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Synthesis and Studies of Pt(II) Compounds of the Types K[Pt(amine)Cl_3] and [Pt(amine)(acetonitrile)Cl_2]

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Abstract

Monoamine Pt(II) compounds of the type K[Pt(am)Cl_3] (am = isopropylamine and t-butylamine) have been synthesized from the reaction of K_2PtCl_4 with the amine in aqueous solution in the presence of KCl. The compounds have been characterized by ^1H NMR and IR spectroscopy. The compounds contain $\frac{1}{2}$ molecule of hydration per Pt atom.

The reaction of K[Pt(am)Cl_3] with acetonitrile in aqueous solution produced *cis*-[Pt(am)(CH_3CN)Cl_2]. The *cis* isopropylamine complex isomerized partly to the *trans* compound in acetonitrile and acetone while the *cis* isomer of t-butylamine remained unchanged. A mixture of *cis* and *trans*-[Pt(am)(CH_3CN)Cl_2] was obtained from the cleavage of iodo-bridged dimers in acetonitrile. All the complexes were studied by ^1H NMR and IR spectroscopy. Some hypotheses on the structures of the iodo-bridged dimers are discussed.

Introduction

Although K[Pt(CH_3CN)Cl_3] and *cis*-[Pt(CH_3CN)$_2Cl_2$] [1–4] have been known for many years, few compounds of the type [PtL(CH_3CN)Cl_2] have been reported. Orchin *et al.* [5, 6] prepared *cis* and *trans*-[Pt(Un)(CH_3CN)Cl_2] where Un = C_2H_4 and CO. The *trans* compounds of C_2H_4 were prepared from the reaction of [Pt(C_2H_4)Cl_2]$_2$ with CH_3CN. Because of the large *trans* effect of C_2H_4, only the *trans* isomer was formed. The *cis* compound was obtained from the reaction of K[Pt(CH_3CN)Cl_3] with C_2H_4. The *trans* effect of CH_3CN is not known, but it is expected to be larger than that of chloride. Therefore the formation of the *cis* compound seems at first surprising. The reaction of K_2PtCl_4 with an excess of CH_3CN produces *cis*-[Pt(CH_3CN)$_2Cl_2$] [4]. It is possible that the *trans* isomer is first formed which might isomerize to the *cis* compound as found for sulfoxide complexes [7, 8]. The (d–d)π bonding is more efficient in the *cis* configuration and all disubstituted Pt complexes with sulfoxides have the *cis* geometry except those with very bulky ligands [9]. CH_3CN is bonded to Pt through the lone-pair of electrons on the nitrogen atom. Acetonitrile is expected to accept electron density from the metal much like CO or other unsaturated ligands which possess available empty π orbitals. It is therefore expected that CH_3CN should have a fairly large *trans* effect but this hypothesis has not been confirmed yet.

Courtot *et al.* [10] prepared four complexes [PtL(CH_3CN)Cl_2] where L = methyl derivatives of pyridine from the cleavage of chloro-bridged dimers.

$$[PtLCl_2]_2 + 2CH_3CN \xrightarrow{CHCl_3} 2[PtL(CH_3CN)Cl_2]$$

For L = pyridine, 4-methylpyridine and 2-methylpyridine, the main product was the *cis* isomer, with the formation of 5–10% of the *trans* isomer. With a very bulky ligand, (L = 2,4,6-trimethylpyridine) only the *trans* isomer was obtained. The geometry of the products was determined by NMR of the methyl protons of coordinated CH_3CN. The protons in the *trans* isomer are slightly more deshielded than in the *cis* isomer. The coupling constants $^4J(^{195}Pt-^1H)$ are also slightly different [10].

Primary amine complexes of platinum(II) with nitriles are not known yet. The main objective of this project was to develop a method to synthesize [Pt(am)(CH_3CN)Cl_2] (am = primary amine). We were mostly interested in the synthesis of the *cis* isomer, but we wanted to synthesize also the *trans* isomer mainly for comparison purposes. *cis* Diamino complexes of platinum have interesting antitumor activities against several tumors. We wanted to develop a general method to synthesize *cis*-[Pt(amine)(CH_3CN)Cl_2] in order to eventually determine the antitumor activity of such compounds.

Experimental

K_2PtCl_4 was bought from Johnson Matthey and Co. Limited and was recrystallized from water before use. The elemental analyses were performed by Galbraith Laboratories. The IR spectra were measured on a P.E. 783 or Digilab FT50 (CsI beamsplitter).

