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Synthesis, multinuclear magnetic resonance and crystal structures of Pt(II) complexes containing amines and bidentate carboxylate ligands

Fernande D. Rochon *, Gassan Massarweh

Université du Québec à Montréal, Département de chimie, C. P. 8888, Succ. Centre-ville, Montréal, Canada H3P 3P8

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Abstract

A novel synthetic method for the synthesis of the complexes *cis*-Pt(amine)$_2$R(COO)$_2$ is compared to two other methods involving the use of either barium dicarboxylate or sodium carboxylate. Pt(II) compounds with monodentate and bidentate amines were studied. The reaction involves the use of a silver dicarboxylato complex, which is the intermediate in the new synthetic procedure. The crystal structure of the silver intermediate with the ligand 1,1-cyclobutanedicarboxylate (1,1-CBDCA) was determined by X-ray diffraction. The crystal Ag$_2$(1,1-CBDCA) has a very interesting 3-D extended structure. The complexes *cis*-Pt(amine)$_2$R(COO)$_2$ were studied in solution by multinuclear (^{1}H, ^{13}C and ^{195}Pt) magnetic resonance spectroscopy, but the solubilities are very low. D$_2$O was found to be the best solvent. In ^{195}Pt NMR, the complexes containing bidentate amines forming five-membered chelates were observed at higher fields than those containing monodentate amines. The resonances of the NH$_3$ compounds were also found at lower fields than the primary amine complexes. All the dicarboxylato ligands form six-membered chelates except 1,2-CBDCA, whose Pt(II) compounds were observed at lower fields than the others. The crystal structures of Pt(en)(1,1-CBDCA), Pt(Meen)(1,1-CBDCA) and Pt(en)(benzylmalonato) were confirmed by X-ray diffraction methods. Several compounds are disordered. The crystals are stabilized by intermolecular hydrogen bonds between the –NH$_2$ groups and the carboxylato O atoms.

Keywords: Platinum; Amine; Carboxylato; Silver; Crystal structure; NMR

1. Introduction

The compound *cis*-Pt(NH$_3$)$_2$Cl$_2$ (*cisplatin*) is still one of the most extensively used anticancer drug in the world [1], although it has numerous side effects and toxicity. It is not very soluble in water and it can hydrolyze inside the cell, where the chloride concentration is low and the pH is neutral, to produce several species, including toxic hydroxo-bridged dimers or other oligomers. A good review of the influence of structure on the activity and toxicity of Pt anti-cancer drugs has been published [2]. The replacement of the chloro ligands by carboxylato ligands produces less toxic compounds, with increased solubility in water. The antitumor compound Pt(NH$_3$)$_2$(1,1-cyclobutanedicarboxylato) (*carboplatin*) is now commercially available in a few countries. It is more soluble in water than *cisplatin* and produces an equally strong antitumor effect, but at a markedly higher dosage due to the delayed formation of the active aquated metabolites. Several other amine-carboxylato Pt(II) compounds have also good antitumor activities like Pt(dach)(oxalato) (*oxaliplatin*) [3] or Pt(dach)(malonato) (dach = 1,2-diaminocyclohexane) and Pt(en)(malonato) (*malonatoplatin*) [4] (en = ethylenediamine).

Two methods have been used in the literature to synthesize diamine dicarboxylato Pt(II) complexes and these were discussed in a previous paper [5]. These methods involve the use of a silver salt to remove the dihalo ligands from Pt(amine)$_2$X$_2$. The product is usually the diaqua compound (in slightly acidic medium) which is very reactive. In basic pH, the diaqua Pt species are hydrolyzed to the dihydroxo

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* Corresponding author. Tel.: +1 514 987 3000x4896; fax: +1 514 987 4054.

E-mail address: rochon.fernande@uqam.ca (F.D. Rochon).

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compound, while in neutral pH, the monoaquamonohydroxo compound, along with hydroxo-bridged dimers and other oligomers, are formed. In these reactions, the quantity of the silver salt is very critical, since a small excess can react with the reactive Pt-aqua species. The crystal structure of one such complex was reported [6]. The structure is a tetranuclear compound containing platinum–silver bonds. Therefore, the quantity of the reactants must be carefully controlled and usually a small deficit of the silver salt is used. Furthermore, the reaction must be done in basic medium to deprotonate the carboxylic acid, where sometimes the ligands might be sensitive to the use of base.

We have now developed a new method, which was compared to the two reported methods. The method involves the formation of a silver carboxylato intermediate, which is then reacted with the diaminodiiodo Pt complex. Compounds with different types of monodentate and bidentate amines were studied. Only bidentate dicarboxylate ligands were chosen. Therefore, all the compounds have the *cis* configuration. The products were analyzed by multinuclear magnetic resonance and a few by crystallographic methods. The silver intermediate was also characterized by X-ray diffraction methods.

2. Experimental

2.1. Chemicals and instrumentation

$K_2[PtCl_4]$ was purchased from Johnson–Matthey and was recrystallized in water before use. The amines were bought from Aldrich, while silver nitrate was purchased from Analar. D_2O, DMF-d_7, MeOD, $CDCl_3$ and CD_3COCD_3 were obtained from CDN Isotopes.

The NMR spectra were measured on a Varian Gemini 300BB. The fields were 300.070, 75.460 and 64.395 MHz for ^1H, ^{13}C and ^{195}Pt, respectively. For the ^{195}Pt NMR spectra, $K_2[PtCl_4]$ (-1628 ppm in D_2O with KCl, relative to $K_2[PtCl_6]$ which was assigned a $\delta(Pt) = 0$ ppm) was the external standard. Most of the NMR spectra of the complexes were measured in D_2O. The solutions were often heated to about 40–45° in order to increase the solubility. For the less soluble compounds, several organic solvents like CD_3COCD_3, DMF-d_7, MeOD and $CDCl_3$ were used, often without success.

2.2. Synthesis

cis-Pt(amine)$_2$I$_2$: These compounds were prepared as described in the literature [7,8].

$Ag_2R(COO)_2$: Two millimoles of aqueous NaOH are added to 1 mmol of the dicarboxylic acid dissolved in a small quantity of water. Two millimoles of $AgNO_3$ are then added to the sodium dicarboxylate solution in the dark. A white precipitate forms immediately. The mixture is stirred for 15–30 min and the silver compound is filtered, washed with water, dried in air and finally in a dessicator. The yields are between 60% and 80%.

Pt(amine)$_2$R(COO)$_2$: The two compounds *cis*-Pt(amine)$_2$I$_2$ and $Ag_2R(COO)_2$ were mixed together in water in a 1:1 proportion. The mixture is stirred in the dark during 2–3 days until the formation of AgI is complete. The yellow precipitate is filtered out and the filtrate is evaporated to dryness.

