990. *Complexes of Acetylenes with Platinum*(II). *Part II.* Hydroxy- and Methoxy-alkylacetylenes.*

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Complexes of the types M[$PtCl_3$ac] and *trans*-[$PtCl_2$ac(amine)], where M = Na or K, and ac = a tertiary α-hydroxyalkyl- or α-methoxyalkyl-acetylene, are described. The stabilities of the complexes depend on the nature of the α-substituents of the acetylene.

The infrared spectra of the complexes show that the C⋮C stretching frequency of the acetylenes is reduced by some 200 cm.$^{-1}$ on complex formation, and that the O–H stretching frequency of the hydroxyacetylenes is similarly reduced by 110—140 cm.$^{-1}$. Evidence is presented for a structure in which the hydroxyacetylene is bonded to the platinum atom through its triple bond and also to the chlorine atoms through its hydroxyl groups. Dipole moments and pertinent features of the infrared and nuclear magnetic resonance spectra are recorded. Allyl alcohol complexes have analogous structures. The methoxyacetylenes form relatively unstable complexes having the methoxyl groups turned away from the platinum atom.

THE best-characterised co-ordination compounds containing olefinic hydrocarbons as ligands are those of platinum(II), first reported in 1827 by Zeise.[1] Their stability depends on the structure of the alkene; electronegative groups (*e.g.*, chloro, phenyl) lower the stability.[2] The corresponding complexes of alkynes have been reported recently,[3,4] and their stability similarly depends critically on the structure of the alkyne RC⋮CR′.[4] Nevertheless the dihydroxyacetylene HO·Me_2C·C⋮C·CMe_2·OH (ac), with electronegative hydroxyl groups attached to the α-carbon atoms, forms relatively stable complexes of the types K[$PtCl_3$ac], *cis*-[$PtCl_2(NH_3)$ac] and *trans*-[$PtCl_2$(amine)ac].[5,6] On finding that the dimethyl ether of this glycol forms similar complexes, and that the corresponding saturated glycol HO·Me_2C·CH_2·CH_2·CMe_2·OH, does not form a complex, Bukhovets [6] concluded that only the triple bond of the acetylene was involved in the formation of the complex.

Since the hydroxyacetylenes contain electronegative groups their complexes should be much less stable than those of the alkynes, yet they are sufficiently stable to suggest that the hydroxyl groups contribute in some direct way. To determine this we thereto have prepared a series of complexes of α-hydroxyalkylacetylenes and examined the effect of complex formation on the stretching frequencies and proton resonance of the hydroxyl group. Here we describe the preparation of complexes of hydroxyalkylacetylenes, and show (1) that the stability of the complex depends on the nature of the α-substituents, (2) that the triple bond is co-ordinated to the metal atom, and (3) that the hydroxyl groups are involved in intramolecular hydrogen bonding.[7]

The complexes are readily prepared by treatment of the hydroxyalkylacetylene (ac)

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* Part I, *J.*, 1961, 827.

[1] Zeise, *Pogg. Annalen*, 1827, **9**, 632.

[2] See, *e.g.*, (*a*) Anderson, *J.*, 1936, 1042; (*b*) Kharasch and Ashford, *J. Amer. Chem. Soc.*, 1936, **58**, 1733; (*c*) Joy and Orchin, *ibid.*, 1959, **81**, 310.

[3] Bukhovets and Pukhova, *Zhur. neorg. Khim.*, 1958, **3**, 1714.

[4] (*a*) Chatt, Duncanson, and Guy, *Chem. and Ind.*, 1959, 430; (*b*) Chatt, Guy, and Duncanson, *J.*, 1961, 827.

[5] Gel'man, Bukhovets, and Meilakh, *Compt. rend. Acad. Sci. U.R.S.S.*, 1945, **46**, 105; Bukhovets and Molodova, *Zhur. neorg. Khim.*, 1957, **2**, 776; 1958, **3**, 1540; Molodova, *ibid.*, 1958, **3**, 2472.

[6] Bukhovets, *Izvest. Sekt. Platiny drug. blagorod. Metal., Inst. obschchei neorg. Khim.*, 1955, **29**, 55.

[7] Cf. Chatt, Duncanson, and Guy, *Nature*, 1959, **184**, 526.

with aqueous potassium tetrachloroplatinate (method 1), potassium trichloro(ethylene)-platinate (Zeise's salt) in acetone (method 2), or ethanolic sodium tetrachloroplatinate (method 3).

$$K_2PtCl_4 + ac \longrightarrow K[PtCl_3ac] + KCl$$
$$K[PtCl_3(C_2H_4)] + ac \longrightarrow K[PtCl_3ac] + C_2H_4$$
$$Na_2PtCl_4 + ac \longrightarrow Na[PtCl_3ac] + NaCl$$

The choice between the methods is largely determined by the structure of the acetylene and its solubility in the solvents mentioned. Method (1) gives the pure complex most readily, but it is only suitable for hydroxyalkylacetylenes which are water-soluble. Method (2) is suitable for both aliphatic and alkylaryl hydroxyacetylenes, but it is sometimes difficult to remove traces of starting material from the product. Method (3) is of least value, as salts of the type $Na[PtCl_3ac]$ are less stable than the corresponding potassium salts, and some decompose during isolation.

Complexes of the type $K[PtCl_3ac]$ are soluble in water, acetone, and ethanol, and insoluble in ether, light petroleum, benzene, and chloroform. They are diamagnetic. The most stable ones form yellow crystals which can be kept in a desiccator without appreciable change for several months; they decompose more rapidly on exposure to air. The least stable complexes are brown solids which decompose in a few days or weeks.

Complexes of the type $K[PtCl_3ac]$ react with amines (am = *p*-toluidine, piperidine, or pyridine) to give mononuclear, diamagnetic complexes of the type *trans*-$[PtCl_2ac(am)]$:

$$K[PtCl_3ac] + am \longrightarrow \textit{trans}\text{-}[PtCl_2ac(am)] + KCl$$

These complexes form yellow crystals, soluble in the common organic solvents except light petroleum. The stable complexes (am = *p*-toluidine) may be kept unchanged for months in a desiccator, but the less stable ones (am = piperidine or pyridine) usually decompose in a few days or weeks. These uncharged complexes decompose more readily in hot solvents or on exposure to air, and are less stable, than the corresponding complexes of alkyne hydrocarbons.[4]

Unsuccessful attempts were made to prepare non-ionic bridged hydroxyalkylacetylene complexes of the type $[Pt_2Cl_4ac_2]$ analogous to the well-known bridged complex, $[Pt_2Cl_4(C_2H_4)_2]$, as follows: [2a,8]

$$[Pt_2Cl_4(C_2H_4)_2] + 2ac \longrightarrow [Pt_2Cl_4ac_2] + 2C_2H_4$$
$$2H[PtCl_3ac] \xrightarrow{\text{Heat}} [Pt_2Cl_4ac_2] + 2HCl$$

This is in marked contrast to the acetylenic hydrocarbons, ac', which form the bridged complexes directly. Most salts of the type $K[PtCl_3ac']$ are unstable in water, eliminating potassium chloride and forming the bridged complex.[4]

Complexes were obtained from: (*a*) aliphatic tertiary hydroxyacetylenes, *e.g.*, series A; (*b*) tertiary aryl-α-hydroxyalkylacetylene, *e.g.*, series B; and (*c*) methyl ethers of group (*a*), *e.g.*, series C. The complexes from the ethers are much less stable than those from the alcohols.

Only intractable decomposition products were obtained by reaction of: (*d*) acetylenes containing an α-CH·OH or α-CH·OMe group (*e.g.*, series D); (*e*) acetylenes containing an α-CPh_2·OH group (*e.g.*, series E); (*f*) conjugated hydroxyalkylacetylenes and their ethers, and those containing a C⋮CAr group (*e.g.*, series F); and (*g*) the ester G.

(1) Examples of acetylenes giving complexes:

Series A: $HO\cdot CMe_2\cdot C⋮C\cdot CMe_2\cdot OH$ $HO\cdot CMeEt\cdot C⋮C\cdot CMeEt\cdot OH$ $Bu^t\cdot C⋮C\cdot CMe_2\cdot OH$

Series B: $HO\cdot CMe_2\cdot C⋮C\cdot CMePh\cdot OH$ $Bu^t\cdot C⋮C\cdot CMePh\cdot OH$
meso- and racemic $HO\cdot CMePh\cdot C⋮C\cdot CMePh\cdot OH$

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[8] Chatt and Duncanson, *J.*, 1953, 2939.

