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Contribution from Inorganic Chemistry 1, Chemical Center, University of Lund, S-221 00 Lund, Sweden,
and Inorganic Chemistry, Chalmers University of Technology, S-412 96 Gothenburg, Sweden

Mechanism for Oxidation of Tetracyanoplatinate(II) by Gold(III) Complexes[1]

Lise Drougge[2a] and Lars I. Elding*[2b]

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Oxidation of $Pt(CN)_4^{2-}$ by $AuCl_4^-$, $AuCl_3OH_2$, and $AuCl_3OH^-$ has been studied at 25.0 °C and 1.00 M ionic strength by use of stopped-flow and conventional spectrophotometry. Oxidation by $AuCl_3OH_2$ is predominant in ca. 10^{-5} M solutions of gold with $[Cl^-] \le 2 \times 10^{-4}$ M and pH 0. This is a two-step reaction, in which an intermediate is formed with the rate law rate = $((9.3 \pm 0.2) \times 10^2\ M^{-1}\ s^{-1})[Pt(CN)_4^{2-}][AuCl_3OH_2]$. In a slow subsequent reaction, which is accelerated by light, Au(0), and free chloride, the intermediate decomposes into *trans*-$Pt(CN)_4ClOH_2^-$ and $AuCl_2^-$. Under certain conditions the displacement of the equilibrium $AuCl_4^- + H_2O \rightleftarrows AuCl_3OH_2 + Cl^-$ becomes rate-determining for the formation of the intermediate. Such experiments give forward and reverse rate constants as $(1.6 \pm 0.2) \times 10^{-2}\ s^{-1}$ and $(1.0 \pm 0.3) \times 10^3\ M^{-1}\ s^{-1}$. Oxidation with $AuCl_4^-$ exclusively has been studied in ca. 10^{-5} M solutions of gold with $[Cl^-] \ge 0.25$ M and pH ca. 0. The reaction products *trans*-$Pt(CN)_4Cl_2^{2-}$ and $AuCl_2^-$ are formed directly without an observable intermediate, with the rate law rate = $(9.4 \pm 0.2\ s^{-1})[Pt(CN)_4^{2-}] \times [Cl^-][AuCl_4^-]$. Experiments with $[Cl^-] \ge 0.25$ M and pH ca. 5 give parallel oxidation with $AuCl_4^-$ and $AuCl_3OH^-$. These indicate that $AuCl_3OH^-$ also oxidizes $Pt(CN)_4^{2-}$ in a process in which $Pt(CN)_4Cl_2^-$ and $AuCl_2^-$ are formed with a rate law of the same form as for reaction with $AuCl_4^-$, and with a very similar rate constant also, ca. $10 \pm 2\ M^{-2}\ s^{-1}$. Those reactions take place via chloride-bridged inner-sphere redox mechanisms. The bridge is most likely formed by chloride ligands of gold(III). The intermediate observed for reaction with $AuCl_3OH_2$ has probably the structure $H_2O \cdots Pt(CN)_4{-}Cl{-}AuCl_2 \cdots OH_2^{2-}$. The first-order chloride dependence observed for oxidation with $AuCl_4^-$ and $AuCl_3OH^-$ can be described as a chloride assistance of the redox reaction with intermediates of the type $Cl \cdots Pt(CN)_4{-}Cl{-}AuCl_2 \cdots X^{4-}$, X = Cl^-, OH^-.

Introduction

Oxidative addition of Cl_2, HOCl, and OCl^- to $Pt(CN)_4^{2-}$ has been studied recently.[3] This paper describes inner-sphere redox reactions between $Pt(CN)_4^{2-}$ and $AuCl_4^-$, $AuCl_3OH_2$, and $AuCl_3OH^-$. There are mechanistic similarities between those reactions and the platinum(II/IV) redox reactions[4] and the halide-accelerated reactions reviewed in a previous report.[5] Only two studies on oxidation of platinum(II) complexes by gold(III) (in both cases as $AuCl_4^-$) seem to have been published so far.[6,7]

The present system can be described by the reaction scheme of Figure 1. The concentration of free chloride and pH determines which of the three parallel reactions is predominant. In reaction with $AuCl_3OH_2$, a stable intermediate can be observed, eq 1a. It decomposes in a slow subsequent process, eq 1b. In some cases

$$Pt(CN)_4^{2-} + AuCl_3OH_2 \rightarrow \text{intermediate} \tag{1a}$$

$$\text{intermediate} \rightarrow \textit{trans}\text{-}Pt(CN)_4ClOH_2^- + AuCl_2^- \tag{1b}$$

the equilibrium displacement between $AuCl_4^-$ and $AuCl_3OH_2$ described by the rate constants k_1 and k_{-1} of Figure 1 becomes rate-determining for reaction 1a.

