Available online at www.sciencedirect.com
ScienceDirect
Inorganica Chimica Acta 360 (2007) 2255–2264
Inorganica Chimica Acta
www.elsevier.com/locate/ica

Synthesis and characterization of complexes of the type $[Pt(amine)_4]I_2$ and *trans*-$[Pt(CH_3NH_2)_2(H_3C{-}N{=}C(CH_3)_2)_2]I_2$ by crystallography and multinuclear magnetic resonance spectroscopy

Fernande D. Rochon *, Christian Tessier, Viorel Buculei

Chemistry Department, Université du Québec á Montréal, C.P. 8888, Succ. Centre-ville Montréal, Que., Canada H3C 3P8

Received 10 October 2006; accepted 5 November 2006
Available online 11 November 2006

Abstract

Complexes of the type $[Pt(amine)_4]I_2$ were synthesized and characterized mainly by multinuclear (^{195}Pt, ^{1}H and ^{13}C) magnetic resonance spectroscopy. The compounds were prepared with different primary amines, but not with bulky amines, due to steric hindrance. In ^{195}Pt NMR, the signals were observed between −2715 and −2769 ppm in D_2O. The coupling constant $^3J(^{195}Pt–^1H)$ for the $MeNH_2$ complex is 42 Hz. In ^{13}C NMR, the average values of the coupling constants $^2J(^{195}Pt–^{13}C)$ and $^3J(^{195}Pt–^{13}C)$ are 18 and 30 Hz, respectively. The crystal structure of $[Pt(EtNH_2)_4]I_2$ was determined by X-ray diffraction methods. The Pt atom is located on an inversion center. The structure is stabilized by H-bonding between the amines and the iodide ions. The compound with n-$BuNH_2$ was found by crystallographic methods to be $[Pt(n\text{-}BuNH_2)_4]_2I_3(n\text{-}BuNHCOO)$. The crystal contains two independent $[Pt(CH_3NH_2)_4]^{2+}$ cations, three iodide ions and a carbamate ion formed from the reaction of butylamine with CO_2 from the air. When the compound $[Pt(CH_3NH_2)_4]I_2$ was dissolved in acetone, crystals identified as *trans*-$[Pt(CH_3NH_2)_2(H_3C{-}N{=}C(CH_3)_2)_2]I_2$ were isolated and characterized by crystallographic methods. Two *trans* bonded $MeNH_2$ ligands had reacted with acetone to produce the two N-bonded Schiff base Pt(II) compound.

Keywords: X-ray crystal structures; Platinum complexes; Amine; IR; NMR; *n*-Butylcarbamate; Imine; Schiff base

1. Introduction

The antitumor complex *cisplatin*, *cis*-$Pt(NH_3)_2Cl_2$ has been known for several decades and the compound is nowadays one of the most widely used anticancer drug. Its chemistry and its mechanism of action have been studied by many authors. Hambley has published a good review of the influence of structure on the activity of Pt drugs [1]. If the ligand NH_3 is replaced by primary amines, the antitumor activity can increase with some amines [2–5], but several of these neutral amine compounds have a more limited activity spectrum. In addition, several of the most active complexes (for example, those with cyclic amines) are too insoluble to be useful anticancer drugs [6].

Most Pt(II)-amine compounds which have antitumour properties have the *cis* configuration, although some *trans* Pt(II) complexes have been shown to possess some anticancer activity, but they seem more limited at the moment. Our research group has recently undertaken a systematic study of complexes of the types *cis*- and *trans*-$Pt(amine)_2I_2$ with different types of amines in order to determine the purity of the complexes and find an easy method to determine the geometry of the compounds [7,8]. We have transformed the diiodo compounds into the dinitrato species and again these were studied by different methods, mainly by IR and multinuclear magnetic resonance [8,9]. Finally, the aqueous reactions of the dinitrato compounds were studied at different pH in order to determine the different species present in solution, especially at neutral pH, where

---

* Corresponding author. Tel.: +1 514 987 3000 4896; fax: +1 514 987 4054.
E-mail address: rochon.fernande@uqam.ca (F.D. Rochon).

0020-1693/$ - see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.ica.2006.11.005

hydroxo-bridged oligomers are formed [8,10]. These oligomers, especially the hydroxo-bridged dimers have been shown to be quite toxic and might be partly responsible for the toxicity of *cisplatin* [11,12].

The *trans*-Pt(amine)$_2$X$_2$ isomers are usually prepared from the tetrasubstituted complex $[Pt(amine)_4]^{2+}$ which have not been much studied in the literature. The synthesis of $[Pt(NH_3)_4]^{2+}$ has been reported by Kaufmann [13] in the sixties and a few crystal structures have been published with the cations $[Pt(amine)_4]^{2+}$. In the latter papers, the anions were usually fairly large like $[MX_4]^{2-}$ (M = Pt or Pd) [14,15]. The only crystal structure reported with a smaller anion like I^-, Br^- or Cl^- is the mixed-valent salt $[Pt(EtNH_2)_4][Pt(EtNH_2)_4Br_2]X_4$ [16–19]. The compounds $[Pt(amine)_4]X_2$ are more soluble and usually more difficult to isolate than the $[Pt(amine)_4]$ $[MX_4]$ complexes.

We have now isolated several tetrasubstituted complexes $[Pt(amine)_4]I_2$, which were characterized mainly by IR and multinuclear (^{1}H, ^{13}C and ^{195}Pt) magnetic resonance spectroscopies. Complexes with several primary amines were studied. Amines cannot accept electron density from the metal. Therefore the σ bonds (ligand → Pt) should cause a deshielding effect on the ligand and a shielding effect on the metal. The strength of the σ bond should then be related to the pK_a value of the protonated amine or the proton affinity of the ligand, although few of the latter values have been reported in the literature.

We have succeeded in obtaining stable single crystals of $[Pt(EtNH_2)_4]I_2$ and we have obtained adequate crystals of the *n*-BuNH$_2$ complex from aqueous solutions. The crystal structure determination of the latter compound has shown that the compound was not as expected. Since the crystal quality was poor with the other amines, we have tried other solvents for their recrystallization. In acetone, we obtained good crystals for the methylamine complex. The crystallographic results on the compound have shown that the structure was quite different, since the amine had partly reacted with the solvent. All these structures will be discussed below.

2. Experimental

$K_2[PtCl_4]$ was obtained from Johnson Matthey and was recrystallized in water before use. The amines were bought from Aldrich and D$_2$O was purchased from CDN Isotopes.

The NMR spectra were measured on a Varian Gemini 300 BB in D$_2$O. The fields were 300.075, 75.460 and 64.311 MHz, respectively, for ^{1}H, ^{13}C and ^{195}Pt. The external reference used for ^{195}Pt was K[Pt(DMSO)Cl$_3$] (in D$_2$O), adjusted at −2998 ppm from $K_2[PtCl_6]$ (δ (Pt) = 0 ppm in D$_2$O).

2.1. Synthesis

The compounds $[Pt(amine)_4]I_2$ were synthesized by a modified version of Kaufmann method described to prepare $[Pt(NH_3)_4]Cl_2$ [13]. The amine (10–12 mmol) is slowly added to the $K_2[PtI_4]$ solution (0.5 mmol of $K_2[PtCl_4]$ dissolved in 5 mL of water with 3 mmol de KI). A yellow precipitate forms immediately. The mixture is stirred for several days until a colourless solution is obtained. The solution is slightly concentrated at room temperature until a white precipitate forms. With some amines, slight heating is required to obtain the tetrasubstituted compound in a larger yield. The precipitate is filtered, washed with cold water, dried in air and in a dessicator under vacuum. The complexes $[Pt(amine)_4]I_2$ were isolated for six aliphatic amines, methylamine (MeNH$_2$), ethylamine (EtNH$_2$), *n*-propylamine (*n*-PrNH$_2$), *n*-butylamine (*n*-BuNH$_2$), *iso*-propylamine (*iso*-PrNH$_2$) and *iso*-butylamine (*iso*-BuNH$_2$) and two cyclic amines, cyclopropylamine (*cyclo*-PrNH$_2$) and cyclobutylamine (*cyclo*-BuNH$_2$).

