Optically Active Co-ordination Compounds. Part 40.† Mixed Complexes of Platinum(II) with L-Proline and Other α-Amino-acids

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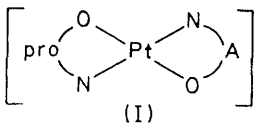
Mixed complexes of the type *trans*-[Pt(proO)A] are described (pro = L-prolinate; A = the anion of sarcosine or of the L enantiomers of alanine, serine, valine, or proline). The amino-acidate ligands are mutually *trans* and are bound to the platinum ion through oxygen and nitrogen. The complexes have been characterized by chemical studies, analyses, and spectra (electronic, c.d., o.r.d., ^{1}H n.m.r., and i.r.). The complex *trans*-[Pt(proO)(sarO)] has been separated into its diastereoisomeric forms, *i.e.* *trans*-[Pt(*S*-proO)(*S*-sarO)] and *trans*-[Pt(*S*-proO)(*R*-sarO)], where *S* and *R* denote the configurations at the asymmetric nitrogen centres. The rates of inversion ($k_{inv.}$) and of deuteriation (k_D) at the asymmetric nitrogen centres of sarcosine have been compared, and $k_D \gg k_{inv.}$.

MIXED amino-acid complexes of the ions copper(II), cobalt(III), and platinum(II) have been described.[1-3] This paper presents the results of our further studies of mixed L-proline–amino-acid (A) complexes of Pt^{II}. We prepared the complexes by heating a mixture of potassium dichloro(L-prolinato)platinate(II), K[Pt(proO)-Cl_2], and the corresponding L-amino-acid in aqueous solution {mol ratio K[Pt(proO)Cl_2]: amino-acid = 1 : 3}. Six new complexes have been obtained. Since all the asymmetric amino-acids in this paper have the L configuration the prefix will now be omitted.

All the complexes possess the *trans* configuration, (I), according to their chemical reaction with thiourea.



(I)

The complexes were most readily characterized by their i.r., absorption, c.d., o.r.d., and ^{1}H n.m.r. spectra. Although we have not been able to use atomic absorption as a means of confirming the geometric configurations of our complexes (since, although there is evidence that for isomeric pairs of platinum complexes the response for the *cis* isomer is greater than that for the *trans*, we have only one isomer of each), we have collected our information on this topic in the Experimental section because it appears potentially useful.

The nitrogen atom of L-prolinate as a bidentate chelate ligand necessarily[4] has the *S* absolute configuration. (This is merely a specific statement deriving from the general case ‡ that the fusion of two five-membered rings is mutually *cis*.) In the case of *trans*-[Pt(proO)(sarO)] the nitrogen atoms of the sarcosinate ion (sarO) may adopt either the *S* or the *R* configuration.

One reason for the recent marked interest in the amino-acidato-complexes of metal ions is that, by virtue of the restriction (by chelation) of rotation about bonds, it may be possible in aqueous media to achieve stereoselective formation of reactive anions (by loss of a proton either from carbon or from nitrogen). For example, some years ago we showed that the exchange with D_2O and the decline of optical rotation for the asymmetric carbon centres of bis(L-alaninato)copper(II) occurred § at unequal rates.

Several studies have been made of rates of N-proton exchange and of N-inversion in cobalt(III) and platinum(II) complexes.[5-7] In such studies the rates of proton exchange were determined by observing the disappearance of n.m.r. signals of protonated species in D_2O solutions of the complexes. Rates of inversion of resolved isomers were determined polarimetrically[5] or by using n.m.r. line-shape analysis alone.[6] Both processes (exchange and inversion) were found to be promoted by hydroxide ion. In one study[5] {for [Co(sarO)$(NH_3)_4$]$^{2+}$} the rate of exchange exceeds the rate of inversion by a factor of 10^3—10^5, *i.e.* on average the proton can be abstracted and replaced many times before inversion takes place. On the other hand,[6] in platinum(II) complexes (DL and *meso*) of *NN'*-dimethylethylenediamine the rates of exchange and inversion were comparable. Erickson *et al.*[7] studied N-proton exchange in several amino-acid complexes of Pt^{II}. We report here kinetic studies (carried out by similar means) of N-proton exchange and inversion of sarcosine in *trans*-[Pt(proO)(sarO)].

† Part 39; R. D. Gillard and L. R. H. Tipping, *J.C.S. Dalton*, 1977, 1241.

‡ *cis*-Fused bicyclo[3.3.0]octanes are more stable than *trans* (R. P. Linstead and E. M. Meade, *J. Chem. Soc.*, 1934, 935).

§ A recent report casts doubt on this finding, on the grounds that with a 2 : 1 ratio of alanine : copper(II) it is impossible to obtain a homogeneous solution at pH 12. This is true, and is the reason why the earlier studies related to concentration conditions 4 : 1 ⩽ L-ala: Cu ⩽ 8 : 1, as specifically mentioned in our detailed paper.[2] Our own recent work shows that redox catalysis is involved in the change of optical rotation, vitiating the earlier conclusions.

