

SYNTHESIS, INFRARED, RAMAN AND PMR SPECTRA OF THE TETRAMER: TETRAKIS(TRIMETHYLTHIOMETHOXYPLATINUM(IV)), $[\text{Pt}(\text{CH}_3)_3\text{SCH}_3]_4$

J.R. HALL, D.A. HIRONS and G.A. SWILE

Department of Chemistry, University of Queensland, Brisbane, 4067 (Australia)

(Received March 5th, 1979)

Summary

Trimethylthiomethoxyplatinum(IV), $\text{Pt}(\text{CH}_3)_3\text{SCH}_3$, has been prepared and characterised. It is tetrameric in CHCl_3 solution and in the vapour state. Infrared and Raman spectra of the solid state have been recorded and also the Raman spectrum of a chloroform solution. Polarized lines at 126, 563, 729, 1255 and 2923 cm^{-1} are assigned to the totally symmetric modes $\nu(\text{Pt}-\text{S})$, $\nu(\text{Pt}-\text{C})$, $\nu(\text{C}-\text{S})$, $\delta(\text{CH}_3)$ and $\nu(\text{C}-\text{H})$, respectively. The PMR spectrum in CHCl_3 has been recorded, $^2J(^{195}\text{Pt}-\text{C}-^1\text{H})$ 69.7 Hz. The thiomethyl proton signal consists of a septet, $^3J(^{195}\text{Pt}-\text{S}-\text{C}-^1\text{H})$ 15.5 Hz, which is expected for a tetramer based on interlocking tetrahedra of four $\text{Pt}(\text{CH}_3)_3$ and four SCH_3 groups.

Introduction

The preparation of trimethylmethoxyplatinum(IV), $\text{Pt}(\text{CH}_3)_3\text{OCH}_3$, was reported by Ivanova and Gel'man in 1958 [1]. The sulphur analogue is reported here for the first time and also its characterization by various spectroscopic techniques. A related molecule, $\text{Pt}(\text{CH}_3)_3\text{SH}$, has been described by Graves et al. [2], but a firm decision as to molecularity was not reached since the substance was sparingly soluble. The thiomethoxy compound, on the other hand, is readily soluble in a number of solvents.

Results and discussion

PMR spectrum

In view of the tetrameric nature of $\text{Pt}(\text{CH}_3)_3\text{SCH}_3$ in CHCl_3 solution and in the vapour state, a likely structure for the molecule is the cage model commonly found for $\text{Pt}(\text{CH}_3)_3\text{X}$ compounds, e.g., $[\text{Pt}(\text{CH}_3)_3\text{OH}]_4$ [3]. The PMR spectrum is consistent with this model. The spectrum in the methyl-platinum

TABLE 1
 INFRARED AND RAMAN SPECTRA (cm^{-1}) OF $[\text{Pt}(\text{CH}_3)_3\text{SCH}_3]_4$

Raman CHCl_3 solution	Raman solid	Infrared solid	Assignment	
63w	66(sh)	113w	Pt_4S_4 skeletal bending	
86m, dp	68w 82s			
125m, p	121m	248vw 270w	$\nu_{\text{sym}}(\text{Pt}-\text{S})$ $\delta(\text{CPtS})$	
150w, dp	146m			
560s, p	247w	312s	$\delta(\text{PtC})$ $\nu_{\text{asym}}(\text{Pt}-\text{S})$	
	260vw ~308vww			
	557vs	713vw	$\nu(\text{Pt}-\text{C})$	
	561m			
566vs				
595(sh)				
729vw, p	714(sh)	845(sh)	$\nu(\text{C}-\text{S})$	
	721w			
	728(sh)			
1220w, dp	750	854w	$\rho(\text{CH}_3(\text{S})), \rho(\text{CH}_3(\text{Pt}))$	
	849vww			
	1253vw, p	1216m		951s
2900w, p	1248w	1224s	$\delta(\text{CH}_3(\text{Pt}))$	
	1300vww	1254s		
	2920vw, p	1421vw	1303m	$\delta(\text{CH}_3(\text{S}))$
		2809vw	1424s	$\delta_{\text{asym}}(\text{CH}_3)$ $2 \times \delta_{\text{asym}}(\text{CH}_3)$
2900w, p	2886m	2808m	$\nu(\text{C}-\text{H})$	
	2909w	2894s		
	2955vw	2918w		
	2980vw	2958s		