$[Pt(MeNH_2)_4]I_2$: yield = 75%; m.p. = 148–155 °C (dec.). IR (cm^{-1}): ν(N–H) 3150 s, ν(C–H) 2970 m, 2885 m, δ(N–H) 1585 s, δ(C–H) 1470 m 1435 s 1390 m, ν(C–N) 1195 m 1170 m, ν(Pt–N) 580 w, other bands 1325 m, 1280 m, 1025 w, 980 m, 710 w. NMR (δ (ppm)): ^{1}H: H$_1$ 2.500 s + d $^3J(^{195}Pt-H_1) = 42$ Hz, ^{13}C: C$_1$ 32.878, $^2J(^{195}Pt-C_1) = 19$ Hz.

$[Pt(EtNH_2)_4]I_2$: yield = 81%; m.p. = 134–162 °C (dec.). IR (cm^{-1}): ν(N–H) 3144 s, ν(C–H) 2963 m 2870 m, δ(N–H) 1523 s, δ(C–H) 1415 s, 1403 s, 1393 m, ν(C–N) 1218 m, 1190 m, ν(Pt–N) 587 m, other bands 1338 m, 1315 m, 1292 m 1031 m, 1020 m, 985 m, 970 m, 830 m, 708 s, 675 s. NMR (δ (ppm)): ^{1}H: H$_1$ 2.756q $^3J(H-H_1) = 7.2$ Hz, H$_2$ 1.263 t $^3J(H-H_1) = 7.2$ Hz, ^{13}C: C$_1$ 41.362 $^2J(^{195}Pt-C_1) = 20$ Hz, C$_2$ 15.529 $^3J(^{195}Pt-C_2) = 34$ Hz.

$[Pt(n\text{-}PrNH_2)_4]I_2$: yield = 71%; m.p. = 132–153 °C (dec.). IR (cm^{-1}): ν(N–H) 3110 s, ν(C–H) 2972 s, 2880 s, δ(N–H) 1610 s, δ(C–H) 1475 s, 1393 m, ν(C–N) 1265 m, 1215 m, ν(Pt–N) 590 m, other bands 1335 m, 1315 m, 1105 m, 1047 m, 995 s, 961 s, 896 m, 747 s, 400 s. NMR (δ (ppm)): ^{1}H: H$_1$ 2.658 t $^3J(H-H_1) = 7.5$ Hz, H$_2$ 1.677 tq $^3J(H-H_1) = 7.5$, 7.2 Hz, H$_3$ 0.931 t $^3J(H-H_1) = 7.2$ Hz, ^{13}C: C$_1$ 48.131 $^2J(^{195}Pt-C_1) = 17$ Hz, C$_2$ 23.983 $^3J(^{195}Pt-C_2) = 30$ Hz, C$_3$ 10.369.

$[Pt(n\text{-}BuNH_2)_4]I_2$: yield = 69%; m.p. = 99–122 °C (dec.). IR (cm^{-1}): ν(N–H) 3150 s, ν(C–H) 2960 s, 2925 s, 2870 s, δ(N–H) 1575 s, δ(C–H) 1470 s, 1375 m, ν(C–N) 1240 m, ν(Pt–N): 580 m, other bands 1630 w, 1360 m, 1305 m, 1110 m, 1090 w, 1055 w, 980 w, 955 w, 895 w, 735 m. NMR (δ (ppm)): ^{1}H: H$_1$ 2.698 t $^3J(H-H_1) = 7.5$ Hz, H$_2$ 1.656 tt $^3J(H-H_1) = 7.5$, 7.2 Hz, H$_3$ 1.368 tq $^3J(H-H_1) = 7.5$, 7.2 Hz, H$_4$ 0.910 t $^3J(H-H_1) = 7.2$ Hz, ^{13}C: C$_1$ 46.204 $^2J(^{195}Pt-C_1) = 14$ Hz, C$_2$ 32.680 $^3J(^{195}Pt-C_2) = 29$ Hz, C$_3$ 19.415, C$_4$ 13.116.

$[Pt(iso\text{-}PrNH_2)_4]I_2$: yield = 74%; m.p. = 141–162 °C (dec.). IR (cm^{-1}): ν(N–H) 3145 s, ν(C–H) 2965 s, 2890 m, δ(N–H) 1590 s, δ(C–H) 1460 m, 1385 m, ν(C–N) 1235 m, 1220 m, ν(Pt–N): 578 m, other bands 1315 m, 1110 w, 1060 w, 980 m, 885 w, 755 w. NMR (δ (ppm)): ^{1}H: H$_1$ 2.934 h $^3J(H-H_1) = 6.3$ Hz, $^3J(^{195}Pt-H_1) = 41$ Hz, H$_2$ 1.357 d, $^3J(H-H_1) = 6.6$ Hz, ^{13}C: C$_1$ 48.799, $^2J(^{195}Pt-C_1) = 15$ Hz, C$_2$ 22.845, $^3J(^{195}Pt-C_2) = 30$ Hz.

[Pt(*iso*-$BuNH_2$)$_4$]I_2: yield = 65%; m.p. = 102–118 °C (dec.). IR (cm^{-1}): ν(N–H) 3090 s, ν(C–H) 2965 s 2875 s, δ(N–H) 1605 m, δ(C–H) 1473 s, 1395 s, 1378 s, ν(C–N) 1265 s, 1215 m, ν(Pt–N): 585 m, other bands 1345 m, 1315 m, 1175 m, 1125 m, 1005 s, 942 m, 815 w, 775 w, 715 w, 480 w, 445 w, 400 w. NMR (δ (ppm)): ^{1}H: H_1 2.574 d, $^3J(H–H_1) = 6.6$ Hz, H_2 1.855 th, $^3J(H–H_1) = 6.9$, 6.0 Hz, H_3 0.944, $^3J(H–H_1) = 6.6$ Hz, ^{13}C: C_1 53.853, $^2J(^{195}Pt–C_1) = 20$ Hz, C_2 29.265, $^3J(^{195}Pt–C_2) = 28$ Hz, C_3 19.157.

[Pt(*cyclo*-$PrNH_2$)$_4$]I_2: yield = 65%. NMR (δ (ppm)): ^{1}H: H_1 2.523tt, $^3J = 3.3$ Hz, H_2 0.823m, $J = 7.3$ Hz, $H_{2'}$ 0.716 m, $J = 3.5$ Hz.

[Pt(*cyclo*-$BuNH_2$)$_4$]I_2: yield = 65%. NMR (δ (ppm)): ^{1}H: H_1 3.387tt, $^3J = 8.0$ Hz, H_2 2.343 m, $H_{2'}$ 2.002 m, $H_{3,3'}$ 1.707 m.