[1] G. Brookes and L. D. Pettit, *J.C.S. Chem. Comm.*, 1974, 813.
[2] R. D. Gillard, S. H. Laurie, D. C. Price, D. A. Phipps, and C. F. Weick, *J.C.S. Dalton*, 1974, 1385.
[3] L. M. Volshtein and O. P. Slyudkin, *Russ. J. Inorg. Chem.*, 1974, **19**, 131.
[4] A. McL. Mathieson and H. K. Welsh, *Acta Cryst.*, 1952, **5**, 599.
[5] B. Halpern, A. M. Sargeson, and K. R. Turnbull, *J. Amer. Chem. Soc.*, 1966, **88**, 4630.
[6] P. Haake and P. C. Turley, *J. Amer. Chem. Soc.*, 1968, **90**, 2293.
[7] L. E. Erickson, A. J. Dappen, and J. C. Uhlenhopp, *J. Amer. Chem. Soc.*, 1969, **91**, 2510.

RESULTS AND DISCUSSION

Hydrogen-1 N.M.R. Studies.—Spectra of complexes (1)—(8) have been recorded for acidic (D_2SO_4) and neutral (D_2O) solutions. The results are summarized in Table 1. The spectra of complexes (1)—(6) in acidic solution contain bands (with ^{195}Pt side bands) due to proline, located, for all the complexes, at *ca.* 6.5 (NH), *ca.* 4 (proton of CH), and [3] 2—3.18 p.p.m. (methylene protons). On the other hand, the spectrum of each complex has its own characteristic bands, for example: [Pt(proO)(alaO)], C-methyl doublet (1.41 p.p.m.); [Pt(proO)(valO)](valO = valinate), band in *ca.* 0.96 p.p.m. region; [Pt(proO)(sarO)], N-methyl doublet (2.6 p.p.m.) (see Table 1). In neutral solutions in D_2O there is very rapid proton–deuteron exchange of amino-groups.

TABLE 1

Hydrogen-1 n.m.r. results for the platinum(II) amino-acid complexes

Complex	N.m.r. spectrum *	
	acidic solution	neutral solution
(1) K[Pt(proO)Cl_2]	6.45(X) 3.96(q,A) 3.18(q,D) 2.0(c,B,C)	 3.94(A) 3.18(t,D) 2.0(c,B—D)
(2) *trans*-[Pt(proO)(alaO)]	6.50(X) 3.80(c,A,E) 3.15(d,D) 1.4(d,Me), J(Me–H_E) 7.6	 3.90(c,A,E) 2.0(c,B,C,D) 1.71(d,Me), J(Me–H_E) 7.6
(3) *trans*-[Pt(proO)(serO)]	6.45(X) 5.9(Y) 3.8(c,A,E) 3.16(d,D) 2.0(c,B,C,K)	 3 84(c,A,E) 3 20(t,D) 2.1(c,B,C,D,K)
(4) *trans*-[Pt(proO)(valO)]	6.4(X) 5.6(Y) 3.5—4.0(c,A,E) 3.18(c,D) 2(c,B,C) 0.96(t,Me)	 3.8(c,A,E) 3.0(c,B—D) 2(M) 0.96(t,Me)
(5) *trans*-[Pt(proO)$_2$]	6.5(X) 3.87(c,A) 3.15(d,D) 2.1(c,B,C)	 3.83(A) 3.18(c,D) 2.1(c,B—D)
(6)[Pt(proO)(*S*-sarO)]	6.45(X) 6.0(Y) 3.9(c,A) 3.5(c,P) 3.14(c,D) 2.6(d,Me), J(Me–H_X) 6 2.0(c,B,C)	 3.90(c,A) 3.6 } (c,P) 3.46 } 3.14(c,D) 2 6(s,Me) 2.0(c,B—D)

* s = Singlet; d = doublet; t = triplet; q = quartet; c = complex. δ in p.p.m.; J in Hz.

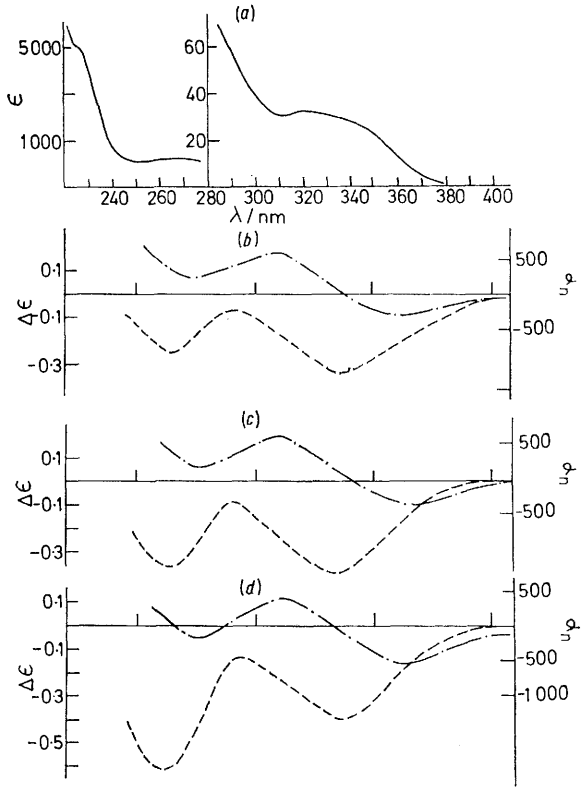


FIGURE 1 Absorption spectrum (——) of *trans*-[Pt(proO)(alaO)] (*a*), and o.r.d. (— · — · —) and c.d. (– – – –) spectra of *trans*-[Pt(proO)(alaO)] (*b*), *trans*-[Pt(proO)(serO)] (*c*), and *trans*-[Pt(proO)(valO)] (*d*). All solutions contained 10^{-3} mol dm^{-3} complex in $HClO_4$

