S-bridged Complexes of Pt(II) and Pt(IV) With Thiophenol and p-Toluenethiol

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[Received 3rd August, 1985, revised 26th May, 1986]

Summary: In iso-ropanol medium, Pt(II) and Pt(IV) form 1:1 and 1:2 (M:L) and 1:1, 1:2 and 1:4 (M:L) complexes, respectively, with each of thiophenol (TP) and p-toluene-thiol (PTT). The stability constant values show that Pt(II) and Pt(IV) complexes are almost equally stable, however (TP) complexes are relatively more stable than those formed with (PTT). The solid complexes have S-bridged polymeric structure, assigning square planar configuration for Pt(II) complexes and octahedral geometry for Pt(IV) complexes.

Introduction

Most Pt(II) complexes with various ligands are predominantly square planar. However, there is an indication that additional, though weaker, bonds may be formed in vacant octahedral sites. In solution, such positions may be occupied by solvent molecules [1]. In catalytic reactions involving Pt complexes, or in ligand displacement reactions, initial attack presumably occurs in the axial positions. Pt(IV) forms a large number of very stable and kinetically inert octahedral complexes [2a], including thiol compounds, owing to its pronounced tendency to be hexa-coordinated.

A number of RS^- or thiocyanate bridged binuclear complexes of Pt(II) have been reported [2b]. Nyholm et al.[3] pointed out that complexes of platinum formed with thiophenol assumed polymeric structure. It has been argued [4,5] that the mercaptide ion often retains its tendency to form S-bridges even in the presence of other groups capable of coordination, in such cases dimerization was frequently encountered.

Thiolato complexes of transition metals have biological and inhibitive characters [6,7]. Some platinum complexes have pronounced anticancer activity [8]. Thiols are usually present as impurities in petrochemicals. Therefore a study of their complexes with platinum, which is used as catalyst in many petrochemical processes, in non-aqueous media is important. In the present work, the formation and properties of platinum (II&IV) complexes with thiophenol (TP) and p-toluenethiol (PTT) are investigated.

Experimental

Stock solution of Pt(II) was prepared by dissolving $PtCl_2$ in concentrated HCl and diluting to the required volume with isopropanol. The Pt(IV) stock solution was prepared by dissolving $PtCl_4.5H_2O$ in isopropanol, adding a few drops of HCl to prevent solvolysis. The Pt(II) and Pt(IV) solutions were standardised potentiometrically. The solutions of thiols were

prepared by dissolving accurate weights in isopropanol, freshly before each experiment.

The formation of Pt-thiol complexes in solution was followed spectrophotometrically in the near uv region. The mole ratio, continuous variation and slope ratio methods were used for the identification of the compositions of the complexes. The spectra were scanned by means of SP-1750 PYE-UNICAM recording spectrophotometer. The overall formation constants of the complexes were evaluated by applying the method of Harvey and Manning [9]. The stepwise formation constants were obtained using the corresponding solutions method [10].

Isopropanol solutions of sodium hydroxide or acetic acid were used to adjust the pH values of solutions, which were measured by means of a CORNING pH-meter 113.

The solid complexes were prepared by mixing the metal ion and thiol solutions, in isopropanol, in varying proportion ratios (1:1 to 1:6). The solutions were left overnight and the precipitated products were filtered, washed thoroughly with ethanol followed by ether and dried in a vacuum desiccator.

The ir spectra were scanned in the range 400-4000 cm^{-1}, using PERKIN-ELMER-337 spectrophotometer by KBr disc technique.

The x-ray powder diffraction patterns of the solid complexes were obtained with a PHILIPS x-ray diffractometer, Type P.W.1051.

Results and Discussion

Greyish-yellow Pt(II) and Pt(IV) complexes with (TP) and (PTT) are formed in isopropanol after heating on a water bath for about 10 minutes at 70°C. In aqueous and other non-aqueous media including methanol, ethanol, n-propanol, n-butanol, isobutanol, n-pentanol, isopentanol and dioxan, the rate of complex formation is invariably slower than in isopropanol.

In acidic solutions, pH < 5.0, there is no significant effect of pH on the formation of Pt(II)-thiol complexes, while in alkaline media, precipitation occurs, due to solvolysis of Pt(II) ions. In case of Pt(IV) complexes, the change of pH in the range 2.0 to 12.0 exerts negligible effect on complex formation. Therefore the formation constants calculated in this article are not conditional, but apparent values.

The sequence of addition of the reagents causes apparently no significant effect on the rate of complex formation.