$Pt(NH_3)_2$(1,1-CBDCA): δ(H) (ppm), 1.716quintet, 2.700t, δ(C) (ppm), 15.41, 31.19, 56.37, 182.0. $Pt(NH_3)_2$(1,2-CBDCA): δ(H) (ppm), 1.806, 3.011, 3.517, δ(C) (ppm), 21.86, 44.20. $Pt(NH_3)_2$(malonato): δ(H) (ppm), 3.018. $Pt(NH_3)_2$(Bumalonato): δ(H) (ppm), 0.77, 1.187, 1.254, 1.77, 2.41, 3.392t, δ(C) (ppm), 13.21, 21.9, 29.30, 31.01, 58.17, 181.32. $Pt(NH_3)_2$(Bzmalonato): δ(H) (ppm), 2.914d, 3.267t, 7.18m, δ(C) (ppm), 36.6, 61.8, 126.2, 128.6, 128.81, 180.7.

Pt(cpa)$_2$(1,1-CBDCA): δ(H) (ppm), 1.753quintet, 2.258t, (cpa) 1.38, 1.48, 1.72, 1.90, 2.66, δ(C) (ppm), 15.61, 29.37, 30.64, 58.0, 179.6, (cpa) 23.51, 33.16, 59. Pt(cpa)$_2$(1,2-CBDCA) in D_2O-DMF: δ(H) (ppm), 1.82, 3.04, (cpa) 1.53, 1.95, δ(C) (ppm), 21.77, 43.38, 164.8, (cpa) 23.53, 32.92, 57.78. Pt(cpa)$_2$(malonato): δ(H) (ppm), 3.52, (cpa) 1.42, 1.56, 1.98, 3.05, δ(C) (ppm), 48.0, 178.0 (cpa) 23.64, 33.11, 57.83. Pt(cpa)$_2$(Bumalonato) measured in D_2O/MeOH δ(H) (ppm), 0.73, 1.17, 3.50, (cpa) 1.48, 1.56, 1.70, 1.90, 3.05, δ(C) (ppm) 13.24, 21.94, 29.0, 30.64, 52.23, 181.76, (cpa) 23.64. Pt(cpa)$_2$(Bzmalonato): δ(H) (ppm), 3.05, 3.40, 7.17, δ(C) (ppm), 36.6, 61.8, 126.98, 129.38, 130.23, 179.9, (cpa) 23.73, 31.87, 52.34.

Pt(en)(1,1-CBDCA): δ(H) (ppm), 1.7, 2.4, δ(C) (ppm), 15.41, 31.03, 56.20, 180.0 (en) 48.02. Pt(en)(1,2-CBDCA): δ(H) (ppm), 1.86, 3.03, 3.50, (en) 2.33, 2.41, $^3J(^{195}Pt–^1H) = \sim 48$ Hz, δ(C) (ppm), 22.07, 44.06, 180.2, (en) 48.22. Pt(en)(malonato): δ(H) (ppm), 3.46, (en) 2.40, $^3J(^{195}Pt–^1H) = \sim 46$ Hz, δ(C) (ppm) 48.01. Pt(en)(Bumalonato): δ(H) (ppm), 0.99t, 1.43, 1.51, 2.01, 3.58t, (en) 2.64, 2.70, $^3J(^{195}Pt–^1H) = \sim 47$ Hz, δ(C) (ppm), 13.2, 22.06, 29.02, 31.55. Pt(en)(Bzmalonato): δ(H) (ppm), 3.06, 3.6, 7.2m, (en) 2.50, 2.83, δ(C) (ppm), 36.40, 60.33, 126.25, 128.65, 128.80, 140.9, 179.10, (en) 48.09, 46.97.

Pt(Meen)(1,1-CBDCA): δ(H) (ppm), 1.695quintet, 2.648t, 2.695t, (Meen) 1.102d, 2.15m, 2.45m, 2.63m, δ(C) (ppm), 15.31, 30.80, 31.26, 56.21, 181.74, (Meen) 15.41, 52.58, 55.82. Pt(Meen)(1,2-CBDCA): δ(H) (ppm), 1.78, 2.98, (Meen) 1.14, 2.23, 2.42, 2.84, δ(C) (ppm), 21.8, 43.33, 184.03 (Meen) 15.25, 52.81, 56.04. Pt(Meen)(malonato): δ(H) (ppm), 3.468, 3.51, (Meen) 1.147d, 2.25dd, 2.50dd, 2.87m, δ(C) (ppm) 48.3, 177.13, (Meen) 15.30, 52.62, 55.87. Pt(Meen)(Bumalonato): δ(H) (ppm), 0.751t, 0.810t, 1.28, 1.722t, 2.46, 3.342t, 3.357t, (Meen) 1.116d, 1.184d, 2.26, 2.53, 2.87, δ(C) (ppm), 13.4, 21.83, 29.34, 31.12, 52.8, 179.3. Pt(Meen)(Bzmalonato): δ(H) (ppm), 3.03d, 3.61t, 7.2, (Meen) 1.14d(minor), 1.15d(major), 2.22(minor), 2.37(major), 2.46(minor), 2.56(major), 2.98(CH_2).

Pt(Me$_2$en)(1,1-CBDCA): δ(H) (ppm), 1.70, 2.65, δ(C) (ppm), 15.43, 30.96, 56.17, 181.67, 181.83 (Me$_2$en) 44.69, 51.57, 68.14. Pt(Me$_2$en)(1,2-CBDCA): δ(H) (ppm), 1.92d,

Table 1
Crystallographic details of the crystals

Name	$\{Ag_2(1,1\text{-CBDCA})\}_n$	Pt(en)(1,1-CBDCA)	Pt(Meen)(1,1-CBDCA)	Pt(en)(Bzmal)
Crystal	**1**	**2**	**3**	**4**
Chemical formula	$C_6H_6O_4Ag_2$	$C_8H_{14}N_2O_4Pt$	$C_9H_{16}N_2O_4Pt$	$C_{12}H_{16}N_2O_4Pt$
Molecular weight	$(357.85)_n$	397.30	411.33	447.36
Space group	$I4_1/a$ (No. 88)	*Pnma* (No. 62)	*Pnma* (No. 62)	$P2/_1$ (No. 4)
a (Å)	22.5966(16)	8.663(2)	9.686(3)	4.603(3)
b (Å)	22.5966(16)	9.618(2)	9.986(3)	10.792(5)
c (Å)	11.692(2)	12.713(2)	11.753(5)	12.916(6)
B (°)				93.61(5)
V (Å^3)	5970.0(12)	1059.3(4)	1136.8(7)	640.3(6)
Z	32	4	4	2
ρ_{calcd} (g cm^{-3})	3.185	2.491	2.403	2.320
μ(Mo Kα) (cm^{-1})	5.212	13.243	12.344	10.968
$F(000)$	5376	744	776	424
Measured reflections	10634	11754	8442	4512
Independent reflections (R_{int})	2919 (0.0488)	1637 (0.0577)	1186 (0.1513)	2262 (0.0949)
Observed reflections [$I > 2\sigma(I)$]	2507	1464	964	1812
R_1 [$F > 2\sigma(I)$]	0.0268	0.0289	0.0459	0.0575
wR_2 (all data)	0.0597	0.0704	0.1072	0.1327
S	1.070	1.064	1.045	1.074

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

3.10, (Me_2en) 2.43, 2.52, 2.566, δ(C) (ppm), 21.50, 41.54, 179.76, (Me_2en) 45.42, 51.91, 68.50. Pt(Me_2en)(malonato): δ(H) (ppm), 3.55, (Me_2en) 2.58, 2.687, δ(C) (ppm) 47.81, 178.5, (Me_2en) 44.71, 51.48, 68.22. Pt(Me_2en)(Bumalonato): δ(H) (ppm), 0.80, 1.28, 2.55, 3.36, (Me_2en) 2.43, 2.94, δ(C) (ppm), 13.24, 21.83, 29.40, 31.24, 58.22, (Me_2en) 44.70, 51.59, 68.22. Pt(Me_2en)(Bzmalonato): δ(H) (ppm), 2.60d, 3.65t, 7.19m, (Me_2en) 2.50, δ(C) (ppm), 37.00, 59.65, 127.17, 128.90, 129.02, 138.26, 179.86.