Absorption, C.D., and O.R.D. Studies.—The absorption, c.d., and o.r.d. spectra of the mixed proline–amino-acid complexes (2)—(8) have been recorded (see Table 2 and Figures 1 and 2) and compared with the corresponding spectra [8] of bis(amino-acidate) complexes [PtA_2] in both *cis* and *trans* configurations.

The electronic-absorption spectra of *trans*-[Pt(proO)A] complexes are extremely similar showing identical patterns, and are akin to the spectra of other complexes of the type *trans*-[PtA_2]. They are quite different from

[8] O. P. Slyudkin, O. N. Adrianova, M. A. Kerzencev, and L. M. Volshtein, *Russ. J. Co-ordination Chem.*, in the press.

the corresponding spectra[8] of *cis*-[PtA_2]. Circular dichroism (c.d.) spectra of mixed proline–amino-acid

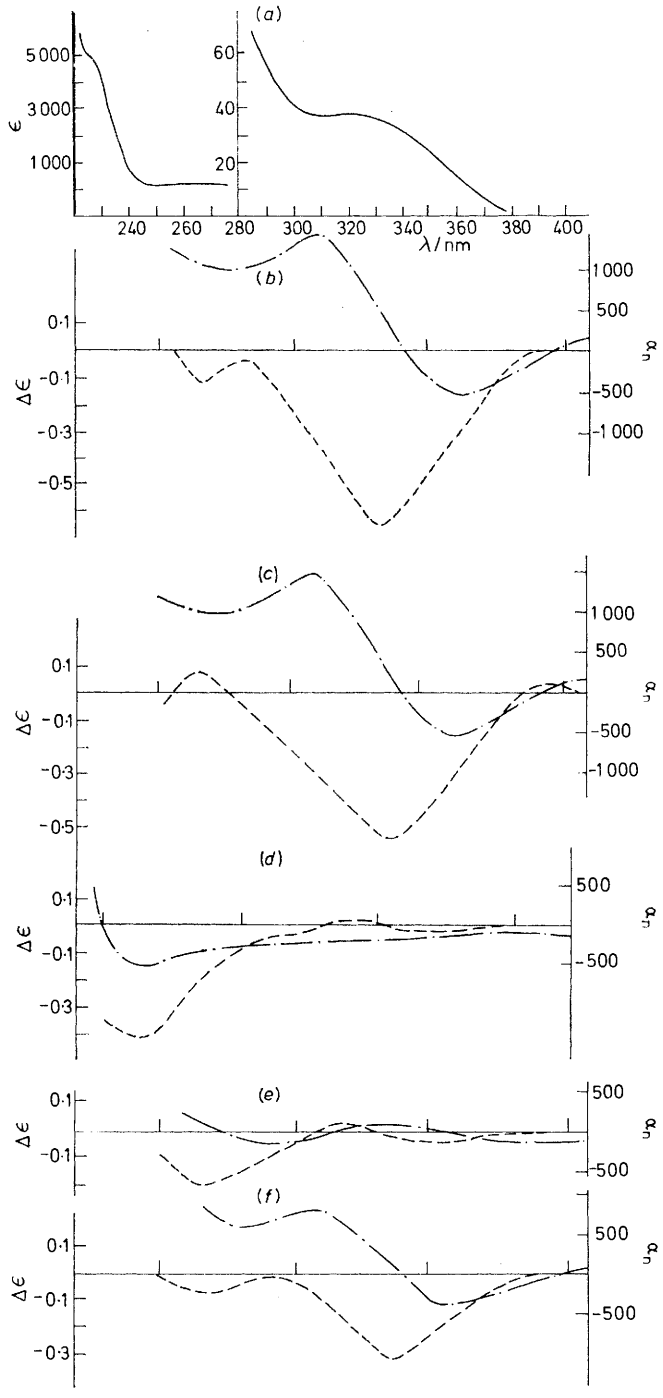


FIGURE 2 Absorption spectrum (——) of *trans*-[$Pt(proO)_2$] (*a*), and o.r.d. (— · — · —) and c.d. (– – – –) spectra of *trans*-[$Pt(proO)_2$] (*b*), *trans*-[Pt(proO)(*S*-sarO)] (*c*), *trans*-[$Pt(alaO)_2$]-(*d*), *trans*-[Pt(proO)(*R*-sarO)] (*e*), and *trans*-[Pt(proO)(*R*,*S*-sarO)] (*f*). All the solutions contained 10^{-3} mol dm^{-3} complex in $HClO_4$

complexes have features similar to those of *trans*-[PtA_2], but the first band (λ *ca.* 336 nm) shows larger values (negative) than the corresponding bands in *trans*-[PtA_2]. Optical rotatory dispersion (o.r.d.) spectra of the mixed complexes, in contrast to those of *trans*-[PtA_2], have regions of positive rotation (see Figures 1 and 2).

