



# A kinetic study of the reduction of tetrachloroaurate(III) ions by the cyano complexes of iron(II), tungsten(IV) and molybdenum(IV)

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## Abstract

The kinetics of the reduction of tetrachloroaurate(III) by the cyano complexes of Fe(II), W(IV) and Mo(IV) have been studied in aqueous acidic medium. The reactions of  $\text{Fe}(\text{CN})_6^{4-}$  and  $\text{W}(\text{CN})_8^{4-}$  display first-order kinetics in both  $[\text{AuCl}_4^-]$  and  $[\text{M}(\text{CN})_n^{4-}]$  ( $\text{M}=\text{Fe}$  and  $n=6$ ,  $\text{W}$  and  $n=8$ ) while  $[\text{H}^+]$  has a retarding effect on the reaction rate for both the Fe and W reactions. An acid dissociation constant,  $K_{a1}$ , for the  $\text{Fe}(\text{CN})_6^{4-}$  reaction has been established kinetically to be  $K_{a1} = (9.1 \pm 0.5) \times 10^{-3}$  M ( $\text{p}K_{a1} = 2.04$ ) at  $\mu = 1.2$  M while the previously unknown  $K_{a1}$  for the  $\text{W}(\text{CN})_8^{4-}$  reaction was found to be  $K_{a1} = 0.33 \pm 0.09$  M ( $\text{p}K_{a1} = 0.48$ ). Alkali metal cations such as  $\text{Na}^+$  and  $\text{Cs}^+$  and denoted as  $(\text{cat}^+)$  accelerate the reaction. Some reactions were performed under second order (stoichiometric) conditions while other were performed under pseudo-first order conditions; rate constants utilizing these two techniques were mutually consistent. From the acid dependence and variation of the ionic strength of the reaction medium and the Bronsted-Bjerrum equation it has been established that  $\text{Au}^{\text{III}}\text{Cl}_4^-$  and  $\text{H}(\text{cat}^+)\text{M}(\text{CN})_n^{2-}$  ( $\text{M}=\text{Fe}$  and  $n=6$  or  $\text{M}=\text{W}$  and  $n=8$ ) are the reactive species during the course of the reactions. The reaction between  $\text{Mo}(\text{CN})_8^{4-}$  and  $\text{AuCl}^-$  is first order in  $[\text{AuCl}^-]$  and second order in  $\text{Mo}(\text{CN})_8^{4-}$ . Reactions were performed under stoichiometric conditions and kinetic data was treated with a third order integrated rate law. The reaction is independent of  $[\text{H}^+]$  and  $[\text{cat}^+]$ . From the retarding effect of  $\text{Cl}^-$  and  $\text{Mo}(\text{CN})_8^{3-}$  on the rate of the  $\text{Au}^{\text{III}}\text{Cl}_4^-$  reduction, it is concluded that the molecular formula of the intermediate gold(II) species en route to  $\text{Au}^{\text{I}}\text{Cl}_2^-$  is  $\text{Au}^{\text{II}}\text{Cl}_3^-$ . Activation parameters for all three reactions have been obtained from the Eyring equation.

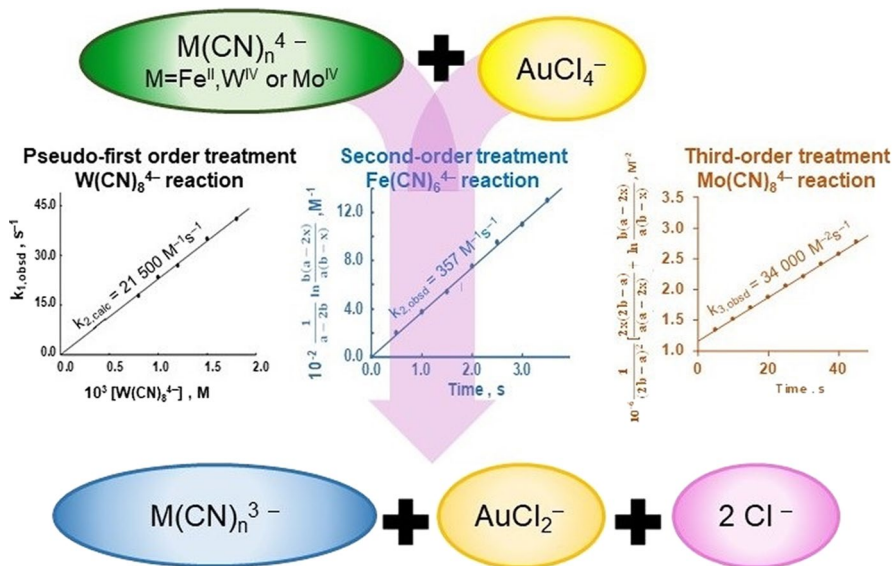
This paper is dedicated to our co-author and friend, Prof Stephen S. Basson, whom passed away on 24 September 2023 at the age of 83 years, for his contribution to the Inorganic and Physical Chemistry research group of the Free State university.

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It was concluded that all three reactions follow the same mechanism but that the reverse reaction in the equilibrium between the intermediate gold(II) species,  $\text{Au}^{\text{II}}\text{Cl}_3^-$ , and the product  $\text{Mo}^{\text{V}}(\text{CN})_8^{3-}$  is only significant in the  $\text{Mo}^{\text{IV}}(\text{CN})_8^{4-}$  reduction of  $\text{Au}^{\text{III}}\text{Cl}_4^-$ . This was also the cause for  $\text{Mo}(\text{CN})_8^{4-}$  showing a second order dependency.

### Graphical abstract

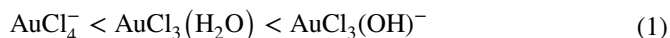


**Keywords** Redox kinetics · Acidic medium · Mechanism · Rate law · Activation parameters

### Introduction

Much less is known about the two-electron reduction of the tetrachloroaurate(III) than about the substitution kinetics of gold(III)  $d^8$  species, of which the tetrachloroaurate(III) ion is a member. Reduction with non-metal ions or molecules as reducing agents such as oxalic acid [1, 2], iodide [3], thiocyanate [4], hydroxylamine [5], L-histidine [6] and hydrazoic acid [7], are some of the reported electron transfer kinetics studies involving the tetrachloroaurate(III) ion. In these studies, except for the oxalic acid reduction, a first order dependence on  $\text{AuCl}_4^-$  and the reducing agent was observed. For the oxalic acid study, a fractional order in oxalic acid was observed. The oxidation of iodide ions was studied at constant  $[\text{H}^+]$ , but for all the other of the above-mentioned studies, an increase in hydrogen ion concentration has a decreasing effect on the reaction rate. The hydrogen ion effect was assigned to the protonation equilibrium of  $\text{AuCl}_4^-$  in the hydroxylamine [5] and

hydrazoic acid [7] studies and to the protonation of oxalate [1, 2] and histidine [6] in these oxidation studies. The reaction rate also decreases with increasing chloride ion concentration. A relative high concentration of chloride ions suppress hydrolysis of the  $\text{AuCl}_4^-$  and the decrease in reaction rate with increasing  $[\text{Cl}^-]$  could be due to the reactivity of the Au(III) species in the order [8]



The reduction of  $\text{AuCl}_4^-$  with the metal ions  $\text{Pt}^{2+}$  and  $\text{Fe}^{2+}$  [8] and the metal ion complex,  $\text{Pt}(\text{CN})_4^{2-}$  [9] as reducing agents has also been reported. The rate of the  $\text{AuCl}_4^-/\text{Pt}^{2+}$  reaction is independent of the chloride ion concentration in the range  $0.25 \text{ M} < [\text{Cl}^-] < 1.0 \text{ M}$  and the rate decrease with increasing  $[\text{H}^+]$ . The rate of the  $\text{AuCl}_4^-/\text{Fe}^{2+}$  reaction show an increase with increasing  $[\text{Cl}^-]$  for  $0.05 \text{ M} < [\text{Cl}^-] < 1.0 \text{ M}$  and a decrease with increasing  $[\text{H}^+]$ . The reaction also shows an inverse first-order dependence on added  $\text{Fe}^{3+}$  ions to the reaction mixture.

The oxidation of tetracyanoplatinate(II) by  $\text{AuCl}_4^-$  show three reactive Au(III) species depending on the amount of  $\text{Cl}^-$  in the reaction mixture. For  $[\text{Cl}^-] < 2 \times 10^{-4} \text{ M}$  and pH 0 the neutral Au(III) species,  $\text{AuCl}_3(\text{H}_2\text{O})$ , is the dominant species. Oxidation with  $\text{AuCl}_4^-$  as the exclusive oxidant has been studied with  $[\text{Cl}^-] \geq 0.25 \text{ M}$  and a pH of ca. 0 [9]. For  $2 \times 10^{-4} < [\text{Cl}^-] < 0.25 \text{ M}$  and at a pH of ca. 5, parallel oxidation with  $\text{AuCl}_4^-$  and  $\text{AuCl}_3(\text{OH})$  was detected [9]. The reactions with the above-mentioned gold(III) species proceed via chloride-bridge inner-sphere electron transfer mechanisms.

The interpretation of a reaction mechanism by which two-electron oxidizing agents, such as gold(III) in the  $\text{Au}^{3+}/\text{Au}^+$  system, reacts, is simplified when it reacts with a stable, one-electron reducing agent such as  $\text{M}(\text{CN})_n^{4-}$  with  $\text{M} = \text{Fe}(\text{II})$ ,  $n = 6$ , or  $\text{M} = \text{W}$  or  $\text{Mo}$  and  $n = 8$ .

Hexacyanoferrate(II) is oxidized to hexacyanoferrate(III) by a number of oxidants in acidic, neutral and alkaline medium [10]. In the oxidation by permanganate [11] and peroxydisulphate [12–14] in aqueous acidic medium, the dependence of the reaction rate on pH indicates that the species  $\text{HFe}(\text{CN})_6^{3-}$  and  $\text{H}_2\text{Fe}(\text{CN})_6^{2-}$  are involved. The oxidation of the metal cyano complexes,  $\text{Mo}(\text{CN})_8^{4-}$  and  $\text{W}(\text{CN})_8^{4-}$  with peroxydisulphate [15, 16] in alkaline medium and with nitrous acid [17, 18] have been studied in our laboratory. An alkali metal ion catalysis was significant in the peroxydisulphate oxidation studies. In the nitrous acid oxidation study, an equilibrium concentration of the nitrosonium ion,  $\text{NO}^+$ , has been proposed as the active oxidizing species.

