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The Reactions of Diamines with the Trichloro(dimethyl sulfoxide)platinum(II)-ate Ion. A Comparison of the Rates of Closing of Seven- and Eight-Membered Rings

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The reactions of $NH_2(CH_2)_nNH_2$ (n = 2–6), $NH_2(CH_2)_2NH_3^+$, and cyclohexylamine with $[Pt(dmso)Cl_3]^-$ in aqueous solution have been followed spectrophotometrically. When n = 2 or 3 the first observed product is $[Pt(dmso)(N{-}N)Cl]^+$, where the diamine (N–N) is acting as a chelate and ring closing is fast compared to the rate of entry of the amine into the complex. When $n \geq 4$, or with monodentate amines, the first observed product is trans-*$[Pt(dmso)(N{-}N)Cl_2]$ with N–N acting as a monodentate, or* trans-*$[Pt(dmso)(am)Cl_2]$ (am = monodentate amine). When n = 4 the second observable stage of reaction is ring closing in competition with displacement of a chloride by a second diamine molecule. When n = 5 and 6, the slower second reaction consists solely of the entry of the second diamine molecule and the competing ring closing reaction makes a negligible contribution to the overall reaction. It is concluded that the rate constant for the closing of the eight-membered ring is at least 40 times smaller than that for the closing of the seven-membered ring.*

Introduction

In our studies of the relationship between the kinetics of ring closing and the size of the chelate ring [1–3] we have observed that the rate of ring closing decreases dramatically as the size of the ring increases. We could not extend our studies beyond the formation of seven-membered rings because, in spite of much effort, we have been unable to synthesise the required reagents such as *cis*- or *trans*-$[Pt(L)(NH_2(CH_2)_nNH_3)Cl_2]^+$ or even their precursors such as $[Pt(L)(NH_2(CH_2)_nNH_2)Cl]^+$ in which the diamine is acting as a monodentate or bidentate ligand respectively (L = NH_3 or $(CH_3)_2SO$ (dmso)) when n > 4. A material that analyses as $[Pt(NH_2(CH_2)_5NH_2)Cl_2]$ [4] proved to be polymeric and could not be converted to a suitable substrate [3]. In a bid to find other ways of studying ring closing in larger rings we have tried to exploit the very large difference between the *trans*- and *cis*-labilising powers of dimethyl sulfoxide [5–7] by studying the reaction between $[Pt(dmso)Cl_3]^-$ and diamines of the type $NH_2(CH_2)_nNH_2$ in the hope that the relatively strong *trans* effect of dmso will speed up the rate of attachment of the first end of the amine to the point where it becomes sufficiently fast compared to the rate of closing of the ring, which occurs at a site *cis* to dmso, for the two steps to be separated kinetically. The results are reported in this paper.

Experimental

Potassium trichloro(dimethyl sulfoxide)platinate(II) was prepared by the method of Kukushkin [8]. *Anal.* Calcd for $C_2H_6Cl_3KOSPt$, C, 5.7; H, 1.4; Cl, 25.4. Found: C, 5.8; H, 1.4; Cl, 25.7.

Trans-Dichloro(dimethyl sulfoxide)(cyclo-hexylamine)platinum(II) was prepared and characterised by the method of Romeo and Tobe [5]. *Anal.* Calcd for $C_8H_{19}NCl_2OSPt$, C, 21.7; H, 4.3; N, 3.2. Found: C, 21.7; H, 4.5; N, 3.4. *Cis*-chloro(dimethylsulfoxide)bis(cyclo-hexylamine)platinum(II) chloride was prepared and characterised by the method of Braddock *et al.* [9]. *Anal.* Calcd. for $C_{14}H_{32}N_2Cl_2OSPt$, C, 31.0; H, 6.0; N, 5.2. Found: C, 30.8; H, 6.0; N, 5.1.

The amines were purchased from Aldrich Chemical Company and purified by refluxing over NaOH pellets and then distilled at reduced pressure. Stock solutions of the amines were standardised by titration with standard hydrochloric acid and reaction solutions were prepared by quantitative dilution. Other reagents were AR grade, dried and stored over P_2O_5.