Pt(dach)(1,1-CBDCA): δ(H) (ppm), 1.735q, 2.713t, (dach) 0.99, 1.13, 1.42, 2.22, 2.32, δ(C) (ppm), 15.41, 31.04, 56.28, 181.75, (dach) 23.98, 31.82, 62.48. Pt(dach)(1,2-CBDCA): δ(H) (ppm), 1.82, 3.05, 3.46, (dach) 0.94, 1.08, 1.36, 2.20, δ(C) (ppm in D_2O–CH_3OD), 20.48, 43.95, (dach) 23.85, 31.5, 63.10. Pt(dach)(malonato): measured in $CDCl_3$, δ(H) (ppm), 3.46, (dach) 0.86, 1.19, 1.23, 2.15, δ(C) (ppm) 181.8, (dach) 23.94, 31.78, 62.48. Pt(dach)(Bumalonato): δ(H) (ppm), 0.97, 1.12, 1.41, 1.73, 1.86d, 2.23, 2.71t. Pt(dach)(Bzmalonato): δ(H) (ppm), 2.60, 2.98d, 3.14, 3.36, 7.11m.

Pt(*sec*-butylamine)(Bzmalonato): δ(H) (ppm), 3.13, 3.3, 7.17m, (*sec*-butylamine) 0.823t, 1.129d. 1.49m, 3.01.

2.3. Crystallographic measurements and structure resolution

The four crystals were recrystallized in water or a mixture of water and acetone. They were selected after examination under a polarizing microscope for homogeneity. The data collection was made at room temperature on a Bruker P4 diffractometer equipped with graphite-monochromatized Mo Kα radiation. The XSCANS program [9] was used for centering the crystals, the data collections and the reducing process. The unit cell parameters were obtained by least-squares refinement of the angles 2θ, ω and χ for well-centered reflections. The coordinates of the heavy atoms were determined from direct methods and the positions of all the other atoms were found by the usual Fourier methods. The intensity data were corrected for absorption (Gaussian integration for crystal **4** and semi-empirical for the others) and for the effects of Lorentz and polarization. The H atoms were fixed at their calculated positions (riding model) with $U_{eq} = 1.2 \times U_{eq}$ of the C atom to which they are bonded, except where there are disorders. In crystals **2**, there are two positions (occupancy of 0.5 each) for the ethylene groups in ethylenediamine, while in crystal **3**, there are two positions for the methylene and the CH_3 groups (occupancy of 0.5 each) of the methyl derivative of ethylenediamine. The refinement of the structures was done on F^2 by full-matrix least-squares analysis. The calculations were done with a SHELXTL system [10]. The crystallographic data and other pertinent information are summarized in Table 1.

3. Results and discussion

3.1. Synthetic procedures

Two different methods have been used in the literature for the synthesis of amine-carboxylato Pt(II) complexes. These have been discussed in a previous publication [5]. The standard method involves the use of sodium carboxylate (NaX or Na_2X_2) which reacts with the diaquadiamine Pt(II) complex in water.

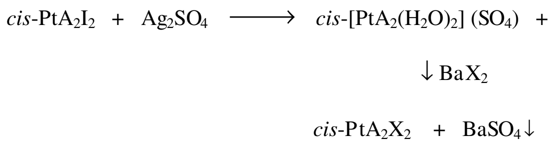
$$cis\text{-}PtA_2I_2 + 2AgNO_3 \xrightarrow{H_2O} cis\text{-}[PtA_2(H_2O)_2](NO_3)_2 + 2AgI\downarrow$$

$$\downarrow Na_2X_2$$

$$cis\text{-}PtA_2X_2 + 2NaNO_3$$

In this reaction, the silver salt should not be in excess, since other species will be produced. Furthermore, since the diaminediiodo compound is very insoluble in water, the reaction in water is very slow. The reaction is faster in acetone and a small excess of the silver salt can then be used, which can increase the yield of the intermediate ionic compound. The second step is done in water and the reaction is quite long depending on the two ligands. It is difficult to evaluate the extent of the reaction since all the products are soluble in water. Furthermore, the complete separation of the Pt compound from sodium nitrate is difficult. Therefore, the overall yields (from $K_2[PtCl_4]$) for this method are not very high, usually between 10% and 50% in water (depending on the two ligands) or slightly higher when the reaction with the silver salt is performed in acetone. A study of the products by ^{195}Pt NMR spectroscopy has shown the presence of more than one species for a few pairs of ligands [5].

In the second method, silver sulfate is used instead of silver nitrate and barium carboxylate (prepared in situ) is used instead of the sodium salt. The reaction is done in water.



$$\begin{aligned} &cis\text{-}PtA_2I_2 + Ag_2SO_4 \longrightarrow cis\text{-}[PtA_2(H_2O)_2](SO_4) + 2AgI\downarrow \\ &\qquad\qquad\qquad\qquad\qquad \downarrow BaX_2 \\ &\qquad\qquad\qquad\qquad cis\text{-}PtA_2X_2 + BaSO_4\downarrow \end{aligned}$$

The diaqua species contains also some cis-$PtA_2(H_2O)(SO_4)$. This method is faster, easier to control since the presence of $BaSO_4$ can be observed and the products are easier to purify. The yields (from $K_2[PtCl_4]$) vary between about 45% and 88%. We have shown that this method is superior to the above one, since it produces pure complexes, while the method described above often lead to a mixture of compounds with some of the different ligands. But this second method cannot be used for the synthesis of the oxalate complexes, since barium oxalate is too insoluble in water. Furthermore, these two methods cannot be used for ligands containing groups which can be attacked in basic medium.

We have now developed a new method where the intermediate is the silver carboxylato compound which can be isolated and characterized. The reactions are as follows:

$$2AgNO_3 + M_2X_2 \overset{H_2O}{\rightarrow} Ag_2X_2 \downarrow + 2M(NO_3) \quad (M = Na \text{ or } K)$$

$$cis\text{-}PtA_2I_2 + Ag_2X_2 \overset{H_2O}{\rightarrow} cis\text{-}PtA_2X_2 + 2AgI \downarrow$$

The second reaction takes about 2 days in water. The addition of acetone will accelerate the reaction in the formation of the diaminedicarboxylato complex. In a water–acetone ratio of 1:4, the reaction time was reduced to about 2 h. If the carboxylate and the amine are monodentate ligands, the addition of acetone is not recommended, since the *cis*-Pt(II) compound can isomerize to the *trans* isomer in acetone. The intermediate silver carboxylato compound must be isolated and purified by washing with water before proceeding to the second step of the reactions. The overall yields (from $K_2[PtCl_4]$) are about 75%.

