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A Study of *cis*-Dichlorobis(methylamine)platinum(II): Crystal and Molecular Structures of Two Crystal Forms

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Abstract

A new synthesis of *cis*-dichlorobis(methylamine)platinum(II) is described. It appears that during the crystallization process at least two types of crystals are formed. Form **A** is monoclinic with space group $P2_1/n$ and unit cell dimensions $a = 6.272$, $b = 15.726$, $c = 7.419$ Å, $\beta = 99.86°$, $V = 721$ Å^3, $Z = 4$, $R = 0.055$. Form **B** is monoclinic, with space group $P2_1/c$ and unit cell dimensions $a = 16.078$, $b = 6.372$, $c = 21.459$ Å, $\beta = 92.7°$, $V = 2196$ Å^3, $Z = 12$, $R = 0.057$. The two forms can be readily distinguished by IR spectroscopy.

Introduction

cis-Dichlorodiammineplatinum(II) (cisplatin or *cis*-DDP) is a leading antitumor drug with a wide spectrum of activity against human tumors. However, due to its severe dose-limiting side effects, an intensive search for analogues of cisplatin with reduced toxicity and more favorable properties has been initiated during the past two decades.

Most of the complexes evaluated either involve the substitution of ammonia molecules with other amino ligands (monodentate or bidentate), or the alteration of the leaving group (monodentate or bidentate) [1, 2].

The antitumor activity of *cis*-$Pt(MeNH_2)_2Cl_2$, the simplest analogue of *cis*-$Pt(NH_3)_2Cl_2$ has been disappointing in spite of its increased solubility in water [2]. As part of a study to compare effects of different ligands on the toxicity and mutagenicity of *cis*-platinum(II) compounds in bacteria [3], the *cis*-dichloro complex of Pt(II) with methylamine was synthesized.

While this complex has been known for some time, it has only been characterized by infrared spectroscopy. Moreover, the various infrared spectral studies [4, 5] are not at all in accordance. The physical properties of the complexes $Pt(am)_2X_2$ vary gradually on replacing one of the protons of NH_3 successively with an alkyl group, but there is a break at the methylamine complex. For example, in the series am = NH_3, $MeNH_2$, $EtNH_2$, $PrNH_2$, $BuNH_2$, the methylamine complex has the highest solubility in water [2a] and the lowest enthalpy of formation and decomposition [6].

In order to resolve the discrepancy in the literature on the infrared spectra of $Pt(MeNH_2)_2Cl_2$, we have re-examined its preparation and physicochemical and X-ray structural investigations were undertaken.

Experimental

Commercially available methylamine (Fluka, 40% in water) was used without further purification. K_2PtCl_4 was obtained from Johnson Matthey.

Preparation of the Complexes

cis-$Pt(MeNH_2)_2Cl_2$

This complex was synthesized by a slight modification of the method of Dhara [7]. A mixture of K_2PtCl_4 (2.4 g, 5.4 mmol) and KI (5.4 g, 32 mmol) was stirred at room temperature for 1 h. The resulting brown solution was filtered and methylamine (1.5 ml, 11 mmol) was added to the stirred solution of $[PtI_4]^{2-}$. The immediate orange precipitate was stirred for 1 h (the precipitate turned slightly paler), filtered, washed with water (several times) and dried *in vacuo* over silica-gel. The yield of the diiodo complex is almost quantitative. Silver nitrate (0.74 g, 4.36 mmol) was added to a solution of $[Pt(MeNH_2)_2I_2]$ (1.12 g, 2.2 mmol) in acetone (40 ml) and the mixture stirred vigorously for 1 h. AgI was removed and the yellow filtrate was evaporated to dryness at room temperature. Addition of a few drops of concentrated hydrochloric acid to the nitrato complex dissolved in either acetone, water or methanol gradually precipitated the *cis*-chloro complex.

The compound can be recrystallised from water or acetonitrile.

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trans-[Pt(MeNH$_2$)$_2$Cl$_2$]

Methylamine (5 ml) was added to a filtered solution of K_2PtCl_4 (0.66 g, 1.59 mmol) in water and the solution warmed for 1 h. The green precipitate of the Magnus salt which formed initially redissolved slowly. The almost clear solution obtained was filtered and concentrated to 5 ml. Concentrated hydrochloric acid (6 ml) was added and the resulting yellow solution warmed gently with stirring for 1 h. A flocculant yellow precipitate gradually separated. The mixture was kept at 5 °C for 15 h, the product was separated, washed with cold water and dried *in vacuo* over silica-gel.

Analysis

C, H and N analyses were carried out by standard procedures by the Interuniversity Microanalytical Services, Ecole Nationale Supérieure de Chimie de Toulouse.

All analytical data are in good accordance with the formula $Pt(MeNH_2)_2Cl_2$.

Spectral Measurements

IR spectra were recorded (4000–200 cm^{-1}) on a Perkin-Elmer 983 spectrophotometer as nujol mulls (CsI plates) or as CsBr discs. There is no reaction of the compounds with CsBr, because the spectra are comparable to those obtained as nujol mulls.

Proton NMR spectra were recorded on a WH 250 Bruker Fourier-transform spectrometer equipped with a wide band probe (23–103 MHz). The δ values are quoted with respect to TMS. Solutions were nearly saturated in DMSO-d$_6$. ^{195}Pt spectra were recorded at 323 K in D_2O as solvent. Typical parameters were: pulse width 20 μs, 2750 transients were collected. ^{195}Pt of H_2PtCl_6 in D_2O solution was used as external reference at 53 770 768 MHz. Data were collected on freshly prepared samples.

