# Kinetics of the $Hg^{2+}$ – assisted Chloride Release of some *cis*-$CoCl(en)_2(py\text{-}X)^{2+}$ Complexes

D. A. HOUSE*

*Department of Chemistry, University of Canterbury, Christchurch, New Zealand*

and W. MARTY

*Institute of Chemistry, University of Neuchâtel, 2100 Neuchâtel, Switzerland*

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We have, for some time, been interested in the properties of Co(III) complexes containing pyridine or substituted pyridines [1–9]. As part of our work on base hydrolysis rates [5], it was desirable to synthesise *cis*-$CoCl(en)_2(R)^{2+}$ where R = 4-amino- and 4-dimethylamino-pyridine for structure-reactivity comparisons.

There are two possible modes of coordination of 4-amino-pyridine, *via* the pyridine nitrogen or *via* the amino nitrogen, but for the dimethylamino analog, the latter is unlikely from steric considerations. The two complexes react with base at almost the same rate [10] and ligand binding *via* the pyridine nitrogen seems more likely.

Preliminary data from a single crystal X-ray analysis of *cis*-$[CoCl(en)_2(py\text{-}NH_2)](NO_3)_2$ (R ~ 6%) confirms the *cis*-configuration and shows the pyridine ligand to be bound *via* the ring nitrogen. The *cis*-configuration for the 4-amino-pyridine complex has also been established by optical resolution.

In this communication, we describe the kinetics of the $Hg^{2+}$-assisted chloride release for these two complexes, together with similar data for the pyridine and 4-methylpyridine analogues.

## Experimental

4-amino and 4-dimethylaminopyridine were purchased from Fluka and used as supplied.

The complexes were prepared by the standard method [11] of grinding an aqueous slurry of *trans*-$[CoCl_2(en)_2]Cl$ [12] with a slight excess of the amine. The red chloropentamine dichloride salts that deposited were twice recrystallised from aqueous 0.05 *M* HCl by the addition of LiCl. Full experimental details will be pubished later but analytical, $^{13}C$ NMR [13] and visible absorption spectral data [14] are fully consistent with the *cis*-$[CoCl(en)_2(py\text{-}X)]Cl_2$ formulation.

Appropriate amounts of $Hg(NO_3)_2 \cdot H_2O$ were dissolved in 1.0 *M* trifluoroacetic acid (TFA) or perchloric acid and the $[Hg^{2+}]$ was determined by titration with standard KCl using diphenylcarbazone indicator [15]. After preliminary spectral scans to establish isosbestic points, kinetic data were obtained by fixed wavelength techniques at 480 nm using a Varian Superscan recording spectrophotometer [16].

## Results and Discussion

The $Hg^{2+}$-assisted halido release reaction (1) of halopentaaminecobalt(III) complexes has been the subject of many kinetic studies [17].

$$CoX(N_5)^{2+} + Hg^{2+} \rightarrow Co(N_5)(OH_2)^{3+} + HgX^{+} \qquad (1)$$

The reaction is first order in both [Co(III)] and $[Hg^{2+}]$ and, in this work, the investigation has been performed under pseudo-first-order conditions with $[Hg^{2+}] > 10[Co(III)]$. In nitrate or perchlorate media, a positive salt effect is observed, and in trifluoroacetate or sulfate media the reaction is independent of ionic strength [16]. Most kinetic studies have used nitrate or perchlorate as the reaction media, but for the aminopyridine complexes under investigation, poor solubility required the use of trifluoroacetate as the background electrolyte.

Table I lists the kinetic data obtained for *cis*-$CoCl(en)_2(py\text{-}X)^{2+}$ (X = H, 4-Me, 4-$NH_2$, 4-$N(Me)_2$) under these conditions and also for X = H at $\mu$ = 1.0 *M*, $HClO_4$. From a comparison of these and previously obtained kinetic data (Table II), it is obvious that the use of TFA as a background electrolyte results in a considerable lowering of the activation energy for reaction (1). Consequently, it is difficult to make meaningful comparisons, in terms of py-X substitution, on the magnitude of the observed rate constants. Nevertheless, the order of increasing rate at 298.2; in 1.0 *M* TFA, is H < 4-Me, < 4-$NH_2$ < 4-$N(Me)_2$ and this is likely to hold over a considerable temperature range, as the activation energies are approximately constant at 60 kJ $mol^{-1}$. This order parallels the base strength of the monoamine ($pK_a$ = 5.23, 6.02, 9.13, 9.61 for X = H, 4-Me, 4-$NH_2$ and 4-$N(Me)_2$ respectively [18]). When all the data in Table II are normalised (Table III) to 1.0 *M* TFA (multiplication of Chan's data at $\mu$ = 0.2 *M* ($NO_3^-$) by a factor of 1.67) a reasonably linear plot of $pK_a$ (amine) *vs.* ln $k_{Hg}$ is obtained with a slope of 0.5 (Fig. 1). A linear plot with slope of 1.0 would suggest that the Co(III) center behaves in a similar manner

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*Author to whom correspondence should be addressed.

