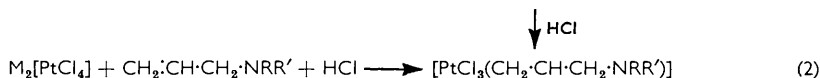


603. Platinum Complexes with Unsaturated Amines. Part I.
Complexes with Allylamines.

By R. G. DENNING and L. M. VENANZI.

Allylamine complexes $\text{PtCl}_2\text{L}\cdot\text{HCl}$, where $\text{L} = \text{CH}_2\text{:CH}\cdot\text{CH}_2\cdot\text{NR}_2$, have been shown to be olefin complexes of the cationic species LH^+ , with structures analogous to that of Zeise's salt. Corresponding complexes of secondary bases $\text{CH}_2\text{:CH}\cdot\text{CH}_2\cdot\text{NHR}$ are probably polymeric; the complex of the mono-octyl derivative is dimeric, the organic ligand acting as a bridging group.

LIEBERMAN and PAAL¹ in 1883 recorded that boiling solutions of hexachloroplatinum(IV) salts of allylamines gave products with the empirical formula (amine H) PtCl_3 . Compounds of the same empirical formula were described more recently by Rubinstein and Derbisher,² and by Helman and Essen.³ These were obtained by the reactions:



Helman and Essen³ formulate the products as olefin complexes (I); Rubinstein and Derbisher² suggest that they are "monoammines," presumably implying structure (II).

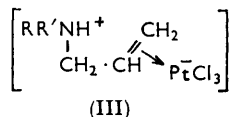


¹ Liebermann and Paal, *Ber.*, 1883, **16**, 530.

² Rubinstein and Derbisher, *Doklady Akad. Nauk S.S.S.R.*, 1950, **74**, 283; 1952, **86**, 961; *Izvest. Sekt. Platiny*, 1951, **26**, 95; 1952, **27**, 99; *Bull. Acad. Sci. U.S.S.R.*, 1953, 209.

³ Helman and Essen, *Doklady Akad. Nauk S.S.S.R.*, 1951, **77**, 273.

Compounds of the Type $[\text{PtCl}_3(\text{NHRR}'\cdot\text{CH}_2\cdot\text{CH}:\text{CH}_2)]$.—We have reinvestigated compounds of this type and find that, irrespective of the method of preparation, they have the empirical formula given where R or R' = H, Et, allyl, or n-octyl and are to be formulated as (III). The compounds are yellow and insoluble in water and in the usual organic solvents, but they dissolve in warm dilute acids. The mono-octyl complex, however, is soluble in a number of polar organic solvents, and therefore, could be investigated more fully.



Our formulation is based on the following evidence: (1) When the cation $[\text{Allyl}\cdot\text{NEt}_3]^+$ is used as a ligand the same type of complex is obtained, thus eliminating structures involving platinum–nitrogen bonds. (2) The only compound examined which was soluble in nitrobenzene, namely, $[\text{PtCl}_3(\text{Et}_3\text{N}\cdot\text{CH}_2\cdot\text{CH}:\text{CH}_2)]$, is a non-electrolyte in this solvent; (3) The infrared spectra of all the complexes (see below) indicate the presence of one co-ordinated double bond and a quaternary nitrogen atom; (4) the visible- and the ultraviolet-light absorption spectra of all the complexes (see below) show that they are structurally analogous to the ethylene complex $\text{K}[\text{PtCl}_3(\text{C}_2\text{H}_4)]$.

Infrared Spectra.—The diagnostic bands for the complexes and some reference compounds are listed in the annexed Table. The salient features are: (i) The compounds show a complex band structure in the region $3300\text{--}2400\text{ cm}^{-1}$, characteristic of quaternary ammonium salts.⁴ (ii) The C=C stretching frequency of the complexes show that they contain one co-ordinated double bond, even when a second allyl group is present in the ligand.^{5,6} (iii) The bands at about 2000 cm^{-1} are assigned to a $=\text{CH}_2$ wagging overtone, corresponding to that at 2047 cm^{-1} observed by Powell and Sheppard for $\text{K}[\text{PtCl}_3(\text{C}_2\text{H}_4)]$.⁷ Co-ordination of the olefin shifts this band by about 100 cm^{-1} towards higher energy.

