

^{195}Pt NMR Studies of Platinum(II) Dimethylsulphoxide Complexes

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Abstract

The solvolyses of the complexes $\text{cis-Pt}(\text{L}_2)\text{X}_2$, where L_2 is two NH_3 molecules or ethylenediamine and $\text{X} = \text{Cl}^-$, Br^- , or I^- , in dimethylsulphoxide solution were studied by ^{195}Pt NMR spectroscopy. The rates followed the order: iodides > bromides > chlorides. Products were identified by their chemical shifts and, where possible, ^{195}Pt – ^{15}N coupling constants. In general, *cis*-bis-dimethylsulphoxide complexes were destabilized and only seen when silver ions were added to remove competing halide ligands. Studies on the interaction of OH^- ions with $\text{Pt}(\text{II})$ DMSO complexes in aqueous and DMSO solutions are also reported.

Introduction

Dimethylsulphoxide (DMSO) is an ambidentate ligand towards many metal ions, binding either through sulphur or oxygen [1]. Wayland *et al.* [2] suggested that $[\text{Pt}(\text{DMSO})_4]^{2+}$ in solution contained two *cis* S-bonded and two *cis* O-bonded DMSO ligands on the basis of NMR and infrared measurements. $[\text{Pd}(\text{DMSO})_4]^{2+}$ is now known from X-ray crystallography to have such a configuration [3]. O-bonded DMSO undergoes more rapid substitution, e.g. by water, than S-bonded DMSO [4]. In $\text{Pt}(\text{II})$ chemistry DMSO is usually considered to exert a high (thermodynamic) *trans* influence (comparable with olefins) and a moderately high (kinetic) *trans* effect [1].

^{195}Pt NMR is useful for probing the structure of $\text{Pt}(\text{II})$ DMSO complexes in solution [5, 6, 7]. However too few data have been reported to allow reliable correlations between ^{195}Pt chemical shifts of the platinum DMSO complexes and their structures to be made. We have therefore extended our previous studies on the solvolysis of $\text{cis-Pt}(\text{NH}_3)_2\text{Cl}_2$ in DMSO to include the analogous bromide, iodide and ethylenediamine complexes. We have also investigated reactions of DMSO complexes with water and hydroxide ions.

Biological interest in $\text{Pt}(\text{II})$ DMSO complexes has recently been stimulated by the finding [8] that complexes of the type $\text{cis-Pt}(\text{amine})_2(\text{DMSO})_2$ are more water soluble and less toxic than the analogous halide complexes.

Experimental

Proton-decoupled ^{195}Pt NMR spectra were recorded on a JEOL FX60 spectrometer at 12.8 MHz, ambient temperature 300 K using 0.5–2 ml of solution in 10 mm tubes, with D_2O as external lock in a coaxial tube. This avoided deuteration of amine ligands which broadens ^{195}Pt signals through ^2H coupling. Typically a 25 kHz sweep width, 70° pulse and 8 k computer points with 0.7 s pulse interval were used, although when ^{14}N ligands were present ^{195}Pt relaxation times were shorter and more rapid pulsing could be employed without distortion of relative signal intensities. A 1M solution of Na_2PtCl_6 in D_2O was used as external chemical shift reference [9].

K_2PtCl_4 was supplied by Johnson Matthey Ltd, *cis*- $\text{Pt}(\text{NH}_3)_2\text{Br}_2$, *cis*- $\text{Pt}(\text{NH}_3)_2\text{I}_2$, $\text{Pt}(\text{en})\text{Cl}_2$ and $\text{Pt}(\text{N-en})\text{I}_2$ were synthesized by the method of Dhara [10] and had satisfactory elemental analyses. ^{15}N -Ethylenediamine $\cdot 2\text{HCl}$ (>96% ^{15}N) was purchased from Prochem (BOC) Ltd. Dimethylsulphoxide was Analar grade.

