364. *The Chemistry of the Transition Elements. Part I. Dimeric Carbonyl Complexes of Platinum.*

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Physical and chemical evidence for the assignment of the " trans-symmetrical " structure of the compounds $[Pt(CO)Cl_2]_2$, $[Pt(CO)Br_2]_2$, and $[Pt(CO)I_2]_2$ is presented.

The reaction of neutral ligands with these compounds leads to derivatives of the types : (i) $Pt(CO)Hal_2L$, where Hal = Cl, Br, or I, and L = a monodentate donor group; and (ii) $[Pt(CO)HalLL]^+[Pt(CO)Hal_3]^-$, where LL = a bidentate donor group.

THE reaction between platinum, carbon monoxide, and chlorine was discovered by Schutzenberger [1] who isolated the compounds $Pt(CO)Cl_2$, $Pt(CO)_2Cl_2$, and $Pt_2(CO)_3Cl_4$. This and later work on platinum carbonyl compounds has been summarized by Sidgwick.[2]

For some time past the compound whose empirical formula is $Pt(CO)Cl_2$ has been assumed to be dimeric, and Chatt and Williams [3] have pointed to the similarity of properties of this compound and certain " trans-symmetrical " platinum(II)–phosphorus trifluoride, –(tertiary phosphine), and –(tertiary arsine) complexes.

Of the three compounds, $Pt(CO)Cl_2$, $Pt(CO)Br_2$, and $Pt(CO)I_2$, the bromide is the only one suitable for molecular-weight determination and even this, owing to its instability and the fact that its saturated solution in benzene at 25° is only 0·035M, gives rather unreliable results. However, the value obtained (750 ± 50) shows that the molecule is definitely dimeric. The analogous physical and chemical properties of the compounds indicate that the chloride and iodide are also dimeric, the general formula being $[Pt(CO)Hal_2]_2$.

Metal carbonyls give rise to sharp absorption bands in the region 2000—2100 cm.$^{-1}$ of the infrared spectrum.[4] Absorption in this region has been shown to indicate terminal carbon monoxide ligands, while a bridging carbonyl group, as in iron enneacarbonyl, absorbs at about 1820 cm.$^{-1}$. Absence of the latter frequency (see Table) shows that, in the dimeric platinum carbonyl halides, the carbonyl groups must be terminal. The structure must therefore be halogen-bridged.

Dilute benzene solutions of each of the metal carbonyl halides exhibited no dielectric loss in the 10 cm. region, showing definitely that the compounds are non-polar and therefore have the annexed " trans-symmetrical " structure. A full discussion of the chemical evidence for halogen-bridged structures has been given by Chatt.[5]

Reaction of the bridged compound with two mols. of neutral monodentate ligand should give the derivative $Pt(CO)Hal_2L$ * and with one mol. of neutral bidentate ligand the salt $[Pt(CO)HalLL]^+[Pt(CO)Hal_3]^-$.*

Infrared absorption peaks (cm.$^{-1}$) in the carbonyl region.

(1)	$[Pt(CO)Cl_2]_2$	2152	(7)	$PyH^+[Pt(CO)Cl_3]^-$	2106
(2)	$[Pt(CO)Br_2]_2$	2130	(8)	$PyH^+[Pt(CO)Br_3]^-$	2096
(3)	$[Pt(CO)I_2]_2$	2112	(9)	$PyH^+[Pt(CO)I_3]^-$	2076
(4)	$[Pt(CO)dipyCl]^+[Pt(CO)Cl_3]^-$				2145, 2102
(5)	$[Pt(CO)dipyBr]^+[Pt(CO)Br_3]^-$				2132, 2096
(6)	$]Pt(CO)dipyI]^+[Pt(CO)I_3]^-$				2115, 2072

In this way the compounds $Pt(CO)(MeAsPh_2)Hal_2$, $Pt(CO)tolI_2$ (tol = *p*-toluidine) and $[Pt(CO)dipyHal][Pt(CO)Hal_3]$ were prepared. The last compound is analogous to that which Chatt reported to be formed by the action of dipyridyl on $[Pt(PR_3)Cl_2]_2$. Addition

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* Where L and LL indicate monodentate and bidentate ligands respectively.