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The ^1H NMR spectra were recorded on a Varian EM-360L (concentrations about 0.05 M).

Synthesis of Complexes

K[Pt(am)Cl$_3$] (am = isopropylamine (iprNH$_2$) and t-butylamine (t-buNH$_2$))

Six ml of am is added to a solution containing 3 mmol of K_2PtCl_4, 12 mmol KCl and 10 ml of water. The solution is heated at 60 °C with stirring. When the solution turns yellow, it is immediately evaporated to dryness under vacuum. The dry product is washed with ether and filtered. It is then dissolved in 15 ml of H_2O and the pH neutralized with 1 M HCl if necessary. The precipitate [Pt(am)$_2$-Cl$_2$] is then removed by filtration and the filtrate is evaporated to dryness under vacuum. Acetone is added to the residue and KCl and K_2PtCl_4 are filtered out. The filtrate is evaporated to dryness. The residue is dissolved in 10 ml H_2O and the mixture is filtered. The filtrate is again evaporated to dryness. The yellow powder is washed with ether, filtered and dried. K[Pt(iprNH$_2$)Cl$_3$]: yield 16%, dec. 177–241 °C. K[Pt(t-buNH$_2$)Cl$_3$: yield 36%, dec. 220–257 °C.

cis-[Pt(am)(CH$_3$CN)Cl$_2$]

K[Pt(am)Cl$_3$] (0.33 g) is dissolved in 2 ml of H_2O and the solution is filtered. The filtrate is slightly concentrated by evaporation under reduced pressure. Acetonitrile (8 drops) is then added to the solution and stirred for 10 min. The mixture is left at room temperature (24 h for iprNH$_2$ and 4 h for t-buNH$_2$) and then the pale yellow precipitate is filtered out, washed with water and dried. A second crop can be obtained by adding a few drops of CH_3CN to the above filtrate. *cis*-[Pt(iprNH$_2$)(CH$_3$CN)Cl$_2$]: yield 93%, dec. 168–182 °C. *cis*-[Pt(t-buNH$_2$)(CH$_3$CN)-Cl$_2$]: yield 94%, dec. 225–235 °C.

Mixture cis and trans-[Pt(am)(CH$_3$CN)Cl$_2$]

The iodo-bridged dimers [Pt(am)I$_2$]$_2$ are synthesized according to ref. 11. 0.4 g of the dimers are dissolved in 25 ml of CH_3CN. The mixture is stirred at room temperature in the dark overnight and then filtered. $AgNO_3$ (0.274 g for iprNH$_2$ and 0.267 g for t-buNH$_2$) is dissolved in 5 ml CH_3CN and added to the above filtrate. The mixture is stirred in the dark at room temperature for 2 h. The AgI precipitate is filtered out, and KCl (0.120 g for iprNH$_2$ and 0.117 g for t-buNH$_2$) is added to the filtrate. The solution is stirred again overnight in the dark. The excess Ag^+ precipitates and AgCl is filtered out. An excess of 0.1 g of KCl is again added to the filtrate, stirred for 6 h in the dark and again filtered to remove completely all the silver ions. The filtrate is evaporated to dryness and the residue is cooled in a freezer overnight. The next day a cold aqueous solution 2 M KCl (10 ml) is added to the residue and the yellow compound is filtered, washed with cold water and dried. [Pt(iprNH$_2$)(CH$_3$CN)Cl$_2$]: yield 32%, dec. 127–147 °C. [Pt(t-buNH$_2$)(CH$_3$CN)Cl$_2$]: yield 34%, dec. 138–155 °C.

K[Pt(CH$_3$CN)Cl$_3$]

Three mmol of CH_3CN (0.123 g) are added to 2 mmol of K_2PtCl_4 dissolved in 10 ml of water and stirred overnight at room temperature. The mixture is then filtered to remove [Pt(CH$_3$CN)$_2$Cl$_2$] and the filtrate is evaporated to dryness under reduced pressure. The residue is dissolved in a small quantity of water, filtered and the filtrate is again evaporated to dryness. The residue is dissolved in 40 ml of acetone and filtered to remove KCl and unreacted K_2PtCl_4. The filtrate is evaporated to dryness and the residue is washed with ether, filtered and dried. Yield 37%, dec. 175–268 °C.