Diagnostic infrared frequencies (cm^{-1}).

Compound (X = allyl) (Y = n-octyl)	NH Stretch	= CH_2 Deformation overtone		C=C Stretch	
		free	bonded	free	bonded
X·NH ₂	3370, 3290	1834		1642	
[XNH ₂] ₂ [SnCl ₆]	Complex	1885		1650	
[PtCl ₃ (X·NH ₂)]	Complex		2060		1504
X ₂ NH	3279	1840		1648	
[PtCl ₃ (X ₂ NH ₂)]	Complex	1935	2070	1650	1500
X·NH ₂ Et	3280	1840		1648	
[PtCl ₃ (X·NH ₂ Et)]	Complex		2058		1503
[PtCl ₃ (X·NH ₂ Et)] ₂	3189		1995		1513
X·NH ₂ Y	3282	1835		1645	
[X·NH ₂ Y]Br	Complex	1925		1647	
[PtCl ₃ (X·NH ₂ Y)]	Complex		1990		1500
[Pt ₂ Cl ₄ (X·NH ₂ Y) ₂]	3195		2000		1513
X·NEt ₂	—	1840		1647	
[X·NH ₂ Et] ₂ [HgI ₄]	Complex	1900		1643	
[PtCl ₃ (X·NH ₂ Et)]	Complex		2011		1495
X ₂ NEt	—	1840		1647	
[X ₂ NH ₂ Et][HgI ₄]	Complex	1900		1643	
[PtCl ₃ (X ₂ NH ₂ Et)]	Complex	1955	2065	1649	1506
[X·NEt ₃][HgI ₄]	—	1920		1640	
[PtCl ₃ (X·NEt ₃)]	—		1990		1495

Visible and Ultraviolet Spectra.—The close similarity of the reflection spectra indicates that the complexes are all of the same type. The spectrum of the mono-octyl complex could be examined in dichloromethane solution; it resembles closely that of a dichloromethane solution of a complex $[\text{n-C}_{16}\text{H}_{33}\cdot\text{NMe}_3][\text{PtCl}_3(\text{C}_2\text{H}_4)]$ (see Fig. 1).

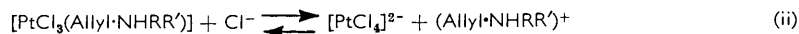
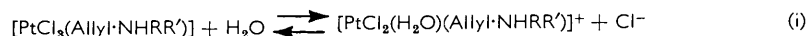
⁴ Heacock and Marion, *Canad. J. Chem.*, 1956, **34**, 1782.

⁵ Cotton, "Modern Co-ordination Chemistry," ed. Lewis and Wilkins, Interscience Publ. Inc., New York, 1960, p. 301.

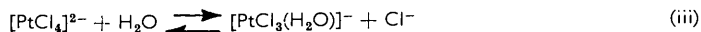
⁶ Kouvenholm, Lewis, and Nyholm, *Proc. Chem. Soc.*, 1961, 220.

⁷ Powell and Sheppard, *Spectrochim. Acta*, 1959, **13**, 69.

Aqueous acid solutions of the complexes do not obey Beer's law and show a strong dependence on chloride concentration, consistently with the equilibria (i) and (ii).

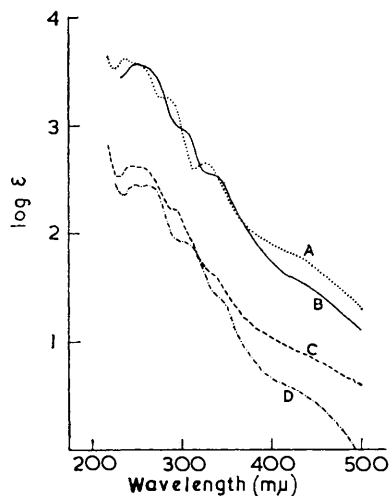


The equilibrium

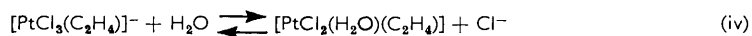


has been neglected because Elleman *et al.*⁸ found $K = 0.015$ and our spectra were measured in solutions with a high chloride concentration.

