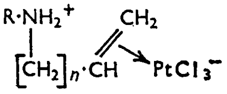
647. *Platinum Complexes with Unsaturated Amines. Part II.*[1] *Complexes with Butenylamines and Pentenylamines.*

By D. V. Claridge and L. M. Venanzi.

Complexes of empirical formula $PtCl_2L,HCl$ $\{L = CH_2{:}CH{\cdot}[CH_2]_n{\cdot}NHR$ ($n = 2,3$; $R = H$, n-C_8H_{15})$\}$ have been shown to be olefin complexes of the cation LH^+. Neutralisation of the complexes produces compounds of formula $PtCl_2L$ which are insoluble, except [$PtCl_2$(n-octylpent-4-enylamine)] which is dimeric and of similar structure to that previously proposed for [$PtCl_2$(n-octylallylamine)].

Compounds of the Type $\{PtCl_3(CH_2{:}CH{\cdot}[CH_2]_n{\cdot}NH_2R)\}$.—These were prepared by the action of olefinic amines on $[PtCl_4]^{2-}$, in acid solution, and have the empirical formula shown, where $R = H$ or n-octyl, and $n = 2$ or 3. They are assigned structure (I) analogous to that previously proposed for the corresponding compounds prepared from allylamines.[1]



(I)

$n = 2$, R = H (I*a*)
$n = 2$, R = n-Oct (I*b*)
$n = 3$, R = H (I*c*)
$n = 3$, R = n-Oct (I*d*)

The complexes are yellow with the exception of compounds (I*a*) and (I*c*) which, as normally prepared, are orange, although (I*c*) could also be obtained in a yellow form. Complexes (I*a*) and (I*c*) are insoluble in water and the usual organic solvents, but soluble in dilute acids. Complexes (I*b*) and (I*d*) are insoluble in dilute acids but soluble in polar organic solvents.

The above formulation is based on the following evidence: (1) The preparation of the complexes in acid solution indicates that only the double bond is available for co-ordination; (2) the infrared spectra (see below) show the presence of a co-ordinated double bond and a quaternary nitrogen atom; (3) the visible and ultraviolet spectra of these compounds (see below) are very similar to that of $K[PtCl_3(C_2H_4)]$ which is known to have a structure of the type shown above.[2]

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

		$:CH_2$ deformation overtone		C:C stretch	
Compound	NH stretch	Free	Bonded	Free	Bonded
$X{\cdot}NH_2$	3373, 3297	1830		1640	
$[X{\cdot}NH_3]_2[SnCl_6]$	Complex	1865		1642	
$[PtCl_3(XNH_3)]$	Complex		2002		*
$X{\cdot}NHZ$	3289	1825		1641	
$[X{\cdot}NH_2Z]Cl$	Complex	1850		1640	
$[PtCl_3(X{\cdot}NH_2Z)]$	Complex		1996		1500
$Y{\cdot}NH_2$	3372, 3296	1820		1640	
$[Y{\cdot}NH_3]_2[SnCl_6]$	Complex	1830		1643	
$[PtCl_3(Y{\cdot}NH_3)]$ (yellow form)	Complex		2018		1505 (sh)
$[PtCl_3(Y{\cdot}NH_3)]$ (orange form)	Complex		2005		*
$Y{\cdot}NHZ$	3290	1820		1640	
$[Y{\cdot}NH_2Z]Cl$	Complex	1850		1643	
$[PtCl_3(Y{\cdot}NH_2Z)]$	Complex		1996		
$X'{\cdot}NHZ$	3288			1666	
$[X'{\cdot}NH_2Z]Cl$	Complex				
$[PtCl_3(X'{\cdot}NH_2Z)]$	Complex				1515
$[PtCl_2(Y{\cdot}NHZ)]_2$	3221		2000		1516

($X = CH_2{:}CH{\cdot}[CH_2]_2-$, $X' = CH_3{\cdot}CH{:}CH{\cdot}CH_2-$, $Y = CH_2{:}CH{\cdot}[CH_2]_3-$, Z = n-octyl, sh = shoulder * = masked by other strong absorption bands, + = not observed.)

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[1] Part I, Denning and Venanzi, *J.*, 1963, 3241.

[2] Wunderlich and Mellor, *Acta Cryst.*, 1954, **7**, 130; 1955, **8**, 57.