[1] Schutzenberger, *Compt. rend.*, 1870, **70**, 1134, 1287; *Bull. Soc. chim. France*, 1870, **14**, 97.
[2] Sidgwick, " The Chemical Elements and Their Compounds," Oxford Univ. Press, London, 1950, Vol. I, pp. 1627—8.
[3] Chatt and Williams, *J.*, 1951, 3061.
[4] Brimm, Lynch, and Sesny, *J. Amer. Chem. Soc.*, 1954, **76**, 3831.
[5] Chatt, *J.*, 1951, 652.

to the bridged carbonyl of more than two mols. of ligand causes expulsion of carbon monoxide and formation of the compound PtL$_2$Hal$_2$.

This excess-ligand reaction does not take place with *p*-toluidine. Further, the *p*-toluidine compound is the most stable of all those prepared. This may be due to the weak *trans*-effect of *p*-toluidine; the CO group is thus not rendered labile and so replacement by *p*-toluidine is not possible.

It should be noted that all the carbonyl compounds are unstable to heat and moisture. The stability of the *p*-toluidine compound is therefore only relative.

The absorption maxima of 2102 and 2106 cm.$^{-1}$ for compounds 4 and 7 of the Table are obviously due to C–O stretching frequencies of carbon monoxide in the identical anions. Similarly, the frequencies 2096 and 2072 cm.$^{-1}$ can be assigned to carbon monoxide in the anions of compounds 5 and 6. Additional evidence for the assignment of the carbonyl frequencies in compounds 1, 2, and 3 to terminal carbonyl groups is that the absorptions are in the same region as those due to the carbonyl groups in compounds 4—9 where they are certainly terminal.

EXPERIMENTAL

Dicarbonyldichloro-μμ'-dichlorodiplatinum(II).—This compound was obtained by methods similar to those employed by Mylius and Foerster.[6] Dry chlorine and dry carbon monoxide were passed over finely divided platinum at about 250°. The yellow sublimate which was slowly formed was dissolved in concentrated hydrochloric acid, and the compound recovered by evaporation under reduced pressure. Alternatively the sublimate was heated at 200° in a stream of dry carbon dioxide, and the compound recrystallized from dry benzene. The yield is considerably better by the second method, but by using the first one may be sure that no dichlorodicarbonylplatinum(II) is present. The compound melts at 192° (Found: Cl, 24·2. Calc. for C$_2$O$_2$Cl$_4$Pt$_2$: Cl, 24·1%).

Dicarbonyldibromo-μμ'-dibromodiplatinum(II).—The yellow sublimate obtained by the action of carbon monoxide and chlorine on heated platinum was dissolved in the minimum quantity of hydrobromic acid and evaporated to dryness on the water-bath.[6] The bromide was recrystallized from dry benzene. The compound melts at 182° (Found: Pt, 50·6. Calc. for C$_2$O$_2$Br$_4$Pt$_2$: Pt, 50·9%).

Dicarbonyldi-iodo-μμ'-di-iododiplatinum(II).—This compound was prepared in the same way as the preceding one, with hydriodic acid in place of hydrobromic acid.[6] The iodide, recrystallized from dry benzene, decomposed between 135° and 140° (Found: I, 53·4; Pt, 40·6. Calc. for C$_2$O$_2$I$_4$Pt$_2$: I, 53·2; Pt, 40·9%).

Methyldiphenylarsinecarbonyldichloroplatinum(II).—Methyldiphenylarsine (0·72 g.) in carbon tetrachloride (50 ml.) was added to dicarbonyldichloro-μμ'-dichlorodiplatinum(II) (0·87 g.) in benzene (100 ml.). The initial yellow solution became paler. Crystals of methyldiphenylarsinecarbonyldichloroplatinum(II) were obtained with some difficulty from the residue. The compound gives a non-conducting solution in nitrobenzene (Found: C, 34·0; H, 2·6; Pt, 33·8. Calc. for C$_{14}$H$_{13}$OAsCl$_2$Pt: C, 31·2; H, 2·4; Pt, 36·25%). The analytical figures indicate contamination with about 0·1 mole of the tertiary arsine per mole of the platinum complex. It proved impossible to purify the compound further without some reduction to metallic platinum. The carbonyl frequencies in the infrared spectra of several preparations of the compound were identical.

