Kinetic investigations of the mechanism of dihydrogen driven catalytic reduction of methylene blue, safranine O, methyl viologen and ferricyanide using platinum carbonyl cluster anions (Chini-clusters) as catalyst

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Abstract

$[Bu_4N]_2[Pt_{12}(CO)_{24}]$ (**1**) catalyses the selective reduction of electron acceptors (**S**), methylene blue (MB^+), safranine O (Saf^+), methyl viologen (MV^{2+}) and ferricyanide by dihydrogen. Macroscopic rate investigations for the cationic substrates in DMF, and for ferricyanide in DMSO have been carried out. In all cases, k_{obs} is given by $k_1 [S] + k_2$, indicating that there are two catalytic cycles. In one of them, the formation of a complex between **S** and $[Pt_{12}(CO)_{24}]^{2-}$ in the rate determining step (rate constant k_1) is followed by electron transfer and/or other fast steps. In the other catalytic cycle, the rate determining step (rate constant k_2) involves formation of the solvated cluster anion $[Pt_{12}(CO)_{24}]^{2-}$. The solvated cluster then undergoes fast reduction by dihydrogen and other reactions. The relative contributions of these two cycles depend on the substrate, and for MB^+, Saf^+, MV^{2+} and $[Fe(CN)_6]^{3-}$ the contribution of the second cycle is about 99%, 55%, 77% and 97%, respectively. Both k_1 and k_2 of ferricyanide are about three orders of magnitude smaller than those of the cationic electron acceptors. The rates of reduction of MB^+ and Saf^+ have also been studied in the presence of added water. Rates increase as the presence of water provides an additional pathway for the reduction of $[Pt_{12}(CO)_{24}]^{2-}$ to $[Pt_9(CO)_{18}]^{2-}$.

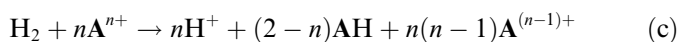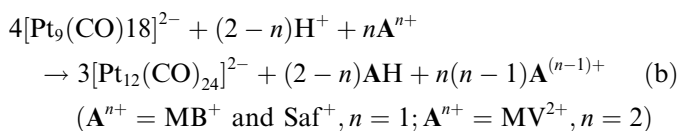*Keywords:* Chini clusters; Kinetics; Catalysis; Reduction by dihydrogen; Organic dyes

1. Introduction

Platinum carbonyl clusters of the general formula $[Pt_3(CO)_6]_n^{2-}$ ($n = 3$, 4, 5 and 6), commonly known as Chini-clusters, are known to equilibrate dihydrogen with two protons and two electrons [1–4]. The tetramer $[Pt_{12}(CO)_{24}]^{2-}$ is thus reduced to the trimer $[Pt_9(CO)_{18}]^{2-}$ according to

$$3[Pt_{12}(CO)_{24}]^{2-} + H_2 \rightleftharpoons 4[Pt_9(CO)_{18}]^{2-} + 2H^+ \qquad (a)$$
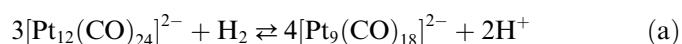
We and others reported mechanistic investigations on this and related reactions [5,6]. We also reported the use of these clusters as catalysts for a variety of selective redox and hydrogenation reactions [7–15]. Recently our findings on the reactions of dihydrogen with $A_n[Pt_{12}(CO)_{24}]$, where A^{n+} is a redox active cation and potential electron acceptor, have also been reported [16]. The redox active cations chosen for these studies were the dyes such as methylene blue (MB^+), safranineO (Saf^+), and methyl viologen (MV^{2+}). Benzyl nicotinamide (BNA^+), a model of NAD^+, was also used as a counter cation. In all cases, reduction of $[Pt_{12}(CO)_{24}]^{2-}$ to $[Pt_9(CO)_{18}]^{2-}$ occurs, and

MB^+, Saf^+, and MV^{2+} are selectively reduced to MBH, SafH and $MV^{+\cdot}$ radical cations, respectively. However, under the same conditions BNA^+ could not be reduced to BNAH. In the above-mentioned work, cyclic voltammetric studies on these cations in DMF are also described. The ability of the clusters to reduce MB^+, Saf^+ and MV^{2+} but not BNA^+ by dihydrogen is found to be in agreement with the redox potentials of the electron acceptors. We had also shown [10,16] that $[Pt_9(CO)_{18}]^{2-}$ could be oxidized back to $[Pt_{12}(CO)_{24}]^{2-}$ according to reaction (b). It is apparent that a combination of reactions (a) and (b) will lead to the *catalytic* reduction of the electron acceptor by dihydrogen according to reaction (c)

$$4[Pt_9(CO)18]^{2-} + (2-n)H^+ + nA^{n+}$$
$$\rightarrow 3[Pt_{12}(CO)_{24}]^{2-} + (2-n)AH + n(n-1)A^{(n-1)+} \quad (b)$$
$$(A^{n+} = MB^+ \text{ and } Saf^+, n = 1; A^{n+} = MV^{2+}, n = 2)$$
$$H_2 + nA^{n+} \rightarrow nH^+ + (2-n)AH + n(n-1)A^{(n-1)+} \quad (c)$$

A simplified catalytic cycle with anions $[Pt_{12}(CO)_{24}]^{2-}$ and $[Pt_9(CO)_{18}]^{2-}$ as catalytic intermediates may thus be proposed (Scheme 1).