The crystal structure of one of the intermediate silver compounds was determined by X-ray diffraction methods. The results have shown that the crystal Ag_2(1,1-CBDCA) (1,1-CBDCA = 1,1-cyclobutyldicarboxylate) which was recrystallized in water is not hydrated. Three diaminedicarboxylato Pt(II) compounds were also studied by crystallographic methods. The results have confirmed the expected structures. The three Pt(II) complexes do not contain any water of hydration contrary to the reported structure $Pt(EtNH_2)_2$(1,1-CBDCA) · H_2O [5].

Compounds with the following amines were studied: NH_3, cyclopentylamine (cpa), ethylenediamine (en), 1,2-diaminopropane (Meen), *N*,*N*-dimethylethylenediamine (Me_2en) and 1,2-diaminocyclohexane (dach). Only dicarboxylate ligands were studied: 1,1-cyclobutanedicarboxylate, *trans*-1,2-cyclobutanedicarboxylate (1,2-CBDCA), malonate (mal), butylmalonate (Bumal) and benzylmalonate (Bzmal). Several other compounds were synthesized (ex. with *sec*-butylamine), but most of these could not be characterized in solution by NMR spectroscopy, since their solubility is too low. A few experiments were performed with the ligand 1,1-cyclohexanediacetate. This ligand forms an eight-membered chelate and the Pt(II) complexes do not seem very stable. Multinuclear magnetic resonance studies of the products have shown the presence of several species in solution, most without the presence of the diacetate ligand.

3.2. Crystal structures

3.2.1. Ag_2(1,1-CBDCA) (**1**)

The results of the crystal structure determination of the 1,1-CBDCA silver complex have shown that there are four independent Ag atoms and two 1,1-CBDCA ligands in the unit cell. The compound did not crystallize with any molecule of solvent and the stoichiometry of the compound is Ag_2(1,1-CBDCA). The independent pattern and a few more atoms (Ag3′, Ag4′, O3′, O4′ and C2′) are shown in Fig. 1.

The most important bond distances and angles are listed in Table 2. The compound has an interesting 3-D extended structure. There seems to be metal–metal bonds although it is difficult to evaluate. The sum of the van der Waals radii of Ag atoms is about 3.4 Å. The Ag1–Ag2 and Ag3–Ag3′ distances are relatively short, 2.9284(6) and 2.9519(7) Å, respectively. The other distances are longer, with Ag4–Ag4′ and Ag3–Ag3″ = 3.1962(8) and 3.2835(7) Å, respectively, probably too long to suggest metal–metal bonds. Therefore, the Ag–Ag distances shorter than 2.96 Å were linked in Fig. 1.

The environment around each Ag atom is quite different. Again, it is difficult to evaluate some bonds since the distances Ag–O vary. In the following discussion, we will assume a maximum Ag–O bond distance of 2.32 Å. There are two such Ag–O bonds around each Ag atom, with O–

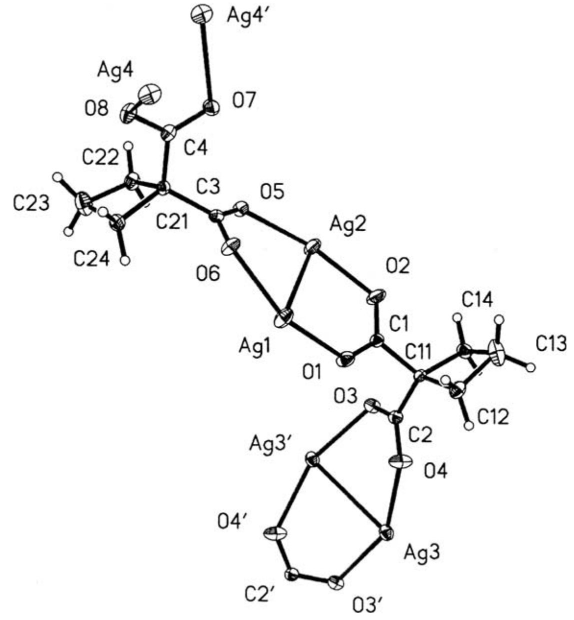


Fig. 1. Labeled diagram of Ag_2(1,1-CBDCA) (the ellipsoids correspond to 30% probability). Ag–Ag distances shorter than 2.96 Å were linked.

Ag–O angles ranging from 151.2° to 165.8° (Table 2). In addition, there are a few other O atoms around each Ag atom at distances between 2.45 and 2.59 Å, suggesting some weaker bonds. Furthermore, if we assume Ag–Ag bonds for distances shorter that 2.96 Å, we can suggest metal–metal bonds between Ag1 and Ag2 and between Ag3 and another Ag3. The angles Ag–Ag–O for these atoms are between 71.18(9)° and 83.04(9)°. The fourth silver atom Ag4 does not seem to be involved in metal–metal bonds.

Each carboxylato group forms bonds with two different Ag atoms as clearly shown in Fig. 1. The angles Ag–O–C vary between 111.6(3)° and 128.1(3)°. The C–O bonds are in the range 1.241(5)–1.267(5) Å and the average carboxylato O–C–O angle is 125.1(4)°. The C atoms of the four-membered rings are in a plane (mean deviation of 0.094 and 0.087 Å) and the internal C–C–C angles vary between 88.5(3)° and 90.7(4)°. The dihedral angles between the two carboxylato planes with its four-membered ring plane are 110.6° and 129.3° for the C11 ring and 46.3° and 84.4° for the C21 ring plane. The two independent four-membered rings are almost co-planar with a dihedral angle of 10.9°. The two carboxylato groups on each 1,1-CBDCA ligand are almost perpendicular to each other. The dihedral angle between the C1 O1 O2 and the C2 O3 O4 planes is 91.2°, while it is 104.9° between the C3 O5 O6 and C4 O7 O8 planes.

