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Cyanide and chloride exchange on homoleptic gold(III) square-planar complexes: variable pressure kinetic investigation by heteronuclear NMR[☆]

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Received 3 September 2001; accepted 15 November 2001

Dedicated to Professor A.G. Skyes

Abstract

Kinetic studies of X⁻ exchange on [AuX₄]⁻ square-planar complexes (where X = Cl⁻ and CN⁻) were performed at acidic pH in the case of chloride system and as a function of pH for the cyanide one. Chloride NMR study (330–365 K) gives a second-order rate law on [AuCl₄]⁻ with the kinetic parameters: $(k_2^{Au,Cl})^{298} = 0.56 \pm 0.03 \text{ s}^{-1} \text{ mol}^{-1} \text{ kg}; \Delta H_2^{\pm Au,Cl} = 65.1 \pm 1 \text{ kJ mol}^{-1}; \Delta S_2^{\pm Au,Cl} = -31.3 \pm 3 \text{ J mol}^{-1} \text{ K}^{-1}$ and $\Delta V_2^{\pm Au,Cl} = -14 \pm 2 \text{ cm}^3 \text{ mol}^{-1}$. The variable pressure data clearly indicate the operation of an I_a or A mechanism for this exchange pathway. The proton exchange on HCN was determined by ¹³C NMR as a function of pH and the rate constant of the three reaction pathways involving H₂O, OH⁻ and CN⁻ were determined: $k_0^{\text{HCN},\text{H}} = 113 \pm 17 \text{ s}^{-1}$, $k_1^{\text{HCN},\text{H}} = (2.9 \pm 0.7) \times 10^9 \text{ s}^{-1} \text{ mol}^{-1} \text{ kg}$ and $k_2^{\text{HCN},\text{H}} = (0.6 \pm 0.2) \times 10^6 \text{ s}^{-1} \text{ mol}^{-1} \text{ kg}$ at 298.1 K. The rate law of the cyanide exchange on [Au(CN)₄]⁻ was found to be second order with the following kinetic parameters: $(k_2^{\text{Au,CN}})^{298} = 6240 \pm 85 \text{ s}^{-1} \text{ mol}^{-1} \text{ kg}$, $\Delta H_2^{\pm \text{Au,CN}} = 40.0 \pm 0.8 \text{ kJ} \text{ mol}^{-1}$, $\Delta S_2^{\pm \text{Au,CN}} = -37.8 \pm 3 \text{ J} \text{ mol}^{-1} \text{ K}^{-1}$ and $\Delta V_2^{\pm \text{Au,CN}} = +2 \pm 1 \text{ cm}^3 \text{ mol}^{-1}$. The rate constant of X⁻ exchange on [AuX₄]⁻ are two or three orders of magnitude faster than the Pt(II) analogue. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: High-pressure NMR; Kinetic; Gold(III) complexes; Ligand exchange; Square planar

1. Introduction

The chemistry of gold(III) knows recent developments with the use of its compounds in the treatment of rheumatism [2] (anti-arthritis Au(I) drugs may be activated in vivo to Au(III) metabolites [3]) and Au(III) complexes hold promise as possible anti-tumour agents [4]. It is therefore of interest to investigate fundamental kinetic properties of the Au(III) complexes in solution. Au(III) is a low spin d⁸ centre which forms square-planar complexes, but the high oxidising power of the Au(III) complexes limits the number of nucleophiles for which ligand substitution can be investigated without complications from redox reactions. Soft nucleophiles are reducing agents and Au(III) is reduced to Au(I). However, chloride and cyanide complexes of Au(III) are thermodynamically stable in aqueous solutions and also labile. These two complexes are therefore ideal candidates for a fundamental study involving temperature, pressure and pH variations.

The reactions of displacement of ligand in squareplanar transition metal complexes have been described in books and reviews published in the last years [5]. The rate law for the general reaction (Eq. (1)) can be expressed by the two term equation (Eq. (2)):

$$[MX_4]^{n-} + 4^* X^- \stackrel{k_2}{\nleftrightarrow} [M^* X_4]^{n-} + 4X^-$$
(1)

$$k_{\rm obs} = k_1 + k_2 \text{ [ligand]} \tag{2}$$

The second-order rate constant k_2 refers to the bimolecular attack of the ligand on the substrate and the pseudo-first order rate constant k_1 to the attack of the

 $[\]approx$ Part 97 of the series High-pressure NMR Kinetics, part 96 is Ref. [1].

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solvent. The k_1 , if observed, will depend on the nature of the solvent. The absence of steric hindrance above and below the plane of the complex produces a characteristic kinetic behaviour with a five-coordinate intermediate or transition state.

The first chloride exchange study on tetrachloroaurate(III) was performed by Rich and Taube [6] under conditions where hydrolysis and oxydo-reduction does not occur. The rate constants were determined using isotopic labelling technique with radioactive chloride (³⁶Cl). ³⁵Cl/³⁷Cl NMR can also be used to extract kinetic information [7]. In this case, the property used to measure the Cl⁻ exchange rate is the free chlorine spin relaxation rate. We have extended the temperature domain studied and for the first time used variable pressure chloride ³⁵Cl NMR to obtain the reaction activation volume.

Early cyanide exchange studies [8] with certain heavy metal cyanides complex were monitored with counting techniques using ¹⁴C-labelled radiocyanide. However, cyanide exchange can be better and easier followed using ¹³C NMR. A preliminary cyanide exchange study on [Au(CN)₄]⁻ was performed by Pesek and Mason [9]. This study was limited to high pH where cyanide is entirely deprotonated. Our first goal was to perform a variable pH study to check if HCN could act as a nucleophile like CN⁻. Further, by using variable temperature and variable pressure ¹³C NMR, we intend to give an answer to the nature of the transition state for the cyanide exchange on this homoleptic complex.

2. Experimental

2.1. Chemicals and solutions

K[Au(CN)₄] was prepared as described in literature [10]. K[AuCl₄] (Aldrich, p.a.), KCl (Merck, p.a.), KCF₃SO₃ (Fluka, purum), K¹³CN (Cambridge isotope, 99% enriched) were of the highest quality available and were used without further purification and dissolved in doubly deionised and distilled water. Solutions containing ~ 0.1 mol kg⁻¹ of [Au(L)₄]⁻ and varying concentration of KL (L = CN⁻ or Cl⁻) were freshly prepared before experiments. The ionic strengths of [AuCl₄]⁻ and [Au(CN)₄]⁻ solutions were adjusted to 0.6 mol kg⁻¹ by adding KCF₃SO₃ and KNO₃, respectively. [AuCl₄]⁻ solutions were protected from light to avoid decomposition. [Au(CN)₄]⁻/CN⁻ solutions were studied from pH 11.5 (initial pH the solution) to pH 0.6 by adding concentrated HNO₃.

2.2. pH measurements

The pH values were determined by potentiometric technique. The instrumentation used consists of a titro-

processor (Titrino 716 from Metrohm), for the addition of titrant and millivolts readings. A combined glass/reference electrode with a symmetrical electrode chain from Radiometer Analytical S.A. (pHC2406L) and Metrohm 713 pH meter were calibrated from titration of HCl with NaOH under the same conditions (T = 298.1 K and I = 0.6 mol kg⁻¹) thus the pH values are defined as $-\log[H^+]$. If the solutions pH values differed by more than 0.1 unit between the beginning and the end of the NMR measurement, the data were not accepted.

2.3. NMR measurements

All NMR spectra were recorded in a 9.4 T magnetic field with Bruker ARX-400 and DPX-400 spectrometers at 100.63 MHz (13 C), 32.633 MHz (37 Cl) and 39.206 MHz (35 Cl). In 13 C NMR experiments, methanol was used as internal standard for chemical shift (49.3 ppm) and for B_0 -homogeneity. In the case of chloride NMR, the 1 H NMR water signal served as reference of the B_0 -homogeneity. All aqueous solutions contained 2% D₂O as an internal lock substance. The temperature was controlled by a Bruker B-VT 3000 unit and measured before and after spectral accumulation by substituting the sample with a Pt-100 resistance (accuracy: 0.5 K) [11].