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TABLE I. Observed and Calculated Rate Constants for the $Hg^{2+}$-Assisted Chloride Release of Some *cis*-$CoCl(en)_2(4\text{-x-py})^{2+}$ Complexes in 1 *M* Trifluoroacetic Acid.

| X | T<br>°C [K] | $Hg^{2+}$ [a]<br>m*M* | $10^3\ k_{obs}$ [b]<br>$s^{-1}$ | $10^2\ k_{Hg}$ [c]<br>$M^{-1}\ s^{-1}$ | $10^2\ k_{Hg}(calc)$ [d]<br>$M^{-1}\ s^{-1}$ |
|---|---|---|---|---|---|
| H[e] | 30.6 [303.8] | 61.3 | 1.54 ± 0.06 | 2.51 ± 0.10 | 2.47 |
| | 31.4 [304.6] | 61.3 | 1.61 ± 0.05 | 2.62 ± 0.07 | 2.63 |
| | 35.2 [308.4] | 61.3 | 2.15 ± 0.05 | 3.51 ± 0.08 | 3.51 |
| | | | 2.13 ± 0.05 | 3.47 ± 0.08 | |
| | 40.9 [314]1] | 61.3 | 3.27 ± 0.08 | 5.33 ± 0.13 | 5.35 |
| | 45.8 [319.0] | 39.1 | 3.00 ± 0.05 | 7.67 ± 0.13 | 7.60 |
| Me | 30.5 [303.7] | 61.3 | 1.88 ± 0.03 | 3.07 ± 0.05 | 3.10 |
| | | 61.3 | 1.93 ± 0.08 | 3.14 ± 0.13 | |
| | 35.2 [308.4] | 61.3 | 2.37 ± 0.08 | 4.45 ± 0.13 | 4.46 |
| | 40.9 [314.1] | 39.1 | 2.67 ± 0.07 | 6.83 ± 0.18 | 6.84 |
| | 45.8 [319.0] | 20.7 | 2.03 ± 0.02 | 9.80 ± 0.09 | 9.77 |
| | | 20.7 | 2.02 ± 0.02 | 9.76 ± 0.09 | |
| $NH_2$[f] | 25.3 [298.5] | 20.7 | 2.05 ± 0.02 | 9.90 ± 0.10 | 10.0 |
| | | 20.7 | 2.11 ± 0.05 | 10.2 ± 0.24 | |
| | 19.9 [293.1] | 20.7 | 1.36 ± 0.03 | 6.58 ± 0.14 | 6.58 |
| | | 39.1 | 2.59 ± 0.06 | 6.62 ± 0.15 | |
| | 16.0 [289.2] | 39.1 | 1.87 ± 0.06 | 4.80 ± 0.15 | 4.82 |
| | | 39.1 | 1.84 ± 0.08 | 4.72 ± 0.20 | |
| | | 61.3 | 2.95 ± 0.07 | 4.81 ± 0.11 | |
| | 11.1 [284.3] | 61.3 | 1.98 ± 0.08 | 3.23 ± 0.13 | 3.21 |
| | | 61.3 | 2.00 ± 0.04 | 3.26 ± 0.07 | |
| $N(Me)_2$[g] | 25.4 [298.6] | 20.7 | 3.15 ± 0.04 | 15.2 ± 0.2 | 15.3 |
| | | 20.7 | 3.20 ± 0.03 | 15.4 ± 0.14 | |
| | 19.9 [293.1] | 20.7 | 2.03 ± 0.04 | 9.81 ± 0.20 | 9.69 |
| | 16.0 [289.2] | 20.7 | 1.38 ± 0.06 | 6.66 ± 0.30 | 6.92 |
| | | 39.1 | 2.80 ± 0.05 | 7.16 ± 0.13 | |
| | 11.1 [284.3] | 39.1 | 1.70 ± 0.06 | 4.35 ± 0.15 | 4.47 |
| | | 39.1 | 1.80 ± 0.08 | 4.60 ± 0.20 | |
| | $\mu$ = 1.0 *M* $HClO_4$ | | | | |
| H[e] | 31.0 [304.2] | 93.4[h] | 2.65 ± 0.05 | 2.83 ± 0.05 | 2.69 |
| | 35.7 [308.9] | 93.4[h] | 3.96 ± 0.04 | 4.24 ± 0.04 | 4.37 |
| | | | 3.87 ± 0.07 | 4.14 ± 0.07 | |
| | 40.6 [313.8] | 64.5[i] | 4.77 ± 0.06 | 7.40 ± 0.09 | 7.15 |
| | | | 4.54 ± 0.17 | 7.04 ± 0.23 | |
| | 45.4 [318.6] | 20.7[j] | 2.40 ± 0.05 | 11.6 ± 0.24 | 11.4 |