Results and Discussion

K[Pt(am)Cl$_3$]

The monoamine complexes were prepared from the reaction of K_2PtCl_4 with the amine in aqueous solution at 60 °C in the presence of KCl. Compounds of isopropylamine (iprNH$_2$) and t-butylamine (t-buNH$_2$) were synthesized.

$$K_2PtCl_4 + am \xrightarrow[60\,°C,KCl]{H_2O} K[Pt(am)Cl_3] + KCl$$

The reaction must be stopped rapidly to reduce the formation of the disubstituted compounds which are insoluble in aqueous medium.

$$K[Pt(am)Cl_3] + am \xrightarrow{H_2O} [Pt(am)_2Cl_2]\downarrow + KCl$$

This method is limited to bulky amines since *cis*-[Pt(am)$_2$Cl$_2$] is formed rapidly with less encumbered ligands. The yield for the synthesis of K[Pt(t-buNH$_2$)-Cl$_3$] is 36% while it is only 16% for the iprNH$_2$ complex.

The results of the elemental analyses have shown that the monoamine complexes crystallize with water of hydration (Table I). The isopropylamine complex has been studied by X-ray diffraction [12]. The oxygen atoms of the water molecules are located on special positions. The chemical formula is therefore K[Pt(iprNH$_2$)Cl$_3$]·$\frac{1}{2}$H$_2$O.

The infrared spectra of the two complexes were measured in the solid state. The main bands are shown in Table II. The two spectra were identical in the ν(O–H) and δ(O–H) regions. We therefore assumed identical structures. Two narrow ν(OH) bonds were observed at 3596 and 3522 cm^{-1}, confirming the presence of molecules of water of hydration. These values of ν(O–H) vibrations are fairly

TABLE I. Elemental Analyses of the Synthesized Complexes

Compound		C (%)	H (%)	Cl (%)
$K[Pt(iprNH_2)Cl_3]\cdot\frac{1}{2}H_2O$	calc.	8.82	2.47	26.03
	obs.	9.03	2.81	25.66
$K[Pt(t\text{-}buNH_2)Cl_3]\cdot\frac{1}{2}H_2O$	calc.	11.37	2.86	25.16
	obs.	11.74	3.35	24.80
$Pt(iprNH_2)(CH_3CN)Cl_2$	calc.	16.40	3.30	19.36
(*cis*)	obs.	16.77	3.57	19.32
(*cis–trans*)	obs.	16.71	3.06	19.12
$Pt(t\text{-}buNH_2)(CH_3CN)Cl_2$	calc.	18.95	3.71	18.65
(*cis*)	obs.	19.12	3.70	18.80
(*cis–trans*)	obs.	18.67	2.92	18.14

high and suggest the absence of hydrogen bonds between the molecules of water and the complex ion $[Pt(am)Cl_3]^-$. The crystal structure determination of $K[Pt(iprNH_2)Cl_3]\cdot\frac{1}{2}H_2O$ [12] has confirmed that the water molecules are not involved in hydrogen bonding. But the O atom is exceptionally close to the potassium ion. Furthermore, there are several Cl atoms in the environment of the K ion suggesting that packing energy around the K ion is an important stabilizing factor in the crystal.

The N–H vibrations appear at lower frequency upon coordination as expected. The values for the ligand (Table II) have been taken from the literature [13]. Coordination through the lone-pair of electrons on the nitrogen atom weakens the N–H bond. The $-NH_2$ groups are also involved in hydrogen bonds with the chlorine atoms as shown in the crystal structure of $K[Pt(iprNH_2)Cl_3]\cdot\frac{1}{2}H_2O$ [12].

The symmetry of the complex ion $[Pt(am)Cl_3]^-$ is approximatively C_{2v}. These compounds should show three ν(Pt–Cl) bands in the far infrared region, two are stretching vibrations of the *cis* bonds A_1 (sym) and B_1 (asym) while the third vibration of symmetry A_1 is the ν(Pt–Cl) *trans* to am [14]. Sometimes the two first vibrations are very close and only two bands are observed. We have observed three bands between 297 and 328 cm^{-1}.

The ^1H NMR spectra of the complexes were measured in D_2O and the results are shown in Table III. All the peaks are shifted towards lower field upon coordination as expected. No $^4J(^{195}Pt-^1H)$ coupling was observed. There seems to be a $^3J(^{195}Pt-^1H)$ coupling in the complex $K[Pt(iprNH_2)Cl_3]$, but the signal of C*H* is a multiplet of low intensity and the coupling constant could not be calculated.

