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The Kinetics of the Mercury(II) Catalyzed Aquation of the Azidopentaamminecobalt(III) Ion

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The kinetics of the mercury(II) catalyzed aquation of $Co(NH_3)_5N_3^{2+}$ to $Co(NH_3)_5OH_2^{3+}$ were studied in the temperature range of 60–80 °C and $\mu = 1.0$ M (H^+, Na^+, ClO_4^-). The isothermal rate is governed by $Rate = kK[Hg^{2+}][Co(III)]/(1 + K[Hg^{2+}])$, which reveals formation of the intermediate $Co(NH_3)_5N_3Hg^{4+}$ complex. The stability constant of the binuclear complex $K = 7.3$ M^{-1} at 25 °C is calculated from the corresponding $\Delta S_o = -15.5 \pm 7.2$ cal mol^{-1} K^{-1} and $\Delta H_o = -5.8 \pm 2.5$ kcal mol^{-1} values. The rate constant $k = 1 \times 10^{-5}$ s^{-1} at 25 °C for the aquation of the binuclear complex is calculated from the activation entropy $\Delta S^{\ddagger} = 9.8 \pm 6.0$ cal mol^{-1} K^{-1} and enthalpy $\Delta H^{\ddagger} = 27.2 \pm 2.1$ kcal mol^{-1}. A comparison with the kinetic and mechanistic behavior of similar complexes is made.

Introduction

Studies on the mercury(II) catalyzed aquation of a halide or pseudo-halide ligand from inert transition metal complexes have been numerous. Catalysis presumably occurs through formation of a mercury(II) adduct in which the halide or pseudo-halide acts as a bridging ligand in the binuclear complex. In some of the studies the existence of the adduct has been demonstrated by observing that the aquation rate dependence on mercury(II) was less than first order. Mercury(II) adduct formation involving a halide ligand was observed only for complexes having an additional halide or pseudo-halide ligand in the *cis*-position [1–5]. Adducts with mercury(II) bridged by a pseudo-halide ligand are more stable and therefore more readily detected [6–12].

The mercury(II) catalyzed aquation of azide ligand from $Cr(H_2O)_5N_3^{2+}$ was previously investigated [13]. Now we report a similar kinetic study on the $Co(NH_3)_5N_3^{2+}$ ion, from which equilibrium parameters for the mercury(II) adduct formation and kinetic parameters for its decomposition to the $Co(NH_3)_5OH_2^{3+}$ ion are determined.

Experimental

Materials

Azidopentaamminecobalt(III) was prepared as the nitrate salt. The product was recrystallized from dilute nitric acid (Found %: Co, 18.9; H, 4.88; N, 48.3; Calc %: Co, 19.0; H, 4.84; N, 45.2). The visible absorption maximum was found at 518 nm with the molar absorptivity of 263 M^{-1} cm^{-1}, in a reasonable agreement with the literature data [14]. Mercury(II) perchlorate solution was prepared and analyzed as previously described [7]. The other chemicals used were analytical grade Merck. Doubly distilled water was used throughout.

Kinetic Measurements

The kinetics were followed spectrophotometrically at 518 nm, an absorbance maximum for $Co(NH_3)_5N_3^{2+}$. A Cary 17 instrument was used. The fitting of the instrument and the technique applied was similar to that previously reported [11]. The ionic strength was maintained at 1.0 M with $NaClO_4$.

Results

The kinetic runs were performed using a high excess of Hg(II) concentration over that of Co(III) and the disappearance of $Co(NH_3)_5N_3^{2+}$ was given by

$$-d[Co(NH_3)_5N_3^{2+}]/dt = k_{obsd}[Co(NH_3)_5N_3^{2+}]$$

The Co(III) product was characterized as $Co(NH_3)_5OH_2^{3+}$ by the UV–visible spectra taken after 10 or more half lives of the reaction. The pseudo first order rate constants, k_{obsd}, observed at the different conditions employed are listed in Table I. The nature of the dependence of k_{obsd} upon mercury(II) concentration and acidity is seen in Fig. 1, where some of the entries from Table I for 80 °C are presented graphically. The data for the different experimental acidities fit the same dependence of k_{obsd} upon [Hg(II)], and though the data for 70 °C are somewhat

