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Platinum-Acetylene Complexes and Amine Reactions

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The reaction of Bukhovets' salt, $K[PtacCl_3]$(ac = $(CH_3)_2C(OH)C{\equiv}C(OH)(CH_3)_2$) and its bromo-analog with amines (Am = NHR_1R_2; $R_1 = H$, $R_2 = H, CH_3, C_2H_5, CH(CH_3)_2, C(CH_3)_3$; $R_1 = CH_3$, $R_2 = CH_3$; $R_1 = C_2H_5$, $R_2 = C_2H_5$) have been studied in aqueous solutions. Zero charged complexes, trans-*$PtacAmX_2$ (X = Cl, Br), were first formed. Consequently, the platinum activated triple bond of acetylene was attacked by a second molecule of amine and two kinds of complexes were isolated: Pt(acAm)$AmCl_2$ (type 1), where (acAm) = $(CH_3)_2C(OH)C{=}C(NHR_1R_2)^{+}C(OH)(CH_3)_2$ is a vinyl ammonium compound; $R_1 = H$, $R_2 = C(CH_3)_3$; $R_1 = C_2H_5$, $R_2 = C_2H_5$; and Pt(acAm-H)AmX (type 2), where (acAm-H) = $(CH_3)_2C(OH)C{=}C(NR_1R_2)C(OH)(CH_5)_2$ is a vinyl amine; $R_1 = H$, $R_2 = H, CH_3, C_2H_5, CH(CH_3)_2$; $R_1 = CH_3$, $R_2 = CH_3$. The structures of these complexes are discussed together with their chemical reactions infrared spectra, mass spectra, nmr spectra, molecular weight determinations and conductivity measurements.*

Introduction

The are not many examples of formation of C-N bonds by the addition of amines to an unsaturated carbon-carbon bond, which has been coordinated to platinum metals.[1] Paiaro *et al.* showed that amines reacted with diene complexes[2,3] and monoolefin[4] complexes of platinum and palladium, and Clark and Colls found that platinum cationic complexes of acetylene could be led to methoxy vinyl complexes in methanol.[5,6] In view of our results on the acetylene platinum complexes with ethylenediamines,[7,8] we were interested in investigating the nucleophilic attack of the triple bond of acetylene in the platinum complexes by amines and diamines.

The present work, therefore, describes several reactions of the acetylenic analogs to Zeise's salt with primary and secondary amines and with diamines of the general formula, $NH_2(CH_2)xNH_2$, where x = 2,4,5,6,7,8. The dinitrogen ligands show unusual stereochemical properties.

Results and Discussion

Complexes of trans-*$PtacAmX_2$.* The platinum salt $K[PtacCl_3]$ (ac = $(CH_3)_2C(OH)C{\equiv}CC(OH)(CH_3)_2$) and its bromo-analog reacted with aliphatic amines in aqueous solutions to give yellow complexes, as precipitates of the formula *trans*-$PtacAmX_2$ (Am=Amine, X = Cl Br), similar to the complexes of *trans*-$PtacpyCl_2$ (py = pyridine, piperidine).[10] Bukhovets claimed[11] to have isolated the complex of trans-$PtacNH_3Cl_2$ by reacting $K[PtacCl_3]$ and aqueous ammonia. However, we repeated this reaction several times without success; only a white insoluble compound was obtained. Its infrared spectrum showed that the coordinated acetylene changed. This compound will be discussed in the next paragraph. We prepared the complex, *trans*-$PtacNH_3Cl_2$ by displacing pyridine or 2,6-lutidine from the complex of *trans*-$PtacpyCl_2$ in benzene solution. The elemental analyses and the characteristic bands of the infrared spectra of these complexes are listed in Tables I and IV, respectively.

Reactions of trans-*$PtacAmX_2$ with amines.* The complexes $K[PtacX_3]$ or trans-$PtacAmX_2$ reacted with excess amines (including ammonia) and two kinds of complexes were isolated, depending on the nature of the amines employed; both of the complexes contained one molecule of acetylene and two molecules of amine per platinum atom. In general, bulky amines gave complexes containing two atoms of chlorine (type 1 complexes), less bulky amines gave complexes containing one atoms of chlorine per platinum atom (type 2 complexes). Complexes 1 are yellow, very similar to those of the series $PtacAmCl_2$ and very soluble in organic solvents, such as benzene, chloroform and methanol. They change slowly in solution and cannot be recrystallized from solutions. Complexes 2 are white or nearly white, except the complex with NH_2CH_3, soluble in methanol and nitromethane, and the complexes with $NH_2CH(CH_2)_2$ and $NH(CH_3)_2$ which are soluble in chloroform. Both types of complexes are air-stable and insoluble in water. Their analytical data and the characteristic bands of the

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[2] G. Paiaro, A. De Renzi, and R. Palumbo, *Chem. Comm.*, 1150 (1967).