Complexes [Pt(amine)(CH₃CN)Cl₂]

Two methods were developed for the synthesis of $[Pt(am)(CH_3CN)Cl_2]$ where am = $iprNH_2$ and t-$buNH_2$. The first method produced pure *cis* isomers

TABLE II. Main IR Bands (cm^{-1}) in Ligands and Complexes

	ν(O–H)	ν(N–H)	δ(O–H)	δ(N–H)	$\delta(CH_3)+\nu$(C–C)	ν(C≡N)	ν(Pt–Cl)
$iprNH_2$		3375		1600			
		3300					
$K[Pt(iprNH_2)Cl_3]\cdot\frac{1}{2}H_2O$	3597	3278	1586	1565			328
	3521	3262					313
		3229					298
		3204					
		3121					
CH_3CN					2290	2254	
$K[Pt(CH_3CN)Cl_3]$					2342	2316	337
							332
							326
							323sh
cis-$[Pt(iprNH_2)(CH_3CN)Cl_2]$		3238		1575	2338	2309	351
		3200					336
		3121					
t-$buNH_2$		3375		1600			
		3300					
$K[Pt(t\text{-}buNH_2)Cl_3]\cdot\frac{1}{2}H_2O$	3595	3274	1590	1564			325
	3522	3219	1582sh				311
		3198					297
		3126					
		3078					
cis-$[Pt(t\text{-}buNH_2)(CH_3CN)Cl_2]$		3240		1578	2340	2309	342
		3201					321
		3125					

TABLE III. ^{1}H NMR Spectra of the Complexes δ (ppm) and Coupling Constants J (Hz)

Compound	Solvent	Amine					CH_3CN	
		$\delta(-CH_3)$	^3J	$\delta(CH)$	^3J	$\delta(-NH_2)$	δ	$^4J(^{195}Pt-H)$
$iprNH_2$	D_2O	1.04d	7	3.02m	7			
	$CDCl_3$	1.05d		3.12m		1.21s		
CH_3CN	D_2O						2.03s	
	$CDCl_3$						1.97s	
$K[Pt(CH_3CN)Cl_3]$	D_2O						2.53s+d	14.5
$\Delta\delta$							0.50	
$K[Pt(iprNH_2)Cl_3]$	D_2O	1.27d	7	~3.1m	7			
$\Delta\delta$		0.23		0.1				
cis-$[Pt(iprNH_2)(CH_3CN)Cl_2]$	$CDCl_3$	1.35d	7	3.42m		1.52s	2.44s+d	13.5
$\Delta\delta$		0.30		0.30		0.31	0.47	
trans-$[Pt(iprNH_2)(CH_3CN)Cl_2]$[a]	$CDCl_3$	1.35d	7	3.45m		1.62s	2.55s+d	15
$\Delta\delta$		0.30		0.33		0.41	0.58	
t-$buNH_2$	D_2O	1.13s						
	$CDCl_3$	1.13s				1.47s		
$K[Pt(t\text{-}buNH_2)Cl_3]$	H_2O	1.32s						
$\Delta\delta$		0.19						
cis-$[Pt(t\text{-}buNH_2)(CH_3CN)Cl_2]$	$CDCl_3$	1.42s				1.59	2.44s+d	13
$\Delta\delta$		0.29				0.12	0.47	
trans-$[Pt(t\text{-}buNH_2)(CH_3CN)Cl_2]$[a]	$CDCl_3$	1.42s				1.64	2.55s+d	15
$\Delta\delta$		0.29				0.17	0.58	

[a]The values for the amine are for mixtures (~65% *cis*, ~35% *trans*).

while mixtures of *cis trans* isomers were obtained by the second method.

The first method involves the simple reaction of CH_3CN with the monoamine complex $K[Pt(am)Cl_3]$ in aqueous solution.

$$K[Pt(am)Cl_3] + CH_3CN \xrightarrow{H_2O} cis\text{-}[Pt(am)(CH_3CN)Cl_2] + KCl$$

Since the *trans* effect of Cl > amine only the *cis* isomer is produced in aqueous medium. The yield is quantitative. The results of the chemical analyses are shown in Table I. The two compounds (am = $iprNH_2$ and t-$buNH_2$) were characterized by ^{1}H NMR and IR spectroscopy.