Oxidation by $AuCl_4^-$ and $AuCl_3OH^-$ is predominant for $[Cl^-] > 0.25$ M and $0 < pH < 5$ where practically no $AuCl_3OH_2$ is present. Reactions 2 and 3 occur without observable intermediates and are both accelerated by free chloride.

$$Pt(CN)_4^{2-} + AuCl_4^- \xrightarrow{Cl^-} \textit{trans}\text{-}Pt(CN)_4Cl_2^{2-} + AuCl_2^- \tag{2}$$

$$\begin{aligned} &Pt(CN)_4^{2-} + AuCl_3OH^- + Cl^- \rightarrow \\ &\qquad \textit{trans}\text{-}Pt(CN)_4Cl_2^{2-} + AuCl_2^- + OH^- \end{aligned} \tag{3}$$

Experimental Section

Chemicals and Solutions. Potassium tetracyanoplatinate(II) trihydrate (Johnson and Matthey), hydrogen tetrachloroaurate(III) trihydrate (Degussa), sodium chloride and hydrochloric acid (Merck p.a.), and perchloric acid (Baker p.a.) were used without further purification. Sodium perchlorate (Baker p.a.) was recrystallized once. Water was doubly distilled from quartz. The ionic strength was 1.00 M with sodium perchlorate as supporting electrolyte in all experiments where not otherwise stated. The distribution of gold(III) among $AuCl_4^-$, $AuCl_3OH_2$, and $AuCl_3OH^-$ for the various pH and chloride concentrations used was calculated by use of $pK_a = 0.63$[8] and $K_1 = k_1/k_{-1} = 1.6 \times 10^{-5}$ M from Table III.

Apparatus. UV-visible spectra were recorded by use of a Beckman 25 spectrophotometer and Hellma Quartz Suprasil cells. Rapid reactions were followed by a modified Durrum-Gibson stopped-flow instrument and slower ones by the use of a Zeiss Quartz PMQ II spectrophotometer with a recorder. The temperature was 25.0 ± 0.1 °C in all experiments. Rate constants given in the tables are average values from three or more measurements and were calculated by a least-squares program directly from the transmittance or absorbance vs. time curves (±ca. 5%).

Spectra. Both $Pt(CN)_4^{2-}$ and the solutions containing mixtures of the gold(III) complexes have high molar absorptivities in the interval 230-350 nm, as compared to the final reaction products *trans*-$Pt(CN)_4Cl_2^{2-}$ and *trans*-$Pt(CN)_4ClOH_2^-$. The reaction product $AuCl_2^-$ is transparent in the wavelength interval studied. Figure 2 shows spectral changes with time.

Kinetics of Reaction 1. Formation of an intermediate in reaction 1a was followed under first-order conditions (with the platinum complex in excess) by stopped-flow techniques, at 312 nm, where $Pt(CN)_4^{2-}$ is transparent and the absorbance decreases; cf. Figure 2c,d. In all experiments, pH = 0. The total concentration of gold, C_{Au}, was low (1×10^{-5} or 2×10^{-5} M). Table I reviews those experiments. Decomposition of the intermediate according to (1b) is accelerated by ordinary light, Au(0), and chloride. In all experiments in Table I, decomposition was negligible; i.e., the intermediate was stable on the time scale of the kinetics of its formation.

(i) Determination of k_2. In the solutions without added extra chloride, the distribution of gold between the three complexes varies with C_{Au}; cf. footnotes *b*-*e* of Table I. Since the acid hydrolysis of $AuCl_4^-$ is slow for these experimental conditions (vide infra), the distribution is the same before and after mixing in the kinetic runs. These were started by mixing 2.0×10^{-5} or 4.0×10^{-5} M stock solutions of gold in 1.00 M $HClO_4$ with equal volumes of $Pt(CN)_4^{2-}$ solutions (0.40-1.00 mM) in 1.00 M $HClO_4$ directly in the stopped-flow instrument. Reaction with $AuCl_3OH_2$ (in rapid equilibrium with $AuCl_3OH^-$) and formation of the intermediate of reaction 1a was observed as a decrease of absorbance. Direct oxidation by both $AuCl_4^-$ and $AuCl_3OH^-$ is very slow (vide infra) and can be neglected for the low concentrations of chloride present. Since acid hydrolysis of $AuCl_4^-$ to $AuCl_3OH_2$ is also slow, the $AuCl_4^-$ present at zero time does not react on the time scale of those experiments, but equilibrium displacement can be observed as a slow subsequent process.

(ii) Determination of $k_1 + k_{-1}[Cl^-]$. The solutions with added chloride (1.00×10^{-4} or 2.00×10^{-4} M) contain mainly $AuCl_4^-$ (cf. Table I). For $[Pt(CN)_4^{2-}] \ge 2 \times 10^{-4}$ M and 4×10^{-4} M, respectively, oxidation of $Pt(CN)_4^{2-}$ by $AuCl_3OH_2$ is fast compared to the displacement of the equilibrium between $AuCl_4^-$ and $AuCl_3OH_2$. After a rapid initial process

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(1) This work is part of a Ph.D. thesis by L.D.

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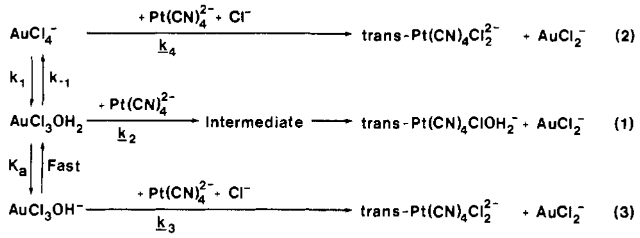

Figure 1. Reaction scheme. Redox reactions are assumed to take place via chloride-bridged inner-sphere mechanisms.

