Bromine, Benzene, Carbon Disulphide, and Chlorinated Methane Adducts of Platinum Dichloride

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β-Platinum dichloride reacts with a variety of small molecules A (A = Br_2, C_6H_6, CS_2, CCl_4, $CHCl_3$, or CH_2Cl_2) to give adducts of stoicheiometry $Pt_6Cl_{12}.nA$ (n = 1 or 0.75). On the basis of spectroscopic, thermal, and X-ray powder results these compounds are formulated as clathrates and tentative assignments of their structures, based on host lattices of Pt_6Cl_{12} molecules, are given.

THE reaction of β-platinum dichloride with bromine to give $Pt_6Cl_{12}\cdot Br_2$ has been described in a preliminary note.[1] Further examination of this system has now revealed that this reaction is far from unique in its type and that β-$PtCl_2$ is extremely versatile in its ability to react with small molecules. A reaction with benzene to give $Pt_6Cl_{12}\cdot C_6H_6$ has already been mentioned briefly by Wiese *et al.*[2] New reactions with carbon disulphide, carbon tetrachloride, chloroform, and dichloromethane are now presented all of which give products of formula $Pt_6Cl_{12}\cdot nA$ (A = added molecule; $n = 1$ except for A = CCl_4 when $n = 0.75$). X-Ray powder diffraction, vibrational spectra, and thermal behaviour of all the adducts have been interpreted in terms of their formulation as clathrates in which the added molecules occupy spaces in different but closely related lattices of Pt_6Cl_{12} molecules.

In the earlier note[1] the bromine compound was reported to undergo a phase change on heating in organic solvents. This description of the reaction is in error; bromine is in fact substituted by solvent to give $Pt_6Cl_{12}\cdot nA$. The X-ray powder results given[1] for ' β-$Pt_6Cl_{12}\cdot Br_2$ ' are really those for $Pt_6Cl_{12}\cdot C_6H_6$.

RESULTS AND DISCUSSION

All the adducts were readily formed under the same very mild conditions (see Experimental section). They are all very similar in physical appearance to the parent compound, varying only slightly in colour, but they are clearly distinguishable by their X-ray powder patterns. These are given in Figure 1 and clearly show that despite the obvious individuality they are all related in that the

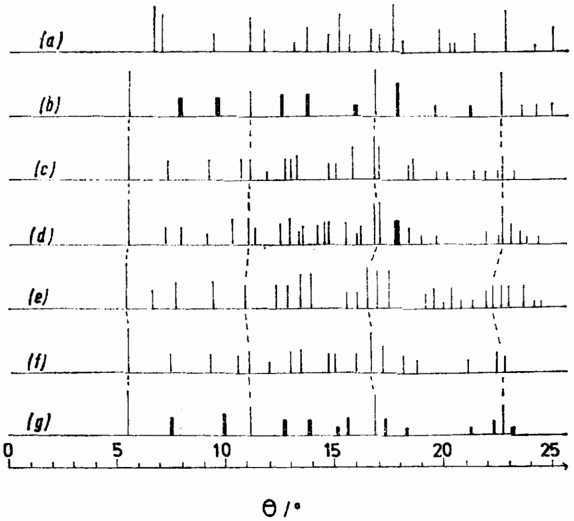

FIGURE 1 X-Ray powder patterns for β-$PtCl_2$ (a) and $Pt_6Cl_{12}\cdot nA$ [A = Br_2 (b), C_6H_6 (c), CS_2 (d), CCl_4 (e), $CHCl_3$ (f), and CH_2Cl_2 (g)]

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[1] V. Bonora, M. Jawork, and M. F. Pilbrow, *J.C.S. Chem. Comm.*, 1974, 616.

