

Rates and Mechanism of Substitution Reactions of Dimethylsulfoxide and Aquo-(diethylenetriamine)platinum(II) Ions

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The kinetics of the replacement of the ligand L in $[\text{Pt}(\text{dien})\text{L}](\text{ClO}_4)_2$ ($\text{L} = \text{H}_2\text{O}$ and dimethylsulfoxide; $\text{dien} = 1,5\text{-diamino-3-aza-pentane}$) by a series of nucleophiles were studied in aqueous solution, using both stopped-flow and conventional spectrophotometry. The reactions go only by way of the direct bimolecular attack of the reagent on the substrate. The reactivity of the biphilic reagents SeCN^- and thiourea, and to a lesser extent of SCN^- , towards these doubly charged substrates, is largely less than expected on the basis of the n_{Pt}° scale. The nucleophilicity scale is then $\text{Cl}^- < \text{N}_3^- < \text{Br}^- < \text{thiourea} < \text{SCN}^- < \text{I}^- < \text{SeCN}^- < \text{S}_2\text{O}_3^{2-}$. The sulphur-bonded dmso is at least three orders of magnitude less labile than H_2O , but the reactivity difference decreases with the nucleophilicity of the entering group.

Introduction

The role of the dimethyl sulfoxide in platinum(II) chemistry has aroused increasing interest both from a kinetic or a preparative point of view. Preparative work [1–4] has been devoted mainly to investigate the bonding mode of dmso which normally occurs through sulphur to the soft metal or through oxygen when the ligand is forced into a sterically crowded environment. Kinetic studies have dealt mainly with the *trans* effect or the *cis* effect of dmso [5–11].

Very little is known on the lability of this ligand, except the empirical observation that the soft–soft Pt–S interaction is reasonably stable when a single dmso is bound to the metal, while it is easily labilized in the presence of another dmso coordinated either in *cis* or *trans* position. In this paper we report the kinetics of the displacement of dmso and H_2O from $[\text{Pt}(\text{dien})\text{L}]^{2+}$ ($\text{L} = \text{dmso}$ or H_2O) in aqueous solution by a range of neutral and charged nucleophiles.

Experimental

Materials

The solvento complex $[\text{Pt}(\text{dien})(\text{dmso})](\text{ClO}_4)_2$ was prepared as follows. The complex $[\text{Pt}(\text{dien})\text{I}]\text{I}$ (0.828 g, 1.5 mmol) was dissolved in dimethyl sulfoxide (20 cm³). Anhydrous silver perchlorate (0.622 g, 3 mmol) dissolved in dmso (10 cm³) was added and the resultant mixture was stirred at room temperature in the dark for 24 h before filtering off the precipitated silver iodide. The excess solvent was removed by solvent extraction with diethylether and the oily residue dried under vacuum over P_2O_5 and vigorously stirred with dichloromethane to give a white solid. This latter was dissolved in methanol, the solution set aside in a refrigerator for one day, after which time some yellow material which had separated was filtered off and the volume of the filtrate reduced to 20 ml under reduced pressure. The white crystals that formed on cooling (0.583 g) were filtered off, washed with ether and air dried. *Anal.* Found: C, 12.59; H, 3.27; N, 7.20; S, 5.42%. $\text{C}_6\text{H}_{19}\text{N}_3\text{SCl}_2\text{O}_9\text{Pt}$ requires: C, 12.54; H, 3.33; N, 7.32; S, 5.57%.

The complexes $[\text{Pt}(\text{dien})\text{X}]\text{X}$ ($\text{X} = \text{NO}_3$, Cl, Br, I) were prepared by methods similar to those previously described in the literature [12–14]. The aquo-complex $[\text{Pt}(\text{dien})(\text{H}_2\text{O})](\text{ClO}_4)_2$ was prepared by following the procedure described by Hartley *et al.* [15].

Reagent grade inorganic salts were dried over P_2O_5 in a vacuum desiccator and used without further purification. Infrared spectra were obtained as Nujol mulls on a Perkin-Elmer PE 577 spectrometer. Nmr spectra were recorded on a 60 M Hz Perkin-Elmer R 24 A spectrometer. Conductivity measurements were performed using a Radiometer CDM 3 conductivity bridge with a glass cell containing platinum electrodes.

