Solvolysis of *cis*-$[Pt(NH_3)_2Cl_2]$ in Dimethyl Sulphoxide and Reactions of Glycine with $[PtCl_3(Me_2SO)]^-$ as Probed by ^{195}Pt Nuclear Magnetic Resonance Shifts and ^{195}Pt–^{15}N Coupling Constants

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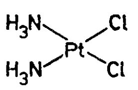
Summary The formation of six products from the solvolysis of *cis*-$[Pt(NH_3)_2Cl_2]$ in Me_2SO has been monitored by ^{195}Pt n.m.r. shifts and ^{195}Pt–^{15}N coupling constants, the products including mono- and tri-ammine species; the same method allows a ready identification of the more thermodynamically stable isomer of $[Pt(glycinate)(Me_2SO)Cl]$ as that with O *trans* to S.

Despite the widespread use of Me_2SO as a solvent for the anti-tumour agent *cis*-$[Pt(NH_3)_2Cl_2]$ in pharmacobiochemical experiments,[1] there appears to be insufficient data available on its solvolytic products, mainly because few methods are available for following such reactions in detail. Me_2SO is known to be a strong (S-bonding) nucleophile toward Pt^{II}, exerting a high (kinetic) *trans* effect[2,3] but since Pt–N bonds are usually considered to be inert[4] the only major solvolysis product might be expected to be *cis*-$[Pt(NH_3)_2Cl(Me_2SO)]^+$, unless acid is present[5] to drive the reaction towards NH_3 release. We describe here the identification of six solvolytic products of (**1**) using ^{195}Pt n.m.r. shifts and ^{195}Pt–^{15}N coupling constants. The same procedure is then simply applied to confirm Erickson and Hahne's interpretation[6] of the course of the glycine–$[PtCl_3(Me_2SO)]^-$ reaction.

Table. Chemical shifts and coupling constants

		$^1\lvert J(^{195}Pt–^{15}N)\rvert$/Hz[c], *trans* to		
Complex[a]	δ/p.p.m.[b]	Cl^-	NH_3	Me_2SO
(**1**)	2097	312·2	—	—
(**2**)	2354	317	278	—
(**3**)	3046	336[d]	—	—
(**4**)	3067	—	—	232
(**5**)	3126	—	287[d]	—
(**6**)	3147	340·0[d]	—	233·8
(**7**)	3224	—	288[d]	232
(**8**)	1602	317	—	—
(**9**)	3110	—	—	244
(**10**)	2747	—	—	226
(**11**)	2902	330[d]	—	—

[a] (**1**)—(**7**) in Me_2SO, (**8**)—(**11**) in H_2O, all at 30 °C. [b] to high field of Na_2PtCl_6 in D_2O (external), ±0·5 p.p.m. [c] ±6 or ±0·6 Hz if quoted to one decimal place. [d] *cis* to Me_2SO.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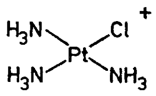
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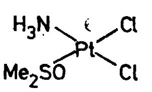
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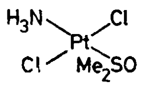
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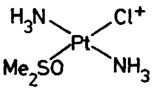
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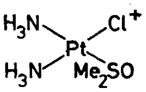
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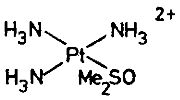
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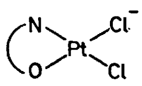
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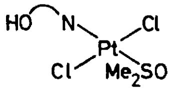
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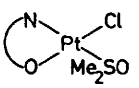
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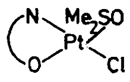
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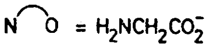
$= H_2NCH_2CO_2^-$

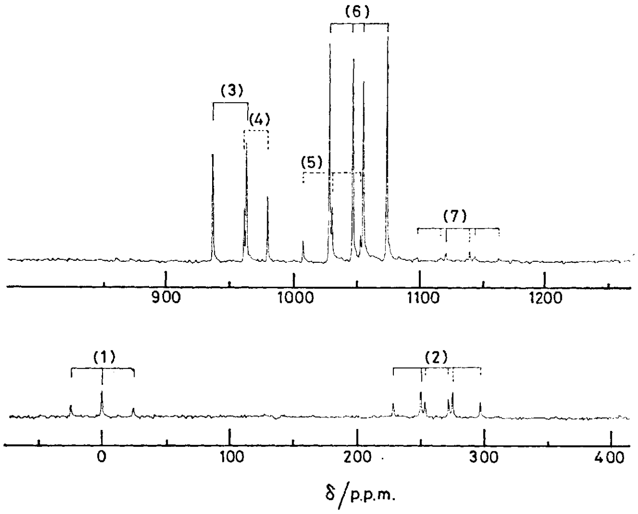

FIGURE 1. 12·8 MHz ^{1}H-noise decoupled ^{195}Pt FT n.m.r. spectrum of a 1 M solution of *cis*-[Pt(^{15}NH$_3$)$_2$Cl$_2$] (**1**), in dimethyl sulphoxide, 30 °C. This accumulation, total time 14 h, began 3 h after dissolution. (Sweep width 25 kHz, pulse interval 0·7 s, 8k computer points, 70° pulse). Shifts are to high field of (**1**), other assignments are given in the Table.