The main bands in the IR spectra of the compounds are shown in Table II. Coordination of CH_3CN through the lone-pair of electrons on the nitrogen atom always increases the ν(C=N) frequency because of kinematic coupling (with ν(Pt–N)) and the increased ionic character of the C–N bond [15]. In free CH_3CN, the ν(C=N) vibration absorbs at 2254 cm^{-1} while it increases to 2309 cm^{-1} in coordinated CH_3CN. IR spectroscopy is often a good method to identify *cis* and *trans* isomers of Pt(II) complexes. Two ν(Pt–Cl) bonds are predicted for *cis*-$[Pt(am)_2Cl_2]$ (C_{2v} point group) while only one band ν(Pt–Cl) is expected for *trans* isomers (C_{2h}). Sometimes there is a coincidence of the two vibrations for some *cis* isomers and only one wider band will be observed. The *trans* complexes always show a single ν(Pt–Cl) band. The compounds *cis*-$[Pt(am)(CH_3CN)Cl_2]$ clearly showed two ν(Pt–Cl) bonds at 351, 336 and 342, 321 cm^{-1} for $iprNH_2$ and t-$buNH_2$ respectively. These values agree well with the values (353 and 344 cm^{-1}) found in *cis*-$[Pt(CO)(CH_3CN)Cl_2]$ [5]. Therefore the complexes $[Pt(am)(CH_3CN)Cl_2]$ synthesized from the reaction of $K[Pt(am)Cl_3]$ with CH_3CN in aqueous medium are the *cis* isomers. The substitution reaction can be explained by the kinetic electrostatic theory applied to an S_N2 mechanism [16]. The most readily formed trigonal bipyramid is that in which the amine ligand with its *trans* Cl ligand, is apical and the entering CH_3CN is trigonal with the other two Cl ligands. The loss of a trigonal Cl ligand leads to a *cis* complex.

The ^{1}H NMR spectra of the two compounds *cis*-$[Pt(am)(CH_3CN)Cl_2]$ were measured in $CDCl_3$. The results are shown in Table III. Natural platinum contains ~33% of the isotope 195 of spin $I = ½$. It can therefore couple with protons in its close environment. The coupling will appear as satellites with relative intensities of 1:4:1 (on a low field NMR instrument). The methyl protons of free CH_3CN appear as a singlet at 1.97 ppm in aqueous solution. In $K[Pt(CH_3CN)Cl_3]$, the protons are observed at lower field (δ = 2.53 ppm) with a coupling constant $^4J(^{195}Pt-^1H) = 14.5$ Hz. In the two

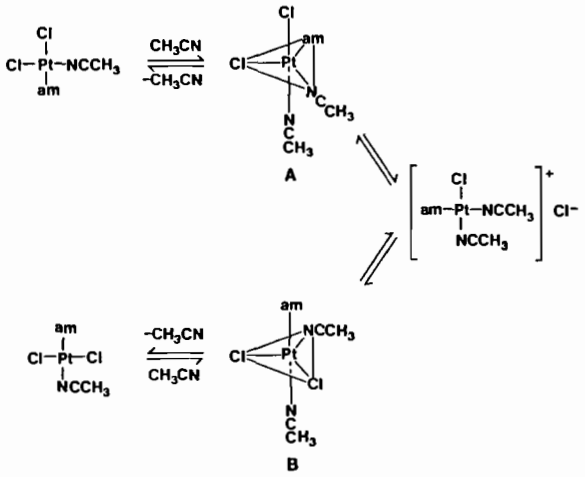


Fig. 1. Suggested mechanism for the isomerization of *cis*-$[Pt(iprNH_2)(CH_3CN)Cl_2]$ in CH_3CN.

