Dicarbonyltetrahalogenoplatinate(I) Salts

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The complex anions $[Pt_2X_4(CO)_2]^{2-}$ (X = Cl or Br) are formed in solution by the reaction of CO with $[PtX_4]^{2-}$ ions in concentrated aqueous HX. Their tetra-n-propylammonium salts have been isolated. Vibrational spectra indicate that the structure of the anions consists of two planar $[PtX_2CO]^-$ units linked by a platinum–platinum bond. Two forms of the salt $(Pr^n_4N)_2[Pt_2Cl_4(CO)_2]$ have been crystallised, both apparently containing anions with the same symmetry but having different vibrational frequencies, suggesting that the two PtX_2CO planes are rotated 45° with respect to each other. The Pt–Pt bond is cleaved by Cl_2, HCl, H_2, and MeHgCl.

CARBONYL derivatives of halogenoplatinum(II) complexes were the first metal carbonyl complexes to be characterised.[1] Booth *et al.*[2,3] showed that a polymeric complex $[Pt(CO)_2]_n$ was formed as a purple colloidal precipitate from the reaction of water with a benzene solution of the complex $[PtCl_2(CO)_2]$. Products variously described as red to black have been obtained from the reaction of CO with aqueous or dilute acid solutions of chloroplatinate(II) anions,[4-6] and, even where not proven, can be assumed to be the same complex.

During attempts to prepare the anion $[PtCl_3CO]^-$, by the action of CO on $K_2[PtCl_4]$ suspended in concentrated hydrochloric acid, we found that after all the red colour of the starting material had been discharged, isolation of the product as a tetra-n-propylammonium salt, resulted in a mixture of the salt $(Pr^n_4N)[PtCl_3CO]$ and another carbonyl species. Rachkovskaya *et al.*[7] have reported that they obtained the complex $[PtCO(HCl)_2]$ from oxidation of $[Pt(CO)_2]_5$ with iron(III) in aqueous hydrochloric acid and prepared a salt $(Et_4N)[PtCl(CO)(HCl)_2]$ from it. They considered the salts, however, to contain Pt–H bonds and presumably regard the complexes as octahedral carbonyltrichlorodihydridoplatinate(IV) anions. We have now isolated our other carbonyl species and its bromo-analogue and investigated their structures by vibrational spectroscopy. Preliminary experiments show that they undergo some very interesting reactions.

RESULTS

Preparation and Isolation.—When a suspension of the salt $K_2[PtCl_4]$ in concentrated hydrochloric acid was stirred with carbon monoxide at atmospheric pressure, it very slowly dissolved to give a pale yellow-green solution. If this solution was monitored in the CO stretching region by Raman spectroscopy, just after all trace of the pink-brown solid $K_2[PtCl_4]$ had disappeared, it showed a prominent polarised band at 2 115 cm^{-1}, together with two other much weaker bands, 2 076 (polarised) and 2 057 cm^{-1} (depolarised). Further treatment of this solution with carbon monoxide caused the weaker bands to grow in unison whilst the high-frequency band diminished. The species initially formed is clearly $[PtCl_3CO]^-$ by comparison with an authenticated sample containing this ion.[8] Consideration of the relative intensities of the carbonyl bands in Raman and i.r. spectra suggests $K_2[PtCl_4]$ can be 90% converted to the two-CO band species in 6 days. Reaction times were found to vary if the preparation was attempted in different locations and it became evident that daylight has an important influence on the rate of formation. An attempt at preparation in a room with only artificial light required 14 days for dissolution of $K_2[PtCl_4]$ and production of only *ca.* 10% of the desired product, compared to reaching the same stage in 3 days of winter daylight. A good indication that the required stage of reaction has been reached is that some of the purple complex $[Pt(CO)_2]_n$ begins to form as a precipitate. Use of $PtCl_2$ instead of $K_2[PtCl_4]$ achieves the same result in the same time.