[2] U. Wiese, H. Schäfer, H. G. von Schnering, C. Brendel, and K. Rinke, *Angew. Chem.*, 1970, **82**, 135.

basic reflections of the primitive cubic $Pt_6Cl_{12}\cdot Br_2$[1] also appear, although slightly shifted, as strong lines in the patterns of the other compounds. This indication that all these adducts have related structures is borne out by the cell constants determined[1] for the bromine (primitive cubic *a* 798 pm) and benzene adducts (rhombohedral, *a* 813 pm, α_R 96.4°) and those now found on indexing the results for $Pt_6Cl_{12}\cdot 0.75\,CCl_4$ (body-centred cubic, *a* 1 624 pm) and $Pt_6Cl_{12}\cdot CHCl_3$ (rhombohedral, *a* 806 pm, α_R 94.9°).

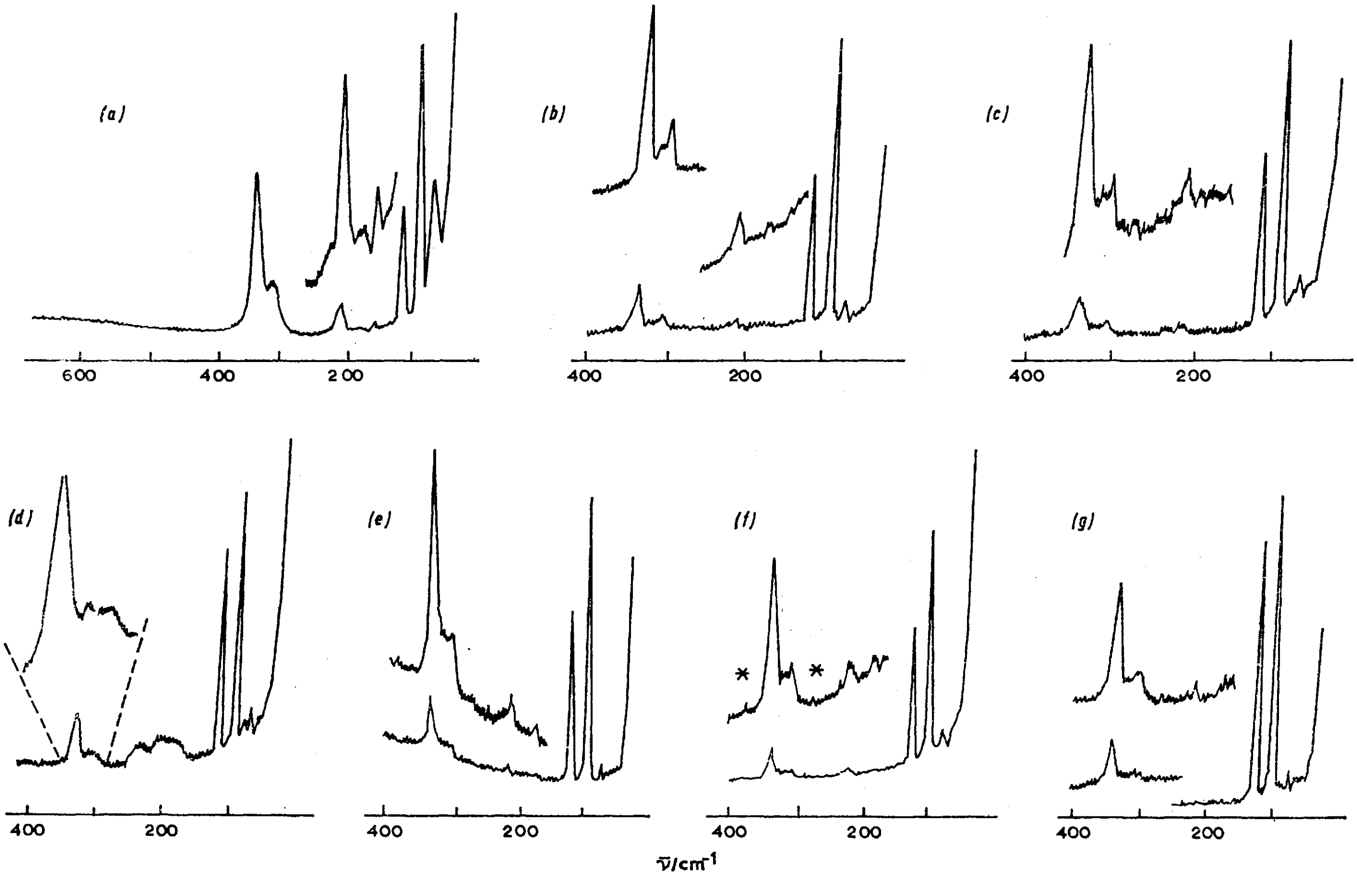

FIGURE 2 Raman spectra of β-$PtCl_2$ (*a*) and $Pt_6Cl_{12}\cdot n$A [A = C_6H_6 (*b*), CS_2 (*c*), Br_2 (*d*), CCl_4 (*e*), and $CHCl_3$ (*f*) (*, bands due to chloroform), and CH_2Cl_2 (*g*)]

These almost constant unit-cell parameters of $a \approx 800$ pm (twice this for A = CCl_4) with an interaxial angle close to or exactly 90° are significantly comparable with those of β-$PtCl_2$ itself (rhombohedral, *a* 809 pm, α_R 108.4°).[3] It is known[3] that this latter crystallises as effectively spherical Pt_6Cl_{12} molecules which are held together only by van der Waals forces, a fact demonstrated in that β-$PtCl_2$ can be sublimed and $[Pt_6Cl_{12}]^+$ molecule ions observed in the mass spectrum.