High-pressure high-resolution liquid NMR spectra were monitored with a home built probe described previously [12]. Tetrachloroethylene was used as pressurisation liquid. The temperature was stabilised to ± 0.2 K by pumping thermostated liquid through the high-pressure vessel.

Slow exchange reactions were followed using labelling techniques by mixing two pre-thermostated solutions using fast injection techniques [13] or manual injection. The temperature of the fast injection unit was stabilised by thermostated ethanol circulation at 298.1 K. The mixing time was measured to be less than 0.5 s in our conditions. About 50 spectra (1–5 scans each) were recorded for each experiment and a supplementary delay between successive spectra was added for slow reactions.

2.4. Programs

The analysis of data using appropriate equations was accomplished with the non-linear least-squares-fitting program SCIENTIST [14]. The reported errors correspond to one standard deviation.

Line widths of NMR signals were obtained by fitting Lorentzian functions to the experimental spectra using NMRICMA 2.7 program [15] for MATLAB [16]. Complete line shape analysis based on the Kubo–Sack formalism, using modified Bloch equations was also performed using NMRICMA 2.7 program to extract rate constants from experimental spectra.

Experimental ¹³C NMR line widths of the HCN/CN⁻ signal and rate constants $k_{obs}^{HCN,H}$ of the proton exchange on HCN at 298.1 K as a function of pH ^a

| pH (±0.1) | $\Delta v_{1/2 exp}$ (Hz) | $k_{\rm obs}^{\rm HCN,H\ b}\ ({\rm s}^{-1})$ | pH (± 0.1) | $\Delta v_{1/2 \exp}$ (Hz) | $k_{\rm obs}^{\rm HCN,H\ b}\ ({\rm s}^{-1})$ |
|-----------|---------------------------|--|------------------|----------------------------|--|
| 2.3 | 21.3 | 1.14×10^{2} | 7.9 | | 6.16×10^{3} |
| 2.4 | 20.4 | 1.20×10^{2} | 8.4 | | 3.04×10^{4} |
| 2.9 | 19.1 | 0.95×10^{2} | 8.7 | 148 | 5.20×10^{4} |
| 3.9 | 19.8 | 1.18×10^{2} | 9.1 | 120 | 1.95×10^{5} |
| 4.6 | 20.7 | 1.34×10^{2} | 9.4 | 119 | 3.34×10^{5} |
| 5.3 | 27.4 | 1.38×10^{2} | 9.7 | 87.8 | 6.67×10^{5} |
| 6.5 | 80.2 | 4.39×10^{2} | 10.1 | 50.6 | 1.07×10^{6} |
| 6.8 | | 9.43×10^{2} | 10.3 | 38.2 | 1.16×10^{6} |
| 7.5 | | 2.80×10^{3} | 10.7 | 13.7 | 1.83×10^{6} |

^a $C_{\rm CN} = 0.410 \text{ mol kg}^{-1}$, $I = 0.594 \text{ mol kg}^{-1}$ (KNO₃).

^b Extracted from the experimental spectra by the Kubo-Sack formalism.

3. Data treatment and results

3.1. Cyanide solutions

Table 1

In our study of CN^- exchange on $[Au(CN)_4]^-$, we had to vary the pH from basic to acidic. Over this large range, the free ligand present in solutions changes from $CN^$ at high pH to HCN at low pH. Therefore we have first determined the dissociation constant K_a^{HCN} and the proton exchange rate constant on HCN.

3.1.1. ¹H exchange on HCN

¹³C NMR spectra were performed from pH 10.7 to 2.3 at 298.1 K with a 0.41 mol kg⁻¹ KCN ($I = 0.6 \text{ mol kg}^{-1}$) solution (Table 1). At low pH, HCN is the major species in the solution. The ¹³C NMR spectra show a doublet with a coupling constant ¹ $J_{CH} = 272$ Hz. The HCN chemical shift and line widths are 112.4 ppm and 20 Hz, respectively. In increasing the pH, the doublet broadens and coalesces around pH 7–8. This phenomenon is due to the decreasing lifetime of the proton on HCN. At pH 8, the NMR sharp coalesced signal broadens and to move strongly towards the CN⁻ resonance frequency at 165.1 ppm. At pH > 10, the CN⁻ form is predominant and the line width of the signal stays around 4–6 Hz.

Because the proton exchange is fast on the NMR time scale, the dissociation constant $K_{\rm a}^{\rm HCN}$ could be determined by fitting the variation of the chemical shift, $\delta_{\rm obs}$, of the coalesced signal as a function of pH (Eq. (3)).

$$\delta_{\rm obs} = \frac{K_{\rm a}^{\rm HCN}}{[{\rm H}^+] + K_{\rm a}^{\rm HCN}} \,\delta_{\rm CN} + \frac{[{\rm H}^+]}{[{\rm H}^+] + K_{\rm a}^{\rm HCN}} \,\delta_{\rm HCN} \tag{3}$$

Under our experimental conditions (T = 298.1 K, I = 0.6 mol kg⁻¹ fixed with KNO₃), a p K_a^{HCN} value of 9.5 ± 0.2 was obtained.

The proton exchange rate law was already reported in different supporting electrolyte and ionic strength by Bednar and Jenks [17] and Banyai et al. [18]. Three different reaction pathways were proposed (Eqs. (4)-(6)).

$$HCN + H_2 O \underset{\substack{k \in N, H \\ k \in N, H \\ \mu \in N, H}}{\overset{k \in N, H}{\rightleftharpoons}} CN^- + H_3 O^+$$
(4)

$$HCN + OH^{-} \underset{\substack{k_{1} \in V, H \\ k_{1} \in V, H}}{\stackrel{R}{\rightarrow}} CN^{-} + H_{2}O$$
(5)

$$HCN + CN^{-2} \rightleftharpoons HCN + CN^{-}$$
(6)

An overall proton exchange rate constant on HCN, $k_{obs}^{HCN,H}$, can be obtained by taking into an account the three pathways (Eq. (7)).

$$k_{obs}^{HCN,H} = -d[HCN]/[HCN]dt$$

= $k_0^{HCN,H} + k_1^{HCN,H}[OH^-] + k_2^{HCN,H}[CN^-]$
= $k_0^{HCN,H} + k_1^{HCN,H}10^{-(pK_w + pH)}$
+ $k_2^{HCN,H}C_{CN}\frac{K_a^{HCN}}{K_a^{HCN} + [H^+]}$ (7)

The inverse of the mean lifetime of ¹³C in the HCN site, $k_r^{\text{HCN}} (1/\tau_{\text{HCN}} = k_r^{\text{HCN}})$, was extracted from experimental spectra by line shape analysis using Kubo–Sack formalism and the following 3 × 3 exchange matrix **D**₁ (Eq. (8), see Appendix A for more details). P^{HCN} and P^{CN} are the populations of HCN and CN⁻. The resonance frequencies of H^{α}CN, H^{β}CN and CN⁻ are fixed to 11441, 11169 and 16638 Hz, respectively.

sites
$$H^{\alpha}CN$$
 $H^{\beta}CN$ CN^{-}
 $\mathbf{D}_{1} = \begin{vmatrix} -k_{r}^{HCN} & 0 & k_{r}^{HCN} \\ 0 & -k_{r}^{HCN} & k_{r}^{HCN} \\ (P^{HCN}/2P^{CN})k_{r}^{HCN} & (P^{HCN}/2P^{CN})k_{r}^{HCN} & -(P^{HCN}/P^{CN})k_{r}^{HCN} \end{vmatrix}$
(8)

The proton exchange rate constants observed on HCN, $k_{obs}^{HCN,H}$, which are directly given by k_r^{HCN} ($k_{obs}^{HCN,H} = k_r^{HCN}$), are shown in Table 1. Eq. (7) was least-squares fitted to the $k_{obs}^{HCN,H}$ values leading to the following rate constants: $k_0^{HCN,H} = 113 \pm 17 \text{ s}^{-1}$, $k_1^{HCN,H} = (2.9 \pm 0.7) \times 10^9 \text{ s}^{-1} \text{ mol}^{-1} \text{ kg}$ and $k_2^{HCN,H} = (0.6 \pm 0.2) \times 10^6 \text{ s}^{-1} \text{ mol}^{-1} \text{ kg}$. The pH variation of $k_{obs}^{HCN,CN}$ together with the relative contributions of the three pathways are shown in Fig. 1.