Methyldiphenylarsinecarbonyldibromoplatinum(II).—Methyldiphenylarsine (0·64 g.) in carbon tetrachloride (100 ml.) was added to dicarbonyldibromo-μμ'-dibromodiplatinum(II) (1·00 g.) in a mixture of benzene (50 ml.) and carbon tetrachloride (100 ml.). The orange solution changed to yellow when warmed on the water-bath. Yellow needles of *methyldiphenylarsinecarbonyldibromoplatinum*(II) slowly crystallized. The compound is non-conducting in nitrobenzene (Found: C, 26·8; H, 2·1; Pt, 31·2. C$_{14}$H$_{13}$OAsBr$_2$Pt requires C, 26·8; H, 2·1%; Pt, 31·1%).

Methyldiphenylarsinecarbonyldi-iodoplatinum(II).—Methyldiphenylarsine (0·26 g.) in benzene (50 ml.) was added to the dimeric iodide (0·54 g.) in benzene (100 ml.). On evaporation, the yellow solution became red and a red oil was obtained. This yielded brown crystals when kept in a dry sealed container in the refrigerator for several days. The *compound* gives a non-conducting solution in nitrobenzene (Found: C, 22·9; H, 1·4; Pt, 27·1. C$_{14}$H$_{13}$OAsI$_2$Pt requires C, 23·3; H, 1·8; Pt, 27·1%).

⁶ Mylius and Foerster, *Ber.*, 1891, **24**, 2424; Foerster, *ibid.*, p. 3751.

2 : 2' - *Dipyridylcarbonylchloroplatinum*(II)   *Carbonyltrichloroplatinate*(II).—2 : 2' - Dipyridyl (0·11 g.) in benzene (50 ml.) was added to the dimeric chloride (0·43 g.) in benzene (200 ml.). A yellow precipitate was formed immediately. This was washed several times with dry benzene. The *compound* is itself sensitive to moisture, and is very often contaminated with decomposition products of the starting materials which are very difficult to remove. The conductivity of 31·4 mhos in M/1000-nitrobenzene solution shows the existence of two ions in solution (Found : Pt, 53·0. $C_{12}H_8O_2N_2Cl_4Pt_2$ requires Pt, 52·5%).

2 : 2' - *Dipyridylcarbonylbromoplatinum*(II)   *Carbonyltribromoplatinate*(II).—2 : 2' - Dipyridyl (0·149 g.) in benzene (50 ml.) was added to the dimeric bromide (0·66 g.) in benzene (200 ml.). A yellow precipitate, formed immediately, was filtered off and washed with benzene. The *compound* is unstable to moisture. The conductivity of 31·6 r.o. in M/1000-nitrobenzene solution shows the existence of two ions in solution (Found : Pt, 42·0. $C_{12}H_8O_2N_2Br_4Pt_2$ requires Pt, 42·3%).

2 : 2' - *Dipyridylcarbonyliodoplatinum*(II)   *Carbonyltri-iodoplatinate*(II).—2 : 2' - Dipyridyl (0·032 g.) in benzene (50 ml.) was added to the dimeric iodide (0·20 g.) in benzene (100 ml.). A yellow precipitate of the compound was formed. It is much more stable than the chloro- and bromo-compounds and can be recrystallized from boiling acetone. The conductivity of 24·2 mhos in M/1000-nitrobenzene solution shows the existence of two ions in solution (Found : C, 13·8; H, 0·8; N, 2·6; Pt, 34·6. Calc. for $C_{12}H_8O_2N_2I_4Pt_2$: C, 12·0; H, 0·7; N, 2·5; Pt, 34·4%).

Pyridinium carbonyltrichloroplatinate(II).—This compound was prepared according to the method of Mylius and Foerster [6] (Found : Pt, 46·8. Calc. for $C_6H_6ONCl_3Pt$: Pt, 47·8%). The conductivity in M/1000-nitrobenzene solution was 32·4 r.o.