Results and Discussion***Cis-Pt(NH₃)₂Br₂***

The solvolysis of 1M (^{14}N) *cis*- $\text{Pt}(\text{NH}_3)_2\text{Br}_2$ in DMSO was studied. Owing to quadrupolar coupling to the ^{14}N ligands, only broad ^{195}Pt NMR resonances were seen. The first spectrum accumulated over a period of 1 h contained two resonances of approximately equal intensity at –2410 and –3218 ppm, assignable to complexes 11 and 8 respectively. The spectrum acquired during the second hour showed only the latter peak. The rate of solvolysis was about twice that previously observed for the chloride complex under similar conditions [6]. The spectrum

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TABLE I. ^{195}Pt NMR Shifts and $^1J(^{195}\text{Pt}-^{15}\text{N})$ Coupling Constants of Species Detected During the Solvolysis of Pt(II) Amines in Dimethylsulphoxide Solutions (SOMe_2 and OSMe_2 Represent S-Bonded and O-Bonded DMSO Respectively). Couplings are given only when ^{15}N -Enriched Ligands were used and the Reasoning behind the Assignments is given in the Text.

Complex	$-\delta$ (ppm)	$^1J(^{195}\text{Pt}-^{15}\text{N})$ (Hz) <i>trans</i> to:		
		NH_3	Br^- or I^-	DMSO
1 <i>cis</i> -[Pt(NH_3)(SOMe_2) $_2$ (H_2O)] $^{2+}$	3426	—	—	274
2 <i>cis</i> -[Pt(NH_3)(SOMe_2) $_2$ Cl] $^+$	3487	—	—	268
3 <i>trans</i> -[Pt(NH_3)(SOMe_2)(H_2O) $_2$] $^{2+}$	2965	—	—	256
4 <i>trans</i> -[Pt(OSMe_2) $_2$ (SOMe_2)(H_2O)] $^{2+}$	2877	—	—	—
5 <i>cis</i> -[Pt(NH_3) $_2$ (SOMe_2) $_2$] $^{2+}$	3512	—	—	268
6 <i>cis</i> -[Pt(NH_3)(SOMe_2) $_2$ Br] $^+$	3613	—	—	268
7 <i>cis</i> -[Pt(NH_3) $_2$ (SOMe_2)Br] $^+$	3315	—	341	232
8 <i>trans</i> -[Pt(NH_3) $_2$ (SOMe_2)Br] $^+$	3218	284	—	—
9 <i>cis</i> -Pt(NH_3)(SOMe_2)Br $_2$	3352	—	335	—
10 <i>trans</i> -Pt(NH_3)(SOMe_2)Br $_2$	3506	—	—	226
11 <i>cis</i> -Pt(NH_3) $_2$ Br $_2$	2410	—	—	—
12 <i>cis</i> -Pt(NH_3) $_2$ I $_2$	3636	—	—	—
13 <i>cis</i> -Pt(NH_3)(SOMe_2)I $_2$	4405	—	—	—
14 [Pt(en)(SOMe_2)I] $^+$	3779	—	345	247
15 [Pt(en)(SOMe_2) $_2$] $^{2+}$	3650	—	—	292
16 Pt(en)Cl $_2$	2345	—	—	—
17 [Pt(en)(SOMe_2)Cl] $^+$	3307	—	—	—

obtained over the next 14 h showed three broad peaks due to complexes 7, 8, and 9.

The assignment of these peaks was aided by spectra from complexes containing ^{15}N ligands in which $^1J(^{15}\text{N}-^{195}\text{Pt})$ couplings were clearly resolved. The only material available for this was a 2-week old solution of *cis*-Pt($^{15}\text{NH}_3$) $_2$ Cl $_2$ in DMSO which had reached equilibrium as described previously [6]. To this, two molar equivalents of AgNO $_3$ were added in two equal steps. This appeared to generate new species 1 to 6, although there are no good arguments for ruling out NO $_3^-$ as a ligand (the detailed reasoning is described in ref. 11). Addition of one equivalent of NaBr to this solution resulted in the appearance of *cis*-[Pt(NH_3)(SOMe_2) $_2$ Br] $^+$, 6. With a further 2 equivalents of NaBr, the species present were *cis*- and *trans*-[Pt(NH_3) $_2$ (SOMe_2)Br] $^+$ and *cis*- and *trans*-Pt(NH_3)(SOMe_2)Br $_2$, 7 and 8, and 9 and 10 respectively, as judged from shifts and coupling constants, see Table I.