The activation parameters for the pathway 0 (Eq. (4)) could be determined at pH 3.7 where its contribution to the proton exchange is predominant. ¹³C NMR



Fig. 1. Variation of the log $k_{\text{obs}}^{\text{HCN,CN}}(\Box)$ and of the relative contributions, k_i , of three proton exchange pathways $(k_0^{\text{HCN,H}}(\blacklozenge); k_1^{\text{HCN,H}}(\blacksquare))$ and $k_2^{\text{HCN,H}}(\blacktriangle)$ as a function of pH at 298.1 K; $C_{\text{CN}} = 0.410$ mol kg⁻¹, I = 0.594 mol kg⁻¹ (KNO₃).



Fig. 2. 100.63 MHz ¹³C NMR of the $[Au(CN)_4]^-/HCN/CN^-$ solution as a function of pH at 298.1 K; $C_{CN} = 0.434 \text{ mol kg}^{-1}$; $C_{Au} = 0.102 \text{ mol kg}^{-1}$; $I = 0.615 \text{ mol kg}^{-1}$ (KNO₃).

spectra were measured between 273.9 and 320.1 K. At higher temperature, decomposition [19] occurs and HCN evaporates from the solution. The HCN chemical shift does not change in the temperature range studied. $k_r^{\rm HCN}$ determined as a function of temperature, were least-squares fitted to the Eyring law (Eq. (9)), leading to activation parameters, $(k_0^{\rm HCN,CN})^{298} =$ $94 \pm 20 \text{ s}^{-1}$, $\Delta H_0^{\ddagger} = 38 \pm 2 \text{ kJ mol}^{-1}$ and $\Delta S_0^{\ddagger} = 80 \pm 6 \text{ J mol}^{-1} \text{ K}^{-1}$.

$$k_{0}^{\text{HCN,H}} = \frac{k_{\text{B}}}{h} T \exp\left[\frac{\Delta S_{0}^{*}}{R} - \frac{\Delta H_{0}^{*}}{RT}\right]$$
$$= (k_{0}^{\text{HCN,H}})^{298} \frac{T}{298.1} \exp\left[\frac{\Delta H_{0}^{*}}{R} \left(\frac{1}{298.1} - \frac{1}{T}\right)\right]$$
(9)

3.1.2. Cyanide exchange on $[Au(CN)_4]^-$

The tetracyanoaurate(III) is known to be very stable in aqueous solution. The stability constant $\log \beta_4$ was estimated to be 85 [20]. A ¹³C NMR pH variation study (from pH 11.6 to 2.0) was performed with a 0.1 mol kg⁻¹ [Au(CN)₄]⁻ aqueous solution at 298.1 K. A singlet was observed at 104.2 ppm with a line width less than 1 Hz. The integral of that singlet was constant during the pH variation indicating that no dissociation or decomposition occurred even if no free cyanide was present in solution. However, when the pH value was increased to 13.9, the complex was reduced completely to Au(I) species after less than 1 h at ambient temperature. The following ¹³C NMR signals could be assigned: $[Au(CN)_2]^-$ (singlet at 153.6 ppm) [21], OCN⁻ (broad triplet at 129 ppm, ${}^1J_{C-N} =$ 10.5 Hz) [22], CO₂ (singlet at 124.9 ppm) and free cyanide. Cyanogen (CN)2 was probably present in the solution with a broad multiplet at 119.6 ppm (the carbon was enriched at 50%) disappearing slowly due to evaporation.

The rate law was determined at pH 11.5 in order to have the major proportion of cyanide in the CN⁻ form. ¹³C NMR signals of the free ligand (165.5 ppm) and of the gold complex (104.2 ppm) broaden by the addition of free cyanide (Fig. 2, first basic spectrum). Preliminary tests showed that varying the ionic strength from 0.1 to 2 mol kg $^{-1}$ had no influence on the line width observed. Therefore, solutions containing 0.1 mol kg⁻¹ of K[Au(CN)₄] were prepared at pH 11.3 and variable amounts of KCN were added successively into the solutions to cover a concentration domain from 0.02 to 1.23 mol kg⁻¹. The cyanide exchange induces line broadening on the ¹³C NMR spectra, therefore, the rate constants $k_{obs}^{Au,CN}$ were extracted using line shape analysis with the Kubo-Sack formalism. The site of the CN⁻ bound to the metal centre (10485 Hz) was added to the exchange matrix \mathbf{D}_1 . The new 4×4 -exchange matrix \mathbf{D}_2 is given in Eq. (10).

Table 2

Variation of the observed cyanide exchange rate constant $k_{obs}^{Au,CN}$ and its concentration normalised value $k'_{obs}^{Au,CN}$ for $C_{CN} = 0.4 \text{ mol kg}^{-1}$ as a function of pH at T = 298.1 K

| | pH (±0.1) | $k_{ m obs}^{ m Au,CN}$ (s ⁻¹) | $C_{\rm CN} \ (\rm mol \ kg^{-1})$ | $\log_{k'^{ m Au,CN}_{ m obs}}$ |
|-----------|--------------|---|------------------------------------|---------------------------------|
| Kubo–Sack | 11.4 | 2605 | 0.434 | 3.38 |
| formalism | 10.8 | 2566 | 0.434 | 3.37 |
| | 10.6 | 2623 | 0.434 | 3.38 |
| | 10.3 | 2600 | 0.434 | 3.38 |
| | 10.1 | 2079 | 0.434 | 3.28 |
| | 9.9 | 1863 | 0.434 | 3.24 |
| | 9.6 | 1444 | 0.434 | 3.12 |
| | 9.4 | 1177 | 0.434 | 3.04 |
| | 9.1 | 840 | 0.434 | 2.89 |
| | 9.0 | 694 | 0.434 | 2.81 |
| | 8.8 | 452 | 0.434 | 2.62 |
| | 8.4 | 179 | 0.434 | 2.22 |
| | 7.8 | 52 | 0.434 | 1.67 |
| | 7.1 | 14 | 0.434 | 1.12 |
| Isotopic | 3.7 | 3.90×10^{-3} | 0.251 | -2.20 |
| exchange | 3.3 | 1.42×10^{-3} | 0.263 | -2.67 |
| | 1.3 | 1.70×10^{-5} | 0.197 | -4.46 |
| | 1.0 | 8.31×10^{-6} | 0.188 | -4.75 |
| | 0.8 | 1.08×10^{-5} | 0.290 | -4.83 |
| | 0.6 | 3.37×10^{-6} | 0.271 | -5.30 |

 $pK_{a}^{HCN} = 9.5$, $C_{Au} = 0.11 \pm 0.01 \text{ mol kg}^{-1}$, $I = 0.7 \pm 0.1 \text{ mol kg}^{-1}$ (KNO₃), $H_2O/D_2O = 5\%$.



Fig. 3. Variation of the rate constant $k_{obs}^{Au,CN}$ of cyanide exchange on $[Au(CN)_4]^-$ as a function of free cyanide concentration at T = 298.1 K and pH 11.3 ± 0.2 . $C_{Au} = 0.090 \pm 0.003$ mol kg⁻¹.