The $[Pt_2Cl_4(CO)_2]^{2-}$ ions are best extracted from hydrochloric acid solution by addition of tetra-n-propylammonium chloride in dichloromethane, most of the colour passing into the non-aqueous phase. The i.r. spectrum in the CO stretching region showed two bands, 2 070 and 2 096 cm^{-1}, which, since they differed in relative intensity for different preparations, cannot be due to the two-CO band species in the aqueous solution. However, after working up the dichloromethane solution, heating the residue for *ca.* 20 min at 60 °C under vacuum, and then washing with acetone, a very bright yellow solid remained, the vibrational spectra of which clearly showed it to correspond to the two-CO band complex produced in the aqueous medium.

Chemical analysis showed the complex to be empirically $(Pr^n_4N)[PtCl_2CO]$. Attempts to find a high-field hydride resonance in the n.m.r. spectrum of the original aqueous solution or a dichloromethane solution of the final product were unsuccessful. The equivalent conductivity of the salt in nitrobenzene at 21 °C is 21·7 Ω^{-1} cm^{-1} which shows it to be an electrolyte but does not give any real insight into the degree of polymerisation of the anion. The presence of two carbonyl stretching vibrations, however, shows that it must be at least dimeric. Titration of the salt with a standard solution of $(Pr^n_4N)[PtI_5(PMe_3)]$, an extremely dark coloured complex which is reduced to the ion $[PtI_3(PMe_3)]^-$ of much

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[1] P. Schutzenberger, *Ann. Chem. Phys.*, 1868, **15**, 100.

[2] G. Booth, J. Chatt, and P. Chini, *Chem. Comm.*, 1965, 639.

[3] G. Booth and J. Chatt, *J. Chem. Soc.* (*A*), 1969, 2131.

[4] I. Sano, *Chem. Abs.*, 1935, **29**, 66; 1940, **34**, 4640.

[5] L. A. Gribov, A. D. Gel'man, F. A. Zakharova, and M. M. Orlova, *Russ. J. Inorg. Chem.*, 1960, **5**, 473.

[6] I. I. Matveev, L. N. Rachovskaya, and N. K. Eremenko, *Izv. sibirsk. Otdel. Akad. Nauk, Ser. khim. Nauk*, 1968, **2**, 81.

[7] L. N. Rachkovskaya, N. E. Eremenko, and K. I. Matveev, *Doklady Phys. Chem.*, 1970, **190**, 174.

[8] M. G. Norton, Ph.D. Thesis, Bristol University, 1968.

paler colour,[9,10] is in agreement with the formulation as a platinum(I) species (equivalent weight: found 474; calc. 480).

The $[Pt_2Cl_4(CO)_2]^{2-}$ complex is readily soluble in dichloromethane and nitromethane, but only sparingly so in acetone or nitrobenzene. It is stable in these solvents at room temperature but decomposes at elevated temperatures. It is insoluble in ether or carbon tetrachloride. It is instantly decomposed by water giving a black precipitate, but seems indefinitely stable, even in damp air, if it is pure.

Attempts were made to prepare the corresponding bromo-complex by an analogous method, starting from $PtBr_2$ in concentrated hydrobromic acid. After 2 weeks of stirring with carbon monoxide, relative to $[PtBr_3CO]^-$, only some 7% of $[Pt_2Br_4(CO)_2]^{2-}$ had been produced; prolonged reaction over a further 4 weeks did not materially alter this ratio which seems to represent equilibrium under these conditions. The reaction of concentrated HBr and $PtBr_2$ with CO at 100 atm for 2 days gave enhancement of the ion $[Pt_2Br_4(CO)_2]^{2-}$ relative to $[PtBr_3CO]^-$ (ratio *ca.* 1 : 3) but a considerable amount of the complex $[Pt(CO)_2]_n$ was also formed. The same extraction procedure was used as for the chloro-complex and again the i.r. spectrum of the initial dichloromethane solution showed species differing from those in the aqueous solution. Reversion to the ion $[Pt_2Br_4(CO)_2]^{2-}$ on removal of the solvent occurs less readily than for the chloro-complex and it seems necessary to go through several cycles of solution in dichloromethane, evaporation under vacuum, and heating of the solid to reproduce the required product to the full extent. Prolonged heating of the residue alone at 100 °C under vacuum has little effect. The final product is quite soluble in nitromethane, slightly soluble in acetone, but only very sparingly so in dichloromethane. Surprisingly, it seems to be very much more soluble in all these solvents in the presence of the salt $(Pr^n_4N)[PtBr_3CO]$, a property which makes the extraction of the complex exceedingly tedious if it is not a substantial proportion of the crude reaction mixture.