FIG. 1. Visible and ultraviolet spectra of (A) $\text{K}[\text{PtCl}_3(\text{C}_2\text{H}_4)]$ in $0.2N\text{-HClO}_4$, (B) $[\text{C}_{16}\text{H}_{35}\text{NMe}_3][\text{PtCl}_3(\text{C}_2\text{H}_4)]$ in CH_2Cl_2 , (C) $[\text{PtCl}_3(\text{Allyl}\cdot\text{NHEt}_2)]$ in $0.2N\text{-HClO}_4$, and (D) $[\text{PtCl}_3(\text{Allyl}\cdot\text{NH}_2\cdot\text{C}_8\text{H}_{17})]$ in CH_2Cl_2 . For (C) and (D) the ϵ scale is ten times that shown.



Evidence for equilibrium (i) is that the analogous equilibrium



is established within two minutes in $0.2N$ -perchloric acid.⁹ From the equilibrium constant it appears that about 90% of the complex is in the aquo-form. We find that this process is accompanied by a hyperchromic shift of the spectrum (see Fig. 1). Similar shifts are observed with our complexes. This is consistent with the observation that the ligand field of water is greater than that of the chloride ion.

Evidence for the formation of the $[\text{PtCl}_4]^{2-}$ ion postulated in equilibrium (ii) is supplied by the chloride-ion dependence of the spectra. In $4N$ -chloride the spectra resemble that of the $[\text{PtCl}_4]^{2-}$ ion (see Fig. 2). Equilibrium (ii) is dependent on the nature of the organic ligand, being shifted towards the right in the order $\text{RR}'\text{NH}_2^+ < \text{R}_2\text{R}'\text{NH}^+$ at a given chloride-ion concentration. The explanation of these differences awaits a quantitative study of the equilibria.

Compounds of the Type $[\text{PtCl}_2(\text{NHR}\cdot\text{CH}_2\cdot\text{CH}:\text{CH}_2)]_x$.—Rubinstein and Derbisher,² and Helman and Essen,³ prepared complexes of this type and attributed to them structures in which the amine acts as a chelating agent. Rubinstein and Derbisher,² using diallylamine, obtained two products of the above empirical formula to which they attribute structures (IV) and (V), where $\text{R} = \text{allyl}$. Molecular models show that monoallylamines cannot act as chelating agents while preserving the orientation of the double bond perpendicular to the plane of co-ordination. This orientation is found in other olefin

⁸ Elleman, Grantham, and Martin, *J. Amer. Chem. Soc.*, 1955, **77**, 2965.

⁹ Leden and Chatt, *J.*, 1955, 2936.

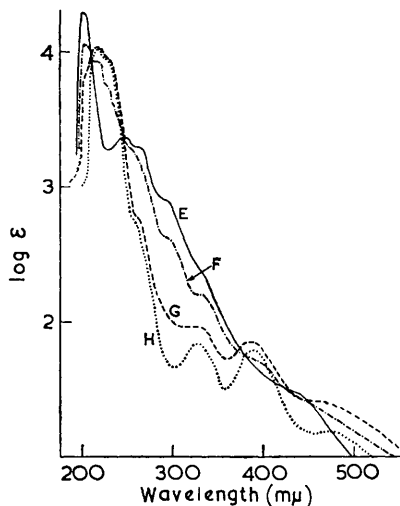


FIG. 2. Chloride-ion dependence of the spectrum of $[\text{PtCl}_3(\text{Allyl}\cdot\text{NHEt}_2)]$: in (E) $\text{N}\cdot\text{HClO}_4$, (F) $0.1\text{N}\cdot\text{HClO}_4 + \text{N}\cdot\text{NaCl}$, and (G) $0.1\text{N}\cdot\text{HClO}_4 + 4\text{N}\cdot\text{NaCl}$. (H) is the spectrum of K_2PtCl_4 in $3\text{N}\cdot\text{HCl}$.

