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Platinum(II) Complexes Containing Dimethylsulphoxide and Linear Aliphatic Diamines Formation of a Seven-membered Chelate Ring

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The synthesis and properties of complexes of the type [Pt(diamine)(dmso)Cl] Cl containing chelate rings of increasing size are reported (dmso = dimethylsulphoxide; diamine = 1,2-diaminoethane (en), 1,3-diaminopropane (tn), and 1,4-diaminobutane (bn)). The 1,4-diaminobutane complex contains the rare seven-membered ring and is formed together with a binuclear complex, trans-*[Pt(dmso)Cl*$_2$*]*$_2$*(NH*$_2$*(CH*$_2$*)*$_4$*NH*$_2$*), in which the amine bridges two platinum atoms. The compounds have been characterised by analysis, conductance, spectroscopic and nuclear magnetic resonance measurements. On heating the en and the tn complexes under reduced pressure dimethylsulphoxide is lost and the corresponding uncharged [Pt(diamine)Cl*$_2$*] species is formed.*

Introduction

Some time ago we started a kinetic study of the reactions of platinum(II) complexes containing dimethylsulphoxide and monodentate amines. Taking advantage of the strong *trans* labilising effect exercised by the S-bonded ligand we were able to overcome the marked inertness of the Pt–N bond towards substitution and study not only the entry of amine into the complex but also the displacement of the amine *trans* to dimethylsulphoxide by chloride. Two systems were studied, namely, *cis*-[Pt(dmso)(am)$_2$Cl] Cl [1] and *trans*-[Pt(dmso)(am)Cl$_2$] [2], where am is one of a wide range of primary, secondary and heterocyclic amines. It was shown that the basicity of the amine controlled both the rate of its displacement and the thermodynamic stability of the complex, in the sense that the most basic amine produced the most stable and least reactive substrate. There was also a very strong basicity related *cis* effect whereby the least basic amine produced the most labile substrate [1]. We now intend to make use of the *trans* labilising effect of dimethylsulphoxide to examine the relationship between ring size and the rates of ring opening and closing in complexes of the type [Pt(dmso)(diamine)Cl]$^+$ in order to extend our understanding of the relationship between ring size and equilibrium constant for chelate formation and we report here the synthesis of the complexes with the 5-, 6- and 7- membered rings.

Experimental

Ethylenediamine, 1,3-diaminopropane and 1,4-diaminobutane were purchased from Fluka and used without further purification.

cis-[Pt(dmso)$_2$Cl$_2$] was prepared from K$_2$PtCl$_4$ and aqueous dimethylsulphoxide by the method of Wayland *et al.* [3]. K[Pt(dmso)Cl$_3$] was prepared by reacting equimolar amounts of K$_2$PtCl$_4$ and dimethylsulphoxide in aqueous solution [4].

Chloro(dimethylsulphoxide)(ethylenediamine)platinum(II) Chloride

To a suspension of *cis*-[Pt(dmso)$_2$Cl$_2$] (1.0 g, 2.35 mmol) in methanol (100 ml) a solution of ethylenediamine (0.142 g, 2.36 mmol) in methanol (10 ml) was added dropwise and the mixture stirred at room temperature until the yellow colour had disappeared. The solution was 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 10 ml under reduced pressure. The white crystals that formed on cooling were filtered off, washed with ether and air dried. *Anal.* Found: C, 11.9; H, 3.31; N, 7.17; Cl, 17.3; S, 7.7. C$_4$H$_{14}$N$_2$OSCl$_2$Pt requires: C, 11.9; H, 3.46; N, 6.93; Cl, 17.5; S, 7.9%. The same compound can be obtained by reacting K[Pt(dmso)Cl$_3$] with an equimolar amount of ethylenediamine in water.

Chloro(dimethylsulphoxide)(1,3-diaminopropane)platinum(II) Chloride

This compound was prepared in the same way as the ethylenediamine complex using equimolar

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amounts of *cis*-[Pt(dmso)$_2$Cl$_2$] and 1,3-diaminopropane except that the complex did not crystallise spontaneously from the concentrated filtrate and required the careful addition of diethylether. *Anal.* Found: C, 14.3; H, 3.89; N, 6.70; Cl, 17.1; S, 7.8. $C_5H_{16}N_2OSCl_2Pt$ requires: C, 14.4; H, 3.82; N, 6.69; Cl, 17.0; S. 7.70%.