Assignment of Configuration of Sarcosine Nitrogen.—To assign configurations in the less-soluble and soluble forms of *trans*-[Pt(proO)(sarO)], we have compared the optical activity of *trans*-[$Pt(proO)_2$], *trans*-[$Pt(alaO)_2$], and both forms of *trans*-[Pt(proO)(sarO)]. Solutions of *trans*-[$Pt(proO)_2$] and the more-soluble forms of *trans*-[Pt(proO)(sarO)] have very similar c.d. and o.r.d. spectra [Figure 2(*a*) and (*b*)]. On the other hand, c.d. and o.r.d. spectra of the less-soluble form of *trans*-[Pt(proO)(sarO)] were similar to the spectra of *trans*-[$Pt(alaO)_2$] [Figure 2(*c*) and (*d*)].

Both nitrogen atoms of bidentate chelating L-prolinate necessarily have the *S* absolute configuration in *trans*-[$Pt(proO)_2$]. It is then possible to assign to the sarcosine asymmetric nitrogen atom in the soluble form of *trans*-[Pt(proO)(sarO)] the *S* absolute configuration. The optical activity of *trans*-[$Pt(alaO)_2$] is due to the ' vicinal ' effect of the asymmetric carbon atoms.[8] The less-soluble form of *trans*-[Pt(proO)(sarO)] has two asymmetric nitrogen atoms of opposite absolute configuration and its optical activity is due only to the ' vicinal ' effect of the asymmetric carbon atom of proline.

The c.d. and o.r.d. curves of neutral and alkaline solutions of the two forms change very quickly with time, to the same final spectra [Table 2, complex (9), Figure 3].

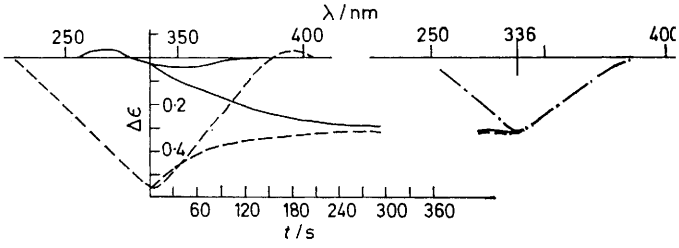


FIGURE 3 C.d. traces typical of those employed to obtain rates of inversion of sarcosine nitrogen. The curve (– – – –) shows the c.d. at 336 nm for solutions of *trans*-[Pt(proO)(*S*-sarO)] at pH 7 and 35 °C as a function of time. This trace is shown as arising (at 336 nm) from the c.d. spectrum of the *trans* (*S*) isomer; its full c.d. spectrum (from 250 to 400 nm) is shown (– – – –) plotted against the upper horizontal axis. Curves (——) are the time course of the c.d. at 336 nm and the c.d. spectrum (258—400 nm) for the *trans* (*R*) isomer against the same horizontal axes. Curves (— · — · —) represent the *limiting* values of Δε at 336 nm from the rate plots (—— and – – – –) and the c.d. spectrum of the equilibrium mixture of *trans*-[Pt(proO)(*R*-sarO)] and -[Pt(proO)(*S*-sarO)]

Equilibria.—Since we have values for the properties of the pure isomers, we have been able to measure the equilibrium constant *K* for equation (1) by determining optical

$$\textit{trans}\text{-[Pt(proO)(}R\text{-sarO)} \rightleftharpoons \textit{trans}\text{-[Pt(proO)(}S\text{-sarO)] \quad (1)}$$

rotations (or circular dichroisms) at differing wavelengths after equilibration. The results are shown in Table 3. The value which we adopt for *K* is 1.3 ± 0.3.

TABLE 2

Absorption and c.d. results for the mixed proline–amino-acid complexes of Pt^{II} (in 10^{-3} mol dm^{-3} $HClO_4$)

Complex	Absorption λ/nm	Absorption ε/dm^3 $mol^{-1}cm^{-1}$	C.d. λ/nm	C.d. Δε
(2) *trans*-[Pt(proO)(alaO)]	350	23		
	318	32	335	−0.34
	275	150	265	−0.25
	227	4 800		
	200	6 500		
(3) *trans*-[Pt(proO)(serO)]	345	23		
	320	35	334	−0.40
	275	150	263	−0.37
	228	5 000		
	200	7 000		
(4) *trans*-[Pt(proO)(valO)]	350	23		
	315	38	336	−0.40
	275	170	260	−0.60
	226	4 900		
	207	6 500		
(5) *trans*-[Pt(proO)$_2$]	352	24		
	320	38	332	−0.65
	275	160	266	−0.12
	230	4 800		
	205	6 500		
(6) *trans*-[Pt(proO)(*S*-sarO)]			395	0.02
	350	19	336	−0.55
	320	34	265	0.08
	275	150		
	229	4 700		
	205	7 000		
(7) *trans*-[Pt(proO)(*R*-sarO)	348	19	354	−0.04
	317	33	308	0.02
	270	130	265	−0.20
	230	4 800		
	205	8 000		
(8) *trans*-[Pt(alaO)$_2$]	350	20	380	−0.03
	318	34	338	0.01
	270	150	262	−0.41
	230	4 000		
	200	6 000		
(9) *trans*-[Pt(proO)(*R*,*S*-sarO)]	348	30		
	318	50	336	−0.32
	275	170		
	230	5 000	262	−0.08
	200	7 000		