[3] R. Palumbo, A. De Renzi, A. Panunzi, and G. Paiaro, *J. Am. Chem. Soc.*, *91*, 3874 (1969).

[4] *Ibid.* *91*, 3879 (1969).

[5] M.H. Chisholm and H.C. Clark, *Inorg. Chem.*, 2557 (1971).

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[9] S.V. Bukhovets, *Izvest sektora platiny*, *29*, 55-60 (1955).

[10] J. Chatt, R.G. Guy, L.A. Duncanson, and D.T. Thompson, *J. Chem. Soc.*, 5170 (1963).

[11] S.V. Bukhovets and K.A. Mobodova, *Z. Neorg. Khim.*, *11*, 776 (1957).

Table I. Analytical data and melting points of the complexes *trans*-$PtacAmX_2$(ac = $(CH_3)_2C(OH)C{\equiv}CC(OH)(CH_3)_2$. X = Cl, Br).

Compound		C	H	N	X	Pt	m.p. °C
$PtacNH_3Cl_2$	cald.	22.59	4.00	3.30			140
	found	22.59	3.96	3.53			
$Ptac(NH_2CH_3)Cl_2$		23.71	3.89	3.20	16.25	42.00	
		22.53	3.21	3.10	16.54		142
$Ptac(NH_2CH_3)Br_2$		20.45	3.60	2.65	30.30		138
		20.98	3.54	2.50	31.45		
$Ptac(NH_2C_2H_5)Cl_2$		26.50	4.63	3.09		42.00	107
		26.63	4.47	3.04		42.80	
		29.94	5.50	2.91		40.50	135
		30.09	5.03	2.77		40.00	
$Ptac(NH(CH_3)_2)Cl_2$		26.50	4.63	3.09			120
		26.51	4.48	3.11			
$Ptac(NH(C_2H_5)_2)Cl_2$		29.94	5.50	2.91		40.54	134
		30.01	5.10	2.69		40.40	
$Ptac'(NH_2(NH_2Et)Cl_2$		29.60	5.14	2.87			80
		30.18	4.98	2.77			

ac′ = $(CH_3)_2C(OCH_3)C{\equiv}CC(OCH_3)(CH_3)_2$.

Table II. Analytical data, melting points and molecular weights of complexes 2, Pt(acAm-H)AmX.
((acAM-H) = $(CH_3)_2C(OH)C{=}C(NR_1R_2)C(OH)(CH_3)_2$, X = Cl, Br)

Compound		C	H	N	X	Pt	m.p. °C	m.w. in CH_3OH
1. $Pt(acNH_2)NH_3Cl$	cald.	23.13	4.34	6.75	8.67		180	
	found	23.31	4.68	6.74	8.81			
2. $Pt(acNHCH_3)(NH_2CH_3)Cl$		27.59	5.52	6.44	8.28	44.39	174	
		27.83	5.07	6.50	8.78	44.83		
3. $Pt(acNHCH_3)(NH_2CH_3)Br$		25.05	5.01	5.85	16.70	40.70	150	
		24.98	4.58	5.55	17.73	40.20		
4. $Pt(acNHC_2H_5)(NH_2C_2H_5)Cl$		31.10	6.05	6.05		42.12	150	463
		30.92	5.47	5.89		42.60		454
5. $Pt(acNHCH(CH_3)_2)(NH_2CH(CH_3)_2)Cl$		34.22	6.52	5.70		39.57	138	487
		34.85	6.48	5.56		30.19		431
6. $Pt(acN(CH_3)_2)(NH(CH_3)_2)Cl$		31.10	6.05	6.05		42.10	110	463
		31.48	5.86	6.05		41.30		436
		31.15	5.92	5.86				
7. $Pt(acNH(CH_2)_6NH_2)Cl$		34.40	5.93	5.72			175	
		34.94	6.28	6.53				
8. $Pt(acNH(CH_2)_8NH_2)Cl$		37.20	6.38	5.32			175	
		37.34	6.52	5.84				
9. $Pt(acNHC_2H_5)(NH_2C_2H_5)Cl$		31.10	6.05	6.05			140	
		31.19	5.95	5.93				
*10. $Pt(acNH_2)(2,6\text{-}Lu)ClH_2O$		35.00	4.86	5.44			115	
		34.94	4.59	5.23				

* 2,6-Lu = 2,6-lutidine.