Series C: $MeO{\cdot}CMe_2{\cdot}C{\vdots}C{\cdot}CMe_2{\cdot}OH$ $MeO{\cdot}CMe_2{\cdot}C{\vdots}C{\cdot}CMe_2{\cdot}OMe$

(2) Examples of acetylenes not giving complexes:

Series D: $HO{\cdot}CH_2{\cdot}C{\vdots}C{\cdot}CH_2{\cdot}OH$ $HO{\cdot}CHMe{\cdot}C{\vdots}C{\cdot}CH_2{\cdot}OH$ $HO{\cdot}CMe_2{\cdot}C{\vdots}C{\cdot}CH_2{\cdot}OH$
$HO{\cdot}CHMe{\cdot}C{\vdots}C{\cdot}CHMe{\cdot}OH$ $HO{\cdot}CMe_2{\cdot}C{\vdots}C{\cdot}CHMe{\cdot}OH$ $HO{\cdot}CMe_2{\cdot}C{\vdots}C{\cdot}CHPh{\cdot}OH$
$MeO{\cdot}CH_2{\cdot}C{\vdots}C{\cdot}CH_2{\cdot}OMe$ $MeO{\cdot}CHMe{\cdot}C{\vdots}C{\cdot}CHMe{\cdot}OMe$

Series E: $HO{\cdot}CMe_2{\cdot}C{\vdots}C{\cdot}CPh_2{\cdot}OH$ $HO{\cdot}CMePh{\cdot}C{\vdots}C{\cdot}CPh_2{\cdot}OH$ $HO{\cdot}CPh_2{\cdot}C{\vdots}C{\cdot}CPh_2{\cdot}OH$
$Bu^t{\cdot}C{\vdots}C{\cdot}CPh_2{\cdot}OH$

Series F: $HO{\cdot}CMe_2{\cdot}C{\vdots}CPh$ $HO{\cdot}CMe_2{\cdot}C{\vdots}C{\cdot}C{\vdots}C{\cdot}CMe_2{\cdot}OH$ $Ar{\cdot}C{\vdots}C{\cdot}Ar$
($Ar = o\text{-}HO{\cdot}C_6H_4$ or *o*- or *p*-$MeO{\cdot}C_6H_4$)

Ester G: $BzO{\cdot}CMe_2{\cdot}C{\vdots}C{\cdot}CMe_2{\cdot}OBz$

Factors Affecting the Stability of the Complexes.—The stabilities of complexes of the hydroxyalkylacetylenes depend greatly on the structure of the acetylene, $HO{\cdot}CR^1R^2{\cdot}C{\vdots}C{\cdot}CR^3R^4{\cdot}OH$. When the groups R are alkyl, stable complexes of the type $Na[PtCl_3ac]$ and $K[PtCl_3ac]$ are readily formed, but the introduction of even one hydrogen atom leads to unstable gums. The stabilising effect of alkyl groups has also been noted in complexes of alkyne hydrocarbons,[4] where it was shown that electronic effects are not of major importance in determining stability. Nevertheless, the relative stabilities of the complexes of the hydroxy- and methoxy-alkylacetylenes can be correlated, perhaps fortuitously, in terms of electronic effects.

As in the alkyne hydrocarbon series, the hydroxyalkylacetylenes seem to behave primarily as electron-donors, and substituents with a high positive inductive effect and an absence of conjugation favour the formation of stable complexes. Phenyl groups lower the stability of the complexes, as would be expected since the electron-withdrawing phenyl group should reduce the π-electron density and donor capacity of the triple bond. In partial compensation for this weakening, the hydroxyl groups are then bound more firmly to the chlorine atoms, as shown by the progressive lowering of the hydroxyl stretching frequency (Table 1) with increasing phenyl substitution. However, presence of two phenyl groups on the same carbon atom prevents stable complex formation. Hydroxyalkylacetylenes having the triple bond conjugated to a phenyl group or to a second triple bond give very unstable complexes which we have not been able to isolate as sodium or potassium salts, but which might possibly be isolated as salts of large organic cations.[3] Complexes of methoxyalkylacetylenes are considerably less stable than those of the corresponding hydroxyalkyl compounds because of the change in structure from type (III) to (IV) (see below) and, as in the hydroxyalkylacetylenes, the presence of hydrogen on the α-carbon atoms as, *e.g.*, in the last example of series D prevents the formation of stable complexes.

Structure of the Hydroxyalkylacetylene Complexes [in collaboration with L. A. DUNCANSON (i.r. spectra) and D. T. THOMPSON (n.m.r. spectra)].—In the di(hydroxyalkyl)acetylene complexes both the triple bond and the hydroxyl groups are involved in bonding, as shown by the infrared (i.r.) and nuclear magnetic resonance (n.m.r.) spectra. With the triple bond perpendicular to the plane of the platinous complex, as is the double bond in ethylene complexes,[9] two structures (I and II) which involve bonding of the hydroxyl groups to the octahedral (z) positions of the platinous complex, are possible, as is a third (III) with hydrogen bonding to the chlorine atoms.

The perpendicular arrangement of the multiple bond is favoured in platinous complexes of olefinic and acetylenic hydrocarbons by the type of bonding shown in ref. 8 where " back-donation " of electrons from the platinum atom into the antibonding π-orbitals of the olefin is assisted by $5d_{xz}6p_z$-hybridisation. Nevertheless, the perpendicular arrangement is easily perturbed by dissymmetry or steric requirement of the unsaturated

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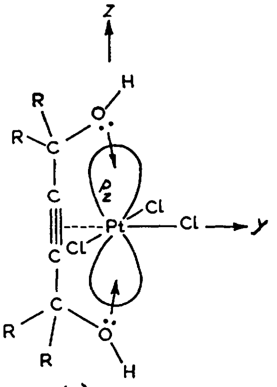
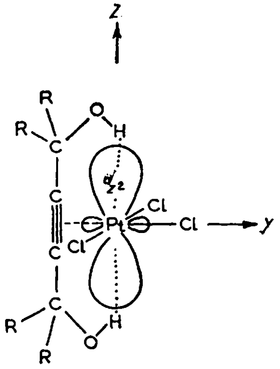
[9] Alderman, Owston, and Rowe, *Acta Cryst.*, 1960, **13**, 149, and references therein.

substance,[10] and it may be assumed that hydroxyalkylacetylene ligands will, where necessary, depart from the exactly perpendicular arrangement to produce a better fit to the remainder of the complex. This type of distortion is likely to be marked in the complexes of the monohydroxyalkylacetylenes.

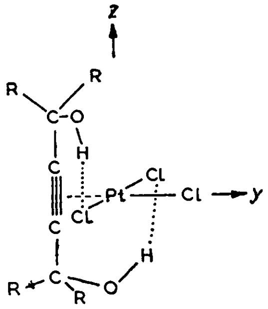
Another electronically possible structure, involving back-donation from the d_{xy}-orbital and having the di(hydroxyalkyl)acetylene in the plane of the complex with the hydroxyl groups hydrogen-bonded to the two chlorine atoms, is sterically impossible. Although we first favoured a structure of the type (I) or (II),[7,11] we are now convinced that structure (III) is correct and that the complexes of the monohydroxyalkylacetylenes have an analogous structure.



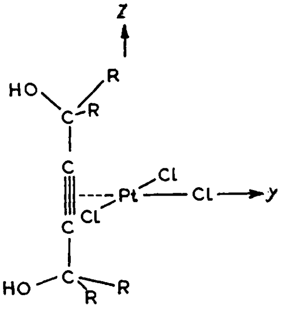
(I)



(II)



(III)



(IV)

The methyl ethers cannot form bonds as in (III), and dipole moments suggest that the methoxyl groups are not fixed, as in a structure such as (I; H = Me) but rather that they are free as in (IV; H = Me).

The above stuctures are suggested on the basis of the following evidence.

Co-ordination of the triple bond. Apart from Bukhovets's observation that the triple bond is essential for the formation of complexes, the infrared spectra gave evidence that the triple bond is attached to the metal.