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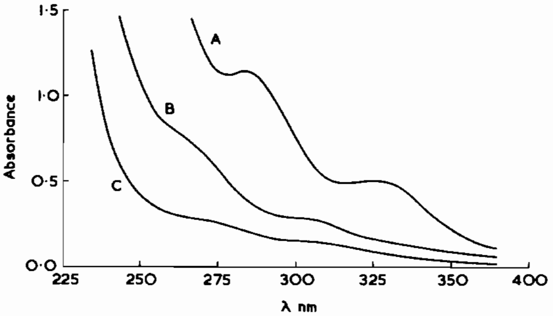


Fig. 1. The reaction between $[Pt(dmso)Cl_3]^-$ and 1,2-diaminoethane in water at 30.0 °C. [complex] = 2.0×10^{-3} *M*. $[Cl^-] = 1.0$ *M*. $\mu = 2.0$ ($NaClO_4$). (A) Spectrum before the addition of the amine. (B) Spectrum measured within 2 minutes of adding the amine, [en] = 0.20 *M*. No significant dilution. (C) Final spectrum (after 30 minutes).

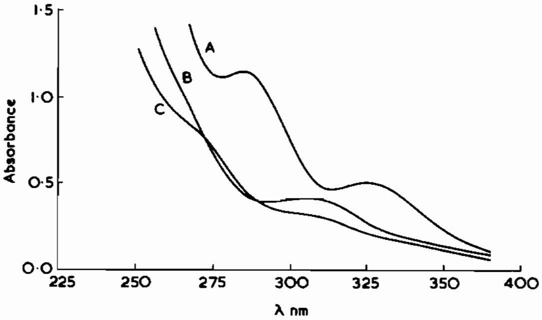


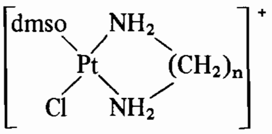
Fig. 2. The reaction between $[Pt(dmso)Cl_3]^-$ and 1,5-diaminopentane in water at 30.0 °C. [complex] = 2.0×10^{-3} *M*. $[Cl^-] = 1.0$ *M*, $\mu = 2.0$ ($NaClO_4$). (A) Spectrum before the addition of amine. (B) Spectrum measured within 2 minutes of adding the amine, [pen] = 0.060 *M*. No significant dilution. (C) Spectrum at the end of the second measurable change. The final spectrum of this system was not determined.

Preliminary measurements to choose the appropriate wavelengths for the kinetic studies were made with a Pye-Unicam SP 1750 spectrophotometer equipped with a thermostatted cell holder. The slowest ($t_{1/2} > 20$ s) kinetic runs were also followed with this machine. The faster reactions were followed with a Durrum D110 Stopped-Flow Spectrophotometer. For the fastest reactions ($t_{1/2} < 1$s) the output from the photon multiplier–log amplifier was stored in a Datalab CL 905 transient recorder and then plotted out on a Servoscribe RE 511.20 potentiometric recorder. For the reactions with $t_{1/2} > 1$ s the output was directly connected to the recorder.

Results

In a preliminary examination of the system using repetitive scanning spectrophotometry, two types of reaction were observed depending upon the nature of the amine used. The first type, found in the reactions with 1,2-diaminoethane (en) and 1,3-diaminopropane (pn), Fig. 1, is characterized by a rapid change of the spectrum from that of $[Pt(dmso)Cl_3]^-$ (peaks at 327 and 285 nm) to one with shoulders at 260 and 310 nm, that is complete before the first measurement can be made and this spectrum changes again at a rate that is proportional to the amine concentration. The second type, Fig. 2, is found in the reactions with 1,4-diaminobutane (bn), 1,5-diaminopentane (pen), 1,6-diaminohexane (hex) and cyclohexylamine (chx) and is characterised by a rapid change to a spectrum with peak at 307 nm which then changes to a spectrum very similar to that of the intermediate in Fig. 1. The subsequent changes are the same in both systems. The spectra of the intermediate in Fig. 1 and the second intermediate (C) in Fig. 2 are virtually identical and are also very similar to the spectra of $[Pt(dmso)(en)Cl]^+$, $[Pt(dmso)(tn)Cl]^+$ [10] and an authentic sample of *cis*-$[Pt(dmso)(chx)_2Cl]^+$. The spectrum of the first intermediate (B) in Fig. 2 is very similar to that of an authentic sample of *trans*-$[Pt(dmso)(chx)Cl_2]$. The final spectrum (not shown in Fig. 2) is very similar to that of $[Pt(en)_2]^{2+}$ which has been isolated and characterised as the final product of the reaction between $[Pt(dmso)Cl_3]^-$ and en. When am is a saturated primary amine, the spectra of complexes of the type $[Pt(dmso)(am)_xCl_{(3-x)}]^{(x-1)+}$ in the region studied are not particularly sensitive to the nature of the amine, nor are they sensitive to whether or not it forms part of a chelate and so we have concluded that the first observed change in the reaction of $[Pt(dmso)Cl_3]^-$ with en and tn is,