μ-(1,4-diaminobutane)bis[dichloro(dimethylsulphoxide)platinum(II)]

A solution of 1,4-diaminobutane (0.41 g, 4.7 mmol) in methanol (10 ml) was added dropwise to a stirred suspension of *cis*-[Pt(dmso)$_2$Cl$_2$] (2.0 g, 4.8 mmol) in methanol (150 ml). Before the addition of amine was complete a yellow compound had started to separate. The mixture was left overnight in the refrigerator and the yellow compound, insoluble in water, methanol and most organic solvents, was filtered off, washed with methanol and ether and air dried. *Anal.* Found: C, 12.4; H, 3.13; N, 3.78; Cl, 18.3; S, 8.2. $C_8H_{24}N_2O_2S_2Cl_4Pt_2$ requires: C, 12.4; H, 3.09; N, 3.61; Cl, 18.6; S, 8.4%.

Chloro(dimethylsulphoxide)(1,4-diaminobutane)platinum(II) Chloride

The filtrate from the above preparation was evaporated to small volume (4–5 ml) under reduced pressure and ether was added until precipitation started. The mixture was left overnight in the refrigerator and the white compound was filtered off, washed with ether and air dried. *Anal.* Found: C, 16.4; H, 4.26; N, 6.34; Cl, 16.1; S, 7.3. $C_6H_{18}N_2OSCl_2Pt$ requires: C, 16.7; H, 4.19; N, 6.48; Cl, 16.4; S, 7.4%.

Trans-*dichloro(dimethylsulphoxide)(1-aminobutane)platinum(II)*

This was prepared by a modification of Kukushkin's method [4]. An equimolar amount of 1-aminobutane was added to an aqueous solution of [K[Pt(dmso)Cl$_3$] and the yellow product extracted by ether and recrystallised from ether. *Anal.* Found: C, 17.0; H, 3.94; N, 3.48. $C_6H_{17}NOSCl_2Pt$ requires: C, 17.3; H, 4.10; N, 3.35%.

Thermal Decomposition of [Pt(dmso)(en)Cl] Cl

0.5 g of [Pt(dmso)(en)Cl] Cl was placed in the bottom of a small flask linked to a vacuum system and immersed in an oil bath. The pressure was reduced to 20 mm Hg and the temperature increased slowly. At 138 °C the colour changed from white to deep yellow and drops of dimethylsulphoxide condensed on the cool parts of the apparatus. The product (0.398 g) was recrystallised from hot water. *Anal.* Found: C, 7.43; H, 2.47; N, 8.48; Cl, 21.7. $C_2H_8N_2Cl_2Pt$ requires: C, 7.36; H, 2.45; N, 8.59; Cl, 21.8%.

Thermal Decomposition of [Pt(dmso)(tn)Cl] Cl

Using the same procedure as above, 0.402 g of product was obtained from the decomposition of 0.50 g of [Pt(dmso)(tn)Cl] Cl. *Anal.* Found: C, 10.69; H, 2.97; N, 8.11; Cl, 20.85. $C_3H_{10}N_2Cl_2Pt$ requires: C, 10.52; H, 2.94; N, 8.23; Cl, 20.85%.

N-deuteration of the Complexes

The complexes were dissolved in D$_2$O and the solutions allowed to stand for several hours at room temperature before they were evaporated to dryness over P$_2$O$_5$.

Physicochemical Measurements

Electrolytic conductances were measured with a Jones conductivity bridge and a conventional cell with shiny platinum electrodes previously calibrated with aqueous KCl. All measurements were made at 25 °C in water.

Infrared spectra were measured with a Perkin–Elmer PE 577 recording spectrophotometer. Samples were in the form of Nujol or hexachlorobutadiene mulls.

Electronic spectra were measured with an Optica CF-4 recording spectrophotometer.

The ^{1}H nmr spectra of D$_2$O solutions of the complexes and of the free ligands were measured with a 60 MHz Perkin–Elmer R 24A spectrometer.