Structure.—Vibrational spectra of various samples containing the $[Pt_2X_4(CO)_2]^{2-}$ anions as solids and in solution are documented in the Table and some of their aspects shown in the Figure. I.r. and Raman spectra of the solids and solutions all showed two very strong bands, within the range 2 007—2 076 cm^{-1}, separated by up to 20 cm^{-1} and coincident between the two techniques; Raman spectra of solutions showed the higher-frequency band to be polarised and the lower depolarised. Thus the complex must be at least dimeric. For the solid platinum(0) carbonyl complex $[Pt(CO)_2]_n$ there are CO stretching bands at 2 068 and 1 891 cm^{-1}, certainly relating to terminal and bridging groups respectively.[2] In the ion $[PtX_3CO]^-$, the CO bands in dichloromethane solution are at 2 098, 2 090, and 2 078 cm^{-1} for chloro-, bromo-, and iodo-complexes respectively.[8] Since CO stretching frequencies tend to be higher in complexes (i) of higher oxidation state, (ii) of less-negative overall charge, and (iii) with a larger number of carbonyl groups on a metal atom, our wavenumbers are clearly indicative of terminally bound carbon monoxide. It is also most improbable that we have two CO groups bound to a single platinum atom.

In the low-frequency region of the Raman spectra of the chloro-complex, by far the most intense band is at *ca.* 170 cm^{-1}, is polarised (ρ = 0·25), and is some 35 cm^{-1} lower

Vibrational spectra (2 100—1 960 and below 600 cm^{-1}) of the salts $(Pr^n_4N)_2[Pt_2X_4(CO)_2]$ (X = Cl or Br)

	$(Pr^n_4N)_2[Pt_2Cl_4(CO)_2]$									$(Pr^n_4N)_2[Pt_2Br_4(CO)_2]$		
Assignment	I.r. (mull) (A)	Raman (solid) (A)	I.r. (mull) (B)	Raman (solid) (B)	I.r. (mull) (C)	Raman (solid) (C)	I.r. (CH_2Cl_2)	Raman ($MeNO_2$)	Raman [HCl(aq)] (D)	I.r. (mull)	Raman (solid)	Raman (solution)
$(CO)_2$ str. (sym)	2 046vs	2 044vs	2 046vs	2 042vs	2 035vs	2 034vs	2 047vs	[a]	2 076s,p	2 028vs	2 027vs	2 066 [b]
$(CO)_2$ str. (asym)	2 030vs	2 032s	2 031vs	2 031s	2 018vs	2 018vs	2 027vs	[a]	2 057ms,dp	2 010vs	2 009vs	2 049 [b]
Other CO region bands	2 011m,bd,sh 1 993w 1 985w		2 012wm,bd,sh 1 993w 1 985w		2 010sh 1 977w	2 009wm				1 971w		
$(PtC)_2$ str. (sym)		529s		519s		528s		523s,p	520s,p	516sh	517s	514s,p [c]
PtCO bend or $(PtC)_2$ str. (asym)	554ms 515vs 510sh	547s 514m	554ms 515vs 510sh	551ms 510sh	$\left.\begin{matrix}543\\541\end{matrix}\right\}$m 514vs 512sh	541s 514m	543m 512vs	542s,p	533s,p	538m 503vs	537ms 502wm	536ms,p [c]
$(PtX)_2$ (*trans* to CO) str. (sym)	*315*m,sh	*319*s	*315*m,sh	*316*m	*324*ms	*325*m	*318*sh	*318*m,bd,p	*317*m,p	*220*wm,sh		
$(PtX)_2$ (*trans* to CO) str. (asym)	*310*s *306*m,sh	*313*sh [d]	*310*s *305*m,sh	*309*sh [d]	*315*s *310*sh	*308*w,bd [d]	*313*s			*214*m		
$(PtX)_2$ (*trans* to Pt) (sym)	*269*w	*268*s	*269*w	*270*s	*274*wm	*275* s	[a]	*272*s,p	*268*s,p		*220* ms	*218*m,p [c]
$(PtX)_2$ (*trans* to Pt) (asym)	*240*vs		*240*vs		*243*vs	*243*vw	*241*vs			*172* s	*ca.* *168*sh	
Pt–Pt str.	171vw	170vvs	171vw	171vvs	176vw	178vvs		173vvs,p	173vvs,p	135vvw	135vvs	135vvs,p [c]
Deformation and lattice modes	140sh 116wm 85w	126s,bd	141vw,sh 131vw,sh 115m 82w	122s,bd 83sh	122m	157s 136s 119ms 101sh *ca.* 80sh			*ca.* 100bd	97w 67vw	84vs	
Cation and other bands	360vvw	340w,bd 313sh [d]	361vvw	375vvw 335vw 309sh [d]	361vvw 345vvw	375vvw 340vvw,sh 308w,bd [d]				362vvw	342wm 314wm	
Limit of study	(40)	(100)	(40)	(70)	(40)	(60)	(200)	(130)	(80)	(40)	(50)	(110)