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TABLE I. Rate Constants for the Mercury(II) Catalyzed Aquation of the $Co(NH_3)_5N_3^{2+}$ Ion at μ = 1.0 *M* ($NaClO_4$).[a]

°C	H^+/m*M*	Hg^{2+}/m*M*	$k_{obsd} \times 10^5/s^{-1}$
80.0	300	14.2	31.2
80.0	300	16.9	36.7
80.0	300	21.1	43.6
80.0	300	25.2	51.3
80.0	300	32.0	64
80.0	300	40.1	80
80.0	300	54.9	100
80.0	300	69.8	131
80.0	300	89.3	158
80.0	300	110	189
80.0	300	129	223
80.0	300	150	251
80.0	300	169	275
80.0	300	190	312
80.0	300	211	355
80.0	300	232	375
80.0	100	12.1	27.5
80.0	100	14.8	32.1
80.0	100	20.0	42.8
80.0	100	29.8	62
80.0	100	39.3	80
80.0	100	60.7	110
80.0	100	88.1	172
80.0	100	121	222
80.0	100	159	275
80.0	100	200	335
80.0	100	236	385
80.0	100	269	420
80.0	100	300	460
80.0	30	10.6	26.9
80.0	30	15.1	38.5
80.0	30	23.6	58
80.0	30	40.1	86
80.0	30	49.5	109
80.0	30	64.8	136
80.0	30	84.9	178
80.0	30	106	209
80.0	30	130	257
80.0	30	141	272
80.0	30	151	308
80.0	30	160	312
80.0	30	172	340
70.0	300	12.0	10.0
70.0	300	14.1	12.8
70.0	300	17.7	16.5
70.0	300	24.7	23.1
70.0	300	33.2	28.8
70.0	300	45.2	38.5
70.0	300	60.1	48
70.0	300	77.8	61
70.0	300	99	75
70.0	300	127	92
70.0	300	152	105
70.0	300	170	112
70.0	300	194	128
70.0	300	212	136
70.0	300	233	149
70.0	100	34.3	25.7
70.0	100	45.8	32.1
70.0	100	64.1	44.4
70.0	100	85.8	58
70.0	100	108	70
70.0	100	130	83
70.0	100	156	96
70.0	100	180	110
70.0	100	200	122
70.0	100	220	132
70.0	100	240	136
70.0	100	260	144
70.0	100	280	154
70.0	100	300	165
70.0	30	29.8	26.0
70.0	30	40.1	33.5
70.0	30	50.4	41.3
70.0	30	69.8	58
70.0	30	90.4	72
70.0	30	108	84
70.0	30	126	96
70.0	30	140	105
70.0	30	153	116
70.0	30	165	122
70.0	30	173	128
70.0	30	175	136
60.0	100	22.9	7.2
60.0	100	50.4	14.5
60.0	100	101	25.7
60.0	100	151	37
60.0	100	195	45
60.0	100	229	48
60.0	100	300	54

[a] $[Co(NH_3)_5N_3^{2+}]$ = (2.9–3.6) × 10^{-4} *M*, λ = 518 nm.

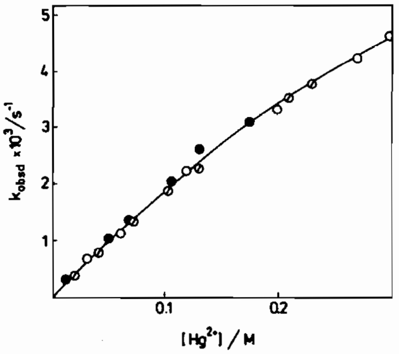

Fig. 1. Pseudo-first-order rate constants for the mercury(II) catalyzed aquation of $Co(NH_3)_5N_3^{2+}$ as a function of $Hg(ClO_4)_2$ concentration at 80 °C and $\mu = 1.0$ *M* ($NaClO_4$) in (⊘) 0.3 *M*, (○) 0.1 *M*, and (●) 0.03 *M* $HClO_4$.