3.2.2. *cis-Pt(amine)$_2$ (dicarboxylato)*

The crystal structure of the compounds Pt(en)(1,1-CBDCA) (**2**), Pt(Meen)(1,1-CBDCA) (**3**) and Pt(en)(Bzmal) (**4**) were studied by X-ray diffraction methods. The three crystals were recrystallized in water or water–acetone

Table 2
Selected bond distances (Å) and angles (°)

*$Ag_2(C_4H_6(COO)_2)$ (**1**)*			
Ag1–O1	2.195(3)	Ag2–O2	2.165(3)
Ag1–O(6)	2.267(3)	Ag2–O5	2.195(3)
Ag1–O(6′)	2.454(3)	Ag2–O3′	2.535(3)
Ag3–O3′	2.282(3)	Ag4–O8	2.235(3)
Ag3–O4	2.293(3)	Ag4–O7′	2.310(3)
Ag3–O5′	2.556(3)	Ag4–O7″	2.591(3)
Ag3–O7′	2.569(3)	Ag1–Ag2	2.9284(6)
Ag3–Ag3′	2.9520(6)	O1–C1	1.248(5)
O2–C1	1.241(5)	O3–C2	1.263(5)
O4–C2	1.261(5)	O5–C3	1.255(5)
O6–C3	1.259(5)	O7–C4	1.267(5)
O8–C4	1.263(5)	C–C (ave.)	1.537(7)
O1–Ag1–O6	154.00(12)	O2–Ag2–O5	165.76(12)
O3′–Ag3–O4	151.19(12)	O7′–Ag4–O8	151.19(11)
Ag1–Ag2–O (ave.)	82.90(9)	Ag1–Ag2–O (ave.)	82.90(9)
Ag3′–Ag3–O (ave.)	77.00(9)	Ag–O–C	111.6(3)–128.1(3)
O–C–O (ave.)	125.1(4)	C–C–C (four-membered ring)	88.5(3)–90.7(4)
C–C–C (others)	106.4(3)–118.2(3)		
*Pt(en)(1,1-CBDCA) (**2**)*			
Pt–O1	2.009(4)	Pt–N1	2.028(5)
O1–C5	1.302(7)	O2–C5	1.226(8)
N1–C6	1.537(13)	N1–C7	1.505(12)
C1–C5	1.512(8)	C1–C2	1.565(12)
C1–C4	1.538(12)	C2–C3	1.479(19)
C3–C4	1.497(19)	C6–C7′	1.486(16)
O1–Pt–O1′	91.8(3)	O1–Pt–N1	91.6(2)
N1–Pt–N1′	84.8(3)	O1–Pt–N1′	175.2(2)
Pt–O1–C5	123.5(4)	Pt–N1–C6	105.8(6)
Pt–N1–C7	108.1(5)	C5–C1–C5′	112.8(7)
C5–C1–C4	114.3(4)	C5–C1–C2	112.3(4)
C2–C1–C4	88.6(7)	C1–C2–C3	88.8(9)
C1–C4–C3	89.2(8)	C2–C3–C4	93.5(9)
O1–C5–O2	120.1(7)	O2–C5–C1	121.0(6)
O1–C5–C1	118.9(6)	N1–C6–C7′	106.9(9)
N1–C7–C6′	105.1(8)		
*Pt(Meen)(1,1-CBDCA) (**3**)*			
Pt–O1	2.021(8)	Pt–N1	2.033(9)
O1–C5	1.286(12)	O2–C5	1.239(12)
N1–C61	1.50(3)	N1–C62	1.49(3)
C1–C5	1.534(12)	C–C (cyclobut. ave.)	1.56(2)
C61–C62′	1.61(3)	C6–C7 (ave.)	1.45(4)
O1–Pt–O1′	87.8(5)	O1–Pt–N1	94.3(4)
N1–Pt–N1′	83.4(5)	O1–Pt–N1′	177.2(3)
Pt–O1–C5	119.1(6)	Pt–N1–C61	109.2(12)
Pt–N1–C62	112.5(11)	C5–C1–C5′	111.1(11)
C5–C1–C4	116.0(7)	C5–C1–C2	111.1(7)
C2–C1–C4	89.7(10)	C1–C2–C3	93.6(12)
C1–C4–C3	86.9(10)	C2–C3–C4	89.9(10)
O1–C5–O2	121.9(9)	O2–C5–C1	119.6(9)
O1–C5–C1	118.5(9)	N1–C61–C62′	104(2)
N1–C62–C61′	105(2)	N1–C61–C7	114(2)
N1–C62–C7	115(2)		
*Pt(en)(Bzmal) (**4**)*			
Pt–O1	2.046(5)	Pt–O2	1.986(7)
Pt–N1	2.043(9)	Pt–N2	2.007(7)

(*continued on next page*)

Table 2 (*continued*)

*Pt(en)(Bzmal) (**4**)*			
O=C (ave.)	1.227(12)	O–C (ave.)	1.310(11)
N1–C5	1.480(12)	N1–C6	1.449(12)
C–C (ave.)	1.533(15)	C–C (ave. aromatic)	1.367(15)
O1–Pt–O2	90.5(2)	N1–Pt–N2	83.8(3)
N1–Pt–O1	94.5(3)	N1–Pt–O2	174.9(3)
N2–Pt–O2	91.1(3)	N2–Pt–O1	172.6(2)
Pt–O1–C1	120.8(4)	Pt–O2–C2	124.7(5)
Pt–N1–C5	104.2(6)	Pt–N2–C6	111.0(5)
O–C–O (ave.)	121.4(7)	C1–C3–C2	108.1(6)
N–C–C (ave.)	107.9(7)	C3–C4–C11	115.1(10)
O–C–C (ave.)	116.2(8)	C1–C3–C2	108.1(6)
C–C3–C2 (ave.)	112.2(13)	C–C–C (ave. aromatic)	120.0(10)

mixture, but the structures do not contain any molecule of solvent.

The crystal Pt(en)(1,1-CBDCA) (**2**) was shown to belong to a centrosymmetric space group. The Pt atom and the four C atoms of the cyclobutyl ring are located in a crystallographic plane, resulting in disorders of the two methylene groups of the ethylenediamine ligand. Its structure is shown in Fig. 2, including the disorder on the amine ligand. The best coordination plane around the Pt atom was calculated (mean deviation of 0.023 Å) and its dihedral angle with the cyclobutane ring is 90° (by symmetry).

The bond lengths and angles are listed in Table 2. The angles around the Pt angles are normal with the five-membered chelate angle of 84.8(3)° and the dicarboxylato six-membered chelate angle is 91.8(3)°. The other *cis* angles are 91.6(2)°, while the *trans* angles are 175.2(2)°. The Pt–O bond distances are 2.009(4), while the Pt–N bonds are 2.028(5) Å, in agreement with published values on similar complexes [5,11–15]. The carbonyl bonds O2–C5 are shorter (1.226(8) Å) than the O1–C5 (1.302(7) Å) distances as expected. The N–C bond lengths are slightly long (1.505(12) and 1.537(13) Å) probably due to the strain inside the chelate five-membered ring. The disorder on the C atoms increases the standard deviations on these bonds. The internal chelate ring angles at the N atoms are 108.1(5)° and 105.8(6)°, while those at the C atoms are 105.1(8)° and 106.9(9)°. In the second chelate, the strain is smaller, since it is a six-membered ring. The internal angles are 123.5(4)° at O1, 118.9(6)° at C5 and 112.8(7)° at C1. The angles inside the four-membered cyclobutane ring are much smaller and vary between 88.6(7)° and 93.5(9)°.

The conformation of the molecule is clearly seen on Fig. 2. The six-membered carboxylato chelate ring has a boat conformation. The best plane was calculated through the four atoms O1, O1′, C5 and C5′ and the Pt and C1 atoms are on the same side of the plane with deviations of 0.444 and 0.623 Å, respectively. This boat conformation was also observed in the structure of Pt(EtNH$_2$)$_2$(1,1-CBDCA) · H$_2$O [5]. The two carbonyl atoms O2 are oriented towards the other side of the plane (deviation of −0.470 Å).