To check that compounds (I*a*) and (I*b*) are but-3-enyl- and not but-2-enyl-derivatives, the compound $[PtCl_3(CH_3{\cdot}CH{:}CH{\cdot}CH_2NH\text{-n-octyl})]$ was prepared and found to be different from (I*b*) (see Table).

Infrared spectra. The diagnostic bands for the complexes and some reference compounds are listed in the Table.

The main features of the spectra are a complex band structure in the region 3300—2400 cm.$^{-1}$ characteristic of quaternary ammonium salts[3] and a weak band at about 1500 cm.$^{-1}$ showing the presence of a co-ordinated olefinic group.[4,5] The weak bands at about 2000 cm.$^{-1}$ are assigned to a $:CH_2$ wagging overtone.[1] Co-ordination of the olefin shifts this band by about 100 cm.$^{-1}$ towards higher energy. The position of this band in the spectra of compounds (I*a*) and (I*c*) serves as a criterion of co-ordination of the olefinic group since in both cases the band at 1500 cm.$^{-1}$ is masked by the edge of an intense band appearing at about 1485 cm.$^{-1}$. The spectra of the two forms of $[PtCl_3(\text{pent-4-enyl}{\cdot}NH_3)]$ differ in the position and intensity of the NH_3^+ stretching and deformation absorptions, suggesting that the NH_3^+ groups are hydrogen-bonded in different ways in the respective crystals.

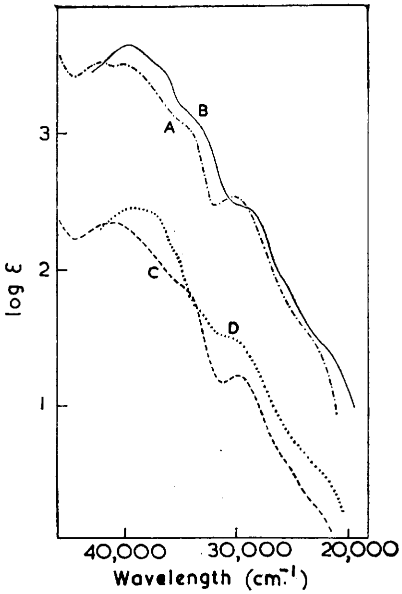

FIG. 1. Visible and ultraviolet spectra.

(A) $PtCl_3(CH_2{:}CH{\cdot}[CH_2]_2NH_3)$ in 1N-$HClO_4$.
(B) $PtCl_3(CH_2{:}CH{\cdot}[CH_2]_3{\cdot}NH_2\text{-n-octyl})$ in CH_2Cl_2.
(C) $K[PtCl_3(C_2H_4)]$ in 1N-$HClO_4$.
(D) $[n\text{-}C_{16}H_{33}{\cdot}NMe_3][PtCl_3(C_2H_4)]$ in CH_2Cl_2.

For (C) and (D) the ε scale is ten times that shown.

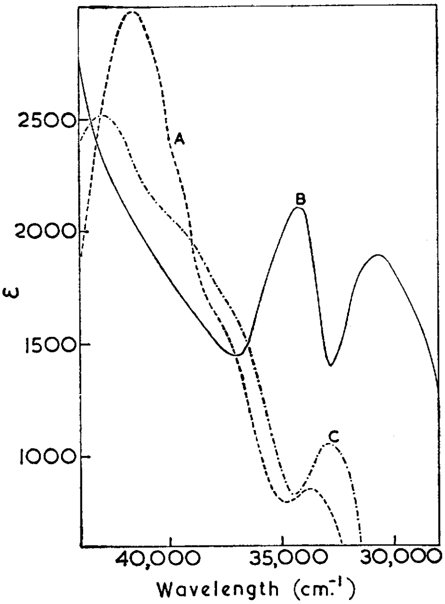

FIG. 2. Visible and ultraviolet spectra.

(A) $\{PtCl_2(CH_2{:}CH{\cdot}[CH_2]_3NH\text{-n-octyl})\}_2$ in CH_2Cl_2.
(B) $\{PtCl_2(CH_2{:}CH{\cdot}CH_2{\cdot}NH\text{-n-octyl})\}_2$ in CH_2Cl_2.
(C) *trans*-$[PtCl_2(C_2H_4)(\text{piperidine})]$ in CH_2Cl_2.