## Experimental

Potassiumnickeltetracyanide,  $\text{K}_2\text{Ni}(\text{CN})_4$ , was prepared as described by Vogel [19] while potassium octacyanotungstate(IV)dihydrate,  $\text{K}_4\text{W}(\text{CN})_8 \cdot 2\text{H}_2\text{O}$  [20], and potassium octacyanomolybdate(IV)dihydrate,  $\text{K}_4\text{Mo}(\text{CN})_8 \cdot 2\text{H}_2\text{O}$  [21], were prepared as described by Leipoldt and co-workers. The latter two complexes were used as primary standards [22] after recrystallization. All other reagents were Merck “pro

analisi” standard and used as received.  $\text{AuCl}_4^-$  solutions were prepared in  $\geq 0.25$  M NaCl and, if required, supplemented with NaCl and/or  $\text{NaClO}_4$  to maintain a constant ionic strength ( $\mu$ ) and standardized with EDTA in the presence of  $\text{K}_2\text{Ni}(\text{CN})_4$  [23]. Fresh solutions of  $\text{K}_4\text{Fe}(\text{CN})_6 \cdot 3\text{H}_2\text{O}$  were prepared every 2 h as aqueous solutions of this complex are unstable towards oxidation [24]. Solutions of  $\text{Fe}(\text{CN})_6^{4-}$  were standardized as described previously [19, 25] directly prior to use. Double distilled water was used throughout. The temperature was controlled to within  $0.1$  °C with a Fryka-Kaltetechnik KB 300 water bath fitted with a Thermomix 1440 thermostat. All reactions were carried out in a diffuse light laboratory as aqueous solutions of especially  $\text{Mo}^{\text{V}}(\text{CN})_8^{3-}$  are sensitive to light [26, 27]. Detailed reaction conditions and obtained kinetic data may be found in Supplementary Information, Tables S1–S9.

Kinetic parameters of reactions as shown in Eq. 2



were obtained under pseudo first order, second order or third order conditions.

## Second and third order reactions

Data collected under almost stoichiometric conditions ( $[\text{M}(\text{CN})_n^{4-}]_0 \sim 2[\text{AuCl}_4^-]_0$  with the subscript “0” denoting initial time or time = 0) were obtained by treatment of time/reactant concentration data either with the second order integrated Eq. 3 if second order kinetics was observed ( $\text{M} = \text{Fe}$ ,  $n = 6$  and  $\text{M} = \text{W}$ ,  $n = 8$ ) or, if third order kinetics prevailed ( $\text{M} = \text{Mo}$ ,  $n = 8$ ), with the third order integrated rate law shown in Eq. 4 [28].

$$\frac{1}{a - 2b} \ln \left[ \frac{b(a - 2x)}{a(b - x)} \right] = k_{2,\text{obsd}} t \quad (3)$$

$$\frac{1}{(2b - a)^2} \left[ \frac{2x(2b - a)}{a(a - 2x)} + \ln \frac{b(a - 2x)}{a(b - x)} \right] = k_{3,\text{obsd}} t \quad (4)$$

In Eqs. 3 and 4,  $a$  = initial concentration of  $\text{M}(\text{CN})_n^{4-}$ ,  $b$  = initial concentration of  $\text{AuCl}_4^-$  and  $x$  = concentration of  $\text{AuCl}_4^-$  that reacted at time  $t$ . This also implies  $2x$  = concentration of  $\text{M}(\text{CN})_n^{4-}$  that has reacted at time  $t$ .

## Pseudo-first order reactions

The variation of  $[\text{AuCl}_4^-]$  for the  $\text{Fe}(\text{CN})_6^{4-}/\text{AuCl}_4^-$  reaction has also been performed under pseudo-first order conditions with  $[\text{AuCl}_4^-]_0$  up to 16-fold in excess over  $[\text{Fe}(\text{CN})_6^{4-}]_0$ . The subscript “0” indicates time zero. In the case of the  $\text{W}(\text{CN})_8^{4-}$  reaction with  $\text{AuCl}_4^-$ , the excess in  $[\text{W}(\text{CN})_8^{4-}]_0$  was up to 13 times over that of  $[\text{AuCl}_4^-]_0$ . These conditions were deemed sufficient for pseudo-order conditions, because Lente provided evidence in his book [29] that an excess of

fourfold is enough for a flooding (pseudo-first order) process in chemical kinetics. We have previously tested this observation of Lente and confirmed it experimentally as valid [30–32]. Electronic limitations of the apparatus in the form of a noisy background at high ionic strengths as well as large extinction coefficients of reactants, compromised data obtained from reactions where a larger than 16-fold excess of one reactant over the other was used. These pseudo-first order experiments were conducted to compare rate constants obtained from pseudo-first order data treatments with those obtained from second order data treatments. Pseudo-first order data were generated from concentration/time traces and fitted either to the exponential rate law shown in Eq. 5 [30, 31] or to its linearised form, Eq. 6, where  $M = \text{Fe}$  and  $n = 6$  or  $M = \text{W}$  and  $n = 8$ .

$$[\text{M}(\text{CN})_n^{4-}]_t = [\text{M}(\text{CN})_n^{4-}]_0 e^{(-k_{1,\text{obsd}} \cdot t)} \quad (5)$$

$$\ln [\text{M}(\text{CN})_n^{4-}]_t = \ln [\text{M}(\text{CN})_n^{4-}]_0 - k_{1,\text{obsd}} \cdot t \quad (6)$$

General reaction conditions for performing each reaction type are as follow:

### The $\text{AuCl}_4^-/\text{Fe}(\text{CN})_6^{4-}$ reaction

Firstly, this reaction was studied under almost stoichiometric conditions ( $[\text{Fe}(\text{CN})_6^{4-}]_0 \sim 2.02[\text{AuCl}_4^-]_0$ ) on a Durrum Gibson model D110 stopped-flow connected to a Tektronix 5103 N oscilloscope. The increase in  $[\text{Fe}(\text{CN})_6^{3-}]$ ,  $\epsilon_{420\text{nm}}\{\text{Fe}(\text{CN})_6^{3-}\} = 1000 \text{ M}^{-1} \text{ cm}^{-1}$  and  $\epsilon_{420}\{\text{AuCl}_4^-\} = 243 \text{ M}^{-1} \text{ cm}^{-1}$ , was measured at 420 nm and  $25.0 \pm 0.1$  °C. The  $\text{AuCl}_2^-$  [3] and  $\text{Fe}(\text{CN})_6^{4-}$  species [30] do not contribute to the absorbance at this wavelength. Electronic spectrums for the  $\text{AuCl}_4^-$ ,  $\text{Fe}(\text{CN})_6^{4-}$  and  $\text{Fe}(\text{CN})_6^{3-}$  species may be found elsewhere [3, 30]. The collected stopped-flow spectrometer volt data for the  $\text{Fe}(\text{CN})_6^{4-}$  reactions were converted to concentration data using Eq. 7 ( $C = \text{concentration}$ ,  $V = \text{volt}$  measured on stopped-flow at times  $t$ , initially (i.e. at  $t = 0$ ) and at the end of the reaction ( $t = \infty$ )) following the ratio approach of Carlyle and Espenson [34] since any measured quantity proportional to concentration, here volt, can only be used directly in pseudo-first order reaction data treatment. Other reaction orders require physically measured data to be converted to concentration data prior to fitting to obtain the correct rate constants. Concentration data were then fitted to the second order integrated rate equation, Eq. 3.

$$[C]_t = [C]_0 \cdot \frac{(V_t - V_\infty)}{(V_0 - V_\infty)} \quad (7)$$

Secondly, the variation of  $[\text{Fe}(\text{CN})_6^{4-}]$  for the reaction of  $\text{AuCl}_4^-$  with  $\text{Fe}(\text{CN})_6^{4-}$  has also been studied on an Olis RSM 1000F stopped-flow spectrophotometer measuring change in  $[\text{Fe}(\text{CN})_6^{4-}]$  with time under pseudo-first order conditions with  $[\text{AuCl}_4^-]_0$  up to 16 fold in excess over  $[\text{Fe}(\text{CN})_6^{4-}]_0$  to compare obtained rate constants under pseudo-order conditions with the second order rate constants obtained under second order reaction conditions.

Tables S1–S5 (Supplementary Information) summarise reaction conditions and kinetic data for the  $\text{AuCl}_4^-/\text{Fe}(\text{CN})_6^{4-}$  reaction.

### The $\text{AuCl}_4^-/\text{W}(\text{CN})_8^{4-}$ reaction

For the  $\text{AuCl}_4^-/\text{W}(\text{CN})_8^{4-}$  reaction the decrease in  $[\text{AuCl}_4^-]$ ,  $\epsilon_{306}\{\text{AuCl}_4^-\} = 4733 \text{ M}^{-1} \text{ cm}^{-1}$ , at 306 nm (an isobestic point for the  $\text{W}(\text{CN})_8^{4-}/\text{W}(\text{CN})_8^{3-}$  system,  $\epsilon_{306}\{\text{W}(\text{CN})_8^{4-}\} = \epsilon_{306}\{\text{W}(\text{CN})_8^{3-}\} = 881 \text{ M}^{-1} \text{ cm}^{-1}$ ) was monitored at  $25.0 \pm 0.1 \text{ }^\circ\text{C}$ , also on a Durrum Gibson model D110 stopped-flow instrument, with firstly, an excess of  $[\text{W}(\text{CN})_8^{4-}]$  ranging from 2.8 to 7.7 over  $[\text{AuCl}_4^-]$  (Fig. 1a) and by applying Eq. 3 in a second order kinetic data treatment, see Tables S6 and S7 reactions 79–124. Electronic spectra for the  $\text{W}(\text{CN})_8^{4-}$  and  $\text{W}(\text{CN})_8^{3-}$  systems may be found elsewhere [31]. The collected volt data from the stopped-flow spectrometer were also converted to concentration following Carlisle's ratio approach [34] and Eq. 7 as describe in A above.

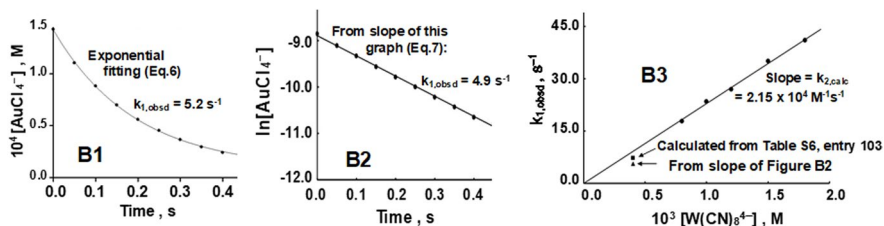
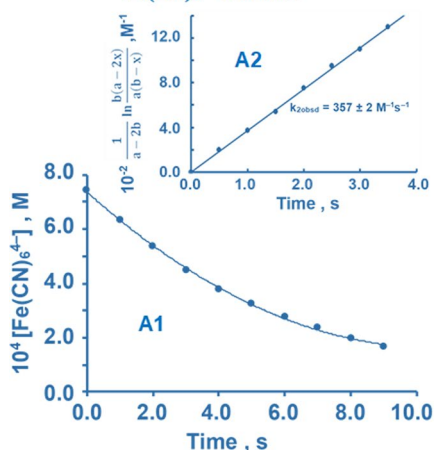
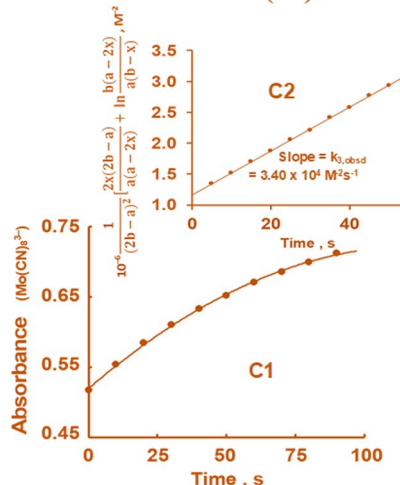
In a second approach of data treatment for this reaction, we considered the data obtained from the same reactions where the  $[\text{W}(\text{CN})_8^{4-}]$  excess ranged from 2.2 to 7.7 over  $[\text{AuCl}_4^-]$  (reactions 86–92 in Table S6) as if the reaction was performed under pseudo-order kinetics. Here, the integrated laws 5 and 6 were applied to data of these seven reactions. We followed this approach because Lente provided evidence in his book [29] that an excess of fourfold is enough for a flooding (pseudo-first order) process in chemical kinetics. The rate constants obtained from second order treatment (Eq. 3) and from the pseudo-first order treatment (data from reactions 75–81 applying Eqs. 5 and 6) were mutually consistent.