Variable pH study represents another possibility also to determine the rate law by varying cyanide concentration. The ¹³C NMR spectra as a function of pH of the $[Au(CN)_4]^-/HCN/CN^-$ solution in aqueous media is represented in Fig. 2. At basic medium, the line width of the bound ¹³CN is broad $(1/T_2^b = 2400 \text{ s}^{-1} \text{ at pH})$

| Site | H∝CN | H ^β CN | CN^{-} | $[Au(CN)_4]^-$ | |
|-------------------------|--|--|---|---|------|
| | $-k_{\rm r}^{\rm HCN}$ | 0 | $k_{\rm r}^{\rm HCN}$ | 0 | |
| | 0 | $-k_{\rm r}^{\rm HCN}$ | $k_{\rm r}^{\rm HCN}$ | 0 | |
| D ₂ = | $(P^{\rm HCN}/2P^{\rm CN})k_{\rm r}^{\rm HCN}$ | $(P^{\rm HCN}/2P^{\rm CN})k_{\rm r}^{\rm HCN}$ | $- (P^{\rm HCN}/P^{\rm CN}) k_{\rm r}^{\rm HCN} \\ - (P^{\rm CNb}/P^{\rm CN}) k_{\rm r}^{\rm Au}$ | $-(P^{\mathrm{CNb}}/P^{\mathrm{CN}})k_{\mathrm{r}}^{\mathrm{Au}}$ | (10) |
| | 0 | 0 | $k_{\rm r}^{\rm Au}$ | $-k_{r}^{Au}$ | |

The inverse of the mean lifetime of cyanide in the $[Au(CN)_4]^-$ site, k_r^{Au} , together with k_r^{HCN} , the inverse of the mean lifetime of proton in HCN site, were determined by fitting to the experimental spectra. k_r^{Au} is defined for the exchange of a particular cyanide bound to the metal centre Au(III), and P^{CNb} is the corresponding population ($P^{CNb} = 4C_{Au}/C_{tot}$). The observed kinetic rate constant of cyanide exchange on Au(III), $k_{obs}^{Au,CN}$ (Eq. (11)) is directly given by k_r^{Au} ($k_{obs}^{Au,CN} = k_r^{Au}$). The $k_{obs}^{Au,CN}$ values determined using the Kubo–Sack formalism are presented in Fig. 3. Analysis of the [CN⁻] dependence showed a clean second-order rate law, without intercept, leading to $k_2^{Au,CN}$ value of 6240 ± 85 s⁻¹ mol⁻¹ kg.

$$k_{\rm obs}^{\rm Au,CN} = -d[{\rm Au}({\rm CN})_4^-]/dt[{\rm Au}({\rm CN})_4]^-$$

= $k_2^{\rm Au,CN}[{\rm CN}^-]$ (11)

11.4) and sharpens when pH is decreased $(1/T_2^b = 12 \text{ s}^{-1} \text{ at pH 4.6})$. The HCN/CN⁻ resonance frequency observed varies only due to the proton exchange between HCN and CN⁻. The p K_a^{HCN} did not change within the experimental error (9.4 ± 0.2).

Due to the large variation of $k_{obs}^{Au,CN}$, two experimental techniques (line shape analysis and isotopic exchange) had to be used. Cyanide and proton rate constants were extracted from spectra when line widths are broad (ca. pH 7.0–12.0). The values of the $k_{obs}^{Au,CN}$ and $k_{obs}^{HCN,H}$ are presented in Table 2. Below pH 7, the exchange reaction is too slow to be observed by line broadening. However, at pH < 4, the exchange is slow enough to be determined by isotopic labelling technique. The exchange reaction was followed by rapidly mixing ¹³C enriched ligand (H¹³CN) to a complex



Fig. 4. (a) Series of ¹³C NMR spectra after rapid mixing of two solution containing H¹³CN and [Au(CN)₄]⁻. The intensity of the complex signal ($\Delta v_{1/2} = 2$ Hz) increased as a function of time and that of the HCN doublet ($\Delta v_{1/2} = 20$ Hz) is decreasing; $C_{Au} = 0.109$ mol kg⁻¹, $C_{CN} = 0.276$ mol kg⁻¹, I = 0.60 mol kg⁻¹ (KNO₃), pH 3.3, D₂O = 2%, $T = (298 \pm 0.2)$ K; Δt between two spectra 11.57 s (the 15 last spectra are not presented). (b) Time evolution of the ¹³C population of HCN (\blacksquare) and [Au(CN)₄]⁻ (\bullet). Fitted parameters (Eq. (2)): [Au(CN)₄]⁻: $x_0 = (0.01 \pm 0.01)$; $x_{\infty} = (0.62 \pm 0.01)$; $k_{obs}^{Au,CN} = (1.416 \pm 0.005) \times 10^{-3}$ s⁻¹.



Fig. 5. Variation of the rate constant $k_{obs}^{Au,CN}$ (normalised by the concentration: $C_{CN} = 0.4 \text{ mol kg}^{-1}$) of cyanide exchange on $[Au(CN)_4]^-$ as a function of pH in water at T = 298.1 K.

solution at the same pH and temperature using fast injection unit. Attention had to be paid to the long relaxation times of bound CN^- . Experimental T_1 values as a function of pH, for $[Au(CN)_4]^-$ and HCN/CN^- (individual and mixed solutions) were determined to be in a time domain from 15 to 25 s. With cyanide present and not purged from O₂, the relaxation time T_1 of $[Au(CN)_4]^-$ was shorter compared to Pesek and Mason results [9]. By monitoring the increase in intensity of the complex signal and the decrease of that of the free ligand, the kinetics constants were determined with the modified McKay equation (Eq. (12)) [23,24].

$$x(t) = x_{\infty} + (x_0 - x_{\infty}) \exp(-k_{obs}^{Au,CN} t / (1 - x_{\infty}))$$
(12)

x(t) represents the mole fraction of the coordinated ¹³CN as a function of the time and x_0 and x_∞ are the limiting conditions at t = 0 and at the exchange equilibrium, respectively. To each of the ~ 50 spectra of the fast injection experiment Lorentzian functions were fitted in order to determine the integrals as a function of time. The analysis of the experimental data using Eq. (12) was done by a non-linear least-squares program with $k_{obs}^{Au,CN}$, x_∞ , x_0 as adjustable parameters. A typical example of the ¹³CN spectra observed as a function of time is given in Fig. 4. The $k_{obs}^{Au,CN}$ values obtained using fast injection, are included in Table 2. Between pH 3.7 and 0.6, the $k_{obs}^{Au,CN}$ value decrease over three orders of magnitude.

A second-order rate law was least-square fitted to all the $k_{obs}^{Au,CN}$ values as a function of pH and C_{CN} concentration leading to rate constant $(k_2^{Au,CN})^{298} = (6950 \pm 460) \text{ s}^{-1} \text{ mol}^{-1} \text{ kg}$ which is within experimental error the same as the one found from [CN⁻] variation at high pH. For visualisation, the second-order rate constants, $k_{obs}^{Au,CN}$, were concentration normalised in $k_{obs}^{Au,CN}$ to a free analytical cyanide concentration of $C_{CN} = 0.4$ mol kg⁻¹ (Fig. 5; Table 2). The strong decrease of the experimental rate observed with pH indicates that the reacting species is CN⁻: no exchange pathway with HCN as a nucleophile could be detected.

Variable temperature study (273.1–327.1 K) was performed at pH 11.5 with a solution containing 0.100 mol kg⁻¹ of K[Au(CN)₄] and 0.455 mol kg⁻¹ of KCN $(I = 0.650 \text{ mol kg}^{-1} \text{ KNO}_3)$ using line shape analysis. At higher temperatures (>330 K) a slight yellow coloration of the solution appears rapidly indicating cyanide destruction and Au(III) reduction. Up to 327 K, no variation of the integrals were observed and the system was fully reversible. This leads, by fitting Eq. to the following activation parameters: (9), $(k_2^{\text{Au,CN}})^{298} = 6300 \pm 100 \text{ s}^{-1} \text{ mol}^{-1} \text{ kg}, \ \Delta H_2^{\ddagger} = 40.0 \pm 100 \text{ s}^{-1} \text{ mol}^{-1} \text{ kg}$ 0.8 kJ mol⁻¹ and $\Delta S_{2}^{\ddagger} = -37.8 \pm 3$ J mol⁻¹ K⁻¹.