Kinetics

The slowness of most reactions of $[\text{Pt}(\text{dien})(\text{dmso})]^{2+}$ made it possible to apply conventional

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spectrophotometry for monitoring. The kinetic runs were followed either by repetitive scanning in the region 420–220 nm with a Cary Mod. 219 spectrophotometer or using a Beckman D.U. single beam monochromator, equipped with a Saitron 301 photometer with scale expansion facilities and a Servoscribe RE 511.20 potentiometer recorder. In this latter case, the reactions were initiated by mixing in a 4 cm cell 1.0 cm³ of 0.006 *M* aqueous solution of the complex and 11.0 cm³ of a solution of the other reagents, previously brought to the reaction temperature in the spectrophotometer cell.

The rates of anation of [Pt(dien)H₂O]²⁺ were followed with a standard Durrum-Gibson stopped-flow spectrophotometer equipped with a photometric log amplifier mod. D-131. Absorbance changes, at a selected wavelength, were displayed on a Gould 054100 storage oscilloscope and traces were recorded on a Radiometer REC 61 potentiometric recorder. The solutions of complex were made up by dissolving in water either [Pt(dien)H₂O](ClO₄)₂ or [Pt(dien)NO₃]₂. In order to avoid acid dissociation by [Pt(dien)(H₂O)]²⁺ (*pK*_a = 6.13 at 25 °C and *μ* = 0.1 *M*) [15] and Schlieren effects on mixing, it was necessary for both the complex and the reagent solution to adjust the pH to 4 by adding the sufficient amount of perchloric acid and to bring the ionic strength to 0.1 *M* (LiClO₄).

In all the cases a large excess of reagent was used to provide pseudo-first-order conditions and to force the reactions to completion. Pseudo-first-order rate constants (*k*_{obsd} s⁻¹) were obtained either from the gradients of plots of log(*A*_t - *A*_∞) vs. time or from a non linear least-squares fit of experimental data to *A*_t = *A*_∞ + (*A*₀ - *A*_∞) exp (-*k*_{obsd} *t*) with *A*₀, *A*_∞ and *k*_{obsd} as the parameters to be optimized (*A*₀ = absorbance after mixing of reactants, *A*_∞ = absorbance at completion of reaction). Activation parameters were obtained from linear least-squares analysis of Eyring plots.

Results

The complex [Pt(dien)(dmsO)](ClO₄)₂ can be isolated as a pure species. The molar conductivity of an aqueous solution (1 × 10⁻⁴ *M*) at 30 °C was 201 ohm⁻¹ cm² mol⁻¹. Dilution conductivity experiments in nitromethane solution (in the range 10⁻²–10⁻⁵ equiv. l⁻¹) gave a plot of λ_c vs. *c*^{1/2} having a slope of 634 ± 31 ohm⁻¹ l^{1/2} equiv^{-1/2} at 25 °C. These values are fully consistent with that of a 1:2 electrolyte [16]. The I.R. spectrum showed characteristic N–H absorptions in region 3300–3100 cm⁻¹ and a strong band at 1560 cm⁻¹ assigned to the NH₂ bending mode. The non-coordinating counter ion ClO₄⁻ gives a sharp peak at 640 cm⁻¹ and a strong broad band at 1080 cm⁻¹. This latter obscures the region

of the S=O stretching mode which usually makes it possible to differentiate between oxygen and sulphur bonding [1, 2]. The ¹H nmr spectrum of the N-deuterated complex in D₂O, showed a main signal centered at 3.58 p.p.m. relative to SiMe₄ with a ¹⁹⁵Pt satellite doublet *J*(¹⁹⁵Pt–¹H) = 21 Hz assigned to the methyl protons of the S-bonded dimethylsulphoxide. A similar peak has been found in the parent compounds K[Pt(dmsO)Cl₃] [4], *cis*-[Pt(dmsO)₂Cl₂] [4] and [Pt(diamine)(dmsO)Cl]Cl [3] (diamine = 1,2-diaminoethane; 1,3-diaminopropane and 1,4-diaminobutane). For uncoordinated dmsO a singlet δ(CH₃) at 2.53 p.p.m. is found whereas oxygen-bonded dmsO gives a downfield shift of at most 0.5 p.p.m. [4]. It is of interest to note that the dien methylene protons are split into three groups at 2.78, 3.12 and 3.27 p.p.m. A two peak split has been already evidenced in the ¹H nmr spectrum of the corresponding Pd(II) compound by Hartley *et al.* [17] and explained with steric restrictions to the conformational freedom of the dien ligand. The electronic spectrum of the compound in water exhibits a band at 272 nm with a molar extinction coefficient of 134 *M*⁻¹ cm⁻¹.