TABLE IV. Chemical Shifts δ (ppm) and $^4J(^{195}Pt-^1H)$ (Hz) of Coordinated CH_3CN in Complexes $[PtL(CH_3CN)Cl_2]$[a]

L	*cis*		*trans*		Reference
	δ	^4J	δ	^4J	
pyridine	2.56	14	2.59	12.5	10
2-picoline	2.50	15.	2.56	13	10
4-picoline	2.55	14	2.59	12	10
2,4,6-trimethylpyridine			2.55	12	10
C_2H_4	2.45	13	2.51		5, 6
isopropylamine	2.44	13.5	2.55	15	this work
t-butylamine	2.44	13	2.55	15	this work
Cl	δ = 2.53 ppm and J = 14.5 Hz				this work

[a]Measured in $CDCl_3$, except for L = C_2H_4 measured in CD_3CN and L = Cl measured in D_2O.

cis-$[Pt(am)(CH_3CN)Cl_2]$ complexes the same protons appeared also as a singlet at 2.44 ppm with the platinum coupling satellites. The coupling constants $^4J(^{195}Pt-^1H)$ are 13.5 Hz (Table III).

Cis amine Pt(II) complexes usually isomerize in certain organic solvents to give the *trans* isomers. In an attempt to synthesize *trans* compounds, mainly for comparison purposes, we have tried to isomerize the two synthesized compounds *cis*-$[Pt(am)(CH_3CN)Cl_2]$ in chloroform, acetone and acetonitrile.

For am = t-buNH$_2$, no isomerization occurred even after refluxing for 10 days. For am = iprNH$_2$ no isomerization was seen in chloroform but the compound did isomerize in acetone and in acetonitrile. The ^1H NMR spectrum of the isomerized product in acetonitrile showed two series of peaks for the coordinated acetonitrile protons. The first series was centered at δ = 2.44 ppm with a $^4J(^{195}Pt-^1H)$ coupling constant of 13.5 Hz as observed for the pure *cis* complex. A second and new series of peaks appeared at δ = 2.55 ppm with a $^4J(^{195}Pt-^1H)$ = 15 Hz. This last resonance was assigned to the methyl protons in *trans*-$[Pt(iprNH_2)(CH_3CN)Cl_2]$. The proportion of the two isomers was 65% *cis* and 35% *trans* in both acetone and acetonitrile. Attempts to increase the proportion of the *trans* isomer were not successful. Each trial gave about the same proportion of isomers. After two weeks in acetonitrile or acetone, the complexes started to decompose. It is difficult at the moment to explain why *cis*-$[Pt(iprNH_2)(CH_3CN)Cl_2]$ partly isomerizes to the *trans* isomer while the corresponding compound of t-butylamine does not isomerize. The suggested mechanism for the isomerization in CH_3CN is shown in Fig. 1. This mechanism is similar to the one suggested by Anderson and Cross [17]. In the first step, the ionic complex $[Pt(iprNH_2)(CH_3CN)_2Cl]^+Cl^-$ is formed. The second step involves the attack of Cl^- on the ionic complex. If intermediate A is formed, the original *cis* compound is reformed, but if intermediate B is formed, the *trans* compound is obtained.

Our ^1H NMR results on the *cis* and *trans* compounds have been compared with the values reported in the literature (Table IV). We can observe that the chemical shifts of the $-CH_3$ protons (of CH_3CN) in the *trans* compounds always appear at lower field than in the *cis* compounds as observed for our complexes. But our coupling constants $^4J(^{195}Pt-^1H)$ are different from those observed in the work of Courtot *et al.* [10]. These authors have observed slightly larger values for the *cis* compounds (14–15 Hz *versus* 12–13 Hz). We have observed larger values for the *trans* complexes (15 Hz *versus* 13 Hz). The difference is probably caused by the second ligand. All Courtot's ligands are pyridine or methyl derivatives of pyridine. The aromatic nature of the pyridine ligands should have an influence on the chemical shifts as well as on the coupling constants. Our values (δ and ^4J) on the two *cis* compounds agree very well with the values obtained for the complex *cis*-$[Pt(C_2H_4)(CH_3CN)Cl_2]$ [5] (Table IV).

The second method which we have developed for the synthesis of $[Pt(am)(CH_3CN)Cl_2]$ is based on the cleavage of halogen-bridged dimers. In the 1950s, Chatt and Venanzi [18–20] prepared mixed-ligand complexes from the cleavage of chloro-bridged dimers (L and L′ = pyridine, aniline, toluidine, PR_3, AsR_3, R_2S, R_2Se, etc.).

$$[PtLCl_2]_2 + 2L' \xrightarrow{\text{acetone}} 2[PtLL'Cl_2]$$

Depending on the ligands, the authors [18–20] obtained mixtures of *cis–trans* isomers or pure *trans* complexes.