Pyridinium carbonyltribromoplatinate(II).—Solid dicarbonyldibromo-μμ'-dibromodiplatinum(II) (0·3 g.) was added to a solution of pyridinium bromide (0·25 g.) in dilute hydrobromic acid. The solution was slowly evaporated to smaller bulk on the water-bath, filtered, and allowed to crystallize. Yellow needles of *pyridinium carbonyltribromoplatinate*(II) were obtained and were recrystallized from dilute hydrobromic acid. The conductivity in M/1000-nitrobenzene solution was 31·6 mhos (Found : Pt, 36·95. $C_6H_6ONBr_3Pt$ requires Pt, 36·9%).

Pyridinium carbonyltri-iodoplatinate(II).—This compound was prepared as above, with pyridinium iodide in place of the bromide. Orange needles were formed on recrystallization from dilute hydriodic acid. The compound decomposes, on storage, to pyridinecarbonyldi-iodoplatinum(II). The conductivity in M/1000-nitrobenzene solution was 31·0 mhos (Found : Pt, 27·5. Calc. for $C_6H_6ONI_3Pt$: Pt, 29·15%).

p-*Toluidinecarbonyldi-iodoplatinum*(II).—p-Toluidine (0·226 g.) in benzene (50 ml.) was added to dicarbonyldi-iodo-μμ'-di-iodoplatinum(II) (1·00 g.) in benzene (40 ml.). The solution changed colour from red to yellow and, after evaporation, masses of yellow fibres gradually separated. The *compound* was diamagnetic and a non-conductor in nitrobenzene. It was stable in air for a long period and was only slowly decomposed by water (Found : Pt, 33·2; I, 43·55. $C_8H_9ONI_2Pt$ requires Pt, 33·4; I, 43·45%).

Molecular Weights.—Many attempts were made to obtain molecular weights by the usual methods applied to inorganic compounds, notably cryoscopic and ebullioscopic methods. Not even very approximate results were possible owing to the instability of the compound sat higher temperatures and the insolubility at low temperatures. The Rast method with camphene (m. p. 48°) seemed to be applicable, but, at the low concentration obtained, results were meaningless. A result was finally obtained by the " isothermic microdistillation " method of Niederl and his co-workers.[7] In this method the capillary tubes, sealed at one end, are placed horizontally, sealed in a larger tube, with the solution of known molar concentration opposing that of the unknown compound. Three tubes were prepared, the same compound being used in each case, 0·015M (on a molecular weight of 766·14 for the bromide). The reference compound (benzoic acid) was prepared in three tubes with concentrations, 0·01M, 0·015M, and 0·02M. Although it is possible to obtain a solution of the bromide of 0·035M concentration, it was necessary to use this weaker solution because of the tendency of the solution to decompose at the liquid–gas interfaces. The lengths of the solution in the tubes were then measured at intervals. They varied as follows :

Strength of known soln.	Original	Final
0·010M	33·1 mm.	30·05 mm.
0·015M	25·0 mm.	25·0 mm.
0·020M	33·5 mm.	35·0 mm.

It was estimated that this indicated a molecular weight for the compound of 750 ± 50.

[7] Niederl, Kasanof, Kisch, and Subba Rao, *Mikrochemie*, 1949, **34**, 132.

Infrared Spectra.—Spectra were measured on a double-beam single-pass instrument designed and built in this School. Compounds were placed between rock-salt plates in paraffin mulls. A sodium chloride prism was used, and the instrument was calibrated with a Polystyrene film.

Dielectric-loss Measurements.—The measurements were made on saturated benzene solutions of the three compounds by a method analogous to that described by Willis Jackson[8] in an apparatus made available by the University of Sydney. The Debye equation for dilute solutions of polar molecules is : [9]

$$\frac{\Delta \tan \delta}{c} = \text{Molar loss tangent} = \frac{\varepsilon_0 + 2}{\varepsilon_0} \cdot \frac{\Pi\, N_0 \mu^2}{6750\, kT} \cdot \frac{\omega\tau}{1 + \omega^2\tau^2}$$

It is apparent, from this equation, that the molar loss will be zero when μ, the dipole moment, is zero. The measurements on the three compounds $[Pt(CO)Hal_2]_2$ thus clearly indicate the molecules to be non-polar.

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[8] Willis Jackson, *Discuss. Faraday Soc.*, 1946, **42**, A, 91, and other papers in the same volume.
[9] Davies, *Quart. Rev.*, 1954, **8**, 253.