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

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Abstract

The solvolyses of the complexes *cis*-Pt(L_2)X_2, where L_2 is two NH_3 molecules or ethylenediamine and X = 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 Pt(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 $[Pt(DMSO)_4]^{2+}$ in solution contained two *cis* S-bonded and two *cis* O-bonded DMSO ligands on the basis of NMR and infrared measurements. $[Pd(DMSO)_4]^{2+}$ 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 Pt(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 Pt(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 *cis*-Pt($^{15}NH_3$)$_2$$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 Pt(II) DMSO complexes has recently been stimulated by the finding [8] that complexes of the type *cis*-Pt(amine)$_2$(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 ^{2}H 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*-Pt$(NH_3)_2Br_2$, *cis*-Pt$(NH_3)_2I_2$, Pt(en)Cl_2 and Pt(^{15}N-en)I_2 were synthesized by the method of Dhara [10] and had satisfactory elemental analyses. ^{15}N-Ethylenediamine·2HCl (>96% ^{15}N) was purchased from Prochem (BOC) Ltd. Dimethylsulphoxide was Analar grade.

Results and Discussion

Cis-Pt(NH$_3$)$_2$Br$_2$

The solvolysis of 1M (^{14}N)*cis*-Pt$(NH_3)_2Br_2$ 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 $^{1}J(^{195}Pt-^{15}N)$ 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	−δ (ppm)	$^{1}J(^{195}Pt-^{15}N)$ (Hz) *trans* to:		
		NH_3	Br^- or I^-	DMSO
1 *cis*-$[Pt(NH_3)(SOMe_2)_2(H_2O)]^{2+}$	3426	–	–	274
2 *cis*-$[Pt(NH_3)(SOMe_2)_2Cl]^{+}$	3487	–	–	268
3 *trans*-$[Pt(NH_3)(SOMe_2)(H_2O)_2]^{2+}$	2965	–	–	256
4 *trans*-$[Pt(OSMe_2)_2(SOMe_2)(H_2O)]^{2+}$	2877	–	–	–
5 *cis*-$[Pt(NH_3)_2(SOMe_2)_2]^{2+}$	3512	–	–	268
6 *cis*-$[Pt(NH_3)(SOMe_2)_2Br]^{+}$	3613	–	–	268
7 *cis*-$[Pt(NH_3)_2(SOMe_2)Br]^{+}$	3315	–	341	232
8 *trans*-$[Pt(NH_3)_2(SOMe_2)Br]^{+}$	3218	284	–	–
9 *cis*-$Pt(NH_3)(SOMe_2)Br_2$	3352	–	335	–
10 *trans*-$Pt(NH_3)(SOMe_2)Br_2$	3506	–	–	226
11 *cis*-$Pt(NH_3)_2Br_2$	2410	–	–	–
12 *cis*-$Pt(NH_3)_2I_2$	3636	–	–	–
13 *cis*-$Pt(NH_3)(SOMe_2)I_2$	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 $^{1}J(^{15}N-^{195}Pt)$ couplings were clearly resolved. The only material available for this was a 2-week old solution of *cis*-$Pt(^{15}NH_3)_2Cl_2$ 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*-$[Pt(NH_3)(SOMe_2)_2Br]^+$, **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 complexes these would appear to be assignable to *cis*-$Pt(NH_3)_2I_2$ 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*-$Pt(NH_3)_2I_2$ would be $-2097 + 2(-965) = -4027$

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

Complex	−δ (ppm) solvent	
	DMSO	H_2O
18 $Pt(SOMe_2)Cl_3^-$	2969	3000
19 *cis*-$Pt(SOMe_2)_2Cl_2$	3459	–
20 *trans*-$Pt(SOMe_2)_2Cl_2$	3650	–
21 $Pt(SOMe_2)_3Cl^+$	3845	–
22 *cis*-$Pt(SOMe_2)_2(OSMe_2)Cl^+$	3241	–
23 *cis*-$Pt(SOMe_2)_2(OSMe_2)_2^{2+}$	3070	–
24 *cis*-$Pt(SOMe_2)Cl_2Br^-$	3213	3244
25 *trans*-$Pt(SOMe_2)Cl_2Br^-$	3101	–
26 *cis*-$Pt(SOMe_2)ClBr_2^-$	3348	3377
27 *trans*-$Pt(SOMe_2)ClBr_2^-$	3457	3494
28 $Pt(SOMe_2)Br_3^-$	3617	–
29 *cis*-$Pt(SOMe_2)Cl_2(OH)^-$	2811	2812
30 *trans*-$Pt(SOMe_2)Cl_2(OH)^-$	2906	–
31 $Pt(SOMe_2)(OH)_3^-$	–	2526
32 *cis*-$Pt(SOMe_2)_2Cl(OH)$	3298	–
33 *cis*-$Pt(SOMe_2)_2(OH)_2$	3167	–
34 *cis*-$Pt(SOMe_2)_2(OH)(OH_2)^+$	–	3095

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 *cis*-$Pt(NH_3)_2Cl_2$ causes a shift of only −312 ppm, much smaller than the substitution shift of *ca.* −450 ppm in the $PtCl_4^{2-}/Br^-$ system [9]. Thus the peak which is initially most intense at −3636 ppm may be the diiodide, **12**. Substitution of DMSO for Cl^- in *cis*-$Pt(NH_3)_2Cl_2$ 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 *cis*-$Pt(NH_3)_2Cl_2$ and *cis*-$Pt(NH_3)(SOMe_2)Cl_2$ is 949 ppm, reasonably close to the shift change under discussion and so the second species may be *cis*-$Pt(NH_3)(SOMe_2)I_2$, **13**, or one or both of the iodide ligands may be further substituted by DMSO.