The environment around the –NH$_2$ groups was examined for possible intermolecular H-bonds. There are two short contacts with N1···O1′ = 2.944 Å and N1···O2′ = 2.879 Å. The angles are favorable for H bonds involving N1 with O1′ with Pt–N1···O1′ = 119.0°, C6(or 7)–N1···O1′ = 107.4° (ave.) and C5′–O1′···N1 = 107.9°. The angles involving possible H-bonds with O2′ are less favorable with Pt–N1···O2′ = 126.4°, C6(or 7)–N1···O2′ = 84.6° (ave.) and C5′–O1′···N1 = 159.8°. The reported compound Pt(EtNH$_2$)$_2$(1,1-CBDCA) crystallized with a molecule of water, which was involved in an extensive H-bonding system. There are no molecules of solvent in crystal **2**, as observed also in the reported structure of Pt(NH$_3$)$_2$(1,1-CBDCA) [11].

In the crystal structure of Pt(Meen)(1,1-CBDCA) (**3**), the –CH$_3$ group on the amine ligand is located on a C atom and the molecule is chiral. The compound belongs to a centrosymmetric space group and the crystal is disordered. Two positions (50:50) were found for the methylene and the methyl groups of the Meen ligand. The disorder is shown in Fig. 3. Again, the Pt atom and the four C atoms of the cyclobutyl group are on a mirror plane. Therefore, the dihedral angle between the Pt plane (mean deviation is 0.0126 Å) and the cyclobutyl ring is again 90° by symmetry.

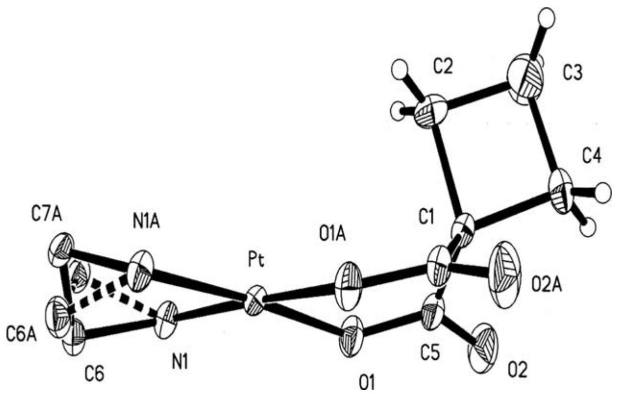


Fig. 2. Labeled diagram of Pt(en)(1,1-CBDCA) (2 conformations for the C atoms of en, and the ellipsoids correspond to 30% probability).

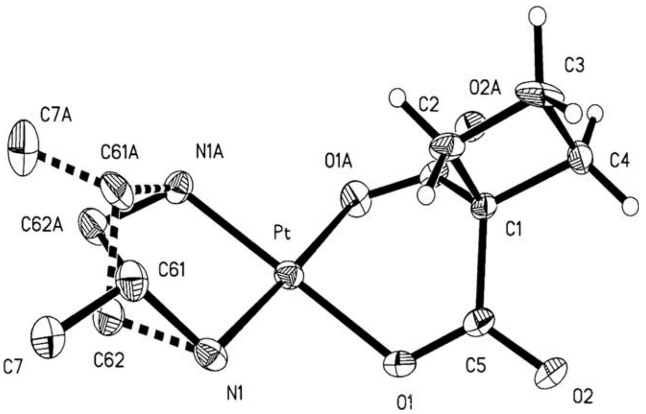


Fig. 3. Labeled diagram of Pt(Meen)(1,1-CBDCA) (2 conformations for the C atoms of Meen and the ellipsoids correspond to 30% probability).

The bond distances and angles in crystal **3** are shown in Table 2. The chelate angles around the Pt atom are smaller than the other *cis* angles, although the five-membered chelate angle is smaller (83.4(5)°) than the six-membered chelate angle (87.8(5)°). The other *cis* angles are 94.3(4)° and the *trans* angles are 177.2(3)°. The Pt–O bond distances are 2.021(8) Å, while the Pt–N bonds are 2.033(9) Å. The average internal angle inside the cyclobutyl ring is 90.0(11)°. The O1–C5 bond is longer (1.286(12) Å) than the C5–O2 bond (1.239(12) Å) as expected.

The carboxylato chelate ring has also a boat conformation as in crystal **2**. The best plane was calculated through the four atoms O1, O1′, C5 and C5′ and the Pt and C1 atoms are on the same side of the plane with deviations of −0.907 and −0.627 Å, respectively. The two carbonyl atoms O2 are oriented towards the other side of the plane (deviation of 0.458 Å) and form intermolecular H-bonds with the $-NH_2$ groups. The distance N1···O2′ is 2.977 Å with angles Pt–N1···O2′ = 105.4°, C6–N1···O2′ = 101.2° (ave.) and C5–O2···N1 = 121.6°, while the distance N1···O2″ is 2.995 Å with favorable angles Pt–N1···O2″ = 116.2°, C6–N1···O2″ = 101.9° (ave.) and C5–O2″···N1 = 127.2°. Therefore, all the amine protons are involved in the H-bonding system with the carbonyl O2 atoms. This H-bonding pattern is quite different from the one of the ethylenediamine analogue described above (crystal **2**).

The third Pt(II) compound Pt(en)(Bzmal) (**4**) belongs to a non-symmetric space group. A drawing of the molecule is shown in Fig. 4. The quality of this crystal was not as good as for the others. The average bond distances are Pt–N = 2.025(8) and Pt–O = 2.016(6) Å. The N–Pt–N chelate angle is smaller (83.8(3)°) than the six-membered chelate ring angle O–Pt–O (90.5(2)°). The other *cis* angles are 92.8(3)° (ave.), while the average *trans* angle is 173.8(3)°. The average C=O bond is shorter (1.227(12) Å) than the two other C–O bonds (ave. 1.310(11) Å) as expected. The other bond distances and angles are listed in Table 2.

The carboxylato chelate ring has also a boat conformation as in crystals **2** and **3**. The best plane was calculated through the four atoms O1, O2, C1 and C2 (mean deviation = 0.039 Å) and the Pt and C3 atoms are on the same side of the plane with deviations of −0.528 and −0.752 Å, respectively. The dihedral angle between this plane and the coordination plane is 19.7°. The two carbonyl atoms O3 and O4 are oriented towards the other side of the plane (deviations of 0.283 and 0.781 Å, respectively) and form intermolecular H-bonds with the $-NH_2$ groups. The distance N1···O4′ is 2.859 Å with angles Pt–N1···O4′ = 115.1° and C5–N1···O4′ = 91.7°, while the angle C2′–O4′···N1 is 136.5°. The distance N2···O3″ is 2.971 Å with favorable angles Pt–N2···O3″ = 110.23°, C6–N2···O3″ = 109.9° and C1″–O3″···N2 = 131.2°. Therefore, each amine group is involved in the intermolecular H-bonding system with the carbonyl O atoms. This H-bonding pattern is slightly different from those of crystals **2** and **3**. The aromatic ring forms a dihedral angle of 43.5° with the Pt plane and 34.7° with the plane of the 4 planar atoms of the boat conformer.