The spectral changes which accompany the displacement of dmsO from [Pt(dien)(dmsO)]²⁺ are often characterised by well-defined isosbestic points and the final spectra always corresponded very closely to that of the isolated and characterised reaction products [Pt(dien)Y]⁺ (Y = entering nucleophile). This leads to exclude any possible interference by ring opening of the ancillary ligand under the *cis* effect of dmsO.

The reactions were studied at least at five nucleophile concentrations (see supplementary material) and the ionic strength was kept constant at 0.1 *M* (LiClO₄). For both complexes the plots of the pseudo-first-order rate constants against the reagent concentration where straight lines which passed virtually through the origin. The apparently large intercepts obtained from early data reported by Gray and Olcott [18] for the anation of [Pt(dien)(H₂O)]²⁺ seem to be due to a larger experimental error involved in the technique used and to the fact that the ionic strength of the medium was not held constant. The same observation has been made recently by Kelm *et al.* [19] who corrected and completed Gray's data, giving a set of rate constants for the anation of [Pt(dien)OH₂]²⁺ at 15 °C and *μ* = 0.1 *M*.

The kinetics follow then the rate law *k*_{obs} = *k*₂[Y] (1). The second order rate constants *k*₂, listed in Table I, were calculated by linear regression analysis of (1) and were extrapolated to zero ionic strength (*k*₂⁰) using the standard relationship for the primary salt effect log *k*₂ = log *k*₂⁰ + 1.02*Z*_A*Z*_B *μ*^{1/2} (1 + *μ*^{1/2})⁻¹, where *Z*_A and *Z*_B are the charges of the substrate and nucleophile respectively.

TABLE I. Second-order Rate Constants (k_2) at Ionic Strength 0.1 M (LiClO₄) and (k_2^0), corrected to $\mu = 0$, for the Reaction: $[\text{Pt}(\text{dien})\text{L}]^{2+} + \text{X}^{n-} \rightarrow [\text{Pt}(\text{dien})\text{X}]^{(2-n)+} + \text{L}^a$

L	X	t, °C	$10^3 k_2$ $M^{-1} s^{-1}$	$10^3 k_2^0$ $M^{-1} s^{-1}$
(CH ₃) ₂ SO	Cl ⁻	30	0.380 ± 0.009	1.17
	Cl ^{-b}	30	0.115 ± 0.008	1.20
	N ₃ ⁻	30	0.756 ± 0.03	2.33
	Br ⁻	30	3.72 ± 0.05	11.5
	SCN ⁻	30	40.4 ± 0.2	125
	SC(NH ₂) ₂	18	25.5 ± 0.8	25.5
	SC(NH ₂) ₂	30	51.4 ± 0.6	51.4
	SC(NH ₂) ₂	40	122 ± 3	122
	I ⁻	18	95.6 ± 3	295
	I ⁻	30	226 ± 0.7	698
	I ⁻	40	471 ± 18	1456
	SeCN ⁻	30	517 ± 6	1600
	S ₂ O ₃ ²⁻	30	10180 ± 133	93700
			k_2 $M^{-1} s^{-1}$	k_2^0 $M^{-1} s^{-1}$
H ₂ O	Cl ⁻	30	0.626 ± 0.011	1.93
	Br ⁻	30	4.64 ± 0.13	14.3
	SCN ⁻	30	54.5 ± 1.6	168
	SC(NH ₂) ₂	10	12.7 ± 0.5	12.7
	SC(NH ₂) ₂	18	22.2 ± 0.48	22.2
	SC(NH ₂) ₂	30	41.2 ± 0.6	41.2
	SC(NH ₂) ₂	40	78.6 ± 1.4	78.6
	I ⁻	10	22.7 ± 0.8	70.1
	I ⁻	18	37.5 ± 1.8	116
	I ⁻	24	57.9 ± 1.6	178
	I ⁻	30	80.6 ± 0.8	249
	I ⁻	40	143 ± 3	443
	S ₂ O ₃ ²⁻	30	3921 ± 10	37445

^aIn water. ^bAt ionic strength 1.0 M (LiClO₄).

Discussion

Since only one ligand substitution is involved without interference from any subsequent step, the replacement of the ligand (Lⁿ⁻) by another Y from [Pt(dien)L]⁽²⁻ⁿ⁾⁺ cations (dien = 1,5-diamino-3-aza-pentane) has been widely investigated. The effect of various entering [18–21] and leaving groups [22, 23] and of the ionic strength [24] upon the substitution kinetics has been demonstrated and activation parameters [23] have been determined.