Thirdly, the variation of  $[\text{W}(\text{CN})_8^{4-}]$  for the reaction of  $\text{AuCl}_4^-$  with  $\text{W}(\text{CN})_8^{4-}$  has been studied on an Olis RSM 1000F stopped-flow spectrophotometer by measuring the change in  $[\text{AuCl}_4^-]$  with time under pseudo-first order conditions. The  $[\text{W}(\text{CN})_8^{4-}]_0$  was up to 13 times larger than  $[\text{AuCl}_4^-]_0$  to compare pseudo-order rate constants with the second order rate constants obtained under second order reaction conditions.

Kinetic data and reaction conditions for each of these  $\text{AuCl}_4^-/\text{W}(\text{CN})_8^{4-}$  reactions may be found in Supplementary Information Tables S2, S6 and S7.

### The $\text{AuCl}_4^-/\text{Mo}(\text{CN})_8^{4-}$ reaction

Kinetic data for the  $\text{AuCl}_4^-/\text{Mo}(\text{CN})_8^{4-}$  reaction was obtained under almost stoichiometric conditions with  $[\text{Mo}(\text{CN})_8^{4-}] \sim 2.02[\text{AuCl}_4^-]$  at  $20 \pm 0.1 \text{ }^\circ\text{C}$  by monitoring the absorbance increase as  $\text{Mo}(\text{CN})_8^{3-}$  is formed at 390 nm on a Pye Unicam SP 1700 double-beam spectrophotometer. Here,  $\epsilon_{390}\{\text{Mo}(\text{CN})_8^{3-}\} = 1333 \text{ M}^{-1} \text{ cm}^{-1}$ ,  $\epsilon_{390}\{\text{AuCl}_4^-\} = 437 \text{ M}^{-1} \text{ cm}^{-1}$  and  $\epsilon_{390}\{\text{Mo}(\text{CN})_8^{4-}\} = 121 \text{ M}^{-1} \text{ cm}^{-1}$ . UV/vis spectrums for  $\text{Mo}(\text{CN})_8^{4-}$  and  $\text{Mo}(\text{CN})_8^{3-}$  may be found elsewhere [31]. The total absorbance measured at time  $t$ ,  $A_t$ , was then converted to the concentration of  $\text{Mo}(\text{CN})_8^{4-}$  that has reacted at time  $t$  (this is  $2 \times$  in Eq. 5) utilising Eq. 8 and by noting the path length,  $\ell$ , is 1 cm.

**B: Pseudo first-order treatment of  $W(CN)_8^{4-}$  reaction showing flooding excess should be  $\geq 4$** 

**A: Second-order treatment of  $Fe(CN)_6^{4-}$  reaction**

**C: Third-order treatment of  $Mo(CN)_8^{4-}$  reaction**


**Fig. 1** **A1** Second order  $Fe(CN)_6^{4-}/AuCl_4^-$  reaction trace obtained with a Durrum Gibson model D110 stopped-flow spectrophotometer with  $[Fe(CN)_6^{4-}] = 7.42 \times 10^{-4}$  M,  $[AuCl_4^-] = 3.67 \times 10^{-4}$  M,  $[H^+]_{(HCl)} = 0.241$  M,  $\mu_{(NaCl)} = 1.27$  M,  $T = 25.0 \pm 0.1$  °C (entry 3 Table S1). **A2** Second order  $\frac{1}{a-2b} \ln \left[ \frac{b(a-2x)}{a(b-x)} \right]$  vs. time plot for this reaction. **B1**  $W(CN)_8^{4-}/AuCl_4^-$  reaction trace using a Durrum Gibson model D110 stopped-flow, and **B2** pseudo-first order  $\ln[W(CN)_8^{4-}]$  vs. time plot for the same reaction.  $[W(CN)_8^{4-}] = 4.00 \times 10^{-4}$  M;  $[AuCl_4^-] = 1.42 \times 10^{-4}$  M;  $[H^+]_{(HCl)} = 0.253$  M;  $\mu_{(NaCl)} = 1.01$  M;  $T = 25.0 \pm 0.1$  °C (entry 86, Table S6). **B3** Graph of  $[W(CN)_8^{4-}]$  vs. pseudo first order rate constants,  $k_{1,obsd}$ , for the  $W(CN)_8^{4-}/AuCl_4^-$  reaction. The middle point at  $[W(CN)_8^{4-}] = 0.4$  mM has a y-coordinate of  $k_{1,obsd} = k_{2,obsd} \times [W(CN)_8^{4-}]$  and  $k_{2,obsd}$  is tabulated in Table S5, entry 103. Other data are from Table S2, obtained on an Olis RSM 1000F stopped-flow instrument. It is clear that a flooding excess of only 2.81 (as in **B1** and **B2**) is not good enough for a pseudo first order data treatment because the bottom point of  $[W(CN)_8^{4-}] = 0.4$  mM deviate much from the line (2<sup>nd</sup> order treatments are then required). An excess of 5.7 do'nt (data from Table S2). **C1** Third order  $Mo(CN)_8^{4-}/AuCl_4^-$  reaction trace obtained with a Pye Unicam SP 1700 double-beam spectrophotometer with  $[Mo(CN)_8^{4-}] = 7.42 \times 10^{-4}$  M;  $[AuCl_4^-] = 3.67 \times 10^{-4}$  M; (reaction 127 in Table S8)  $[H^+]_{(HCl)} = 0.241$  M;  $\mu_{(NaCl)} = 1.27$  M;  $T = 20.0 \pm 0.1$  °C, and **C2** third order  $\frac{1}{(2b-a)^2} \left[ 2x(2b-a) + \ln \frac{b(a-2x)}{a(b-x)} \right]$  vs. time plot for this reaction

$$[Mo(IV)]_{\text{reacted at time } t} = 2x = \frac{A_t / \ell - \epsilon_{Mo(IV)} \cdot [Mo(IV)]_o - \epsilon_{Au(III)} \cdot [Au(III)]_o}{\epsilon_{Mo(V)} - \epsilon_{Mo(IV)} - \frac{1}{2} \epsilon_{Au(III)}} \quad (8)$$

The obtained data was then inserted into the third order integrated rate equation, Eq. 4 [33], and fitted (Fig. 1c) to obtain third order rate constants by noting that  $[\text{Mo}^{\text{IV}}(\text{CN})_8^{4-}]_0 = a$  and  $[\text{Au}^{\text{III}}\text{Cl}_4^-]_0 = b$  in Eq. 4.

Kinetic data and reaction conditions for each of these  $\text{AuCl}_4^-/\text{Mo}(\text{CN})_8^{4-}$  reactions may be found in Supplementary Information Tables S8 and S9 (reactions 125–166).

The stoichiometry of the  $\text{M}(\text{CN})_8^{4-}$  reactions ( $\text{M} = \text{Mo}, \text{W}$ ) were determined volumetrically by titrating the formed  $\text{M}(\text{CN})_8^{3-}$  with ascorbic acid in the presence of  $\text{CdCl}_2$ , using Variamine Blue B hydrochloride (CI37255) as indicator. The obtained ratio of  $\text{M}(\text{CN})_8^{4-}:\text{AuCl}_4^-$  was 2:1 and mirrored the 2:1 stoichiometry of the  $\text{Fe}(\text{CN})_6^{4-}/\text{AuCl}_4^-$  reaction determined by Zacharov et al. [33]. This stoichiometry is reflected in Eq. 2 above.

## Results and discussion

### Reactant orders

#### The $\text{AuCl}_4^-/\text{Fe}(\text{CN})_6^{4-}$ reaction

This reaction was first studied under almost stoichiometric conditions ( $[\text{Fe}(\text{CN})_6^{4-}]_0 \sim 2.02[\text{AuCl}_4^-]_0$ ). Reaction conditions are summarised in Table S1; five reactions were performed. Fig. 1A shows an example of the treatment of data utilising the integrated second order rate equation, Eq. 3. Linearity of such plots for reactions 1–5 implies the order with respect to each reactant is one. Since the obtained second order rate constants are constant (average  $k_{2,\text{obsd}} = 352 \text{ M}^{-1} \text{ s}^{-1}$  for reactions 1–5) irrespective of the initial concentration of the reactants (e.g. the  $\text{Fe}(\text{CN})_6^{4-}$  concentration range was  $4.45 \times 10^{-4} \leq [\text{Fe}(\text{CN})_6^{4-}]_0 \leq 1.04 \times 10^{-3} \text{ M}$ ), it follows that the mechanism of these reactions is not subject to any dominant equilibrium reaction at  $\mu = 1.27 \text{ M}$ .

The choice of stoichiometric concentration conditions came about because electronic limitations of the apparatus in the form of a noisy background at high ionic strengths compromised kinetic results when the concentration of one reactant was in a very large excess over the other. Historically, pseudo-first order reaction conditions required one reactant in excess over the other in the range 10–100 fold or even more.