Table III. Analytical data and melting points of complexes 1, $Pt(acAm)AmCl_2$.
((acAm) = $(CH_3)_2C(OH)C{=}C(NHR_1R_2)C(OH)(CH_3)_2$)

Compound		C	H	N	Cl	Pt	m.p. °C
$Pt[acNH_2C(CH_3)_3](NH_2C(CH_3)_3)Cl_2$	cald.	34.78	6.47	5.05	12.97	35.20	101
	found	34.49	6.00	4.96	13.56	34.95	
$Pt[acNH(C_2H_5)_2](NH(C_2H_5)_2)Cl_2$		34.78	6.47	5.05	12.97	35.20	119
		34.53	6.34	4.99	13.66	35.42	
		33.94	6.34	4.65	13.12		
* $Pt[acNH(CH_3)_2](2,6\text{-}Lu)Cl_2$		36.43	5.36	4.51	12.67		147
		36.79	5.22	5.00	12.74		

* 2,6-Lu = 2,6-lutidine.

infrared spectra are given in Tables II, III, V and VI. Both types of complexes showed that the $\nu C{\equiv}C$ band around 2030 cm^{-1} of the acetylene disappeared on reaction with the amines and a new very strong band was observed at ~1650 cm^{-1}. Their mass spectra showed strong peaks between 142 (m.w. of ac) and 195 (a.w. of Pt), no such peaks were found in the mass spectra of their starting materials, i.e., $K[PtacCl_3]$ and *trans*-$PtacAmX_2$ (see Table VIII). Amines were found to be good nucleophiles for at-

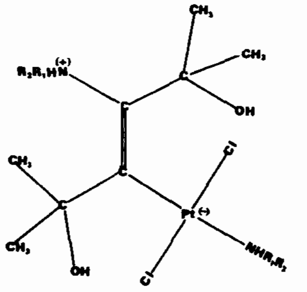
Table IV. Characteristic infrared bands and assignments of the complex *trans*-PtacAmX_2. (ac$=(CH_3)_2C(OH)C\equiv CC(OH)(CH_3)_2$ X = Cl, Br)

Compound *	νOH cm⁻¹	νNH	νC≡C	δNH_2	νPt-X
PtacNH_3Cl_2	3475 vs	3305 s 3260 m 3190 m 3120 sh	2030 vs	1610 w	335 s
Ptac$(NH_2CH_3)_2Cl_2$	3496 sh 3450 vs br	3372 vs 3195 vs 3118 m	2035 vw	1586 vs	334 vs
Ptac$(NH_2CH_3)Br_2$	3504 sh 3449 vs br	3272 s 3198 m 3123 m	2030 vw	1587 s	235 s
Ptac$(NH_2C_2H_5)Cl_2$	3486 vs 3463 vs	3249 vs 3194 vs 3115 m	2032 vw	1585 vs	334 vs
Ptac$(NH_2CH(CH_3)_2)Cl_2$	3470 vs 3410 sh	3260 m 3190 vs 3110 vs	2030 vw	1585 vs	334 vs
Ptac$(NH_2C(CH_3)_3)Cl_2$	3466 vs 3412 vs	3240 sh 3212 vs 3133 m	2033 vw	1585 vs	331 s
Ptac$(NH(CH_3)_2)Cl_2$	3505 vs br 3430 sh	3222 vs	2030 vw		335 s
Ptac$(NH(C_2H_5)_2)Cl_2$	3440 sh 3408 vs br	3190 vs	2033 vw		337 vs br

Intensities: * v = very, s = strong, w = weak, vs = very strong, vw = very weak, br = broad, sh = shoulder, m = medium.

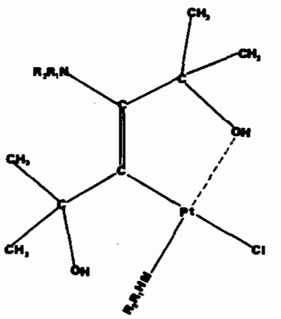
tacking dienes in platinum and palladium complexes.[2,3] The methanol can also act as a nucleophile and attack the triple bond of the acetylene in the platinum complexes with the formation of methoxy vinyl complexes.[5,6]

The above reports led us to carry out nucleophilic additions with amines to the triple bond of the coordinated acetylene. The complexes formed may be represented by the following vinyl amine structures:



type 1

$R_1 = C(CH_3)_3$, $R_2 = H$
$= C_2H_5$ $= C_2H_5$



type 2

$R_1 = H$ $R_2 = H$
$= CH_3$ $= H$
$= C_2H_5$ $= H$
$= CH(CH_3)_2$ $= H$
$= CH_3$ $= CH_3$

Whenever a secondary amine was added to the triple bond, the amine attacked the triple bond of the acetylene and an N-disubstituted vinylamine was obtained, as follows:

$$-C\equiv C- + NHR_1R_2 \rightarrow -CH=C(NR_1R_2)-$$

The vinyl amine cannot be tautomerized into an anil derivative (with a C=N bond) as in the primary amines,[12] example,

$$-C\equiv C- + NH_2R \rightarrow -CH=C(NHR)- \rightleftarrows -CH_2-C=NR$$

The strong band at 1650 cm⁻¹ in the above complexes is a νC=C stretching frequency; it could not be a νC=N stretching frequency, because both types of complexes can be obtained with secondary amines.