Results and Discussion

The reaction between *cis*-[Pt(dmso)$_2$Cl$_2$] and linear aliphatic diamines yields white crystalline compounds which, on the basis of their elemental analysis, conductivities, electronic and infrared spectra, can be formulated as [Pt(dmso)(diamine)Cl]-Cl. The complex with chelated ethylenediamine has been previously described by Johnson [5] who prepared it by the solvolysis of [Pt(en)Cl$_2$] in dimethylsulphoxide. All three complexes are 1:1 electrolytes in water (Table I). The preparation of the 1,4-diaminobutane complex also affords an uncharged yellow complex which analyses as Pt$_2$(dmso)$_2$Cl$_4$(bn). The electronic spectra of the three [Pt(dmso)(diamine)Cl] Cl species in water or methanol are similar and consist of an absorption rising into the far u.v. with an inflection at 260 nm. The molar extinction coefficients at this wavelength are 470, 430 and 430 M^{-1} cm^{-1} for the en, tn and bn complexes respectively. These spectra are also very similar to those of *cis*-[Pt(dmso)(am)$_2$Cl] Cl [1] where am is an alicyclic primary amine, such as cyclohexylamine. All the compounds reported in this paper have a strong infra-red absorption in the range 1112–1145 cm^{-1}, which can be assigned to ν(S–O) of the coordinated dimethylsulphoxide. This occurs at higher frequency than the corresponding vibration in the

TABLE I. Conductivity and Some Characteristic Infra-red Absorptions of Some Platinum(II) Amine Complexes Containing Dimethylsulphoxide.

Complex	λ_M/ohm^{-1} cm^2 mol^{-1} ^{a}	ν(S–O)/cm^{-1}	ν(Pt–S)/cm^{-1}	ν(Pt–Cl)/cm^{-1}
[Pt(dmso)(en)Cl]Cl	139	1145	434	344
[Pt(dmso)(tn)Cl]Cl	131	1112	438	340
[Pt(dmso)(bn)Cl]Cl	131	1130	436	338
cis-[Pt(dmso)(chx)$_2$Cl]Cl^b		1130	442	336
trans-[Pt(dmso)Cl$_2$]$_2$(bn)		1122	439	343
trans-[Pt(dmso)(Bu^{n}NH$_2$)Cl$_2$]		1123	436	339
cis-[Pt(dmso)(chx)Cl$_2$]^{b,c}		1129, 1116	443	342, 329

^{a}2.5 × 10^{-4} *M* aqueous solution at 25 °C. ^{b}chx = cyclohexylamine. ^{c}Data from Ref. 2.

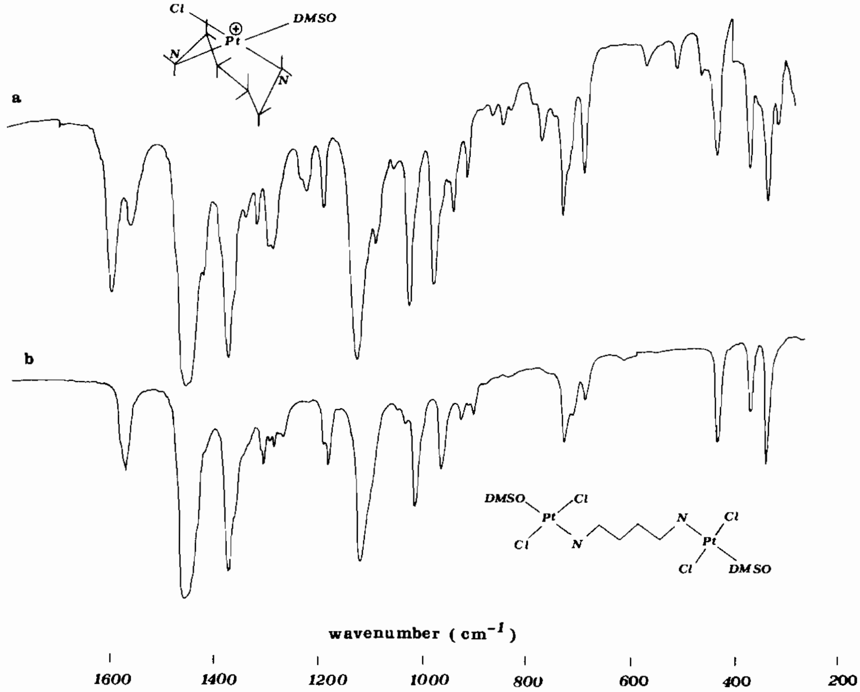

Figure 1. Infrared spectra of the chelate (a) and the bridged (b) platinum(II)–1,4-diaminobutane complexes in the region 1750–250 cm^{-1} (Nujol mulls).