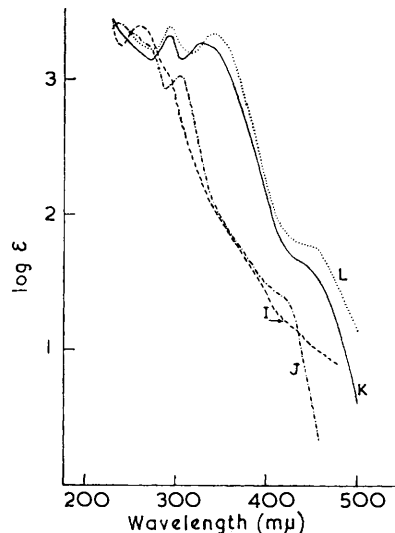
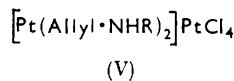
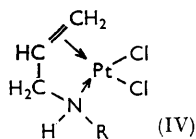


FIG. 3. Visible and ultraviolet spectra of (I) *cis*- and (J) *trans*- $[\text{PtCl}_2(\text{C}_2\text{H}_4)(\text{Piperidine})]$ in CH_2Cl_2 and of $[\text{Pt}_2\text{Cl}_4(\text{Allyl}\cdot\text{NH}\cdot\text{C}_8\text{H}_{17})_2]$ in (K) CH_2Cl_2 and (L) tetrahydrofuran.

complexes of platinum(II).¹⁰ It was, therefore, of interest to establish whether mono-allylamines act as chelating agents or, as appeared more likely, as bridging molecules with the two donor groups attached to different metal atoms.

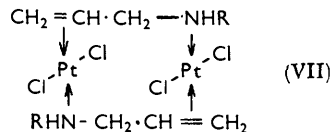
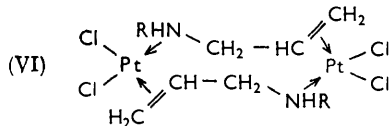


We were unable to repeat Rubinstein and Derbisher's work and obtained only amorphous powders of variable composition.

Neutralization reactions of the type



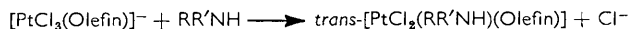
similar to that described by Helman and Essen³ gave crystalline products of the empirical formula shown. While the complex where R = ethyl was only sparingly soluble, that where R = *n*-octyl was soluble in polar organic solvents. In the latter compound both the nitrogen atom and the olefin group are co-ordinated to the platinum atom, as shown



by the infrared spectrum (see Table). The compound is a non-electrolyte in nitrobenzene and is dimeric in naphthalene solution. Of the two possible formulations, (VI)

¹⁰ Wunderlich and Mellor, *Acta Cryst.*, 1954, **7**, 130; 155, **8**, 57; Alderman, Owston, and Rowe, *Acta Cryst.*, 1960, **13**, 149.

and (VII), we think the latter is more likely because (1) the complex was obtained by a reaction of the type



which is known to give only products of *trans*-configuration,¹¹ and (2) the visible and the ultraviolet spectra are very different from that of typical *cis*- or *trans*- $[\text{PtCl}_2(\text{RR}'\text{NH})(\text{Olefin})]$ complexes (see Fig. 3).

The large bathochromic shift of the first spin-allowed transition could arise from interaction of two platinum atoms which, in structure (VII), would be about 3 Å apart. Electrostatic repulsion could raise the energy of the d_{z^2} orbitals sufficiently for the $d_{z^2} \longrightarrow d_{x^2-y^2}$ transition to be that of lowest energy. This is supported by a further bathochromic shift in this band when the solvent is changed from dichloromethane to tetrahydrofuran (see Fig. 3) (cf., e.g., Chatt *et al.*¹²).

One interesting property of the octyl complex $[\text{Pt}_2\text{Cl}_4(\text{Allyl}\cdot\text{NHR})_2]$ is its resistance to boiling alkali. This could be accounted for by the steric hindrance to $\text{S}_{\text{N}}2$ attack by the octyl group implicit in structure (VII).

These observations indicate that other compounds of the type $[\text{PtCl}_2(\text{Allyl}\cdot\text{NHR})]_x$ are not monomeric and thus do not contain allylamine acting as a chelating agent.