Cis-Pt(NH_3) $_2$ I $_2$

The rate of solvolysis of this complex in DMSO was even faster than that of the bromide complex. Within 6 min. of dissolution two species with chemical shifts of -3636 ppm and -4405 ppm were present in approximately equal concentrations. The former rapidly lost intensity to the latter. These peaks were much sharper (linewidths of *ca.* 75 Hz) than those from the corresponding chloride and bromide complexes. By analogy with the species obtained on solvolysis of the chloride and bromide

TABLE II. ^{195}Pt NMR Shifts of some of the Suggested Products from the Solvolysis of Pt(II) Halides in Dimethylsulphoxide.

Complex	$-\delta$ (ppm) solvent	
	DMSO	H $_2$ O
18 Pt(SOMe_2)Cl $_3^-$	2969	3000
19 <i>cis</i> -Pt(SOMe_2) $_2$ Cl $_2$	3459	—
20 <i>trans</i> -Pt(SOMe_2) $_2$ Cl $_2$	3650	—
21 Pt(SOMe_2) $_3$ Cl $^+$	3845	—
22 <i>cis</i> -Pt(SOMe_2) $_2$ (OSMe_2)Cl $^+$	3241	—
23 <i>cis</i> -Pt(SOMe_2) $_2$ (OSMe_2) $_2^{2+}$	3070	—
24 <i>cis</i> -Pt(SOMe_2)Cl $_2$ Br $^-$	3213	3244
25 <i>trans</i> -Pt(SOMe_2)Cl $_2$ Br $^-$	3101	—
26 <i>cis</i> -Pt(SOMe_2)ClBr $_2^-$	3348	3377
27 <i>trans</i> -Pt(SOMe_2)ClBr $_2^-$	3457	3494
28 Pt(SOMe_2)Br $_3^-$	3617	—
29 <i>cis</i> -Pt(SOMe_2)Cl $_2$ (OH) $^-$	2811	2812
30 <i>trans</i> -Pt(SOMe_2)Cl $_2$ (OH) $^-$	2906	—
31 Pt(SOMe_2)(OH) $_3^-$	—	2526
32 <i>cis</i> -Pt(SOMe_2) $_2$ Cl(OH)	3298	—
33 <i>cis</i> -Pt(SOMe_2) $_2$ (OH) $_2$	3167	—
34 <i>cis</i> -Pt(SOMe_2) $_2$ (OH)(OH $_2$) $^+$	—	3095

complexes these would appear to be assignable to *cis*-Pt(NH_3) $_2$ I $_2$ and *cis*-[Pt(NH_3) $_2$ (SOMe_2)I] $^+$. However, chemical shift considerations make at least one of these assignments unlikely. The chemical shift of PtI $_4^{2-}$ is reported [5] to be -2097 ppm compared to -1631 ppm for PtCl $_4^{2-}$ and the predicted shift for *cis*-Pt(NH_3) $_2$ I $_2$ would be $-2097 + 2(-965) = -4027$

ppm (using an average I^- for Cl^- substitution shift of -965 ppm). This is unlikely to be the low-frequency limit for the resonance of this complex, since substitution of the two Cl^- ligands by two Br^- ligands in $\text{cis-Pt}(\text{NH}_3)_2\text{Cl}_2$ causes a shift of only -312 ppm, much smaller than the substitution shift of *ca.* -450 ppm in the $\text{PtCl}_4^{2-}/\text{Br}^-$ system [9]. Thus the peak which is initially most intense at -3636 ppm may be the diiodide, **12**. Substitution of DMSO for Cl^- in $\text{cis-Pt}(\text{NH}_3)_2\text{Cl}_2$ causes a shift of -1050 ppm, and thus a substitution of I^- by DMSO is expected to produce a shift to low frequency of a minimum of 85 ppm, but probably not much greater than this. Thus 769 ppm separating the initial two species is not due to the halide/DMSO substitution as seen for the chloride and bromide complexes. The chemical shift separation of $\text{cis-Pt}(\text{NH}_3)_2\text{Cl}_2$ and $\text{cis-Pt}(\text{NH}_3)(\text{SOMe}_2)\text{Cl}_2$ is 949 ppm, reasonably close to the shift change under discussion and so the second species may be $\text{cis-Pt}(\text{NH}_3)(\text{SOMe}_2)\text{I}_2$, **13**, or one or both of the iodide ligands may be further substituted by DMSO.