The work described in this paper was undertaken with the following objectives: first, to find out to what extent the hypothetical catalytic cycle of Scheme 1 is valid; second, we wanted to see if the general mechanism proposed in Scheme 1 operates for all A^{n+} irrespective of the number of electrons and protons involved in the reduction; third, we wanted to compare the quantitative effects of an *anionic* electron acceptor with that of the *cationic* ones on the rates. Based on simple electrostatic considerations, the reaction between the anionic cluster and an anionic acceptor should be less facile than that involving a cationic acceptor. Finally, we wanted to study the effect of added water, a potential proton donor, on the kinetics of MB^+ and Saf^+ reduction.

All these questions have been addressed by carrying out macroscopic rate studies on the reaction of A^{n+} with dihydrogen in the presence of $[Bu_4N]_2[Pt_{12}(CO)_{24}]$ (1) as the precatalyst. We have also carried out kinetic studies on the catalytic reduction of the *anionic* acceptor ferricyanide. It may be noted that both MB^+ and Saf^+ are two electron and one proton acceptors, but like MV^{2+}, $[Fe(CN)_6]^{3-}$ is a single electron, zero proton acceptor. Our results show that for all the four substrates (**S**), the rate expressions are sim-ilar, and the proposed mechanism (Scheme 1), with some modifications, does operate in all the cases.

2. Results and discussion
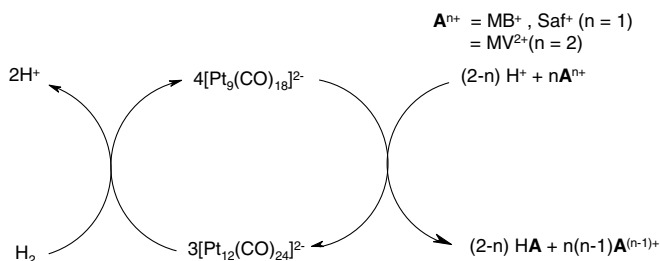
2.1. General background

In our earlier work [16], it was shown that in the *stoichiometric* reactions of $A_n[Pt_{12}(CO)_{24}]$ with dihydrogen, MB^+, Saf^+ and MV^{2+} undergo *selective* reduction. Before commencing rate measurements, it was first established by NMR and ESR spectrometry that under the *catalytic* conditions, i.e. with a large excess of the electron acceptor and **1** as the precatalyst, the selectivity is still maintained and there is no over-reduction or degradation of MBH, SafH or $MV^{+\cdot}$. This indeed is found to be the case (see Section 3).

The rates of catalytic reduction of MB^+ and Saf^+ by dihydrogen were measured by monitoring the rate of disappearance of the characteristic absorbances of the dyes at 665 and 535 nm, respectively. In contrast, for MV^{2+} the rate was measured by monitoring the rate of appearance of $MV^{+\cdot}$ at 398 nm. The extinction coefficients of all the dyes are greater than that of the platinum clusters [16]. Also, since the measurements were carried out in all the cases with a large excess of the dyes (see Section 3), the absorption due to the clusters could therefore be ignored.

However, in the case of ferricyanide, due to much stronger absorptions by the cluster anions, the kinetic measurements could not be monitored by UV–Vis spectrophotometry. The rate of catalytic reduction of $[Fe(CN)_6]^{3-}$ to $[Fe(CN)_6]^{4-}$ by dihydrogen was therefore measured by monitoring changes in the IR (v_{CN}) spectra. Due to good solubility of dihydrogen, the organic electron acceptors and **1** in DMF, the kinetic studies on MB^+, Saf^+ and MV^{2+} were carried out in this solvent. This allows pseudo zero order condition with respect to the concentration of dihydrogen to be maintained and literature reported quantitative data on the reduction of $[Pt_{12}(CO)_{24}]^{2-}$ to $[Pt_9(CO)_{24}]^{2-}$ in DMF to be used for comparison [5,6]. Due to poor solubility of potassium ferricyanide in DMF, dimethylsulfoxide was used as the solvent for this substrate. Preliminary rate measurements at different temperatures showed negligible effect on rates. This observation is similar to what was observed earlier for the redox reactions of $[Pt_{12}(CO)_{24}]^{2-}$ with hydrogen and acid [5,6]. In this work, measurements of activation parameters by Arrhenius and Eyring plots have therefore not been attempted.

2.2. Rate expressions

All the reactions are found to be pseudo first order with respect to the concentration of **1**. As shown in Fig. 1, reasonable straight lines are obtained in the [**1**] vs. initial rate plots. The empirical rate expression is therefore as shown in Eq. (d). It is also clear from Fig. 1(d) that the rates of reduction of $[Fe(CN)_6]^{3-}$ are about three orders of magni-