(A), Product from evaporation of CH_2Cl_2 extract; (B), product from acetone recrystallisation; (C), product from nitromethane recrystallisation; and (D), HCl (aq) reaction mixture prior to extraction (also showed 2 115m,p and 341m,p from $[PtCl_3CO]^-$). M–X modes are indicated in italics.

[a] Not investigated or obscured by solvent. [b] As component of mixture in HBr (aq) formed in the preparation. [c] In $MeNO_2$. [d] Alternative assignments.

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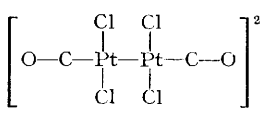
[9] D. A. Duddell, P. L. Goggin, R. J. Goodfellow, M. G. Norton, and J. G. Smith, *J. Chem. Soc.* (*A*), 1970, 545.

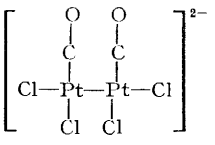
[10] P. L. Goggin, R. J. Goodfellow, S. R. Haddock, J. R. Knight, F. J. S. Reed, and B. F. Taylor, *J.C.S. Dalton*, to be published; F. J. S. Reed, Ph.D. Thesis, Bristol University, 1972.

in the bromo-complex. In the very large number of platinum-(II) and -(IV) chloro-complexes that we have studied we have noticed no case in which skeletal deformations in this region are so much more intense than the most intense Pt–Cl stretching vibrations or have such a low depolarisation ratio.[9,10] Metal–metal bond stretching vibrations generally have a characteristically high Raman intensity,[11] and the wavenumbers of our very intense bands are practically the same as those in the corresponding mercury(I) halides (Hg_2Cl_2 169 cm^{-1}, Hg_2Br_2 136 cm^{-1}).[12] The most probable structure of the $[Pt_2X_4(CO)_2]^{2-}$ ions, therefore, seems to be a dimer with a Pt–Pt bond in which each platinum atom carries 16 valence electrons and would be expected to display square-planar geometry. There are three basic isomeric possibilities (I)—(III) and, for each, there is also the question of the relative orientation of the two planes. The carbonyl stretching vibrations of structure (I) should be essentially mutually exclusive between the Raman and i.r. spectra, regardless of the orientation of the planes, which does not fit the spectra of our complexes. The linear unit, Cl–Pt–Pt–Cl, of structure (II) resembles Hg_2Cl_2 which has Hg–Cl stretching bands at 279 (sym) and 250 cm^{-1} (asym) [12] and thus agrees well with the character of the Pt–Cl stretching bands at about 270 and 240 cm^{-1} in the complex $[Pt_2Cl_4(CO)_2]^{2-}$. For structure (III), the most acceptable assignment of these bands would be as the symmetric stretch of the linear $PtCl_2$ unit and the Pt–Cl (*trans* to Pt) stretch respectively. However, the former is some 50 cm^{-1} lower than the equivalent vibration [13] in the ion $[PtCl_3CO]^-$ which seems excessive for a unit reduction of oxidation state and the Pt–Cl (*trans* to Pt) stretch would be expected to be active in the Raman effect. As structure (III) is also chemically unsatisfactory in having CO in two different environments, one *trans* to a metal–metal bond, we will not consider it further. The coplanar, *trans*-form of structure (II) can be excluded as it is centrosymmetric, but any other orientation of the planes would fit the spectra. Compared to the coplanar arrangement, an angle of 90° between the planes would minimise the repulsions between groups on adjacent platinum atoms, whilst an angle of 45° would position the filled interaxial *d* orbitals as remote from each other as possible, so minimising any antibonding interaction between them. The 45° arrangement has two forms, *cisoid* where the dihedral angle between CO groups is 45° and *transoid* where it is 135°. As we obtain two crystalline forms of the chloro-complex which, from their spectra, are of the same basic type but differ more in the frequency of the bands than would be expected for merely different crystal arrangements of the same molecule, we favour the 45° forms. As the symmetry of all these forms is C_2 or C_{2v}, the assignments that follow are not affected by this choice.



