Reaction of Platinum Dichloride with Bromine: Two Crystal Modifications of a New Mixed Halide

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Summary Platinum dichloride reacts with molecular bromine to give a new mixed halide, $Pt_6Cl_{12}Br_2$, which exists in two crystal modifications for which *X*-ray powder and i.r. results are given.

In extending the study of the preparations, properties, and structures of binary platinum halides[1] to mixed halides we have repeated the work of Batsanov and Ruchkin,[2] who described six compounds of the type PtX_2Y_2 (X,Y = Cl, Br, or I; X ≠ Y). The complete results on these systems will be presented elsewhere, but the recent report[3] of the formation of $Pt_6Cl_6Br_6$ by reaction of BBr_3 with Pt_6Cl_{12} prompts preliminary communication of our results on the platinum dichloride–bromine system.

Although it was reported earlier[2] that on shaking platinous chloride in a stream of bromine at *ca.* 25 °C $PtCl_2Br_2$ was formed, we obtained a red product of stoicheiometry $Pt_6Cl_{12}Br_2$† (*cf.* green-brown Pt_6Cl_{12}). The same product is also obtained by stirring Pt_6Cl_{12} in liquid bromine. A second structural modification, brown β-$Pt_6Cl_{12}Br_2$, is formed by heating a suspension of the initial product (α) in inert organic solvents.

Thermal gravimetric analyses of both products show bromine loss (8·8 ± 0·5% for α, 9·1 ± 0·5% for β; calc. 9·2%) at 200 ± 20 °C with production of Pt_6Cl_{12}.

TABLE

X-Ray powder results for α- and β-$Pt_6Cl_{12}Br_2$

	α			β[a]	
θ	*I*	*hkl*	θ	*I*	*hkl*
5·5	s	100	5·5	s	101
7·8	m	110	7·3	m	110
			9·2	m	021
9·6	m	111	10·7	m	003
11·1	m	200	11·1	m	202
			11·8	w	211
12·5	m	210	12·7	m	030
			13·0	w	113
13·7	m	211	13·3	m	122
			14·7	m	220
			15·0	w	104
16·0	w	220	15·8	m	131
16·8	s	300	16·8	s	303,024
			17·0	m	312
17·8	m	310	18·4	w	214,223
			18·6	w	042,015
22·7	m	400	22·7	w	404,413

[a] Hexagonal indexing.

X-ray powder results for α indicate a primitive cubic lattice with $a = 798$ pm, $Z = 1$, $D_c = 5·72$, $D_m = 5·5$ g cm^{-3}. The powder pattern of β has been rationalised in terms of a rhombohedral unit cell with $a = 813$ pm,

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† The *X*-ray data reported earlier[2] show that that product was probably a mixture of that found here and unchanged platinum dichloride. Of the twenty three lines reported, seven coincide, in position and intensity, with the strongest lines of our product and all but three of the rest can be ascribed to residual Pt_6Cl_{12}.

$\alpha = 96°24'$, $Z = 1$, $D_c = 5{\cdot}52$, $D_m = 5{\cdot}4$ g cm^{-1}; the equivalent hexagonal lattice has $a = 1212$, $c = 1242$ pm. *X*-ray results are given in the Table.

The far i.r. spectra of α and β are very similar to that of Pt_6Cl_{12} with the characteristic vibrations[4] of the hexamer at 318(vs), 203(s), and 107(m) cm^{-1} still present. Additional peaks for α at 352(w), 250(wsh), 238(m), and 228(w) cm^{-1} and for β at 360(m) and 237(mbr) cm^{-1}.‡ These i.r. results strongly suggest that in the $Pt_6Cl_{12}Br_2$ compounds the hexameric Pt_6Cl_{12} units are retained, as is also indicated by the mild conditions used for preparation (*cf. ca.* 350 °C for normal oxidation of $PtCl_2$ to $PtCl_4$ and *ca.* 500 °C for decomposition of $PtCl_2$ into Pt and Cl_2), and that bromine is absorbed by a Pt_6Cl_{12} crystal lattice with concomitant increase in the unit cell size [unit cell volumes ($\times 10^6$): Pt_6Cl_{12}[1] = 426 pm^3, α = 508 pm^3, β = 526 pm^3]. The i.r. bands in α and β at *ca.* 240 cm^{-1} are tentatively assigned to Pt–Br interaction, with 352 (α) and 360 (β) cm^{-1} bands due to Pt–Cl vibrations arising from slight distortion of the hexameric units.

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‡ No Raman spectra could be obtained because of decomposition into Pt_6Cl_{12} at the point of laser incidence.

[1] K. Brodersen, G. Thiele, and H. G. von Schnering, *Z. anorg. Chem.*, 1965, **337**, 120; K. Brodersen, G. Thiele, and B. Holle, *ibid.*, 1969, **369**, 154; G. Thiele and P. Woditsch, *Angew. Chem. Internat. Edn.*, 1969, **8**, 672; M. F. Pilbrow, *J.C.S. Chem. Comm.*, 1972, 270.

[2] S. S. Batsanov and E. D. Ruchkin, *Russ. J. Inorg. Chem.*, 1959, **4**, 779; *ibid.*, 1965, **10**, 1415.

[3] P. M. Druce and M. F. Lappert, *J. Chem. Soc.* (*A*), 1971, 3595.

[4] D. M. Adams, *Proc. Chem. Soc.*, 1961, 335; D. M. Adams, M. Goldstein, and E. F. Mooney, *Trans. Faraday Soc.*, 1963, **59**, 2228; R. Mattes, *Z. anorg. Chem.*, 1969, **364**, 290.