Table I. Observed Rate Constants for Oxidation of $Pt(CN)_4^{2-}$ by $AuCl_3OH_2$, Reaction 1[a]

$10^4[Cl^-]_{added}$/M	$10^4[Pt(CN)_4^{2-}]$/M	10^5C_{Au}/M	$10k_{exptl}$/s^{-1}
0	2.00	1.0[b]	1.48
	2.50		1.74
	3.0		2.18
	3.3	2.0[c]	2.54
	4.0		2.95
	5.0		3.7
1.00[d]	1.00	1.0	0.87
	2.00		1.15
	2.10		1.07
	2.60		1.12
	3.1		1.20
	3.7		0.91
	4.3		0.96
	5.7		1.18
2.00[e]	1.00	1.0	0.72
	2.00		1.47
	2.50		1.92
	4.0		2.08
	5.0		2.03
	6.0		2.10
	8.0		2.25

[a] 1.00 M $HClO_4$ medium, 25.0 °C, 312 nm. [b-e] The distribution of gold between various complexes calculated from $pK_a = 0.63$[8] and $K_1 = 1.6 \times 10^{-5}$ M from Table III (in percent), for $AuCl_4^-$, $AuCl_3OH_2$, and $AuCl_3OH^-$, respectively: (*b*) 38, 50, 12; (*c*) 50, 40, 10; (*d*) 84, 13, 3; (*e*) 91, 7, 2.

in which $AuCl_3OH_2$, originally present in equilibrium with $AuCl_3OH^-$, reacts with $Pt(CN)_4^{2-}$ to its steady-state concentration, the reaction $AuCl_4^- \rightleftarrows AuCl_3OH_2$ can be observed as a subsequent process, independent of the platinum concentration.

(iii) Determination of k_1. The following rate constants were observed in a series of experiments at 312 nm, in which 2.0–6.0 mM $Pt(CN)_4^{2-}$ in 1.00 M $HClO_4$ was mixed with 0.1 mM gold solution in 1.00 M $HClO_4$, without any extra chloride added. $10^2k_{exptl}/s^{-1}$: 1.43, 1.82, 1.86, 1.30, 1.67, 1.40, 1.29, 1.77. These experiments give k_1 directly.

Kinetics of Reactions 2 and 3. The kinetics of reactions 2 and 3 were followed by conventional spectrophotometry under pseudo-first-order conditions with excess $Pt(CN)_4^{2-}$, 0.25 M < $[Cl^-]$ < 1.00 M, and 0 < pH < ca. 5. The disappearance of gold(III) complexes was observed as an absorbance decrease at 312 nm. For $[H^+]$ = 0.50 and 0.75 M, all gold(III) was present as $AuCl_4^-$, but in the 1.00 M $Na(ClO_4^-, Cl^-)$ solution at pH ca. 5 (determined by the protolysis of $AuCl_3OH_2$), between 44 and 57% of the gold(III) was present as $AuCl_3OH^-$ at zero time. The concentration of $AuCl_3OH_2$ was negligible in all cases. Table II summarizes those experiments.

Results

Spectral Changes. Figure 2 shows spectral changes observed when equimolar concentrations of $Pt(CN)_4^{2-}$ and gold(III) are mixed in solutions with different chloride concentrations and pH. In the experiments of Figure 2a,b with $[Cl^-]$ = 1.00 M, there are no isosbestic points, and the product *trans*-$Pt(CN)_4Cl_2^{2-}$ is obtained directly without any observable intermediate. Reaction is slower in the experiment of Figure 2a (74% $AuCl_4^-$ and 26% $AuCl_3OH^-$ at zero time) than in that of Figure 2b (100% $AuCl_4^-$). Conversion between $AuCl_4^-$ and $AuCl_3OH^-$ is rapid on the time scale of those experiments. Oxidation with $AuCl_4^-$ is faster than that with $AuCl_3OH^-$ in this case (vide infra).

Table II. Observed Rate Constants for Oxidation of $Pt(CN)_4^{2-}$ by $AuCl_4^-$ and $AuCl_3OH^-$, Reactions 2 and 3

$10^3 \times [Pt(CN)_4^{2-}]$/M	10^5C_{Au}/M	$[Cl^-]$/M	$[H^+]_{added}$/M	10^3k_{exptl}/s^{-1}
0.40	2.0	0.25	0[a]	0.96
0.40		0.50		2.22
0.40		0.75		3.6
0.40		1.00		4.5
0.20	2.0	0.50	0.50[b]	1.08
0.40		0.50		2.19
0.40		0.75		3.5
0.40		0.75	0.75	3.4
0.40	1.00	0.50	4.6	
0.50	0.50		2.46	
1.00		0.50		5.2
2.00		0.50		9.3
2.00		0.25		5.1
2.50	5.0	0.50		12.7
3.00		0.50		13.5
3.20		0.50		14.5
4.00		0.50		18.2
5.00		0.50		23.5

[a] 1.00 M $NaClO_4$; pH varies between ca. 5 and 5.2. [b] 1.00 M $(Na^+, H^+)(ClO_4^-, Cl^-)$ medium, 25.0 °C, 312 nm.