Three series of variable pressure experiments were performed from 0.1 to 200 MPa at pH 11.5 (298.1 and 278.1 K) and pH 9.5 (279.6 K) with solutions containing 0.10 ± 0.01 mol kg⁻¹ of K[Au(CN)₄] and K¹³CN.



Fig. 6. Variation of the rate constant $k_2^{Au,CN}$ of cyanide exchange on $[Au(CN)_4]^-$ as a function of pressure. (□): T = 298.1 K, pH 11.5, $C_{CN} = 0.457$ mol kg⁻¹; (○): T = 278.1 K, pH 11.5, $C_{CN} = 0.390$ mol kg⁻¹; (△): T = 298.1 K, pH 9.5, $C_{CN} = 0.443$ mol kg⁻¹.

The pressure effect on the cyanide exchange on gold(III) is represented in Fig. 6. The pressure dependence of the rate constant (Eq. (13)) leads to an average activation volume of $\Delta V_2^{\dagger} = +2 \pm 1 \text{ cm}^3 \text{ mol}^{-1}$. The activation volumes were assumed to be pressure independent.

$$k_2^{\text{Au,X}} = (k_2^{\text{Au,X}})_0 \exp\left(-\frac{\Delta V_2^{\ddagger}}{RT}P\right)$$
(13)

3.2. Chloride exchange on $[AuCl_4]^-$

The kinetics study of Cl^- exchange on the $[AuCl_4]^-$ complex (Eq. (1), with $X^- = Cl^-$) can be complicated by the aquation of the complex (Eq. (14)) and deprotonation of the aquo complex (Eq. (15)).

 $[\operatorname{AuCl}_4]^- + \operatorname{H}_2 \operatorname{O} \rightleftharpoons [\operatorname{AuCl}_3(\operatorname{H}_2 \operatorname{O})] + \operatorname{Cl}^-$ (14)

$$[\operatorname{AuCl}_3(\operatorname{H}_2\operatorname{O})] \rightleftharpoons^{\operatorname{A}_a} [\operatorname{AuCl}_3(\operatorname{OH})]^- + \operatorname{H}^+$$
(15)

The stability constant $\log \beta_4$ of $[AuCl_4]^-$ was estimated to 26 relative to the hypothetical $[Au(H_2O)_4]^{3+}$ [25] and a p K_a value of 0.6 was determined by Bekker and Robb [26] for $[AuCl_3(H_2O)]$. According to the calculations made by Peck et al. [27] for $[AuCl_4]^-$ in 1 M NaCl and using stability constants from various authors, the hydrolysis is negligible below pH 6.0.

For chlorine nuclei in complexes of diamagnetic metal ions, the quadrupolar relaxation rates are large (from 10^4 to 10^7 s⁻¹) due to a strong electric field gradient [7]. Consequently, the signal of bound chlorine is too broad to be observed and only signals of the free halide can be measured. The study of the line width of pairs of isotopes ³⁵Cl/³⁷Cl allows the separation of quadrupolar relaxation from broadening due to chemical exchange. On systems where a quadrupolar nucleus

is undergoing slow chemical exchange between two magnetically distinct environments, the transverse relaxation rate is given by Eq. (16) [28] where $1/T_{2Q}^{f}$ is the quadrupolar relaxation rate of the free halide in absence of exchange and $\tau_{\rm f}$, the mean lifetime of the chloride in the free environment.

$$1/T_2^{\rm f} = 1/T_{2\rm O}^{\rm f} + 1/\tau_{\rm f} \tag{16}$$

This lifetime, in the free state, is related to the lifetime in the bound one, $\tau_{\rm b}$, and its inverse, $k_{\rm b}$, by Eq. (17). $P^{\rm b}$ and $P^{\rm f}$ represent the population of bound and free ligand.

$$1/\tau_{\rm f} = (P^{\rm b}/P^{\rm f})(1/\tau_{\rm b}) = (P^{\rm b}/P^{\rm f})k_{\rm b}$$
(17)

The ratio of the quadrupolar relaxation rates of different chlorine isotopes is proportional to the squared ratio of their nuclear electric quadrupole moments according to Eq. (18) [7].

$$(1/T_{2Q}^{35})/(1/T_{2Q}^{37}) = [Q^{35}/Q^{37}]^2 = 1.610$$
(18)

In an exchanging system, at a given temperature, the line widths $(\Delta v_{1/2} = 1/(\pi T_2^{\rm f}))$, Eq. (16)) for two different isotopes will only differ in the quadrupolar relaxation term $1/T_{2Q}^{\rm f}$. Note that we neglect the kinetic isotopic effect on the exchange rate constant that Hall et al. [29] have estimated to a few percent for chloride.

A set of seven aqueous solutions was prepared with 0.10 mol kg⁻¹ [AuCl₄]⁻ complex concentration and with free Cl⁻ concentration varying from 0.04 to 0.5 mol kg $^{-1}$. The pH values of the solutions were between 2.7 and 3.7, without adding acid, which allowed to neglect hydrolysis and deprotonation. ³⁵Cl and ³⁷Cl relaxation rates, $1/T_2^{f}$, were recorded as a function of temperature between 273.1 and 364.9 K using all solutions. The observed $1/T_2^f$ values were found to be independent, within experimental error, of the Clconcentration at all temperatures. Therefore, an average value was calculated for $1/T_2^{\rm f}$ at each temperature (Fig. 7). This finding allowed to simplify Eq. (19) (combination of Eqs. (2), (16) and (17) and $P^{\rm b}/P^{\rm f} =$ 4[AuCl₄]/[Cl⁻]) by neglecting the term including the rate constant k_1 (Eq. (20)).

$$1/T_{2}^{\rm f} = 1/T_{2Q}^{\rm f} + 4[{\rm AuCl}_{4}^{-}](k_{1}^{\rm Au, Cl}/[{\rm Cl}^{-}] + k_{2}^{\rm Au, Cl})$$
(19)

$$1/T_2^{\rm f} = 1/T_{2\rm Q}^{\rm f} + 4k_2^{\rm Au, Cl}[{\rm AuCl}_4^-]$$
(20)

Even if the temperature domain, where the exchange contribution is predominant, is relatively large, the extrapolated rate constant at 298.1 K cannot be determined without important experimental error. Two different studies of chloride exchange on [AuCl₄]⁻ were performed using ³⁶Cl isotopic exchange [6] and NMR techniques [30]. The rate constant values obtained by Sharps et al. are in a good agreement with our values at



Fig. 7. Temperature dependence of the averaged observed relaxation rates normalised by the complex concentration, $1/(T_2^f \times 4[Au(CN)_4^-])$ for ${}^{35}Cl(\blacksquare)$ and ${}^{37}Cl(\textcircled)$ in aqueous solution (average values from seven solutions with free Cl⁻ concentration ranging from 0.05 to 0.4 mol kg⁻¹) and temperature dependence of $\ln k_2^{AuCl}$ from Ref. [2] (\blacktriangle). The dotted lines represent exchange ($-\cdot -$) and quadrupolar relaxation contributions (----).

high temperature, but an important deviation¹ is observed at 298.1 K with their extrapolated $(k_2^{\text{Au,Cl}})^{298}$. However, the data obtained at low temperature by



Fig. 8. Pressure dependence of the observed ³⁵Cl relaxation rate, $1/T_2^{f}$, of a 0.102 mol kg⁻¹ [AuCl₄]⁻ and 0.527 mol kg⁻¹ free Cl⁻ solution; (**I**) 277.5 K; (**O**) 340.8 K; (**A**) 351.5 K.