$A^{n+} = MB^+$, Saf^+ (n = 1)
$= MV^{2+}(n = 2)$

$2H^+$ $4[Pt_9(CO)_{18}]^{2-}$ (2-n) H$^+$ + nA^{n+}

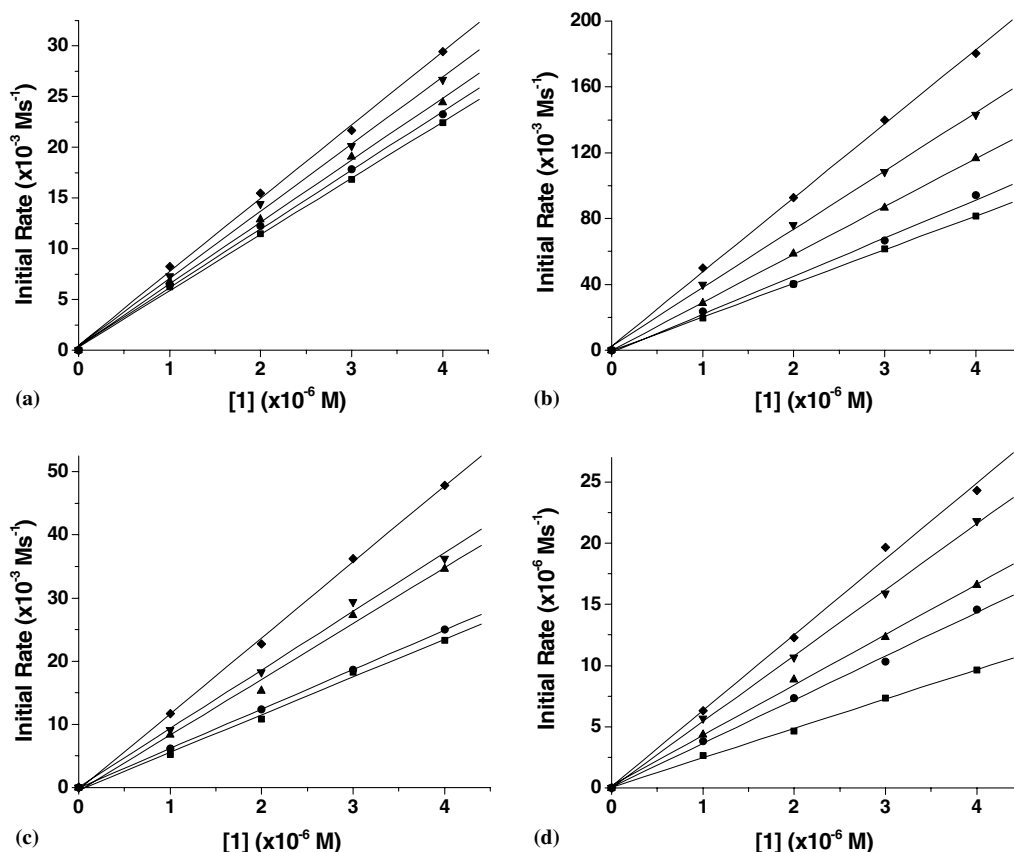H_2 $3[Pt_{12}(CO)_{24}]^{2-}$ (2-n) H**A** + n(n-1)**A**$^{(n-1)+}$

Scheme 1.

Fig. 1. Initial rate vs. [**1**] plot for the dihydrogen driven reduction of electron acceptors (**S**). (a) methylene blue] ($P \times 10^{-5}$ M): P = ■, 3.125; ●, 4.6875; ▲, 6.25; ▼, 9.375; ♦, 12.5, (b) safranine O], ($Q \times 10^{-5}$ M): Q = ■, 7.464; ●, 9.95; ▲, 11.38; ▼, 15.17; ♦ 18.98 , (c) [methyl vilologen], ($R \times 10^{-5}$ M): R = ■, 4.66; ●, 7.46; ▲, 9.33; ▼, 11.66; ♦ 15.55 and (d) [ferricyanide] ($S \times 10^{-5}$ M): S = ■, 101; ●, 151.48; ▲, 176.748; ▼, 252.5 and ♦, 303. One unit of [**1**] ($\times 10^{-6}$ M) is 3.43, 14.25, 5.72 and 14.3 for MB^+, Saf^+, MV^{2+} and $[Fe(CN)_6]^{3-}$, respectively.

tude slower than those of the other electron acceptors. This is also apparent from the observation that measurable spectroscopic change in the catalytic reduction of $[Fe(CN)_6]^{3-}$ takes several hours, while that of the organic substrates takes only a few seconds
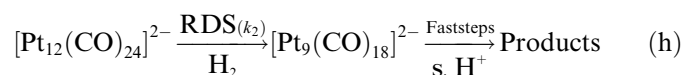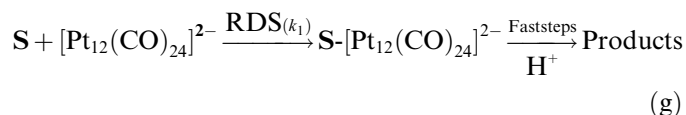
$$-\frac{d[S]}{dt} = k_{obs}\,[\mathbf{1}] \qquad (d)$$