In another experiment $Pt(CN)_4^{2-}$ was allowed to react with a gold(III) solution in 1.00 M $NaClO_4$ without added chloride, where practically all gold is present as $AuCl_3OH^-$. The redox reaction was observed to be extremely slow.

Parts c and d of Figure 2 show spectral changes in solutions with pH = 0 and low concentrations of chloride. There are two isosbestic points at 263 and 300 nm, and the product of reaction has a spectrum different from that of the sum of the final Pt(IV) and Au(I) products. There is an increase of absorbance between the two isosbestic points.[9]

In those solutions with low chloride concentration, redox reaction with $AuCl_4^-$ and $AuCl_3OH^-$ is much slower than that with $AuCl_3OH_2$ and can be neglected, whereas transformation between $AuCl_3OH_2$ and the other two gold(III) complexes is still fast on the time scale of the experiment. Reaction is faster in the experiment of Figure 2c (40% $AuCl_3OH_2$) than in that of Figure 2d (7%).

The reacting solutions contain three absorbing species, viz. the two reactants $Pt(CN)_4^{2-}$ and Au(III) (which remain in a 1:1 molar ratio during the course of the second-order reaction) and the product, which is the intermediate of reaction 1. At the isosbestic point at 263 nm, the absorbance of the sum of the reactants equals that of the reaction product. At 300 nm, $Pt(CN)_4^{2-}$ is transparent, and the absorbance of the disappearing gold(III) equilibrium mixture equals that of the reaction product.

The intermediate formed in those two experiments is characterized by spectrum 5 of Figure 2c and spectrum 4 of Figure 2d. These spectra remain constant for 48 h when the solutions are protected from illumination. Exposure to light causes spectral changes corresponding to formation of Pt(IV) and Au(I) according to eq 1b (dashed curves of Figure 2). Similarly, addition of chloride as the sodium salt accelerates the decomposition of the intermediate, which, however, is still slow with a half-life of several hours for 1.00 M chloride.

Kinetics of Reaction 1. (i) Calculation of k_2. In the solutions without extra chloride added and with low total concentrations of gold (1×10^{-5} to 2×10^{-5} M), the rate constant for displacement of the hydrolysis equilibrium of $AuCl_4^-$, $(k_1 + k_{-1}[Cl^-]) \approx k_1 = 1.6 \times 10^{-2}\ s^{-1}$, is small compared to the observed rate constants of Table I.

Consequently, the concentrations of $AuCl_4^-$ and Cl^- remain approximately constant during the course of reaction 1a. The rate of formation of the intermediate is given by eq 4. The rate is

$$\text{rate} = k_2[Pt(CN)_4^{2-}][AuCl_3OH_2] \qquad (4)$$

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[9] A slight deviation of the final spectra from the isosbestic points is caused by a much slower subsequent reaction (which is not the decomposition of the intermediate).