[4] It is thus strongly implied that in $Pt_6Cl_{12}\cdot n$A the integrity of the hexamers is maintained and that it is this large structural unit which dictates the sizes of the unit cells. That the character of the Pt_6Cl_{12} molecules is maintained in the adducts and that the interaction with A is non-bonding is indicated by the mild conditions of formation and also by thermal-gravimetric and differential-thermal analyses. All the adducts dissociate quantitatively at *ca.* 470 K (±20 K) to β-$PtCl_2$ and A, as identified by *X*-ray powder and i.r. methods. An approximate estimate of the magnitude of the endothermicity of dissociation based on the value[5] of $\Delta H = +804$ kJ mol^{-1} for $Pt_6Cl_{12} \longrightarrow 6Pt + 6Cl_2$ as internal standard gives an average value (they are all very similar) of $\Delta H \approx +105$ kJ mol^{-1}, *i.e.* very much less than expected for bond fission but consistent with a lattice energy change plus ΔH_v of A.

Vibrational spectra confirm this conclusion. Far-i.r. measurements show that for all the adducts the vibrations of β-$PtCl_2$ at 316vs, 203s, and 110s cm^{-1} (refs. 6 and 7) are maintained without major variations in intensity and with changes in position of only ±3 cm^{-1}. The adducts' spectra showed additional weak bands at 352 ± 2 cm^{-1}, and for A = Br_2 further extra bands at 250(sh),

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[3] K. Brodersen, G. Thiele, and H. G. von Schnering, *Z. anorg. Chem.*, 1965, **337**, 120.

[4] H. Schäfer, U. Wiese, K. Rinke, and K. Brendel, *Angew. Chem.*, 1967, **79**, 244.

[5] H. Schäfer and U. Wiese, *J. Less-Common Metals*, 1971, **24**, 55.

[6] D. M. Adams, *Proc. Chem. Soc.*, 1961, 335; D. M. Adams, M. Goldstein, and E. F. Mooney, *Trans. Faraday Soc.*, 1963, **59**, 2228.

[7] R. Mattes, *Z. anorg. Chem.*, 1969, **364**, 290.