region should consist of a principal resonance accompanied by satellites (^{195}Pt , $I = 1/2$, 34% abundance) whose coupling constant value should correspond to that found for *trans* S atoms [4]. This pattern * is observed and the coupling constant value, 69.7 Hz (τ 9.03 ppm), compared with the result for $\text{Pt}(\text{CH}_3)_3\text{-SH}$, 73.4 Hz [2], indicates a stronger Pt-S bond in the former case. The methyl-sulphur signal consists of a septet of lines attributed to proton coupling with zero, one, two and three ^{195}Pt nuclei. The intensity distribution is approximately correct [5] and $^3J(^{195}\text{Pt}-\text{S}-\text{C}-^1\text{H})$ 15.5 Hz (τ 7.73 ppm), agrees with the value for $\text{Pt}(\text{CH}_3)_3\text{SH}$ (15.2 Hz) [2].

Vibrational spectrum

Infrared and Raman spectra of $[\text{Pt}(\text{CH}_3)_3\text{SCH}_3]_4$ in the solid state and the Raman spectrum of a CHCl_3 solution are set down in Table 1.

The spectra consist essentially of features typical of the $\text{Pt}(\text{CH}_3)_3$ [6,7] and SCH_3 [8] groups, together with additional stretching and bending modes of the

* The relative peak heights were found to be approximately 1/8/1 rather than the expected ratio of 1/4/1 for trimethylplatinum mononuclear species. We are currently investigating this effect.

cage atoms. Assignments are indicated in Table 1. The value of 560 cm^{-1} for Pt—C stretching is consistent with $\nu(\text{Pt—C})$ for other sulphur compounds, e.g., $[\text{Pt}(\text{CH}_3)_3\text{SCN}]_4$ [9] and $\text{Pt}(\text{CH}_3)_3\text{SH}$ [2]. It indicates further the sensitivity of this mode to the nature of the *trans* donor atom [7,10]. The assignment of the Raman line at 125 cm^{-1} to symmetric Pt—S stretching is guided by its polarization. In $[\text{Pt}(\text{CH}_3)_3\text{SCN}]_4$, bands about 250 cm^{-1} were attributed to this type of mode [9].

Experimental

Preparation of $[\text{Pt}(\text{CH}_3)_3\text{SCH}_3]_4$

$\{\text{Pt}(\text{CH}_3)_3\}_2\text{SO}_4 \cdot 4\text{ H}_2\text{O}$ (1.0 g) was dissolved in 25 ml water and aqueous NaSCH_3 solution ($\sim 1\text{--}2\text{ ml}$, 20–25% by weight obtained from Tokyo Kasei) was added dropwise until no more precipitate formed. The solid was filtered off, washed with water and air-dried (yield 1.03 g). According to PMR spectra, the solid (dissolved in benzene) is a mixture of the various tetramers $[\{\text{Pt}(\text{CH}_3)_3\text{OH}\}_x\{\text{Pt}(\text{CH}_3)_3\text{SCH}_3\}_{4-x}]$, $x = 0\text{--}4$. A similar system has been reported previously [11]. Disproportionation of the mixed tetramers into the parent compounds was effected by suspending the solid product in boiling benzene ($\sim 15\text{ ml}$) for 30 min. The solution was then evaporated to dryness and the residue extracted with four 25 ml aliquots of *n*-hexane. A small amount of solid identified as $[\text{Pt}(\text{CH}_3)_3\text{OH}]_4$ remained undissolved. The yellow hexane solution was boiled with activated charcoal and filtered. The filtrate was concentrated on a water-bath to the point of crystallisation, cooled in ice-water and filtered. Recrystallization was effected by dissolving the crystals in the minimum volume of CHCl_3 and precipitating with ethanol. Fine, white crystals were filtered from the solution. Yield 0.3 g, dec. p. $220\text{--}240^\circ\text{C}$, Found: C, 16.9; H, 4.2; S, 11.2. $\text{C}_4\text{H}_{12}\text{SPt}$ calcd.: C, 16.7; H, 4.2; S, 11.2%. The compound is soluble in benzene, chloroform and *n*-hexane. Mol. wt. (CHCl_3): 1240; tetramer calcd.: 1149.