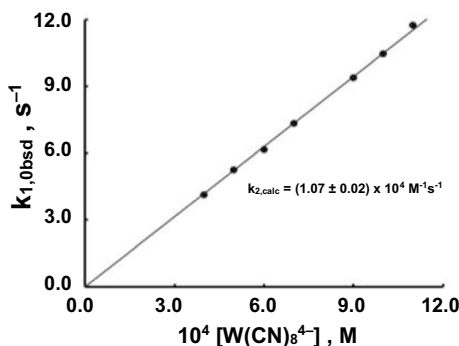
However, secondly, the availability of a new Olis RSM 100 stopped flow with improved optics over a 1976 Durrum Gibson model D110 stopped-flow instrument allowed us to also study this reaction under the best possible pseudo-order kinetic conditions with the concentration of the limiting reagent, here  $\text{Fe}(\text{CN})_6^{4-}$ , between 6 and 16 times less than that of the other reactant,  $\text{AuCl}_4^-$ , Table S2. We consider this concentration range sufficient for pseudo-order conditions because, as noted above, Lente provided evidence in his book [29] that an excess of fourfold is enough for a flooding (pseudo-first order) process in chemical kinetics. We have previously tested this observation of Lente and confirmed it experimentally as valid [30–32]. The rate constants obtained from the second order treatment (Eq. 3) and from the pseudo-first order treatment applying Eqs. 5 and 6 and plotted in Fig. S1 (data from



reactions 21–26 in Table S2) were mutually consistent ( $k_{2,\text{obsd}}=357 \text{ M}^{-1} \text{ s}^{-1}$  using Eq. 3 (Fig. 1A) and  $k_{2,\text{obsd}}=510 \text{ M}^{-1} \text{ s}^{-1}$  from the  $k_{1,\text{obsd}}$  vs  $[\text{AuCl}_4^-]$  plot in Fig S1. The non-zero intercept of Fig. S1 (Supplementary Information) implies a second reaction is also consuming  $\text{Fe}(\text{CN})_6^{4-}$  even when no  $\text{AuCl}_4^-$  is present. Elding and co-workers also reported [35] a non-zero intercept in reactions between  $\text{AuCl}_4^-$  and sulfite at  $[\text{Cl}^-]=0.20 \text{ M}$  but at high  $[\text{Cl}^-]$  (1.0 M) zero intercepts were found. These authors proposed that the non-zero intercepts are the result of noticeable quantities of  $\text{AuCl}_3(\text{OH})^-$  (or  $\text{AuCl}_3(\text{H}_2\text{O})$  depending on pH) that may form during mixing of reactants, and that these newly formed species reacts fast in parallel with  $\text{AuCl}_4^-$  as oxidant of  $\text{Fe}(\text{CN})_6^{4-}$ . As our results paralleled this, we did not research the exact nature of this non-zero Y-axis intercept any further, but we shall show below that  $\text{Na}^+$  and  $\text{Cs}^+$  ions have a catalytic effect on the  $\text{AuCl}_4^-/\text{Fe}(\text{CN})_6^{4-}$  reaction, and that Prussian Blue forms during the course of the reaction as  $\text{AuCl}_2^-$  forms and abstracts  $\text{CN}^-$  ions from  $\text{Fe}(\text{CN})_6^{4-}$  and or  $\text{Fe}(\text{CN})_6^{3-}$ . Both these observations may also contribute to the observed non-zero Y-intercept.

### The $\text{AuCl}_4^-/\text{W}(\text{CN})_8^{4-}$ reaction

This reaction was first monitored by measuring disappearance of the limiting reagent,  $\text{AuCl}_4^-$ , with time. The  $[\text{W}(\text{CN})_8^{4-}]$  excess over  $[\text{AuCl}_4^-]$  ranged from 2.8 to 7.7, Table S6 (Supplementary Information), reactions 86–92. By applying Eq. 3 in a second order graphic kinetic data treatment, see for example Fig. S2 in Supplementary Information, second order rate constants,  $k_{2,\text{obsd}}$ , were obtained. The obtained  $k_{2,\text{obsd}}$  rate constants were within experimental error constant, Table S6, implying here also that the orders of the reaction with respect to each reactant is one and that the mechanism of this reactions is not subject to any dominant equilibrium reaction



**Fig. 2** First order graph for the reaction of  $\text{AuCl}_4^-$  and  $\text{W}(\text{CN})_8^{4-}$ .  $[\text{AuCl}_4^-]=1.423 \times 10^{-4} \text{ M}$ ;  $[\text{HCl}]=0.253 \text{ M}$ ;  $\mu=0.26 \text{ M}$ ;  $T=25 \pm 0.1 \text{ }^\circ\text{C}$ ;  $\lambda=306 \text{ nm}$ . This graph was obtained by treating the raw voltage data from the Durrum Gibson model D110 stopped-flow spectrophotometer to obtain  $k_{1,\text{obs}}$  rate constants for entries 86–92 (Table S6) as if they were pseudo first order utilizing Eq. 6. The calculated second order rate constant  $k_{2,\text{calc}}$  from the above graph came very close to the rate constants in Table S6 obtained from a second order treatment utilising Eq. 4 (the average  $k_{2,\text{obsd}}$  for reactions 86–92 utilizing Eq. 4 was  $1.36 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$ , i.e. 79% agreement)

step. The average  $k_{2,\text{obsd}}$  value for reactions 86–92 is  $1.30 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$  under the conditions of Table S6.

Secondly, we applied Lente's suggestion that a flooding excess of 4 over the limiting reagent is enough to satisfy pseudo-order conditions. We therefore treated the same data of the reactions 86–92 above as if they were valid for a pseudo-order reaction and found pseudo-first order rate constants. Fig. 1B1 and B2 give an example of this treatment type for the  $\text{Fe}(\text{CN})_6^{4-}/\text{AuCl}_4^-$  reaction. The flooding excess in these reactions was between 2.8 and 7.7. The obtained  $k_{1,\text{obsd}}$  rate constants were plotted against the  $[\text{W}(\text{CN})_8^{4-}]$  (Fig. 2) and gave a second order rate constant of  $k_{2,\text{calc}} = 1.07 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$ . This rate constant is mutually consistent with the rate constant calculated during the second order treatment using Eq. 3 for these reactions ( $1.30 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$ ) and implies once again the order with respect to each reactant is one. This result also proves again Lente's results in his book [29] that a flooding excess of 4 over the limiting reagent is enough to satisfy pseudo-order conditions. In fact, our results showed that even an excess of 2.8 still fitted the same line and indicates that under suitable conditions, even a flooding excess of 3 rather than 4 may be enough, but see also the results of the next paragraph.

In a third attempt to place the order determination of  $\text{W}(\text{CN})_8^{4-}$  and  $\text{AuCl}_4^-$  beyond doubt, a complete new set of reactions were performed on the newly available Olis RSM100 stopped-flow instrument with improved optics, this time with the  $[\text{W}(\text{CN})_8^{4-}]$  excess 4–14 times that of the  $[\text{AuCl}_4^-]$ . Data are summarised Table S2, reactions 27–31, and the obtained pseudo-first order plot of rate constant ( $k_{1,\text{obsd}}$ ) vs  $[\text{W}(\text{CN})_8^{4-}]$  are shown in Fig. 1B3. The so-obtained rate constant,  $k_2 = 2.15 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$ , is mutually consistent with the rate constant of reaction 103 in Table S6,  $k_{2,\text{obs}} = 1.84 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$ , obtained under equivalent conditions 46 years before on a Durrum Gibson model D110 stopped-flow instrument utilising a second order data treatment with Eq. 3. We therefore confidently report rate constants and first order behaviour for both  $\text{W}(\text{CN})_8^{4-}$  and  $\text{AuCl}_4^-$  in this reaction.

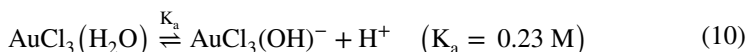
### The $\text{AuCl}_4^-/\text{Mo}(\text{CN})_8^{4-}$ reaction

This reactions was studied with  $[\text{Mo}(\text{CN})_8^{4-}] \sim 2.02[\text{AuCl}_4^-]$ , i.e. stoichiometric conditions. Results are summarised in Tables S8 and S9, Supplementary Information. However, the second order integrated rate equation, Eq. 3, did not result in any linear plots. Rather, third order plots with Eq. 4 were linear, see Fig. 1C2. This indicated a first order dependence on  $\text{AuCl}_4^-$  and a second order dependence on  $\text{Mo}(\text{CN})_8^{4-}$ . Rate constants did not remain constant with increase in reactant concentrations but decreased (entries 125–130, Table S8). This is indicative of a reverse (equilibrium) step of appreciable rate in the reaction mechanism of this reaction. The equilibrium step was observed and will be discussed below when the  $\text{Cl}^-$  ion dependence and influence of the oxidised product,  $\text{Mo}^{\text{V}}(\text{CN})_8^{3-}$  are discussed. It also explains the non-zero intercept with the Y-axis in Fig. 1C2. The third order rate constant of the reaction under conditions of reaction 127 in Table S8 is  $k_{3,\text{obsd}} = 3.4 \times 10^6 \text{ M}^{-2} \text{ s}^{-1}$ .

## Reactive form of reactants.

### Chloride dependence of $\text{AuCl}_4^-$

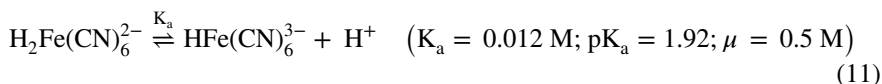
The tetrachloroaurate(III) ion can exist in different forms in solution depending on the concentration of chloride ions in the solution [9].



To ensure the gold(III) species to be in the  $\text{AuCl}_4^-$  form, the  $[\text{Cl}^-]$  was never allowed to drop below 0.25 M to drive equilibrium 9 sufficiently to the left [9, 36–38]. It was calculated from the reported dissociation constants that at no stage during the study did  $\text{AuCl}_4^-$  undergo chloride displacement to a larger extent than 1% under the reaction conditions used ( $[\text{Cl}^-] > 0.25 \text{ M}$ ,  $\text{pH} < 3.33$ ).

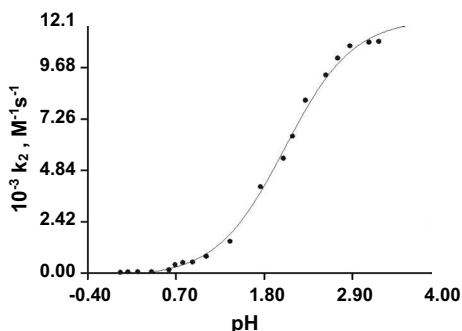
### $\text{H}^+$ dependence of cyanide complexes

Redox studies on the oxidation of hexacyanoferrate(II) in acidic medium by  $\text{MnO}_4^-$  [11] and  $\text{S}_2\text{O}_8^{2-}$  [12–14] have reported the involvement of the species  $\text{H}_2\text{Fe}(\text{CN})_6^{2-}$  ( $\text{p}K_a = 1.92$  at  $\mu(\text{ionic strength}) = 0.5 \text{ M}$  [39]) and  $\text{HFe}(\text{CN})_6^{3-}$  ( $\text{p}K_a = 2.72$  T  $\mu = 0.5 \text{ M}$  [39]) in the reaction mechanism. Since the oxidation of hexacyanoferrate(II) by  $\text{AuCl}_4^-$  was studied in an acidic medium of  $\geq 0.24 \text{ M HCl}$ , the  $\text{Fe}(\text{CN})_6^{4-}$  ion exists mainly in the double protonated form,  $\text{H}_2\text{Fe}(\text{CN})_6^{2-}$ , and equilibrium 11 plays a role in the reaction mechanism.