2.2. Crystal structures

The crystallographic study of the $EtNH_2$ (**I**), *n*-$BuNH_2$ (**II**) and the $MeNH_2$ (**III**) complexes were made at room temperature on a Bruker P4 diffractometer using graphite-monochromatized Mo Kα ($\lambda = 0.71073$ Å) radiation. The crystals were selected after examination under a polarizing microscope for homogeneity. The cell dimensions were determined at room temperature, from a least-squares refinement of the angles 2θ, ω and χ obtained for well-centered reflections. The data collections were made by the $2\theta/\omega$ scan technique using the XSCANS program [20]. The coordinates of the Pt atoms were determined by direct methods. All the other non-hydrogen atoms were found by the usual Fourier methods. For crystal **II**, there are two independent cations in the unit cell. Three iodide ions were easily found but the fourth ion was found different. After many trials, the residual electronic density was assigned to a *n*-butylcarbamate ion. Two C atoms (C63 and C64) on one of the butyl chains were found to be disordered on two positions with 70:30 proportions in crystal **II**. For crystal **III**, two ligands in *trans* positions were found to be rearranged to imine ligands, which are disordered on two positions (proportions 63–37). The refinement of all the structures was done on F^2 by full matrix least-squares analysis. The hydrogen atom positions were fixed in their calculated position with $U_{eq} = 1.2\ U_{eq}$ (or 1.5 for methyl groups) of the carbon to which they are bonded. Corrections were made for absorption (from ψ-scans), Lorentz and polarization effects. The residual peaks were located in the close environment of the platinum atoms. The calculations were done using the Bruker SHELXTL system [21]. The pertinent crystal data and the experimental details are summarized in Table 1.

3. Results and discussion

3.1. Synthesis

The tetrasubstituted complexes $[PtL_4]X_2$ (X = Cl or I) have been used as intermediates in the preparation of the compounds *trans*-PtL_2X_2. In the literature, the $[PtL_4]I_2$ compounds were synthesized from the reaction of $[PtL_4]Cl_2$ (L = pyridine and its derivative) with potassium iodide [22]. The intermediate $[PtL_4]Cl_2$ was synthesized by Kaufmann method [13] with a large excess of ligand (Pt:L ~20)

$$K_2[PtCl_4] \xrightarrow[\Delta]{L/H_2O} [PtL_4]Cl_2 \xrightarrow[-KCl]{KI/H_2O} [PtL_4]I_2$$

Table 1
Crystallographic data for the three crystals

Crystal	I	II	III
Name	$[Pt(EtNH_2)_4]I_2$	$[Pt(n\text{-}BuNH_2)_4]I_3$ (n-BuNHCOO)	$[Pt(MeNH_2)_2(H_3C{-}N{=}C(CH_3)_2)_2]I_2$
Chemical formula	$C_8H_{28}I_2N_4Pt$	$C_{37}H_{98}I_3N_9O_2Pt_2$	$C_{10}H_{28}I_2N_4Pt$
M_w	629.23	1472.12	653.25
Space group	$P\bar{1}$	$P2_1/n$	*Pbca*
Unit cell dimensions			
a (Å)	7.3094(9)	17.547(4)	12.912(3)
b (Å)	7.7600(16)	16.369(4)	11.082(3)
c (Å)	8.5369(12)	21.209(5)	13.229(3)
α (°)	92.205(14)	90	90
β (°)	113.391(10)	98.92(1)	90
γ (°)	97.860(14)	90	90
V (Å^3)	437.95(12)	6018(2)	1892.9(8)
Z	1	4	4
ρ_{calc} (g cm^{-3})	2.386	1.625	2.292
μ (Mo Kα) (mm^{-1})	11.519	6.216	10.665
$F(000)$	288	2856	1200
Measured reflections	4012	21503	16164
Independent reflections (R_{int})	2006 (0.026)	10591 (0.088)	2173 (0.083)
$R_1(I > 2\sigma(I))$	0.0317	0.0671	0.0351
wR_2 (all data)	0.0866	0.1640	0.0853
S	1.052	0.972	1.126

$R_1 = \sum(|F_o - F_c|)/\sum|F_o|$, $wR_2 = [\sum(w(F_o^2 - F_c^2)^2)/\sum(w(F_o^2)^2)]^{1/2}$.

The product usually contains an impurity of the type $[PtL_4][PtX_4]$ which cannot be separated from the main complex. In order to eliminate the formation of this impurity, the method was modified in our laboratories and the results have shown a great purity of the products. The starting material is now $K_2[PtI_4]$ instead of the tetrachloro salt. A large excess of amine is used. The cis yellow diiodo species is formed immediately and slowly react with the excess ligand to form the white tetrasubstituted compound. The total time of reaction is 2–4 days, depending on the amine.

$$K_2[PtI_4] \xrightarrow[-2KI]{\text{amine/ } H_2O} cis\text{-}Pt(amine)_2I_2 \downarrow \xrightarrow[\Delta]{\text{amine/}H_2O} [Pt(amine)_4]I_2$$

This type of compound cannot be prepared with bulky amines. For dimethylamine and *sec*-butylamine, the reaction with an excess amine produced *trans*-$Pt(amine)_2I_2$ as shown by multinuclear magnetic resonance spectroscopy [7]. For these more bulky amines, the ionic trisubstituted species $[Pt(amine)_3I]I$ probably formed but readily decomposed to the insoluble more stable neutral *trans*-Pt $(amine)_2I_2$ compound. For the more sterically demanding ligands like diethylamine and *t*-butylamine, it has been shown that it is not possible to coordinate 2 amine ligands in *cis* position [7]. The reaction of these amines with $K_2[PtI_4]$ produces the iodo-bridged dimers I(amine)Pt-$(\mu\text{-}I)_2$Pt(amine)I, which can be rearranged to *trans*-$Pt(amine)_2I_2$ when heated for 20 min at about 50–60 °C [23].

The yields (between 65% and 81%) and the decomposition points of the compounds $[Pt(amine)_4]I_2$ are listed in Section 2. The decomposition points are related to the transformation of the white ionic complexes into the yellow neutral *trans*-$Pt(amine)_2I_2$ compounds. The latter complexes decompose at much higher temperatures [7]. The compounds $[Pt(amine)_4]I_2$ decompose at lower temperature as the length of the alkyl group increases (148–155 °C for $MeNH_2$ and 99–122 °C for *n*-$BuNH_2$). Ramification of the alkyl group increases the stability of the complexes as expected (132–153 °C for *n*-$PrNH_2$ and 141–162 °C for *iso*-$PrNH_2$).

3.2. IR spectroscopy

The IR spectra were measured in the solid state in KBr pellets. All the compounds have shown a large band around 3100 cm^{-1} corresponding to ν(N–H) vibrations. The deformation mode was observed as a single very intense band around 1600 cm^{-1}.

The far IR region was closely examined in order to assign the Pt–N vibrations. According to group theory, the symmetry for the skeletal PtN_4 group is D_{4h}. One non-symmetric stretching ν(Pt–N) (E_u) vibration and two deformation modes (A_{2u} and E_u) are active in IR spectroscopy [24–26], but the two latter modes could not be seen on our instrument. A few studies on $[Pt(NH_3)_4]Cl_2$ have been reported in the literature. The single ν(Pt–N) band was assigned between 510 and 542 cm^{-1} [25,27,28]. The IR spectra of the complexes $[Pt(MeNH_2)_4]X_2$ have shown one band at 536 cm^{-1} for X = Cl [24,29] and at 532 cm^{-1} for X = Br [29]. These results are shown in Table 2. Based on these reported values, we have assigned a band observed between 578 and 590 cm^{-1} to a stretching ν(Pt–N) vibration (Table 2). It seems that the energy of the ν(Pt–N) bands is larger in the iodide compounds than in the bromides or chlorides. The H-bonding system should be more important in the chloride complexes than in the iodide compounds, which might partially explain the higher energy of the ν(Pt–N) bands in the iodide compounds. The assignments of these bands are not easy, since they are usually very weak and they often couple with other vibrations. Therefore, these results should be taken only as suggested assignments at the moment.