The stretching frequency of the triple bond, $\nu(\mathrm{C}\vdots\mathrm{C})$, of disubstituted acetylenes occurs between 2190 and 2260 cm.$^{-1}$.[12] In complexes of the type K[PtCl$_3$ac] (ac = hydroxyalkylacetylene) there is usually a weak absorption in the region 1994—2010 cm.$^{-1}$; in complexes

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[10] Holden and Baenziger, *J. Amer. Chem. Soc.*, 1955, **77**, 4987.

[11] Chatt, Duncanson, and Guy, Proceedings of the Symposium on the Chemistry of Co-ordination Compounds, Agra, 1959, Part I, Nat. Acad. Sci. India, 1960, p. 118.

[12] See Bellamy, " The Infra-red Spectra of Complex Molecules," Methuen, London, 1958, p. 59.

TABLE 1.

Infrared bands (cm.$^{-1}$) of complexes of α-hydroxyalkylacetylenes and their methyl ethers with platinum(II).

Compound [a]	ν(C⋮C)	ν(OH)	ν(NH)	ν(CH) [b]
HO·CMe$_2$·C⋮C·CMe$_2$·OH (ac)	2248 [c] 2224	3612	—	—
K[PtCl$_3$ac]	2010	*d*	—	—
trans-[PtCl$_2$ac(py)]	2035	3500	—	—
trans-[PtCl$_2$ac(pip)]	2045	3502	3229	—
trans-[PtCl$_2$ac(*p*-tol)]	2030	3500	3324 3265	—
K[PtBr$_3$ac]	2015 2003	*d*	—	—
trans-[PtBr$_2$ac(py)]	2032	3497	—	—
trans-[PtBr$_2$ac(pip)]	2036	3504	3214	—
trans-[PtBr$_2$ac(*p*-tol)]	2024	3505	3319 3255	—
HO·CMe$_2$·C⋮C·CMe$_2$·OMe (ac)	*e*	3610	—	2822
K[PtCl$_3$ac]	2004	*d*	—	—
trans-[PtCl$_2$ac(py)]	2030	3494	—	2830
trans-[PtCl$_2$ac(pip)]	*f*	3495	3221	2826
trans-[PtCl$_2$ac(*p*-tol)]	2015	3500	3326 3259	2831
MeO·CMe$_2$·C⋮C·CMe$_2$·OMe (ac)	*e*	—	—	2824
K[PtCl$_3$ac]	1994	*d*	—	—
trans-[PtCl$_2$ac(py)]	2037	—	—	2830
trans-[PtCl$_2$ac(pip)]	2032	—	3216	2829
trans-[PtCl$_2$ac(*p*-tol)]	2035	—	3319 3250	2830
HO·CMeEt·C⋮C·CMeEt·OH (ac)	*e*	3615	—	—
K[PtCl$_3$ac]	2010	*d*	—	—
Na[PtCl$_3$ac]	2014	*d*	—	—
trans-[PtCl$_2$ac(py)]	2030	3491	—	—
trans-[PtCl$_2$ac(pip)]	*f*	3497	3227	—
trans-[PtCl$_2$ac(*p*-tol)]	2020	3501	3325 3260	—
HO·CMe$_2$·C⋮C·CMePh·OH (ac)	*e*	3606	—	—
K[PtCl$_3$ac]	2004	*d*	—	—
trans-[PtCl$_2$ac(pip)]	2026	3478	3224	—
meso-HO·CMePh·C⋮C·CMePh·OH (ac)	*e*	*h*	—	—
K[PtCl$_3$ac]	*e*	*d*	—	—
trans-[PtCl$_2$ac(pip)]	*e*	3462	3226	—
racemic HO·CMePh·C⋮C·CMePh·OH (ac)	*e*	3602	—	—
K[PtCl$_3$ac]	*e*	*d*	—	—
trans-[PtCl$_2$ac(pip)]	*e*	3463	3226	—
Bu^t·C⋮C·CMe$_2$·OH (ac)	2273 [g] 2228	3612	—	—
K[PtCl$_3$ac]	2008	*d*	—	—
trans-[PtCl$_2$ac(pip)]	2046	3500	3223	—
trans-[PtCl$_2$ac(*p*-tol)]	2026	3507	3326 3259	—
Bu^t·C⋮C·CMePh·OH (ac)	2259 2224	3603	—	—
K[PtCl$_3$ac]	2009	*d*	—	—
trans-[PtCl$_2$ac(pip)]	2041	3475	3224	—

[a] py = pyridine; pip = piperidine; *p*-tol = *p*-toluidine. [b] In methoxy groups. [c] Raman spectrum (Cleveland and Murray, *J. Amer. Chem. Soc.*, 1940, **62**, 3186). [d] Not investigated. [e] Not visible. [f] Viscous oil. [g] Liquid film. [h] The glycol is insoluble in CCl$_4$.

of the type *trans*-[PtCl$_2$ac(am)] (am = *p*-toluidine, piperidine, or pyridine) the absorption occurs in the region 2015—2046 cm.$^{-1}$ (Table 1). We attribute these weak absorptions to a C⋮C stretching vibration whose frequency is lowered some 200 cm.$^{-1}$ by co-ordination of the triple bond to the metal atom. A similar lowering of about 200 cm.$^{-1}$ was observed in hydrocarbon alkyneplatinum(II) complexes,[4] and one of some 150 cm.$^{-1}$ in ν(C⋮C) of olefin–platinum(II) complexes.[8,13]

Bonding by the hydroxyl groups. The hydroxyl groups are profoundly modified when the hydroxyalkylacetylenes form complexes. This is shown by the lowering of 110—140 cm.$^{-1}$ in the OH stretching frequency on complex formation (Table 1) and a downfield shift of about 1·5 τ in the proton resonance of the hydroxyl proton, both consistent with hydrogen bonding (Table 2).

Typical infrared spectra in the OH stretching region and the effect on them of adding dioxan are shown in Figs. 1 and 2. The spectrum (Fig. 1) of the free hydroxyalkylacetylene, $\mathrm{Bu^t{\cdot}C{⋮}C{\cdot}CMePh{\cdot}OH}$ (ac), shows a strong, sharp band at 3603 cm.$^{-1}$ due to free hydroxyl groups, with a half band width ($\Delta\gamma_{\frac{1}{2}}$) of 28 cm.$^{-1}$, and a weak, broad band at 3463 cm.$^{-1}$ due to intermolecularly bonded hydroxyl groups. The complex *trans*-[$\mathrm{PtCl_2}$ac(piperidine)], shows a single absorption at 3473 cm.$^{-1}$, with $\Delta\gamma_{\frac{1}{2}} = 112$ cm.$^{-1}$ (Fig. 2), which we assign to ν(OH) lowered by 130 cm.$^{-1}$ owing to strong intramolecular hydrogen bonding. Intermolecular hydrogen bonding is excluded because that common to all the hydroxyalkylacetylene complexes examined would occur either between hydroxyl groups, or the hydroxyl group and a chlorine atom, and neither would have sufficient strength to be complete at low concentrations. Hence we should find bands assignable to free hydroxyl groups in the spectra of the complexes in solution: these were not found (cf. Figs. 1 and 2). Further, the hydroxyl groups in the spectra of the complexes are virtually unchanged on addition of a strong electron-donor, which should split association caused by intramolecular hydrogen bonding. Thus the addition of dioxan to a solution of *trans*-[$\mathrm{PtCl_2(Bu^t{\cdot}C{⋮}C{\cdot}CMePh{\cdot}OH)}$(piperidine)] in carbon tetrachloride only alters ν(OH) from 3473 to 3466 cm.$^{-1}$ and $\Delta\gamma_{\frac{1}{2}}$ from 112 to 114 cm.$^{-1}$ (Fig. 2). This behaviour should be contrasted with the effect of adding dioxan to a similar solution of the free hydroxyalkylacetylene where intermolecular hydrogen bonding obviously occurs (Fig. 1).

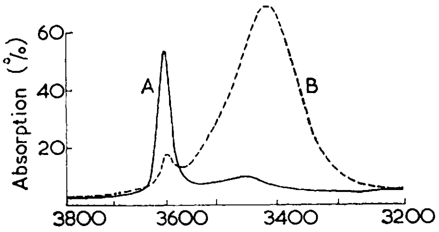

FIG. 1. Infrared spectrum of $\mathrm{Bu^t{\cdot}C{⋮}CMePh{\cdot}OH}$ in (A) $\mathrm{CCl_4}$ (0·1M) and (B) $\mathrm{CCl_4}$–dioxan (0·1M).