free ligand and is fully consistent with bonding through sulphur [6]. This is the normal mode of bonding of dimethylsulphoxide to platinum(II) and palladium(II) although there are many examples of mixed S- and O-bonded or even totally O-bonded sulphoxide Pd^{II} and Pt^{II} complexes [3, 7–9] but generally these are only found in sterically hindered systems. The absorptions in the region 3300–3100 cm^{-1} are broad and, since they shift when the materials have been allowed to stand in D$_2$O solution, they can be assigned to ν(N–H). For the [Pt(dmso)(bn)Cl] Cl complex, whose i.r. spectrum is typical of all three species, the best defined peak in this region shifts from 3235 to 2410 cm^{-1} on deuteration (ν(N–H)/ν(N–D) = 1.34). A band at 1600 cm^{-1} also disappears on deuteration and is assigned to an NH$_2$ bending mode. There are four weak peaks in the ν(C–H) region (3000–2880 cm^{-1}) that are not affected by the deuteration treatment. The i.r. spectrum in the range 1750–300 cm^{-1} is shown in Fig. 1. Of the many bands present, that at 436 cm^{-1} is assigned to ν(Pt–S) and that at 338 cm^{-1} to ν(Pt–Cl).

The evidence is thus strongly in favour of a chelating diamine in all three cases so that, in the case of

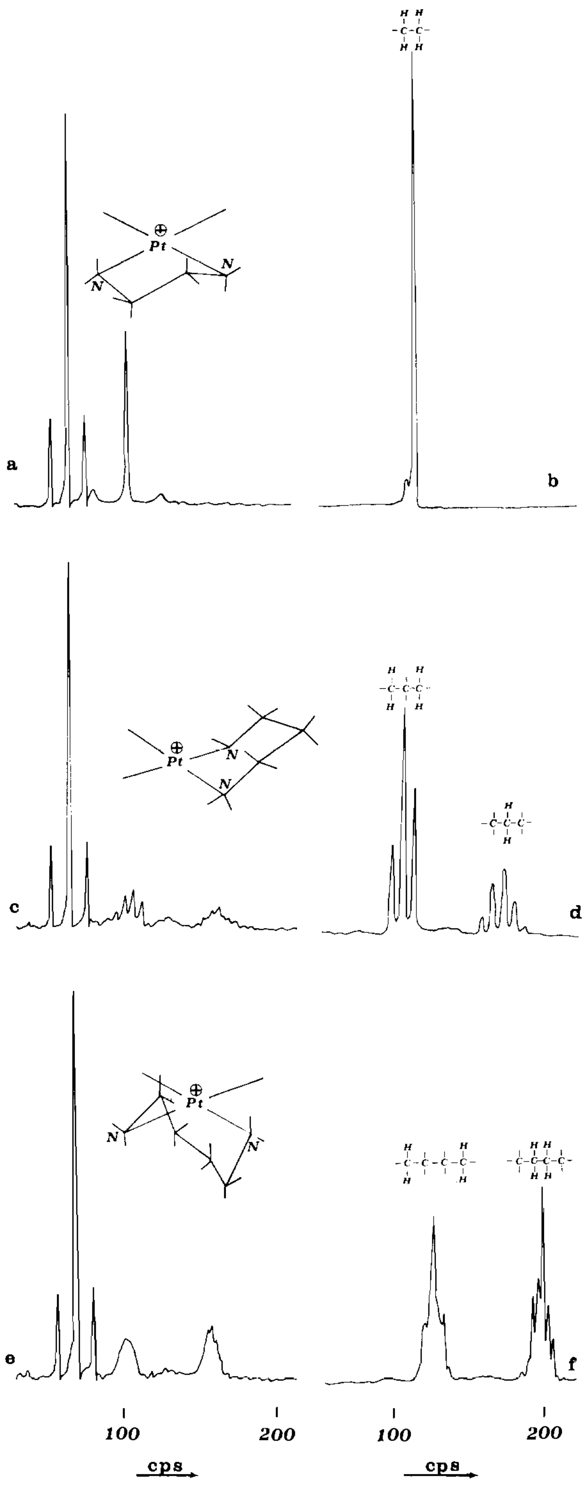

Figure 2. The 60 MHz pmr spectra of free diamines and platinum(II) diamine compounds in D_2O: (a) N-deuterated [Pt(DMSO)(en)Cl] Cl; (b) enthylenediamine; (c) N-deuterated [Pt(DMSO)(tn)Cl] Cl; (d) 1,3-diaminopropane; (e) N-deuterated [Pt(DMSO)(bn)Cl] ; (f) 1,4-diaminobutane.