The relative ease of replacement of the halide ions as outgoing groups was found to depend on the nature of the reagent [25, 26]. Lability sequences can be derived from reactivity data pertaining to pyridine [22] or thiourea [23] as entering nucleophiles. This latter series can now be extended to include

H₂O and dmso, so that H₂O > I⁻ > Br⁻ > Cl⁻ > dmso ≅ SCN⁻ > N₃⁻ > NO₂⁻. The difference in reactivity spans a range of 5 orders of magnitude. The lability of the sulphur bonded dmso appears to be comparable to that of SCN⁻, even though some caution must be taken in comparing reactivity data of differently charged substrates.

The correlation of the rates of reaction of [Pt(dien)(dmso)]²⁺ with the n_{Pt}^0 values of different nucleophiles in Fig. 1 shows very large negative deviations for SeCN⁻, thiourea and to a lesser extent for SCN⁻. We recall that the n_{Pt}^0 values refer to reactivity data pertaining to a standard uncharged substrate *trans*-[Pt(pyridine)₂Cl₂]. However the phenomenon is hardly due to electrostatic interactions between the reagents. The so-called *biphilic* groups, which have the capacity to stabilize the 5-coordinate transition state through metal to ligand

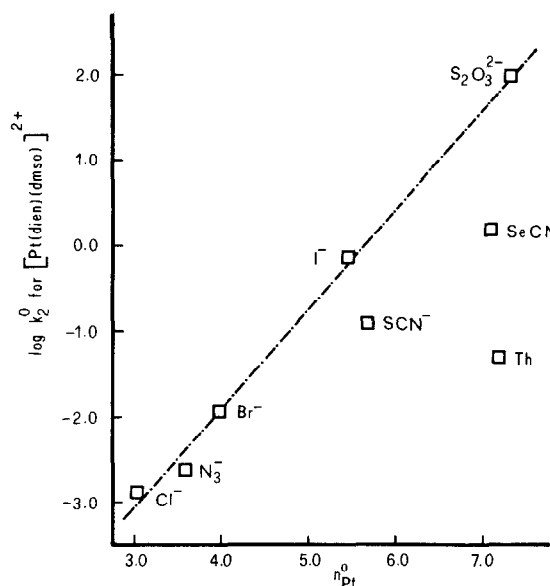


Fig. 1. Correlation of the rates of reaction of $[\text{Pt}(\text{dien})(\text{dmsO})]^{2+}$ with the n_{Pt}^0 values of different nucleophiles.

π interactions, are less reactive than predicted because of the positive charge which reduces the disposibility of non bonding electrons on the metal. This is a well-known phenomenon which has been discussed at length in connection with the behaviour of other charged substrates [27] and very recently by Tobe, Cattalini *et al.* [11], in a study of the *cis* effect in the cationic complexes $[\text{Pt}(\text{en})(\text{dmsO})\text{Cl}]^+$ and $[\text{Pt}(\text{en})(\text{NH}_3)\text{Cl}]^+$ (*en* = 1,2-diaminoethane). However in this doubly charged substrate the deviations are so particularly striking (3 orders of magnitude for $\text{SC}(\text{NH}_2)_2$) to lead to inversions in the sequence of nucleophilic reactivity, *viz.* $\text{Cl}^- < \text{N}_3^- < \text{Br}^- < \text{thiourea} < \text{SCN}^- < \text{I}^- < \text{SeCN}^- < \text{S}_2\text{O}_3^{2-}$. Similar reasonings apply also for $[\text{Pt}(\text{dien})(\text{H}_2\text{O})]^{2+}$ which exhibits the same departures from the reactivity order predicted.

It should be noted on passing that the reactivity of the biphilic reagents and hence a good fit of the kinetic data with the customary set of nucleophilic reactivity constants n_{Pt}^0 are not strictly related only to the formal charge of the substrate, but depend also on the amount of electron density brought about by the coordinated ligands to the metal atom in the ground state. Both factors control the expansion of the non bonding Pt(II) orbitals, making them more or less available for overlap with empty orbitals of the incoming biphilic ligand. In fact enhancement of reactivity and positive deviations from a simple linear free energy relationship were shown to occur for uncharged *trans*- $[\text{Pt}(\text{PEt}_3)_2(\text{R})\text{Cl}]$ complexes [28] (PEt_3 = triethylphosphine;