In 1978 Courtot *et al.* [10] also prepared mixed-ligand complexes by a similar method. The authors prepared CH_3CN complexes from the cleavage of chloro-bridged dimers (py = methylpyridine derivatives).

$$[Pt(py)Cl_2]_2 + 2\ CH_3CN \xrightarrow{CHCl_3} [Pt(py)(CH_3CN)Cl_2]$$

We have made several attempts to isolate chloro-bridged dimers with amines but were not successful. Recently our research group has reported the synthesis of iodo-bridged dimers with amine ligands [11]. We have therefore tried to cleave the dimers $[Pt(am)I_2]_2$ (am = $iprNH_2$ and t-$buNH_2$) with acetonitrile, and then convert the iodo ligands to chloro ligands by the standard methods. Since the dimers $[Pt(am)I_2]_2$ and $[Pt(am)(CH_3CN)I_2]$ are insoluble in water, the cleavage could not be performed in aqueous medium. The reaction was done directly in CH_3CN. The new method developed for the synthesis of $[Pt(am)(CH_3CN)Cl_2]$ is therefore as follows:

$$[Pt(am)I_2]_2 + 2CH_3CN \xrightarrow{CH_3CN} [Pt(am)(CH_3CN)I_2]$$

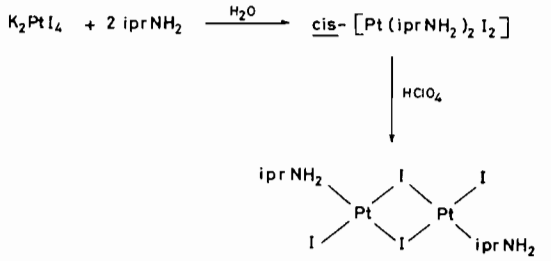
$$[Pt(am)(CH_3CN)I_2] \xrightarrow{Ag^+,\ -AgI} \text{solvolyzed species} \xrightarrow[H_2O]{KCl} [Pt(am)(CH_3CN)Cl_2]$$

The step involving the precipitation of the iodo ligands is critical and all the silver ions must be completely removed before isolating the final product.

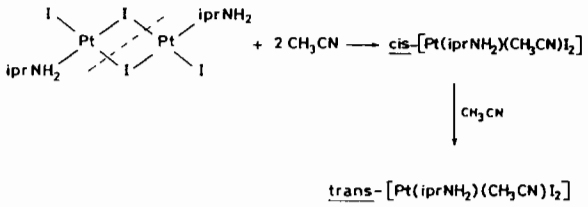
The results of the chemical analysis of the two complexes (am = $iprNH_2$ and t-$buNH_2$) have confirmed the right composition. The ^1H NMR spectra of the two compounds measured in $CDCl_3$ have shown the presence of two isomers, since there are two series of signals for the resonance of the methyl protons of coordinated CH_3CN. The first series was centered at $\delta = 2.44$ ppm with $^4J(^{195}Pt-^1H) = 13.5$ Hz and the second series was centered at $\delta = 2.55$ ppm with $^4J(^{195}Pt-^1H) = 15$ Hz similarly to the isomerized product of *cis*-$[Pt(iprNH_2)(CH_3CN)Cl_2]$. The peaks centered at $\delta = 2.44$ ppm are caused by the *cis* isomers while those at $\delta = 2.55$ ppm are from the *trans* isomers. It is interesting to note that both $iprNH_2$ and t-$buNH_2$ compounds gave the same pattern. The proportion of the *cis*-isomer is 70% ($iprNH_2$) and 60% (t-$buNH_2$) and 30% and 40% respectively for the *trans* compound.

Since the cleavage of the iodo-bridged dimer was performed in acetonitrile, it is not surprising that a mixture of isomers is obtained with $iprNH_2$. We can assume that *cis*-$[Pt(iprNH_2)(CH_3CN)I_2]$ is first formed and then partial isomerization occurs in acetonitrile. A mixture of isomers is obtained in the same proportion as in the previous isomerization experiment.

The iodo-bridged dimer of $iprNH_2$ is probably the *trans* isomer. It was synthesized from the *cis* disubstituted complex [11].