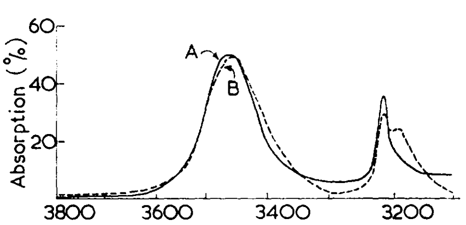

FIG. 2. Infrared spectrum of the complex, *trans*-[$\mathrm{PtCl_2(Bu^t{\cdot}C{⋮}C{\cdot}CMePh{\cdot}OH)}$ (piperidine)] in (A) $\mathrm{CCl_4}$ (0·1M) and (B) $\mathrm{CCl_4}$–dioxan (0·1M).

The proton magnetic resonance spectra give supporting evidence (Table 2). In the spectrum of the free alcohol (A) in dilute deuteriochloroform solution, the hydroxyl proton resonance occurs at a much higher field (8·10 τ) than in the spectrum of the complex (B), *i.e.*, *trans*-[$\mathrm{PtCl_2}$A(pyridine)], where 6·58 τ is consistent with hydrogen bonding in the complex. On increasing the concentration of the solution of (A) the resonance moves to lower fields, whereas in the complex (B) it moves only slightly and is constant (6·58 τ) at concentrations lower than 0·04M. Since the proton resonance of a free hydroxyl group usually depends on concentration,[14] as it has been shown to do in compound (A,) it can be concluded that in complex (B) the protons are involved in hydrogen bonding and that no

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[13] Adams and Chatt, *J.*, 1962, 2821 and references therein.

[14] Jackman, " Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press, London, 1959, pp. (*a*) 66, (*b*) 69.

TABLE 2.

Proton magnetic resonance spectra (τ values) (solutions in $CDCl_3$).

	(A) $HO{\cdot}CMe_2{\cdot}C{\vdots}C{\cdot}CMe_2{\cdot}OH$		(B) *trans*-[$PtCl_2A$(pyr)] *	
Concn. (M)	OH	Me	OH	Me
0·7	6·53	8·45	6·25	8·13
0·4	7·07	8·45	6·40	8·13
0·2	7·52	8·47	6·48	8·13
0·09	7·88	8·47	—	—
0·07	—	—	6·52	8·13
0·04	8·00	8·47	6·58	8·13
0·02	—	—	6·58	8·13
0·01	8·10	8·47	6·58	8·13

* In the spectrum of the complex (B) the ratio of the areas under the proton peaks were in the ratio pyridine : hydroxyl : methyl = 5 : 2·0 ± 0·1 : 12·2 ± 0·6, indicating that no hydroxyl-hydrogen resonance could be expected at τ values other than those above. No resonance on the high-field side of the tetramethylsilane signal was observed.

dissociation occurs even in dilute solution. This is strong evidence for intramolecular hydrogen bonding.

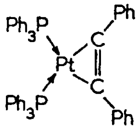
These results are consistent only with structures (II) and (III). Structures (I) and (IV) both have free hydroxyl-hydrogen which should form bonds to dioxan, and so should suffer a shift of ν(OH) on addition of dioxan to their carbon tetrachloride solutions, which was not observed.

Structures (II) and (III) may be distinguished by their nuclear magnetic resonance spectra. In the structure (II), the hydroxyl-hydrogen atom becomes closely associated with the transition-metal atom and would therefore be expected to show a large up-field shift to a τ value lying somewhere between that of hydrogen in an organic hydroxy-compound and hydrogen in a transition-metal hydrido-complex. Also, the resonance should show a splitting by the platinum isotope of spin $\frac{1}{2}$, cf. *trans*-[$PtHCl(PEt_3)_2$].[15] In fact a down-field shift was observed and no splitting, which is consistent only with structure (III) (Table 2).

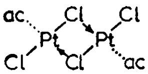
For comparison of the infrared spectra, a model compound [16] (C)

$$[Pt(HO{\cdot}CMeEt{\cdot}C{\vdots}C{\cdot}CMeEt{\cdot}OH)(PPh_3)_2] \quad (C)$$

was prepared, in which hydrogen bonding to chlorine could not occur. This compound probably has a planar structure like (V), containing platinum(II), although a structure similar to this, but having the acetylene turned so that it is perpendicular to the P–P–Pt plane and with the triple bond co-ordinated to platinum(0), is possible. Whatever the detailed structure, the infrared spectrum shows that the hydroxyl groups are free, and we find a single hydroxyl stretching frequency in the spectrum of a carbon tetrachloride solution at 3615 cm.$^{-1}$. This is identical with that of the parent glycol and on addition of dioxan is lowered to 3457 cm.$^{-1}$, in contrast to the behaviour of the hydroxyalkylacetylenes in the platinous chloride complexes.



(V)



(VI)

Further to compare the behaviour of the hydroxyalkylacetylenes in their complexes with those of hydroxyalkenes some complexes of allyl alcohol were prepared. The infrared results (Table 3) show that hydrogen bonding occurs in allyl alcohol complexes because ν(OH) is lowered by some 140 cm.$^{-1}$. This hydrogen bonding probably explains the good stability of allyl alcohol complexes. It is to be noted that ν(C:C) is lowered by some 150 cm.$^{-1}$. The allyl alcohol complexes are thus closely analogous to the complexes of the hydroxyalkylacetylenes.

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[15] Chatt, *Proc. Chem. Soc.*, 1962, 318; Chatt and Shaw, *J.*, 1962, 5075.

[16] Cf. Chatt, Rowe, and Williams, *Proc. Chem. Soc.*, 1957, 208.

TABLE 3.

Infrared data of olefin complexes of platinum(II).

Compound [a]	ν(C⋮C)	ν(OH)	ν(NH)	ν(CH) [b]
$CH_2{:}CH{\cdot}CH_2{\cdot}OH$ (un)	1652	3621	—	—
$K[PtCl_3un]$	1499	*d*	—	—
trans-$[PtCl_2un(py)]$	*e*, *f*	3473	—	—
trans-$[PtCl_2un(pip)]$	*e*, *f*	3484	3228	—
trans-$[PtCl_2un$(*p*-tol)$]$	*e*	3478	3328 3263	—
$CH_2{:}CH{\cdot}CH_2{\cdot}OMe$ (un)	1647	—	—	2820
$K[PtCl_3un]$	1496	*d*	—	—
trans-$[PtCl_2un(py)]$	1509	—	—	2820
trans-$[PtCl_2un(pip)]$	1506, *f*	—	3227	2820
trans-$[PtCl_2un$(*p*-tol)$]$	*e*	—	3330 3264	2821

The symbols have the same meaning as in Table 1.

Structure of the Methoxyalkylacetylene Complexes.—The complexes of the methoxyalkylacetylenes are much less stable than those of the corresponding alcohols. This is readily explained since they cannot have a hydrogen-bonded structure such as (III; H = Me). Either of structures (I) and (IV) (H = Me) would agree with the infrared spectra (Table 1), but the dipole moments suggest that the methoxyl groups are turned away from the platinum atoms.

The dipole moments of some complexes of the type *trans*-$[PtCl_2ac(am)]$, where ac is an acetylenic substance and am is an amine, are listed in Table 4. That of the free di(hydroxyalkyl)acetylene is 2·0 D and of its dimethyl ether, 1·45 D.

TABLE 4.

Dipole moments (Debye units) of complexes of the type *trans*-$[PtCl_2ac(am)]$.

	$Bu^t{}_2C_2$	$Bu^t{\cdot}C⋮C{\cdot}CMe_2{\cdot}OH$	$(HO{\cdot}CMe_2)_2C_2$	$(MeO{\cdot}CMe_2)_2C_2$
p-Toluidine	1·6 *	3·05	3·45	3·65
Pyridine	2·75 *		4·45	4·7

* Taken from ref. 4*b*.

In the di-t-butylacetylene complex the amine is at the positive end of the dipole, which from symmetry must be directed along the N–Pt axis. The dimethoxyalkylacetylene complexes have moments about 2 D greater than that of the corresponding di-t-butylacetylene complex. This difference is appreciably greater than the total moment of the free ether. Evidently the co-ordinated ligand has a moment greater than that of the free ligand, which suggests that the free rotation of the two halves of the di(methoxyalkyl)-acetylene molecule, relative to each other has been restricted. Further, this moment must be directed in the same direction as in the di-t-butylacetylene complex, which suggests that the electronegative methoxyl groups tend to be orientated away from the platinum atoms, as in Fig. 3 which shows the steric requirements of one end of the acetylene in the structure (IV; H = Me).