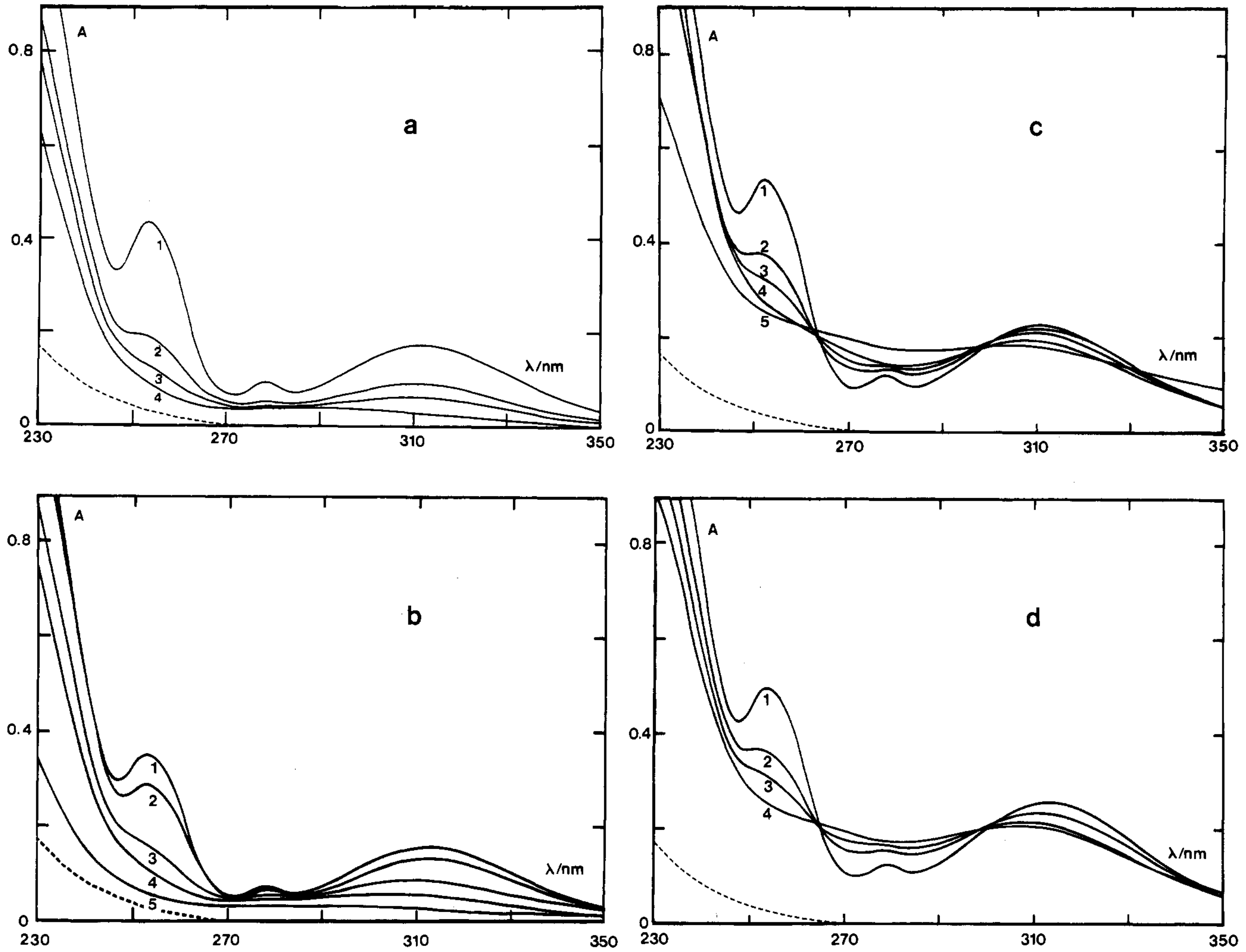

Figure 2. Spectral changes for second-order reactions between $Pt(CN)_4^{2-}$ and gold(III) complexes ($C_{Pt} = C_{Au} = 4.0 \times 10^{-5}$ M, $d = 1$ cm) for various pH and chloride concentrations: (a) 1.00 M NaCl (74% $AuCl_4^-$ and 26% $AuCl_3OH^-$ at zero time), 15 min (1), 2 h (2), 4 h (3), and 24 h (4) after mixing; (b) 1.00 M HCl (100% $AuCl_4^-$), 10 min (1), 30 min (2), 2.5 h (3), 6 h (4), and 20 h (5) after mixing; (c) 1.00 M $HClO_4$ (50% $AuCl_4^-$, 40% $AuCl_3OH_2$, 10% $AuCl_3OH^-$ at zero time), ca. 30 s (1), 10 min (2), 40 min (3), 3 h (4), and 18 h (5) after mixing;[9] (d) 1.00 M $HClO_4$ with $[Cl^-]_{added} = 2.0 \times 10^{-4}$ M (91% $AuCl_4^-$, 7% $AuCl_3OH_2$, 2% $AuCl_3OH^-$), ca. 30 s (1), 2.5 h (2), 5 h (3), and 24 h (4) after mixing.[9] Dashed curves indicate calculated equilibrium spectra. The product $AuCl_2^-$ is transparent in the wavelength interval.

independent of $[Cl^-]$, which varies with C_{Au}; cf. Table I. If only $AuCl_3OH_2$ is reactive and is in rapid equilibrium with its conjugate base, (cf. Figure 1), we arrive at eq 5, where $C_{Au}' = [AuCl_3OH_2]$

$$\text{rate} = k_2[Pt(CN)_4^{2-}]\frac{[H^+]}{K_a + [H^+]}C_{Au}' \qquad (5)$$

$+ [AuCl_3OH^-]$, $[H^+] = 1.00$ M, and $pK_a = 0.63$.[8] This gives the pseudo-first-order rate constant of eq 6. In agreement with eq

$$k_{exptl} = 0.81k_2[Pt(CN)_4^{2-}] \qquad (6)$$

6, the plot of k_{exptl} vs. platinum concentration for these experiments is linear. The slope is $(7.5 \pm 0.2) \times 10^2$ M^{-1} s^{-1}, which gives the value of k_2 in Table III.

(ii) Calculation of k_{-1} and K_1. In the solutions buffered with chloride (1.00×10^{-4} or 2.00×10^{-4} M), $AuCl_4^-$ is the predominant gold complex at zero time. When the condition of (7) is

$$k_1 + k_{-1}[Cl^-] < k_2[Pt(CN)_4^{2-}] \qquad (7)$$

fulfilled, the rate of displacement of the equilibrium between $AuCl_4^-$ and $AuCl_3OH_2$ becomes rate-determining for the overall redox process according to the scheme of Figure 1. This is true for the entries of Table I with $[Pt(CN)_4^{2-}] \geq 2 \times 10^{-4}$ M, $[Cl^-] = 1 \times 10^{-4}$ M and $[Pt(CN)_4^{2-}] \geq 4 \times 10^{-4}$ M, $[Cl^-] = 2 \times 10^{-4}$ M. Consequently, the observed rate constant becomes independent of $[Pt(CN)_4^{2-}]$ in this region of concentration and eq 8 is valid.

$$k_{exptl} = k_1 + k_{-1}[Cl^-] \qquad (8)$$

These experiments give $k_1 + k_{-1}[Cl^-] = (1.1 \pm 0.3) \times 10^{-1}$ s^{-1} for 1.00×10^{-4} M chloride and $(2.1 \pm 0.3) \times 10^{-1}$ s^{-1} for 2.00×10^{-4} M chloride. Combination with the value of k_1 determined separately (Table III) gives the rate constant k_{-1} and the equilibrium constant $K_1 = k_1/k_{-1}$ recorded in Table III. The agreement between these values and those reported earlier[8,10] is relatively close if differences in experimental method and ionic media are taken into account.