Visible and Ultraviolet Spectra.—The spectra of the n-octyl complexes could be examined in dichloromethane or methyl cyanide solution. They are practically identical and resemble closely that of a solution of the complex $[n\text{-}C_{16}H_{33}{\cdot}NMe_3][PtCl_3(C_2H_4)]$ in dichloromethane (see Fig. 1). The spectra of $[PtCl_3(\text{but-3-enyl}{\cdot}NH_3)]$ and

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[3] Heacock and Marion, *Canad. J. Chem.*, 1956, **34**, 1782.

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

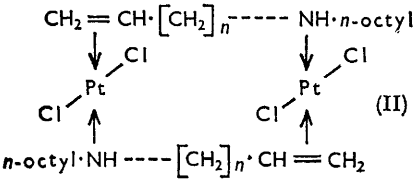
[5] Kouvenholm, Lewis, and Nyholm, *Proc. Chem. Soc.*, 1961, 220.

$K[PtCl_3(C_2H_4)]$ in $1N$-$HClO_4$ are also very similar (see Fig. 1). The two forms of $[PtCl_3(\text{pent-4-enyl}\cdot NH_3)]$ gave identical spectra in $1N$-$HClO_4$, closely resembling that of $[PtCl_3(\text{but-3-enyl}\cdot NH_3)]$.

Compounds of the Type $\{PtCl_2(CH_2{:}CH\cdot[CH_2]_n\cdot NHR)\}$.—These are obtained by addition of base to compounds of type (I), *e.g.*:

$$[PtCl_3(\text{Allyl}\cdot NH_2R)] + OH^- \longrightarrow [PtCl_2(\text{Allyl}\cdot NHR)] + H_2O + Cl^-$$

When R = n-octyl the compound was found to be dimeric and was formulated thus ($n = 1$):[1]



(II)

The visible and ultraviolet spectrum of this compound differed considerably from that of a typical *trans*-$[PtCl_2(RR'NH)(\text{olefin})]$ complex and this was explained in terms of platinum–platinum interaction.

A similar compound of empirical formula $[PtCl_2(\text{pent-4-enyl}\cdot NH\cdot\text{n-octyl})]$ was prepared by neutralisation of $[PtCl_3(\text{pent-4-enyl}\cdot NH_2\cdot\text{n-octyl})]$. Both the olefinic group and the nitrogen atom are co-ordinated to platinum in this. It is soluble in polar organic solvents, is a non-electrolyte in nitrobenzene, and dimeric in naphthalene solution. Its visible and ultraviolet spectrum resembles closely that of *trans*-$[PtCl_2(\text{piperidine})(C_2H_4)]$ (see Fig. 2). This indicates structure (II), with $n = 3$.

The explanation of the anomalous ultraviolet spectrum of $[PtCl_2(\text{allyl}\cdot NH\cdot\text{octyl})]_2$ given in Part I,[1] can be seen to be essentially correct, since in the compound with $n = 3$ molecular models show the platinum atoms to be more than 5 Å apart and free from interaction.

As expected, neutralisation of $[PtCl_3(\text{but-2-enyl}\cdot NH_2\cdot\text{octyl})]$ produced a compound almost identical to $[PtCl_2(\text{allyl}\cdot NH\text{-n-octyl})]_2$, showing the same type of unusual ultraviolet spectrum. In all other cases, neutralisation produced insoluble solids which are probably polymeric. It is surprising that a compound $[PtCl_2(\text{but-3-enyl}\cdot NH\text{n-octyl})]_2$, *i.e.*, with $n = 2$ in structure (II), could not be isolated. Polymer formation might be due to steric factors: models show that in such a dimer there would be some steric hindrance between the platinum atoms and the bridging $:CH_2$ groups. This may be sufficient to cause the formation of an insoluble, open-chain polymer.

EXPERIMENTAL

But-3-enylamine was prepared by the method of Ettlinger and Hodgkins,[7] and an exactly similar procedure was used to convert pent-4-en-1-ol, prepared as described in *Organic Syntheses*,[8] into pent-4-enylamine. Pent-4-en-1-ol (130 g.) and pyridine (3 ml.) were treated with thionyl chloride (185 g.) giving 112 g. (70%) 5-chloropent-1-ene (b. p. 104—106°). This halide (31·5 g.), potassium phthalimide (60 g.), potassium iodide (0·5 g.), and dimethylformamide (200 ml.) were heated at 120° for 2 hr. and 160° for ½ hr. From the mixture 43·2 g. of crude 5-phthalimidopent-1-ene was isolated. This was refluxed with 99% hydrazine hydrate solution (11 ml.) in ethanol (150 ml.) for 2 hr. The yield of pent-4-enylamine was 10·5 g. (b. p. 105—106°).