The electronic spectra of solutions exhibit broad bands in the near uv region, with maximum absorption occuring at 350 and 330 nm in case of Pt(II) complexes with (TP) and (PTT), respectively, and at 335 nm in case of Pt(IV) complexes with each of the two thiols. In case of Pt(II) and Pt(IV) salt solutions, shoulders appear around 360 and 350 nm, respectively.

Stoichiometry of the complexes:

Platinum (II) forms 1:1 and 1:2 (M:L) complexes, while Pt(IV) forms 1:1, 1:2 and 1:4 complexes with TP and PTT. These results are confirmed by calculating the number of absorbing species in solution applying the graphical methods of Coleman to the absorbance data obtained by the mole ratio method [11].

The formation constants of the complexes are calculated from the mole

ratio data [9]. The stepwise formation constants are calculated using the corresponding solutions method [10]. In this method the formation function, $\bar{n}$, and the free ligand concentration [L] are calculated for each system, then $\bar{n}/[L]$ values are plotted against [L]. The application of Olerup's method [12] to those plots gives β_1 and β_2 in each case, representative curves are given in figures 1A and 1B. From the plots of $\bar{n}$ against pL, log k_n values are determined by the half values method, representative curve is given in figure 1C.

The plots of n/[L] vs.[L], cf. Fig.1B,give different measurable values of $[L]_i$ and the corresponding values of n/[L]. These values are used to calculate the integral $\zeta_0^L \bar{n}/[L]$ d[L] using the appropriate computer programme [13]. The integral values obtained are used to evaluate β_n of the complexes. The logarithmic values of the successive formation constants of the complexes obtained by the various methods are given in Table 1. It is noteworthy that TP forms more stable complexes with Pt(II&IV) than PTT. This may be due to steric effect of the methyl group of p-toluenethiol.

Composition and Structure of Solid Complexes:

The solid Pt(II) complexes with TP and PTT are brick-red and greyish-yellow in colour, respectively, while Pt(IV) complexes with each of the thiols are yellow. The results of chemical analysis (Table 2) as well as those of ir spectra and x-ray diffraction patterns proposed the following hexameric and dimer structures for Pt(II) and Pt(IV) complexes, respectively.

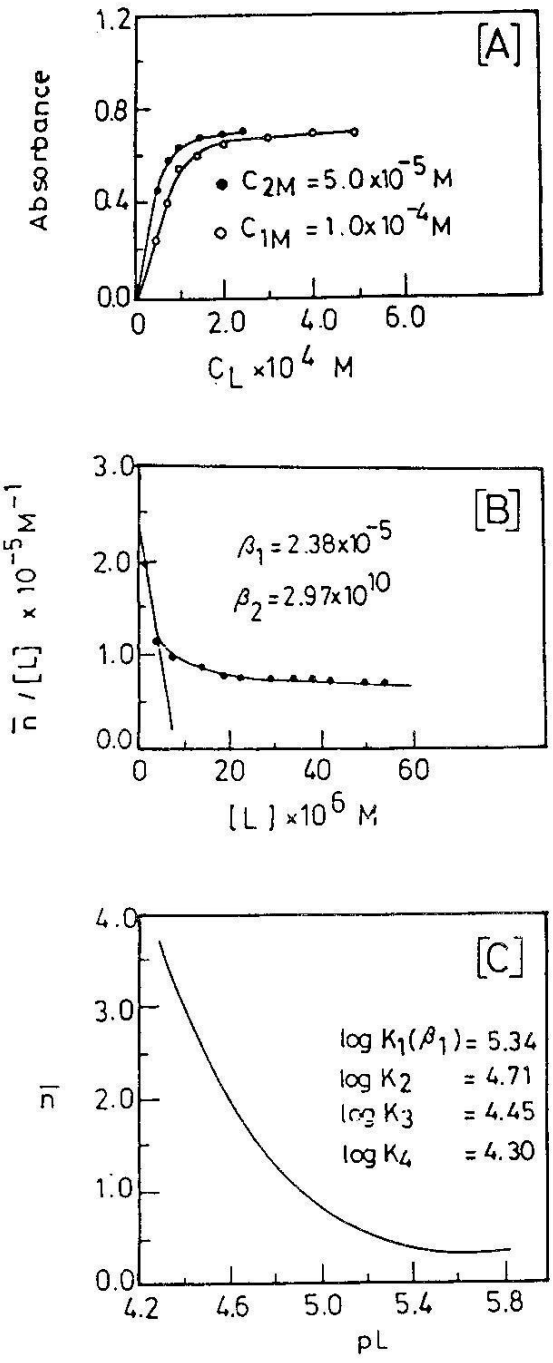
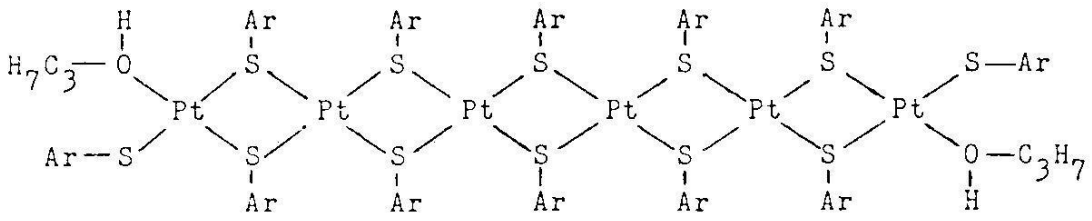
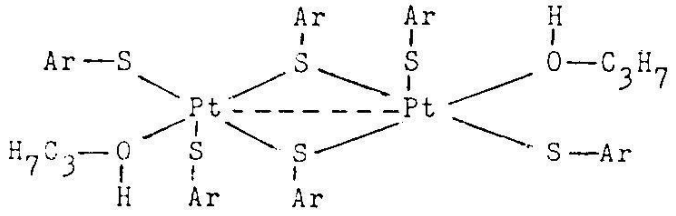