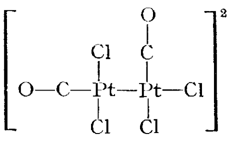
$$\left[\mathrm{O{-}C{-}Pt(Cl)_2{-}Pt(Cl)_2{-}C{-}O}\right]^{2-}$$

(I)



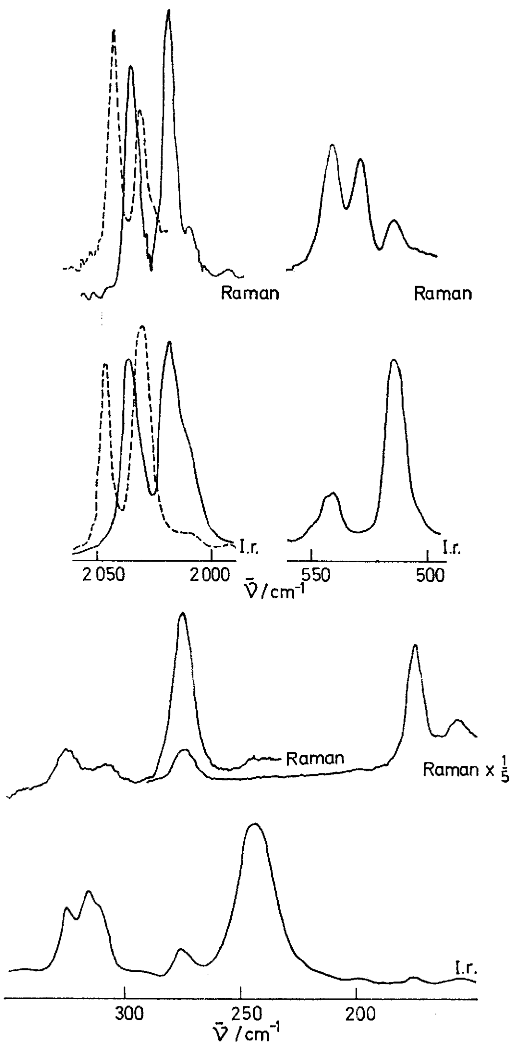
$$\left[\mathrm{Cl{-}Pt(CO)(Cl){-}Pt(CO)(Cl){-}Cl}\right]^{2-}$$

(II)



$$\left[\mathrm{O{-}C{-}Pt(Cl)_2{-}Pt(CO)(Cl){-}Cl}\right]^{2-}$$

(III)



I.r. (absorbance) and Raman spectra of the salt $(Pr^n{}_4N)_2[Pt_2Cl_4(CO)_2]$, as recrystallised from nitromethane. (— — —), CO stretching region of form obtained from acetone solution

For the chloro-complex, the vibrational spectra of the form from nitromethane [(C) in the Table] are less complicated by solid-state effects and assignments will be based on this. The higher-frequency Pt–Cl stretching bands not so far assigned must relate to Pt–Cl (*trans* to CO) modes. The Pt–C stretching and Pt–CO bending vibrations may be expected in the region of 500 cm^{-1} and for a structure of C_2 symmetry there are six such modes. Only three features are seen both in the i.r. and the Raman spectrum, not necessarily coincident between the two. Pt–C Stretching bands are generally more intense in Raman spectra than are

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[11] T. Spiro, *Progr. Inorg. Chem.*, 1970, **11**, 1.