Table 2
υ(Pt–N) (cm^{-1}) vibrations for the complexes $[Pt(amine)_4]I_2$ and analogous examples from the literature

Complex	υ(Pt–N)	Reference
$[Pt(NH_3)_4]Cl_2$	510	[27]
	522	[28]
	542	[25]
$[Pt(MeNH_2)_4]Cl_2$	536	[24]
	535	[29]
$[Pt(MeNH_2)_4]Br_2$	532	[29]
$[Pt(MeNH_2)_4]I_2$	580	
$[Pt(EtNH_2)_4]I_2$	587	
[Pt(*n*-$PrNH_2)_4]I_2$	590	
[Pt(*n*-$BuNH_2)_4]I_2$	580	
[Pt(*iso*-$PrNH_2)_4]I_2$	578	
[Pt(*iso*-$BuNH_2)_4]I_2$	585	

3.3. Crystal structures

The crystallographic study of the $EtNH_2$ (**I**) compound confirmed the structure of the ionic complex. A drawing

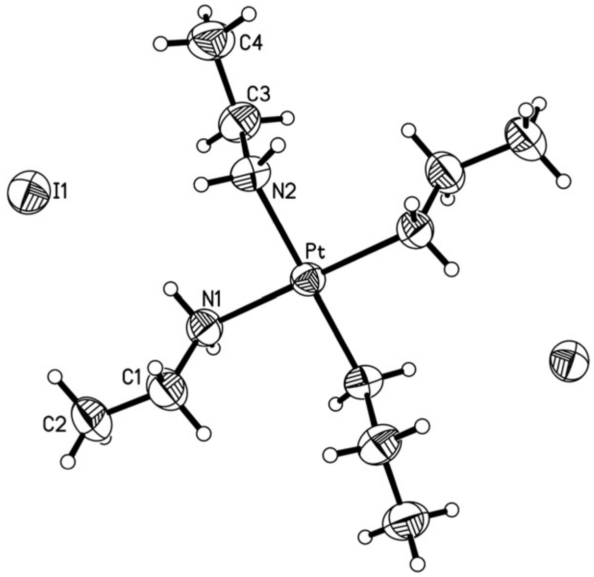

Fig. 1. Labelled diagram of $[Pt(EtNH_2)_4]I_2$. The ellipsoids correspond to 50% probability.

of the structure is shown in Fig. 1. The crystal belongs to the centric $P\bar{1}$ space group and the Pt atom is located on an inversion centre. The environment around the Pt(II) atom is a perfect square plane. The Pt–N bond distances are 2.052(5) and 2.059(4) Å (Table 3). The *trans* N–Pt–N angles are 180° by symmetry, while the *cis* angles are 89.6(2) and 90.4(2)°. The amine bond distances are normal with average N–C = 1.491(8) Å and C–C = 1.517(9) Å. The average Pt–N–C angle is 117.3(4)°, and the mean N–C–C angle is 111.6(6)°. The dihedral angles between the amine ligands (N–C–C) and the Pt plane are 71.7(4) and 80.4(4)°.

The crystal structure of a few $[Pt(EtNH_2)_4]^{2+}$ salts have been reported with larger anions like $[PtX_4]^{2-}$ [14] and in the mixed-valence compound $[Pt(EtNH_2)_4][Pt(EtNH_2)_4Br_2]X_4$ [16–19]. The present crystal is stabilized with hydrogen bonds between the amine groups and the iodide ions. All the N–H groups are involved in hydrogen bonding. The distances and angles are shown in Table 3. The distances N···I vary between 3.673(5) and 3.888(5) Å and the angles N–H···I are between 142.0 and 177.8°.

The structure of the *n*-$BuNH_2$ complex (crystal **II**) was also examined. There are two independent Pt atoms in the unit cell. The two cations $[Pt(n\text{-}BuNH_2)_4]^{2+}$ and three I^- ions were readily located, but the fourth I^- ion could not be found. There were several residual peaks present and after numerous efforts of interpretation, they were assigned to a *n*-butylcarbamate anion. This ion was obtained from the reaction of *n*-butylamine with CO_2 from the air. The reaction mixture for the synthesis of the tetrasubstituted complex is basic, since a rather large excess of amine must be used to accelerate the reaction. Steric hindrance is an important factor in the preparation of this type of compound. A good review on the methods to convert CO_2 into carbamato derivatives was published in 2003 [30]. In our work, the presence of carbamate ions in our solution was probably very limited. It might have formed during the synthetic procedure or during the recrystallization process. The compound was recrystallized in air several times in water, before crystals adequate for diffraction studies could be obtained.

The crystal structure of only one related compound was found in the literature. It contains the same *n*-butylcarbamate ion, although it was prepared in a different way [31]. A Co(III) compound $[Co(nBuNH_2)_4(CO_3)](n\text{-}BuNHCOO)\cdot H_2O$ was very slowly crystallized from a mixture containing cobalt(II) oxalate, *n*-butylamine and water. The oxalate was oxidized to CO_2, which was trapped by the basic medium and converted into carbonate and *n*-butylcarbamate ions. The *n*-butylcarbamate anion is not bonded to the metal atom, but it is involved in the H-bonding system.

The structure of one of the cation in our compound $[Pt(n\text{-}BuNH_2)_4]_2I_3$ (*n*-BuNHCOO) (**II**) is shown in Fig. 2. The replacement of one iodo ion by the larger *n*-butylcarbamate anion brings a larger stability to the crystal, which contains the very large cations $[Pt(n\text{-}BuNH_2)_4]^{2+}$. Carbamate anions were probably present in small concentration, but compound **II** would crystallized before the totally iodo complex, since it would be slightly less soluble in water. Free carbamate ions are not common in reported crystal structures. There are a few structures containing a carbamate

Table 3
Selected bond lengths (Å) and angles (°) for the three crystals

*$[Pt(EtNH_2)_4]I_2$ (**I**)*			
Pt–N1	2.052(5)	Pt–N2	2.059(4)
N1–C1	1.482(8)	N2–C3	1.500(7)
C1–C2	1.509(9)	C3–C4	1.524(9)
N1···I1	3.888(5)	N1···I1[b]	3.755(5)
N2···I1	3.682(5)	N1···I1[c]	3.673(5)
N1–Pt–N2	89.64(19)	N1–Pt–N2[a]	90.36(19)
N1–Pt–N1[a]	180	N2–Pt–N2[a]	180
Pt–N1–C1	116.6(4)	Pt–N2–C3	117.9(4)
N1–C1–C2	112.8(6)	N2–C3–C4	110.3(5)
N1–H···I1	142.0	N1–H···I1[b]	152.9
N2–H···I1	156.7	N1–H···I1[c]	177.8
[a]$-x, -y+1, -z+1$; [b]$x-1, y, z$; [c]$-x+1, -y+1, -z+1$.			
*$[Pt(n\text{-}BuNH_2)_4]_2I_3$ (n-BuNHCOO) (**II**)*			
$[Pt(nBuNH_2)_4]^{2+}$			
Pt1–N1	2.074(12)	Pt2–N5	2.055(13)
Pt1–N2	2.047(13)	Pt2–N6	2.031(14)
Pt1–N3	2.036(13)	Pt2–N7	2.050(13)
Pt1–N4	2.062(12)	Pt2–N8	2.003(16)
N–C (ave.)	1.46(2)		
N–Pt1–N (*cis*)	89.3(5)–90.1(5)	N–Pt2–N (*cis*)	89.8(6)–90.7(6)
N–Pt1–N (ave. *trans*)	179.2(6)	N–Pt2–N (ave. *trans*)	179.3(6)
Pt1–N–C (ave.)	117.1(11)	Pt2–N–C (ave.)	116.6(13)
N–C–C (ave.)	111.7(19)		
$nBuNHCOO^-$			
C1–O1	1.26(2)	C1–O2	1.26(2)
C1–N1′	1.283(17)	N1′–C2	1.459(16)
C–C (ave.)	1.51(4)		
O1–C1–O2	119.5(16)	O1–C1–N1′	121.9(15)
O2–C1–N1′	118.3(15)	C1–N1′–C2	123.9(19)
*$[Pt(MeNH_2)_2(H_3C{-}N{=}C(CH_3)_2)_2]I_2$ (**III**) (the imine ligands are disordered on two positions with the two sets of atoms labeled ′ and ″, respectively)*			
Pt1–N1	2.046(5)	Pt1–N2′	2.045(9)
Pt1–N2″	2.026(14)	N1–C1	1.474(9)
N2′–C3′	1.255(11)	N2″–C3″	1.238(14)
N2′–C2′	1.487(15)	N2″–C2″	1.48(2)
C3′–C5′	1.495(12)	C3″–C5″	1.499(14)
C3′–C4′	1.501(11)	C3″–C4″	1.499(13)
N1–Pt1–N1[a]	180	N2–Pt1–N2[a]	180.
N1–Pt1–N2′	90.5(2)	N1–Pt1–N2′[a]	89.5(2)
N1–Pt1–N2″	89.3(4)	N1–Pt1–N2″[a]	90.7(4)
Pt1–N1–C1	116.4(4)	Pt1–N2′–C3′	124.0(9)
Pt1–N2″–C3″	124.2(15)	Pt1–N2′–C2′	116.5(10)
Pt1–N2″–C2″	113.9(18)	C2′–N2′–C3′	119.5(13)
C2″–N2″–C3″	122(2)	N2′–C3′–C5′	122.1(15)
N2″–C3″–C5″	127(2)	N2′–C3′–C4′	125.2(13)
N2″–C3″–C4″	123(2)	C5′–C3′–C4′	112.7(14)
C5″–C3″–C4″	110(2)		
N1···I1	3.610(5)	N1···I1[b]	3.622(5)
N1–H1A···I1	156.4	N1–H1A···I1[b]	156.5

