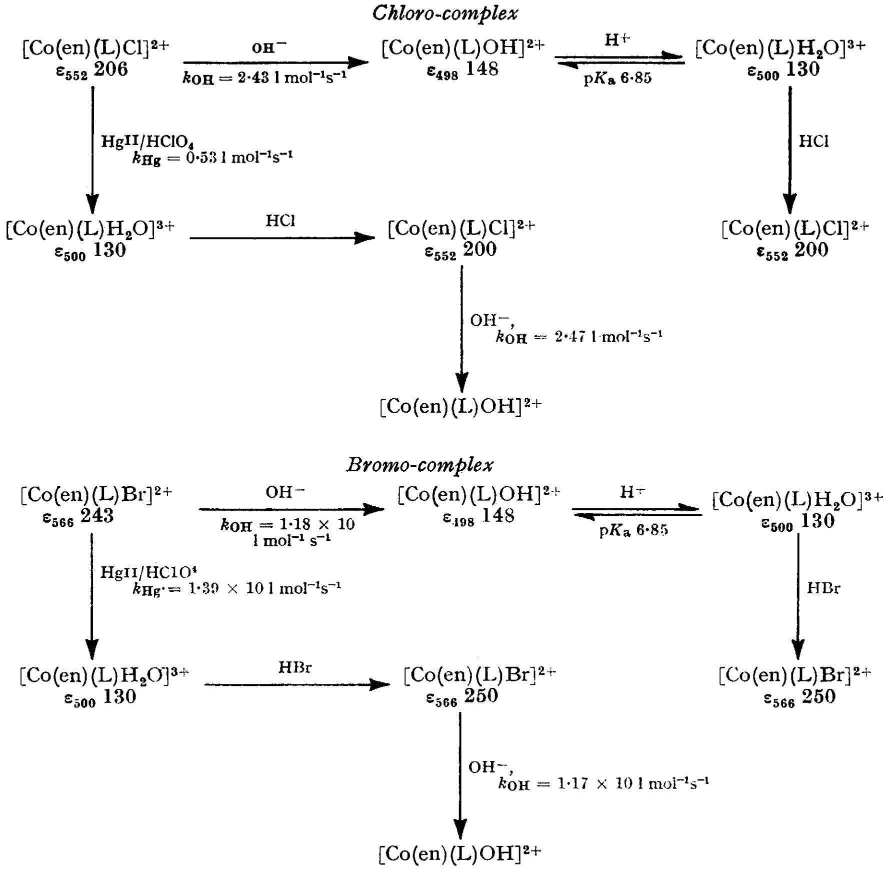


The product of base hydrolysis is the hydroxopenta-amine.

The practical ionisation constant for equilibrium (1)

$$[Co(en)\{NH_2{\cdot}CH_2{\cdot}CH_2{\cdot}C(NH_2){:}N{\cdot}CH_2{\cdot}CH_2{\cdot}NH_2\}OH_2]^{3+} \rightleftharpoons [Co(en)\{NH_2{\cdot}CH_2{\cdot}CH_2{\cdot}C(NH_2){:}N{\cdot}CH_2{\cdot}CH_2{\cdot}NH_2\}OH]^{2+} + H^+ \quad (1)$$

was determined potentiometrically ($pK_a$ 6·81 ± 0·03) and spectrophotometrically ($pK_a$ 6·87 ± 0·03) at 25 °C and $I = 0{\cdot}1$M ($NaClO_4$). Good isosbestic points were observed in the spectrophotometric measurements at 368, 428, and 527 nm, providing evidence for only a single isomer. The reactions shown in Scheme 1 were then carried out. Treatment of the hydroxopenta-amine, produced on base hydrolysis, with the appropriate concentrated hydrogen halide regenerated the original halogenopenta-amine complex (confirmed by visible spectra). Mercury(II)-catalysed aquation, which normally occurs with full retention of configuration, gave the same aquopenta-amine complex as that prepared by base hydrolysis and subsequent acidification. Treatment of this aquopenta-amine with the appropriate hydrogen halide gave a halogenopenta-amine complex, which had the same spectral characteristics as, and underwent base hydrolysis at an identical rate to, an authentic sample of (I; X = Cl). It is clear therefore that base hydrolysis occurs with essentially complete retention of configuration.