Taube are consistent with our experimental values. Therefore, we have added the rate constant k_2 determined at 273.1 and 283.1 K using isotopic exchange (same analysis was reported [31]). Both values were expressed in s⁻¹ and divided by a factor of 4 according to Taube, for comparison with our data. Eq. (9) together with Eqs. (18) and (20) and were fitted to the averaged experimental relaxation rates and to both Taube values, leading to the relaxation parameters (1/ $T_{2Q,35}^{f}$)²⁹⁸ (or (1/ $T_{2Q,37}^{f}$)²⁹⁸), E_{Q}^{f} and to the activation parameters ΔH_{2}^{\ddagger} and ΔS_{2}^{\ddagger} (or k_{2}^{298}) (Table 3; Fig. 7).

$$1/T_{2Q}^{f} = (1/T_{2Q}^{f})^{298} \exp\left[\frac{E_{Q}^{f}}{R}\left(\frac{1}{T} - \frac{1}{298}\right)\right]$$
(21)

The activation volume related to the quadrupolar relaxation process, ΔV_Q^{\dagger} , and the activation volumes ΔV_2^{\dagger} for Cl⁻ chemical exchange were determined from the pressure dependence of $1/T_2^{f}$ at three different temperatures using Eqs. (20), (16) and (22).

$$1/T_{2Q}^{f} = (1/T_{2Q}^{f})_{0} \exp\left(-\frac{\Delta V_{Q}^{*}}{RT}P\right)$$
(22)

 35 Cl high-pressure NMR experiments were performed at 277.5 K (99.9% of quadrupolar relaxation contribution), 340.8 K (22.9% of exchange contribution) and

Table 3

Kinetic and quadrupolar parameters for Cl⁻ (0.04–0.5 mol kg⁻¹) exchange on $[AuCl_4]^-$ (0.1 mol kg⁻¹) (I = 0.6 mol kg⁻¹ KCF₃SO₃)

| Quadrupolar parameters | | | | Kinetic parameters | | | | |
|--|---|--|---|--|--|--|--|--|
| $(1/T_{2Q}^{\rm f})^{298}$ (s ⁻¹) | | $E_{\rm Q}^{\rm f}$ (kJ mol ⁻¹) | $\frac{\Delta V_{\rm Q}^{*}}{(\rm cm^3mol^{-1})}$ | $\frac{(k_2^{\text{Au,Cl}})^{298}}{(\text{s}^{-1} \text{ mol}^{-1} \text{ kg})}$ | ΔH_2^{\ddagger} (kJ mol ⁻¹) | ΔS_2^* (J mol ⁻¹ K ⁻¹) | $\frac{\Delta V_2^*}{(\mathrm{cm}^3 \mathrm{mol}^{-1})}$ | |
| ³⁵ Cl | ³⁷ Cl | _ | | | | | | |
| 40 ± 1 38.1 ± 0.8 ^a | 25 ± 1 26.1 ± 0.6 ^a | 9.4 ± 1 8.8 ± 0.4 ^a | -0.3 ± 0.2 -0.2 ± 0.5 ^a | 0.56 ± 0.03 | 65.1 ± 1 | -31.3 ± 3 | -14 ± 2 | |

^a For comparison: values obtained with a 0.6 mol kg⁻¹ KCl solution.

¹ According to Fig. 4 of Ref. [30], the $k_{\rm ex}$ should be e^{2.03} and probably not 10^{2.03}.

| Fable 4 | |
|--|------|
| Rate constants $(s^{-1} M^{-1})$ of proton exchange on HCN in aqueous medium at 298 K for reaction pathway | /s i |

| i | Catalyst | pK _a | $\log k_i^{b}$ | $\log k_{-i}$ | Conditions | Reference |
|---|------------------|--------------------------------------|--|--|--|-----------------------------------|
| 0 | H ₂ O | | $\begin{array}{c} 1.6 \\ 1.6 \pm 0.1 \\ 2.05 \pm 0.07 \end{array}$ | 10.6 ° 10.7 ° 11.6 ° | 293.1 K; $I = 1.0$ M (KCl) 298.1 K; $I = 1.0$ M (NaClO ₄) 298.1 K, $I = 0.6$ mol kg ⁻¹ (KNO ₃) | [17] [18] this work |
| 2 | CN- | 9.0 9.09 9.5 | <5 6.5 ± 0.1 5.8 ± 0.2 9.6 ^d | | 293.1 K; $I = 1.0$ M (KCl) 298.1 K; $I = 1.0$ M (NaClO ₄) 298.1 K, $I = 0.6$ mol kg ⁻¹ (KNO ₃) I = 0.01-0.05 M | [17] [18] this work [37] |
| 1 | OH- | 15.74 13.80 13.75 ^f | 9.9 ± 0.2 9.5 ± 0.1 9.5 ± 0.2 a | 3.2 ^b 4.8 ^e 5.3 ^c | 295.1 K; <i>I</i> = 1.0 M (KCl) 298.1 K; <i>I</i> = 1.0 M (NaClO ₄) 298.1 K, <i>I</i> = 0.6 mol kg ⁻¹ (KNO ₃) | [17] [18] this work |

^a Except k_i of this work expressed in s⁻¹ mol⁻¹ kg and k_0 in s⁻¹.

^b Experimental value.

^c Calculated value.

^d Ultrasonic absorption value.

^e Recalculated value: $\log k_{-1}^{\text{HCN,H}} = \log k_{1}^{\text{HCN,H}} - pK_{w} + pK_{a}^{\text{HCN}} = 9.5 - 13.8 + 9.09 = 4.8.$

^f Ref. [38].

351.5 K (40.5% of exchange contribution) allowing to separate both activation volumes ΔV_Q^{\dagger} and ΔV_2^{\dagger} (Fig. 8). Ideally, a higher temperature should have been used to better define ΔV_2^{\dagger} . However, this was not feasible due to irreversible decomposition of $[AuCl_4]^-$ above 370.0 K. From the eight adjustable parameters (two activation volumes, three zero-pressure rate constants and three quadrupolar relaxation rates at the different temperatures) two values were fixed as obtained from the variable temperature study $(k_2^{277.5} \text{ and } (1/T_{2Q}^{f})^{351.5})$ due to their minor individual contribution to $1/T_{2Q}^{f}$. The activation values resulting from the fitting procedure are given in Table 3.

4. Discussion

4.1. Proton exchange on HCN

Values of pK_a^{HCN} have been determined in a number of studies under a large range of experimental conditions. The formation of HCN occurs below pH 11 and depends upon the ionic strength, the nature of the supporting electrolyte and the temperature of the solution. The general trend observed is the following: the higher the ionic strength, the higher the pK_a^{HCN} value. The data published are included in the range between 8.78 (318.1 K, extrapolated to $I=0 \mod \text{kg}^{-1}$) and 10.01 (298.1 K, $I=5 \mod \text{kg}^{-1}$) [32–35]. Our value of 9.5, measured at $I=0.6 \mod \text{kg}^{-1}$, is in good agreement with the observed trend.

The proton exchange on HCN proceeds via three pathways (Eqs. (4)–(6)) involving H₂O, OH⁻ and CN⁻, respectively (Fig. 1). At low pH (<4) the predominant pathway 0 is H₂O catalysed and $k_{obs}^{HCN,H}$ is pH indepen-

dent. The CN⁻ catalysed pathway 2 (Eq. (6)) contributes between pH 5 and 10 with a maximum of 50% to the overall rate. The OH⁻ catalysed pathway 1 (Eq. (5)) contributes to ~40% between pH 7 and 9 and becomes predominant above pH 9.5. If the general observation is similar to that of Glaser and co-workers [18], we found different values for the individual rate constant (Table 4) mainly due to a difference of a factor 2 in the exchange matrices.

With a $pK_a^{\text{HCN}} = 9.5$, we calculate $(pK_a^{\text{HCN}} = \log k_{-0}^{\text{HCN},\text{H}} - \log k_0^{\text{HCN},\text{H}})$ a reverse rate constant $k_{-0}^{\text{HCN},\text{H}} = 4 \times 10^{11} \text{ M}^{-1} \text{ s}^{-1}$ indicating a diffusion-controlled reaction [36]. Our reverse rate constant is about one order of magnitude faster than those from literature (Table 4) which can be partially attributed to our higher pK_a^{HCN} value. The activation parameters ΔH_0^{\ddagger} (Table 5) is close to the thermodynamic enthalpy $\Delta H_0^{\circ} = 44.6 \text{ kJ mol}^{-1}$ (0.5 M, NaCl) determined by Solis et al. [34] for HCN dissociation (Eq. (3)) as excepted for a reverse diffusion-controlled reaction.