The observed rate constants (k_{obs}) have been measured at different concentrations of the substrates, while maintaining the general condition that [**S**]/[**1**] remains greater than one in all the cases, and much greater than one in most of the cases (see Section 3). Plots of k_{obs} versus [**S**] are given in Fig. 2. The linearity of the plots indicates that for all **S**, Eqs. (e) and (f) give the rate expression and k_{obs}, respectively. Within the concentration range of **S** employed in these studies, saturation kinetics is not observed. Also, as can be seen from Fig. 2, the straight lines for the cationic substrates have very similar intercepts, but different slopes

$$-\frac{d[S]}{dt} = k_1[S][\mathbf{1}] + k_2[\mathbf{1}] \qquad (e)$$

$$k_{obs} = k_1[S] + k_2 \qquad (f)$$

It is clear from the rate law that there are two independent pathways through which the catalytic reduction of **S** by dihydrogen takes place. The first terms of both Eqs. (e) and (f) suggest that there is a pathway where the transition state of the rate-determining step involves **S** and **1**. The slopes of the straight lines in Fig. 2 give the rate constants k_1 that correspond to this pathway. The intercepts of the straight lines in Fig. 2 give k_2 and correspond to the second term of Eqs. (e) and (f). They show that there is another pathway, the rate of which is independent of the concentration of **S**. A mechanism consistent with the observed rate law must therefore involve two rate-determining steps (RDS) as shown by

$$S + [Pt_{12}(CO)_{24}]^{2-} \xrightarrow{\text{RDS}(k_1)} S\text{-}[Pt_{12}(CO)_{24}]^{2-} \xrightarrow[H^+]{\text{Faststeps}} \text{Products}$$

$$(g)$$

$$[Pt_{12}(CO)_{24}]^{2-} \xrightarrow[H_2]{\text{RDS}(k_2)} [Pt_9(CO)_{18}]^{2-} \xrightarrow[s,\ H^+]{\text{Faststeps}} \text{Products} \qquad (h)$$

Further evidence for the proposed rate expression as shown by (f) comes from good agreement between the experimental data and theoretical predictions based on (f), where the values of k_1 and k_2 are optimized for the best
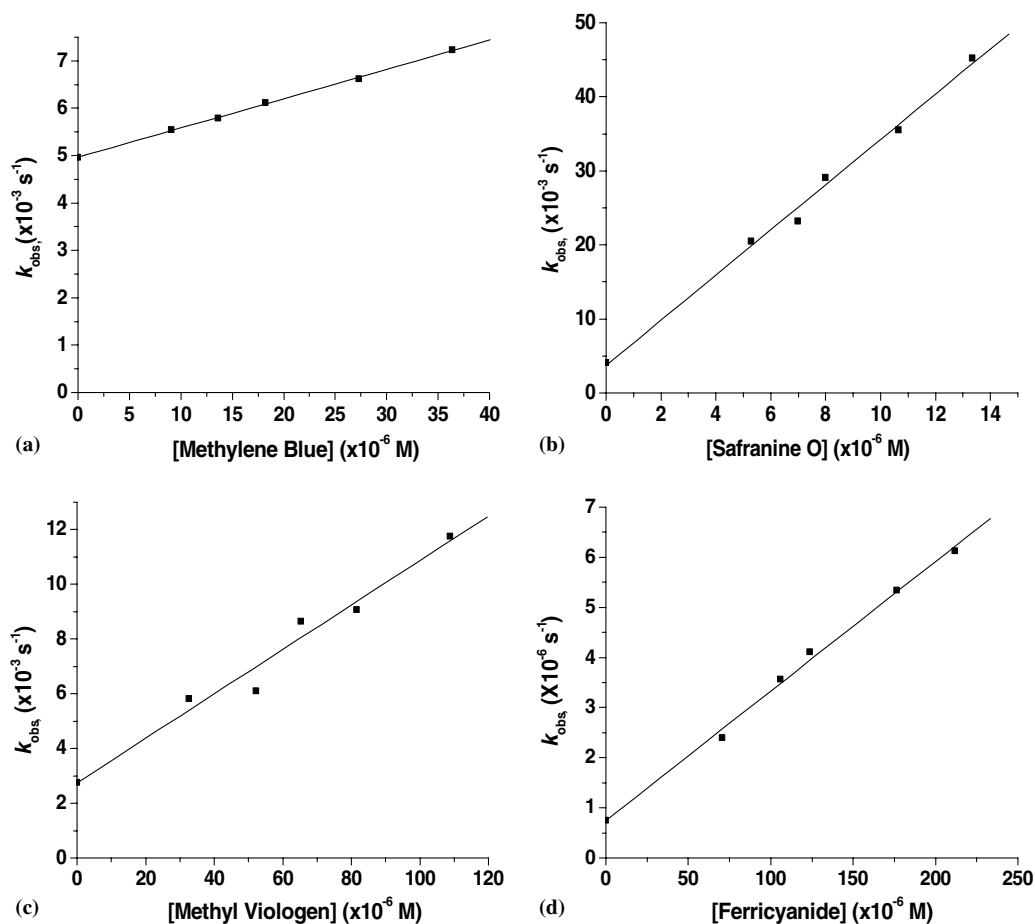
Fig. 2. k_{obs} (calculated from Fig. 1) vs. [substrate] plot for the dihydrogen driven reduction reactions of electron acceptors (**S**). (a), (b), (c) and (d) indicate data for methylene blue, safranine O, methyl viologen and ferricyanide, respectively.