EXPERIMENTAL

Preparation of the Organic Ligands.—*N*-Ethylallylamine and ethyldiallylamine were prepared as described by Weston *et al.*,¹³ and *NN*-diethylallylamine by the method of Cope and Towle.¹⁴ Commercial diallylamine was used after fractionation.

n-Octylallylamine. *n*-Octyl bromide (50 g.) and allylamine (44 g.) were heated at 150° in a sealed tube for 4 hr. The products were acidified and steam-distilled to remove octyl bromide. After neutralization, the organic layer of the residue was separated, dried, and fractionated. The fraction boiling at 65—75°/1 mm. was collected. Since it still contained octyl bromide it was acidified with hydrochloric acid, extracted repeatedly with ether, and then neutralized to liberate the *amine* which was dried and redistilled (b. p. 68—69°/0.4 mm.) (Found: C, 78.0; H, 13.7; N, 8.5. $\text{C}_{11}\text{H}_{23}\text{N}$ requires C, 78.1; H, 13.6; N, 8.3%). A cold aqueous solution of sodium bromide was added to the amine (2 g.) in concentrated hydrochloric acid (5 c.c.). The white hydrobromide was filtered off, washed with a little ice-cold water, dried, and recrystallized from ethyl acetate; it had m. p. 183—184° (Found: Br, 32.0. $\text{C}_{11}\text{H}_{24}\text{BrN}$ requires Br, 31.9%).

Triethylallylammmonium chloride. Triethylamine (10 c.c.) and allyl chloride (7.5 c.c.) were refluxed for 2 hr., then extracted twice with water. The extracts were united and extracted twice with ether. The aqueous layer was boiled with charcoal, filtered, and evaporated to give a crude product (4.5 g.) that was used for the preparation of the complexes.

Preparation of the Complexes.—*Trichloro(allylammmonium)platinum(II).* (1) Allylamine (1 g.) in 3*N*-hydrochloric acid (ca. 5 c.c.) was added to potassium tetrachloroplatinate (1 g.) in 3*N*-hydrochloric acid (20 c.c.). The solution was boiled until it became yellow, filtered hot, and left overnight. The product (0.4 g.) that crystallized decomposed at 205—220° (Found: Cl, 30.2; N, 4.1; Pt, 54.7. Calc. for $\text{C}_3\text{H}_9\text{Cl}_3\text{NPt}$: Cl, 29.8; N, 4.0; Pt, 54.6%).

Trichloro(diallylammmonium)platinum(II). (1) This was prepared by method 1 above, and recrystallized from 3*N*-hydrochloric acid (yield 57.2%). It decomposed at 188—205° (Found: Cl, 26.9; N, 3.4; Pt, 48.6. Calc. for $\text{C}_6\text{H}_{12}\text{Cl}_3\text{NPt}$: Cl, 26.7; N, 3.5; Pt, 48.8%). (2) Diallylamine (ca. 0.5 c.c.) was added to a solution of hydrogen tetrachloroplatinate (1 g.) in water (15 c.c.) and ethanol (5 c.c.), and the solution was refluxed for 15 min., then evaporated to small volume. On cooling, the product was obtained in 16% yield. (3) The amine (0.5 c.c.) was added to potassium tetrachloroplatinate (1 g.) in water (ca. 10 c.c.) and after 20 min. the precipitate was filtered off, washed with water and ethanol, dried, and dissolved in boiling 3*N*-hydrochloric acid (30 c.c.). The solution was evaporated to a small volume. The product (23%) crystallized on cooling. The products from methods (1)—(3) had identical infrared spectra.

¹¹ Basolo and Pearson, "Mechanisms of Inorganic Reactions," Wiley, New York, 1958, p. 172.

¹² Chatt, Gamlen, and Orgel, *J.*, 1958, 486.

¹³ Weston, Ruddy, and Suter, *J. Amer. Chem. Soc.*, 1943, **65**, 676.

¹⁴ Cope and Towle, *J. Amer. Chem. Soc.*, 1949, **71**, 3423.

Trichloro-N-ethylallylammoniumplatinum(II). This material was prepared and purified by methods (1) (yield 69%) and (2) (very poor yield). It decomposed at 188—221° (Found: Cl, 27.4; N, 3.5; Pt, 50.5. Calc. for $C_5H_{12}Cl_3NPt$: Cl, 27.4; N, 3.6; Pt, 50.2%).