The di(hydroxyalkyl)acetylene complexes have moments of about 1·8 D greater than those of the di-t-butylacetylene complex, *i.e.*, the increment in moment is slightly less than the total moment of the free ligand. This fact in itself indicates that the hydroxyalkylacetylenes do not form complexes analogous to those of the methoxyalkylacetylenes.

The lower increment in dipole moment made by the di(hydroxyalkyl)acetylenes compared with the dimethoxy-analogues is explained by the spatial requirements of the atoms in structure (III), shown in Fig. 4 as compared with Fig. 3. Here the moments of the two highly dipolar hydroxyl groups will partly counterbalance. It is to be noted that the mono(hydroxyalkyl)acetylene complex, where counterbalancing cannot occur, has a moment almost as great as that of the di(hydroxyalkyl)acetylene complex. Thus, although the moments of acetylene complexes cannot be calculated with certainty, they are in qualitative agreement with the proposed structures.

Above we noted that hydroxyalkylacetylenes do not form complexes of the type $[(\mathrm{PtCl_2ac})_2]$ (structure VI), whereas the acetylenic hydrocarbons formed this dimer in preference to the salt, $\mathrm{K[PtCl_3ac]}$. It seems that in aqueous solution there may be equilibria involving very small concentrations of the above dimer,[17] *e.g.*:

$$\mathrm{K[PtCl_3ac]} + \mathrm{H_2O} \rightleftharpoons trans\text{-}[\mathrm{PtCl_2(H_2O)ac}] + \mathrm{KCl}$$

$$2\ trans\text{-}[\mathrm{PtCl_2(H_2O)ac}] \rightleftharpoons [(\mathrm{PtCl_2ac})_2] + 2\mathrm{H_2O}$$

When the dimer contains an acetylenic hydrocarbon it is likely to be very insoluble in water, and in the above equilibrium its solubility may be exceeded, the more so the larger the hydrocarbon part of the molecule. This would explain why the acetylenic hydrocarbons except $\mathrm{Bu^t{\cdot}C{\vdots}C{\cdot}Me}$ (the acetylenic hydrocarbon of lowest molecular weight to give stable complexes) form salts of the type $\mathrm{K[PtCl_3ac]}$ as stable entities in acetone, but form the dimer rapidly on addition of water.

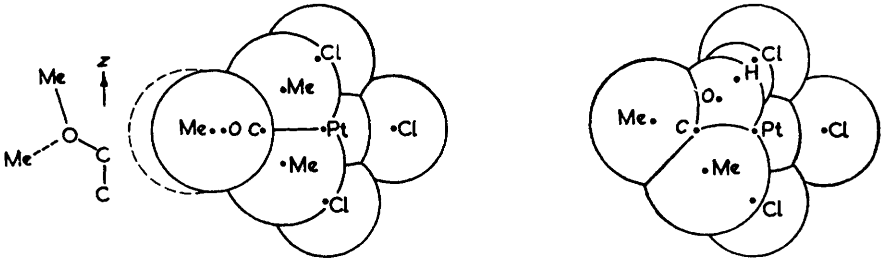

FIG. 3.

FIG. 4.

FIGS. 3 and 4. Views of the ions $[\mathrm{PtCl_3(MeO{\cdot}CMe_2{\cdot}C{\vdots}C{\cdot}CMe_2{\cdot}OMe)}]^-$ and $[\mathrm{PtCl_3(HO{\cdot}CMe_2{\cdot}C{\vdots}C{\cdot}CMe_2{\cdot}OH)}]^-$ along the *z*-axis. FIG. 3. On the basis of structure (IV; H = Me). Two extreme positions of the rotating methoxyl group are indicated. The centres of obscured atoms essential to the understanding of the structure are labelled in italics. FIG. 4. On the basis of structure (III). The centres of obscured atoms essential to the understanding of the structure are labelled in italics.

We were not able to isolate the dimer derived either from $\mathrm{Bu^t{\cdot}C{\vdots}C{\cdot}Me}$ or from the hydroxyalkylacetylenes. These dimers should be more soluble in water than those derived from acetylenic hydrocarbons of higher molecular weight and thus may not separate from the equilibrium mixtures in water, but this scarcely explains our inability to prepare them by direct displacement of ethylene from the compound $[\mathrm{PtCl_2(C_2H_4)_2}]_2$ or by thermal decomposition of the acid $\mathrm{H[PtCl_3ac]}$ in absence of water. It seems that the dimer has a rather poor stability and our structure (III) explains this in the case of the complexes of the di(hydroxyalkyl)acetylenes (although possibly a more general explanation is needed).

In the salt $\mathrm{K[PtCl_3ac]}$ and in the amine complexes *trans*-$[\mathrm{PtCl_2(am)ac}]$ the di(hydroxyalkyl)acetylene (ac) has two singly bound or terminal chlorine atoms for the formation o the two hydrogen bonds with the hydroxyl groups. In the dimer of structure (VI), one of the two *trans*-chlorine atoms is already taking part in bridging. It should, therefore, have a lower negative charge than the terminal chlorine atoms and a smaller affinity for hydrogen bonding to the hydroxyl group. Thus hydrogen bonding should not contribute so strongly to the stability of the dimer as to the stability of compounds containing only terminal chlorine atoms in *trans*-positions to the di(hydroxyalkyl)acetylenes, as have all the di(hydroxyalkyl)acetylene complexes described in this paper.

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[17] Cf. corresponding equilibria in olefin complex chemistry (Leden and Chatt, *J.*, 1955, 2936; Martin and Lokken, Abs. Papers, 142nd Meeting American Chem. Soc., Sept. 1962, p. 31N).

In compounds of the type *trans*-[$PtCl_2L$ am] (am = piperidine or *p*-toluidine) the N–H stretching frequencies depend on the *trans*-ligand L. A great variety of ligands L has been studied including ethylene,[18] and we now add results for the hydroxyalkylacetylene and allyl alcohol complexes.

In our new complexes (Tables 1 and 3) the N–H frequencies are fairly constant, but not so constant as in the series of acetylenic hydrocarbon complexes *trans*-[$PtCl_2$ac′(piperidine)] [ac′ = $Bu^t\cdot C⋮C\cdot R$ (R = Me, Et, Pr^n, Bu^t, or CMe_2Ph)], where values of 3221 and 3222 $cm.^{-1}$ were found, as compared with 3230 $cm.^{-1}$ in the corresponding ethylene complex[19] and a range from 3216 to 3229 $cm.^{-1}$ amongst the complexes in Tables 1 and 3. The only clear regularities to be noted are that methylation of the hydroxyalkylacetylenes causes a significant lowering of ν(N–H), whereas methylation of allyl alcohol scarcely affects ν(N–H); also the complexes of dissymmetric hydroxyalkylacetylenes appear to have slightly lower ν(N–H) than might be expected from the values of the symmetrical analogues. Generally, however, there is nothing remarkable about the values of ν(N–H), which provides further evidence that the hydroxy- and methoxy-alkylacetylenes are bound to the metal in much the same manner as acetylenic hydrocarbons in their complexes. On the other hand, had the hydroxyl group also been bound to the metal as in structure (I) or (II) the values of ν(N–H) might have been affected greatly by the presence of the hydroxyl or methoxyl groups. In Tables 1 and 3 ν(C–H) of the methoxyl groups are also given, and again it is noted that slight changes occur on co-ordination of the triple bond of the methoxyalkylacetylenes to the metal but not on co-ordination of allyl methyl ether to the metal. These differences, however, are probably not very significant and may reflect the more tightly packed structure which is necessary to accommodate the bulky methoxyalkylacetylenes in comparison with the relatively small allyl methyl ether molecule.

EXPERIMENTAL

Microanalyses were carried out in these laboratories. M. p.s of non-ionic complexes were determined on a Kofler hot-stage and are corrected. M. p.s of ionic complexes were determined in capillary tubes and are uncorrected.

Hydroxy-derivatives of Acetylenes.—Except where otherwise stated, the hydroxyalkyl acetylenes were prepared by the condensation of carbonyl compounds with acetylenic Grignard reagents in ether.[20]

They were purified by fractional distillation or recrystallisation until their physical constants agreed with those recorded in the literature,[21] and elemental analyses were satisfactory.