fit. As shown in Fig. 3, for typical catalytic runs, for both MB^+ and Saf^+ the theoretical prediction and the experimental data match well.
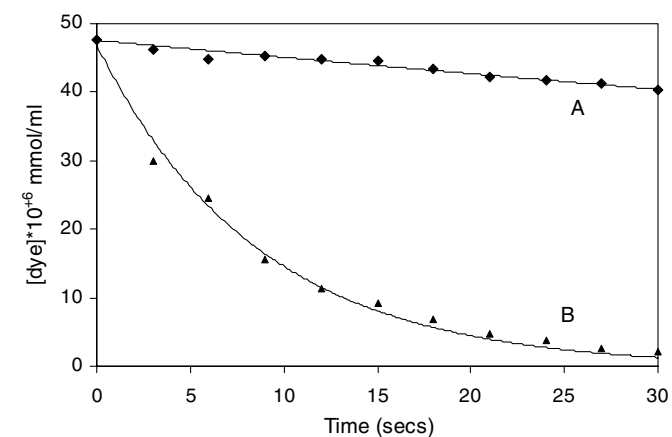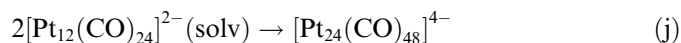

Fig. 3. Comparison of model (continuous line) and experimental data (points). A: Dye = Saf^+Cl^-; [**1**] $= 5.95 \times 10^{-6}$ mmol/ml; B: Dye = MB^+Cl^- and [**1**] $= 20.6 \times 10^{-6}$ mmol/ml.

2.3. Catalytic cycles

A catalytic cycle that corresponds to Eq. (g) is proposed in Scheme 2. The rate determining step involves one $[Pt_{12}(CO)_{24}]^{2-}$ anion and one **S**. To satisfy the stoichiometry of the overall reactions, this is then followed by fast reactions with more $[Pt_{12}(CO)_{24}]^{2-}$, and either proton or more **S** (for **S** = MV^{2+} and $[Fe(CN)_6]^{3-}$) to give $[Pt_{15}(CO)_{30}]^{2-}$ and
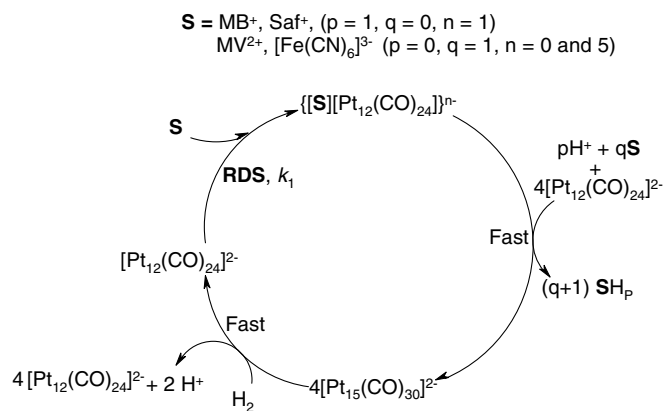
Scheme 2.

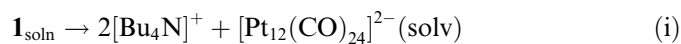the reduced substrate. The reduction of $[Pt_{15}(CO)_{30}]^{2-}$ by dihydrogen in DMF is known to be a fast reaction, and this reaction then completes the catalytic cycle [5,6]. Keeping in mind the inherent limitations of the experimental techniques employed in this work (time scale, detection limit, etc.), it is not possible to say in which precise step(s) the electron transfer(s) take place. In other words, the redox states of $\mathbf{S}$ and the cluster in the species $\{[\mathbf{S}][Pt_{12}(CO)_{24}]\}^{n-}$ are not known.

The catalytic cycle shown in Scheme 1 is consistent with Eq. (h), provided the known rate expression for the reduction of $[Pt_{12}(CO)_{24}]^{2-}$ to $[Pt_9(CO)_{18}]^{2-}$ by dihydrogen is slightly modified. The modifications are required for the following reason. In our earlier report [5], the reduction of $[Pt_{12}(CO)_{24}]^{2-}$ to $[Pt_9(CO)_{18}]^{2-}$ by dihydrogen was shown to be *second order* with respect to the concentration of $\mathbf{1}$. However, the second term of rate expression (h) indicates a rate-determining step that is *first order* with respect to the concentration of $\mathbf{1}$. In other words in the presence of a large excess of $\mathbf{S}$, the order of the reaction, with respect to the concentration of $\mathbf{1}$, changes from second to first

$$\mathbf{1}_{\text{soln}} \rightarrow 2[Bu_4N]^+ + [Pt_{12}(CO)_{24}]^{2-}(\text{solv}) \qquad (i)$$

$$2[Pt_{12}(CO)_{24}]^{2-}(\text{solv}) \rightarrow [Pt_{24}(CO)_{48}]^{4-} \qquad (j)$$

The reactions that may bring about this change are shown by Eqs. (i) and (j). *In the absence of* $\mathbf{S}$, formation of fully solvated $[Pt_{12}(CO)_{24}]^{2-}$, as shown by reaction (i), is fast. The subsequent reaction where two $[Pt_{12}(CO)_{24}]^{2-}$ ions react to form a loose dimer, i.e. reaction (j), is the rate determining step [16]. However, *in the presence of a large excess of* $\mathbf{S}$, formation of solvated $[Pt_{12}(CO)_{24}]^{2-}$ i.e. reaction (i), becomes the rate determining step as far as reduction of $[Pt_{12}(CO)_{24}]^{2-}$ to $[Pt_9(CO)_{18}]^{2-}$ is concerned. This is reasonable since $\mathbf{S}$ may provide the counter cation to $[Pt_{12}(CO)_{24}]^{2-}$ to form loose ion-pairs rather than free fully solvated $[Pt_{12}(CO)_{24}]^{2-}$. A catalytic cycle that takes into account *both the pathways*, (g) and (h) for MB^+ and Saf^+, is shown in Scheme 3. It may be noted that the upper and lower cycles of Scheme 3 correspond to those of Schemes 1 and 2, respectively. Similar cycles can also be drawn for MV^{2+} and ferricyanide.