In the methoxy vinyl complexes prepared from platinum acetylene complexes,[5,6,13] the nmr spectrum[13] was consistent with the methoxy group being *trans* to the platinum.[14] In the present complexes it was not possible to make a molecular model by keeping the two bulky groups, $-C(OH)(CH_3)_2$ in the *cis*-position of the double bond. Since there are two amines per molecule of complex, it should be interesting to react the acetylene complex with a diamine ligand. Diamines, $NH_2(CH_2)_xNH_2$ were used, and it was found that with x = 2, the cationic complex $[Ptac(NH_2(CH_2)_2NH_2)Cl]^+Cl^-$ was obtained and both nitrogens were coordinated to the platinum,[7] if x = 4,5 no complexes were isolated, and if x = 6,7,8, complexes 2 were obtained with both nitrogens coordinated, one to the metal atom and one to the carbon of the triple bond. They were characterized by their infrared spectra, analytical data and chemical properties (see Tables II and V). The reactivity of the diamines indicates that the two nitrogen atoms in the complex were very far apart. Thus the amino group attacking the carbon atom is in the *trans*-position in the double bond, with respect to the platinum atom.

Both types of complexes were non-electrolytes in methanol and nitromethane. When methyl iodide

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(13) M.H. Chisholm, H.C. Clark, and L.E. Manzer, *Inorg. Chem.*, 1269 (1972).

(14) B.E. Mann, B.L. Shaw, and N.I. Tucker, *Chem. Comm.*, 1333 (1970).

Table V. Characteristic infrared bands and assignments of complexes 2, Pt(acAm-H)AmX

Compound	νOH cm^{-1}	νNH	νC=C	δNH$_2$	νPt-X
1 $\mathrm{Pt(acNH_2)NH_3Cl}$	3472 vs	3317 vs br	1672 vs	1616 vs	314 s
		3172 vs			
		3095 vs			
2 $\mathrm{Pt(acNHCH_3)(NH_2CH_3)Cl}$	3430 vs	3122 sh	1667 vs	1575 vs	317 s
	3322 w	3190 m			
		3106 vs			
3 $\mathrm{Pt(acNHCH_3)(NH_2CH_3)Br}$	3425 s	3292 m	1658 sh	1593 vs	235 m
	3381 s	3250 s	1647 vs		
	3335 m	3164 w			
		3117 vs			
4 $\mathrm{Pt(acNHC_2H_5)(NH_2C_2H_5)Cl}$	3340 s	3227 m	1672 vs	1590 s	315 s
5 $\mathrm{Pt(acNHCH(CH_3)_2)(NH_2CH(CH_3)_2)Cl}$	3310 m	3150 s			
	3480 sh	3275 vs	1650 vs	1592 s	321 s
	3360 vs	3226 w			
		3190 s			
		3150 m			
6 $\mathrm{Pt(acN(CH_3)_2)(NH(CH_3)_2)Cl}$	3530 s	3334 vs	1676 sh		313 s
	3351 vs		1662 vs		
			1636 sh		
7 $\mathrm{Pt(acNH(CH_2)_6NH_2)Cl}$	3420 s br	3230 vs	1655 vs br	1580 s br	315 m
		3130 s			
8 $\mathrm{Pt(acNH(CH_2)_8NH_2)Cl}$	3430 s br	3230 vs	1655 vs br	1580 s br	316 m
		3130 s			
9 $\mathrm{Pt(acNHC_2H_5)(NH_2C_2H_5)Cl}$	3290 vs	3210 sh	1665 vs	1595 vs	332 s
	3265 s	3190 vs	1630 s		
		3130 s			
10 $\mathrm{Pt(acNH_2)(2,6Lu)ClH_2O}$	2648 s*	3253 w	1644 vs br	1580 m	326 s
	3563 s	3185 vs	1621 sh		
	3376 vs	3089 vs	1606 sh		

* νOH of H_2O

Table VI. Characteristic infrared bands and assignments of complexes 1, Pt(acAm)AmCl$_2$

Compound	νOH cm^{-1}	νNH	νC=C	δNH$_2$	νPt-Cl
$\mathrm{Pt[acNH_2C(CH_3)_3][NH_2C(CH_3)_3]Cl}$	3470 m	3293 s	1653 vs	1577 vs	319 s
	3390 s	3245 s	1634 sh	1557 sh	
		3228 s	1618 sh		
		3118 m			
		3075 m			
$\mathrm{Pt[acNH(C_2H_5)_2][NH(C_2H_5)_2]Cl_2}$	3487 vs	3216 m	1623 vs		326 s
	3400 sh	3111 m			
$\mathrm{Pt[acNH(CH_3)_2][2,6\text{-}Lu]Cl_2}$	3465 vs	3050 s	1635 vs		332 s
		3019 m			316 w
$\mathrm{Pt[acNHCH_3(C_2H_5)](NH_2C_2H_5)ICl}$	3480 sv br	3160 sv br	1675 vs br	1606 s br	320 w

* The Pt-I absorption is too low to be observed with our instrument.

Table VII. Infrared band assignments of νOH, νNH, νNH(in cm^{-1}) and their deuterated groups in the complexes.