[a] Initial $[Hg^{2+}]$. [Co(III)] ~ 2 m*M*. [b] Observed pseudo-first-order rate constant. [c] $k_{Hg} = k_{obs}\ [Hg^{2+}]^{-1}$. [d] Calculated from the activation parameters cited in Table II. [e] Isosbestic points at 508, 416, 355 and 331 nm. [f] Isosbestic points at 513, 426 and 368 nm. [g] Isosbestic point at 522 nm. [h] $[HClO_4]$ = 0.76 *M*. [i] $[HClO_4]$ = 0.82 *M*. [j] $[HClO_4]$ = 0.94 *M*.

TABLE II. Activation Parameters for the $Hg^{2+}$-Assisted Chloride Release of Some *cis*-$CoCl(en)_2(py\text{-}X)^{2+}$ Complexes at 298.2 K.

| X | $10^2\ k_{Hg}$<br>$(M^{-1}\ s^{-1})$ | $\mu$<br>(*M*) | $E_a$<br>(kJ $mol^{-1}$) | log PZ | $\Delta S^{\#}$<br>($JK^{-1}\ mol^{-1}$) | Ref. |
|---|---|---|---|---|---|---|
| H | 1.51 | 1.0 ($ClO_4^-$) | | | | a |
| | 1.41 | 1.0 ($ClO_4^-$) | 80.1 ± 3.2 | 12.316 | −17 ± 6 | b |
| | 1.58 | 1.0 (TFA) | 59.5 ± 0.7 | 8.635 | −88 ± 2 | b |

*(continued overleaf)*

TABLE II. *(continued)*

| X | $10^2$ $k_{Hg}$ ($M^{-1}$ $s^{-1}$) | $\mu$ (*M*) | $E_a$ (kJ $mol^{-1}$) | log PZ | $\Delta S^{\#}$ ($JK^{-1}$ $mol^{-1}$) | Ref. |
|---|---|---|---|---|---|---|
| | 0.87 | 0.2 ($NO_3^-$) | 84.6 ± 1.6 | 12.762 | −9 ± 3 | c |
| 3-Me | 1.17 | 0.2 ($NO_3^-$) | 80.4 ± 2.4 | 12.159 | −20 ± 5 | c |
| 4-Me | 1.99 | 1.0 (TFA) | 60.4 ± 0.4 | 8.881 | −83 ± 1 | b |
| | 1.30 | 0.2 ($NO_3^-$) | 79.5 ± 0.5 | 12.044 | −23 ± 1 | c |
| 3-Et | 1.31 | 0.2 ($NO_3^-$) | 78.6 ± 1.3 | 11.880 | −26 ± 3 | c |
| 4-Et | 1.40 | 0.2 ($NO_3^-$) | 80.3 ± 2.0 | 12.209 | −19 ± 4 | c |
| 3,5-$Me_2$ | 1.73 | 0.2 ($NO_3^-$) | 73.2 ± 2.4 | 11.058 | −41 ± 5 | c |
| 3,4-$Me_2$ | 2.02 | 0.2 ($NO_3^-$) | 70.5 ± 1.9 | 10.653 | −49 ± 4 | c |
| 4-$NH_2$ | 9.79 | 1.0 (TFA) | 56.4 ± 0.6 | 8.867 | −83 ± 2 | b |
| 4-$N(Me)_2$ | 14.8 | 1.0 (TFA) | 60.7 ± 1.4 | 9.822 | −65 ± 3 | b |

[a] C. Bifano and R. G. Linck, *Inorg. Chem.*, *7*, 908 (1968). [b] This work. [c] S. C. Chan and S. F. Chan, *Austral. J Chem.*, *24*, 2071 (1971). The data in Table II have been recalculated from the variation in $k_{Hg}$ *vs.* T given in this reference.