238s, and 228m cm^{-1} were observed.* The Raman spectrum of β-$PtCl_2$ appears not to have been published. It is given in Figure 2 together with those of the adducts in the same region. I.r. and Raman spectra also show that in $Pt_6Cl_{12}{\cdot}nA$ the character of A is little changed from that as a free molecule.

All these results indicate that under the influence of certain small molecules the van der Waals forces in β-$PtCl_2$ are disturbed and the Pt_6Cl_{12} molecules caused to adopt new arrangements which involve encagement of the small molecules.

The *X*-ray results show that the reorganisation of the hexamers is basically that from the almost body-centred cubic packing in β-$PtCl_2$ (α_R 108.4°, *cf.* the tetrahedral angle) to a primitive cubic ordering (Figure 3). It is now suggested that, when suitably adjusted with respect to the individual characters of A, the extra free volume created by this reordering (cubic P packing of spheres represents 47.6% free-cell volume, *cf.* 32% for cubic I)[9] is occupied by guest molecules and that these provide van der Waals contacts which compensate for the stability loss incurred by lowering the co-ordination number from eight to six.

Thus, for $Pt_6Cl_{12}{\cdot}Br_2$ it is suggested that bromine symmetrically occupies the spatial diagonal in Figure 3.† With a = 798 pm, the length of a Br_2 molecule = 618 pm, and assuming the Pt_6Cl_{12} units to be spherical with radius 404 pm (packing separation in β-$PtCl_2$),[2] the Br · · · Pt_6Cl_{12} distance is 577 pm, *cf.* a van der Waals contact of 404 + 195 = 599 pm. Thus allowing for a reasonable compressibility or distortion of the hexamers (see vibrational spectra) the guest–host separation is fully consistent with a clathrate formulation.

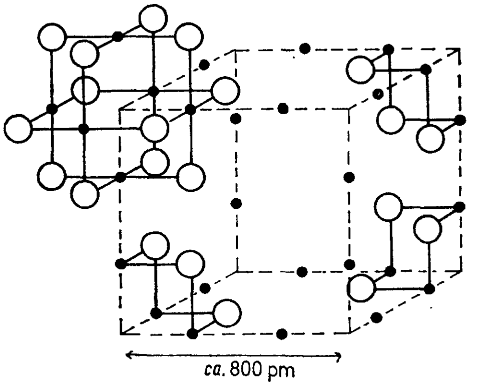
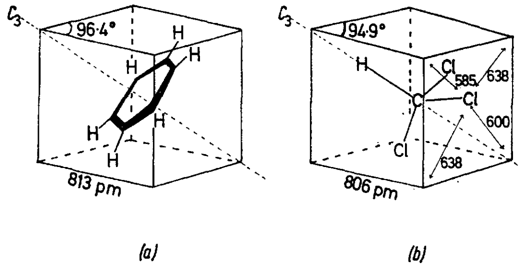


FIGURE 3 Suggested basic host unit cell of Pt_6Cl_{12} molecules. Only one hexamer is shown in full; the others are indicated by only some of their atoms. The hexamer separation is exaggerated for the sake of clarity

Although it is impossible to accommodate benzene in Figure 3 and still maintain reasonable van der Waals contacts, the *X*-ray results for $Pt_6Cl_{12}{\cdot}C_6H_6$ indicate a rhombohedral unit cell and indeed by compression of the basic cubic model along a three-fold axis space is created which can be filled by C_6H_6 so that such contacts do occur as shown in Figure 4(*a*). A similar rhombohedral distortion of Figure 3 is necessary to accommodate chloroform and to conform with the *X*-ray results; a possible structure is given in Figure 4(*b*).