Compound	νOH	νNH	νNH
1 *trans*-$\mathrm{Ptac(NH(CH_3)_2)Cl_2}$	3505 vs br	3222 vs	
	3430 sh		
2 $\mathrm{Pt(acN(CH_3)_2)(NH(CH_3)_2)Cl}$	3530 s	3334 vs	
	3351 vs		
3 $\mathrm{Pt(acNH(CH_3)_2)(2,6\text{-}Lu)Cl_2}$	3465 s		3050 s
			3019 m
4 Deuterated of 3	2920 m br		2283 m br
	(H/D=1.20)		2260 sh
			(H/D=1.34)
5 $\mathrm{Pt(acNH(C_2H_5)_2)(NH(C_2H_5))Cl_2}$	3487 vs	3216 m	3111 m
	3400 sh		
Deuterated	2588 s	2397 m	2317 m
	2513 m	(H/D=1.34)	(H/D=1.34)
	(H/D=1.35)		
6 *trans*-$\mathrm{Ptac(NHC_2H_5)Cl_2}$	3408 vs br	3190 vs	
7 *trans*-$\mathrm{Ptac''(NH(CH_3)_2)Cl_2}$		3200 vs	

ac″ = $\mathrm{(CH_3)_3CC{\equiv}CC(CH_3)_3}$

Table VIII.* Mass spectra of the complexes m/e.

Compound														
trans-Ptac(NH(C_2H_5)$_2$)Cl_2	481	446	411	392	358	340	322	296	268	238				
Pt(acNH(C_2H_5)$_2$)(NH(C_2H_5)$_2$)Cl_2						319	286	271	256	244	195	180	162	
Pt(acNHCH_3)(N$H_2$$CH_3$)Cl			414			346	327	295	265	255		156	155	
Pt(acNHCH_3)$_2$)(NH_2CH(CH_3)$_2$)Cl	471			370				291	250	234	183	180	152	
Pt(acN(CH_3)$_2$)(NH(CH_3)$_2$)Cl	497**	462	445	410	362	320	315	290	260	240	186	170	152	
*** Pt(acNHC_2H_5)(NH_2H_5)Cl	480		417	380	343			280	240	235	169	156	144	143

* Bands under 142 were not listed. Above 200, only the strongest bands were listed. ** This band is greater than the molecular weight, the spectra were taken around the temperature of the melting point. A disproportionation has probably taken place and some species of Pt(acNH(CH_3)$_2$)Cl_2 were produced. *** This is complex No. 9 in Tables II and V.

was added to a nitromethane solution of complexes 1, there was no apparent change in conductance, however the conductance changed rapidly for complexes 2 (see Figure 1). This is indicative of one free amino group in complexes 2.[15] The νPt-Cl stretching frequencies of complexes 1 (320-335 cm^{-1}) were stronger and broader compared to those of complexes 2 (313-320 cm^{-1}). The intensities and shapes of νPt-Cl bands of complexes 1 are similar to those of PtacAmCl_2 and PtC_2H_4AmCl_2.[16] When formulated the two chlorine atoms in *trans*-position and in order to balance the charges in complexes 1 an ammonium salt is required. A stretching frequency of νN-H was indeed found in the complexes 1, for example the complex Pt(acNH(CH_3)$_2$)(2,6-Lu)Cl_2 (2,6-Lu = 2,6-lutidine) and its deutero-analog (see Table VII). The complexes 1, being non-electrolytes, behave like the olefin complex $PtCl_3^-[Et_3N^+CH_2CH = CH_2]$ reported by Denning and Venanzi.[17]

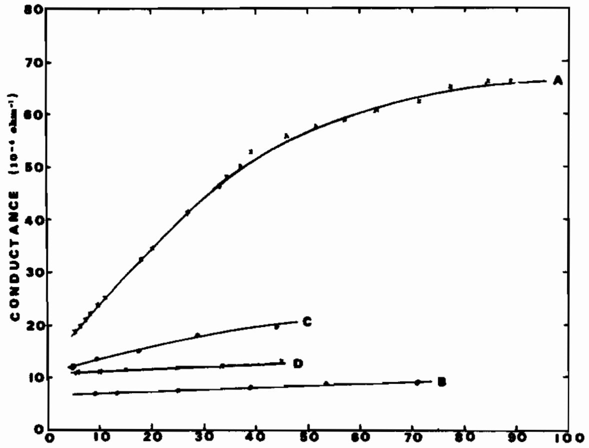

Figure 1. Conductivity changes of the complexes in nitromethane. Pt(acNHC_2H_5)N$H_2$$C_2H_5$Cl, with methyl iodide (A), without methyl iodide (B), Pt(acNH_2C(CH_3)$_3$)NH_2C(CH_3)$_3$$Cl_2$, with methyl iodide (C), without methyl iodide (D). The concentration of each solution is 1 mmole, the mixture of nitromethane and methyl iodide is 23: 2 by volume. The data were taken at 22°C.