Pt(^{15}N-en)I$_2$

During the first four minutes after dissolution of $Pt(^{15}N\text{-en})I_2$ in DMSO a 1:1:1:1 quartet at −3779 ppm was seen with corresponding $^1J(^{195}Pt-^{15}N)$ 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 *cis*-$Pt(NH_3)_2I_2$ at −3636 ppm but no intact $Pt(^{15}N\text{-en})I_2$, 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 $[Pt(en)(SOMe_2)I]^+$ to give a new species at −3650 ppm, a triplet with $^1J(^{195}Pt-^{15}N)$ of 292 Hz. This can only be due to $[Pt(SOMe_2)_2(en)]^{2+}$, **15**, and lies 138 ppm to low frequency of *cis*-$[Pt(NH_3)_2(SOMe_2)_2]^{2+}$. 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.

Pt(en)Cl$_2$

A ^{195}Pt NMR peak at −2345 ppm was visible within a few min (500 pulses) after dissolution of $(^{14}N)-Pt(en)Cl_2$ (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 $Pt(en)Cl_2$ and $[Pt(en)(SOMe_2)Cl]^+$, **16** and **17**. Their separation is 962 ppm, close to the 1050 ppm for the *cis*-$Pt(NH_3)_2Cl_2$ system. Both peaks were relatively sharp for ^{195}Pt bonded to ^{14}N with linewidths 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$_2$PtCl$_4$

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 $[Pt(SOMe_2)Cl_3]^-$ and *cis*-$Pt(SOMe_2)_2Cl_2$ respectively. The former is assigned by its shift, since Goggin *et al.* [5] have reported a value of −3000 ppm for $[(iPr)_4N][Pt(SOMe_2)Cl_3]$ 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 *cis*-$Pt(NH_3)Cl_2$: −949 ppm for the first and −466 ppm for the second. Sharply diminishing substitution shifts may by general for S-bonding ligands. In the $PtCl_4^{2-}$/N-acetylmethionine system the fourth substitution shift appears to be almost zero*.

The kinetically-preferred product is likely to be *trans*-$Pt(SOMe_2)_2Cl_2$ 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 *cis*-$Pt(SOMe_2)_2Cl_2$ as the only product. $AgClO_4$ was then added in an attempt to remove bound Cl^- and allow for futher 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 *cis*-$[Pt(SOMe_2)_2(OSMe_2)Cl]^+$. All trace of *cis*-$Pt(SOMe_2)_2Cl_2$ dis-

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*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 *cis*-$[Pt(SOMe_2)_2(OSMe_2)_2]^{2+}$, **23**, and the latter, which was also seen during reactions of $AgNO_3$ with *cis*-$Pt(NH_3)_2Cl_2$ in DMSO, was assigned to a complex containing an H_2O ligand, **24**. When H_2O (50 μl) was added, all of complex **22** disappeared and the concentration of complex **24** increased, with notable increases in linewidth 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*-$Pt(SOMe_2)_2Cl_2$ is then 386 ppm, which is quite large, but a similar value is observed for *cis*- and *trans*-$[Pt(NO_2)_2Cl_4]^{2-}$ [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 $[PtCl_3(SOMe_2)]^-$ together with a small amount of *cis*-$PtCl_2(SOMe_2)_2$ as precipitate. To this were added 4 equivalents of NaOH. The ^{195}Pt NMR spectrum (3000 pulses) showed two species: $[PtCl_3(SOMe_2)]^-$ at −3000 ppm and presumably either complex **29** or **30** *cis*- or *trans*-$[PtCl_2(SOMe_2)(OH)]^-$ 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 $PtCl_2(SOMe_2)(H_2O)$ but left only $[PtCl_3(SOMe_2)]^-$ and $PtCl_2(SOMe_2)_2$ 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*-$PtCl(OH)(SOMe_2)_2$, **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*-$PtCl_2(SOMe_2)_2$ 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*-$[PtCl_2(SOMe_2)(OH)]^-$, **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*-$[PtCl_2(SOMe_2)(OH)]^-$, **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*-$Pt(NH_3)_2Cl_2$ 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*-$Pt(NH_3)_2Cl_2 <$ *cis*-$Pt(NH_3)_2Br_2 <$ *cis*-$Pt(NH_3)_2I_2$. 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 $Pt(en)I_2$ was also very rapid. The rates are presumably a reflection of the stabilities of five-coordinate intermediates and the strengths of the Pt(II)–halide bonds, since the solvation enthalpies for the halide ions follow the order $I^- < Br^- < Cl^-$, although the differences are not large [15]. Reasonable assignments for hydroxo Pt(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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