(iii) Calculation of k_1. In the solutions with no extra chloride added, low concentration of gold (0.02 mM), and relatively large platinum concentrations (1.0–3.0 mM), conditions 9 and 10 are valid. When these are fulfilled, the rate-determining reaction

$$d[AuCl_3OH_2]/dt = 0 \qquad (9)$$

$$k_2[Pt(CN)_4^{2-}] \gg k_{-1}[Cl^-] \qquad (10)$$

is the conversion of $AuCl_4^-$ (which amounts to ca. $0.5C_{Au}$ at zero time) to $AuCl_3OH_2$ with the rate constant of eq 11. The platinum

$$k_{exptl} = k_1 \qquad (11)$$

complex acts as a scavenger for $AuCl_3OH_2$ in these experiments, which give directly the value of k_1 in Table III.

Kinetics of Reactions 2 and 3. The experiments of Table II give the rate law of eq 12.

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$$\text{rate} = k'[\text{Cl}^-][\text{Pt(CN)}_4^{2-}]C_{\text{Au}} \qquad (12)$$

The reaction is first-order with respect to chloride, contrary to the formation of the intermediate in the reaction between $AuCl_3OH_2$ and $Pt(CN)_4^{2-}$; cf. eq 4. For the high concentrations of chloride used, the equilibrium between the gold(III) complexes is established rapidly on the time scale of the experiments, and their concentrations are defined by

$$[\text{AuCl}_4^-] = [\text{H}^+][\text{Cl}^-]C_{\text{Au}}/D \qquad (13a)$$

$$[\text{AuCl}_3\text{OH}_2] = [\text{H}^+]K_1C_{\text{Au}}/D \qquad (13b)$$

$$[\text{AuCl}_3\text{OH}^-] = K_aK_1C_{\text{Au}}/D \qquad (13c)$$

where the denominator is

$$D = [\text{H}^+][\text{Cl}^-] + [\text{H}^+]K_1 + K_aK_1 \qquad (13d)$$

(i) For the solutions with $[H^+] = 0.50$ and 0.75 M and $[Cl^-] = 0.5$–1.0 M (cf. Table II), the two last terms of eq 13d are negligible compared to $[H^+][Cl^-]$, and practically all gold is present as $AuCl_4^-$. According to the rate law of eq 12, $AuCl_4^-$ is the reactant in these cases. Reaction via $AuCl_3OH_2$ or $AuCl_3OH^-$ can be excluded. Under the present conditions, reactions with these complexes should result in rate expressions with factors $[Cl^-]^{-1}$ and $[H^+]^{-1}[Cl^-]^{-1}$, respectively, which is not in accordance with the experimental rate law, eq 12. The first-order chloride dependence is discussed below. These experiments give the value of k_4 in Table III.

(ii) The experiments without added strong acid (four first entries of Table II) give observed rate constants very similar to those measured in strongly acidic solution for comparable concentrations of chloride and platinum. They also satisfy the rate equation (12). In these experiments the pH of ca. 5 is determined by the protolysis of $AuCl_3OH_2$ and varies with C_{Au} during the course of reaction. $[H^+]K_1$ of eq 13 is negligible in these cases, and the gold present is $AuCl_4^-$ and $AuCl_3OH^-$. The form of the rate law of eq 12 rules out reaction via $AuCl_3OH_2$ in steady state with the other two complexes. Reaction via $AuCl_4^-$ exclusively can also be excluded, since the observed rate constants equal those for the experiments with 100% $AuCl_4^-$, in spite of the fact that here only between 43 and 56% of the gold is present as $AuCl_4^-$ at the start of the kinetics (the percentage decreases during the course of reaction).

The third possibility, two parallel reactions via $AuCl_4^-$ and $AuCl_3OH^-$, gives a factor in the rate law of the form (14). For

$$F = \frac{k_4[\text{H}^+][\text{Cl}^-] + k_3K_aK_1}{[\text{H}^+][\text{Cl}^-] + K_aK_1} \qquad (14)$$

the experimental conditions used, the two terms in the denominator of (14) are of similar magnitude (ca. 10^{-5} to 4×10^{-6} M^2). Since these four experiments also satisfy the simple rate law of eq 12 and there is no $[H^+]$ or $[Cl^-]$ dependence as indicated by (14), it can be concluded that

$$k' = k_4 \approx k_3 \qquad (15)$$

Thus, $AuCl_4^-$ and $AuCl_3OH^-$ oxidize $Pt(CN)_4^{2-}$ with very similar rates and with a rate law of the same form. A first-order chloride dependence for the $Pt(CN)_4^{2-}$–$AuCl_3OH^-$ reaction is further supported by the observation that the reaction is extremely slow in the absence of chloride (spectral changes, above). These four experiments give an approximate value of k_3; cf. Table III.