n-Octylbut-3-enylamine.—n-Octylamine (26 g.) and 4-chlorobut-1-ene[7] (10 g.) were refluxed in benzene (100 ml.) for 10 days. When cool, the reaction mixture was shaken with 2N-potassium hydroxide solution (100 ml.), which was then extracted with ether (50 ml.). The

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[6] Chatt, Duncanson, and Venanzi, *J.*, 1955, 4461; 1956, 2712.
[7] Ettlinger and Hodgkins, *J. Amer. Chem. Soc.*, 1955, **77**, 1831.
[8] *Org. Synth.*, Coll. Vol. III, Wiley, New York, 1955, p. 698.

extract was united with the benzene layer and dried (KOH). The ether and benzene were then distilled off and the residue fractionated under reduced pressure through a vacuum-jacketed, glass-packed column. Yield 12·0 g. (67%) (b. p. 71°/1·4 mm.) (Found: C, 78·3; H, 13·5; N, 7·9. $C_{12}H_{25}N$ requires C, 78·6, 13·7; N, 7·7%). White crystals of *n-octylbut-*3*-enylamine hydrochloride* were recrystallised from water (decomp. 205°) (Found: Cl, 16·2. $C_{12}H_{26}ClN$ requires Cl, 16·2%).

*n-Octylpent-*4*-enylamine*.—This *amine* was prepared from n-octylamine (26 g.) and 5-chloropent-1-ene (10 g.) as described for n-octylbut-3-enylamine yield 13·8 g. (70%) (b. p. 90°/1·4 mm.) (Found: C, 78·5; H, 13·5; N, 7·7. $C_{13}H_{27}N$ requires C, 79·2; H, 13·7; N, 7·1%). *n-Octylpent-*4*-enylamine hydrochloride* (decomp. 200°) (Found: Cl, 15·1. $C_{13}H_{28}ClN$ requires Cl, 15·2%).

*n-Octylbut-*2*-enylamine*.—Under the conditions described by Tiollais,[9] crotonaldehyde (35 g.) was condensed with n-octylamine (64 g.), to form an aldimine. The freshly distilled compound (27 g.) (b. p. 75°/0·8 mm.) was dissolved in dry ethanol (150 ml.) and cooled in ice in a 5 l. flange-neck flask fitted with two long, wide-bore condensers. Sodium (12·5 g.) in small pellets was added in one portion. The mixture was left overnight and then treated with water (100 ml.) followed by excess of 5N-hydrochloric acid. The acidic solution was evaporated to dryness under reduced pressure and the residue treated with a solution of potassium hydroxide (25 g.) in water (100 ml.). The *n-octylbut-*2*-enylamine* was extracted with ether and the solution dried (KOH). The ether was distilled off and the product fractionated under reduced pressure (yield 12·2 g.) (b. p. 67°/0·8 mm.) (Found: C, 77·9; H, 13·7; N, 7·7. $C_{12}H_{25}N$ requires C, 78·6; H, 13·7; N, 7·7%). *n-Octylbut-*2*-enylamine hydrochloride* (decomp. 195°) (Found: Cl, 16·2. $C_{12}H_{26}ClN$ requires Cl, 16·2%).

Preparation of the Complexes.—*Trichloro(but-*3*-enylammonium)platinum*(II). (Method 1) But-3-enylamine (0·5 g.) in 3N-hydrochloric acid (10 ml.) was added to a solution of potassium tetrachloroplatinate (1 g.) in 3N-hydrochloric acid (20 ml.) and the mixture heated on a boiling-water bath until it became yellow. The solution was evaporated under reduced pressure to about 15 ml., filtered, and left to crystallise (yield 0·45 g.) (decomp. 185°) (Found: Pt, 52·1; C, 13·3; H, 2·9. $C_4H_{10}Cl_3NPt$ requires Pt, 52·2; C, 12·9; H, 2·8%).

*Trichloro(pent-*4*-enylammonium)platinum*(II).—(*a*) *Orange form*. This was prepared by method 1 above (yield 75%) (decomp. 172°) (Found: Pt, 50·0; C, 16·1; H, 3·3. $C_5H_{12}Cl_3NPt$ requires Pt, 50·3; C, 15·6; H, 3·2%).