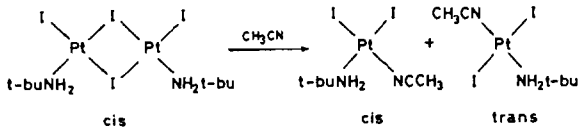


It was not possible to determine with certainty the configuration of the dimer since the $\nu(Pt-I)$ vibrations absorb below 200 cm^{-1} and the compounds are too insoluble for NMR studies. But from the synthetic procedure since the starting compound is the *cis* isomer, we can suggest that it has the *trans* configuration as observed in the chloro-bridged dimer $[Pt(2,6\text{-lutidine})Cl_2]_2$ [21]. The cleavage of the *trans* dimer will first produce the *cis* compound (the *trans* effect of I > amine) which will partly isomerize in acetonitrile.



The isolation of a mixture of isomers of $[Pt(t\text{-}buNH_2)(CH_3CN)Cl_2]$ cannot be explained by the same reasoning, since we have shown that the *cis* compound does not isomerize in acetonitrile. But we know that the formation of the iodo-bridged dimer of t-$buNH_2$ does not follow the same pattern as $iprNH_2$ or other amines. K_2PtI_4 usually reacts with amines in aqueous solution to form insoluble yellow *cis*-$[Pt(am)_2I_2]$ which, in the presence of perchloric acid, can be transformed to the *trans* iodo-bridged dimer. But with t-butylamine, which is a very bulky ligand, the reactions are different. We have tried to isolate *cis*-$[Pt(t\text{-}buNH_2)_2Cl_2]$ by several methods without success. The reaction of K_2PtCl_4 with t-$buNH_2$ in aqueous solution produced *trans*-$[Pt(t\text{-}buNH_2)_2Cl_2]$ [22]. Because of steric hindrance, the *cis* isomer which is usually obtained in these conditions cannot be isolated. Similarly the reaction of K_2PtI_4 with t-$buNH_2$ does not produce yellow *cis*-$[Pt(t\text{-}buNH_2)_2I_2]$. The product obtained is brownish in colour which is indicative of the formation of iodo-bridged dimers. It also contains *trans*-$[Pt(t\text{-}buNH_2)I_2]$. The brownish

precipitate can be completely converted to the iodo-bridged dimers which can now be a mixture of isomers. The cleavage of the *trans* isomer will produce *cis*-[Pt(t-buNH$_2$)(CH$_3$CN)I$_2$] similar to the reaction of isopropylamine, but will not isomerize. The cleavage of a *cis* isomer will produce a mixture of *cis* and *trans* isomers as shown below:



Since *cis*-[Pt(t-buNH$_2$)(CH$_3$CN)I$_2$] does not isomerize in acetonitrile, a 50:50% mixture of *cis* and *trans* iodo-bridged dimers will produce 75% of *cis* and 25% of *trans*-[Pt(t-buNH$_2$)(CH$_3$CN)I$_2$]. We have obtained 60% of *cis* and 40% of the *trans* complex. From this reasoning, we can calculate that about 20% of the iodo-bridged dimers have the *trans* configuration while 80% of the dimers have the *cis* configuration.

We have made several attempts to separate *cis* and *trans*-[Pt(am)(CH$_3$CN)Cl$_2$] in order to characterize the *trans* compounds but we were not successful.

We have tried another method to synthesize [Pt(am)(CH$_3$CN)Cl$_2$] as follows:

$$K_2PtCl_4 + CH_3CN \xrightarrow{H_2O} K[Pt(CH_3CN)Cl_3]$$

$$K[Pt(CH_3CN)Cl_3] \xrightarrow[H_2O]{am} [Pt(am)(CH_3CN)Cl_2]$$

K[Pt(CH$_3$CN)Cl$_3$] has been isolated and characterized (Tables II and III). But its reaction with the two amines at room temperature resulted in decomposed products. When the reaction was done in ice close to 0 °C, we were able to isolate a yellow product but the results of the chemical analysis indicated a mixture of several products including [Pt(am)$_2$Cl$_2$] and [Pt(am)(CH$_3$CN)Cl$_2$]. We were unable to separate and purify the products. The reaction of K[Pt(CH$_3$CN)Cl$_3$] with amines was done in other solvents but again without success.

We are continuing this project since it is important to isolate pure *trans*-[Pt(am)(CH$_3$CN)Cl$_2$].
Our assignment of the configuration of the *cis* isomers was based on IR spectroscopy. We believe that *trans* compounds would show only one ν(Pt–Cl) band in the IR spectrum but this still remains to be verified. We have also tried to prepare adequate crystals for X-ray diffraction studies but without success.

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