[a]$-x, -y, -z$; [b]$-x+1/2, y-1/2, z$.

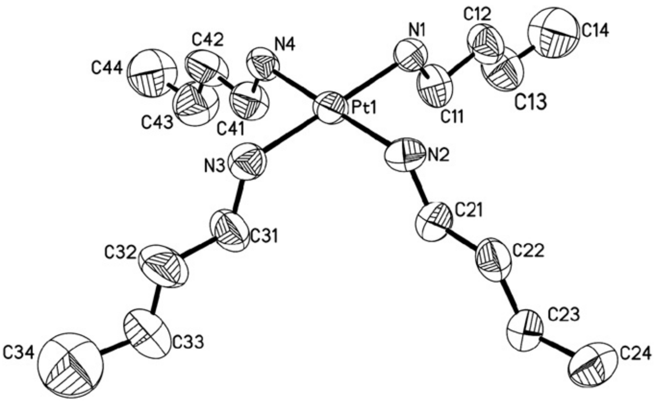

Fig. 2. Labelled diagram of one cation $[Pt(nBuNH_2)_4]^{2+}$ in crystal **II**. The ellipsoids correspond to 25% probability.

coordinated to a metal center [32–34]. Our compound (**II**) is a rare example of a free carbamate ion, besides the Co(III) complex [31] mentioned above and the two Cu(II) compounds containing anions of *N*-carboxyglycine and ethylenediaminebiscarboxylic acid [35].

The Pt–N bonds in **II** vary between 2.003(16) to 2.074(12) Å and the N–Pt–N angles are close to the ideal values (Table 3). The average Pt–N–C angle is 116.9(12)°. All the *n*-butylamine ligands adopt the fully extended all-*anti* conformation, except one ligand bonded to Pt2. In the latter, the two terminal C atoms are disordered on two positions. The most populated one (70%) has the all-*anti* conformation, while the minor component has a *gauche* conformation. The relative conformation of the ligands in the two cations is very interesting. For each complex cation, all the four N–C bonds point away on the same side of the Pt square plane. The two cations are arranged in pairs as shown in Fig. 3, where all the C–N point upward for the Pt1 cation and downward for the Pt2 cation. The anions are located between the pairs of cations.

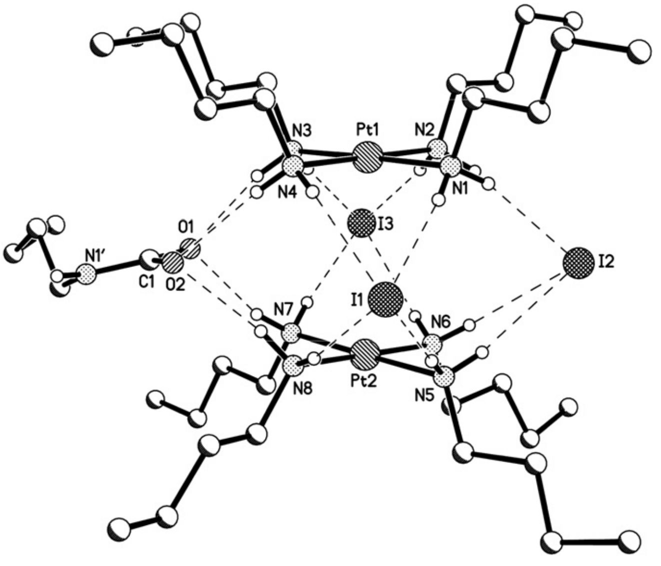

Fig. 3. Diagram of the two cations and the anions in crystal **II** showing the conformation of the two cations and some H-bonds. A diagram showing the more elaborate H-bonding system can be visualized in Fig. S1 (deposit).

The C–O bonds in the carbamate anion are 1.26(2) Å. The C1=N1′ is 1.283(17) Å, while the N1′–C2 bond is longer (1.459(16) Å). The angles around C1 and N1′ are close to 120°.

The compound is stabilized by an extensive hydrogen-bonding system, which is maximized in crystal **II**. All the NH_2 groups of the amines and the NH group of the carbamate anion act as donors, while the two O atoms of the carbamate ion and the three iodide ions are acceptors. Some of the H-bonds are shown in Fig. 3. A more elaborate drawing of the H-bonding system is available in the Supplementary material (Fig. S1).

The N···I distances are between 3.617(14) and 3.734 (14) Å and the angles N–H···I range from 165.9 and 175.9°, while the distances N···O are between 2.79(2) and 3.00(2) Å and the N–H···O angles range from 158.2 and 167.0°.

Several other tetrasubstituted compounds were recrystallized in water, but the quality of the crystals was too poor for crystallographic methods. Therefore several other solvents were tried. The $MeNH_2$ compound was recrystallized in acetone and crystals of good quality were obtained. The results of its crystal structure determination were quite surprising. The crystal belongs to a centrosymmetric space group and the Pt atom is located on an inversion center. Two $MeNH_2$ ligands (in *trans* position by symmetry) were easily determined, but the two other ligands were found to be quite different. The two other amines had reacted with the solvent (acetone) used for recrystallization generating bonded imine ligands. The structure of the new ligands was found to be $H_3C{-}N{=}C(CH_3)_2$, bonded to Pt through the N atom. Since the Pt atom is on an inversion center the compound has a *trans* geometry. Crystal **III** is therefore the ionic compound *trans*-$[Pt(MeNH_2)_2(H_3C{-}N{=}C(CH_3)_2)_2]I_2$.