The mass spectrum consisted of multiplets due to the variety of Pt and S isotopes and their possible combinations in the tetramer. The highest molecular weight multiplet maximised on 1148 amu and the feature of the spectrum was a series of these multiplets of decreasing molecular weight separated by 15 amu.

Infrared spectra in the $4000\text{--}200\text{ cm}^{-1}$ region were recorded on a Perkin—Elmer Model 225 spectrophotometer. Samples were examined as Nujol or hexachlorobutadiene mulls between CsI plates. Spectra in the region $400\text{--}50\text{ cm}^{-1}$ were obtained from samples in the form of Nujol mulls between polythene plates using a Beckman-RIIC IR-720 far-infrared spectrophotometer.

Raman spectra were recorded on a Cary Model 82 laser spectrophotometer. An argon laser emitting 514.5 nm was used to excite the polycrystalline sample which was held in a capillary. Laser power at the sample was 250 mW. Spectral slit widths down to 2 cm^{-1} were used. Infrared and Raman frequencies are considered accurate to $\pm 2\text{ cm}^{-1}$ below 2000 cm^{-1} and $\pm 4\text{ cm}^{-1}$ above 2000 cm^{-1} .

Molecular weight measurements were made using a Hewlett—Packard 302 Mechrolab high-temperature vapour pressure osmometer (reproducibility $\sim 10\%$).

The mass spectrum was recorded on an MS9025 instrument.

Magnetic resonance spectra were recorded in CDCl_3 on a Jeol PS100 spectrometer. Chemical shifts are reported in ppm downfield from internal TMS.

Acknowledgements

The authors thank the Australian Research Grants Committee for funds to purchase the infrared and Raman spectrometers; Mr. J. Kent for C and H analyses; Mr. G.A. MacFarlane, through the courtesy of Dr. R.F. Evans for recording the mass spectrum and Miss L. Lambert for the NMR spectra.

References

- 1 O.M. Ivanova and A.D. Gel'man, *Zh. Neorg. Khim.*, 3 (1958) 1334.
- 2 R. Graves, J.M. Homan and G.L. Morgan, *Inorg. Chem.*, 9 (1970) 1592.
- 3 H.S. Preston, J.C. Mills and C.H.L. Kennard, *J. Organometal. Chem.*, 14 (1968) 447.
- 4 D.E. Clegg, J.R. Hall and G.A. Swile, *J. Organometal. Chem.*, 38 (1972) 403.
- 5 G.L. Morgan, R.D. Rennick and C.C. Soong, *Inorg. Chem.*, 5 (1966) 372.
- 6 D.E. Clegg and J.R. Hall, *Spectrochim. Acta*, 21 (1965) 375.
- 7 D.E. Clegg and J.R. Hall, *J. Organometal. Chem.*, 22 (1970) 491.
- 8 I.W. May and E.L. Pace, *Spectrochim. Acta, A*, 24 (1968) 1605.
- 9 G.C. Stocco and R.S. Tobias, *J. Coordin. Chem.*, 1 (1971) 133.
- 10 D.E. Clegg and J.R. Hall, *Austral. J. Chem.*, 20 (1967) 2025.
- 11 J.R. Hall and G.A. Swile, *J. Organometal. Chem.*, 44 (1972) 201.