1,4-diaminobutane complex, we have an example of the uncommon seven-membered chelate ring in a bidentate complex. This has been found previously in, for example, the bis(L-ornithinato)palladium(II) complex where a seven-membered ring with two nitrogen donors seems to be preferred over a five-membered ring with one nitrogen and one oxygen donor [10]. There is spectroscopic evidence that 1,4-bis(diphenylphosphine)butane (dpb) forms complexes with ruthenium(II) [11] and cobalt(II) [12] where the diphosphine can form seven-membered chelate rings and another bridges two metals. Shaw has reported the synthesis [13] and structure [14] of mononuclear complexes of Pt^{II} and Ir^{I} with Bu^t_2P-$CH_2)_nPBu^t_2$ (n = 9 or 10) in which there is not only a large ring but also a spanning of *trans* positions. Most of the other examples of large rings involve multidentate ligands where the large ring is perhaps stabilised by the formation of other and smaller rings. Thus the tetraamine, spermine, $NH_2(CH_2)_3NH$-$(CH_2)_4NH(CH_2)_3NH_2$, acts as a quadridentate when coordinated to Cu(II) in [Cu(spermine)]$(ClO_4)_2$ and forms a seven-membered central ring [15]. Paoletti has suggested, on the basis of emf measurements, that $NH_2(CH_2)_2NH(CH_2)_4NH_2$ can act as a terdentate and form a small amount of a Cu(II) complex with a five- and a seven-membered ring [16].

In addition to the white 1:1 electrolyte [Pt(dmso)-(bn)Cl] Cl, 1,4-diaminobutane forms a yellow, non-electrolyte species containing one butanediamine for every Pt(dmso)Cl_2 residue. The infra-red spectrum in the range 1750–300 cm^{-1} is given in Fig. 1, where it is compared with the chelate bn complex. When the vibrational modes of coordinated dimethylsulphoxide are subtracted the spectrum is much simpler than that of the chelate complex as a number of vibrations of the aliphatic chain are no longer active. A similar pattern was found by Powell and Sheppard [17] when they compared the infra-red spectrum of the ethylenediamine bridged $[Pt(C_2H_4)Cl_2]_2(NH_2CH_2$-$CH_2NH_2)$ with that of the chelate [Pt(en)Cl_2]. This would suggest a similar formulation for the dmso complex, with the 1,4-diaminobutane acting as a bridging ligand. There is also a close similarity between the characteristic absorptions of the bridged complex and *trans*-[Pt(dmso)(n-butylamine)Cl_2]. The monoamine complex has three sharp ν(N–H) peaks at 3295, 3218 and 3124 cm^{-1} and a bending mode at 1575 cm^{-1} which can be compared to the peaks at 3260, 3220, 3135 and 1575 cm^{-1} in the complex with the bridging diamine. The presence of only one metal–chlorine stretching band at 343 cm^{-1} is consistent with the *trans* geometry. Compounds of the type *cis*-[Pt(dmso)(am)Cl_2] have at least two strong peaks in this region [2].

Proton Magnetic Resonance Spectra

All the ^1H nmr spectra of the N-deuterated complexes in D_2O show a main signal centered 70 cps upfield from the HOD resonance with a ^{195}Pt satellite doublet ($J_{^{195}Pt-^{1}H}$ = 23Hz) which is assigned to the methyl protons on the coordinated dimethylsulphoxide and is strong evidence that the ligand retains its S-bonded attachment in solution. The spectrum of [Pt(dmso)(en)Cl] Cl has already been described [5] and also shows a sharp peak at 110 cps with two ^{195}Pt satellites ($J_{^{195}Pt-^{1}H}$ = 42Hz) assigned to the methylene protons. The single peak is consistent with the expected rapid exchange between the two conformations of the chelate ring [18]. The methylene proton peaks of the tn and bn complexes are relatively broad but resemble the corresponding peaks of the free ligands. They too are consistent with rapid conformational equilibration of the chelate rings, already discussed for other tn complexes [19]. The spectra are shown in Fig. 2.

The Thermal Decomposition of [Pt(dmso)(diamine)-Cl] Cl

On heating the complexes under reduced pressure dimethylsulphoxide is displaced by the anionic chloride and the non-electrolyte $[Pt(diamine)Cl_2]$ complexes are obtained in quantitative yield. This preparation route appears to be simpler, faster and more specific than the usual method which involves reaction between K_2PtCl_4 and the diamine. On solvolysis in dimethylsulphoxide the ionic complexes are reformed. The first-order rate constants for the solvolysis are 1.9×10^{-4} s^{-1} and 2.8×10^{-4} s^{-1} for $[Pt(en)Cl_2]$ and $[Pt(tn)Cl_2]$ respectively at 30 °C.

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