2-*Methylhex*-3-*yne*-2,5-*diol* was prepared in 63% yield from but-3-yn-2-ol and acetone as a pale yellow, viscous liquid, b. p. 116—117°/12 mm., n_D^{25} 1·4644 (Found: C, 65·35; H, 9·5. $C_7H_{12}O_2$ requires C, 65·6; H, 9·45%).

5,5-*Dimethyl*-2-*phenylhex*-3-*yn*-2-*ol*, prepared (33%) from 3,3-dimethylbut-1-yne and acetophenone, crystallised from light petroleum (b. p. 40—60°) as prisms, m. p. 48—48·5° (Found: C, 83·35; H, 9·2. $C_{14}H_{18}O$ requires C, 83·1; H, 9·0%).

Di-(o-*hydroxyphenyl*)*acetylene*. Di-(*o*-methoxyphenyl)acetylene[22] (1·2 g., 1 mol.) in ether (100 ml.) was added to a solution of magnesium iodide (8 mol.) in ether (50 ml.), and the solution heated under reflux for 10 min. Evaporation of the solvent at 15 mm. left a cream-coloured solid which was heated at 140°/0·1 mm. for 1 hr. Addition of dilute hydrochloric acid to the cooled mixture gave a white solid which was extracted with benzene. Extraction of the benzene solution with aqueous sodium hydroxide, followed by neutralisation of the alkaline extract with dilute sulphuric acid, gave a solid which on two crystallisations from light petroleum (b. p. 80—100°) yielded *di*-(o-*hydroxyphenyl*)*acetylene* as needles (0·67 g., 63%), m. p. 129·5—130·5° (Found: C, 80·25; H, 4·95; OMe, 0·0. $C_{14}H_{10}O_2$ requires C, 80·0; H, 4·8%).

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[18] Chatt, Duncanson, Shaw, and Venanzi, *Discuss. Faraday Soc.*, 1958, **26**, 131.

[19] Chatt, Duncanson, and Venanzi, *J.*, 1955, 4461.

[20] Raphael, " Acetylenic Compounds in Organic Synthesis," Butterworths Scientific Publ., London, 1955, p. 15.

[21] See Johnson, " The Chemistry of the Acetylenic Compounds," Edward Arnold and Co., London, 1946.

[22] Coleman, Holst, and Maxwell, *J. Amer. Chem. Soc.*, 1936, **58**, 2310.

Acetylenic Ethers.—1,4-Dimethoxybut-2-yne, b. p. 58—59°/17 mm., n_D^{21} 1·4340, was prepared from but-2-yne-1,4-diol and dimethyl sulphate.[23] 2,5-Dimethoxyhex-3-yne, b. p. 64—65°/15 mm., n_D^{21} 1·4282, was similarly prepared from hex-3-yne-2,5-diol. Treatment of 2,5-dimethylhex-3-yne-2,5-diol (14·2 g.) with dimethyl sulphate [23] gave a mixture of mono- and di-ethers, b. p. 56—90°/12 mm., which was adsorbed on a silica-gel column (55 × 3 cm.) from light petroleum (b. p. 40—60°). Elution with this solvent gave 2,5-dimethoxy-2,5-dimethylhex-3-yne (3·5 g., 20%), b. p. 62—63·5°/12 mm., n_D^{21} 1·4270 (Found: C, 70·65; H, 10·75. Calc. for $C_{10}H_{18}O_2$: C, 70·55; H, 10·65%). Elution with light petroleum–ether (3 : 1) gave 5-methoxy-2,5-dimethylhex-3-yn-2-ol (7·05 g., 45%), b. p. 86°/12 mm., n_D^{24} 1·4401 (Found: C, 69·2; H, 10·35; Me, 19·5. Calc. for $C_9H_{16}O_2$: C, 69·2; H, 10·3; OMe, 19·85%).

2,5-*Dibenzoyloxy*-2,5-*dimethylhex*-3-*yne*.—This was prepared by the action of benzoyl chloride on 2,5-dimethylhex-3-yne-2,5-diol in pyridine at 0°. Recrystallisation from methanol yielded the *dibenzoate* as prisms (70%), m. p. 114—116° (Found: C, 75·15; H, 6·5. $C_{22}H_{22}O_4$ requires C, 75·4; H, 6·35%).

Complexes of the Type K[PtCl$_3$ac].—*Method* 1. A solution of potassium chloroplatinate(II) (4·15 g., 1 mol.) and the hydroxyalkylacetylene (2 mol.) in water (30 ml.) was set aside at room temperature until the colour was orange-yellow (5—10 days). The filtered solution was taken to dryness at <40°/15 mm., yielding an orange solid which was washed with ether and then extracted with acetone. Removal of solvent from the filtered solution at 15 mm. yielded the salt, K[PtCl$_3$ac], as yellow prisms, which were washed with ether and dried *in vacuo* at room temperature. Complexes of the type K[PtBr$_3$ac] were similarly prepared from potassium tetrabromoplatinate(II).

Method 2. A solution of Zeise's salt (1 mol.) and the hydroxyalkylacetylene (2 mol.) in acetone was left at room temperature for 2—3 days (10—14 days for hydroxyalkylacetylenes containing phenyl groups). The filtered solution was taken to dryness at 15 mm., and the salt, K[PtCl$_3$ac] was washed with ether and dried *in vacuo* at room temperature. The aliphatic alcohols gave crystalline yellow complexes, and phenyl compounds gave yellow-brown or brown complexes.

Complexes of the Type Na[PtCl$_3$ac].—*Method* 3. A solution of sodium chloroplatinate(II) tetrahydrate (4·55 g., 1 mol.) and the hydroxyalkylacetylene (2 mol.) in ethanol (40 ml.) was left at room temperature until deposition of sodium chloride had ceased and the colour was orange-yellow (5—10 days). The yellow complex Na[PtCl$_3$ac], was then isolated as described in method 1.

The following complexes were prepared by methods 1 or 2: Potassium trichloro-(2,5-dimethylhex-3-yne-2,5-diol)platinate(II), yellow prisms, 60% (method 1), 83% yield (method 2), decomp. 140—145° (Found: C, 20·15; H, 2·85. Calc. for $C_8H_{14}Cl_3KO_2Pt$: C, 19·9; H, 2·9%); *potassium tribromo*-(2,5-*dimethylhex*-3-*yne*-2,5-*diol*)*platinate*(II), orange prisms [75% (method 1)], decomp. 115—118° (Found: C, 15·8; H, 2·35. $C_8H_{14}Br_3KO_2Pt$ requires C, 15·6; H, 2·3%); *potassium trichloro*-(3,6-*dimethyloct*-4-*yne*-3,6-*diol*)*platinate*(II), yellow prisms [78% (method 1), 88% (method 2)], decomp. 122—124° (Found: C, 23·45; H, 3·65. $C_{10}H_{18}Cl_3KO_2Pt$ requires C, 23·5; H, 3·55%); *potassium trichloro*-(5-*methoxy*-2,5-*dimethylhex*-3-*yn*-2-*ol*)*platinate*(II), pale yellow prisms [70% yield (method 1)], decomp. 155—160° (Found: C, 21·5; H, 3·25. $C_9H_{16}Cl_3KO_2Pt$ requires C, 21·75; H, 3·3%); *potassium trichloro*-(2,5-*dimethoxy*-2,5-*dimethylhex*-3-*yne*)*platinate*(II), yellow-brown prisms [43% (method 1)], decomp. 140—145° (Found: C, 23·65; H, 3·55. $C_{10}H_{18}Cl_3KO_2Pt$ requires C, 23·5; H, 3·55%); *potassium trichloro*-(2,5,5-*trimethylhex*-3-*yn*-2-*ol*)*platinate*(II), yellow prisms [10% (method 1)], decomp. 152—162° (Found: C, 22·6; H, 3·4. $C_9H_{16}Cl_3KOPt$ requires C, 22·5; H, 3·35%); *potassium trichloro*-(2-*methyl*-5-*phenylhex*-3-*yne*-2,5-*diol*)*platinate*(II), yellow prisms [80% (method 2)], decomp. 133—138° (Found: C, 28·8; H, 3·05. $C_{13}H_{16}Cl_3KO_2Pt$ requires C, 28·65; H, 2·95%); *potassium trichloro*-(5,5-*dimethyl*-2-*phenylhex*-3-*yn*-2-*ol*)*platinate*(II), yellow prisms [81% (method 2)], decomp. 130—135° (Found: C, 30·85; H, 3·45. $C_{14}H_{18}Cl_3KOPt$ requires C, 31·0; H, 3·35%); *potassium trichloro*-(meso-2,5-*diphenylhex*-3-*yne*-2,5-*diol*)*platinate*(II), brown powder [61% (method 2)], decomp. 84—88° (Found: C, 35·85; H, 3·1. $C_{18}H_{18}Cl_3KOPt$ requires C, 35·6; H, 3·0%); *potassium trichloro*-(racemic 2,5-*diphenylhex*-3-*yne*-2,5-*diol*)*platinate*(II), yellow-brown powder [70% (method 2)], decomp. 129—130° (Found: C, 35·45; H, 3·1%). The diol isomers of m. p. 164—164·5° and 129—130° have been designated as *meso*- and racemic 2,5-diphenylhex-3-yne-3,5-diol, respectively.