Yatsimirskii and co-workers [40] reported that the  $\text{Fe}(\text{CN})_6^{4-}/\text{AuCl}_4^-$  reaction does not proceed to completion when  $[\text{H}^+] > 1 \text{ M}$ . In such a strong acid medium the hexacyanoferrate(II) ion exists as a mixture of double and higher protonated

**Fig. 3**  $k_{2,\text{obsd}}$  vs. pH for the oxidation of  $\text{Fe}(\text{CN})_6^{4-}$  by  $\text{AuCl}_4^-$ .  $[\text{Fe}(\text{CN})_6^{4-}] = 7.42 \times 10^{-4} \text{ M}$ ;  $[\text{AuCl}_4^-] = 3.67 \times 10^{-4} \text{ M}$ ;  $\mu = 1.21 \text{ M}$  (NaCl);  $T = 25.0 \pm 0.1 \text{ }^\circ\text{C}$ . Data from Table S3 (Supplementary Information)



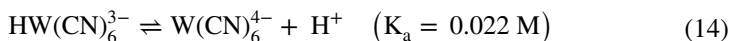
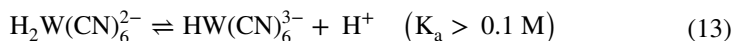
ions. This is mutually consistent with results from our study. The sigmoid curve shown in Fig. 3 shows the rate of the reaction at  $[H^+] = 1.20 \text{ M}$  ( $\text{pH} = -0.079$ ) strives asymptotically to zero. The rate of the oxidation of  $\text{Fe}(\text{CN})_6^{4-}$  by  $\text{AuCl}_4^-$  decrease with an increase in  $[H^+]$  in the range  $4.7 \times 10^{-4} < [H^+] < 1.2 \text{ M}$  (Table S3, entries 32–50, Fig. 3). Calculated from the reported  $K_a = 0.012 \text{ M}$  ( $\text{p}K_a = 1.92$ ) [39] for Eq. 11, the existence of  $\text{HFe}(\text{CN})_6^{3-}$  is  $< 3\%$  at the higher end of the  $[H^+]$ -range (i.e. at  $\text{pH} = -0.079$ ). The rate data show that the reaction rate at  $[H^+] = 1.20 \text{ M}$  is the slowest ( $k_{2,\text{obsd}} = 19 \text{ M}^{-1} \text{ s}^{-1}$ ); it is ca. 5600 times slower than at  $[H^+] = 0.000816 \text{ M}$  ( $k_2 = 1.07 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$ ). We conclude that the double protonated species,  $\text{H}_2\text{Fe}(\text{CN})_6^{2-}$ , is not a strong enough reducing agent to react at a significant rate with  $\text{AuCl}_4^-$  ions and is thus considered as a species in the  $\text{Fe}(\text{CN})_6^{4-}/\text{AuCl}_4^-$  redox system with negligible contribution compared to the reducing contribution of the species  $\text{HFe}(\text{CN})_6^{3-}$  under our experimental conditions. The species  $\text{HFe}(\text{CN})_6^{3-}$  is the dominant reactive species in the  $\text{Fe}(\text{CN})_6^{4-}/\text{AuCl}_4^-$  redox system.

The influence of the  $[H^+]$  on the reaction rate for the  $\text{Fe}(\text{CN})_6^{4-}/\text{AuCl}_4^-$  reaction (Table S3) as well as the sigmoid-shaped graph of  $k_{2,\text{obsd}}$  versus  $\text{pH}$  (Fig. 3,  $\text{pH}$  calculated from  $\text{pH} = -\log [H^+]$ ) indicate a  $\text{p}K_a$  value in the acidic range. A  $K_a$  value of  $(9.1 \pm 0.2) \times 10^{-3} \text{ M}$  ( $\text{p}K_a = 2.04$ ) at  $\mu = 1.2 \text{ M}$  was obtained from a non-linear least squares fit of the kinetic data to Eq. 12 [41–43].

$$k_{\text{obsd}} = \frac{k_{\text{HA}} [H^+] + k_A K_a}{[H^+] + K_a} \quad (12)$$

This kinetically determined  $\text{p}K_a = 2.04$  value for the equilibrium shown in Eq. 11 corresponds well with the potentiometrically determined literature value [39] of the first protonation of  $\text{Fe}(\text{CN})_6^{4-}$ ,  $\text{p}K_a = 1.92$  at  $\mu = 0.5 \text{ M}$ .

The oxidation of  $\text{W}(\text{CN})_8^{4-}$  by  $\text{AuCl}_4^-$  also shows a decrease in reaction rate with an increase in  $[H^+]$  in the range  $0.241 < [\text{HCl}] < 1.203 \text{ M}$  (Table S6 entries 93 to 99). This is an indication that an acid equilibrium of  $\text{W}(\text{CN})_8^{4-}$  play a role in the reaction mechanism. Two protonated octacyanotungstate(IV) species,  $\text{H}_2\text{W}(\text{CN})_8^{3-}$  and  $\text{HW}(\text{CN})_8^{4-}$ , could be involved via their acid dissociation reactions.



From Eq. 14 with  $K_a = 0.022 \text{ M}$  [17, 18] at  $[H^+] = 0.241 \text{ M}$ , the equilibrium is such that more than 92% of the tungsten complex will be in the form of  $\text{HW}(\text{CN})_8^{3-}$ . From Eq. 13 with  $K_a > 0.1 \text{ M}$ , less than 70% tungsten complex will be in the form of  $\text{H}_2\text{W}(\text{CN})_8^{2-}$ . This indicates that the observed  $[H^+]$  dependence of the reaction involves Eq. 13 [44–46]. The rate data in Table S6 entries 93 to 99 indicate that the  $\text{H}_2\text{W}(\text{CN})_8^{3-}$  species is not as strong a reducing agent as  $\text{HW}(\text{CN})_8^{4-}$  while reacting with  $\text{AuCl}_4^-$  ions and the  $\text{HW}(\text{CN})_8^{4-}$  species is therefor considered the more reactive reducing species in the  $\text{W}(\text{CN})_8^{4-}/\text{AuCl}_4^-$  redox system under our experimental conditions.

The variation of the hydrogen ion concentration for the oxidation of  $\text{W}(\text{CN})_6^{4-}$  by  $\text{AuCl}_4^-$  (Table S6 entries 93 to 99 and Fig S3, Supplementary Information) fitted to Eq. 12 yield a  $K_a$  value of  $0.33 \pm 0.09$  M ( $\text{p}K_a = 0.48$ ) at  $\mu = 1.2$  M for the equilibrium shown in Eq. 13. A value for  $K_a$  for  $\text{W}(\text{CN})_6^{4-}$  has not been reported previously in the literature although it has been approximated as  $K_a > 0.1$  M. In addition, from Fig. S3,  $\text{HW}(\text{CN})_8^{4-}$  reacts almost twice as fast ( $k_{2,\text{obsd}} = 5.85 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$ ) with  $\text{AuCl}_4^-$  than  $\text{H}_2\text{W}(\text{CN})_8^{3-}$  ( $k_{2,\text{obsd}} = 3.31 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$ ) under the conditions indicated.

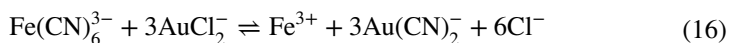
The rate of oxidation for  $\text{Mo}(\text{CN})_8^{4-}$  by  $\text{AuCl}_4^-$  in an acidic medium in the ranges  $0.241 \leq [\text{HCl}] \leq 1.20$  M (Table S9 entries 151 to 155) is independent of the hydrogen ion concentration. As calculated from the acid dissociation constant,  $K_a(\text{Mo}(\text{CN})_8^{4-}) = 0.47$  M [17] at  $I = 1.0$  M, at the lower limit of the acid concentration range, i.e.  $[\text{H}^+] = 0.241$  M, the reducing species exist entirely in the unprotonated  $\text{Mo}(\text{CN})_8^{4-}$  form. As the  $[\text{H}^+]$  increased, the concentration of the monoprotonated species,  $\text{HMo}(\text{CN})_8^{3-}$ , increased until it reached a maximum of ca. 72%  $\text{HMo}(\text{CN})_8^{3-}$  at the higher acid concentration end. The rate constant data of  $k_{3,\text{obsd}}$  in Table S8 thus indicate that the reactivity of the  $\text{Mo}(\text{CN})_8^{4-}$  and  $\text{HMo}(\text{CN})_8^{3-}$  species with respect to  $\text{AuCl}_4^-$  reduction under our experimental conditions are similar.

The  $\text{HFe}(\text{CN})_6^{3-}/\text{AuCl}_4^-$  and the  $\text{HW}(\text{CN})_8^{3-}/\text{AuCl}_4^-$  redox systems are independent of the product concentration,  $[\text{Fe}(\text{CN})_6^{3-}]$  and  $[\text{W}(\text{CN})_6^{3-}]$  respectively (Tables S4 entries 58 to 62 and Table S7 entries 114 to 116) and also of the  $[\text{Cl}^-]$  (Tables S4 entries 51 to 57 and S7 entries 122 to 124 respectively) in the reaction mixture. Ionic strength was kept constant with  $\text{NaClO}_4$  during  $[\text{Cl}^-]$  variations. In contrast, the rate data for the oxidation of  $\text{Mo}(\text{CN})_8^{4-}$  by  $\text{AuCl}_4^-$  show a decrease in the reaction rate with an increase of the product,  $[\text{Mo}(\text{CN})_8^{3-}]$  as well as when the  $[\text{Cl}^-]$  is increased in the reaction mixture (Figs. S4 and S5 in Supplementary Information respectively). This is indicative of an equilibrium step in the reaction mechanism.

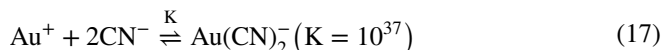
Although the  $\text{AuCl}_2^-$  ions (the reduced product of the reaction) are known to disproportionate [8, 9] according to



precipitation of metallic gold was not observed on the time scale of the kinetic runs of the reaction. In line with Zakharov and co-workers [33], formation of “Prussian Blue” during the latter stages of the reaction was detected for the hexacyanoferrate(II) oxidation. This means that free  $\text{Fe}^{3+}$  ions are generated at the end of the reaction according to the cyanide coordination reaction (Eq. 16).



That  $\text{CN}^-$  is captured by  $\text{AuCl}_2^-$  from the reaction product,  $\text{Fe}(\text{CN})_6^{3-}$ , is the consequence of the affinity of Au(I) for  $\text{CN}^-$  [47] and the stability of  $\text{Au}(\text{CN})_2^-$  according to Eq. 17.



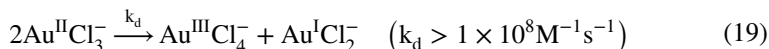
The influence of the ferric ion on the reaction rate in the region  $0.0000 \text{ M} < [\text{Fe}^{3+}] < 4.44 \times 10^{-4} \text{ M}$  was found to be slightly retarding (Table S4 entries 63 to 65). Since  $\text{Fe}^{3+}$  are only generated at the end of the reaction, it was not regarded as an inherent property of the  $\text{HFe}(\text{CN})_6^{3-}/\text{AuCl}_4^-$  redox system.

Before a reaction mechanism for the  $\text{HM}(\text{CN})_n^{3-}/\text{AuCl}_4^-$  ( $\text{M} = \text{Fe}$  and  $n = 6$  or  $\text{M} = \text{W}, \text{Mo}$  with  $n = 8$ ) redox systems can be proposed, it is important to consider the possible formulation of the intermediate gold(II) chloro complex that forms when  $\text{AuCl}_4^-$  is reduced to  $\text{AuCl}_2^-$ . Rich and Taube [48] reported that the formulation of this gold(II) chloro intermediate could either be  $\text{AuCl}_4^{2-}$  or  $\text{AuCl}_3^-$ . From the retarding effect that was observed by variation of  $\text{Mo}(\text{CN})_8^{3-}$  ions as well as  $\text{Cl}^-$  ions in the reaction mixture of the  $\text{Mo}(\text{CN})_8^{4-}$  reduction of  $\text{AuCl}_4^-$ , the gold(II) intermediate is suggested to be  $\text{Au}^{\text{II}}\text{Cl}_3^-$  as shown in Eq. 18.