$[Pt(dmso)Cl_3]^- + NH_2(CH_2)_nNH_2 \rightarrow$



$+ 2Cl^-$ (n = 2 or 3).

The study of this change by stopped-flow spectrophotometry shows it to occur in a single stage and we conclude that the rate determining step is the entry of the first end of the diamine, subsequent ring closing being fast. Further evidence in support of this conclusion comes from the kinetics which are discussed below. In the reactions of the other amines, depicted in Fig. 2, we conclude that the first observable change is,

$[Pt(dmso)Cl_3]^- + am \rightarrow$

trans-$[Pt(dmso)(am)Cl_2] + Cl^-$,

and the second stage is the displacement of the chloride *cis* to dmso by another RNH_2 group. This may

TABLE I. Rate Constants for the Reactions:*

$$\text{(a) } [\text{Pt(dmso)Cl}_3]^- + \text{N–N (or N)} \rightarrow \textit{trans}\text{-}[\text{Pt(dmso)(N–N)Cl}_2] + \text{Cl}^-$$
$$\text{or } \textit{trans}\text{-}[\text{Pt(dmso)(N)Cl}_2] + \text{Cl}^-$$
$$k_{obs} = k_1^a + k_2^a\,[\text{N–N}]\ (\text{or } [\text{N}])$$
$$\text{(b) } \textit{trans}\text{-}[\text{Pt(dmso)(N–N)Cl}_2 + \text{N–N} \rightarrow \left\{\begin{array}{l}[\text{Pt(dmso)(N–N)Cl}]^+ + \text{Cl}^- + \text{N–N}\\ + \textit{cis}\text{-}[\text{Pt(dmso(N–N)}_2\text{Cl}]^+ + \text{Cl}^-\end{array}\right.$$
$$\text{or } \textit{trans}\text{-}[\text{Pt(dmso)(N)Cl}_2] + \text{N} \rightarrow \textit{cis}\text{-}[\text{Pt(dmso)(N)}_2\text{Cl}]^+ + \text{Cl}^-$$
$$k_{obs} = k_{cl} + k_1^b + k_2^b\,[\text{N–N}]\ (\text{or } [\text{N}])$$

Amine		k_1^a/s^{-1}	$k_2^a/M^{-1}\ s^{-1}$	$10^2\ (k_{cl} + k_1^b)/s^{-1}$	$k_2^b/M^{-1}\ s^{-1}$
1,2-diaminoethane	(en)	0.03 ± 0.12	46.9 ± 1.1	–	–
1,3-diaminopropane	(tn)	0.17 ± 0.15	40.6 ± 1.1	–	–
1,4-diaminobutane	(bn)	–0.26 ± 0.21	38.4 ± 1.6	13.8 ± 0.8	0.54 ± 0.05
1,5-diaminopentane	(pen)	0.12 ± 0.16	41.7 ± 1.5	0.2 ± 0.2	0.54 ± 0.02
1,6-diaminohexane	(hex)	0.00 ± 0.13	42.8 ± 1.0	0.1 ± 0.6	0.67 ± 0.05
cyclohexylamine	(chx)	0.02 ± 0.09	13.9 ± 0.8	–0.9 ± 0.3	0.77 ± 0.03
2-aminoethylammonium	(enH^+)	0.13 ± 0.06	18.0 ± 0.5	–	–