more scattered, it can be concluded that there is no acidity dependence. At a particular temperature the reaction is less than first order with respect to the Hg^{2+} concentration and the function is defined by expression 1, in accordance with the two stage process described by the reaction scheme 2–3, the general form of

$$k_{obsd} = kK[Hg^{2+}]/(1 + K[Hg^{2+}]) \qquad (1)$$

$$Co(NH_3)_5N_3^{2+} + Hg^{2+} \xrightleftharpoons{K} Co(NH_3)_5N_3Hg^{4+} \qquad (2)$$

$$Co(NH_3)_5N_3Hg^{4+} \xrightarrow{k} Co(NH_3)_5OH_2^{3+} + HgN_3^{+} \qquad (3)$$

$$HgN_3^{+} \underset{\text{fast}}{\overset{H^+}{\rightleftharpoons}} Hg^{2+} + HN_3$$

which has been well established for a number of Co(III) and Cr(III) complexes having halide or pseudohalide ligands undergoing catalytic dissociation [1–5, 7, 9, 11, 12]. Plots of k_{obsd}^{-1} *vs.* $[Hg^{2+}]^{-1}$, yielding straight lines as shown in Fig. 2 and in agreement with expression 1, have been used to obtain trial values for computation of the corresponding reaction parameters. All the runs from Table I were treated simultaneously according to expression 4, using a

$$k_{obsd} = \frac{2.084 \times 10^{10} T e^{(\Delta S^{\ddagger}/R - \Delta H^{\ddagger}/RT)} [Hg(II)] e^{(\Delta S_o/R - \Delta H_o/RT)}}{1 + [Hg(II)] e^{(\Delta S_o/R - \Delta H_o/RT)}} \qquad (4)$$

non-linear least-squares computer program. The values obtained are $\Delta S_o = -15.5 \pm 7.2$ cal mol^{-1} K^{-1} and $\Delta H_o = -5.8 \pm 2.5$ kcal mol^{-1} for the changes of the standard entropy and enthalpy of the equilibrium reaction 2, and $\Delta S^{\ddagger} = 9.8 \pm 6.0$ cal mol^{-1} K^{-1} and $\Delta H^{\ddagger} = 27.2 \pm 2.1$ kcal mol^{-1} for the activation entropy and enthalpy of the aquation reaction 3. The uncertainties quoted are standard deviations. The corresponding constants calculated for 25 °C have the values $K = 7.3$ *M*$^{-1}$ for the equilibrium reaction 2 and $k = 1.0 \times 10^{-5}$ s^{-1} for the aquation reaction 3.

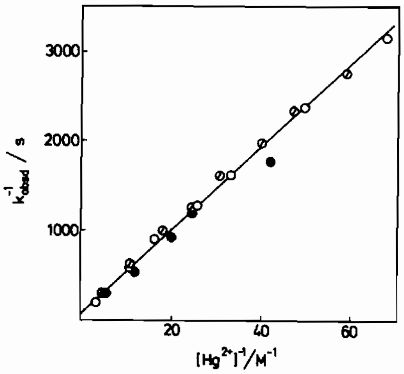

Fig. 2. Plot of k_{obsd}^{-1} as a function of $[Hg(II)]^{-1}$ for the mercury(II) catalyzed aquation of $Co(NH_3)_5N_3^{2+}$ at 80 °C and $\mu = 1.0$ *M* ($NaClO_4$) in (⊘) 0.3 *M*, (○) 0.1 *M*, and (●) 0.03 *M* $HClO_4$.