(a) (b)

FIGURE 4 Possible orientations of (*a*) benzene and (*b*) chloroform molecules in their rhombohedral unit cells. Corner positions are occupied by Pt_6Cl_{12}, *cf.* Figure 3

Calculated A · · · Pt_6Cl_{12} separations for compounds for which the *X*-ray powder results have been rationalised are given in Table 1 together with the pertinent van der Waals radii sums. A noticeably bad fit is that for the CCl_4 adduct and even allowing for compressibility or reasonable distortion the contacts are too small to be compatible with a clathrate formulation. This means that the three-fold axes of the unit cell in Figure 3 and CCl_4 cannot be coincident. This is reflected in the double unit-cell dimension compared with the other systems and in the unique stoicheiometry of this compound. These results can be rationalised if the space group for this system is *I*23 (T^3) with the Pt_6Cl_{12} molecules and carbon atoms of CCl_4 located as shown in Figure 5 (locations 8c and 6b respectively). With chlorine atoms in the 24f positions with parameters of *ca.* $x = 0.563$,

TABLE 1

Separation between Pt_6Cl_{12} groups and A based on structures in which A occupies the centre of a cubic or rhombohedral unit cell with $a \approx 800$ pm, and sums of the respective van der Waals radii (pm)

Contact	Calculated separation	Sum of van der Waals radii
Pt_6Cl_{12} · · · Br–Br	577	598
Pt_6Cl_{12} · · · H–C_6H_5	546	523
Pt_6Cl_{12} · · · Cl–CCl_3	527	583
Pt_6Cl_{12} · · · Cl–$CHCl_2$[a]	638, 600, 585[b]	583
Pt_6Cl_{12} · · · H–CCl_3	528	523

[a] The carbon atom of $CHCl_3$ is assumed to occupy the position $\frac{1}{2},\frac{1}{2},\frac{1}{2}$. [b] See Figure 4(*b*).

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*Although these bands, as also similar ones in the Raman spectrum, are indicative of Pt–Br interaction, the fact that $Pt_6Cl_{12}{\cdot}Br_2$ resembles all the other compounds in all other respects suggests that these more likely result from perturbation of the hexameric groups. An unambiguous identification of ν(Br–Br) in the Raman spectrum, which would verify this, was precluded since several bands common to all the adducts were observed in the pertinent (*ca.* 317 cm^{-1})[8] region.

† Although with Br_2 in this position the cubic symmetry is lost, a statistical occupation of all four diagonals would allow for its retention; evidence for this is provided by the fact that the *X*-ray powder diffraction lines for this compound are very diffuse.

[8] H. Stammreich, F. Forneris, and Y. Tavares, *Spectrochim. Acta*, 1961, **17**, 1173.

[9] R. Hoppe, *Angew. Chem.*, 1970, **82**, 7.

$y = 0$, and $z = 0.088$ the $CCl_3{-}Cl \cdots Pt_6Cl_{12}$ separation is 571 pm. The X-ray results for the CS_2 and CH_2Cl_2 compounds have so far eluded rationalisation. Although clearly related to the structures of the above compounds, no further comment can be made except that the actual structures may well be of low symmetry. This is to be expected when one considers the size of CS_2 (678 pm *cf.* Br_2) and the low molecular symmetry of CH_2Cl_2 (C_{2v}).

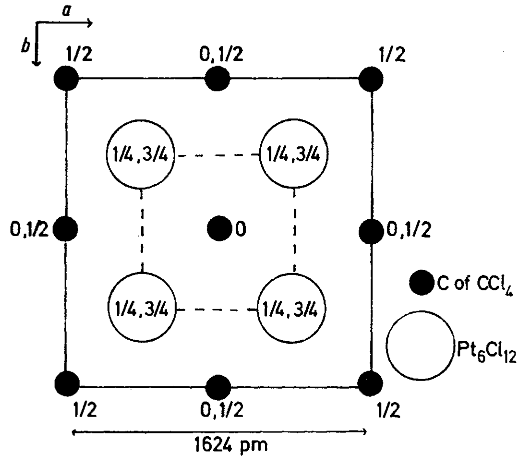

FIGURE 5 Suggested unit cell for $(Pt_6Cl_{12})_8 \cdot 6CCl_4$. The basic unit cell (Figure 3) is indicated by broken lines