TABLE III. Rate Constants for the $Hg^{2+}$-Assisted Chloride Release from Some *cis*-$CoCl(en)_2(py\text{-}X)^{2+}$ Complexes Normalised to 1.0 *M* TFA at 298.2 K.

| No. | X | $10^2$ $k_{Hg}$ | $pK_a$ (py-X) |
|---|---|---|---|
| 1 | H | 1.58 | 5.23 |
| 2 | 3-Me | 1.96 | 5.70 |
| 3 | 4-Me | 1.99 | 5.99 |
| 4 | 4-Et | 2.34 | 6.03 |
| 5 | 3,5-$Me_2$ | 2.90 | 6.14 |
| 6 | 3,4-$Me_2$ | 3.38 | 6.48 |
| 7 | 4-$NH_2$ | 9.79 | 9.13 |
| 8 | 4-$N(Me)_2$ | 14.8 | 9.61 |

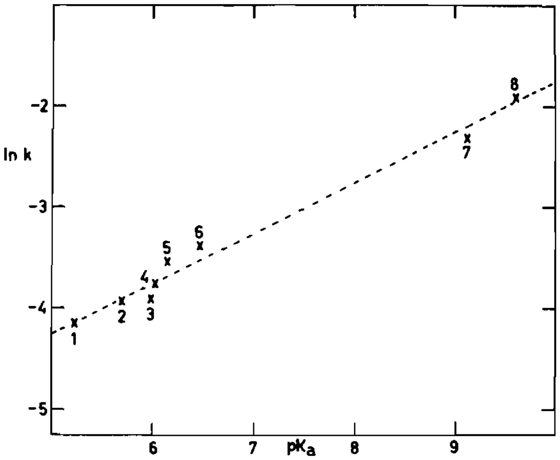

Fig. 1. Plot of ln $k_{Hg}$ (298.2) *vs.* $pK_a$ (py-X) for the data in Table III.

to a proton in terms of the effect of electron delocalisation. The deviation of the slope from unity may reflect some perturbation of the electronic effects due to back-bonding of the Co(III) orbitals and the conjugated π-system of the ligand. Such an interaction has been proposed previously [2, 8] to account for the subtle differences in behaviour between *cis*-$CoCl(en)_2(amine)^{2+}$ complexes with aliphatic and heterocyclic amine ligands.

Although no acid dependence studies have been made (apart from variation of [$HClO_4$] from 0.76–0.94 *M* to maintain ionic strength), the constancy of the activation parameters within the series suggests that the non-bonded $-NH_2$ and $-N(Me)_2$ amino groups are not protonated under the reaction conditions.

## References

1 I. J. Kindred and D. A. House, *Inorg. Nucl. Chem. Lett.*, *10*, 25 (1974).
2 D. A. House and R. S. Visser, *J. Inorg. Nucl. Chem.*, *38*, 1157 (1976).
3 D. R. Fenemor and D. A. House, *J. Inorg. Nucl. Chem.*, *38*, 1559 (1976).
4 D. R. Fenemor and D. A. House, *Int. J. Chem. Kinetics*, *8*, 573 (1976).
5 J. McKenzie and D. A. House, *J Inorg. Nucl. Chem.*, *39*, 1843 (1977).
6 Foo Chuk Ha, D. A. House and J. W. Blunt, *Inorg. Chim. Acta*, *33*, 269 (1979).
7 Foo Chuk Ha and D. A. House, *Inorg. Chim. Acta*, *38*, 167 (1980).
8 D. A. House, P. R. Norman and R. W. Hay, *Inorg. Chim. Acta Lett.*, *45*, 117 (1980).

9 G. Bombieri, F. Benetollo, A. Del Pra, M. L. Tobe and D. A. House, *Inorg. Chim. Acta, 50, 89 (1981).*

10 D. A. House and W. Marty, to be published.

11 J. C. Bailar and L. B. Clapp, *J. Am. Chem. Soc., 67,* 171 (1954).

12 G. G. Schlessinger, 'Inorganic Laboratory Preparations', Chemical Publishing Co., N.Y., 237 (1962).

13 D. A. House and J. W. Blunt, *Inorg. Nucl. Chem. Lett., 11,* 219 (1975).

14 S. C. Chan and S. F. Chan, *Austr. J. Chem., 24,* 2071 (1971).

15 A. I. Vogel, 'Quantitative Inorganic Analysis', 3rd Edn., Longmans Green, London, 274 (1962).

16 D. A. House, *Inorg. Chim. Acta, 51,* 273 (1981).

17 D. A. House, *Coord. Chem. Rev., 23,* 223 (1977), Table 19.

18 D. D. Perrin, 'Dissociation Constants of Organic Bases in Aqueous Solution', Supplement 1972, I.U.P.A.C., Butterworths, London 5010, 5181.