Fig-1: Application of the corresponding solutions method to the calculation of the formation constants of the Pt(IV)-thiophenol complexes.
(A) Absorbance-C_L plots, (B) $\bar{n}/[L]$ vs. [L] plot & (C) Plot of $\bar{n}$ vs. pL.



Pt(II)-thiol hexameric complex



Pt(IV)-thiol dimer complex

Table-1: Collective data of the formation constants of the Pt(II) and Pt(IV) complexes with thiophenol (TP) and p-toluenethiol (PTT).

Experiment	Method	Pt(II)-TP		Pt(II)-PTT		Pt((IV)-TP				Pt(IV)-PTT			
		$\log\beta_1$	$\log\beta_2$	$\log\beta_1$	$\log\beta_2$	$\log\beta_1$	$\log\beta_2$	$\log\beta_3$	$\log\beta_4$	$\log\beta_1$	$\log\beta_2$	$\log\beta_3$	$\log\beta_4$
1) M.R.* method	Harvey & Manning	5.02	9.79	4.30	8.26	5.13	10.00		19.41	4.34	8.27		15.77
2) C.S.** method	a) Olerup.	5.27	10.30	4.32	8.24	5.38	10.47			4.42	8.55		15.78
	b) Half values	5.37	10.05	4.50	8.37	5.34	10.05	14.50	18.80	4.58	8.54	12.24	15.78
	c) Integration	5.23	9.97	4.28	8.24	5.38	10.11	14.20	18.86	4.42	8.24	11.65	15.87
	Mean	5.22±	10.02±	4.35±	8.28±	5.31±	10.15±	14.35±	19.02±	4.44±	8.40±	11.94±	15.81±
	value	0.15	0.21	0.10	0.06	0.12	0.21	0.21	0.34	0.10	0.17	0.42	0.06

* M.R. = Mole Ratio.

** C.S. = Corresponding Solutions.

Table-2: Microchemical Analysis of the separated complexes.

Complex	C%		H%		S%		M%		Cl%
	Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found	Found
Pt(II)-TP	35.99	36.00	2.92	2.70	14.76	15.05	45.10	44.87	Nill
Pt(II)-PTT	39.00	39.45	3.61	3.70	13.87	13.67	42.27	42.30	Nill
Pt(IV)-TP	43.25	43.60	3.95	3.70	16.84	16.04	33,49	33.36	Nill
Pt(IV)-PTT	46.10	45.85	4.64	4.50	15.37	15.12	31.23	31.05	Nill

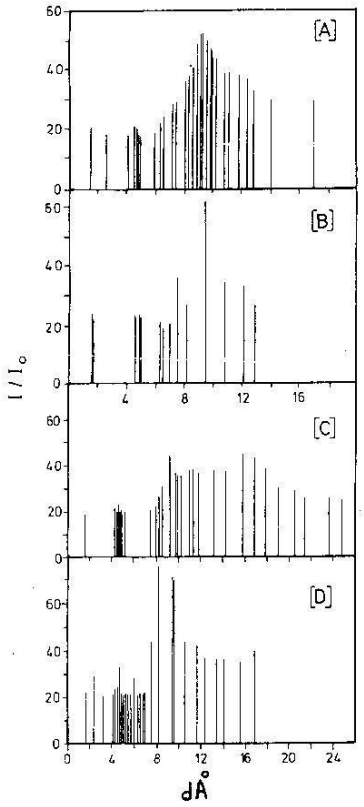


Fig-2: The d-spacing and relative intensities of Pt(II) and Pt(IV) compexes with thiophenol (Plots A&C, respectively) and with p-toluenethiol (Plots B&D, respectively).