[12] J. R. Durig, K. K. Lau, G. Nagarajan, M. Walker, and J. Bragin, *J. Chem. Phys.*, 1969, **50**, 2130.

[13] R. J. Goodfellow, P. L. Goggin, and D. A. Duddell, *J. Chem. Soc.* (*A*), 1968, 504.

Pt–CO bending bands and the reverse is frequently true of i.r. spectra. Accordingly the 519 cm^{-1} Raman feature is probably the symmetric Pt–C stretch, but the intense i.r. band at similar wavenumber probably relates to Pt–CO bending. In solution, the Raman band at 542 cm^{-1} is polarised as well as the Pt–C stretching band at 523 cm^{-1} and is thus probably the totally symmetric in-plane Pt–CO bending vibration. This may particularly gain Raman intensity from coupling with the Pt–Pt stretch because the motion is in the same direction as the metal–metal bond whereas the symmetric Pt–C and –CO stretching motions are perpendicular to it.

Spectra of the form recrystallised from acetone (B) may be assigned by analogy to the other form. We assume that the presence of three Pt–Cl (*trans* to CO) stretching features in the i.r. spectrum arises from solid-state effects. It is worth noting that the Raman spectrum of the CO region shows the lower-frequency band to be significantly less intense than the higher-frequency band, whereas in form (C) they are practically of the same intensity. In the i.r. spectrum, the integrated intensities suggest that the low-frequency band is greater relative to the high-frequency band in the sample (B) than in (C). These observations tentatively suggest that the form (B) has the *transoid*-structure.

The product initially obtained in the preparation gives spectra which do not completely correspond to those of either of the recrystallised forms but most closely resemble those of the complex from acetone solution. The spectra, in the CO stretching region, of solutions of either form, only show two strong bands which are the same for either form but differ in frequency between solvents. They seem to be consistent with either a freely rotating model or with the presence of a single structure in any particular solvent, but if the latter is the case we do not have any means of deciding what the structure is.

The spectra of the bromo-complex $[Pt_2Br_4(CO)_2]^{2-}$ can also be interpreted on the same basis but the products obtained from acetone and from nitromethane recrystallisation were identical. The relative intensities of the bands in the CO stretching region suggest that the complex corresponds structurally to form (C) of the chloro-complex.

Reactions.—As mentioned above, the initial extract in dichloromethane shows two CO stretching bands which cannot be ascribed to the species in the original acidic aqueous solution but on working-up the salt $(Pr^n{}_4N)_2[Pt_2Cl_4(CO)_2]$ is regenerated. One of the species in this initial dichloromethane extract had ν(CO) 2 096 cm^{-1} which corresponds to the salt $(Pr^n{}_4N)[PtCl_3CO]$ in this solvent.[8] When the aqueous solution before extraction was essentially free of $(Pr^n{}_4N)[PtCl_3CO]$, then the relative intensity of the i.r. band at 2 096 cm^{-1} was approximately equal to that of the band at 2 070 cm^{-1} due to the other complex present. The same spectrum was generated from the salt $(Pr^n{}_4N)_2[Pt_2Cl_4(CO)_2]$ in dichloromethane solution immediately on treatment with gaseous hydrogen chloride. The ^1H n.m.r. spectrum of this solution showed a hydride resonance which was broad at ambient magnet temperature but sharp at 240 K (τ 25·12, J_{PtH} 1 273 Hz). Re-examination of the i.r. spectrum showed an additional weak feature at 2 208 cm^{-1} in the region of other Pt–H stretching vibrations (*e.g.*, ref. 14). We propose that this species is *cis*-$[PtCl_2(H)CO]^-$ formed by the addition of HCl across the Pt–Pt bond [equation (1)]. Evaporation of this solution in the air at

$$[COCl_2Pt\text{–}PtCl_2CO]^{2-} + HCl \longrightarrow [COCl_2PtH]^- + [PtCl_3CO]^- \quad (1)$$

room temperature followed by re-examination of a dichloromethane solution of the product showed a largely unchanged spectrum with weak additional absorptions due to the ion $[Pt_2Cl_4(CO)_2]^{2-}$. Removal of the solvent *in vacuo* and pumping of the solid residue regenerates the platinum(I) anion. We conclude that the HCl in the initial reaction mixture does not cleave the Pt–Pt bond because it is present as $H_3O^+Cl^-$, but that it is extracted into dichloromethane as undissociated hydrogen chloride which does.