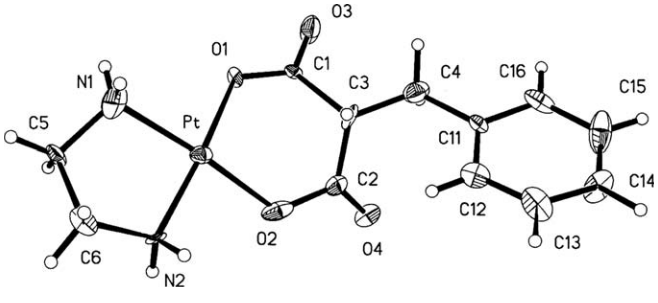


Fig. 4. Labeled diagram of Pt(en)(Bzmalonato) (the ellipsoids correspond to 30% probability).

3.3. NMR

The majority of the multinuclear magnetic resonance spectra of the diamine dicarboxylato complexes were measured in D_2O. Since most of the compounds are only sparingly soluble in water, very long accumulating times were required especially for the ^{195}Pt and ^{13}C NMR spectra. The solutions were often heated to about 40–45° in order to increase the solubility. One ^{1}H NMR spectrum was measured at 50°. Even then, some weaker signals (especially in ^{13}C NMR) could not be detected. A few compounds were too insoluble for NMR spectroscopy. Several organic solvents were tested, but the solubilities were even lower. A few spectra were measured in a mixture of D_2O with an organic solvent. Some of the complexes decomposed when heated.

3.3.1. ^{195}Pt NMR

Most of the ^{195}Pt NMR spectra were recorded overnight. The ^{195}Pt chemical shifts of the Pt(II) compounds are shown in Table 3. Most of the complexes have shown only one signal. They can be approximately classified into three groups according to the amines. The complexes containing NH_3 are observed at lowest fields (−1610 to −1742 ppm), those containing a monodentate primary amine (cyclopentylamine) (−1646 to −1861 ppm) and finally the bidentate amines, ethylenediamine, its methyl derivatives and dach (−1851 to −1978 ppm) compounds. The presence of a five-membered chelate (like ethylenediamine) moves the chemical shifts to higher fields because of the strain inside the ring and the increased electron density on the Pt atom caused by the chelate effect. All the carboxylato ligands are bidentate and form six-membered chelate rings, except the ligand 1,2-CBDCA, which forms a seven-membered chelate ring upon complexation. This removes the strain inside the dicarboxylate chelate ring along with a decrease of stability due to the chelate effect and the chemical shifts of all the 1,2-CBDCA complexes are observed at lower fields than the others.

It is difficult to compare the chemical shifts of the different compounds, since several are very different. We might

Table 3
δ(Pt) (ppm), δ(H) (ppm) and $^2J(^{195}\mathrm{Pt}–^1\mathrm{HN})$ (Hz) of the complexes in D_2O

Amine	Carboxylato	δ(Pt)	δ (^{1}HN)	$^2J(^{195}\mathrm{Pt}–^1\mathrm{H})$
NH_3	1,1-CBDCA	−1742	4.025	72
NH_3	1,2-CBDCA	−1610, −1506 (30%)	3.945	99
NH_3	malonato		5.3	
NH_3	Bumalonato	−1686	4.077	90
cpa	1,2-CBDCA	−1647, −1720 (20%)		
cpa	malonato	−1861		
cpa	Bzmalonato		5.4	
en	1,1-CBDCA	−1908		
en	1,2-CBDCA	−1860	4.094	
en	malonato	−1997	5.310	68
en	Bumalonato	−1954	5.28 (D_2O), 4.80 (acetone)	65
en	Bzmalonato	−1907	5.15, 5.47, 5.58	
Meen	1,1-CBDCA	−1951	5.5, 5.3	
Meen	1.2-CBDCA	−1867	5.05, 5.25, 5.44	
Meen	malonato	−1963	5.4	72
Meen	Bumalonato	−1914		
Meen	Bzmalonato	−1916		
Me_2en	1,1-CBDCA	−1968	5.56	70
Me_2en	1,2-CBDCA	−1851	5.21	
Me_2en	malonato	−1978		
Me_2en	Bumalonato	−1930		
Me_2en	Bzmalonato	−1928	5.33	
dach	1,1-CBDCA	−1946		
dach	1,2-CBDCA	−1888, −1713 (35%)	5.43	63
dach	malonato		4.28, 4.39	
dach	Bumalonato		5.56	62

look at the malonato complexes and its benzyl and butyl derivatives. The presence of a butyl or benzyl group on the malonato ligand seems to shift the resonance towards lower fields. This might be caused by the solvent effect. For the malonato compounds, the solvent (water) can approach the metal atom on both sides of the Pt(II) plane, which increases the electron density on the Pt atom. For the benzyl and butyl malonato derivatives, the bulkiness of these ligands reduces the extent of hydration around the Pt atom, thus reducing the electron density around the metal atom, when compared to the unsubstituted malonato ligand. A shift towards lower fields is often observed when the bulkiness around the Pt atom increases. Similar results were obtained for the Me_2NH and Me_4en complexes [5]. It is interesting to note that the ^{195}Pt resonances of the butylmalonato and benzylmalonato complexes are almost identical indicating that the presence of an electrorepulsive or electroattracting group on the carboxylato ligand does not seem to have an important influence on the ^{195}Pt chemical shifts. But the butyl or the benzyl groups are quite far for the Pt atom.

It might be different for the amine ligand. For the 1,1-CBDCA complexes of ethylenediamine ($\delta = -1908$ ppm) and its methyl ($\delta = -1951$ ppm) and dimethyl ($\delta = -1972$ ppm) derivatives, a shift towards higher fields can be observed when methyl groups are present. For the Me_4en complex, the reported value is −1966 ppm [5]. The presence of electrorepulsive groups on the amine should increase the strength of the Pt–N σ bond, therefore increasing the electron density on the Pt atom resulting in a shielding on the metal as observed in ^{195}Pt NMR.

The NH_3, cpa, and dach Pt(II) complexes containing 1,2-CBDCA have shown a second signal (Table 3), which could be attributed to some hydrolyzed or aqua species. In the $Pt(NH_3)_2$ system, the diaqua compound *cis*-$[Pt(NH_3)_2(D_2O)_2]^{2+}$ has been reported at −1590 [16], the monohydroxo-bridged dimer *cis*-$[Pt(NH_3)_2(D_2O)(\mu\text{-}OH)Pt(NH_3)_2(D_2O)]^{3+}$ between −1516 and −1547 depending on the pH [17] and the cyclic trimer at −1499 ppm [17–19]. The *cis*-$[Pt(cpa)_2(D_2O)_2]^{2+}$ compound was found at −1721 ppm [20] very close to the second peak observed for the cpa-1,2-CBDCA compound (−1720 ppm). For the dach compound, we have not found any report on monohydroxo-bridged dimers, but their chemical shifts should be around the observed second signal (−1713 ppm).