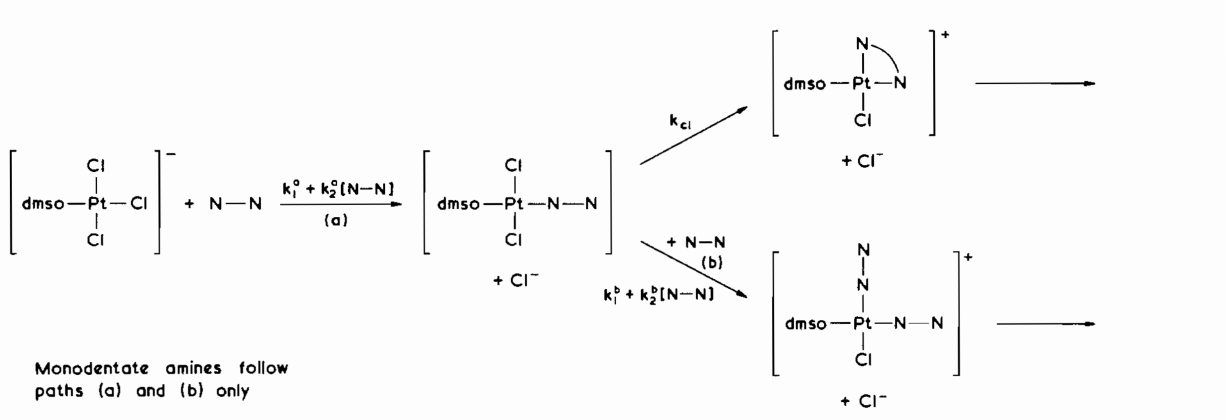
*In water at 30.0 °C, [NaCl] = 1.0 *M*, [Complex] = 2.0×10^{-3} *M*, $\mu = 2.0$ (NaClO_4).

come from the diamine already coordinated, in which case there is ring closing, or else from an independent amine, in which case the product is *cis*-$[\text{Pt(dmso)(am)}_2\text{Cl}]^+$, where am can be a monodentate diamine. The two processes are spectroscopically indistinguishable and may run in parallel. The final stage, which we have not examined kinetically, is probably the displacement of the third chloride by RNH_2 followed by the loss of dmso.

In order to examine the kinetics of the displacement of the first two chlorides it was necessary to use the stopped flow technique which involves the mixing of solutions that had aged for periods of at least 10 minutes. The reactions were therefore carried out in the presence of a large excess of Cl^- ([NaCl] = 1.0 *M*, $\mu = 2.0$ (NaClO_4)) so as to avoid complications from the deprotonation of the coordinated water in the solvolysed substrate, *trans*-$[\text{Pt(dmso)(H}_2\text{O)Cl}_2]$, when the amine was added. Using the published value of 5.3×10^{-3} *M* for the solvolytic equilibrium constant ($\mu = 1.0$, 25.0 °C) [7] it can be calculated that 99.4% of the substrate is present in the form of the trichloro- anion when $[\text{Cl}^-] = 1.0$ *M*. The change in μ to 2.0 and the change in the temperature to 30.0 °C would not alter this value significantly. The concentration of the amine was always considerably greater than that of the complex (20 to 100 times) and so simple first-order kinetics were ensured. The individual stages of the reaction differed sufficiently in rate for there to be no need for elaborate data processing methods to separate the rate constants. It was often possible to choose a value for 'A_∞' that gave a plot of $\ln(A_t - A_\infty)$ against time (A_t is the absorbance at time t) that was linear for at least four half-lives and when this was not convenient, the rate constants were calculated by Guggenheim's method (k_{obs} is the slope of the plot of $\ln(A_t - A_{(\Delta+t)})$ against time, where A_t and $A_{(\Delta+t)}$ are the absorbances of the reaction mixture at time t and Δ + t respectively and Δ is a constant time interval, generally between two and three half lives for the reaction). The first-order rate constants, k_{obs}, obtained by these methods vary linearly with concentration of amine and the slopes and intercepts of these lines; obtained by a least squares regression, are collected in Table I.