TABLE 3

Values for K [a] obtained by analysis of equilibrated solutions at pH 6

λ/nm	K o.r.d.[b]	K c.d.
500	1.3	
370	1.6	
360		1.3
357	1.6	
345		1.3
333	1.5	
330		1.2
315		1.3

[a] K = [*trans*-Pt(proO)(*S*-sarO)]/[*trans*-Pt(proO)(*R*-sarO)].
[b] Some values ($K \simeq 1.1$) obtained at $526 < \lambda < 588$ have been rejected, because values of α_λ for the separated isomers and (therefore) the equilibrated mixture are rather close together in this region.

The rate constants which we obtain for equilibration are of course functions of k_f and k_b. However, we have enough results (as shown in Table 4) to extract k_f and k_b

TABLE 4

Kinetic results for exchange ($k_{exch.}$) and inversion ($k_{inv.}$)

pH	$10\,c$ / mol dm^{-3}	$10^5\,k_{exch.}^{obs.}$ / s^{-1}	$10^3 k_{inv.}^{obs.} = (k_f + k_b)$ / s^{-1}
4.2	1.4	36	
	1.5	33	
4.6	0.7	77	
	1.2	73	
5.4	0.7	180	
	0.6	190	
	0.09 *		0.9
6.05	0.07		1.43
	0.10		1.3

* D_2O as solvent.

for inversion, and $k_{exch.}$ for exchange. Both processes are described by the rate expression $k_{obs.} = k[\text{complex}][OH^-]$. $k_{inv.} = (k_f + k_b)$ is $\simeq 10^{-5}$ dm^3 mol^{-1} s^{-1} whereas $k_{exch.}$ is $\simeq 4 \times 10^{-4}$ dm^3 mol^{-1} s^{-1}. This we take to indicate that, as shown in Figure 4, the intermediate anion has a barrier to inversion larger than that for reprotonation, *i.e.* many acts of exchange may occur before the first act of inversion.

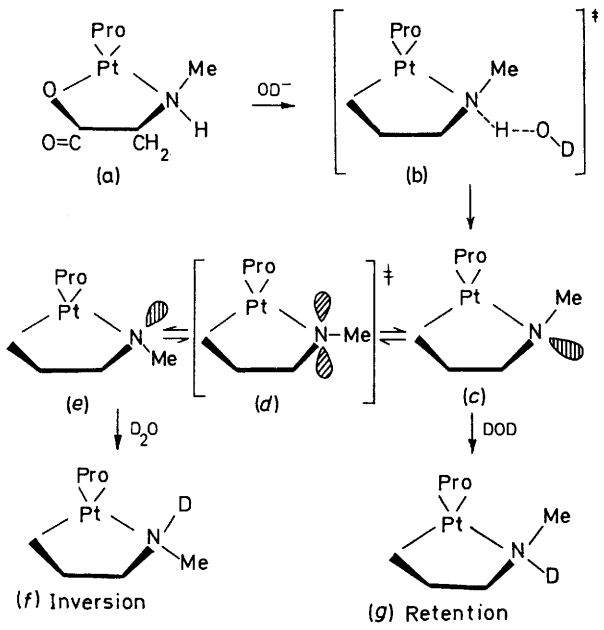
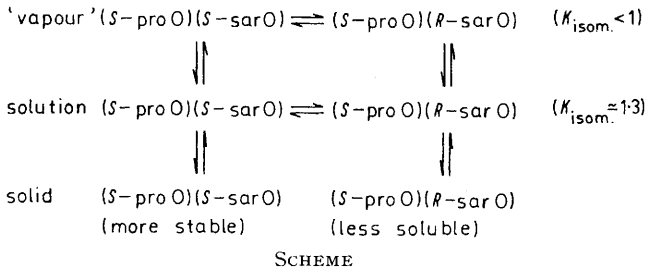


FIGURE 4 Mechanism for proton–deuteron exchange and inversion at the nitrogen atom of sarcosine in *trans*-[Pt(proO)(*S*-sarO)]

The modest value for the equilibrium constant, *determined in water*, re-emphasizes a point which is often ignored. This is that conformational conclusions for chelated compounds based on interatomic repulsion potentials refer at present only to isolated molecules, *i.e.* those in the vapour phase. There is no doubt that predictions of favoured structure based on hydrogen–hydrogen potentials are valuable for establishing the isolated conformation of minimum energy. In the

same way, the use of atomic models will usually suggest a conformational preference. In the present case, this would quite clearly be for the (*S*-proO)(*S*-sarO) structure. However, experimentally, there is little difference, *in aqueous solution*, between the *SS* and *RS* structures, and such as there is lies in the ' wrong ' direction.