Trichloro-(N-octylallylammonium)platinum(II). (Method 4) gaseous hydrogen chloride was passed through a solution of the amine (0.5 g.) in ethanol (10 c.c.), the solution heated to the b. p., treated slowly with sodium tetrachloroplatinate tetrahydrate (1 g.) in ethanol (20 c.c.), refluxed for 15 min., filtered hot, and treated with dilute hydrochloric acid. The product crystallized on cooling and, when recrystallized (yield 70%) from 40% aqueous ethanol acidified with a little hydrochloric acid, decomposed at 150—165° (Found: Cl, 22.9; N, 3.0; Pt, 41.3. $C_{11}H_{24}Cl_3NPt$ requires Cl, 22.6; N, 3.0; Pt, 41.4%). It was also obtained in 45% yield by method 1. It is soluble in ethanol, methylene chloride, tetrahydrofuran, and ethyl methyl ketone.

Trichloro-(N-ethylallylammonium)platinum(II). This complex was prepared by method 1 in 95% yield and recrystallized by slow evaporation of an allyl chloride solution to which ethanol had been added (Found: Cl, 24.7; N, 3.3; Pt, 45.4. $C_8H_{16}Cl_3NPt$ requires Cl, 24.9; N, 3.3; Pt, 45.6%).

Trichloro-(NN-diethylallylammonium)platinum(II) was prepared by method 4 in 65% yield, by method 1 in 55% yield, and by method 2 in 45% yield; it decomposed at 190—207° (Found: Cl, 25.4; N, 3.3; Pt, 46.6. $C_7H_{16}Cl_3NPt$ requires Cl, 25.6; N, 3.4; Pt, 46.9%).

Trichloro-(NNN-triethylallylammonium)platinum(II) was prepared by method 1 in 80% yield and had decomp. pt. 207—227°, Λ_M , in $10^{-3}M$ -nitrobenzene solution 3.0 mho (Found: Cl, 23.7; N, 3.1; Pt, 44.2. $C_9H_{20}Cl_3NPt$ requires Cl, 24.0; N, 3.2; Pt, 44.0%).

Dichloro-(N-ethylallylamine)platinum(II). The complex $[PtCl_2(Allyl \cdot NH_2Et)]$ (1.25 g.) was dissolved in warm hydrochloric acid (50 c.c.), the solution was cooled in ice-water, chloroform was added (25 c.c.), and the mixture was neutralized with 0.1N-sodium hydroxide at 0° with stirring. Evaporation of the chloroform layer gave the product (10%) which does not dissolve in chloroform and was recrystallized from ethyl methyl ketone-cyclohexanone, then decomposing at 170—184° (Found: Cl, 20.4; N, 3.4; Pt, 54.9. $C_8H_{11}Cl_2NPt$ requires Cl, 20.0; N, 3.6; Pt, 55.2%).

Dichloro-(N-octylallylamine)platinum(II)dimer. The complex $[PtCl_2(Allyl \cdot NH \cdot C_8H_{17})]$ (1.48 g.) in ethanol (1 l.) was cooled to -40° and neutralized with the exact equivalent of $\sim 0.1N$ -sodium ethoxide. The solution was allowed to warm gradually and at -18° precipitation began; this was complete when the solution reached room temperature. The solid was filtered off, dried, and recrystallized from dioxan at $>80^\circ$. This complex decomposed at 177—181° [Found: Cl, 15.9; N, 3.4; Pt, 44.7%; M (cryoscopic in naphthalene), 920, 835, 801, 896, 865. $C_{22}H_{46}Cl_4N_2Pt_2$ requires Cl, 16.3; N, 3.2; Pt, 44.8%; M , 871]. It is soluble in tetrahydrofuran and slightly soluble in ethyl methyl ketone and dichloromethane.

Trichloroethylene(hexadecyltrimethylammonium)platinum(II). Zeise's salt (1 g.) in water was treated with an excess of hexadecyltrimethylammonium chloride, and the precipitated complex was filtered off, dried, and recrystallized from cyclohexane. The pale yellow needles decomposed at 113—115° (Found: Pt, 31.7. $C_{21}H_{46}Cl_3NPt$ requires Pt, 31.7%).