Complexes 2 have an usaturated site of cordination. Generally, such complexes have the tendency to pick up a molecule of solvent containing a donor atom or to pick up another molecule of complex and from a bridged complex. However, complexes 2 were isolated from H_2O-amine mixtures and recrystallized from methanol-ether mixtures. We could not find any evidence of the existance of solvent molecule present in the complexes, because they were isolated from solutions with excess amine (e.g., for $NH_2CH(CH_3)_2$, H_2O: amine = 2: 1 by volume; Pt: amine ≈ 1:20 in moles). It is unlikely that the supposedly chlorine bridged complexes could survive under such conditions.[18,19] Only one νPt-Cl stretching frequency was observed in the narrow region of 313-320 cm^{-1}, also a narrow and sharp is not at all indicative of chlorine bridged complexes.[20,21,22] On the other hand, the free (uncoordinated) amino group was found at the *trans*-position of the double bond. It would be impossible sterically to make bridged complexes through the free amino group as in the case of diene complexes.[3] The complexes 2 were found to be monomers in methanol by normal molecular weight measurements (see Table II). From the above results we proposed a structure for complexes 2 in which the oxygen atom of one hydroxyl group of the acetylene occupies the fourth coordinated position and forms a five membered ring (see structure II). We could not take an nmr spectrum to see whether the hydrogen of the one hydroxyl group is lost, because several bands of the amine mask this region. However, it seems unlikely that the hydrogen is lost. If it were, we should have a platinum(III), which would be a very interesting case. The νPt-Cl stretching frequencies are low and thus, we assigned the Cl, as being *trans* to the carbon atom. The two compounds (No. 4 and No. 9 Tables II and V), have the same chemical constitution. The νPt-Cl stretching frequency of No. 9 at 332 cm^{-1} is much higher than that of No. 4 and the chlorine atom of No. 9 is probably not *trans* to the carbon atom.

The reaction of complexes 2 with methyl iodide in nitromethane gave the complexes of type 1, for example,

$$\underset{\text{type 1}}{\mathrm{Pt(acNHC_2H_5)(NH_2C_2H_5)Cl}}\xrightarrow{\mathrm{CH_3I}}$$

$$\underset{\mathrm{A}}{\mathrm{Pt[acNH(CH_3)(C_2H_5)(NH_2C_2H_5)Cl]I}}\rightarrow$$

$$\underset{\mathrm{B}}{\mathrm{Pt(acNH(C_3)(C_2H_5))(NH_2C_2H_5)ICl}}$$

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The compound B isolated from the above reaction is a nonelectrolyte in nitromethane; the methyl group was found by nmr spectra to be linked to the nitrogen. ($\tau NCH_3 = 6.60$, $\tau CH_3I = 7.73$). The conductivity increased rapidly when CH_3I was added to a nitromethane solution of complexes 2. At first, compound A is formed, then it turned into compound B, having the structure of compounds 1.

It is interesting to examine the following reactions:

$$\textit{trans}\text{-Ptac(2,6-Lu)}Cl_2 \xrightarrow[H_2O]{NH(CH_3)_2} \text{Pt(acNH}(CH_3)_2\text{)(2,6-Lu)}Cl_2 \quad \text{type 1} \tag{1}$$

$$\textit{trans}\text{-PtacNH}(CH_3)_2Cl_2 \xrightarrow[H_2O]{NH(CH_3)_2} \text{Pt(acN}(CH_3)_2\text{)NH}(CH_3)_2Cl \quad \text{type 2} \tag{2}$$

$$\textit{trans}\text{-Ptac(2,6-Lu)}Cl_2 \xrightarrow[H_2O]{NH_3} \text{Pt(acNH}_2\text{)(2,6-Lu)ClH}_2O \quad \text{type 2} \tag{3}$$

The formation of the new complexes depends on the nature of the starting complexes ($PtacAmCl_2$) and also on the nature of the amines employed. The complex isolated from reaction (3) contains a molecule of water (No. 10 in Tables II and V). The νOH stretching frequency of crystalline water absorbs at 3648 cm^{-1}, which is much higher than the absorption of the hydroxyl groups of acetylene (see Figure 2).

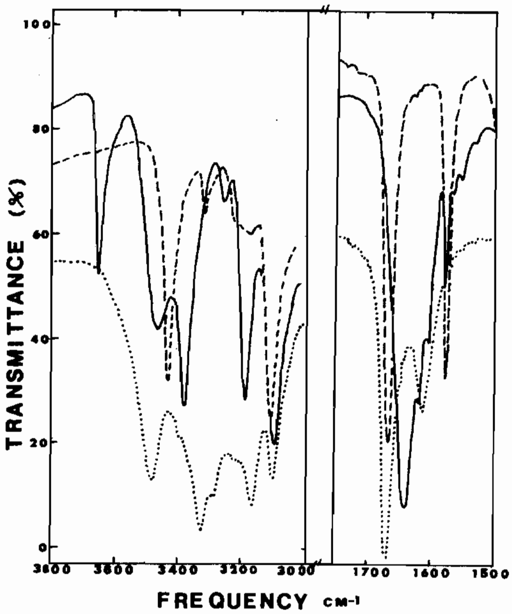

Figure 2. The infrared spectra of $Pt(acNH_2)NH_3Cl$(. . . .), $Pt(acNHCH_3)NH_2CH_3Cl$(- - -) and $Pt(acNH_2)(2.6\text{-}Lu)H_2OCl$ (———).