Discussion

The reactions of interest to this work are summarised in the scheme. In the reactions with N–N = en and tn the rate constant for ring closing k_{cl}, is large compared to $k_1^b + k_2^b$ [N–N] and therefore ring closing dominates the fate of the monosubstituted intermediate. Furthermore, k_{cl} is large compared to $k_1^a + k_2^a$ [N–N] and so the formation of the chelated product $[\text{Pt(dmso)(N–N)Cl}]^+$ appears to be a single stage process with the entry of N–N as the rate determining step. The slopes and intercepts of this stage are therefore identified with k_2^a and k_1^a. With all the other amines the two stages are separate. The slopes and intercepts of the first stage are still identified with k_2^a and k_1^a but the second stage aggregates the various pathways leading to the consumption of the *trans*-$[\text{Pt(dmso)(N–N)Cl}_2]^+$ intermediate, consequently $k_{obs} = k_{cl} + k_1^b + k_2^b$ [N–N]. Consumption of this species by bridge formation, *i.e.*, the free end of the monodentate diamine attacking a different Pt(II) centre, can be



Scheme

ruled out because this would require a second-order dependence upon the concentration of complex and there is no evidence for this over the range of concentration that we have chosen to use. The slope of the plot of k_{obs} for the second step against [N–N] is therefore k_2^b and the intercept = $k_{cl} + k_1^b$.

The second-order rate constants for the entry of the diamine into $[Pt(dmso)Cl_3]^-$, k_2^a, are virtually independent of the nature of the diamine. This would be expected if the reaction being followed was the direct entry of an amine since the rate constants for such a reaction at Pt(II) are generally insensitive to the basicity of the amine [5]. These results are at variance with those of Kukushkin and Ukraintsev [11, 12] who studied the reaction between $[PtCl_4]^{2-}$ and diamines at 25 °C ($\mu = 1.0$) and found that k_2 for the entry of the diamine decreased along the series n (2.02×10^{-3} M^{-1} s^{-1}) > tn (1.57×10^{-3} M^{-1} s^{-1}) > hex (0.70×10^{-3} M^{-1} s^{-1}) and approached the values obtained for the mono amines, *e.g.*, NH_3 (0.42×10^{-3} M^{-1} s^{-1}) and n-$BuNH_2$ (0.55×10^{-3} M^{-1} s^{-1}). In view of the complicated nature of the substitution of chloride by amine in $PtCl_4^{2-}$ with considerable interference from subsequent stages [13] care should be taken in interpreting the raw kinetic data. The rate constants for the entry of the monodentate chx and enH^+ into $[Pt(dmso)Cl_3]^-$ are smaller by a factor of roughly 2 which would be expected if the difference was dominated by the statistical effect of having two equivalent nucleophilic sites per molecule of diamine. This also indicates that anchimeric effects are only of secondary importance in this system. The data for enH^+ as an entering nucleophile were obtained by using an equimolar mixture of diaminoethane and HCl as the source of the amine. This was done in the hope that the ring closing process would be slowed down sufficiently to appear as a second step but it still proved to be too fast. Further increase in acid concentration would reduce the rate of entry of the amine as well as that of ring closing and not separate the stages further. This type of behaviour has already been observed in the pH dependence of the reaction between $PtCl_4^{2-}$ and tn [14].

The value of 13.9 M^{-1} s^{-1} for k_2^a for the entry of cyclohexylamine into $[Pt(dmso)Cl_3]^-$ can be compared to 2.2 M^{-1} s^{-1} for the same reaction in methanol at the same temperature, but at a lower ionic strength [5]. This is a bigger solvent effect than that found for the reaction *cis*-$[Pt(dmso)(chx)Cl_2]$ + chx → *cis*-$[Pt(dmso)(chx)_2Cl]^+$ + Cl^- ($k_2(H_2O)/k_2(MeOH) = 2.2$ [1]), but the charge type is different. The absence of a significant intercept in any of the plots of k_{obs} *vs.* [N–N] for the first stage is consistent with the value of 0.145 s^{-1} for the solvolysis of $[Pt(dmso)Cl_3]^-$ in water at 30.0 °C, $\mu = 1.0$, interpolated from the data of Elding and Gröning [7] which would represent a maximum value for k_1^a since there is likely to be mass-law retardation by the large amount of chloride present. The error limits are greater than the expected value.