$\text{Pt}^{15}\text{N-en}\text{I}_2$

During the first four minutes after dissolution of $\text{Pt}^{15}\text{N-en}\text{I}_2$ in DMSO a 1:1:1:1 quartet at -3779 ppm was seen with corresponding $^1J(^{195}\text{Pt}-^{15}\text{N})$ coupling constants of 247 and 345 Hz, assignable to amine ligands *trans* to S-bonded DMSO and I^- respectively, as in complex **14**. This signal is quite close to that of the assumed $\text{cis-Pt}(\text{NH}_3)_2\text{I}_2$ at -3636 ppm but no intact $\text{Pt}^{15}\text{N-en}\text{I}_2$, which would have given rise to a triplet, was seen.

Precipitation of iodide using either two equivalents of AgNO_3 or AgClO_4 led to a further reaction of $[\text{Pt}(\text{en})(\text{SOMe}_2)\text{I}]^+$ to give a new species at -3650 ppm, a triplet with $^1J(^{195}\text{Pt}-^{15}\text{N})$ of 292 Hz. This can only be due to $[\text{Pt}(\text{SOMe}_2)_2(\text{en})]^{2+}$, **15**, and lies 138 ppm to low frequency of $\text{cis-}[\text{Pt}(\text{NH}_3)_2(\text{SOMe}_2)_2]^{2+}$. It is notable that these *cis* DMSO species were produced only when Ag^+ ions were added to the DMSO solutions. Lanza *et al.* [12] have recently discussed the curious mutual destabilization of a pair of *cis* sulphoxides and have noted that one DMSO ligand of **15** is readily displaced by solvent or any other nucleophile (in aqueous or methanolic solutions) but that the other is more difficult to displace.

$\text{Pt}(\text{en})\text{Cl}_2$

A ^{195}Pt NMR peak at -2345 ppm was visible within a few min (500 pulses) after dissolution of $(^{14}\text{N})\text{-Pt}(\text{en})\text{Cl}_2$ (1 M) in DMSO. After 25 min a second peak at -3307 ppm had appeared, and after 2.5 h *ca.* 15% remained in the initial form. After 21 h it had all reacted. The two peaks are assumed to be due to $\text{Pt}(\text{en})\text{Cl}_2$ and $[\text{Pt}(\text{en})(\text{SOMe}_2)\text{Cl}]^+$, **16** and **17**. Their separation is 962 ppm, close to the 1050 ppm

for the $\text{cis-Pt}(\text{NH}_3)_2\text{Cl}_2$ system. Both peaks were relatively sharp for ^{195}Pt bonded to ^{14}N with line-widths of *ca.* 120 and 70 Hz respectively. Again the absence of a bis-substituted complex containing *cis* sulphoxides in the presence of chloride ions is notable.

K_2PtCl_4

A 0.5 M solution of K_2PtCl_4 in DMSO gave rise to two ^{195}Pt NMR signals at -2969 ppm and -3459 ppm. Immediately after dissolution (*ca.* 2 min) two further small peaks at -3650 and -3845 ppm were visible but these disappeared after the sample was heated at 100°C for 10 min, leaving the major species in approximately equal proportions. There was no sign of any signal near to -1630 ppm, the region expected for PtCl_4^{2-} , at least in H_2O . The first two species are assigned to $[\text{Pt}(\text{SOMe}_2)\text{Cl}_3]^-$ and $\text{cis-Pt}(\text{SOMe}_2)_2\text{Cl}_2$ respectively. The former is assigned by its shift, since Goggin *et al.* [5] have reported a value of -3000 ppm for $[(\text{iPr})_4\text{N}][\text{Pt}(\text{SOMe}_2)\text{Cl}_3]$ in water, the same value as we have found for the K^+ salt in aqueous solution. The second species was assigned as the *cis* bis DMSO complex since it was prepared by a similar method to that used by Wayland *et al.* and the structure has been confirmed by X-ray crystallography [13].