Our experimental value for the rate constant $k_1^{\text{HCN},\text{H}}$, obtained for the OH⁻ catalysed pathway, is consistent with literature data obtained by NMR techniques and ultrasonic absorption measurements [37]. The value of

Table 5

Activation parameters of the proton exchange on HCN catalysed by H_2O at acidic pH in water (pathway i = 0)

| I (M) | pK ^{HCN} | $\frac{\Delta H_0^{\dagger}}{(\text{kJ mol}^{-1})}$ | $\frac{\Delta S_0^{\dagger}}{(\mathrm{J} \ \mathrm{mol}^{-1} \ \mathrm{K}^{-1})}$ | Reference |
|-----------------------------------|-------------------|---|---|-----------|
| 1.0 M (NaClO ₄) | 9.09 | 45 ± 4 | -64 ± 12 | [18] |
| 0.8 mol kg ⁻¹ (KCN) | 9.5 | 38 <u>+</u> 2 | -80 ± 6 | this work |

the reverse rate constant $k_{-1}^{\text{HCN,H}}$ was calculated (p $K_{w} - pK_{a}^{\text{HCN}} = \log k_{1}^{\text{HCN,H}} - \log k_{-1}^{\text{HCN,H}}$) using pK_{a}^{HCN} and pK_{w} determined for our ionic medium (p $K_{w} = 13.75$) [38] and this value is in good agreement with the Glaser recalculated value.

The value of the rate constant $k_2^{\text{HCN},\text{H}}$, of the proton exchange catalysed directly by CN⁻, is similar to the ones already published. This pathway is mainly active at pH values just below the pK_a^{HCN} around pH 7 where the sum of the catalysis by H₃O⁺ and OH⁻ is at its minimum.

4.2. X^- exchange on $[AuX_4]^-$

The general mechanistic picture for substitution reactions on square-planar complexes is well established and involves a concurrent bimolecular attack by the solvent and the ligand on the metal centre (rate = $(k_1 + k_2)$ k_2 [ligand] × [complex]) [39]. The k_1 term is the rate constant for the solvolytic pathway, the k_2 term corresponds to the direct attack by the incoming ligand. In an early study of Cattalini and Tobe [40] of ligand substitution on gold(III) complexes, it was concluded that rates of ligand substitution in gold(III) complexes are very sensitive on the nature of both the incoming and the leaving group [25]. Furthermore it was found that the bond formation and bond breaking are nearly synchronous processes. The substitution on Au(III) involves a pentacoordinated transition state rather than a pentacoordinated intermediate. This proposal is compatible with Baddley and Basolo suggestions [41]. Cattalini [42,43] underlined also that the solvent plays at least two different roles in the substitution reaction. On one hand, it can behave as a nucleophile (pathway k_1). On the other hand, factors such as solvation changes of the reacting species and solvent-structure variations of the transition state must be also taken into account (for both pathways). The symmetrical ligand exchange on square-planar complexes usually follow a second-order kinetic with negative entropy and volume of activation leading to the assignment of an associative mode of activation [44]. The solvolytic pathway k_1 , is usually negligible.

The cyanide exchange on $[Au(CN)_4]^-$ follows a purely second-order rate law. If a $k_1^{Au,CN}$ first-order term would exist, it should be less than 10^{-5} s^{-1} with regard to the order of magnitude of the observed rate at low pH, where the cyanide ligand is still active even if its concentration is less than 10^{-9} mol kg⁻¹. The absence of the $k_1^{Au,CN}$ term allows to conclude that HCN does not react as a nucleophile and the absence of a solvolytic pathway.

We found by chlorine NMR that the rate law for the chloride exchange on $[AuCl_4]^-$ is second order in the temperature range of 330.1–365.1 K. Rich and Taube [6] worked using radioactive isotopic technique with

more dilute solutions (0.008–0.07 M for free chloride and 0.01 M for the [AuCl₄]⁻) at 273.1 and 283.1 K. They could therefore also observe a $k_1^{\text{Au,Cl}}$ pathway beside the $k_2^{\text{Au,Cl}}$ pathway. With the NMR technique, needing a much higher Cl⁻ concentration, it was not possible to detect the $k_1^{\text{Au,Cl}}$ pathway and a pure second-order rate law was observed under our experimental conditions ($k_1^{\text{Au,Cl}} \ll k_2^{\text{Au,Cl}}$ [Cl⁻]). The combined analysis of our high-temperature data and of Taube's low temperature data allows to define the activation parameters well, ΔS^{\ddagger} and ΔH^{\ddagger} , for the $k_2^{\text{Au,Cl}}$ pathway (Table 6).

The cyanide exchange is 10^5 times faster than the chloride one on the homoleptic gold(III) complexes. The effectiveness of the nucleophile attack is not only due to its basicity but also to its polarisability [40,41]. From the infrared and Raman spectra of aqueous $[Au(CN)_{4}]^{-}$ solution, Jones and Smith [45] have deduced high CN and AuC force constants indicative of a strong metal-ligand σ -bonding and a weak metal-ligand π -back-bonding. Cyanide will increase the effective positive charge on the metal centre as compared to chloride, which has no metal-ligand π -back-bonding, and thus facilitates bond formation with the incoming nucleophile. The difference in reactivity between the cyanide and the chloride exchange is reflected in a large difference in the ΔH^{\ddagger} terms whereas the ΔS^{\ddagger} terms are very similar (Table 6).

Even if the entropy values are similar for both chloride and cyanide substitutions, we observed significantly different activation volumes. In the case of CN⁻, the $\Delta V_2^{\ddagger Au,CN} = +2 \pm 1 \text{ cm}^3 \text{ mol}^{-1}$ is less negative compared to $\Delta V_2^{\ddagger Au,Cl} = -14 \pm 2 \text{ cm}^3 \text{ mol}^{-1}$, and even slightly positive. The value observed for the chloride exchange corresponds to an associative interchange I_a or to a limiting associative mechanism A. However, there is no straightforward explanation for the cyanide exchange. Small ΔV^{\ddagger} values for ligand exchange on homoleptic square-planar complexes have already been reported with the assignment of an associative activation mode [44]: $-2.2 \text{ cm}^3 \text{ mol}^{-1}$ for $[Pd(H_2O)_4]^{2+}$, $-0.2 \text{ cm}^3 \text{ mol}^{-1} \text{ for } [Pd(DMF)_4]^{2+}, -3.1 \text{ cm}^3 \text{ mol}^{-1}$ for $[Pd(MeNC)_4]^{2+}$, -4.6 cm³ mol⁻¹ for $[Pt(H_2O)_4]^{2+}$ and $-3.7 \text{ cm}^3 \text{ mol}^{-1}$ for $[Pt(MeNC)_4]^{2+}$. The interpretation of these volumes in molecular terms is not trivial, as these solvates undergo large changes in coordination geometry on going from ground state to transition state. Tetrasolvate species may have their two axial sites occupied by loosely bound solvent molecules. The simultaneous loss of one of the axially bound solvent molecules with the formation of a new bond with the second solvent molecule in going to a five-coordinate transition state or intermediate may mean that through compensation, the overall volume change is small or negligible. The difference between the chloride and the cyanide can be explained by specific solvation changes F.J. Monlien et al. / Inorganica Chimica Acta 331 (2002) 257-269

Table 6 Exchange rate constant $(k_2^{M,X})^{298}$ and activation parameters for X exchange on $[MX_4]^{n-1}$ in water for M = Au(III) and Pt(II) a

| Complex | Entering ligand | $(k_2^{M,X})^{298}$ (s ⁻¹ M ⁻¹) | ΔH^{\ddagger} (kJ mol ⁻¹) | $\Delta S^{\ddagger} (\text{J mol}^{-1} \text{ K}^{-1})$ | ΔV^{\ddagger} (cm ³ mol ⁻¹) | Method | Reference |
|--------------------------------------|---|---|---|--|---|---------------------------------------|--------------------------|
| [Au(CN) ₄] ⁻ | CN ⁻ CN ⁻ | 6240 ± 85 ^ь 3900 (297.0 K) | 40.0 ± 1 28 ± 1 | -37.8 ± 3 -100 ± 3 | $+2\pm1^{\circ}$ | NMR | this work [21] |
| [AuCl ₄] ⁻ | Cl ⁻ H ₂ O H ₂ O | 0.56 ± 0.03^{b} $2.7 \times 10^{-5 d}$ $1 \times 10^{-4 d}$ | 65.1 ± 1 64.9 | -31.3 ± 3 | -14 ± 2 | NMR and isotopic isotopic UV | this work [6] [50] |
| $[Pt(CN)_4]^{2-}$ $[PtCl_4]^{2-}$ | CN ⁻ H ₂ O | $11 \pm 1^{\text{ b}}$ $1.8 \times 10^{-7 \text{ d}}$ | 25.1 ± 0.4 87.9 | -142 ± 2 | -27 ± 2 -17 ± 2 | NMR isotopic | [48] [47,49] |

^a The rate constant reported are for the exchange of a particular coordinated X⁻. The rate constant for an unspecified X⁻ is therefore four times greater and the corresponding ΔS^{\ddagger} value is R ln 4 = 11.5 greater.