TABLE 2

Thermal gravimetric and C,H analyses (%) [a] of $Pt_6Cl_{12} \cdot nA$

Compound	A [b]	Pt [b]	C	H
$Pt_6Cl_{12} \cdot Br_2$	9.1 (9.10)	66.7 (66.65)		
$Pt_6Cl_{12} \cdot C_6H_6$	4.3 (4.65)	70.5 (69.9)	3.90 (4.30)	0.30 (0.35)
$Pt_6Cl_{12} \cdot CS_2$	4.3 (4.55)	70.3 (70.0)	0.85 (0.70)	
$Pt_6Cl_{12} \cdot 0.75CCl_4$	7.5 (6.75)	69.0 (68.4)	0.70 (0.55)	
$Pt_6Cl_{12} \cdot CHCl_3$	6.7 (6.95)	69.0 (68.25)	0.75 (0.70)	0.05 (0.05)
$Pt_6Cl_{12} \cdot CH_2Cl_2$	5.1 (5.05)	68.6 (69.65)	0.75 (0.70)	0.10 (0.10)

[a] Calculated values are given in parentheses. [b] The values are the average for at least three samples; maximum deviations from the mean values are: A and Pt, 1%; C, 0.3%; and H, 0.05%.

In view of the well known relation between β-$PtCl_2$ and the lower halides of niobium and tantalum in that they have common M_6X_{12} units in their structures, it is interesting to compare the present results with those for the compounds $[C_5H_5NH]_2[Nb_6X_{12}]Y_6$ (X, Y = Cl or Br). These have been assigned structures[10] in which two pyridinium ions occupy the middle of approximately cubic unit cells of $[Nb_6X_{12}]^{4+}$ ions.

The present study has limited attention to the clathrates of β-$PtCl_2$ with only a selected few, readily available, small molecules. It is expected that this list is far from comprehensive and work is continuing on extensions to the series, including attempts to grow single crystals and with $PtBr_2$ and β-$PdCl_2$ as hosts, since like β-$PtCl_2$ these also crystallise as M_6X_{12} molecules.[3,4]

EXPERIMENTAL

I.r. spectra (10—500 cm^{-1}) were recorded on a Polytec FIR 30 spectrometer as polyethylene discs. Raman spectra were recorded on a Cary 82 instrument using focused krypton-ion laser radiation (Spectra Physics) with a 647.1 nm exciting line. Samples were presented as pressed discs without diluant which were rotated at *ca.* 2 000 revolutions per min. (Control X-ray powder photographs showed that the applied pressures of *ca.* 10 ton cm^{-2} had no effect on the structures.) The power at the samples was *ca.* 140 mW. X-Ray powder photographs were recorded with a Nonius–Guinier de Wolff II camera using Cu-K_α (154.18 pm) radiation and were calibrated using lead nitrate; the error in cell constants was ±1 pm. Differential-thermal and thermal-gravimetric analyses were obtained with Dupont 900 and 950 instruments respectively.

Preparation of $Pt_6Cl_{12} \cdot nA$ *Compounds.*—All the compounds (A = Br_2, C_6H_6, CS_2, $CHCl_3$, CH_2Cl_2, $n = 1$; A = CCl_4, $n = 0.75$) were prepared by the same method. A suspension of β-$PtCl_2$ (*ca.* 0.5 g) (Heraeus GMBH, Hanau) in analytically pure reagent grade A (*ca.* 50 cm^3) (E. Merck, Darmstadt) was stirred for *ca.* 48 h or better heated under reflux for 5 h. The solid *product* (100%) was collected and dried at the pump. Analyses are given in Table 2.

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[5/260 *Received*, 10*th February*, 1975]

[10] B. Spreckelmeyer and H. G. von Schnering, *Z. anorg. Chem.*, 1971, **386**, 27.