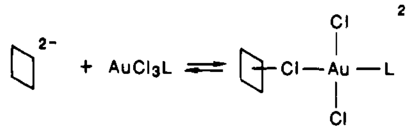
Discussion

$AuCl_4^-$ has previously been used to oxidize some platinum(II) complexes in acetonitrile.[6] The rate laws contain one term that has the same form as the present eq 12 and corresponds to an inner-sphere chloride-bridged redox reaction. In the present cases, formation of chloroplatinum(IV) complexes as final reaction products indicates bridged electron transfer via chloride also.

The chloride bridge might be formed either by one of the ligands of the gold(III) complexes or by a chloride from the solution. Since reaction 1a takes place readily in solutions with very low concentration of free chloride, it is likely that the bridge is formed in a direct reaction between the two complexes, according to eq 16, where L = H_2O. This is one of the alternatives discussed earlier by Peloso[6] for oxidation with $AuCl_4^-$.

Table III. Rate and Equilibrium Constants for the Reactions Defined by Figure 1 at 25.0 °C

constant		μ/M	ref
k_1/s^{-1}	$(1.6 \pm 0.2) \times 10^{-2}$	1.00	this work
	2.2×10^{-2}	0.8	8
$k_{-1}/M^{-1}\ s^{-1}$	$(1.0 \pm 0.3) \times 10^{3}$	1.00	this work
	2.32×10^{3}	2	10
$k_2/M^{-1}\ s^{-1}$	$(9.3 \pm 0.2) \times 10^{2}$	1.00	this work
$k_3/M^{-2}\ s^{-1}$	$\sim 10 \pm 2$	1.00	this work
$k_4/M^{-2}\ s^{-1}$	9.4 ± 0.2	1.00	this work
$K_1 = k_1/k_{-1}$/M	$(1.6 \pm 0.6) \times 10^{-5}$	1.00	this work
	9.5×10^{-6}	0.8, 2	10



(16)

If a bridged complex between $AuCl_3OH_2$ and $Pt(CN)_4^{2-}$ can be readily formed in this manner, it is very likely that $AuCl_4^-$ and $AuCl_3OH^-$ also form bridged complexes with $Pt(CN)_4^{2-}$ via their chloride ligands, in spite of the fact that these reactions are first order with respect to chloride according to eq 12 and that oxidation of $Pt(CN)_4^{2-}$ by $AuCl_3OH^-$ in the absence of added chloride was observed to be extremely slow.

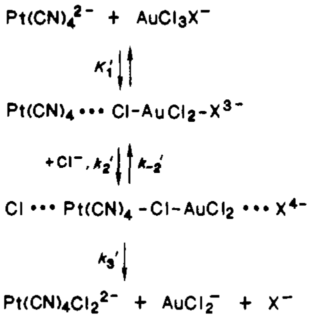
A mechanism according to eq 17 and 18 followed by electron transfer and rapid split of the bridged complex, which also agrees with the observed rate law, does not seem very likely. We have

$$\text{AuCl}_4^- + \text{Cl}^- \rightleftarrows \text{AuCl}_5^{2-} \qquad (17)$$

$$\text{Pt(CN)}_4^{2-} + \text{AuCl}_5^{2-} \rightarrow \text{Pt(CN)}_4\text{-Cl-AuCl}_4^{4-} \qquad (18)$$

previously shown that five-coordinate complexes such as $Pt(CN)_4Cl^{3-}$, $PtCl_5^{3-}$, and $PdCl_5^{3-}$ formed in reactions of type 17 are probably not intermediates in redox or bridge-formation reactions of square-planar complexes.[5,4d,11]

A more probable mechanism, which is very similar to the halide assistance mechanism for ligand substitution discussed in detail elsewhere,[5] is shown by eq 19, where X denotes Cl^- or OH^-. The



(19)

rapid formation of a bridged complex according to eq 16 with L = X is followed by a reversible association of chloride to the platinum(II) side, which is assumed to facilitate electron transfer within the dimeric intermediate. With $K_1'[Pt(CN)_4^{2-}] \ll 1$ and steady state for the intermediates, we arrive at the pseudo-first-order rate constant of eq 20, which agrees with eq 12.

$$k = \frac{K_1'k_2'(k_3'/k_{-2}')[\text{Pt(CN)}_4^{2-}][\text{Cl}^-]}{1 + k_3'/k_{-2}'} \qquad (20)$$

The reaction between $AuCl_3OH_2$ and $Pt(CN)_4^{2-}$ has to be studied in solutions containing very low concentrations of free chloride ($<2 \times 10^{-4}$ M). In these experiments, insufficient chloride is present to assist the redox process, which means that an in-

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(11) Elding, L. I.; Olsson, L.-F. *Inorg. Chem.* **1977**, *16*, 2789.