The reaction of acetone with bonded $MeNH_2$ can be explained in organic chemistry. The reaction of aldehydes or ketones with amines is known to form imine derivatives also known as Schiff bases. Water is eliminated in the process

$$\begin{aligned} CH_3COCH_3 + C'H_3NH_2 &\rightarrow C'H_3NH\text{–}C(CH_3)_2(OH) \\ &\rightarrow C'H_3N = C(CH_3)_2 + H_2O \end{aligned}$$

A Pt(II) compound containing a tridentate ligand (pip_2NCN) was recently reported containing the same imine, which was also produced from the reaction of CH_3NH_2 with acetone used as solvent and bonded to the Pt(II) atom [36]. The complex $[Pt(pip_2NCN)Cl]^+$ was first reacted with $AgCF_3SO_3$ in acetone and after the removal of AgCl, the compound $[Pt(pip_2NCN)(acetone)]^{2+}$ probably formed in acetone solution. The N-bonded Schiff base adduct $[Pt(pip_2NCN)CH_3N{=}C(CH_3)_2][CF_3SO_3]$ was produced in good yield after the addition of CH_3NH_2. Kozelba and Bois had previously suggested that the Pt(II) center could activate a coordinated acetone ligand towards condensation with a primary amine [37]. In our case, the reverse situation was observed. The amine was bonded to the Pt(II) atom, since the characterization of the product in the solid state and by NMR in aqueous solution confirmed that the compound isolated was indeed $[Pt(CH_3NH_2)_4]I_2$. Amines are usually stronger ligands for Pt(II) than acetone. The reaction probably took place between bonded CH_3NH_2 and free acetone. Only two ligands in trans positions reacted with acetone. The other two amine ligands remained unchanged.

The Pt atom in crystal **III** is located on an inversion center and the coordination around the metal atom is square planar. The imine ligands in the crystal *trans*-$[Pt(MeNH_2)_2(H_3C{-}N{=}C(CH_3)_2)_2]I_2$ are disordered on two positions (proportions 63–37%), as shown in Fig. 4. The first set of atoms is labeled ′ and the second set is labeled ″. It is interesting to observe that in the crystal structure reported for $[Pt(pip_2NCN)CH_3N{=}C(CH_3)_2]$ $[CF_3SO_3]$, the imine moiety is also disordered over two positions in similar proportions (65–35%) [36].

The Pt–N bond distances with CH_3NH_2 are 2.046(5) Å, while the N1–C1 bonds are 1.474(9) Å. The *cis* N1–Pt–N2 angles are between 89.3(4) and 90.7(4)°, while the *trans* bond angles are 180° by symmetry. The Pt–N1–C1 angles are 116.4(4)°, while the torsion angles C1–N1–Pt1–N2 are 91.4(5) and 67.4(6)°.

The Pt–N bond distances with the imine ligands are 2.026(14) and 2.045(9) Å (Table 3). The N=C bonds = 1.238(14) and 1.255(11) Å and the other bond lengths are normal. The angle C4–C3–C5 is smaller (ave. 112(2)°) than the N2–C3–C (ave. 124(2)°) and C2–N2–C3 (ave. 121(2)°) angles as expected. The angles Pt–N2–C2 (ave. 115.2(14)°) are also smaller than the Pt–N2–C3 angles (ave. 124.1(12)°). The imine ligands are perpendicular to the platinum(II) plane. All the non-H atoms of the two conformers of the imine ligands are in a plane (mean deviation = 0.006 and 0.055 Å), with dihedral angles of 89.4(4) and 89.6(4)° with the Pt(II) coordination square plane. This conformation reduces the steric hindrance around the Pt atom to a minimum, leading to the most stable structure.

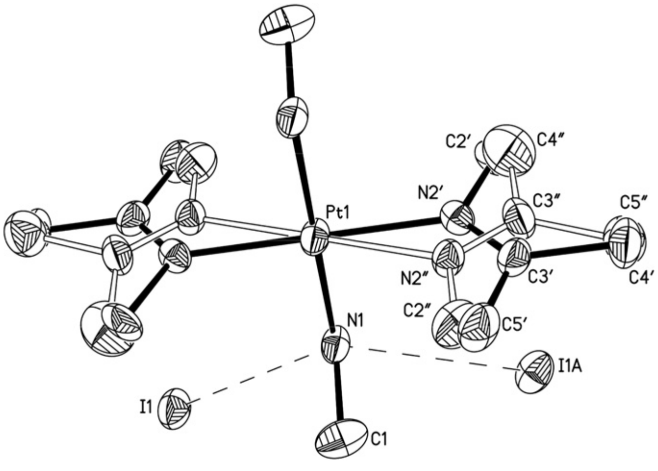

Fig. 4. Labelled diagram of *trans*-$[Pt(MeNH_2)_2(H_3C{-}N{=}C(CH_3)_2)_2]I_2$ (crystal **III**). The ellipsoids correspond to 40% probability. The H atoms have been omitted for clarity.

The crystal is stabilized by hydrogen bonding between the NH_2 groups and the iodo ions as shown in Fig. 2. The N1···I1 distances are 3.610(5) and 3.622(5) Å and the angles N1–H···I1 are 156.4 and 156.5°.

3.4. NMR

The ^{195}Pt, ^{1}H and ^{13}C NMR spectra of all the tetrasubstituted complexes were measured in D_2O. The compounds are quite soluble, but the times of accumulations were increased in order to obtain good data on the coupling constants. The ^{13}C spectra were accumulated during 12–15 h.

3.4.1. ^{195}Pt NMR

The $\delta(^{195}Pt)$ chemical shifts of all the compounds are listed in Table 4. They vary between −2715 and −2769 ppm. For all the products, only one signal was observed confirming the purity of the complexes. In the literature, the complex ion $[Pt(NH_3)_4]^{2+}$ was reported at −2580 ppm [38]. The Pt(II) complexes containing primary amines are usually found at higher fields than the corresponding NH_3 compounds, as observed in this work.

Amines cannot form π-bonds with the Pt atom. Therefore the ^{195}Pt chemical shifts of the metal complex should depend on the strength of the σ bonds. A stronger bond will transfer more electron density to the Pt atom and its $\delta(^{195}Pt)$ will be observed at higher fields. The pK_a values of the protonated amines should be a good criterion for the strength of the σ bonds. These are shown in Table 4. The pK_a values of the non-cyclic protonated amines are very close to each other (10.62–10.78 [39]) and their errors are not negligible. The error of the ^{195}Pt chemical shifts is also a few ppm. Therefore no relation can be found at this moment. The pK_a values are influenced by the solvent and its effect cannot be neglected, especially in relation to the steric hindrance around the N atom. The influence of a solvent like water is most important. The proton affinity of the amines might be a better criterion for the basicity of a ligand, since it is measured in the gas phase. But these

Table 4
$\delta(^{195}Pt)$ (ppm) of the complexes $[Pt(amine)_4]I_2$ (in D_2O), pK_a and proton affinity (AP, kJ/mole)

Amine	AP	pK_a [39]	$\delta(^{195}Pt)$
NH_3	854	9.25	−2580 [38]
$MeNH_2$	914	10.62	−2769
$EtNH_2$	930	10.67	−2753
n-$PrNH_2$	933	10.708	−2741
n-$BuNH_2$	924	10.777	−2743
iso-$PrNH_2$		10.63	−2724
iso-$BuNH_2$		10.72	−2748
cyclo-$PrNH_2$		8.67	−2715
cyclo-$BuNH_2$		9.34	−2766

data are not very common in the literature. Those of the linear amines have been published and they are shown in Table 4. Again the values (proton affinity and δ(Pt)) are too similar to reach any conclusion.

For the non-cyclic amines, the lowest field signal was observed for the *iso*-propylamine compound. This amine is the most sterically hindered close to the binding N atom. The solvent effect is an important phenomenon in ^{195}Pt NMR and it is particularly important for a solvent like water. In aqueous solution, the water molecules can approach the Pt atom on both sides of the square plane, which increases the electron density of the Pt atom. When there is steric hindrance close to the binding atom of the ligand, the molecules of solvent cannot approach the Pt atom so easily and the electron density on the Pt atom will slightly decrease, which will bring a deshielding effect in ^{195}Pt NMR. Therefore, the complex containing *iso*-propylamine should be observed at lower field (−2724 ppm) than the one containing *n*-propylamine (−2741 ppm). Here the difference is not very large since the steric hindrance on *iso*-propylamine is not very large. It is not possible to synthesize this type of tetrasubstituted complex with more sterically demanding amines.