The complexes with secondary amines gave simple spectra in the νNH stretching frequency region and we were able to distinguish the stretching frequencies of νNH and $\nu\overset{+}{N}H$ by comparison of the spectra of the *trans*-$PtacAmCl_2$ with those of $Pt(acAm)AmCl_2$. For the complex $Pt(acNH(CH_3)_2)(2,6\text{-}Lu)Cl_2$ the $\nu\overset{+}{N}H$ stretching frequency was very clearly shown at 3050 cm^{-1} (see Table VII).

We have tested the following reaction,

$$\text{type 1} \underset{-HCl}{\overset{+HCl}{\rightleftarrows}} \text{type 2}$$

Unfortunately, no pure compounds were isolated. It is also worth mentioning the displacement reactions in which pyridine displaced ammonia from the complex *trans*-$PtacNH_3Cl_2$[11] in water. The reaction is reversible in benzene.

$$\textit{trans}\text{-Ptacpy}Cl_2 \underset{py,\ H_2O}{\overset{NH_3,C_6H_6}{\rightleftarrows}} \textit{trans}\text{-PtacNH}_3Cl_2$$

Attempts to make the analogs of complexes of type 1 or of type 2 with $(CH_3)_3CC\equiv CC(CH_3)_3$ and $(CH_3)_2C(OCH_3)C\equiv CC(OCH_3)(CH_3)_2$ were unsuccessful. This is indicative of the importance of having the hydroxyl groups on the acetylenic ligands for the above nucleophilic reactions.

Experimental Section

Chemicals. Potassium chloroplatinite, K_2PtCl_4 and potassium bromoplatinite, K_2PtBr_4 (water solution, 100-300 g per liter) were obtained from Johnson Matthey and Mallory Ltd. 2,5-dimethyl-3-hexyne-2,5-diol, $(CH_3)_2C(OH)C \equiv C\ C(OH_3)_2$, was purchased from Airco Chemical Co. Methylamine 40% solution in water, ethylamine 70% solution in water, isopropylamine, b.p. 31-32°, tert-butylamine, b.p. 44-45°, and dimethylamine 25% in water, were Eastman Organic Chemicals.

Instruments and analyses. Microanalyses were performed by Chemalytics Inc., Tempe, Arizona, U.S.A. Platinum analyses were carried out by us, using a Lindberg Hevi-Duty Furance. Molecular weights were measured with a Hitachi-Perkin-Elmer 115. Nmr spectra were obtained on a Varian T 60 spectrometer, as solutions in $CDCl_3$ using TMS as internal reference. Conductivities were measured with E 365 B Conductoscope, Metrohm Ltd., Heresau, Switzerland. Mass spectra were obtained on a Hitachi-Perkin-Elmer R.M.U.-6D apparatus. Infrared spectra were obtained as nujol or C_4Cl_6 mulls on a Perkin-Elmer 621 spectrophotometer. Melting points were measured on a Fisher-John appartus and are uncorrected.

Preparations of the complexes. All the complexes were dried under vacuum overnight in the presence of P_2O_5 and $CaCl_2$.

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Potassium (2,5-dimethyl-3-hexyne-2,5-diol)trichloroplatinite $K[PtacCl_3]$, *trans*-(2,5-dimethyl-3-hexyne-2,5-diol)pyridinedichloroplatinite $PtacpyCl_2$, and *trans*-(2,5-dimethyl-3-hexyne-2,5-diol) (2,6-lutidine)dichloroplatinite, $Ptac(2,6\text{-}Lu)Cl_2$, were prepared as described in the literature.[23]

Trans-$PtacAmCl_2$ (Am = NH_3, NH_2CH_3, see Table I). The *trans*-$PtacAmCl_2$ complexes were obtained by the addition of an aqueous solution of amine (0.5 ml of a concentrated NH_4OH or NH_2CH_3 40%) to 20 ml benzene solution of 0.3 g $Ptac(2,6\text{-}LuCl_2$ or $PtacpyCl_2$ at room temperature with constant and vigorous stirring. A yellow precipitate appeared and the benzene solution became slightly yellow (nearly colorless). The precipitate was recrystallized from ether-benzene, washed with benzene, and dried. Yield 90%.

