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ORGANOPLATINUM COMPOUNDS

III *. $[Me_3PtClO_4]_4$, PREPARATIVE AND STRUCTURAL ASPECTS OF A NEW ORGANOPLATINUM CLUSTER COMPOUND

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Summary

Several methods for the preparation of Me_3PtClO_4 have been investigated: anhydrous, pure Me_3PtClO_4 was obtained by treating $AgClO_4$ with Me_3PtI in dry benzene. The compound is sensitive to moisture and explodes on heat or shock treatment. Molecular weight determination indicates a tetrameric structure $[Me_3PtClO_4]_4$, and spectroscopic data are consistent with this. Preliminary X-ray investigation of a single crystal indicates a crystal symmetry $I4_1/amd$ (Schoenflies: D_{4h}^{19}) with four $[Me_3PtClO_4]_4$ units in a tetragonal cell ($a = b = 11.267(5)$; $c = 25.09(1)$) and local symmetry D_{2d} of the $[Me_3PtClO_4]_4$ structure.

Results and discussion

The perchlorate anion ClO_4^- functions as a monodentate [1,2], a bidentate, or a bridging ligand [3] in many coordination compounds which exhibit quite different thermodynamic stabilities. Perchlorates of the heavy metals and of the transition series are predominantly covalent, and therefore potentially dangerous explosives.

Trimethylplatinum perchlorate has so far only been studied in solutions, which has given information on the spectroscopic characteristics associated with the solvated cation $(Me_3Pt)^+_{solv.}$ and the tetrahedral ClO_4^- anion [4]. We (with Von Dahlen [5]) have attempted the synthesis of pure, anhydrous Me_3PtClO_4 through the following reactions:

$$(Me_3Pt)_2SO_4 \times 4\,H_2O + 5\,Ba(ClO_4)_2 \nrightarrow$$
$$2\,Me_3PtClO_4 + BaSO_4 + 4\,Ba(ClO_4)_2 \cdot x\,H_2O$$

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* For Part II see ref. 7.

$Me_3PtOH + HClO_4 \nrightarrow Me_3PtClO_4 + H_2O$

(Caution! At higher concentrations of $HClO_4$ this procedure leads to violent explosions)

$Me_3PtN_3 + AgClO_4 \nrightarrow Me_3PtClO_4 + AgN_3$

$Me_3PtCl + AgClO_4 \nrightarrow Me_3PtClO_4 + AgCl$

$Me_3PtI + AgClO_4 \rightarrow Me_3PtClO_4 + AgI$

Of these experiments only the last was successful: Me_3PtClO_4 was obtained in good yield as colourless plates. The compound is extremely sensitive to moisture, decomposes when exposed to light, and explodes on heat or shock treatment.

Trimethylplatinum perchlorate is sparingly soluble in benzene or toluene, but more soluble in ether or 1,4-dioxane. Solutions of Me_3PtClO_4 in these solvents turn yellow after a few hours (oxidation) and platinum metal is formed. For this reason CCl_4 is recommended for recrystallization and for storage of the compound in solution. Me_3PtClO_4 is relatively stable thermally; dry crystals may be handled under an inert gas without danger, but often electrostatic effects are observed. The compound decomposes gradually at 125°C (Kofler-block), but single crystals survive prolonged exposure to X-ray radiation.

Unfortunately, Me_3PtClO_4 was too unstable to give reliable and reproducible mass spectra. ^1H NMR data are in the expected range for $[Me_3PtX]_n$ derivatives:

TABLE 1

VIBRATIONAL SPECTRA OF Me_3PtClO_4 IN VARIOUS SOLVENTS

Assignment	IR		Raman		
	Nujol/Host.	CCl_4	CCl_4	D_2O	Lit. [1]
		3090vs			
		3070s		3000vw	2978m(br)
		3040vs			
ν_{as}(C—H)	2960	2910m	2920w	2920w	2909s
	2890			2880vw	2851vw
		1955m			2823m
		1820m			
		1520w	1540—50w(br)		
		1480vs		1450vw	1427m
		1390w			1329w
	1260vs	1270vw	1270vw	1290vw	1290m
		1240w		1250vw	1250s
δ(C—H)	1225vs	1230vw	1225w	1220vw	1194w
				(2 × 600?)	
		1180w			
	1095w(br)				
	1020w(br)	1040s	1010vw	1020vw	
		975vw		930m	
$\rho(CH_3)$		850w		830w	882w
	790s				
	770(sh)				
		680vs			
$\nu_{as,s}(Pt—C_3)$				600vs	600vs
			565vs		

$\delta(\mathrm{Pt{-}C\underline{H}_3})$: 1.74 ppm (ext. TMS); $^2J(^{195}\mathrm{Pt{-}C\underline{H}_3})$: 76 Hz. Raman spectra were obtained on CCl_4 and D_2O solutions and IR spectra on Nujol/polyoil emulsions and CCl_4 solutions. Crystalline material decomposed in the laser-beam of the Raman spectrometer. The principal infrared and Raman data are given in Table 1.

From the (crystallographic) local symmetry D_{2d} we would expect alternative vibrations in the IR and Raman spectra. However, there are already differences between the IR spectra of CCl_4 solutions and Nujol mulls. Taking into account the intensities in both the IR and Raman effect we assign $\nu_{as,s}(\mathrm{Pt{-}C_3})$ to the 680vs band in the IR and $\nu_s(\mathrm{Pt{-}C_3})$ to the 565vs band in the Raman spectrum.

Preliminary X-ray investigation of Me_3PtClO_4 reveals a tetragonal cell with the crystallographic symmetry $I4_1/amd$ (Schoenflies: D_{4h}^{19}) with four tetramer units $[Me_3PtClO_4]_4$ of local symmetry $\bar{4}2m$ (D_{2d}). Cubic structures have been reported for $[Me_3PtCl]_4$ and $[Me_3PtOH]_4$. In $[Me_3PtClO_4]_4$ we observe a different packing leading to elongation of the c-axis: $a = b = 11.267(5)$; $c = 25.09(1)$.

Experimental

IR spectra were recorded on PE 457 and 577 grating instruments. For Raman spectra a CARY 83 model was used. NMR spectra were recorded on VARIAN T 60 and XL 100 instruments.

Elemental analyses were performed by A. Bernhardt, Analytical Laboratories, D-5250 Elbach über Engelskirchen, BRD. Anhydrous silver perchlorate was purchased from Alfa Inorganics. Me_3PtI was prepared from K_2PtCl_6 and MeLi [6].

Me_3PtClO_4. 2.45 g (11.8 mmol) of $AgClO_4$ were dissolved in 100 ml dry benzene (free of tiophene); a solution of 4.33 g (11.8 mmol) of Me_3PtI in 100 ml benzene was added, and the mixture stirred at room temperature in the dark for 4 h. Cream yellow AgI was precipitated and gradually turned grey on exposure to light. Al_2O_3 was added (W 200 neutral, activity super I, ICN Pharmaceuticals GmbH, West-Germany), and the mixture stirred for another 2 h. The benzene was removed in vacuo and the residue treated with 120 ml dry CCl_4 for 30 min at ambient temperature. After filtration (nitrogen) through a G4 sintered disc the solvent was partly evaporated until crystallization occured. Crystallization was completed over night at −22°C, yielding fine, colourless crystals, m.p. 125—130°C (dec.). Isolated yield: 1.66 g (73% theory). AgI was isolated in 96% yield.

Elemental analysis: Found: C, 10.24; H, 2.44; Cl, 10.35. $C_3H_9ClO_4Pt$ calcd.: C, 10.61; H, 2.67; Cl, 10.44; O, 18.84; Pt, 57.44%.

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