If we consider only the four linear amine complexes, the ^{195}Pt chemical shifts were observed at higher fields for the smaller amines. These results are in agreement with the solvent effect as mentioned above. The amines with longer chains will reduce the approach of the water molecules in the close environment of the metallic atom, leading, to a reduced electron density around the Pt atom. The ^{195}Pt chemical shifts should therefore be observed at slightly lower fields for the larger amines.

Complexes with only two cyclic amines were studied. The compound with cyclopropylamine was observed at slightly lower field, while the cyclobutylamine complex is similar to the methylamine compound. Tension inside the ring is probably a factor, but there are not enough data at the moment to comment on its effect on ^{195}Pt NMR chemical shifts.

3.4.2. ^{1}H NMR

The proton chemical shifts of the complexes are shown in Section 2. The δ(NH) signals were not observed in D_2O. The signals of all the protons in the bonded amines were observed at lower fields than in the free amine, except for H_1 in the *iso*-propylamine complex. The bonding of the amines to Pt will increase the electron density on the metal atom, but will decrease it on the ligand. Therefore, there should be a linear relation between the $\delta(^{195}\mathrm{Pt})$ and the $\Delta\delta(^{1}\mathrm{H})$ (δ of complex − δ of the free amine in the same solvent) values. A plot of the different values for the non-cyclic amines is shown in Fig. 5. The H closest to the Pt atom was chosen (H_1) and $\Delta\delta = \delta_{\mathrm{complex}} - \delta_{\mathrm{free\ amine}}$. Fig. 5 shows that the $\delta(^{195}\mathrm{Pt})$ is shifted to higher fields as $\Delta\delta$ increases (shift towards lower fields). Therefore, there is a good agreement between the values observed in ^{195}Pt NMR with those observed in ^{1}H NMR. An increase of electron density on the Pt atom will cause a decrease in electron density on the H atoms of the ligands.

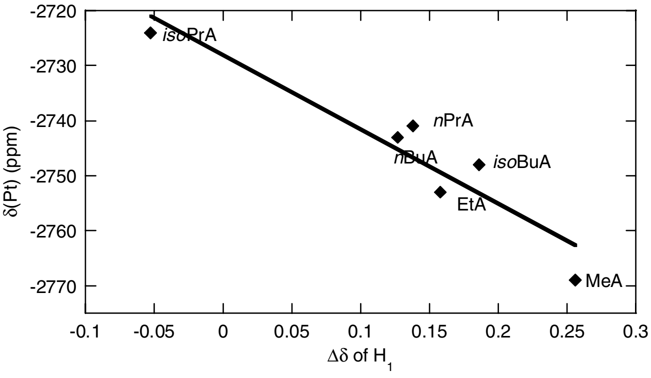

Fig. 5. δ(Pt) vs. $\Delta\delta$ of H_1 for the complexes $[\mathrm{Pt(amine)_4}]\mathrm{I_2}$ (non-cyclic amines).

For the cyclic amines complexes, the two H atoms on all the CH_2 groups are not equivalent. The H atom closer to the N atom of the ligands will be more deshielded upon coordination than the second H atom on the same C atom. In the free amine, the difference is small, but in the complex, the difference is much larger. For example, in the *cyclo*-$\mathrm{BuNH_2}$ complex, the two H protons on C_2 were observed at 2.34 and 2.00 ppm, while the two H protons on C_3 were too close to be separated (ave. 1.707 ppm). All these signals are multiplets since they can couple with all the H present (^{2}J–^{4}J).

The $^{3}J(^{195}\mathrm{Pt}$–$^{1}\mathrm{H})$ coupling constant of only the $\mathrm{MeNH_2}$ compound could be calculated. The value is 42 Hz. There is no comparable values in the literature for this type of complexes, but it is very similar to those reported for *cis*-Pt(amine)$_2$X$_2$ (45 Hz for X = I [7], 40 Hz for X = NO_3 [9], 43 Hz for X = D_2O [10] and 43 Hz for X = OD [10]). The $^{3}J(^{195}\mathrm{Pt}$–$^{1}\mathrm{H})$ coupling constants with the other ligands were not observed, because the latter signals are multiplets of low intensity and the satellites were not observed, even with long accumulation times.

3.4.3. ^{13}C NMR

The $\delta(^{13}\mathrm{C})$ chemical shifts of the compounds are shown in Section 2. The ^{13}C NMR spectra of the free amines were also measured in water and the $\Delta\delta(\delta_{\mathrm{complex}} - \delta_{\mathrm{free\ amine}})$ values are shown in Table 5. Again, these results are in agreement with the results observed in the ^{195}Pt and ^{1}H NMR spectra as discussed in the ^{1}H NMR section. An increase of electron density on the Pt atom (^{195}Pt NMR) will correspond with a decrease of electron density on the ligand (^{1}H and ^{13}C NMR). A linear relationship between the $\delta(^{195}\mathrm{Pt})$ and the $\Delta\delta(^{13}\mathrm{C})$ values of the complexes containing the linear amines can be observed in Fig. 6. For the *iso*-propylamine and *iso*-butylamine compounds, other local factors based on the structure of the ligand play a more important role on the ^{13}C chemical shifts.

Most of the $^{2}J(^{195}\mathrm{Pt}$–$^{13}\mathrm{C}_1)$ coupling constants could be calculated and are shown in Table 5. They vary between

Table 5
$\Delta\delta$(C) (ppm) and $J(^{195}Pt–^{13}C)$ (Hz) of the complexes $[Pt(amine)_4]I_2$ in D_2O

Amine	C_1	C_2	C_3	C_4	$^2J(^{195}Pt–C_1)$	$^3J(^{195}Pt–C_2)$
$MeNH_2$	6.238				19	
$EtNH_2$	6.010	−1.382			20	34
n-$PrNH_2$	5.600	−0.911	−0.304		17	30
n-$BuNH_2$	5.935	−1.169	−0.045	0.878	14	29
iso-$PrNH_2$	6.951	−1.290			15	30
iso-$BuNH_2$	5.282	−0.759	−0.243		20	28

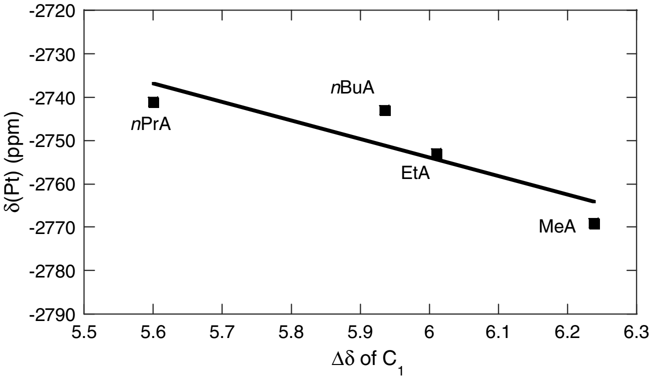

Fig. 6. δ(Pt) vs. $\Delta\delta$ of C_1 for the complexes $[Pt(amine)_4]I_2$ (linear amines).

14 and 20 Hz. No such values exist in the literature on similar compounds, but we can compare with the compounds $Pt(amine)_2I_2$, where the reported average values are 18 Hz for the *cis* isomers and 11 Hz for the *trans* analogues [7]. For most of the complexes, the $^3J(^{195}Pt–^{13}C_2)$ coupling constants were detected and they vary between 28 and 34 Hz. Again no such values have been reported yet in the literature for this type of complexes. They are close to the values reported for *trans*-$Pt(amine)_2I_2$ [7].