This means that solvation has stabilized one conformer relative to the other, and that the conformational equilibrium predicted for isolated molecules is upset in solution, as shown in the Scheme. Such cases are not



SCHEME

unknown: conformational changes in organic molecules produced by solvation are established, and there are a few parallel situations in chelated compounds, for example of Cu^{II}.*

The distinction between cases where the most stable conformations are determined by intramolecular effects and those where the intramolecular stability pattern is over-ridden by such intermolecular effects as solvation is presumably equivalent to including solvation enthalpy and *entropy* terms in the steric argument.

EXPERIMENTAL

Absorption, c.d., and o.r.d. spectra were obtained using a Unicam SP 800B spectrophotometer, Jouan Dichrographe model B, and Bendix spectropolarimeter respectively. Hydrogen-1 n.m.r. spectra were recorded at 90 MHz with a Perkin-Elmer R14 instrument. Infrared spectra of complexes in Nujol and hexachlorobutadiene mulls were obtained using a Perkin-Elmer model 257 spectrometer calibrated with polystyrene. Amino-acids were obtained from B.D.H., and $K_2[PtCl_4]$ was obtained from Johnson, Matthey Chemicals.

Preparation and Isolation of Mixed L-*Proline–Amino-acid Complexes of* Pt^{II}.—The initial complex $K[Pt(proO)Cl_2]$ and *trans*-$[Pt(proO)_2]$ were prepared according to the original procedure.[9,10] Complexes of the type *trans*-[Pt(proO)A] were prepared according to a general procedure, given below for *trans*-[Pt(proO)(alaO)]; isolation of each complex needs special attention, as described. Analysis data are in Table 5.

trans-[Pt(proO)(alaO)]. The complex $K[Pt(proO)Cl_2]$ (0.5 g) and L-alanine (0.32 g) (mol ratio 1 : 3) were dissolved in water (25 cm^3). The solution was heated on a steam-bath for 3 h keeping the volume constant. It was then evaporated (to *ca.* 10 cm^3) and cooled, and a white product precipitated. The complex was collected, washed with cold water, alcohol, and diethyl ether, and dried at 70 °C. Solubility ≃ 20 g dm^{-3} (by evaporation of a saturated solution).

trans-[Pt(proO)(serO)]. The preparative solution was evaporated to 5 cm^3 and cooled. After light scratching of the container, the solution was left overnight. The white product precipitated very slowly. It was separated, washed with a small volume of cold water, alcohol, and diethyl ether, and dried at 70 °C; solubility *ca.* 30 g dm^{-3}.

trans-[Pt(proO)(valO)]. The preparative solution was evaporated (*ca.* 5 cm^3) and cooled. Precipitated valine was removed and the filtrate was passed through a mixed-bed ion-exchange column (H^+ and OH^- forms). The eluate was checked for the absence of chloride ion and free amino-acid. After evaporation, *trans*-[Pt(proO)(valO)] was extracted by a small volume of water.

trans-[Pt(proO)(sarO)] (*mixed isomers*). The complex $K[Pt(proO)Cl_2]$ (0.5 g) and sarcosine (0.32 g) (mol ratio

TABLE 5

Analytical results and i.r. spectra for amino-acid complexes of Pt^{II}

	Analysis (%)						I.r. spectra (cm^{-1}) [a]			
	Found			Calc.						
Complex	C	H	N	C	H	N	$\nu_{asym}(CO_2^-)$	ν(NH) str	ν(ND) str	ν(NH) : ν(ND)
(1) [b]	14.55	2.05	3.45	14.3	1.90	3.35				
(2)	24.4	3.35	7.35	24.2	3.55	7.05	1 630	3 225	2 410	1.34
								3 120	2 330	1.34
								3 060	2 280	1.34
(3)	23.15	3.20	6.75	23.2	3.40	6.80	1 635	3 218	2 410	1.34
								3 120	2 330	1.34
								3 060	2 280	1.34
(4)	27.75	4.10	6.85	28.2	4.25	6.60	1 640	3 210	2 412	1.33
								3 120	2 330	1.34
(5)	28.3	3.90	7.30	28.35	3.80	6.60				
(6)	24.0	3.65	6.90	24.2	3.55	7.05	1 637 [c]	3 150		
(7)	24.1	3.45	6.90	24.2	3.55	7.05	1 632	3 090		
								3 050		
(8)	19.15	2.90	7.55	19.4	3.25	7.55				
(9)	24.25	3.25	7.20	24.2	3.55	7.50	1 635	3 150	2 260	1.39
								3 050		

[a] In Nujol or hexachlorobutadiene mulls. [b] Found: Cl, 16.6. Calc.: 16.9%. [c] The Raman spectrum in 10^{-3} mol dm^{-3} $HClO_4$ solution showed $\nu_{asym}(CO_2^-)$ at 1 657 cm^{-1}.

* Recently, it has been shown, using c.d., that, for $R \rightleftharpoons S$ isomers of $[Pt(N_2\text{-Me-S-pm})]Cl_2$, K is 1.2 at 40 ± 10 °C, *i.e.* the axial isomer is slightly (55%) preferred in water (B. Bosnich and E. A. Sullivan, *Inorg. Chem.*, 1975, **14**, 2768).

[9] L. M. Volshtein and O. P. Slyudkin, *Russ. J. Inorg. Chem.*, 1972, **17**, 236.