SCHEME 1 Reactions of the ring-closed amidine (L) complexes (I; X = Cl or Br) (Absorption coefficients in l $mol^{-1}$ $cm^{-1}$.)

*Mercury*(II)-*catalysed Aquation of the Ring-closed Complexes*.—Mercury(II)-catalysed aquations of the penta-amine complexes (I; X = Cl or Br) were studied at $I = 2{\cdot}04$M and 25 °C (Table 4). The aquation rates of the bromo-complex were quite rapid even at quite low mercury(II) concentrations and it was necessary to employ a stopped-flow spectrophotometer to follow the reactions. Aquation rates were studied using a $HClO_4$

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[16] See, for example, M. T. Barnet, H. C. Freeman, D. A. Buckingham, I. N. Hsu, and D. Vander Helm, *Chem. Comm.*, 1970, 367; R. D. Gillard, P. M. Harrison, and E. D. McKenzie, *J. Chem. Soc.* (*A*), 1967, 618; R. D. Gillard, E. D. McKenzie, R. Mason, and G. B. Robertson, *Co-ordination Chem. Rev.*, 1966, **1**, 263.

concentration of 1·15M. At this acidity the reactions are first order in [Complex] and [Hg$^{II}$]. Mercury(II) was always in large excess and values of the second-order rate constant $k_{Hg}$ were obtained from the expression $k_{Hg} = k_{obs}/[Hg^{II}]$. Values of $k_{Hg}$ are (5·28 ± 0·17) × $10^{-1}$ (chloro-complex) and (1·39 ± 0·06) × 10 l mol$^{-1}$ s$^{-1}$ (bromo-complex) so that $k_{Hg}{}^{Br}/k_{Hg}{}^{Cl}$ is *ca.* 25. This ratio is somewhat larger than might be expected. Bifano and Linck [17] have studied the kinetics of Hg$^{II}$ catalysed aquation of various cobalt(III) complexes of types *cis*- and *trans*-$[Co(en)_2(L)Cl]^{n+}$ at 25 °C and $I$ = 1·0M. For the ion *cis*-$[Co(en)_2(NH_3)Cl]^{2+}$ they quote $k_{Hg} = 1{\cdot}46 \times 10^{-2}$ l mol$^{-1}$ s$^{-1}$, while for *trans*-$[Co(en)_2(NH_3)Cl]$ $k_{Hg} = 4{\cdot}7 \times 10^{-3}$ l mol$^{-1}$ s$^{-1}$. The more rapid reactions of the present complexes may be indicative of strain present in the tridentate ligand which is released on formation of the five-co-ordinate intermediate generally considered to occur in mercury(II)-catalysed aquations.

TABLE 4

Mercury(II)-catalysed aquations of the halogeno-ligands in the ring-closed complexes at 25 °C and $I$ = 2·04M

Chloro-complex *

| [Hg$^{II}$]/M | [HClO$_4$]/M | $10^2k_{obs}$/s$^{-1}$ | $10^1k_{obs}/[Hg^{II}]$ / l mol$^{-1}$ s$^{-1}$ |
|---|---|---|---|
| 0·02 | 1·15 | 1·04 | 5·20 |
| 0·04 | 1·15 | 2·10 | 5·25 |
| 0·06 | 1·15 | 3·27 | 5·45 |
| 0·08 | 1·15 | 4·19 | 5·23 |

Bromo-complex †

| | | $10^1k_{obs}$/s$^{-1}$ | $10^{-1}k_{obs}/[Hg^{II}]$ / l mol$^{-1}$ s$^{-1}$ |
|---|---|---|---|
| 0·01 | 1·15 | 1·33 | 1·33 |
| 0·025 | 1·15 | 3·63 | 1·45 |
| 0·05 | 1·15 | 6·90 | 1·38 |

* Rate constants determined spectrophotometrically at 550 nm. † Rate constants determined by stopped-flow measurements at 568 nm.