The rate constants k_1 and k_2 for all the substrates are given in Table 1. From the data, the following conclusion may be drawn. First, as already mentioned both k_1 and k_2 of the $[Fe(CN)_6]^{3-}$ reduction are about three orders of magnitude smaller than those for the cationic substrates.

Where solvation is not the rate-determining step, solvent effects of about one order of magnitude or less on rate constants have been reported in the literature [17–19]. Thus, apart from the solvent effect, other factors must also contribute to the observed large decrease in k_1. A speculative rationalization for this observation is as follows. Since $[Fe(CN)_6]^{3-}$ is a triply charged anion, substantial electrostatic repulsion between $[Pt_{12}(CO)_{24}]^{2-}$ and $[Fe(CN)_6]^{3-}$ is expected. This is expected to contribute substantially to
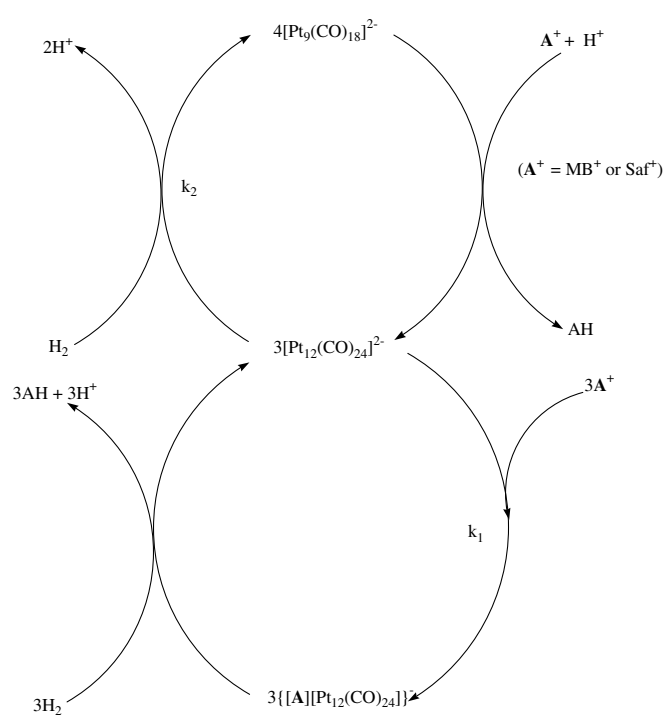
Scheme 3.

Table 1
Rate constants at 27 °C (k_1 and k_2) for the *Chini*-cluster catalyzed dihydrogen driven reduction reactions of different electron acceptor ($\mathbf{S}$)

Electron acceptor ($\mathbf{S}$)	k_1 (10^{-3} M^{-1} s^{-1})	k_2 (10^{-3} s^{-1})	Solvent
Methylene blue	0.06	4.96	DMF
Safranine O	3.05	3.71	DMF
Methyl viologen	0.08	2.74	DMF
Ferricyanide	0.03×10^{-3}	0.7×10^{-3}	DMSO

the decrease in k_1. Further, the ionic strengths of one molar substrate solutions are expected to be 1, 3, and 6 for ACl ($A = MB^+$, Saf^+), ACl$_2$ ($A = MV^{2+}$) and $K_3[Fe(CN)_6]$, respectively. The low k_1 of $[Fe(CN)_6]^{3-}$ is therefore probably due to a combination of electrostatic repulsion, solvent, and kinetic salt effect [20–22].

Second, within the family of the cationic substrates the variation in k_1 for MB^+ and MV^{2+} on the one hand and Saf^+ on the other is notable. It is interesting to note that the electrochemical response of MB^+ and MV^{2+} was also found be similar but different [16] from that of Saf^+. The transition state for the reaction step corresponding to k_1 involves one $\mathbf{S}$ ion. The variation in k_1 between different cationic $\mathbf{S}$, a 50-fold increase between MB^+ and MV^{2+} on the one hand and Saf^+ on the other, is thus ascribed to various factors such as the difference in the Brønsted basicity of the amino side chains (for MB^+ and Saf^+), cationic charge (for MV^{2+}), overall polarity etc.

The variation in k_2, within the family of the cationic substrates, is much less. The transition state for k_2 does not involve $\mathbf{S}$. Therefore, small secondary effects due to the changes in the ionic strength, dielectric constant, etc.

of the solutions, are expected for Saf$^+$, MB$^+$ and MV^{2+}. However, for [Fe(CN)$_6$]$^{3-}$, the *solvation* properties of DMSO would certainly have a direct and major bearing on k_2. The decrease in k_2 in this case must also be partly due to the presence of excess potassium ions, rather than organic cations.