The chemical shift change for the first substitution of Cl^- by DMSO in PtCl_4^{2-} is not known, since PtCl_4^{2-} itself is not observed. However, in H_2O it is from -1631 ppm to -3000 ppm *i.e.* -1369 ppm. The change for the second substitution in DMSO, from -2969 ppm to -3459 ppm is -490 ppm and much smaller than the first. However, much the same effect was found for Cl^-/DMSO substitutions in $\text{cis-Pt}(\text{NH}_3)\text{Cl}_2$: -949 ppm for the first and -466 ppm for the second. Sharply diminishing substitution shifts may be general for S-bonding ligands. In the $\text{PtCl}_4^{2-}/\text{N}$ -acetylmethionine system the fourth substitution shift appears to be almost zero*.

The kinetically-preferred product is likely to be *trans*- $\text{Pt}(\text{SOMe}_2)_2\text{Cl}_2$ and may give rise to the small signal at -3650 ppm seen within the first four minutes of dissolution of K_2PtCl_4 in DMSO.

AgClO_4 Addition

Prolonged heating of K_2PtCl_4 in DMSO produced $\text{cis-Pt}(\text{SOMe}_2)_2\text{Cl}_2$ as the only product. AgClO_4 was then added in an attempt to remove bound Cl^- and allow for further DMSO coordination. However, such reactions appeared to be more complicated than previously suggested by Price *et al.* [2]. Addition of one molar equivalent of AgClO_4 produced a new peak at -3241 ppm assumed to be $\text{cis-}[\text{Pt}(\text{SOMe}_2)_2(\text{OSMe}_2)\text{Cl}]^+$. All trace of $\text{cis-Pt}(\text{SOMe}_2)_2\text{Cl}_2$ dis-

*I. M. Ismail and P. J. Sadler, unpublished work.

appeared on addition of the third equivalent of AgClO_4 giving new species at -3070 ppm and -2870 ppm. The former was assigned to $\text{cis}[\text{Pt}(\text{SOMe}_2)_2(\text{OSMe}_2)_2]^{2+}$, **23**, and the latter, which was also seen during reactions of AgNO_3 with $\text{cis-Pt}(\text{NH}_3)_2\text{Cl}_2$ in DMSO, was assigned to a complex containing an H_2O ligand, **24**. When H_2O ($50\ \mu\text{l}$) was added, all of complex **22** disappeared and the concentration of complex **24** increased, with notable increases in line-width from about 30 to 105 Hz of both **24** and **23**, suggesting that, with H_2O present, O-bonded DMSO is kinetically labile. Perchlorate may also be involved in the exchange process.

The assignments of species **20** and **21** may be interchanged, in which case the chemical shift differences between complexes **19** and **22** and **21** and **20** are similar at 213 and 195 ppm respectively. The chemical shift difference between *cis* and *trans*- $\text{Pt}(\text{SOMe}_2)_2\text{Cl}_2$ is then 386 ppm, which is quite large, but a similar value is observed for *cis*- and *trans*- $[\text{Pt}(\text{NO}_2)_2\text{Cl}_4]^{2-}$ [**14**].

Hydroxide Complexes

One equivalent of DMSO was added to a 0.4 M aqueous solution of K_2PtCl_4 (2 ml). This gave predominantly $[\text{PtCl}_3(\text{SOMe}_2)]^-$ together with a small amount of *cis*- $\text{PtCl}_2(\text{SOMe}_2)_2$ as precipitate. To this were added 4 equivalents of NaOH. The ^{195}Pt NMR spectrum (3000 pulses) showed two species: $[\text{PtCl}_3(\text{SOMe}_2)]^-$ at -3000 ppm and presumably either complex **29** or **30** *cis*- or *trans*- $[\text{PtCl}_2(\text{SOMe}_2)(\text{OH})]^-$ at -2812 ppm. Over the next 12 h the pH of the solution dropped from 12.7 to 7.2 and the amount of the new species increased to 35% of the total Pt in solution. Further NaOH was added to give a total of 14 equivalents but no further change in the spectrum was observed.