Preparation of the Alkylammonium Salts.—*Di(allylammonium) hexachlorostannate(IV)*. Allylamine in concentrated hydrochloric acid at 0° was added to a solution of stannic chloride dihydrate (2 g.) in concentrated hydrochloric acid at 0°, until precipitation was complete. The white crystalline product was filtered off and dried in a vacuum-desiccator; it decomposed at 295—300° (Found: Sn, 26.2. $C_6H_{16}Cl_6N_2Sn$ requires Sn, 26.5%).

Di(ethylallylammonium) tetraiodomercurate(II). An excess of the amine in dilute hydrochloric acid was added to a solution of mercuric chloride in an excess of aqueous potassium iodide. The solid product was filtered off, washed with water, dried, and recrystallized from ethyl acetate. It had m. p. 131—132° (Found: Hg, 20.3. $C_{16}H_{32}HgI_4N_2$ requires Hg, 20.9%).

Allyltriethylammonium tri-iodomercurate(II), prepared and purified as in the preceding case, had m. p. 104—106° (Found: Hg, 28.2. $C_9H_{20}HgI_3N$ requires Hg, 27.9%).

Allyldiethylammonium tri-iodomercurate(II) was prepared similarly but separated as an oil which was dissolved in ethanol and crystallized on spontaneous evaporation of the solvent. It had m. p. 71—73° (Found: Hg, 28.2. $C_7H_{16}HgI_3N$ requires Hg, 28.8%).

Molecular-weight Determinations.—These were done by the cryoscopic method. The solubility of the octyl complex $[Pt_2Cl_4(Allyl \cdot NHR)_2]$ in molten naphthalene is about 3.5% w/w, which, with a molecular weight of about 1000, gives a freezing-point depression of about 0.1°.

Infrared Spectra.—These were taken on a Perkin-Elmer model 221 spectrophotometer in Nujol and hexachlorobutadiene mulls. Commercial hexachlorobutadiene showed C-H stretching frequencies; it was distilled through a vacuum-jacketed Widmer fractionating column (b. p. 92—93°/15 mm.) and then had effectively no C-H absorption.

Conductivity Measurements.—These were done by means of a Cambridge conductivity bridge with visual indicator and a cell with bright platinum electrodes. The nitrobenzene solutions of the complexes were $\sim 10^{-3}M$.

Magnetic-susceptibility Measurements.—These were made by using a Faraday-type magnetic balance.¹⁵ The octyl complex $[Pt_2Cl_4(Allyl)_2NHR]_2$ gave χ_M (uncorr.) -442×10^{-6} c.g.s. units at 293°K, from which χ_M (corr.) -15×10^{-6} was obtained.

Analyses.—Tin was determined volumetrically,^{16a} and mercury gravimetrically as the salt $[Cu en_2][HgI_4]$ (after ashing of the sample with 70% perchloric acid and concentrated nitric acid and neutralization of the resulting solution).^{16b} Bromide ion was determined gravimetrically as silver bromide, and platinum spectrophotometrically by Sandel's method.¹⁷

Chloride ion was determined by the method of Zall *et al.*,¹⁸ modified as follows to give greater sensitivity: the aqueous colorimetric solutions, which were 0.05M in ferric ion, $2 \times 10^{-4}M$ in mercuric thiocyanate, and 1.0N in acid, gave suitable absorbances at 450 m μ in 10-cm. silica cells at chloride concentrations up to 5 p.p.m. The absorbance-concentration graph is a continuous curve. Perchloric or sulphuric acid may be used; the former gives a lower blank absorption. The complexes were destroyed by digestion with *N*-sodium hydroxide and portions of 0.1N-hydrazine. The excess of the latter was catalytically decomposed by the metallic platinum formed, this being filtered off before addition of the colorimetric reagents. The experimental error is *ca.* 2%.

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¹⁵ Hartley and Venanzi, *J.*, 1962, 182.

¹⁶ Vogel, "Quantitative Inorganic Chemistry," 2nd edn., Longmans, London, 1951, pp. (a) 363, (b) 424.

¹⁷ Sandel, "Colorimetric Metal Analysis," Interscience Publ. Inc., New York, 1959, p. 726.

¹⁸ Zall, Fisher, and Garner, *Analyt. Chem.*, 1956, **28**, 1665.