The salt $(Pr^n{}_4N)_2[Pt_2Cl_4(CO)_2]$ does not undergo a rapid reaction with hydrogen at atmospheric pressure, but treatment of a dichloromethane solution of it with hydrogen at 100 atm produced a solution which, after filtration, was shown by its i.r. spectrum to contain $[PtCl_2(H)CO]^-$ as the sole platinum carbonyl complex. Not surprisingly, chlorine effects a similar oxidative addition to the metal–metal bond to give solely the ion $[PtCl_3CO]^-$. The ion $[Pt_2Cl_4(CO)_2]^{2-}$ also reacts immediately with chloro(methyl)mercury(II), the i.r. spectrum showing two bands, 2 061 and 2 028 cm^{-1}, of comparable intensity and the ^1H n.m.r. spectrum, a methyl resonance (τ 9·0; $^2J_{PtH}$ 78·6 Hz). The i.r. wavenumbers suggest that the higher one is due to the ion $[PtCl_2(Me)CO]^-$ and the lower to $[PtCl_2CO(HgCl)]^-$, The solution slowly decomposes at room temperature, depositing mercury. Decomposition is complete in 1 day, the i.r. spectrum of the final solution indicating that the complex assigned as $[PtCl_2CO(HgCl)]^-$ has disappeared to be replaced by $[PtCl_3CO]^-$. These preliminary observations suggest that the dicarbonyltetrahalogenoplatinum(I) anions will participate in a variety of interesting reactions which may also lead to novel platinum(II) species.

DISCUSSION

There seems to be only one platinum(I) complex previously reported,[15] $[Pt_2Cl_2\{(Ph_2P)_2CH_2\}_2]$. Thus the complexes reported here represent a significant contribution to the chemistry of platinum. If our structural deductions are correct they also provide an example of a rare form of isomerism. We have previously argued that interaction between filled *s* orbitals on metal atoms and lone-pairs of electrons on ligands may play a significant role in affecting metal–ligand bond strengths and determining geometries in complexes and the evidence here lends support to such ideas.[16]

The i.r. bands reported by Rachkovskaya *et al.*[7] for their various complexes can all be accounted for as mixtures of $[PtCl_3CO]^-$, $[Pt_2Cl_4(CO)_2]^{2-}$, and $[PtCl_2(H)CO]$ in the various solvents. In particular, for the 'monocarbonyl' in aqueous hydrochloric acid, the bands assigned as ν(PtH) correspond to the carbonyl stretching vibrations of the ion $[Pt_2Cl_4(CO)_2]^{2-}$, whilst the carbonyl band agrees with that of $[PtCl_3CO]^-$. Hence, their

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[14] P. W. Atkins, J. C. Green, and M. L. H. Green, *J. Chem. Soc.* (*A*), 1968, 2275.

[15] F. Glockling and R. J. I. Pollock, *J.C.S. Chem. Comm.*, 1972, 467.

[16] P. L. Goggin, R. J. Goodfellow, and F. J. S. Reed, *J. Chem. Soc.* (*A*), 1971, 2031.

formulations are unlikely to be correct. Our results shed some light on some other related reports in the literature. During our studies on the salt $(Pr^n_4N)[PtCl_3CO]$, it became clear that we could not reconcile our Raman spectrum with that reported by Denning and Ware[17] in a detailed account of the vibrational spectra of the ion $[PtCl_3CO]^-$. Their measurements were made on a solution prepared from $[PtCl_2(CO)_2]$ and 5N-hydrochloric acid and the bands, which have no counterpart in our authenticated complex, correspond to those reported here for the ion $[Pt_2Cl_4(CO)_2]^{2-}$. The complex $[PtCl_2(CO)_2]$ is known to react with water to give $[Pt(CO)_2]_n$ and evidently is also partially reduced by fairly concentrated acids, and may be the basis of the preparation we report here. Some other papers on the ion $[PtX_3CO]^-$ also include extra features in the CO stretching region which may arise from the presence of reduced species (*e.g.*, ref. 18).