In the first experiment on the synthesis of the complex $Pt(Me_2en)$(1,2-CBDCA), three signals were observed in ^{195}Pt NMR at −1861, −1851 and −1738 ppm. The sample was probably heated for a longer time before the measurement in order to dissolve it. The monohydroxo-bridged dimer with Me_2en was reported between −1740 and −1764 (several isomers [21]), close to the lowest field value observed in the NMR spectrum of $Pt(Me_2en)$(1,2-CBDCA) (−1738 ppm). The diaqua compound $[Pt(Me_2en)(D_2O)_2]^{2+}$ was reported at −1867 ppm [21], close to the −1861 found here.

The bidentate ligand 1,2-CBDCA forms upon coordination a seven-membered chelate, whose stability is much decreased compared to five or six-membered chelates. Therefore, its reaction with Pt(II) is probably slower and other hydrolyzed or aqua species are observed in solution. Similar results were reported for two other dicarboxylato ligands, (1,1-cyclopentanediacetato and1,1-cyclohexanediacetato) which form eight-membered chelates [5].

As mentioned earlier, we have performed several experiments with the ligand 1,1-cyclohexanediacetate. Multinuclear magnetic resonance studies of the products have shown the presence of several species in solution, most without the presence of the diacetate ligand.

3.3.2. ^1H and ^{13}C NMR

The ^{1}H NMR signals are listed in Section 2. For a few complexes, the malonate protons exchange with the D atoms of the solvent. Therefore, the signals of –CH_2 or –CH groups of the malonato derivatives were often weaker than expected. The N–H groups of the bonded amines could be observed for several complexes and are shown in Table 3. Their chemical shifts vary between 3.95 and 5.58 ppm. Exchange with D_2O is usually limited for Pt(II) bonded amines. For several compounds, they were not observed. The long accumulation times along with slight heating of the solutions in order to dissolve as much sample as possible increased the amine proton exchange with D_2O. A few coupling constants $^2J(^{195}Pt–^1HN)$ could be calculated, but the values in Table 3 are very approximate. These vary between 62 and 99 Hz. For *cis*-Pt(amine)$_2$I$_2$ complexes with monodentate amines, values between 65 and 70 Hz were reported [8].

The ligand 1,2-diaminopropane (Meen) is a chiral molecule. When bonded to Pt(II), the H atoms on the –NH_2 and –CH_2 groups are not equivalent, since one H atom is located on the same side as the –CH_3 group and the second is on the opposite side. In the complex, Pt(Meen)(mal), the two H atoms in the malonato ligand are not equivalent, since one H atom is on the same side as the –CH_3 group and the second is on the opposite side. These are observed at 3.47 and 3.51 ppm, with relative intensity, respectively, of 2:1. Furthermore, in the Pt(II)–Meen complexes, the CH group in the *n*-butylmalonate and benzylmalonate ligands is prochiral. Therefore, the complexes Pt(Meen)(Bumal or Bzmal) will have four diastereoisomers with two pairs of enantiomers. This is clearly seen in the ^{1}H NMR spectra of these molecules, especially for the two –CH_3 groups. Two well-defined triplets at 0.751 and 0.810 ppm (–CH_3 of Bumal) and two doublets at 1.166 and 1.188 ppm (–CH_3 of Meen) are observed in the ^{1}H spectrum of Pt(Meen)(Bumal). Two triplets at 3.342 and 3.357 ppm are also observed for the CH butylmalonato ligand.

The coupling constants $^3J(^{195}Pt–^1H)$ are usually difficult to determine for these type of complexes on a 300 MHz instrument, especially since the compounds are quite insoluble. They were well observed in the complex of Pt(en)(mal) where the $^3J(^{195}Pt–^1H)$ was found to be 46 Hz. They could also be calculated for the compound Pt(en)(1,2-CBDCA) (48 Hz). For comparison, values between 44 and 54 Hz have been reported in the literature for other complexes containing the moiety Pt(en) [22].

The accumulation times for the ^{13}C NMR spectra were 48–72 h. The background noise was still important. Several weaker peaks were doubtful and are not included in Section 2. For this reason, no $J(^{195}Pt–^{13}C)$ coupling constants are reported. The carboxylato C atoms are observed at around 180 ppm and the signal is extremely low. In the Meen and Me$_2$en complexes, the two carboxylato C atoms are not equivalent. For Pt(Me$_2$en)(1,1-CBDCA), two well resolved signals were observed at 181.67 and 181.83 ppm.

4. Conclusion

The already reported method for the synthesis of Pt(amine)$_2$(RCOO)$_2$ using silver sulfate and barium carboxylate has been found superior to the conventional method involving the reaction of the diaqua species [Pt(amine)$_2$(H$_2$O)$_2$](NO$_3$)$_2$ with the carboxylate salt of sodium or potassium. This latter method produces usually a mixture of products and the yields of Pt(amine)$_2$(RCOO)$_2$ are low (~30%), especially for monodentate ligands. The yields using the barium carboxylate method are better, usually 40–60% and with a few bidentate ligands up to 85%. The new method described in this paper is slightly different, since it involves synthesizing the silver carboxylate intermediate, which is formed quite rapidly. The crystal structure of Ag$_2$(1,1-cyclobutyldicarboxylate) was determined. Surprisingly, this complex is quite stable (few months) in the presence of light. It was recrystallized in water and the compound is free from molecules of solvent. Its reaction with Pt(amine)$_2$I$_2$ in water is simple. Both reactants are dried and can be easily weighed. If the reaction is done in a mixture of water and acetone, the reaction is faster, but acetone should be used with care when monodentate amines and carboxylate ligands are used, since isomerization may occur. The product Pt(amine)$_2$(RCOO)$_2$ is pure after the removal of AgI. The yields with bidentate carboxylate ligands are excellent (~80%).

The NMR characterization of these compounds is difficult due to their low solubility. Water was found to be the best solvent, although the spectra of several compounds could not be measured, since the aqueous concentration was too low. For the monodentate amine ligands, the complexes containing the moiety Pt(NH$_3$)$_2$ were found more soluble than the Pt(cyclopentylamine)$_2$ species. The ethylenediamine complexes and its derivatives are slightly more soluble than the Pt(NH$_3$)$_2$ and Pt(cpa)$_2$ species. In the ethylenediamine series, the Meen complexes were found to be the least soluble. Finally, the dach complexes are probably the least soluble in the reported series.

The ^{195}Pt chemical shifts are observed at higher fields when complexation involves the formation of five-membered chelates as observed for the ethylenediamine derivatives, compared to the monodentate cyclopentylamine complexes. The same observation can be made for the dicarboxylato complexes. The signals of the six-membered chelates are found at higher fields than the seven-membered chelates as observed for the 1,1-CBDCA and the 1,2-CBDCA complexes. The 1,2-CBDCA compounds might contain other Pt(II) species, especially aqua or hydrolyzed compounds, where the dicarboxylato ligand is absent.

5. Supplementary material

The four CIF lists have been deposited at the Cambridge Structural Database, CCDC 298125–298128.

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