termediate can accumulate. Under these conditions mechanism 19 can be written as eq 21, in which the formed dinuclear complex

$$\begin{tikzcd}[row sep=large]
\mathrm{Pt(CN)_4^{2-} + AuCl_3OH_2} \arrow[d, shift left, "K_1''"'] \\
\mathrm{Pt(CN)_4 \cdots Cl\text{-}AuCl_2\text{-}OH_2^{2-}} \arrow[u, shift left] \arrow[d, "k_2''"', "+H_2O"] \\
\mathrm{H_2O \cdots Pt(CN)_4\text{-}Cl\text{-}AuCl_2 \cdots OH_2^{2-}}
\end{tikzcd} \qquad (21)$$

represents the intermediate produced in reaction 1a. With $K_1''[\mathrm{Pt(CN)_4^{2-}}] \ll 1$, the pseudo-first-order rate constant is

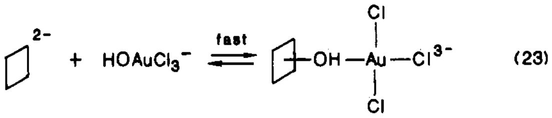
$$k = K_1''k_2''[\mathrm{Pt(CN)_4^{2-}}] \qquad (22)$$

which agrees with rate law 4. The intermediate $H_2O\cdots Pt(CN)_4\text{–}Cl\text{–}AuCl_2\cdots OH_2^{2-}$ is best described as a precursor complex. Electron transfer to Pt(IV) and Au(I) (or Pt(III) and Au(II)) is expected to result in rapid split of the dimer since both Pt(III) and Au(I) complexes are substitution-labile. However, a certain amount of electron displacement within the dimer must have taken place, since the intense UV peak of $Pt(CN)_4^{2-}$ around 253 nm disappears when it is formed; cf. the spectra of Figure 2c,d.

The presence of an aqua ligand at the platinum side of the dimer is supported by the fact that *trans*-$Pt(CN)_4ClOH_2^-$ is formed as the product of electron transfer and split. The acceleration of this split by addition of chloride can be interpreted as a replacement of the aqua ligand at platinum by chloride, which facilitates electron transfer and split according to mechanism 19.

Oxidation of $PtCl_4^{2-}$ by $AuCl_4^-$ in aqueous solution with high concentrations of chloride (>0.25 M) has also been reported to be independent of the concentration of chloride,[7] with a rate law of the same form as the present eq 4 and with a rate constant of the same order of magnitude (830 $M^{-1}\ s^{-1}$) as that of reaction 1a. Since no product analysis was made in that study, it is not possible to relate those results to the present ones, however.

For reaction with $AuCl_3OH^-$, hydroxide bridging with $Pt(CN)_4^{2-}$ might also occur, for instance according to eq 23. This



(23)

is not expected to result in electron transfer. The somewhat slower reaction observed in the experiment of Figure 2a (26% $AuCl_3OH^-$) compared to that of Figure 2b (100% $AuCl_4^-$) might be due to such hydroxide bridging.[12]

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Registry No. $Pt(CN)_4^{2-}$, 15004-88-3; $AuCl_4^-$, 14337-12-3; $AuCl_3OH_2$, 16561-67-4; $AuCl_3OH^-$, 56781-99-8.

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(12) Such decrease in rate is only observed when reactions are studied under second-order conditions.

Contribution from the Department of Chemistry,
Peking University, Beijing, China

Localized INDO Study on the Dimer of Bis(η^5-methylcyclopentadienyl)ytterbium Chloride

Jian Li, Jingqing Ren, and Guang-Xian Xu (K.-H. Hsu)*

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An INDO calculation has revealed that the dimer $(Yb(CH_3C_5H_4)_2Cl)_2$ is a covalent compound. Among the AO's of Yb atoms, the 5d orbitals make the main contribution to bonding, while the 4f orbitals are localized. With use of the Edmiston–Ruedenberg technique, the canonical orbitals of the dimer were transformed to localized molecular orbitals. The nonbonding mixing of atomic orbitals in some canonical molecular orbitals is discussed. The weak interaction between Yb atoms is due to the existence of chlorine bridges that consist of Yb–Cl σ bonds and Cl→Yb dative bonds.

Introduction

Because of the longstanding controversy over the nature of chemical bonding of lanthanide compounds, the electronic structure of these molecules is one of the most attractive topics. Although a series of papers published previously by us[1-8] have revealed some characteristics of the chemical bonds in monomeric lanthanide compounds, there are few theoretical papers concerning the electronic structure of dimers. Recently, we have presented a study on the dimer of bis(η^5-cyclopentadienyl)methylytterbium based on delocalized INDO wave functions,[9] in which the main conclusions obtained in the case of monomers were confirmed. However, there were some unexpected results in it. For example, the 4f orbitals on two different Yb atoms are mixed to form 4f-like molecular orbitals, while the bond orders between the 4f subshells of the atoms are of negligible values. Moreover, the assignment of molecular orbitals to chemical bonds, which are more acceptable for chemists, is rather difficult in terms of these delocalized MO wave functions.

In this investigation, the electronic structure of the dimer of bis(η^5-methylcyclopentadienyl)ytterbium chloride, which is the first organolanthanide dimer characterized by X-ray analysis,[10] is studied by INDO calculation. The wave functions obtained were transformed by a localization procedure and therefore are comparable with the traditional chemical bonds. As expected, the formal mixing of the 4f orbitals from different Yb atoms and that of the 4f orbitals and ligand atoms vanished after localization.

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