Kingston and Scollary[19] reported the characterisation of the salt $(AsPh_4)[PdCl_2(H)CO]$, mainly basing their claim on the observation of a strong 'terminal CO' stretching band at 1 900 cm^{-1} and a weaker 'PdH' stretching band at 1 960 cm^{-1}. We do not regard these assignments as sensible in view of the CO band at 2 132 cm^{-1} in the ion $[PdCl_3CO]^-$, somewhat higher than in the platinum analogue.[8] The CO and Pt–H bands in the ion $[PtCl_2(H)CO]^-$ make it clear that their formulation cannot be correct.

EXPERIMENTAL

Preparations.—Bis(tetra-n-propylammonium) dicarbonyltetrachlorodiplatinate(I), $(Pr^n_4N)_2[Pt_2Cl_4(CO)_2]$. $PtCl_2$ (2·5 g) and conc. HCl (15 cm^3) in a 3 l flask were stirred in an atmosphere of carbon monoxide for 6 days at room temperature in a position accessible to daylight. In this time virtually all the $PtCl_2$ dissolved (3 days), the solution turned pale greenish yellow, and some purple $[Pt(CO)_2]_n$ had started to form (5 days). The solution was filtered and shaken with Pr^n_4NCl (3 g) in dichloromethane (40 cm^3). Most of the colour extracted into the organic phase which was separated and a second extraction was performed with dichloromethane (30 cm^3). The extracts were combined and dried over $MgSO_4$ and, after filtration, the solution was evaporated on a rotary evaporator at room temperature and the residue heated (20 min) at 60 °C. After cooling, it was washed thoroughly with 3 aliquot portions (5 cm^3) of acetone, rinsed with ether, and dried at 80 °C in an oven, leaving a bright yellow *solid* (0·5 g, 78% yield), m.p. 188 °C (decomp.) (Found: C, 32·55; H, 5·8; Cl, 15·0; N, 2·9. Calc. for $C_{26}H_{56}Cl_4N_2O_2Pt_2$: C, 32·5; H, 5·9; Cl, 14·75; N, 2·9%). Products of the same elemental composition were obtained by recrystallisation from acetone [yellow needles, m.p. 191—193 °C (decomp.)] and from nitromethane [yellow blocks, m.p. 202—204 °C (decomp.)].

Bis(tetra-n-propylammonium) tetrabromodicarbonyldiplatinate(I), $(Pr^n_4N)_2[Pt_2Br_4(CO)_2]$. $PtBr_2$ (3 g) was dissolved overnight in conc. HBr (15 cm^3). The filtered solution was treated with CO (100 atm) for 2 days. The resulting solution was filtered free from the complex $[Pt(CO)_2]_n$ and shaken with Pr^n_4NBr (3 g) in CH_2Cl_2 (40 cm^3). The organic (less-dense) phase was separated off and dried over dry $MgSO_4$. The solvent was removed on a rotary evaporator and the residue heated slowly to 100 °C. More CH_2Cl_2 (50 cm^3) was added and the evaporation repeated and followed by two further cycles of the same treatment. The residue was washed with four successive aliquot portions (5 cm^3) of CH_2Cl_2, and dried at 80 °C, leaving only the required complex as a canary-yellow solid. It was recrystallised from nitromethane (yield 0·53 g, 11%). The complex turns black above 205 °C and melts with rapid decomposition at 240—245 °C (Found: C, 27·5; H, 4·95; Br, 28·0; N, 2·45. Calc. for $C_{26}H_{56}Br_4N_2O_2Pt_2$: C, 27·55; H, 4·95; Br, 28·05; N, 2·45%).

I.r., Raman, and ^1H n.m.r. spectra were recorded as outlined previously,[10] except that, to reduce decomposition in the laser beam, the Raman spectra in nitromethane were recorded with samples spinning at *ca.* 30 Hz.

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