2.4. Effect of added water

Detailed kinetic studies on the reaction of [Pt$_{12}$(CO)$_{24}$]$^{2-}$ with water had been reported by us several years ago [23,24]. In our earlier work, we also reported the reduction of NAD$^+$ and BNA$^+$, where in a biphasic medium (dichloromethane and water) [Saf]$_2$[Pt$_{12}$(CO)$_{24}$] was used as a catalyst [11,16]. In these reactions, Saf$^+$ is reduced to SafH by the cluster which in turn reduces NAD$^+$ and BNA$^+$. As the reduction of Saf$^+$ (and MB$^+$) requires one proton, the presence of trace quantities of water in the organic layer may be expected to have an effect on the reaction rates. For this reason, only a few kinetic runs on the catalytic reduction of Saf$^+$ and MB$^+$, in the presence of added water, have been carried out. For both the dyes, the initial rate increases linearly with increasing concentrations of water (Fig. 4).

The linearity and positive intercepts for both the dyes suggest an empirical rate expression as shown

$$\text{Rate} = k'_1[\text{H}_2\text{O}] + k'_{\text{obs}} \qquad (k)$$

The first term of this rate expression indicates that in the presence of trace amounts of water, there is an additional product-forming pathway. The second term corresponds to the rate in the absence of water, i.e., the rate arising out of the pathways shown in Scheme 3. The reduction of [Pt$_{12}$(CO)$_{24}$]$^{2-}$ to [Pt$_9$(CO)$_{18}$]$^{2-}$ by water is known to exhibit saturation kinetics [23,24]. In the presence of trace quantities of water, if the rate determining step of the water assisted pathway happens to be the reduction of [Pt$_{12}$(CO)$_{24}$]$^{2-}$ to [Pt$_9$(CO)$_{18}$]$^{2-}$ by water, then the rate is

expected to show approximately first order dependence. This is experimentally observed and has not been studied in any further detail.

2.5. Conclusions

Our results show that similar mechanisms operate in the catalytic reductions of the four electron acceptors by dihydrogen. There are two independent pathways: one involving both the cluster and the acceptor in the rate determining step, and the other where only the cluster is involved. Between the two, the second pathway is the dominant one. For ferricyanide the rate constants for both these pathways are orders of magnitude less than those of the cationic dyes.

3. Experimental

3.1. Materials

The Dyes, ACl$_n$ (A = MB$^+$, Saf$^+$ and MV^{2+}, $n = 1$, 1 and 2, respectively) and H$_2$PtCl$_6 \cdot$ 6H$_2$O, were purchased from Aldrich and Johnson and Mathey, respectively, and used without further purification. [Bu$_4$N]$_2$[Pt$_{12}$(CO)$_{24}$] was synthesized according to the literature reported procedures [1]. Unless stated otherwise all synthetic operations were carried out by using standard Schlenk line techniques, with dry glassware, under an inert atmosphere. The solvents were dried, distilled under an atmosphere of pre-purified argon atmosphere and degassed prior to use.

3.2. Physical measurements

Infrared and UV–Vis spectra were recorded on Nicolet Impact 400 and Shimadzu UV 2100 spectrometers, respectively. NMR and ESR spectra were recorded on a Varian VXR-300S and 109C E-line X band spectrometer, respectively.
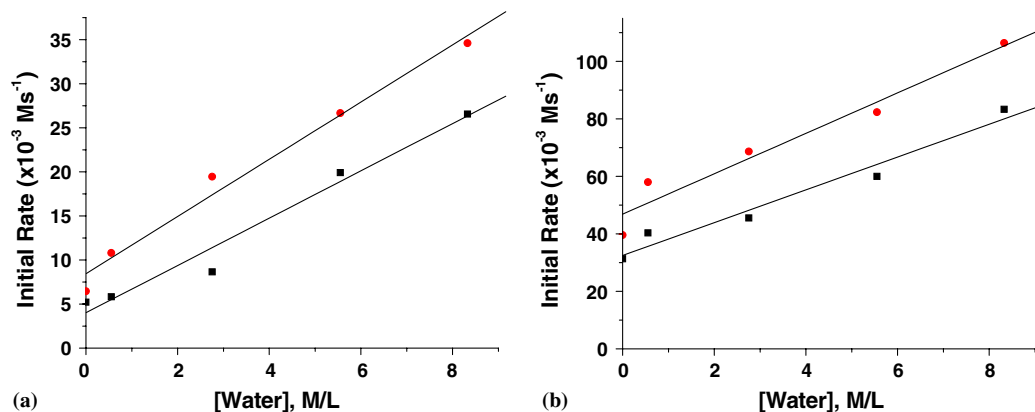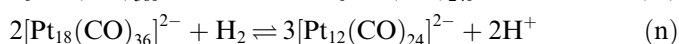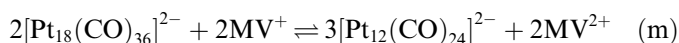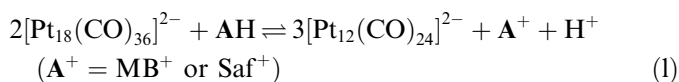

Fig. 4. Initial rate vs. [water] (ML^{-1}) plot for **1** catalyzed dihydrogen driven water added reduction of (a) [methylene blue] (A × 10^{-5} M): A = ■, 2.526; ●, 3.36 with [**1**], 0.297 × 10^{-5} M for both and (b) safranine O (B × 10^{-5} M): B = ■, 1.292; ●, 1.939 with [**1**], 0.238 × 10^{-5} M for both.