Trans-$PtacAmCl_2$ (Am $\neq$ NH_3, see Table I). The trans-$PtacAmCl_2$ complexes were obtained by the addition of a solution of potassium chloride* at 0°C dropwise with strong agitation. A yellow precipitate appeared immediately with each drop of amine. Amine was added with agitation until the solution became slightly yellow. The compound was washed with cold saturated solution of KCl and dried. The compound was further separated from KCl by extracting it with ether and it was recrystallized from ether by evaporation of from n-haxane-methanol solution Yield 30-60%.

Pt(acAm-H)AmCl (see Table II). The complexes of Pt(acAm-H)AmCl were obtained by the dropwise addition of the amine to a solution of 0.3 g $K[PtacCl_3]$ in 2 ml of water at 0°C. At first, a yellow precipitate appeared. Addition of amine was continued until the yellow precipitate disappeared and the solution became slightly yellow-green. The solution was then left at rom temperature and 40 minutes later withe crystals were formed. The crystals were washed with cold water and dried. Yield 25-40%.

Pt(acAm)AmCl$_2$ (see Table III). The complexes $Pt(acAm)AmCl_2$ were obtained by the dropwise addition of the amine to a solution of 0.3 g $K[PtacCl_3]$ in 2 ml of water at 0°C. A yellow precipitate appeared immediately which disappeared on continued addition of amine and a yellow solution was obtained. The solution was then left at room temperature and a yellow precipitate was formed. The yellow precipitate was washed with cold water and dried. Yield 40-60%.

$Pt[acNH(CH_3)_2](2,6\text{-}Lu)Cl_2$ (see Table III). The complex $Pt[acNH(CH_3)_2](2,6\text{-}Lu)Cl_2$ was obtained by the dropwise addition of 2 ml aqueous solution of $NH(CH_3)_2$ (25%) to a suspension of 0.3 g of *trans*-$Ptac(2,6\text{-}Lu)Cl_2$ in 2 ml of water at 0°C. A new compound was formed on the walls of the beaker which was rubbed with a glass rod and one hour later the yellow precipitate was washed with cold water and dried. Yield 30%.

Trans-$Ptac(NH_2CH_3)Br_2$ (see Tables I and IV). The complexes trans-$PtacNH_2CH_3Br_2$ were obtained by the addition of a few drops of cold aqueous solution of NH_2CH_3 (40%) to a cold solution of $K[PtacBr_3]$ with constant agitation and by using a stirring rod to rub the walls of the beaker until a yellow precipitate appeared. The continued addition of amine solution turned the solution slightly yellow, from which a yellow precipitate was collected by filtration and washed with cold water and dried.

$Pt(acNHCH_3)(NH_2CH_3)Br$ (see Tables II and IV). The complex $Pt(acNHCH_3)NH_2CH_3Br$ was obtained by the addition of one ml of aqueous solution of NH_2CH_3 (40%) to a suspension of *trans*-$PtacNH_2CH_3Br_2$ (0.3 g) in 5 ml of water at 0°C with constant stirring. The suspension was then left at room temperature with a continued agitation until the suspension became ivory in color. The complex was filtered and washed with cold water. It was washed again with methanol and white crystals were obtained. Yield 40%.

$Pt(acNH(CH_2)_xNH_2)Cl$ (x = 6,7,8, see Table II). The complexes $Pt(acNH(CH_2)_xNH_2)Cl$ were obtained by the dropwise addition of an aqueous solution of $NH_2(CH_2)_xNH_2$ (0.3 g in 1.5 ml of water) to a 2 ml ice-cold solution of $K[PtacCl_3]$ (0.3 g) at 0°C. At first, a yellow precipitate appeared, which turned into a slightly yellow paste. The clear supernatant solution was decanted and the paste was washed with cold water three times. The beaker with the paste was transfered to an ice bath, and the compound was rubbed against the walls of the beaker, yielding slightly-yellow crystals which were washed with cold water and dried. Yield 35-40%.

$Pt(acNH_2)(2,6\text{-}Lu)Cl\ H_2O$. The complex $Pt(acNH_2)(2,6\text{-}Lu)Cl\ H_2O$ was obtained by the dropwise addition of 2 ml of an aqueous ammonia ($\sim$6%) to a suspension of 0.3 g of *trans*-$Ptac(2,6\text{-}Lu)\ Cl_2$ in 2 ml of water at 0°C. The yellow color of the suspension decayed and became slightly yellow. One hour later the yellowish compound was filtered and washed with cold water. After being dried completely, it was washed again with carbon tetrachloride yielding white crystals. Yield 20%.

$Pt(acNHC_2H_5)(NH_2C_2H_5)Cl$. (No. 9 in Tables II and V). During the preparation of the complex $Pt(acNHC_2H_5)(NH_2C_2H_5)Cl$ (No. 4 in Tables II and V), the filtrate was left at room temperature overnight and colourless neddle-like crystals were obtained, collected by filtration and washed with cold water.

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(*) The presence of KCl is particularly necessary for the complexes of NH_2CH_3 and $NH(CH_3)_2$. For the other amines KCl improved the yields, however, if KCl is not used the complex can be isolated from water further without further purification.