*Mercury*(II)-*catalysed Reactions of* cis-$[Co(en)_2(NH_2CH_2CN)X]^{2+}$ *Ions*.—Buckingham *et al.*[6] have reported that treatment of the ion *cis*-$[Co(en)_2(NH_2CH_2CN)Br]^{2+}$ with Hg$^{II}$ in 0·09—0·89M-HClO$_4$ gave *ca.* 95% yield of $[Co(en)_2(NH_2{\cdot}CH_2{\cdot}CO{\cdot}NH_2)]^{3+}$ containing *O*-bonded glycine amide. This complex is orange ($\lambda_{max.}$ 487 nm, ε 104 l mol$^{-1}$ cm$^{-1}$). We have studied the kinetics of this reaction spectrophotometrically at [HClO$_4$] = 0·537 and $I$ = 2·037M for the chloro- and bromo-complexes (Table 5). In both cases, the reactions are first order in [Hg$^{II}$] and [Complex]. For the chloro- and bromo-complexes $k_{Hg} = (8{\cdot}99 \pm 0{\cdot}43) \times 10^{-4}$ and $(1{\cdot}58 \pm 0{\cdot}04) \times 10^{-1}$ l mol$^{-1}$ s$^{-1}$ respectively. The latter rate constant compares well with that of $1{\cdot}4 \times 10^{-1}$ l mol$^{-1}$ s$^{-1}$ quoted by Buckingham *et al.*[6] at $I$ = 1·2—1·6M and 25 °C.

It has been concluded that the ion *cis*-$[Co(en)_2(NH_2{\cdot}CH_2{\cdot}CO{\cdot}NH_2)(H_2O)]^{3+}$ containing the *N*-co-ordinated amide is not an intermediate in the reaction. It is well established that this ion rapidly forms $[Co(en)_2(NH_2{\cdot}CH_2{\cdot}CO_2H)]^{2+}$, containing chelated glycine ($t_{\frac{1}{2}}$ *ca.* 2 min at 25 °C), and not $[Co(en)_2(NH_2{\cdot}CH_2{\cdot}CO{\cdot}NH_2)]^{3+}$ containing the chelated amide.

In the present reaction, Hg$^{II}$ will initially give a highly reactive five-co-ordinate intermediate, which could then give the chelated aminoacetonitrile complex and/or the aquopenta-amine. Formation of the *N*-bonded nitrile will obviously not be favoured due to strain in the five-membered chelate ring caused by the *sp*-hybridised carbon atom of the nitrile group. In addition, hydrolysis of such a chelated species would give the *N*-bonded amide rather than the *O*-bonded species observed. Jordan *et al.*[3] have observed that hydrolysis of cobalt *N*-bonded nitriles gives rise to *N*-bonded amides.

TABLE 5

Mercury(II)-catalysed reactions of the $[Co(en)_2(NH_2CH_2CN)X]^{2+}$ ions at 25 °C and $I$ = 2·037M

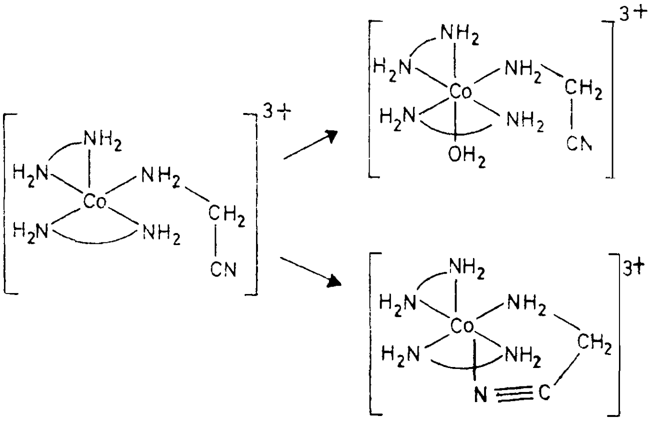
(*a*) Chloro-complex, [HClO$_4$] = 0·537M, reaction monitored at 489 nm.