[10] L. M. Volshtein and O. P. Slyudkin, *Russ. J. Inorg. Chem.*, 1972, **17**, 1168.

1 : 3) were dissolved in water (25 cm³). The solution was evaporated (*ca.* 10 cm³), cooled, and added to 1N K[OH] (giving a pH ≃ 7). The solution was left overnight, when the white product had precipitated. It was separated and washed with a small volume of cold water and alcohol. This product was a mixture of the two forms of *trans*-[Pt(proO)(sarO)], with the less-soluble product predominant.

Separation of the two forms of trans-[Pt(proO)(sarO)]. The mixture of the two forms was dissolved in water and the solution made slightly alkaline. It was then heated on a

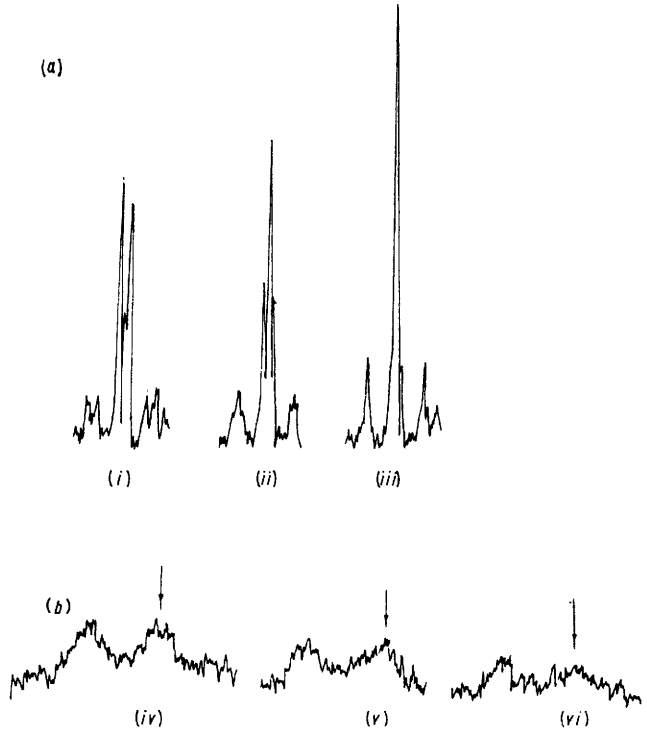


FIGURE 5 Hydrogen-1 n.m.r. traces typical of those employed to obtain rates of proton exchange of *trans*-[Pt(proO)(*S*-sarO)] at 35 °C: (*a*) in D_2O at pH 5.4 after 1 (*i*), 5.3 (*ii*), and 10 min (*iii*) respectively; (*b*) in D_2O at pH 4.42 after 4.25 (*iv*), 9.3 (*v*), and 33 min (*vi*) respectively

steam-bath for *ca.* 10 min; after cooling it was treated with a mixed-bed ion-exchange resin (H^+ and OH^- forms). The solution was concentrated and quickly cooled. The *R* isomer precipitated and was collected, washed with water, alcohol, and diethyl ether, and dried at 70 °C; solubility 10 g dm^{-3}. The filtrate was collected, immediately frozen, and dried *in vacuo*. The complex *trans*-[Pt(proO)(*S*-sarO)] was extracted with a small volume of very cold water and the solution was freeze-dried. Solubility in water ≃ 150 g dm^{-3}.

Equilibration to trans-[Pt(proO)(*R*,*S*-sarO)]. Samples of the solid *trans*-[Pt(proO)(*S*-sarO)] or *trans*-[Pt(proO)(*R*-sarO)] were dissolved in water and after *ca.* 30 min the equilibrium mixture obtained (tested by c.d.) was very quickly evaporated, and dried at 70 °C.

All the mixed proline–amino-acid complexes were characterized by their i.r. spectra which are quite complicated. Table 4 gives only assignments of the anti-symmetric mode of the CO_2^- groups and the N–H stretching mode. The assignments [11] are supported by comparison with the spectra of derivatives which were deuteriated in the NH and NH_2 positions.

Procedure for Kinetic Runs.—(*i*) H–D *Exchange in trans*-[Pt(proO)(*S*-sarO)]. Solutions for ^{1}H n.m.r. kinetic runs were prepared by dissolving the solid complex *trans*-[Pt(proO)-(*S*-sarO)] in buffered D_2O solution. Spectra were recorded at 35 °C as a function of time. Rates of N–H proton exchange were determined by analyses of the slow spectral changes of D_2O solutions. The N–H (6.00 p.p.m.) and methyl (2.6 p.p.m.) regions of the proton resonance spectrum which were employed in these kinetic runs are shown in Figure 5. Our n.m.r. rate measurements were made by determining areas under the N–H (sarcosine) peak and/or the extent of deuteriation from the relative heights of the methyl doublet as the exchange proceeded (Table 6).