Titration of K_2PtCl_4 with NaOH in DMSO

Addition of H_2O (final concentration 5 M) to 0.5 ml of 0.5 M K_2PtCl_4 in DMSO did not produce $\text{PtCl}_2(\text{SOMe}_2)(\text{H}_2\text{O})$ but left only $[\text{PtCl}_3(\text{SOMe}_2)]^-$ and $\text{PtCl}_2(\text{SOMe}_2)_2$ in solution in approximately equal amounts. Addition of one equivalent of NaOH caused reaction of about 50% of the latter species and appearance of a new species at -3298 ppm. This presumably represented a Cl^-/OH^- substitution to give *cis*- $\text{PtCl}(\text{OH})(\text{SOMe}_2)_2$, **32**. Addition of a second equivalent of NaOH gave three further species at -3167 , -2890 and -2906 ppm, and a third equivalent of NaOH gave rise to species with resonances at -2793 and 2811 ppm. The peak at -2890 ppm was clearly different from the other species shifting by 5.25 ppm per equivalent of NaOH added, the others by only +1.0 ppm/equiv. The nature of the equilibrium affecting the shift of this species was not clear.

The two species with peaks at lowest frequency, -3298 and -3167 ppm probably contain two S-

bonding DMSO ligands since the chemical shift of *cis*- $\text{PtCl}_2(\text{SOMe}_2)_2$ is known to be -3459 ppm. The peaks probably represent successive substitution of Cl^- by OH^- and the substitution shifts are therefore +161 and +131 ppm respectively. These shift changes are of the same order of magnitude, although of opposite sign, as the shifts for Br^-/Cl^- substitution in the same *cis*-bis-DMSO system. Using this analogy, it is possible to estimate the shifts for *cis*- and *trans*- $[\text{PtCl}_2(\text{SOMe}_2)(\text{OH})]^-$, **29** and **30**, as -2710 ppm and -2610 ppm and the trihydroxy species should be found near -2500 ppm. It is therefore reasonable to assign one of the species at -2793 and -2811 ppm to *cis*- $[\text{PtCl}_2(\text{SOMe}_2)(\text{OH})]^-$, **29**, and one of the two peaks at -2890 and -2906 ppm to the corresponding *trans* isomer, **30**.

Conclusion

Studies of the solvolysis of platinum complexes in dimethyl sulphoxide are important in relation to anticancer screening. DMSO is often a biologically acceptable solvent, at least for *in vitro* cytotoxicity tests. We have shown previously [6], by ^{195}Pt NMR, that solvolysis of *cis*- $\text{Pt}(\text{NH}_3)_2\text{Cl}_2$ in DMSO leads to a variety of products within a few hours, including mono-ammine, *trans*-diammine and triammine complexes, but no bis DMSO complexes. From the studies reported here, the rates of solvolysis appear to follow the order: *cis*- $\text{Pt}(\text{NH}_3)_2\text{Cl}_2 < \text{cis-Pt}(\text{NH}_3)_2\text{Br}_2 < \text{cis-Pt}(\text{NH}_3)_2\text{I}_2$. In both the bromide and iodide cases, monoammines also appear to be products, a consequence of the high *trans* influence of S-bonded DMSO. The solvolysis of $\text{Pt}(\text{en})\text{I}_2$ was also very rapid. The rates are presumably a reflection of the stabilities of five-coordinate intermediates and the strengths of the $\text{Pt}(\text{II})$ -halide bonds, since the solvation enthalpies for the halide ions follow the order $\text{I}^- < \text{Br}^- < \text{Cl}^-$, although the differences are not large [15]. Reasonable assignments for hydroxo $\text{Pt}(\text{II})$ DMSO complexes were possible from the patterns of ^{195}Pt shifts observed, but more definitive assignments clearly require isolation and characterization of the products.

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