| [Hg$^{II}$]/M | $10^4k_{obs}$/s$^{-1}$ | $10^4k_{obs}/[Hg^{II}]$ / l mol$^{-1}$ s$^{-1}$ |
|---|---|---|
| 0·1 | 0·90 | 8·97 |
| 0·2 | 1·83 | 9·17 |
| 0·3 | 2·57 | 8·55 |
| 0·4 | 3·63 | 9·08 |
| 0·5 | 4·55 | 9·15 |

(*b*) Bromo-complex, [HClO$_4$] = 0·537M, reaction monitored at 489 nm.

| | $10^3k_{obs}$/s$^{-1}$ | $10^1k_{obs}/[Hg^{II}]$ / l mol$^{-1}$ s$^{-1}$ |
|---|---|---|
| 0·025 | 3·90 | 1·56 |
| 0·05 | 8·05 | 1·61 |
| 0·075 | 12·11 | 1·61 |
| 0·1 | 15·40 | 1·54 |

Rearrangement of the *N*- to the *O*-bonded amide would be expected to be a slower process since it requires rupture of the chelate ring.



The slow step in the reaction is considered to be aquation. The chelation step *cis*-aquopenta-amine ⟶ $[Co(en)_2(NH_2{\cdot}CH_2{\cdot}CO{\cdot}NH_2)]^{3+}$ was not observed and must therefore occur rapidly. Since mercury(II)-catalysed aquations normally occur with retention of configuration, a *cis*-configuration is assigned to the aquopenta-amine complex. *cis*-Aquopenta-amine complexes of the type $[Co(en)_2(NH_2R)(OH_2)]^{3+}$ normally have $\lambda_{max.}$ at *ca.* 504 ± 3 nm for the lowest-energy ligand-field

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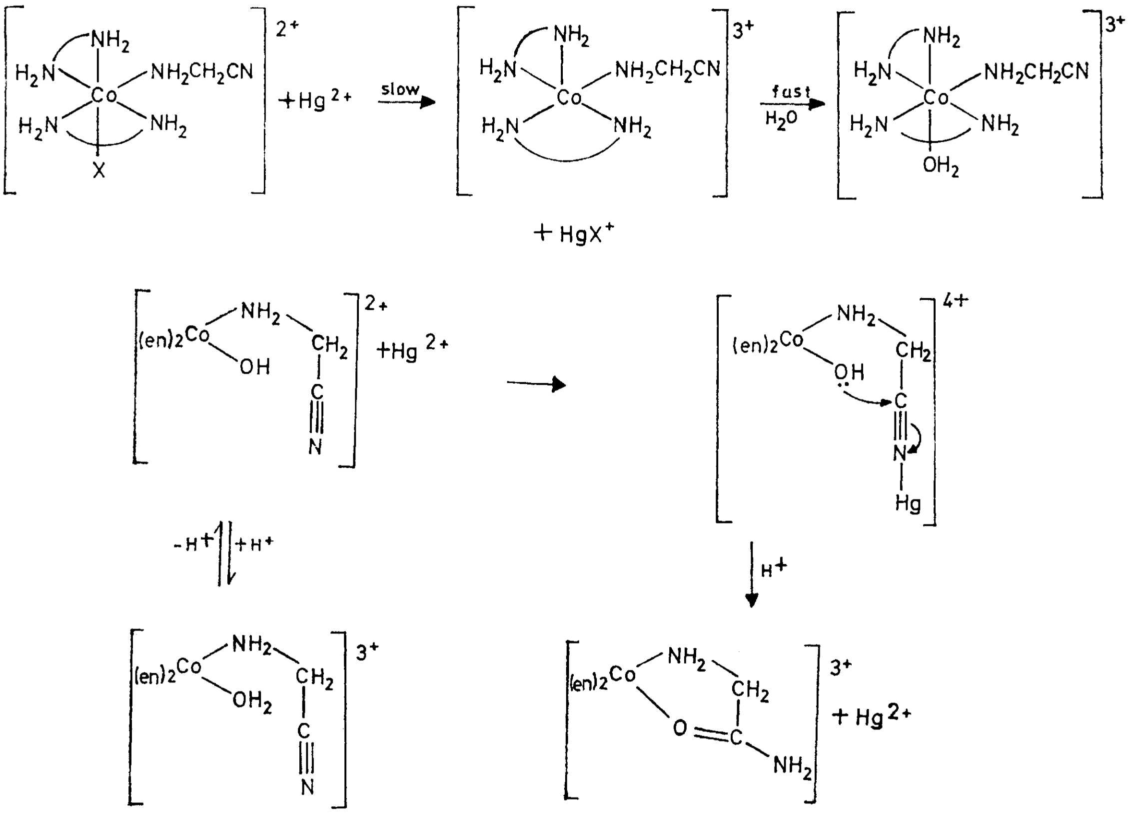
[17] C. Bifano and R. G. Linck, *Inorg. Chem.*, 1968, **7**, 908.