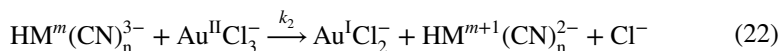
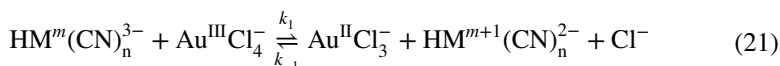
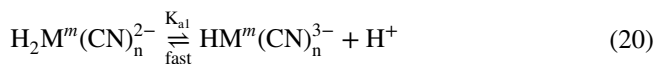
Hence we present our results using  $\text{AuCl}_3^-$  as the gold(II) intermediate complex.

The rapidness by which the  $\text{Au}^{\text{II}}\text{Cl}_3^-$  ion undergoes self-disproportionation [44] according to the Reaction 19



is a side reaction which must also be considered before a mechanism can be proposed. Although Reaction 19 has been reported [48] to be much faster than the reduction of gold(II) to gold(I) by  $\text{Fe}(\text{o-phen})_3^{2+}$ , we do not believe that the self-disproportionation reaction of gold(II) plays a role in the mechanism of the reduction of  $\text{AuCl}_4^-$  to  $\text{AuCl}_3^-$  by the reducing agents  $\text{M}(\text{CN})_n^{4-}$  ( $\text{M} = \text{Fe}$  and  $n = 6$  or  $\text{M} = \text{W}, \text{Mo}$  with  $n = 8$ ). Although  $k_d$  is very large, the probability of two  $\text{Au}^{\text{II}}\text{Cl}_3^-$  ions colliding for self-disproportionation are (especially during the early stages of the reaction) much less than the probability of collision between the gold(II) and the  $\text{M}^{\text{IV}}(\text{CN})_n^{4-}$  ions. Since the standard reduction potential of the  $\text{Fe}(\text{o-phen})_3^{3+}/\text{Fe}(\text{o-phen})_3^{2+}$  couple (1.147 V [49]) is much larger than the reported standard reduction potential of the  $\text{HFe}(\text{CN})_6^{2-}/\text{HFe}(\text{CN})_6^{3-}$  (0.56 V [50]),  $\text{W}(\text{CN})_6^{2-}/\text{W}(\text{CN})_6^{3-}$  (0.57 V [51]) and  $\text{Mo}(\text{CN})_6^{2-}/\text{Mo}(\text{CN})_6^{3-}$  (0.84 V [51]), it follows that the phenanthroline complex is a much weaker reducing agent than the cyano species. It is therefore reasonable to assume that the  $\text{HM}(\text{CN})_n^{3-}$  would react much faster with the gold(II) intermediate than the  $\text{Fe}^{\text{II}}(\text{o-phen})_3^{2+}$  complex would. Therefore we propose the gold(II) intermediate, at least for the reactions reported in this paper, is predominantly removed from the reaction medium by a fast redox reaction with  $\text{M}(\text{CN})_n^{4-}$  or the protonated species  $\text{HM}(\text{CN})_n^{3-}$  ( $\text{M} = \text{Fe}$  and  $n = 6$  or  $\text{M} = \text{W}, \text{Mo}$  with  $n = 8$ ) and not by disproportionation.

Based on the arguments above we propose the mechanism for the reduction of  $\text{AuCl}_4^-$  by  $\text{M}(\text{CN})_n^{4-}$  (for  $\text{M}=\text{Fe}$ ,  $m=\text{II}$  and  $n=6$  or  $\text{M}=\text{W}$ ,  $\text{Mo}$ ,  $m=\text{IV}$  and  $n=8$ ) in acidic medium, to be:



Equation 21 is proposed to be a slow equilibrium and the rate determining step. Application of a steady state approximation to the Au(II) intermediate,  $\text{Au}^{\text{II}}\text{Cl}_3^-$ , yield the theoretical rate law 23 for the oxidation of  $\text{HM}(\text{CN})_n^{3-}$  ( $\text{M}=\text{Fe}^{\text{II}}$  and  $n=6$ , or  $\text{M}=\text{W}^{\text{IV}}$ ,  $\text{Mo}^{\text{IV}}$  with  $n=8$ ) by  $\text{AuCl}_4^-$ .

$$\frac{d[\text{HM}^{m+1}\text{M}(\text{CN})_n^{2-}]}{dt} = \frac{2k_1k_2[\text{HM}^m(\text{CN})_n^{3-}]^2[\text{AuCl}_4^-]}{k_{-1}[\text{Cl}^-][\text{HM}^{m+1}(\text{CN})_n^{2-}] + k_2[\text{HM}^m(\text{CN})_n^{3-}]} \quad (23)$$

To marry the mechanism's rate law, Eq. 23, with what were observed experimentally, the assumptions described below are relevant. Firstly, third order kinetics was observed experimentally for the  $\text{HMo}^{\text{IV}}(\text{CN})_8^{3-}$  oxidation (Fig. 1C). The order with respect to  $\text{HMo}^{\text{IV}}(\text{CN})_8^{3-}$  is two while the order with respect to  $\text{AuCl}_4^-$  is one. Experimentally, an equilibrium step was also indicated by the decrease in the reaction rate with an increase in  $\text{HMo}^{\text{V}}(\text{CN})_8^{2-}$  concentration as well as  $[\text{Cl}^-]$ . Equation 23 satisfies these requirements if  $k_2 \ll k_{-1}$  which implies the term  $k_2[\text{HM}^m(\text{CN})_n^{3-}]$  can be regarded as negligible. The  $\text{HMo}^{\text{IV}}(\text{CN})_8^{3-}$  oxidation is independent of  $[\text{H}^+]$ , which is an indication that equilibrium 21 for this reaction is far to the right.

The oxidations of  $\text{HFe}^{\text{II}}(\text{CN})_6^{3-}$  and  $\text{HW}^{\text{IV}}(\text{CN})_8^{3-}$  by  $\text{Au}^{\text{III}}\text{Cl}_4^-$  are first-order in all reactants, and independent of the product concentration in the reaction mixtures (Tables S4 and S6). This is consistent with the proposed theoretical rate law in Eq. 23 if  $k_2 \gg k_{-1}$  implying the  $k_{-1}[\text{Cl}^-][\text{HM}^{m+1}(\text{CN})_n^{2-}]$  term becomes negligible.

A hydrogen ion dependency was observed for both the tungsten and iron reactions (Fig. 3 and S3) which indicate that equilibrium 20 is significant for these reactions. The observations above lead to the rate law shown in Eq. 24 describing the rate of  $\text{HM}^{m+1}(\text{CN})_n^{2-}$  formation

$$\frac{d[\text{HM}^{m+1}(\text{CN})_n^{2-}]}{dt} = 2k_1[\text{HM}^m(\text{CN})_n^{3-}][\text{AuCl}_4^-] \quad (24)$$

Following the arguments presented in Supplementary Information, Eq. 24 may be written as

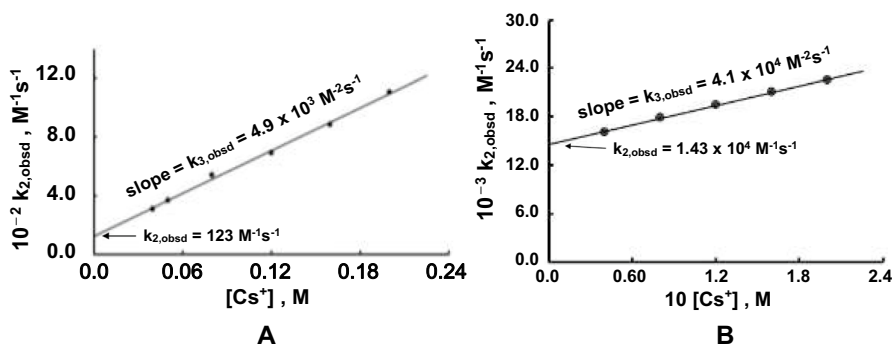
$$\frac{d[\text{HM}^{m+1}(\text{CN})_n^{2-}]}{dt} = \frac{2k_1 K_{a1}}{[\text{H}^+] + K_{a1}} [\text{M}(\text{CN})_n^{4-}]_T [\text{AuCl}_4^-] \quad (25)$$

and

$$k_{\text{obsd}} = \frac{2k_1 K_{a1}}{[\text{H}^+] + K_{a1}} \quad (26)$$

Equation 25 is consistent with the retarding effect that was experimentally observed during an increase in  $[\text{H}^+]$  on the rate of both the tungsten and iron reactions. Additionally, a non-linear least squares fit of the  $[\text{H}^+]$  variation data for the oxidation of  $\text{HFe}(\text{CN})_6^{3-}$  by  $\text{AuCl}_4^-$  (Table S2) to Eq. 26 yield the theoretically predicted values  $k_1 = (5.78 \pm 0.08) \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$  and  $K_{a1} = (9.6 \pm 0.5) \times 10^{-3} \text{ M}$  ( $\text{p}K_{a1} = 2.02$ ). The value of  $K_{a1}$  obtained this way is similar to the experimentally determined value described above ( $K_a = (9.1 \pm 0.2) \times 10^{-3} \text{ M}$ ,  $\text{p}K_a = 2.04$  at  $\mu = 1.2 \text{ M}$ ) and also to the literature value [39],  $\text{p}K_a = 1.92 \text{ M}^{20}$  at  $\mu = 0.5 \text{ M}$ .