In the reaction corresponding to the loss of the second chloride, observed in the case of the entry of bn, pen, hex and chx, k_{obs} is also found to have a linear dependence upon the concentration of amine and, with the exception of the entry of 1,4-diaminobutane, the intercept is negligible. In the case of the monodentate cyclohexylamine this intercept can only be identified with k_1^b indicating that the major part of the large intercept found for the reaction with bn must be due to k_{cl} the ring closing rate constant = 0.14 ± 0.01 s^{-1}. If the dependence of the rate constant for ring closing on ring size is the same in this system as elsewhere one would expect as increase of k_{cl} by 2 to 3 orders of magnitude on going from bn to tn to en. This would make k_{cl} large compared to k_{obs} for the first stage, except at the highest nucleophile concentrations, and explains why chelation is observed as a single stage process. The most important observation in this paper is the decrease in the value of the intercept on going from 1,4-diaminobutane to 1,5-diaminopentane. While it is not possible to assign a value to k_{cl} it is clear that it must be at least 40 times smaller than that for the closing of the seven-membered ring. In an attempt to obtain a more precise value for k_{cl}, the kinetics were studied at low concentrations of diamine and complex in the presence of sufficient base to prevent protonation of the diamine. Unfortunately in addition to preventing the competition from an external amine in the loss of the second chloride it also prevented the amine entering in the first step since, in basic solution, the *trans*-[Pt(dmso)(H_2O)-Cl_2] formed by the k_1^a pathway is deprotonated before it can react with the amine or even the chloride and the Pt–OH bond remains unbroken. The only observed products were *trans*-[Pt(dmso)-(OH)Cl_2]$^-$ and *cis*-[Pt(dmso)$(OH)_2$Cl]$^-$. An attempt was made to reduce the importance of these solvolytic pathways by changing the solvent to methanol, using Et_4N[Pt(dmso)Cl_3], LiCl and $LiClO_4$ because of solubility problems. While the reactions are clear cut for the smaller ring sizes, except that the rate of ring closing appears to be faster with respect to the entry of the first amine in this solvent, it was still not possible to prevent the solvolytic pathways in slightly basic solution. However, preliminary experiments at higher pen concentrations would suggest that the estimate of a factor of 40 as the minimum extent to which the rate constant for ring closing decreases on going from bn to pen is an underestimate and this factor is $\geqslant 10^2$. Similar considerations apply to the reactions with 1,6-diaminohexane. If we relate the first-order ring closing rate constants to second-order direct substitution rate constants by assigning an 'effective molarity', M_{eff}, to the free end of the diamine, then, since M_{eff} for 1,4-diaminobutane lies in the range 0.5 to 1 *M* [2, 3], that for 1,5-diaminopentane must be $<10^{-2}$ *M*.

The values for k_2^b for the direct entry of the second amine are again not very sensitive to the nature of the amine concerned. Indeed we see no indication of the statistical factor of 2 that distinguished the entry of the diamines in [Pt(dmso)Cl_3]$^-$ and the rate constant for cyclohexylamine is the largest of the four reported. As the number of amine ligands present increases it is likely that steric hindrance will assume a more important role. There is considerable evidence for this elsewhere [9] but much more work is needed before this problem can be discussed in depth.

It is clear now that our inability to synthesise the chelated [Pt(L)(N–N)Cl]$^{n+}$ complexes (L = Cl, n = 0; L = dmso or NH_3, n = 1) with 8-membered rings is due to the fact that the ring closing cannot compete with other pathways for the displacement of the second chloride and that, in the concentrated solutions used in the preparations, the free end of the monodentate diamine is more likely to bind to a second platinum than to close the ring, thus leading to polymeric product. Attempts to minimise this by working in very dilute solution failed because of solvolytic competition. It is possible that the problem will be solved by working in a very dilute solution in a suitable dipolar aprotic but non-coordinating solvent but until now we have been unsuccessful.

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