band, while the chelated glycine amide product has $\lambda_{max.}$ 487 nm. Quite marked spectral changes would therefore be expected in the chelation step.



SCHEME 2 Possible mechanism for formation of the ion $[Co(en)_2(NH_2{\cdot}CH_2{\cdot}CO{\cdot}NH_2)]^{3+}$

Buckingham *et al.*[6] have suggested a mechanism of the type shown in Scheme 2. The reaction is assisted by electrophilic catalysis of the $Hg^{II}$ ion co-ordinated to the nitrogen atom of the nitrile. Specific acid-catalysed hydrolysis of nitriles is considered to occur by the mechanism [18] in Scheme 3, *i.e.* rapid pre-equilibrium protonation to form a mesomeric cation, followed by slow nucleophilic attack of a water molecule on the electron-deficient carbon atom. Buckingham *et al.*[6] have suggested that intramolecular nucleophilic attack by a cobalt-bound hydroxide ion occurs in the present reaction. Nitriles are very weak bases [$pK(BH^+)$ for benzonitrile $= -10{\cdot}45$ [19] and $= -4{\cdot}3$ [20] for acetonitrile]. Thus acetonitrile is half protonated in *ca.* 8M-$HClO_4$. Complexes of the $NH_2$-co-ordinated nitrile carry a charge of $+2$ or $+3$ so that protonation would be expected to be very unfavourable. It is probably for this reason that co-ordination of mercury to the CN group is favoured even in quite acidic solution. The $pK_a$ value for the $[N_5Co{-}OH_2]^{3+} \rightleftharpoons [N_5Co{-}OH]^{2+} + H^+$ ionisation would be expected to be *ca.* 6·5. At the acidities employed (*ca.* 0·9M-$HClO_4$) the ratio $[N_5Co{-}OH^{2+}] : [N_5Co{-}OH_2^{3+}]$ species must be *ca.* $10^{-6}$—$10^{-7}$, indicating that the Co–OH species must be at least $10^6$—$10^7$ times more reactive than the aquo-complex.

The main evidence for the ' metal–hydroxide ' rather than the ' metal–aquo ' mechanism is based on analogous reactions of the aminopropiononitrile complex.[6] It was expected that formation of the species $[Co(en)_2(NH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CO{\cdot}NH_2)]^{3+}$, containing the larger six-membered chelate ring, would be slower than that of $[Co(en)_2(NH_2{\cdot}CH_2{\cdot}CO{\cdot}NH_2)]^{3+}$. Preliminary kinetic studies showed that in the presence of 0·1M-$Hg^{II}$ there was a slow reaction ($t_{\frac{1}{2}}$ *ca.* 108 min at 25 °C and $[H^+] = 0{\cdot}1M$) following rapid removal of bromide. This reaction was first order in $[Hg^{II}]$ and was *inversely* proportional to $[H^+]$. The observed spectral change was consistent with a *cis*-aquo-complex giving a chelated product. If this mechanism is confirmed it will provide an interesting example of specific base catalysis occurring in solutions which are *ca.* 1M in hydrogen ion.

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[3/1900 *Received, 14th September,* 1973]

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[19] M. Liler and D. Kosanovic, *J. Chem. Soc.*, 1958, 1084.

[20] M. A. Paul and F. A. Long, *Chem. Rev.*, 1957, **57**, 1.