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[23] Rapp, D.R.-P. 742,650/1943.

The following complexes were prepared by method 3. *Sodium trichloro*-(2,5-*dimethylhex*-3-*yne*-2,5-*diol*)*platinate*(II), yellow prisms (53%), decomp. 100—105° (Found: C, 20·9; H, 3·1. $C_8H_{14}Cl_3NaO_2Pt$ requires C, 20·6; H, 3·0%); *sodium trichloro*-(3,6-*dimethyloct*-4-*yne*-3,6-*diol*)*platinate*(II), yellow prisms (60%), decomp. 100—107° (Found: C, 24·45; H, 3·7. $C_{10}H_{18}Cl_3NaO_2Pt$ requires C, 24·3; H, 3·65%): *sodium trichloro*-(2,5-*dimethoxy*-2,5-*dimethylhex*-3-*yne*)*platinate*(II), pale yellow prisms (15%), decomp. 100—120° (Found: C, 23·85; H, 3·9. $C_{10}H_{18}Cl_3NaO_2Pt$ requires C, 24·3; H, 3·65%); *sodium trichloro*-(2,5,5-*trimethylhex*-3-*yn*-2-*ol*)-*platinate*(II), yellow prisms (61%), decomp. 107—111° (Found: C, 23·9; H, 3·6. $C_9H_{16}Cl_3NaOPt$ requires C, 23·25; H, 3·45%).

By method 1 were prepared potassium trichloro(prop-2-en-1-ol)platinate(II), yellow prisms (95%), decomp. 136—140° (Found: C, 9·35; H, 1·6. Calc. for $C_3H_6Cl_3KOPt$: C, 9·05; H, 1·5%), and *trichloro*(3-*methoxyprop*-1-*ene*)*platinate*(II), bright yellow prisms (80%), decomp. 134—140° (Found: C, 11·85; H, 2·0. $C_4H_8Cl_3KOPt$ requires C, 11·65; H, 1·95%).

Complexes of the Type trans-[PtCl$_2$ac(am)].—*General methods.* (1) am = *p*-Toluidine. A solution of a salt K[PtCl$_3$ac] or Na[PtCl$_3$ac] (0·001 mole) in ice-cold water (5—10 ml.) was treated with an ice-cold solution of *p*-toluidine (0·001 mole) in the minimum quantity of dilute hydrochloric acid. The resulting yellow suspension was neutralised by 3% sodium hydroxide solution. The yellow product was collected, washed with ice-cold water, and dried *in vacuo* at room temperature.

(2) am = Piperidine or pyridine. Piperidine or pyridine (0·001 mole) was added dropwise with shaking to an ice-cold solution of a salt K[PtCl$_3$ac] or Na[PtCl$_3$ac] (0·001 mole) in water (5—10 ml.). The precipitate was often an oil which later crystallised. The yellow product was then isolated as in (1). Except where otherwise stated, the compounds prepared by these methods required no further purification.

Prepared in this way (all prisms) were: trans-*dichloro*-(2,5-*dimethylhex*-3-*yne*-2,5-*diol*)-p-*toluidineplatinum*(II), bright yellow, m. p. 147—148° (decomp.) (72% yield) (Found: C, 35·05; H, 4·6; N, 2·9. $C_{15}H_{23}Cl_2NO_2Pt$ requires C, 34·95; H, 4·55; N, 2·7%); trans-*dichloro*-(2,5-*dimethylhex*-3-*yne*-2,5-*diol*)*piperidineplatinum*(II), yellow (40%), m. p. 112—114° (decomp.) (Found: C, 31·8; H, 5·25; N, 2·9. $C_{13}H_{25}Cl_2NO_2Pt$ requires C, 31·65; H, 5·1; N, 2·85%); *trans*-dichloro-(2,5-dimethylhex-3-yne-2,5-diol)pyridineplatinum(II), yellow (63%), m. p. 114—116° (decomp.) [Found: C, 32·4; H, 4·05; N, 2·85%; *M*, ebullioscopically (under nitrogen) in 1·027% acetone solution, 495, in 2·097% acetone solution, 483. Calc. for $C_{13}H_{19}Cl_2NO_2Pt$: C, 32·05; H, 3·95; N, 2·85%; *M*, 487); trans-*dibromo*-(2,5-*dimethylhex*-3-*yne*-2,5-*diol*)-p-*toluidineplatinum*(II), orange-yellow (85%), m. p. 132—134° (decomp.) (Found: C, 30·2; H, 3·9; N, 2·55. $C_{15}H_{23}Br_2NO_2Pt$ requires C, 29·8; H, 3·85; N, 2·3%); trans-*dibromo*-(2,5-*dimethylhex*-3-*yne*-2,5-*diol*)*piperidineplatinum*(II), bright yellow (38%), m. p. 106—110° (decomp.) (Found: C, 26·9; H, 4·4; N, 2·45. $C_{13}H_{25}Br_2NO_2Pt$ requires C, 26·8; H, 4·35; N, 2·4%); trans-*dibromo*-(2,5-*dimethylhex*-3-*yne*-2,5-*diol*)*pyridineplatinum*(II), bright yellow (77%), m. p. 112—114° (decomp.) (Found: C, 27·05; H, 3·45; N, 2·2. $C_{13}H_{19}Br_2NO_2Pt$ requires C, 27·05; H, 3·5; N, 2·45%); trans-*dichloro*-(3,6-*dimethyloct*-4-*yne*-3,6-*diol*)-p-*toluidineplatinum*(II), bright yellow (63%), m. p. 103—104° (decomp.) (Found: C, 37·5; H, 5·0; N, 2·6. $C_{17}H_{27}Cl_2NO_2Pt$ requires C, 37·55; H, 5·0; N, 2·6%); trans-*dichloro*-(3,6-*dimethyloct*-4-*yne*-3,6-*diol*)*pyridineplatinum*(II) bright yellow (50%), m. p. 46—50° (Found: C, 34·9; H, 4·6; N, 2·75. $C_{15}H_{23}Cl_2NO_2Pt$ requires C, 34·95; H, 4·5; N, 2·7%); trans-*dichloro*-(5-*methoxy*-2,5-*dimethylhex*-3-*yn*-2-*ol*)-p-*toluidineplatinum*(II), pale yellow (83%), m. p. 99—101° (decomp.) (Found: C, 36·65; H, 4·8; N, 2·65. $C_{16}H_{25}Cl_2NO_2Pt$ requires C, 36·3; H, 4·75; N, 2·65%); trans-*dichloro*-(5-*methoxy*-2,5-*dimethylhex*-3-*yn*-2-*ol*)*pyridineplatinum*(II), pale yellow (72%), m. p. 62—65° (Found: C, 33·6; H, 4·35; N, 2·9. $C_{14}H_{21}Cl_2NO_2Pt$ requires C, 33·55; H, 4·2; N, 2·8%); trans-*dichloro*-(2,5-*dimethoxy*-2,5-*dimethylhex*-3-*yne*-p-*toluidineplatinum*(II), yellow-brown (87%), m. p. 123—125° (decomp.) (Found: C, 37·15; H, 5·0; N, 2·75. $C_{17}H_{27}Cl_2NO_2Pt$ requires C, 37·55; H, 5·0; N, 2·6%); trans-*dichloro*-(2,5-*dimethoxy*-2,5-*dimethylhex*-3-*yne*)*piperidineplatinum*(II), yellow-brown (33%), m. p. 77—79° (decomp.) (Found: C, 34·55; H, 5·75; N, 2·7. $C_{15}H_{29}Cl_2NO_2Pt$ requires C, 34·55; H, 5·6; N, 2·7%); trans-*dichloro*-(2,5-*dimethoxy*-2,5-*dimethylhex*-3-*yne*)*pyridineplatinum*(II), yellow-brown (78%), m. p. 101—103° (decomp.) (Found: C, 34·85; H, 4·5; N, 2·7. $C_{15}H_{23}Cl_2NO_2Pt$ requires C, 34·95; H, 4·5; N, 2·7%); trans-*dichloro*-(2-*methyl*-5-*phenylhex*-3-*yne*-2,5-*diol*)*piperidineplatinum*(II). yellow-brown [from benzene–light petroleum (b. p. 60—80°)] (81%), m. p. 115—118° (decomp.) (Found: C, 39·35; H, 5·2; N, 2·6. $C_{18}H_{27}Cl_2NO_2Pt$ requires C, 38·95; H, 4·9; N, 2·5%);