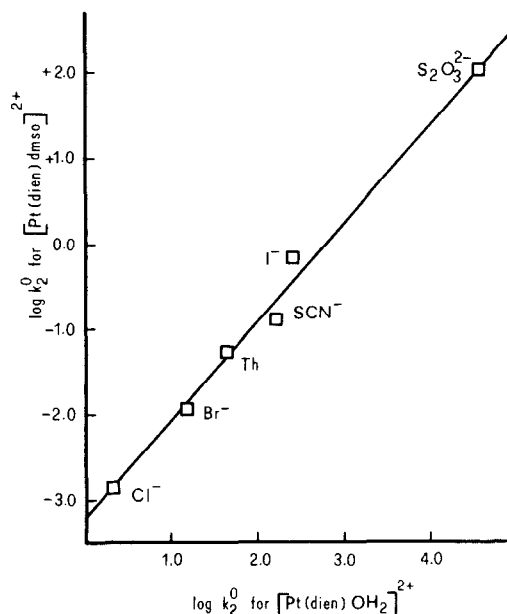


Fig. 2. $\log k_2^0$ for the reactions of $[\text{Pt}(\text{dien})(\text{dmsO})]^{2+}$ plotted against $\log k_2^0$ for the reactions of $[\text{Pt}(\text{dien})(\text{H}_2\text{O})]^{2+}$.

$\text{R} = \text{H}^-$, alkyl or substituted aryl groups) where the strong σ donor *trans* ligand R, through the agency of different activation processes, is able to differentiate between σ donor and π acceptor entering nucleophiles.

In order to correct the effects on the nucleophilicity scale arising from the charge difference between these substrates and the original standard *trans*- $[\text{Pt}(\text{pyridine})_2\text{Cl}_2]$, the $\log k_2^0$ for various nucleophiles reacting with the dmsO complex have been plotted against $\log k_2^0$ for the same nucleophiles reacting with the aquo-complex (see Fig. 2). According to this procedure the rate data for $[\text{Pt}(\text{dien})(\text{H}_2\text{O})]^{2+}$, reacting at 30 °C in water, are taken as a more suitable set of nucleophilic reactivity constants towards 2+ charged substrates. A similar way of rationalising kinetic data for monocationic complexes has required the use of $[\text{Pt}(\text{en})(\text{NH}_3)\text{Cl}]^+$ as a new standard substrate [11]. The slope of the plot, 1.147 ± 0.06 , indicates that the discrimination power of the dmsO complex is 15% greater than that of the aquo-complex. This effect of dmsO as outgoing group, as well as that when it is in *trans* [7–10] or *cis* [11] position, is clearly carried out in the transition state where this ligand is better able than H_2O to accommodate electron density brought about by the reagent. Whether this charge withdrawal occurs through the σ or the π bonding framework is controversial, even because some lengthening of the Pt–S bond must be taken into account. This small but significant difference in the nucleophilic discrimination factors of the two substrates implies that the

TABLE II. Activation Parameters for the Reactions:
 $[\text{Pt}(\text{dien})\text{L}]^{2+} + \text{Y}^{n-} \rightarrow [\text{Pt}(\text{dien})\text{Y}]^{(2-n)+} + \text{L}$
 in Water and at Ionic Strength 0.1 M (LiClO_4).

L	Y	$\Delta H^\ddagger$ ^a	$\Delta S^\ddagger$ ^b
H ₂ O	I [−]	42.7 ± 0.4	−67 ± 2
dmsO	I [−]	52.3 ± 0.8	−84 ± 4
H ₂ O	SC(NH ₂) ₂	41.4 ± 0.8	−77 ± 4
dmsO	SC(NH ₂) ₂	51.0 ± 0.3	−100 ± 17

^a KJ mol^{−1}. ^b J K^{−1} mol^{−1}.

large difference of reactivity between the dmsO and the aquo-complex does not stem completely from the stronger Pt–S bond.

The temperature dependence of the rate of reaction of the aquo- and dmsO-complexes with I[−] and SC(NH₂)₂ has been studied and yielded the activation parameters listed in Table II. The data fit well in the simplified picture of an associative process [23] and their changes are in the direction that might be predicted on changing the leaving group from H₂O to (CH₃)₂SO. It is reasonably self-evident that the enthalpy of activation increases as result of the stronger Pt–S bond, while the steric hindrance arising from methyl groups of the S-bonded dimethylsulphoxide reduces the number of possible ways of arranging the atoms and energy levels in the transition state and thereby leads to a decrease in the entropy of activation.

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Supplementary Material Available

A listing of observed rate constants, k_{obsd} as a function of the temperature and of the nucleophile concentration (6 pages).

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