^b k_2 in s⁻¹ mol⁻¹ kg.

^c Averaged value (see Fig. 6).

^d k_1 in s⁻¹ M⁻¹ = k_1 (in s⁻¹)/4[H₂O], for the exchange of a particular X⁻.

of the reactant and the transition state. In particular, coordinated and free CN^- are well known to form hydrogen bond with water and even protonation can occur [20]. For $[Au(CN)_4]^-$ the slightly positive ΔV^{\ddagger} value could as well be assigned to a synchronous I mechanism. This is further supported by the early observations that the ligand substitution rate is sensitive on the nature of both the incoming and the leaving group [25].

It is of interest to compare the reactions of Au(III) complexes with the analogous Pt(II) ones. The Au(III) complexes are more reactive than the Pt(II) complexes towards substitution (Table 6) [46,47]. The ligand exchange is 600 times faster on $[Au(CN)_4]^-$ than $[Pt(CN)_4]^2^-$ [48] and occurs in both cases only through a CN⁻ nucleophilic attack. The exchange of chloride on $[AuCl_4]^-$ and $[PtCl_4]^2^-$ occurs by fundamentally different processes. Depending on the chloride concentration and on the temperature, the exchange on $[AuCl_4]^-$ involves a nucleophilic attack by Cl⁻ or by H₂O [49]. The chloride attack is negligible on $[PtCl_4]^2^-$. For the aquation pathway, Au(III) [50] is approximately 150 times faster than Pt(II) (Table 6).

In conclusion, the chloride exchange on $[AuCl_4]^-$ can occur either through a direct nucleophilic attack of Cl⁻ or an aquation pathway. The variable pressure experiment $(\Delta V_2^{\pm Au,Cl} = -14 \pm 2 \text{ cm}^3 \text{ mol}^{-1})$ clearly indicate the operation of an I_a or A mechanism. For the cyanide exchange on $[Au(CN)_4]^-$, the observed rate constant varies about nine orders of magnitude depending on the pH domain where HCN does not act as nucleophile.

5. Supplementary material

Supplementary material including table listing the reactions conditions, the rate constants obtained, the

values calculated based on the fitted parameters of the rate laws and supplementary figures are available from the authors upon request.

Acknowledgements

Financial support for this research provided by the Swiss National Science Foundation is acknowledged.

Appendix A

The line shape of the ¹³C NMR spectra of KCN dissolved in water as a function of pH are affected by proton exchange on HCN and can be calculated with the Kubo–Sack formalism which allows for a calculation of the NMR line shape with chemical exchange between different sites [51]. Due to the spin–spin coupling between ¹H and ¹³C a three sites exchange has to be considered. A site is therein characterised by a resonance frequency, $\omega_i = 2\pi v_i$, a population P_i and a transverse relaxation in the absence of exchange, $1/T_{2i}$.

The NMR line width is calculated with Eq. (A1).

$$V(\omega) = C \times \operatorname{Re}(\mathbf{1}\mathbf{K}^{-1}\mathbf{P}) \tag{A1}$$

where $\mathbf{1}$ is the unity vector, *C* is a scaling factor and \mathbf{P} is a column vector with fractional populations of the different sites and the matrix \mathbf{K} is given by Eq. (A2).

$$\mathbf{K} = \mathbf{D} + \mathbf{R} - \mathbf{i}(\mathbf{\Omega} - \omega \mathbf{I}) \tag{A2}$$

where I is a three-dimensional unit matrix and R and Ω are the diagonal matrices of resonance frequencies and transverse relaxation rates given by Eqs. (A3) and (A4)

$$\mathbf{R} = \begin{vmatrix} -1/T_{2\text{HCN}} & 0 & 0\\ 0 & -1/T_{2\text{HCN}} & 0\\ 0 & 0 & -1/T_{2\text{CN}} \end{vmatrix}$$
(A3)

$$\Omega = \begin{vmatrix} -\omega_{\rm HCN} + J_{\rm CH}/2 & 0 & 0\\ 0 & -\omega_{\rm HCN} - J_{\rm CH}/2 & 0\\ 0 & 0 & -\omega_{\rm CN} \end{vmatrix}$$
(A4)

The exchange matrix, D_1 , for the proton exchange on HCN in water is given by Eq. (A5).

$$\mathbf{D}_{1} = \begin{bmatrix} 1/\tau_{\rm HCN} & \mathbf{H}^{\beta}\mathbf{CN} & \mathbf{CN}^{-} \\ 1/\tau_{\rm HCN} & 0 & 1/\tau_{\rm HCN} \\ 0 & -1/\tau_{\rm HCN} & 1/\tau_{\rm HCN} \\ 1/(2\tau_{\rm CN}) & 1/(2\tau_{\rm CN}) & -1/\tau_{\rm CN} \end{bmatrix}$$
(A5)

We distinguish two sites (H^{α}CN and H^{β}CN) depending on the α/β state of the proton spin) accessible from the initial CN⁻ site by a single step exchange. The lifetime $\tau^{\rm HCN}$ and the fractional population $P^{\rm HCN}$ are exactly the same for both HCN sites and the probability of a direct ' $\alpha\beta$ flip-flop' exchange being negligible.

 D_1 can be expressed in terms of k_r^{HCN} , the inverse of the mean lifetime in HCN site.

with $P^{\text{CN}}/\tau_{\text{CN}} = P^{\text{H}^{\alpha}\text{CN}}/\tau_{\text{HCN}} + P^{\text{H}^{\beta}\text{CN}}/\tau_{\text{HCN}} P^{\text{CN}}/\tau_{\text{CN}} = P^{\text{HCN}}/\tau_{\text{HCN}} P^{\text{CN}}/\tau_{\text{CN}} = P^{\text{HCN}}k_{\text{r}}^{\text{HCN}}$

At pH > 7 the Kubo–Sack formalism was also used to extract rate constant of cyanide exchange on $[Au(CN)_4]^-$. The exchange matrix accounts for two exchange processes, the proton exchange on HCN (as described before) and the cyanide exchange on the $[Au(CN)_4]^-$ complex which is introduced as a fourth site in the matrix **D**₂.

We consider that the exchange can occur only via a CN^{-} ion and HCN itself is inactive. This consideration was confirmed by the rate law found for the Au(III) metal centre.

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$$\mathbf{D_{l}} = \left| \begin{array}{ccc} -k_{\rm r}^{\rm HCN} & 0 & k_{\rm r}^{\rm HCN} \\ 0 & -k_{\rm r}^{\rm HCN} & k_{\rm r}^{\rm HCN} \\ P^{\rm HCN}/(2P^{\rm CN})k_{\rm r}^{\rm HCN} & P^{\rm HCN}/(2P^{\rm CN})k_{\rm r}^{\rm HCN} & -P^{\rm HCN}/P^{\rm CN}k_{\rm r}^{\rm HCN} \end{array} \right|$$



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