trans-*dichloro*-(meso-2,5-*diphenylhex*-3-*yne*-2,5-*diol*)*piperidineplatinum*(II), brown (63%), m. p. 62—65° (decomp.) (Found: C, 44·6; H, 4·7; N, 2·2. $C_{23}H_{29}Cl_2NO_2Pt$ requires C, 44·75; H, 4·75; N, 2·25%); trans-*dichloro*(*racemic* 2,5-*diphenylhex*-3-*yne*-2,5-*diol*)*piperidineplatinum*(II), yellow-brown (86%), m. p. 55—57° (decomp.) (Found: C, 44·6; H, 4·7; N, 2·2%); trans-*dichloro*-(2,5,5-*trimethylhex*-3-*yn*-2-*ol*)-p-*toluidineplatinum*(II), yellow (88%), m. p. 124—128° (decomp.) (Found: C, 37·45; H, 5·0; N, 3·05. $C_{16}H_{25}Cl_2NOPt$ requires C, 37·45; H, 4·9; N, 2·75%); trans-*dichloro*-(2,5,5-*trimethylhex*-3-*yn*-2-*ol*)*piperidineplatinum*(II), pale yellow (49%), m. p. 83—86° (Found: C, 34·7; H, 5·65; N, 3·05. $C_{14}H_{27}Cl_2NOPt$ requires C, 34·2; H, 5·55; N, 2·85%); trans-*dichloro*-(5,5-*dimethyl*-2-*phenylhex*-3-*yn*-2-*ol*)*piperidineplatinum*(II), dark yellow prisms [from light petroleum (b. p. 60—80°)] (89%), m. p. 107—109·5° (decomp.) (Found: C, 41·4; H, 5·35; N, 2·75. $C_{19}H_{29}Cl_2NOPt$ requires C, 41·25; H, 5·3; N, 2·55%).

TABLE 5.

Dipole moments of acetylene complexes of platinum(II) in benzene at 25°.

$10^3\omega$	$\Delta\varepsilon/\omega$	$10^2\Delta n/\omega$	$-\delta v/\omega$	$_TP$	$_EP$	$_OP$	μ ($\pm$0·2 D)
trans-$[PtCl_2(HO\cdot CMe_2\cdot C\vdots C\cdot CMe_2\cdot OH)C_5H_5N]$							
4·105	4·603	—	—	—	—	—	—
4·551	4·596	—	—	—	—	—	—
2·539	—	4·77	—	—	—	—	—
3·245	—	4·40	—	—	—	—	—
4·833	—	—	0·623	—	—	—	—
5·617	—	—	0·600	511	88	409	4·45
trans-$[PtCl_2(HO\cdot CMe_2\cdot C\vdots C\cdot CMe_2\cdot OH)$*p*-$Me\cdot C_6H_4\cdot NH_2]$							
1·127	2·696	—	—	—	—	—	—
1·443	2·706	—	—	—	—	—	—
1·121	—	—	0·535	—	—	—	—
1·566	—	—	0·575	353	(97)	241 *	3·45 *
trans-$[PtCl_2(MeO\cdot CMe_2\cdot C\vdots C\cdot CMe_2\cdot OMe)C_5H_5N]$							
1·108	4·876	—	—	—	—	—	—
1·176	4·907	—	(0·60)	559 *	(96)	449 *	4·7 *
trans-$[PtCl_2(MeO\cdot CMe_2\cdot C\vdots C\cdot CMe_2\cdot OMe)$*p*-$Me\cdot C_6H_4\cdot NH_2]$							
2·232	2·960	—	—	—	—	—	—
2·450	3·050	—	(0·60)	396 *	(105) *	276 *	3·65 *
trans-$[PtCl_2(Bu^t\cdot C\vdots C\cdot CMe_2\cdot OH)$*p*-$Me\cdot C_6H_4\cdot NH_2]$							
2·188	2·344	—	—	—	—	—	—
2·549	2·239	—	—	—	—	—	—
3·808	2·137	—	—	—	—	—	—
14·32	—	4·71	—	—	—	—	—
22·06	—	4·19	—	—	—	—	—
2·484	—	—	0·604	—	—	—	—
3·356	—	—	0·596	300	94	192	3·05
$HO\cdot CMe_2C\cdot C\vdots C\cdot CMe_2\cdot OH$							
6·269	3·354	—	—	—	—	—	—
6·872	3·359	—	—	—	—	—	—
20·21	—	5·52	—	—	—	—	—
26·45	—	5·38	—	—	—	—	—
8·023	—	—	0·062	—	—	—	—
9·620	—	—	0·062	136	49·2	81·7	2·0
$MeO\cdot CMe_2\cdot C\vdots C\cdot CMe_2\cdot OMe$							
6·429	1·695	—	—	—	—	—	—
8·941	1·684	—	—	—	—	—	—
48·49	—	8·14	—	—	—	—	—
49·65	—	8·06	—	—	—	—	—
7·487	—	—	0·080	—	—	—	—
7·703			0·091	108	60·4	41·6	1·45

* Calc. by using estimated values of densities and refractivities, given in parentheses.[24]

The following olefin complexes were similarly prepared: trans-*dichloro*-(*prop*-2-*en*-1-*ol*)-p-*toluidineplatinum*(II), bright yellow prisms (81%), m. p. 114—116° (decomp.) (Found: C, 28·15; H, 3·65; N, 3·3. $C_{10}H_{15}Cl_2NOPt$ requires C, 27·85; H, 3·5; N, 3·25%); trans-*dichloro*-(3-*methoxyprop*-1-*ene*)-p-*toluidineplatinum*(II), bright yellow prisms (92%), m. p. 120—124° (decomp.) (Found: C, 29·75; H, 3·9; N, 3·3. $C_{11}H_{17}Cl_2NOPt$ requires C, 29·65; H, 3·85; N, 3·15%); trans-*dichloro*-(3-*methoxyprop*-1-*ene*)*pyridineplatinum*(II), pale yellow prisms (74%) (Found: C, 26·05; H, 3·25; N, 3·45. $C_9H_{13}Cl_2NOPt$ requires C, 25·9; H, 3·15; N, 3·35%).

Bis(*triphenylphosphine*)(3,6-*dimethyloct*-4-*yne*-3,6-*diol*)*platinum*.—The glycol (1·0 g.) and *cis*-dichlorobistriphenylphosphineplatinum (1·0 g.) in ethanol (40 ml.) were treated with hydrazine hydrate (1 ml.). The resulting clear yellow solution was left overnight, the complex separating as colourless prisms (0·5 g.). m. p. 158—160°, which were collected and washed with ethanol (Found: C, 61·8; H, 5·95. $C_{46}H_{48}O_2P_2Pt$ requires C, 62·1; H, 5·45%).

Dipole Moments.—These were determined as in ref. 24, where the meanings of the symbols used in Table 5 are given.

Nuclear Magnetic Resonance Spectra.—These were determined for deuteriochloroform solutions of a range of concentrations (Table 4) on a Varian Associates A60 spectrometer. Tetramethylsilane was used as internal reference.

Infrared Spectra.—The infrared spectra were measured at 20° with a Grubb-Parsons GS2A prism-grating spectrometer. For determination of ν(C⋮C) (stretching) the finely powdered solids were suspended in Nujol; for ν(NH) (stretching), ν(OH) (stretching), and ν(CH) (stretching) in methoxyl groups a dilute solution of the compound in carbon tetrachloride was used.

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[24] Chatt and Shaw, *J.*, 1959, 705.