The Pt-Pt bonds in Pt(IV) complexes are quite possible as evident from the reaction of Pt(III) with alpha-pyridone [14]. Also the insoluble nature of the solid complexes in almost all common solvents confirms the presence of sulphur linkage in their structure [2a,15&16].

Infrared Spectra:

The assignment of the main bands manifested in the ir spectra of the complexes are given in table 3. It is noteworthy that in the spectra of all complexes, the characteristic stretching vibrations of the S-H group, located at 2570 cm^{-1} in case of TP and at 2580 cm^{-1} in case of PTT have disappeared. This reveals the formation of M-S-M bridges [17]. Other evidences for the presence of these bridges are the appearance of the M-S and C-S-M stretching vibration bands in all the spectra at 490 cm^{-1} and 695 cm^{-1}, respectively [18]. The bands of C-S-M at 695 cm^{-1} are originally located as C-S stretching vibration at 730 cm^{-1} and 750 cm^{-1} in the spectra of TP and PTT, respectively. It is apparent that the decrease in wavenumber is a result of restriction caused by the coordination.

The presence of solvent molecules in the complex causes the appearance of two bands at about 1310 cm^{-1} and 3500 cm^{-1} due to bending and stretching vibrations of the O-H group, respectively [19]. The infrared bands due to vibrations of the other active groups and skeletons of the complex molecule are also assigned [19,20] in table 3.

X-ray Diffraction Patterns:

The d-spacings and intensities of the x-ray diffraction spectra of Pt(II&IV) complexes are shown in figure 2. The d_1, d_2 and d_3 values of Pt(II)-TP complex are 9.50, 9.20 and 9.05 Å with intensities 50.0, 52.3 and 51.2, respectively, whereas those obtained for Pt(IV)-TP complex are 16.81, 15.78 and 9.25 Å, with intensities 43.2, 45.0 and 44.4, respectively. Pt(II)-PTT and Pt(IV)-PTT complexes yield d-spacings of (10.69, 9.42 and 7.45 Å) and (9.59, 9.50 and 8.22 Å), respectively. The respective intensities are (34.5, 61.6 and 36.1) and (70.2, 70.6 and 76.0). The differences in the d-spacings of Pt(II) and Pt(IV) complexes with the same ligand are criteria of different

Table-3: Band assignment of ir spectra of platinum complexes with TP and PTT.

Mode of Vibration	Reported Location	Pt(II)-TP	Pt(II)-PTT	Pt(IV)-TP	Pt(IV)-PTT
M-S stretching	490[17]	480 m	490 s	490 sh	510 sh
C-S-M str.	497[17]	680 s	695 w	700 vs	695 m
C-H out of plane bending	950-650[19]	1210vw,	1188m,	1190m,	1210m,
		1070w,	1123vw,	1165m	1180s,
		1028m,	1100m,	1080s,	1115m,
$C-CH_3$ Rocking	1150-850	1005w,	1055m&	1032s,	1085m,
		965vw,	1020m	1010s,	1020s,
				970w	995m,
C-H in plane deformation	1225-950	905vw&		920m&	940w&
		885vw		815m.	880m.
O-H bending	1400-1300[18]	1325sh	1310w	1310m	1300m
$-C_6H_5$ skel.	1600-1500[18]	1582m,	1570vw,	1580s,	1595m,
		1481m,	1490vs&	1480s&	1480vs &
		1445m	1450w	1442s.	1440m.
S-H str.	2600-2550[19]	--	--	--	--
C-H str.	3100-3000[18]	3090w	3050m	3062m	3000m
O-H str. in secondary alcohols.	3625-3620[18]	3500vw	3500b	3510vw	3500w.

vw = very weak, w = weak, m = medium, s = strong, vs = very strong, sh = shoulder & b = broad.

structures, viz. square planar for the Pt(II)- and octahedral for the Pt(IV)-thiol complexes. The intensities of the x-ray diffraction patterns of the investigated complexes suggest that they are not perfectly crystalline, which provides supporting evidence to the proposed polymeric structure.

The analytical aspects of the formation of Pt(II&IV) complexes with TP and PTT in isopropanol have been studied elaborately [21] and found to be very useful.

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