TABLE 6
Rate constants for H–D sarcosine nitrogen exchange in *trans*-[Pt(proO)(*S*-sarO)] at 35 °C

pH [a]	pOD [b]	10^{10}[OD$^-$] / mol dm^{-3}	$10^5 k_{obs.}$ / s^{-1}	$10^5 k_{obs.}$ / [OD$^-$]
4.0	10.3	0.5	21 [c]	42
4.2	10.1	0.8	(34) [d]	42
4.6	9.7	2	75 [c] (69)	38
(4.65)				

[a] Measured by pH meter. [b] pOD = pK_w(D_2O) − [pH$_{(meter)}$ + 0.4]. [c] Results were obtained using the NMe doublet. [d] Results were obtained using the NH peak.

(*ii*) *Epimerization* {*inversion at nitrogen of trans*-[Pt(proO)(*S*-sarO)] *and trans*-[Pt(proO)(*R*-sarO)]}. Solutions for c.d. kinetic runs were prepared by dissolving the solid complexes *trans*-[Pt(proO)(*S*-sarO)] or *trans*-[Pt(proO)-(*R*-sarO)] in 10^{-3} mol dm^{-3} $HClO_4$. Then the necessary volume of the complex solution was diluted with buffer solution. The pH was determined (E.I.L. model 23A pH-meter) before and after each kinetic run. The band (λ 336 nm) of both diastereoisomers employed in the kinetic runs is shown in Figure 3. The epimerization rate measurements were made by determining Δε with time as the epimerization proceeded (Table 7).

The first-order rate constant for exchange ($k_{exch.}$) and for epimerization ($k_{inv.} = k_f + k_b$) for each run was obtained from a plot of log (areas or peak height of doublets) against time and log Δε against time, respectively.

TABLE 7
Rate constants * for N-sarcosine inversion of *trans*-[Pt(proO)(*S*-sarO)] at 35 °C

pH	pOH	10^{10}[OH$^-$] / mol dm^{-3}	$10^5 k_{obs.}$ / s^{-1}	$10^5 k_{obs.}$ / [OH$^-$]
6.05	7.95	112	145(143)	1.29(1.28)
6.55	7.45	355	333(317)	0.94(0.89)
7.0	7.00	1 000	832(810)	0.83(0.81)

* Values for the rate of N-inversion of sarcosine in *trans*-[Pt(proO)(*R*-sarO)] are given in parentheses.

Atomic Absorption of Platinum(II) *Complexes of Amino-acids.*—Several papers describe differences of atomic absorption in platinum(II) complexes,[12–14] arising from causes such as geometric isomerism. Atomic-absorption spectra of platinum(II) amino-acid complexes were obtained using a

[11] K. Nakamoto and P. J. McCarthy, 'Spectroscopy and Structure of Metal Chelate Compounds,' Wiley, New York, 1968.
[12] J. P. Macquet and T. Theophanides, *Spectrochim. Acta*, 1974, **B29**, 271.
[13] J. P. Macquet, J. Hubert, and T. Theophanides, *Analyt. Chim. Acta*, 1974, **72**, 251.
[14] J. P. Macquet and T. Theophanides, *Analyt. Chim. Acta*, 1974, **72**, 261.

Perkin-Elmer 403 spectrophotometer equipped with a platinum lamp (λ 2 659 Å). The solutions of all the complexes contained 50 p.p.m. of platinum. A solution of $K_2[PtCl_4]$ was used for calibration of the flame. The results are given as a ratio of the absorption of two comparable complexes, *e.g.* of the atomic absorption of the *trans* isomer to the atomic absorption of the *cis* isomer (in solution). Only the ligands are listed: $(NH_3)_2Cl_2$, 1.4; $(alaO)_2$, 1.3; $(valO)_2$, 1.5; $(proO)_2$, 1.5; $(ala)_2Cl_2$, 1.4; $(val)_2Cl_2$, 1.7 : 1. However, the ratio for the two *trans* epimers (proO)(*S*-sarO) and (proO)(*R*-sarO) was 1.05 : 1. The nature of the ligand also has an effect. For three pairs of analogous complexes of prolinate and alaninate, the ratios (proO : alaO) were: $K[Cl_2]$, 1.2; *trans*-$[A_2]$, 1.4; *cis*-$[A_2]$, 1.2 : 1. The effect of ligand variation and chelation was also studied: *trans*-$(ala)_2Cl_2$: *trans*-$(alaO)_2$, 1.5; *trans*-$(val)_2Cl_2$: *trans*-$(valO)_2$, 1.3; *trans*-(pro)(sar)Cl_2: *trans*-(proO)(sarO), 1.3; *cis*-$(ala)_2Cl_2$: *cis*-$(alaO)_2$, 1.2; *cis*-$(val)_2Cl_2$: *cis*-$(valO)_2$, 1.1 : 1.

In the absence of interference inhibitors (La^{3+}, Cu^{2+}, phosphate, *etc.*) a significant difference in atomic absorbance between *cis*- and *trans*-(amino-acid)platinum(II) complexes was found. Thus, whereas the *trans* complexes gave higher atomic absorbances than their *cis* isomers, the two diastereoisomers of *trans*-[Pt(proO)(sarO)] gave very similar readings. All the types of proline complexes gave higher absorbances than the analogous alanine complexes. The absorbances of the complexes with unidentate ligands were higher than those when the same ligands were chelated. The ratio for NH_4[(pro)(proO)Cl]: K[(pro)(proO)Cl] is 1.6 : 1; potassium ion has a depressing effect.

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