The spectrum of a 1 M solution of *cis*-[Pt(^{15}NH$_3$)$_2$Cl$_2$]† (**1**) in (AnalaR) Me$_2$SO 5—15 min after dissolution showed a signal due to a single species: a 1 : 2 : 1 triplet 2097 p.p.m. upfield of Na$_2$PtCl$_6$ with $^1|J(^{195}\text{Pt}-^{15}\text{N})|$ 312·2 Hz. This was assigned to intact (**1**), which may be solvated in the fifth and sixth positions. The first new species to appear, 1050 p.p.m. upfield of this, *ca.* 40 min later, and with four peaks of equal intensity was assigned to *cis*-[Pt(^{15}NH$_3$)$_2$Cl(Me$_2$SO)]$^+$, (**6**), the only possible square-planar complex containing two nonequivalent nitrogen atoms. An upfield shift of *ca.* 1000 p.p.m. is expected for Cl$^-$ substitution by Me$_2$SO.[7] 2 h later a further three species can be seen: a 1 : 2 : 1 triplet with a similar chemical shift to (**6**) and identified as *trans*-[Pt(^{15}NH$_3$)$_2$Cl(Me$_2$SO)]$^+$ (**5**), and about 80 p.p.m. downfield of this a pair of doublets assigned to *cis*- (**3**) and *trans*-[Pt(^{15}NH$_3$)Cl$_2$(Me$_2$SO)], (**4**). Their shifts, relative to (**5**), are as expected for NH$_3$ replacement by Cl$^-$. The final species to appear in the spectrum each give a doublet of triplets and therefore contain three co-ordinated nitrogen atoms. They have a chemical shift difference of 870 p.p.m. and are assigned to [Pt(^{15}NH$_3$)$_3$Cl]$^+$ (**2**), and [Pt(^{15}NH$_3$)$_3$(Me$_2$SO)]$^{2+}$ (**7**). Figure 1 illustrates the spectra of all these species, and Figure 2 the variation of their concentrations with time.

The correct assignment of (**3**) and (**4**) is provided by their $^1|J(^{195}\text{Pt}-^{15}\text{N})|$ coupling constants, which are proportional to the *s* character of the Pt–N bond.[8] This depends on the nature of the *trans* ligand and increases in the order Me$_2$SO $<$ NH$_3$ $<$ Cl$^-$. The Table shows that Me$_2$SO also exerts a small *cis* effect (*ca.* +15 Hz in ^1J).

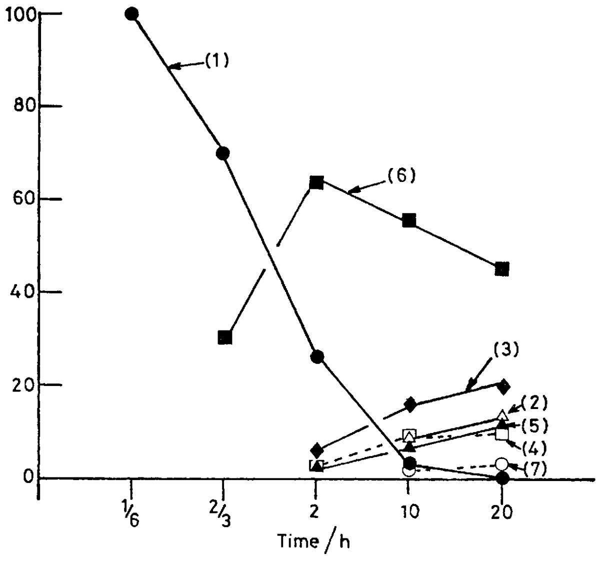

FIGURE 2. Variation of the composition of a 1 M solution of (**1**) in Me$_2$SO with time, as determined from ^{195}Pt n.m.r. peak heights (errors due to T_1 and nuclear Overhauser effect differences are unknown, but may be small since T_1's are expected to be short and all species have a two-bond Pt–H coupling).

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† Prepared from K$_2$PtCl$_4$, ^{15}NH$_4$Ac, and KCl following the method of V. V. Lebedinskii and V. A. Golovnya, *Neorg. Khim. Acad. Nauk. S.S.S.R.*, 1947, **20**, 95 (*Chem. Abs.*, 1947, **44**, 5257).

Pt^{II}–glycine complexes provide a neat application of this pattern of couplings. Reaction of $PtCl_4^{2-}$ with excess of $[^{15}N]$glycine in H_2O gives a doublet with ^1J = 317 Hz, due to a complex (**8**) with N *trans* to Cl^-. $[PtCl_3MeSO_2]^-$, on the other hand, reacts with 1 equiv. (0·25 M) of $[^{15}N]$glycine in H_2O to give initially a mixture of (**9**) and (**10**), but predominantly (**10**) on addition of 1 equiv. of OH^-. Complex (**10**), with ^1J 226 Hz and N *trans* to S, isomerises on heating the solution to the more thermodynamically stable isomer (**11**), which has ^1J 330 Hz, confirming[6] that here N is *trans* to Cl^- and *cis* to Me_2SO.

The quadrupole moment of ^{14}N ($I = 1$) leads to linewidths of *ca.* 200 Hz for *cis*-$[Pt(^{14}NH_3)_2Cl_2]$‡ in Me_2SO, compared to *ca.* 8 Hz with ^{15}N. Despite this and higher order multiplicities all species except (**7**) were again observed during solvolysis. [The concentration of (**7**) can be increased by addition of $AgNO_3$.] Complexes (**2**) and (**3**) appear to account for $> 50\%$ of the species present in a day-old solution at 90 °C, although some precipitation occurs.

We thank the S.R.C. for a grant to purchase the Pt n.m.r. probe and a studentship (to S.J.S.K.), and Johnson Matthey Ltd. for some support and loan of Pt.

(*Received*, 22*nd August* 1977; *Com.* 887.)

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‡ As a check that some of the solvolysis products from ^{15}N-(**1**) were not due to impurities in the starting material, this compound was prepared by a different route; from K_2PtCl_4, KI, and NH_4OH–Ag^+–Cl^- following the method of S. C. Dhara, *Indian J. Chem.*, 1970, **8**, 193.

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