Alkali metal ion catalysis was significant in previous redox studies of some cyano complex ions in alkaline medium [15, 16]. The highly negatively charged  $\text{M}(\text{CN})_n^{4-}$  species suggests alkali metal cation association and relatively high association constants,  $K_{\text{ass}}$ , for alkali metal cation association with  $\text{Fe}(\text{CN})_6^{4-}$  have been reported [52]. The respective  $K_{\text{ass}}$ 's are in the order  $K_{\text{ass,Na}^+} < K_{\text{ass,K}^+} < K_{\text{ass,Cs}^+}$ . This led to an investigation of alkali metal ion catalysis by varying the  $\text{Cs}^+$ -ion concentration in the reaction medium. Due to prerequisite reaction conditions, it was however not possible to vary  $[\text{Na}^+]$  at a constant ionic strength. Results in Table S9 entries 156 to 158 indicate that variation of  $[\text{Cs}^+]$  in the reaction medium has no effect on the rate of the  $\text{HMo}(\text{CN})_8$



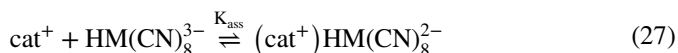
**Fig. 4** Plots of second order rate constant,  $k_{2,\text{obsd}}$ , versus  $[\text{Cs}^+]$  (source =  $\text{CsCl}$ ) with  $T = 25.0 \pm 0.1 \text{ }^\circ\text{C}$  for the **A**  $\text{Fe}(\text{CN})_6^{4-}/\text{AuCl}_4^-$  redox system.  $[\text{Fe}(\text{CN})_6^{4-}] = 7.42 \times 10^{-4} \text{ M}$ ;  $[\text{AuCl}_4^-] = 3.67 \times 10^{-4} \text{ M}$ ;  $[\text{H}^+] = 0.134 \text{ M}$ ;  $[\text{Cl}^-] = 0.334 \text{ M}$ ,  $\mu = 0.34 \text{ M}$ . **B**  $\text{W}(\text{CN})_8^{4-}/\text{AuCl}_4^-$  redox system.  $[\text{W}(\text{CN})_8^{4-}] = 4.00 \times 10^{-4} \text{ M}$ ;  $[\text{AuCl}_4^-] = 1.43 \times 10^{-4} \text{ M}$ ;  $[\text{H}^+] = 0.253 \text{ M}$ ;  $[\text{Cl}^-] = 0.453 \text{ M}$ ,  $\mu = 0.46 \text{ M}$ . The Y-axis intercepts give the rate constant in the absence of  $\text{Cs}^+$  cations but in the presence of  $\text{Na}^+$  cations that also catalyses these reactions. Experimentally, under the conditions employed but in the absence of  $\text{Cs}^+$  cations, the rate constant for the  $\text{Fe}(\text{CN})_6^{4-}$  reaction is  $k_{2,\text{obsd}} = 148 \text{ M}^{-1} \text{ s}^{-1}$  (entry 72, Table S5) and for the  $\text{W}(\text{CN})_8^{4-}$  reaction  $k_{2,\text{obsd}}$  is exactly  $1.43 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$  (entry 117, Table S7)



$^{3-}/\text{AuCl}_4^-$  redox system. Alkali metal ion catalysis for the  $\text{Mo}(\text{CN})_8^{4-}$  ions has mainly been reported for studies in alkaline medium [15, 16] and not for studies in acidic medium [17, 18].

However, results presented in Tables S5 entries 66 to 78 and S7 entries 117 to 121 show an increase in reaction rates of the  $\text{HFe}(\text{CN})_6^{3-}/\text{AuCl}_4^-$  and  $\text{HW}(\text{CN})_8^{3-}/\text{AuCl}_4^-$  redox system with an increase in  $[\text{Cs}^+]$  in the reaction medium. A plot of  $[\text{Cs}^+]$  against  $k_{\text{obsd}}$  for both the  $\text{HFe}(\text{CN})_6^{3-}/\text{AuCl}_4^-$  and  $\text{HW}(\text{CN})_8^{3-}/\text{AuCl}_4^-$  reactions (Fig. 4A and B respectively) confirms the catalytic influence of the alkali metal cation on the reaction rate. The graphs also show an intercept which is the rate constant for the reaction without additionally added  $\text{Cs}^+$  cations. This is because the reaction is performed in the presence of  $\text{Na}^+$  cations as well (a necessity to ensure  $[\text{Cl}^-]$  is high enough to prevent  $\text{AuCl}_4^-$  hydrolyses; the source of  $\text{Cl}^-$  was  $\text{NaCl}$ ). The non-zero intercept signifies the rate of the reaction as catalysed by  $\text{Na}^+$  cations. It is not expected that cation association with the oxidized product,  $\text{Fe}(\text{CN})_6^{3-}$ , plays a major role in the  $\text{Fe}(\text{CN})_6^{4-}/\text{AuCl}_4^-$  redox system, for  $\text{Fe}(\text{CN})_6^{3-}$  has a much lesser tendency towards cation association than the  $\text{Fe}(\text{CN})_6^{4-}$  species [44, 53].

The accelerating effect of the alkali metal cation,  $\text{cat}^+$ , is a clear indication that the alkali metal should be a constituent of the activated complex during electron transfer. Equation 27 should then be an integral part of the reaction mechanism when  $\text{Fe}^{\text{II}}(\text{CN})_6^{4-}$  and  $\text{W}^{\text{IV}}(\text{CN})_8^{4-}$  reduces  $\text{Au}^{\text{III}}\text{Cl}_4^-$ .

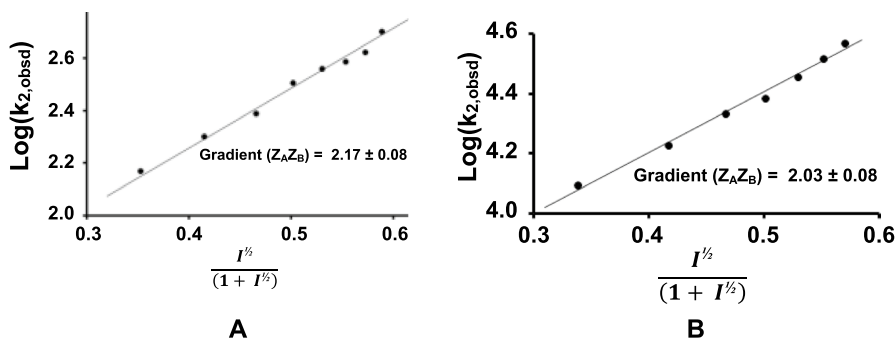


This would then append the rate law shown in Eq. 25 for the  $\text{M}(\text{CN})_n^{4-}/\text{AuCl}_4^-$  redox systems to

$$\frac{d[\text{HM}^{m+1}(\text{CN})_n^{2-}]}{dt} = \frac{2k_1 K_{\text{a1}} K_{\text{ass}} [\text{cat}^+]}{[\text{H}^+] + K_{\text{a1}}} [\text{M}(\text{CN})_n^{4-}]_{\text{T}} [\text{AuCl}_4^-] \quad (28)$$

As per Fig. 4, when more than one alkali metal cation is present in the system, the  $K_{\text{ass}}[\text{cat}^+]$  term in Eq. 28 should be  $\{K_{\text{ass1}}[\text{alkali metal 1}] + K_{\text{ass2}}[\text{alkali metal 2}] + \dots\}$

The influence of the ionic strength of the reaction medium on the reaction rate has been investigated by varying the ionic strength with the addition of sodium chloride to the reaction mixture. Davies [54] and also Pethybridge and Prue [55] reported that the Bronsted-Bjerrum equation [56] for the ionic strength is only valid for ionic strength's smaller than 0.1 M. However, Howlett and Sarsfield [57] applied the Bronsted-Bjerrum equation with success on reactions with ionic strength up to 1.4 M. Dennis et al. [58] in our laboratory also applied it with success at concentrations higher than 0.1 M. Because  $[\text{Cl}^-] > 0.2 \text{ M}$  is compulsory in this study and with the result of Howlett and Sarsfield as basis, the ionic strength of the reaction medium was varied between 0.25 M and 2.0 M (Tables S1 and S6). The results for the  $\text{HFe}(\text{CN})_6^{3-}/\text{AuCl}_4^-$  and the  $\text{HW}(\text{CN})_8^{3-}/\text{AuCl}_4^-$  redox systems clearly show a positive ionic strength dependence while the  $\text{HMo}(\text{CN})_8^{3-}/\text{AuCl}_4^-$  system show a negative ionic strength dependence (Table S9 entries 159 to 166).



**Fig. 5** Bronsted-Bjerrum plot of  $\text{Log}(k_{2,\text{obsd}})$  vs.  $\frac{I^{1/2}}{(1+I^{1/2})}$  ( $I$ = ionic strength) for the **A**  $\text{Fe}(\text{CN})_6^{4-}/\text{AuCl}_4^-$  redox system.  $[\text{Fe}(\text{CN})_6^{4-}] = 7.42 \times 10^{-4}$  M;  $[\text{AuCl}_4^-] = 3.67 \times 10^{-4}$  M. **B**  $\text{W}(\text{CN})_8^{4-}/\text{AuCl}_4^-$  redox system.  $[\text{W}(\text{CN})_8^{4-}] = 4.00 \times 10^{-4}$  M;  $[\text{AuCl}_4^-] = 1.42 \times 10^{-4}$  M. In both cases  $[\text{H}^+] = 0.241$  M;  $T = 25.0 \pm 0.1$  °C; data from Supplementary Information Tables S1 (entries 1–6) and S6 (entries 100–106)

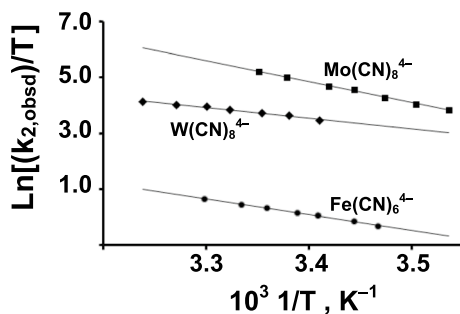
To interpret the data, the logarithmic form of the Bronsted–Bjerrum equation [56, 57], where  $A$  is the Debye–Hückel solvent constant, can be written as

$$\log k = \log k_0 + 2Z_A Z_B A \left( \frac{I^{1/2}}{1 + I^{1/2}} \right) \quad (29)$$

The increase in the ionic strength of the reaction medium resulted in an increase in the reaction rate which indicate that the activated complex is formed by species with the same charge. The data was fitted to the Bronsted-Bjerrum equation with the Debye–Hückel solvent constant for water,  $A \sim 0.51$  at 25 °C (implying  $Z_A Z_B A \approx Z_A Z_B$  in Eq. 29).

A plot of  $\log k$  vs  $\frac{I^{1/2}}{(1+I^{1/2})}$  for the  $\text{HFe}(\text{CN})_6^{3-}/\text{AuCl}_4^-$  and  $\text{HW}(\text{CN})_8^{3-}/\text{AuCl}_4^-$  reactions, Fig. 5A (data from Table S1 entries 6 to 13) and Fig. 5B (data from Table S6 entries 100 to 106), yield a gradient ( $Z_A Z_B$ ) of  $2.17 \pm 0.08$  and  $2.03 \pm 0.08$  respectively. This is consistent with the reactive species for the formation of the activated complex to be  $\text{AuCl}_4^-$  and  $\text{H}(\text{cat}^+)\text{M}(\text{CN})_n^{2-}$  where ( $\text{cat}^+$ ) is an alkali metal ion. The intercept,  $\log k_0$ , yields a value for  $k_0$  of  $25 \pm 1$   $\text{M}^{-1} \text{s}^{-1}$  and  $3.39 \pm 0.04$   $\text{M}^{-1} \text{s}^{-1}$  respectively for the electron transfer rate at zero ionic strength for the above-mentioned redox reactions.