4. Conclusion

The ionic complexes $[Pt(amine)_4]I_2$ were synthesized and characterized in the solid state by IR spectroscopy and by X-ray diffraction methods. The compounds were also studied in aqueous solution by multinuclear (^{195}Pt, ^1H and ^{13}C) magnetic resonance spectroscopy. Our new method is slightly different from the published method and prevents the formation of side-products such as $[Pt(amine)_4][PtX_4]$, which are impossible to separate completely from $[Pt(amine)_4]X_2$. If the tetrasubstituted compounds are used for the preparation of *trans*-$Pt(amine)_2X_2$, the products will be contaminated with $[Pt(amine)_4][PtX_4]$.

The tetrasubstituted amine complexes are important molecules for the synthesis of trans diamine compounds, but it cannot be isolated for bulky ligands. Therefore its use is limited to less hindered amines. The halide complexes are interesting since they are quite soluble. The compounds are stable in aqueous medium. $[Pt(CH_3NH_2)_4]I_2$ was found to react partly when dissolved in acetone to form a Schiff base Pt adduct, *trans*-$[Pt(MeNH_2)_2(H_3C{-}N{=}C(CH_3)_2)_2]I_2$. This type of reaction seems new in the literature. A Pt complex containing a tridentate ligand and an acetone ligand was reported to produce a Pt compound containing the same $H_3(C{-}N{=}C(CH_3)_2)_2$ ligand [36]. But the reaction took place between bonded acetone and free CH_3NH_2. We have observed the reverse process. Bonded CH_3NH_2 reacted with free acetone used as a solvent. Therefore, not only the Pt(II) center can activate a coordinated acetone ligand towards condensation with primary amines, but it can also activate a coordinated amine ligand towards condensation with acetone.

This work has shown that special care should be taken to ascertain the purity of reaction products especially if the compounds were recrystallized in an organic solvent. This is particularly important if the Pt complexes are prepared for antitumor evaluation. It is already known that *cis*-$Pt(amine)_2Cl_2$ can isomerise to the *trans* compounds in several organic solvents, particularly acetone. The two novel compounds discussed in this paper seem to indicate that the rearrangement of amines is not uncommon although not very well known. In one case, the amine reacted with CO_2 of air and in the second case, it reacted with acetone, a solvent commonly used to recrystallize and purify the Pt products. Therefore, the end-products should always be characterized just prior to antitumor evaluation and multinuclear (especially ^1H) magnetic resonance seems a very adequate method. Again, the solvent for recording the spectrum should be carefully chosen.

Acknowledgement

The authors are grateful to the Natural Sciences and Engineering Research Council of Canada for financial support of the project.

Appendix A. Supplementary material

CCDC 623134, 623135 and 623136 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2006.11.005.

References

[1] T.W. Hambley, Coord. Chem. Rev. 166 (1997) 181.

[2] M.J. Cleare, Coord. Chem. Rev. 12 (1974) 349.

[3] M.J. Cleare, P.C. Hydes, B.M. Malerbi, D.M. Watkins, Biochimie 60 (1978) 835.

[4] P.D. Braddock, T. Connors, M. Jones, A.R. KhorHar, D.H. Melzack, M.L. Tobe, Chem. Biol. Interact 11 (1975) 145.

[5] F.D. Rochon, R. Melanson, Acta Crystallogr. C42 (1986) 1291.

[6] M. Nicolini, Platinum and other metal coordination compounds in cancer chemotherapy, University of Padua, Italy, 1987.

[7] F.D. Rochon, V. Buculei, Inorg. Chim. Acta 357 (2004) 2218.

[8] F.D. Rochon, V. Buculei, Inorg. Chim. Acta 358 (2005) 2040.

[9] F.D. Rochon, V. Buculei, Can. J. Chem. 82 (4) (2004) 524.

[10] F.D. Rochon, V. Buculei, Can. J. Chem. 82 (4) (2004) 1606.

[11] J.A. Broomhead, D.P. Fairlie, M.W. Whitehouse, Chem.-Biol. Interact. 31 (1980) 113.

[12] S.K. Aggarwal, J.A. Broomhead, D.P. Fairlie, M.W. Whitehouse, Cancer Chemother. Pharmacol. 4 (1980) 249.

[13] G.B. Kauffman, Inorg. Synth. 7 (1963) 249.

[14] M.E. Cradwick, D. Hall, R.K. Phillips, Acta Crystallogr. B27 (1971) 480.

[15] M.L. Rodgers, D.S. Martin, Polyhedron 6 (1987) 225.

[16] K.L. Brown, D. Hall, Acta Crystallogr. Sect. B Struct. Crystallogr. Cryst. Chem. 32 (1976) 279.

[17] B.M. Craven, D. Hall, Acta Crystallogr. 21 (1966) 177.

[18] H. Endres, H.J. Keller, B. Keppler, R. Martin, Acta Crystallogr. Sect. B Struct. Crystallogr. Cryst. Chem. 36 (1980) 760.

[19] S. Sato, K. Kobayashi, Acta Crystallogr. Sect. C Cryst. Struct. Commun. 43 (1987) 1863.

[20] XSCANS (V. 2.20) Program, Bruker Analytical X-ray Systems.

[21] SHELXTL (PC version 5, 1995) Programs, Bruker Analytical X-ray Systems.

[22] C. Tessier, F.D. Rochon, Inorg. Chim. Acta 295 (1999) 25.

[23] F.D. Rochon, V. Buculei, Inorg. Chim. Acta 358 (2005) 3919.

[24] Y.Y. Kharitonov, I.K. Dymina, T.N. Leonova, Russ. Inorg. Chem. 13 (5) (1968) 709.

[25] L.A. Degen, A.J. Rowlands, Spectrochim. Acta 47A (1991) 1263.

[26] P.J. Hendra, N. Sadasivan, Spectrochim. Acta 21 (1967) 1275.

[27] J. Hiraishi, I. Nakagawa, T. Shimanouchi, Spectrochim. Acta 24A (1968) 819.

[28] P.J.D. Park, P.J. Hendra, Spectrochim. Acta 25A (1969) 909.

[29] G.B. Watt, B.B. Hutchinson, D.S. Klett, J. Am. Chem. Soc. 89 (1967) 2007.

[30] D.B. Dell'Amico, F. Calderazzo, L. Labella, F. Marchetti, G. Pampaloni, Chem. Rev. 103 (2003) 3857.

[31] T.D. Keene, M.B. Hursthouse, D.J. Price, Acta Crystallogr. E60 (2004) m381.

[32] O. Blacque, H. Brunner, M.M. Kubicki, J.-C. Leblanc, W. Meier, C. Moize, Y. Mugnier, A. Sadorge, J. Wachter, M. Zabel, J. Organomet. Chem. 634 (2001) 47.

[33] A. Duatti, A. Marchi, V. Bertalasi, V. Ferretti, J. Am. Chem. Soc. 113 (1991) 9680.

[34] S. Schmid, J. Strähle, Z. Naturforsch. Teil. B46 (1991) 235.

[35] L.A. Kovbasyuk, I.O. Fritsky, V.N. Kokozay, T.S. Iskenderov, Polyhedron 16 (1997) 1723.

[36] H. Jude, J.A. Krause Bauer, W.B. Connick, Inorg. Chem. 41 (2002) 2275.

[37] J. Kozelka, C. Bois, Inorg. Chem. 27 (1988) 3866.

[38] Y. Qu, N. Farrell, M. Velsecchi, L. de Greco, S. Spinelli, Magn. Res. Chem. 31 (1993) 920.

[39] D.D. Derrin, Dissociation Constants of Organic Bases in Aqueous Solution, Butterworths, London, 1965, pp. 140–183.