Discussion

It appears that there have been no quantitative data on the stability of binuclear complexes in which azide ligand acts as a bridge between mercury(II) and an inert transition metal center. In an attempt to induce the aquation of an azide ligand from *cis*-$Co(en)_2(N_3)^{+}$ by the addition of excess Hg(II) Loelinger and Taube obtained a qualitative evidence for the formation of a relatively stable mercury(II) adduct [6]. In a kinetic study of the catalysed aquation of $Cr(H_2O)_5N_3^{2+}$ the reaction was found to be strictly first order in [Hg(II)] over the range of concentrations used, indicating a value <7 *M*$^{-1}$ at 25 °C for the stability constant of the mercury(II) adduct [13,*]. The stability constant $K = 7.3$ *M*$^{-1}$ of the mercury(II) adduct with $Co(NH_3)_5N_3^{2+}$ determined by this work is compared with other relevant data in Table II. This value is six orders of magnitude smaller than the stability constant for mercury(II) binding to the uncoordinated azide ligand. Thus, stability constants for Hg(II) binding to CN^-, N_3^-, or SCN^- ligand, when the nitrogen atom of the ligands is coordinated to the $Cr(H_2O)_5^{3+}$ or $Co(NH_3)_5^{3+}$ moiety, are reduced by a factor of 10^7 to 10^4 as compared to the stability constants for the binding to the uncoordinated ligand. Also, from the three pairs of data in Table II it is seen that the stability of the mercury(II) bond in the binuclear complexes bridged by N_3^- or SCN^- (there is no data for CN^-) is higher for the $Co(NH_3)_5^{3+}$ than for the $Cr(H_2O)_5^{3+}$ moiety, an observation which has been previously discussed for the isothiocyanate ligand [9].

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[*] Estimated from the upper limit of K at 60 °C for the acid-independent reaction and assuming $\Delta H_o = -5$ kcal mol^{-1}.

TABLE II. Stability Constants of Mercury(II) Complexes Formed with Some Coordinated of Free Pseudo-Halide Ligands at 25 °C and $\mu = 1.0\,M$.

Coordinated or Free Ligand	K/M^{-1}	Coordinated or Free Ligand	K/M^{-1}
$Co(NH_3)_5N_3$	7.3[a]	$Cr(H_2O)_5N_3^{2+}$	<7[b]
N_3^-	1.4×10^7 [c]	–	
$Co(NH_3)_5SCN^{2+}$	1.2[d]	$Cr(H_2O)_5SCN^{2+}$	<1[e]
$Co(NH_3)_5NCS^{2+}$	9.8×10^4 [f]	$Cr(H_2O)_5NCS^{2+}$	1.7×10^4 [g]
SCN^-	1.2×10^9 [h]	–	
CN^-	1×10^{18} [i]	$Cr(H_2O)_5NC^{2+}$	6.5×10^{10} [d]

[a] This work. [b] Ref. 13. [c] At 28 °C and $\mu = 0.25\,M$; T. R. Musgrave and R. H. Keller, *Inorg. Chem., 4,* 1793 (1965). [d] Ref. 11. [e] Ref. 7. [f] Ref. 10; $\mu = 0.1\,M$. [g] Ref. 9. [h] L. Ciavatta and M. Grimaldi, *Inorg. Chim. Acta, 4,* 312 (1970). [i] G. Aderegg, *Helv. Chim. Acta, 40,* 1022 (1957). [j] S. N. Frank and F. C. Anson, *Inorg. Chem., 11,* 2938 (1972).

TABLE III. Rate Constants for the Aquation or Aquation and Isomerisation of the Pseudo-Halide Ligand From Some Co(III) Complexes at 25 °C and $\mu = 1.0\,M$.

Complex I	k/s^{-1}	Complex II	k/s^{-1}	Ratio of Constants I/II
A $Co(NH_3)_5N_3Hg^{4+}$	1×10^{-5} [a]	$Co(NH_3)_5N_3^{2+}$	2×10^{-9} [b]	5×10^3
B $Co(NH_3)_5NCSHg^{4+}$	$<10^{-6}$ [c]	$Co(NH_3)_5NCS^{2+}$	4×10^{-10} [d]	$<2.5 \times 10^3$
C $Co(NH_3)_5SCNHg^{4+}$	0.23[c]	$Co(NH_3)_5SCN^{2+}$	8×10^{-7} [e]	2.9×10^5

[a] This work. [b] Ref. 14. [c] Ref. 11. [d] D. L. Gay and G. C. Lalor, *J. Chem. Soc. A*, 1179 (1966). [e] D. A. Buckingham, J. J. Creaser, and A. M. Sargeson, *Inorg. Chem., 9,* 655 (1970).