The negative ionic strength effect obtained for the  $\text{HMo}(\text{CN})_8^{3-}/\text{AuCl}_4^-$  redox system (Table S9 entries 159 to 166) could be explained by the equilibrium step, Eq. 20 in the reaction mechanism with  $M = \text{Mo}$  and  $n = 8$ . To explain, it has been establish that increasing the  $[\text{Mo}(\text{CN})_8^{3-}]$  in the reaction medium, a decrease in the reaction rate is observed (Table S8 entries 131 to 136). An increase in the  $[\text{Cl}^-]$  also have a decreasing effect on the reaction rate (Table S8 entries 137 to 143). The ionic strength of the reaction medium was varied by the addition of  $\text{NaCl}$  to the reaction mixture. This implies that an increase in  $\text{Cl}^-$  ions in the reaction mixture will enhance the reverse reaction of the equilibrium. The negative effect of the



**Fig. 6**  $\text{Ln}(k_{2,\text{obsd}}/T)$  versus  $1/T$  from the linearized Eyring equation for the oxidation of the cyano complexes of Fe, W and Mo by  $\text{AuCl}_4^-$ . Top:  $[\text{Mo}(\text{CN})_8^{4-}] = 7.42 \times 10^{-4}$  M;  $[\text{AuCl}_4^-] = 3.67 \times 10^{-4}$  M;  $[\text{H}^+] = 0.241$  (HCl) M;  $\mu$  (NaCl) = 1.27 M (Supplementary Information, Table S8, entries 144–150). Middle:  $[\text{W}(\text{CN})_8^{4-}] = 4.00 \times 10^{-4}$  M;  $[\text{AuCl}_4^-] = 1.42 \times 10^{-4}$  M;  $[\text{H}^+] = 0.253$  M (HCl);  $\mu$  (NaCl) = 0.26 M (Supplementary Information, Table S6 entries 107–113). Bottom:  $[\text{Fe}(\text{CN})_6^{4-}] = 7.42 \times 10^{-4}$  M;  $[\text{AuCl}_4^-] = 3.67 \times 10^{-4}$  M;  $[\text{H}^+] = 0.241$  M (HCl);  $\mu$  (NaCl) = 1.27 M (Supplementary Information, Table S1 entries 14–20)

**Table 1** Activation parameters for the oxidation of cyano complexes of Fe(II), W(IV) and Mo(IV) by  $\text{AuCl}_4^-$  in acidic medium

Reaction	$\Delta H^\ddagger$ (kJ mol <sup>-1</sup> )	$\Delta S^\ddagger$ (J K <sup>-1</sup> mol <sup>-1</sup> )
$\text{Fe}(\text{CN})_6^{4-}$	47 ± 1	-37 ± 3
$\text{W}(\text{CN})_8^{4-}$	31 ± 2	-63 ± 6
$\text{Mo}(\text{CN})_8^{4-}$	62 ± 2	52 ± 5

variation in the ionic strength thus implies that  $k_{-1}$  becomes significantly large and the reverse reaction of equilibrium 21 has a greater influence on the reaction rate than the expected positive ionic strength influence of the reaction medium. The  $\text{W}^{\text{IV}}(\text{CN})_8^{4-}$  and  $\text{Fe}^{\text{II}}(\text{CN})_6^{4-}$  induced reduction of  $\text{AuCl}_4^-$  did not suffer these complications as neither  $\text{Fe}^{\text{III}}(\text{CN})_6^{3-}$  or  $\text{W}^{\text{V}}(\text{CN})_8^{3-}$  nor  $\text{Cl}^-$  have a retarding effect on these reactions.

The activation parameters for the reactions were obtained by the temperature data in Tables S1, S6 and S8. The parameters  $\Delta H^\ddagger$  and  $\Delta S^\ddagger$  were obtained from the Eyring equation (Eq. 30) where  $k_B$  and  $h$  is the Boltzmann and Planck constants respectively

$$k = \frac{k_B T}{h} e^{\left[ \frac{\Delta S^\ddagger}{R} - \frac{\Delta H^\ddagger}{RT} \right]} \quad (30)$$

A non-linear least-squares fit of the variation of temperature data (Tables S1 entries 14 to 20, S6 entries 107 to 113 and S8 entries 144 to 150 and Fig. 6) to Eq. 30 yield the activation parameters  $\Delta H^\ddagger$  and  $\Delta S^\ddagger$  (Table 1). This is the more accurate and modern way of obtaining  $\Delta H^\ddagger$  and  $\Delta S^\ddagger$  and is preferred over graphical methods involving the logarithmic form of Eq. 30 [60]. The obtained values have been validated by the method of Lente et al. [30, 59, 61] using Eq. 31 for each

reaction. Adherence to Eq. 31 proved the expected direct proportionality between the experimental errors of activation enthalpy,  $\sigma\Delta H^\ddagger$ , and activation entropy,  $\sigma\Delta S^\ddagger$ .

$$\sigma\Delta S^\ddagger = \frac{1}{T_{\text{av}}}\sigma\Delta H^\ddagger \quad (31)$$

$T_{\text{av}}$  is the average temperature where experiments have been performed.

## Conclusions

Although the reduction of the  $\text{AuCl}_4^-$  ion by complex cyanides of iron, tungsten and molybdenum takes place by the same mechanism, only the molybdenum reaction exhibited third order kinetics. Both the other reactions exhibited second order kinetics. The order change with respect to  $\text{Mo}(\text{CN})_8^{4-}$  from one to two compared to the first order behaviour of  $\text{Fe}(\text{CN})_6^{4-}$  and  $\text{W}(\text{CN})_8^{4-}$  is the result of the much faster reverse step reaction rate in the equilibrium between  $\text{Au}^{\text{III}}\text{Cl}_4^-$  and  $\text{Mo}^{\text{IV}}(\text{CN})_8^{4-}$  with  $\text{Au}^{\text{II}}\text{Cl}_3^-$ ,  $\text{Mo}^{\text{V}}(\text{CN})_8^{3-}$  and  $\text{Cl}^-$  than the ensuing reaction step rate between  $\text{Au}^{\text{II}}\text{Cl}_3^-$  and  $\text{Mo}^{\text{IV}}(\text{CN})_8^{4-}$  giving the final products  $\text{Au}^{\text{I}}\text{Cl}_2^-$ ,  $\text{Cl}^-$  and  $\text{Mo}^{\text{V}}(\text{CN})_8^{3-}$ , see Eq. 22 in the main text. For the other two reductants, the reaction between either  $\text{Fe}^{\text{II}}(\text{CN})_6^{4-}$  or  $\text{W}^{\text{IV}}(\text{CN})_8^{4-}$  and  $\text{Au}^{\text{II}}\text{Cl}_3^-$  to generate  $\text{Au}^{\text{I}}\text{Cl}_2^-$ ,  $\text{Cl}^-$  and either  $\text{W}^{\text{V}}(\text{CN})_8^{3-}$  or  $\text{Fe}^{\text{III}}(\text{CN})_6^{3-}$  is much faster than the reverse reaction step between either  $\text{W}^{\text{V}}(\text{CN})_8^{3-}$  or  $\text{Fe}^{\text{III}}(\text{CN})_6^{3-}$  and  $\text{Au}^{\text{II}}\text{Cl}_3^-$ . This conclusion is supported by the retarding effect that  $\text{Mo}^{\text{V}}(\text{CN})_8^{3-}$  and  $\text{Cl}^-$  has on the overall molybdenum reaction rate, but no such retarding effect was observed in the ferrocyanide- or the octacyanotungstate(IV)-induced reductions of  $\text{Au}^{\text{III}}\text{Cl}_4^-$ . This also points to the fact the standard reduction potential of the  $\text{Au}^{\text{III}}\text{Cl}_4^- // \text{Au}^{\text{II}}\text{Cl}_3^- / \text{Cl}^-$  couple must be close to that of the  $\text{Mo}^{\text{V}}(\text{CN})_8^{3-} / \text{Mo}^{\text{IV}}(\text{CN})_8^{4-}$  couple exhibiting  $E^\circ = 0.73$  V at  $\mu = 0$  M [62].  $E^\circ$  for the  $\text{W}^{\text{V}}(\text{CN})_8^{3-} / \text{W}^{\text{IV}}(\text{CN})_8^{4-}$  and  $\text{Fe}^{\text{III}}(\text{CN})_6^{3-} / \text{Fe}^{\text{II}}(\text{CN})_6^{4-}$  couples are 0.46 and 0.35 V at  $\mu = 0$  M [62] respectively. The fact that a reverse reaction between  $\text{Au}^{\text{II}}\text{Cl}_3^-$  and  $\text{Mo}^{\text{V}}(\text{CN})_8^{3-}$  was observed is also indicative that the self-disproportionation reaction between two  $\text{Au}^{\text{II}}\text{Cl}_3^-$  anions to give  $\text{Au}^{\text{III}}\text{Cl}_4^-$  and  $\text{Au}^{\text{I}}\text{Cl}_2^-$  is not a major contributing side reaction in the present redox systems. The retarding effect that  $\text{Cl}^-$  has on the overall molybdenum reaction rate is also consistent with a gold(II) molecular formulation of  $\text{Au}^{\text{II}}\text{Cl}_3^-$  rather than  $\text{Au}^{\text{II}}\text{Cl}_4^{2-}$ .

The reaction rate of the iron and tungsten reaction systems decreased with an increase of  $[\text{H}^+]$  in the reaction mixture, but alkali metals such as  $\text{Na}^+$  and  $\text{Cs}^+$  had a large rate enhancing effect on the  $\text{Fe}(\text{CN})_6^{4-}$  reaction and a smaller rate enhancing effect on the  $\text{W}(\text{CN})_8^{4-}$  reaction. The latter observation is consistent with specific alkali metal cation binding taking place in the case of  $\text{Fe}(\text{CN})_6^{4-}$ , while non-specific alkali metal ion association is prevalent in the case of  $\text{W}(\text{CN})_8^{4-}$  reactions. The insensitivity of the  $\text{Mo}(\text{CN})_8^{4-} / \text{AuCl}_4^-$  reaction system towards both  $\text{H}^+$  and  $\text{Cs}^+$  implies a much lesser tendency towards cation association of the reductant.

The ionic strength study of the  $\text{W}(\text{CN})_8^{4-}/\text{AuCl}_4^-$  and  $\text{Fe}(\text{CN})_6^{4-}/\text{AuCl}_4^-$  redox systems showed gradients of 2.03 and 2.17 for  $\log k$  vs  $\frac{I^{1/2}}{(1+I^{1/2})}$  Bjerrum plots. This is consistent, at least for these two reactions, with the charge of the oxidant ( $\text{AuCl}_4^-$ ) being minus one and the charge of the reductant being minus two. Bearing also in mind the results of the  $[\text{H}^+]$  variation and  $[\text{Cs}^+]$ , we conclude the molecular formula for the reductants are most likely  $\text{HCsFe}(\text{CN})_6^{2-}$  and  $\text{HCsW}(\text{CN})_8^{2-}$ . The  $\text{Cs}^+$  alkali metal cation was also shown to be interchangeable with other alkali metal cations, here  $\text{Na}^+$ .

We also conclude from the kinetic results obtained from experiments performed under pseudo-first order and second order conditions in this study, that a flooding excess of 4 over the limiting reagent (rather than the traditionally accepted 10 as a minimum requirement) is enough for interpretable kinetic studies. This mirrors the conclusions published by Lente earlier [29].

Finally, we have demonstrated how the interpretation of a reaction mechanism by which two-electron oxidizing agents, such as gold(III) in the  $\text{Au}^{3+}/\text{Au}^+$  system, reacts, may be simplified when it reacts with stable, one-electron reducing agents such as  $\text{Mo}(\text{CN})_8^{4-}$ ,  $\text{W}(\text{CN})_8^{4-}$  or  $\text{Fe}(\text{CN})_6^{4-}$ .

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## Declarations

**Conflict of interest** The authors are not aware of any conflict of interests.

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