3.3. Kinetic studies

Unless mentioned otherwise, all UV–Vis spectroscopic monitoring were carried out within the UV–Vis cuvette at 27 °C by using the standard rubber septa for air-sensitive compounds. All studies have been carried out within the range where Lambert-Beer's law is valid. A constant rate of hydrogen flow has been maintained in all experiments by using a flow meter. Kinetic studies of catalytic reactions on the basis of initial rate measurements are well documented in the literature, and two typical references are given [25,26]. From the slope of change in absorbance versus time plots, initial rates were determined. The time intervals for MB^+, Saf^+, and MV^{2+} were 6 s and for ferricyanide 600 s. In most cases (>80%), the initial rate corresponded to less than 20% of the reaction. Representative absorbance versus time plots and details of initial rate data used in the Figures are given in the supplementary material.

In all cases the reaction was initiated by injecting a solution of $[Bu_4N]_2[Pt_{12}(CO)_{24}]$ of known concentration into a hydrogen saturated solution of the maintained under a constant flow of hydrogen. Variable induction times are observed in all the kinetic runs. The observed induction time is essentially a function of the redox equilibrium expected between A^{n+} and $[Pt_{12}(CO)_{24}]^{2-}$ some of which have been discussed in our earlier papers [5,11,16]. The reactions involved are:

$$2[Pt_{18}(CO)_{36}]^{2-} + AH \rightleftharpoons 3[Pt_{12}(CO)_{24}]^{2-} + A^+ + H^+$$
$$(A^+ = MB^+ \text{ or } Saf^+) \qquad (l)$$

$$2[Pt_{18}(CO)_{36}]^{2-} + 2MV^+ \rightleftharpoons 3[Pt_{12}(CO)_{24}]^{2-} + 2MV^{2+} \quad (m)$$

$$2[Pt_{18}(CO)_{36}]^{2-} + H_2 \rightleftharpoons 3[Pt_{12}(CO)_{24}]^{2-} + 2H^+ \qquad (n)$$

Due to the fact that the catalytic runs are carried out with large excess of A^{n+}, at the start of the kinetic run the equilibriums (l) and (m) are shifted to the left to a variable extent. The cluster $[Pt_{18}(CO)_{30}]^{2-}$ is known to undergo very fast reduction by dihydrogen and once it is converted to $[Pt_{12}(CO)_{24}]^{2-}$, the catalytic cycles involving $[Pt_{15}(CO)_{24}]^{2-}$, $[Pt_{12}(CO)_{24}]^{2-}$ and $[Pt_9(CO)_{18}]^{2-}$ take over. The induction times for MB^+ and Saf^+ are much less in most cases, in fact, negligible compared to that for MV^{2+} (see Supplementary material). This is because oxidation by the latter does not require protons, and protons are expected to be scarce at the start of the reaction. Consequently equilibrium (m) lies considerably more to the left than equilibrium (l). For all the catalytic runs, the initial rate measurements were made after the induction time.

Kinetic experiments with added water were carried out in a similar fashion by adding in the DMF solution of the substrate a known quantity of water by a micro-liter syringe and then adding the catalyst to initiate the reaction. The concentration data of the substrates and catalyst are provided in the figure captions and in the supplementary material. For the convenience of rate measurements, the molar ratios of acceptor to catalyst for MB^+, Saf^+,

MV^{2+} and $[Fe(CN)_6]^{3-}$ were kept within 2.2–36.4, 1.3–13.3, 8.2–108.8 and 17.6–211.9, respectively. Out of 84 independent catalytic runs in 81 runs, the molar ratio of substrate to catalyst was $\geqslant 4$.

Changes in the concentrations of MB^+, Saf^+ and MV^{2+} were monitored by recording the changes in absorption at 665, 560 and 398 nm, respectively. The salts ACl ($A = MB^+$, Saf^+) have good solubilities in DMF. However, dissolutions of potassium ferricyanide in DMSO, and $MVCl_2$ in DMF required the help of a sonicator. The reduction of potassium ferricyanide was carried out in DMSO by monitoring the disappearance of ν_{CN}^- peak of $[Fe(CN)_6]^{3-}$ at 2049 cm^{-1} (within characteristic region) [27,28] and appearance of ν_{CN}^- of $[Fe(CN)_6]^{4-}$ at 2023 cm^{-1}.

Control experiments to check the *chemo- and regio-selectivity* of the reductions were carried out with a substrate to catalyst molar ratio ranging from 1:5 to 1:20 in DMSO-d_6. The NMR (H^1) spectra of the bleached solutions (for MB^+ and Saf^+) were recorded; peaks were observed at $\delta = 7.83$, 5.73 and 4.6, respectively, for MBH and $\delta = 4.63$ for SafH. New peaks at $\delta = 4.6$ (s, 1H) and 4.63 (s, 1H), respectively, were observed for MBH and SafH that disappeared on D_2O treatment. The spectra were compared with those of reported [4] ones for MBH and SafH and found to be identical. For MV^{2+}, on reduction, the NMR signals at $\delta = 9.2$ (d, 4H), 8.7 (d, 4H), and 4.5 (s, 6H) disappeared and an ESR signal with $g_{isotropic} = 2.003$ (at both 77 and 300 K) appeared. On treatment with hydrazine hydrate, the NMR signals reappeared without any loss in intensity.

Acknowledgements

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2006.03.033.

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