Crystal Structure of Platinum Tetrachloride

By M. F. PILBROW

(*Institut für Anorganische Chemie I der Universitat Erlangen-Nürnberg, 8520 Erlangen, Fahrstrasse 17, West Germany*)

Summary Platinum tetrachloride has been shown by *X*-ray powder methods to be isostructural with α-PtI_4 and $PtBr_4$.

THE tetrahedral, SnI_4-type structure assigned to $PtCl_4$ by Falqui,[1] is surprising in view of the pronounced tendency of Pt^{IV} to be six co-ordinate and also because $PtCl_4$ may be expected to be paramagnetic and volatile[2] and have a simple i.r. spectrum.

These irregularities of the assigned structure prompted reinvestigation of the system and *X*-ray powder data are now presented which show that $PtCl_4$ is isostructural with α-PtI_4[3] and $PtBr_4$.[4] *X*-ray studies of single red needles, prepared by chemical transport of the powder in 1 atm. Cl_2 (900—300 °C), have so far been precluded because of the hygroscopic nature of the product.

Powdered samples, prepared by three methods,[5] all gave the same *X*-ray powder pattern (see Table).† The low angle reflexions are sharp and distinct but with progression to higher Bragg angle the lines become broad and diffuse. The data have been rationalised in terms of an orthorhombic unit cell with $a = 11{\cdot}37$, $b = 13{\cdot}65$, $c = 5{\cdot}95$ Å. Assuming $Z = 8$, $D_c = 4{\cdot}85$ g cm^{-3} ($D_m = 4{\cdot}5$, lit.[6] 4·302).

α-PtI_4 and $PtBr_4$ crystallise with $Z = 8$ in the *Pbca* space group[3,4] and the Guinier powder patterns of all three halides are markedly similar with higher Bragg angles for reflexions from similarly assigned *hkl* planes in the order $PtI_4 > PtBr_4 > PtCl_4$. Hence it is presumed that $PtCl_4$ has a $[PtCl_{4/2}Cl_2]_\infty$ structure identical with that of α-PtI_4 and $PtBr_4$ (Figure). The isomorphism is further demonstrated by the agreement between the observed $PtCl_4$ line intensities and those calculated using the iodide and bromide structures[3,4] as models.

† Attempts to obtain material having the previously described[1] *X*-ray reflexion characteristics have so far been unsuccessful.

$[PtX^4/_2X_2]_\infty$ has C_2 symmetry which is lowered to C_1 if the different Pt–X bond lengths are considered ($X_a \neq X_b \neq X_c \neq X_d$).[3,4] Thus the molecule should have all its 21 vibrational modes i.r. active.‡ 15 bands (377 s, 364 sh, 345 wm, 337 s, 324 sh, 310 w, 290 m, 274 s, 235 wbr, 200 w, 182 s, 167 sh, 140 w, 130 w, 110 wm)§ consistent with the existence of terminal and bridging Cl atoms, are observed in the $PtCl_4$ spectrum.

X-Ray powder data for $PtCl_4$

θ	*hkl*	I_{obs}	I_{calc}
6·52	020	s	55
8·45	210	vs	100
9·03	111	vw	6
9·90	021	m	15
10·65	121	m	25
11·30	211	vw	7
12·50	230	w	7
12·92	131	m	23
14·35—14·65	311, 231	wbr	18
15·10—15·60	041 321 240, 102 141	wbr	15
15·89	112	vw	13
16·90—17·20	122 202 241, 420 331	sbr	60
18·3—18·7	132 151 430, 421	wbr	19
19·2—19·5	302, 341, 312	mbr	11, 23, 20
21·8—22·1	351, 441	wbr	22
24·5—24·7	213 361 270	vwbr	11
25·0—25·5	062 502 223, 541 133 512, 611	wbr	34

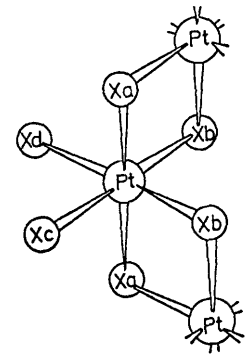

FIGURE. *The configuration of* $[PtX^4/_2X_2]_\infty$ *molecules*

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‡ The tetrahedral symmetry,[1] modified by the C_3 site symmetry has only 6 i.r. active modes.

§ These bands are compatible with the seven reported earlier,[7] but they are better resolved.

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