(*b*) *Yellow form*. The above preparation was repeated except that after evaporation under reduced pressure, the solution was seeded with one of the orange crystals previously obtained. A mixture of two types of crystal resulted, the orange crystals described above and some yellow plates. A further preparation, seeded with one of these yellow crystals, gave only the yellow form (yield 65%) (decomp. 160°) (Found: Pt, 49·8; C, 15·9; H, 3·3. $C_5H_{12}Cl_3NPt$ requires Pt, 50·3; C, 15·6; H, 3·2%).

Trichloro(N*-octylbut-*3*-enylammonium)platinum*(II).—(Method 2.) Hydrogen chloride was passed for a few minutes through a solution of the amine (0·5 g.) in ethanol (10 ml.), the solution added to sodium tetrachloroplatinate tetrahydrate (1 g.) in ethanol (20 ml.), heated to boiling on a water-bath, filtered hot, and treated with sufficient dilute hydrochloric acid to produce incipient precipitation. The product crystallised on cooling (yield 0·9 g.). When recrystallised from methyl cyanide, it decomposed at 160° (Found: Pt, 39·9; C, 29·9; H, 5·5. $C_{12}H_{26}Cl_3NPt$ requires Pt, 40·1; C, 29·8; H, 5·4%).

Trichloro(N*-octylpent-*4*-enylammonium)platinum*(II).—This was prepared in 65% yield by method 2. It was deposited as a yellow oil on dilution of the alcoholic solution with 2N-hydrochlorid acid. The product crystallised on standing and with care could be recrystallised from methyl cyanide (m. p. 147° with some decomp.) (Found: Pt, 39·0; C, 31·4; H, 5·7. $C_{13}H_{28}Cl_3NPt$ requires Pt, 39·0; C, 31·3; H, 5·7%).

Trichloro(N*-octylbut-*2*-enylammonium)platinum*(II).—This was prepared in 75% yield by method 2. The product, after recrystallisation from methyl cyanide, decomposed at 147° (Found: Pt, 40·3; C, 30·1; H, 5·5. $C_{12}H_{26}Cl_3NPt$ requires Pt, 40·1; C, 29·8; H, 5·4%).

Dichloro(N*-octylpent-*4*-enylamine)platinum*(II) *Dimer*.—(Method 3.) A solution of the complex [$PtCl_3$-(pent-4-enyl·NH_2-n-octyl)] (0·76 g.) in ethanol (250 ml.) was cooled to 0° and treated for 1 hr. with an exactly equivalent quantity of 0·02N-ethanolic potassium hydroxide. The mixture

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[9] Tiollais, *Bull. Soc. chim. France*, 1947, 708.

was stirred at room temperature for 1 hr., the precipitated yellow solid collected (yield 0·51 g.) and recrystallised from 1,1-dichloroethane. The *complex* decomposed at 130° (Found: Pt, 41·8; C, 34·5; H, 6·1%: *M*(cryoscopic in naphthalene), 950. $C_{26}H_{54}Cl_4N_2Pt_2$ requires Pt, 42·2; C, 33·8; H, 5·9%; *M*, 927).

Dichloro(N-*but-2-enylamine*)*platinum*(II) *Dimer.*—This *dimer*, prepared in 50% yield by method 3, decomposed at 143° (Found: Pt, 43·2; C, 31·6; H, 5·7. $C_{24}H_{50}Cl_4N_2Pt_2$ requires Pt, 43·3; C, 32·0; H, 5·6%).

Infrared Spectra.—These were taken on a Perkin-Elmer model 221 spectrophotometer in Nujol and hexachlorobutadiene mulls.

Visible and Ultraviolet Spectra.—These were taken on a Unicam S.P. 700 Recording ultra-violet spectrophotometer.

Analyses.—Chloride ion was determined gravimetrically as silver chloride using a filter beaker,[10] and platinum spectrophotometrically by Sandell's method.[11] Carbon, hydrogen, and nitrogen were determined by Dr. A. Bernhardt in the Mikroanalytisches Laboratorium im Max Planck Institut, Mülheim (Ruhr), Germany.

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[10] Vogel, "Quantitative Inorganic Analysis," 3rd edn., Longmans, London, 1961, pp. 640, 1107.

[11] Sandell, "Colorimetric Metal Analysis," Interscience Publ. Inc., New York, 1959, p. 726.