TABLE IV. Equilibrium and Activation Parameters for the $Co(NH_3)_5N_3Hg^{4+}$ and $Co(NH_3)_5(SCN)Hg^{4+}$ Complexes at 25 °C and $\mu = 1.0\,M$.

Complex	ΔS_o/cal $mol^{-1}\,K^{-1}$ [a]	ΔH_o/kcal mol^{-1} [a]	$\Delta S^{\ddagger}$/cal $mol^{-1}\,K^{-1}$ [b]	$\Delta H^{\ddagger}$/kcal mol^{-1} [b]
[c] $Co(NH_3)_5N_3Hg^{4+}$	−15.5	−5.8	9.8	27.2
[d] $Co(NH_3)_5(SCN)Hg^{4+}$	−17	−5.2	10	21.4

[a] Reaction $Co(NH_3)_5X^{2+} + Hg^{2+} \rightleftarrows Co(NH_3)_5XHg^{4+}$. [b] Rupture of Co(III)–nitrogen or Co(III)–sulfur bond. [c] This work. [d] Ref. 11.

The value of the stability constant for $Co(NH_3)_5N_3Hg^{4+}$ ($K = 7.3\,M^{-1}$) lends support to the conclusion [11] that the soft mercury(II) adds to the soft, terminal, uncoordinated sulfur atom in the isothiocyanato Co(III) complex $Co(NH_3)_5NCS^{2+}$ ($K = 9.8 \times 10^4\,M^{-1}$). The value is, however, of a similar magnitude as the stability constant for the mercury(II) addition to the thiocyanato Co(III) complex $Co(NH_3)_5SCN^{2+}$ ($K = 1.2\,M^{-1}$). It was, thus, reasonable to assume previously [11] that the magnitude of the constant $K = 1.2\,M^{-1}$ did not by itself offer an indication on the mode of mercury(II) binding to the thiocyanato ligand in $Co(NH_3)_5SCN^{2+}$. The value $K = 1.2\,M^{-1}$ complies with both possibilities of mercury(II) binding to either hard, terminal, uncoordinated nitrogen atom or to the soft but coordinated sulfur atom in $Co(NH_3)_5SCN^{2+}$, which is here positioned in a less favorable steric and electronic surrounding for Hg(II) binding than in $Co(NH_3)_5NCS^{2+}$.

The kinetic effect of mercury(II) bound to a pseudo-halide ligand on the rupture of the bond between the ligand and the Co(III) center is seen from the data collected in Table III. Within the binuclear reactant *A* and *B* mercury(II) is presumably bound to the terminal atom of the pseudo-halide ligand and its kinetic effect on the rupture of the

Co(III)–nitrogen bond expressed as the ratio I/II is of a similar extent for *A* and *B*. A higher kinetic effect of mercury(II) within the binuclear complex *C* on the rupture of the Co(III)–sulfur bond has been previously discussed [11].

Table IV contains the values of the equilibrium parameters for binding of mercury(II) to $Co(NH_3)_5N_3^{2+}$ and $Co(NH_3)_5SCN^{2+}$ and the activation parameters for the rupture of Co(III)–nitrogen and Co(III)–sulfur bonds in the respective binuclear complexes. Both ΔS_0 and ΔH_0 values for the formation of $Co(NH_3)_5N_3Hg^{4+}$ and $Co(NH_3)_5(SCN)Hg^{4+}$ are very similar. A pertinent question is whether this similarity indicates a mechanism in which mercury(II) adds to the same kind of atom, *i.e.* to the terminal nitrogen of the –SCN and –NNN ligand. However, the error limits on the values of ΔS_0 and ΔH_0 are too large to allow such differentiation of mechanisms.

The mercury(II) catalyzed aquation of $Co(NH_3)_5N_3^{2+}$ was not found to be acidity dependent, in conformity with the low acidity of the aquo ligands coordinated to Hg^{2+} [15]. A marked acidity dependence of the analogous reaction of $Cr(H_2O)_5N_3^{2+}$ previously observed [13] originated obviously from a different reactivity of the hydrolytic species derived from the Cr(III) complex.

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