Measurements of electrolytic conductance were carried out with 10^{-3} M dimethyl sulfoxide solutions at 25 °C using a Beckman conductivity bridge.

Solutions and Refinement of the Structures

The X-ray measurements for forms **A** and **B** were carried out on a Nonius CAD4 diffractometer using monochromated Mo Kα radiation (λ = 0.71069 Å) at room temperature. The cell dimensions for forms **A** and **B** were calculated from 25 reflections. The structures were determined by the heavy atom method. A Patterson map revealed the position of the platinum atom. All non-hydrogen atoms were located by the usual combination of the Fourier and least squares calculations. Hydrogen atoms were introduced with a theoretical bond length of 0.97 Å, but were left free in the last cycle of refinement. Crystal data and other parameters related to data collection are summarized in Table I.

TABLE I. Summary of Crystal Data and Intensity Collection

	A	**B**
Compound	$PtCl_2N_2C_2H_{10}$	$(PtCl_2N_2C_2H_{10})_3$
Crystal system	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1/c$
a (Å)	6.272	16.078(2)
b (Å)	15.726	6.372(1)
c (Å)	7.419	21.459(4)
β (°)	99.86	92.7(2)
Z	4	4
V (Å^3)	721	2196
F(000)	1776	1776
μ (Mo Kα) (cm^{-1})	200.1	200.1
ρ_{calc} (g cm^{-3})	3.02	2.977
Temperature (K)	293	293
Instrument	Nonius CAD4 diffractometer	
Radiation	Mo Kα from monochromator (λ Mo Kα = 0.71069 Å)	
Take-off angle (°)	3	4
Scan mode	$\theta/2\theta$	$\theta/2\theta$
Max. Bragg angle (°)	26	26
Periodicity	3600 s 100 reflections	3600s 100 reflections
No. independent reflections	2070	3496
No. observed reflections	2058	3419
No. refined parameters	65	191
$R = \Sigma\|\|F_o\|-K\|F_c\|\|/\Sigma\|F_o\|$	0.055	0.057
$R_w = [\Sigma_w(\|F_o\| - K\|F_c\|)^2/\Sigma_x\|F_o\|^2]^{1/2}$	0.063	0.068

Results and Discussion

The complex *cis*-[Pt(MeNH$_2$)I$_2$] was prepared by the method of Dhara [7] and converted to *cis*-[Pt(MeNH$_2$)$_2$(ONO$_2$)$_2$] using silver nitrate in acetone. The conversion of the nitrate complex to the chloro analogue using hydrochloric acid was tried in various solvents (water, acetone, methanol), but this resulted in the formation of two types of crystals or sometimes a mixture of two. Under these mild conditions it is anticipated that the *cis*-isomer is formed exclusively.

No special conditions could be found favorizing the formation of one of the modifications. Both forms are yellow, but form **A** is paler than form **B**. Recrystallization of the compound from acetonitrile or water would either: (i) not change the compound, (ii) cause one form to change to the other, or (iii) give a mixture of the two forms. All these compounds analysed as [Pt(MeNH$_2$)$_2$Cl$_2$]. The two forms **A** and **B** can easily be differentiated using IR (*vide infra*) and their melting points (form **A**: m.p. = 185–187 °C, form **B**: m.p. = 171–175 °C).

Isomers of the composition PtL$_2$X$_2$ can exist as [PtL$_4$][PtX$_4$], [PtL$_3$X][PtLX$_3$] or as *cis*- or *trans*-[PtL$_2$X$_2$]. The geometric isomers of PtL$_2$X$_2$ can also cocrystallize to give a mixed crystal [8]. Polymorphism is known amongst ionic compounds, e.g. [Pt(NH$_3$)$_4$][PtCl$_4$] [9], and neutral monomeric compounds, e.g. Pt(2,2'-bipyridine)Cl$_2$ [10] and *cis*-Pt(N-methylimidazole)$_2$Cl$_2$ [11].

In our case, forms **A** and **B** cannot be ionic isomers as they are both non-electrolytes in DMSO*.

IR Spectra

There have been two independent studies of the IR spectra of *cis*-[Pt(MeNH$_2$)$_2$Cl$_2$] [4, 5]. However, the IR spectrum of the compound published by Watt *et al.* [4] differs considerably from that of Kharitonov *et al.* [5]. In our work, the IR spectrum of form **A** corresponds to that published by Kharitonov and coworkers, while form **B** corresponds to that published by Watt *et al.*

The main differences in the spectra are in the region for δNH$_2$ and in the region for the Pt–Cl stretch (see Table II). The positions of the other bands are similar for the two forms, except that the relative intensities are different. A distinct splitting of the ν(Pt–N) band is observed for both modifications, as expected for a *cis*-complex, but form **B** has slightly higher frequencies than form **A**. In both modifications, the lower frequency band is the more intense of the two.

Modification **A**, instead of showing two absorptions in the Pt–Cl stretching region as expected for a *cis*-isomer, shows only a broad band (width at half height = 20 cm^{-1}) which is normally indicative of a *trans*-isomer. It is important that the *cis*-compounds of the type [PtL$_2$X$_2$] tested for antitumor activity are isomerically pure as the *trans*-isomers have no activity [2].

To settle the possibility that *cis-trans* isomerization** might have occurred during the preparation of *cis*-Pt(MeNH$_2$)$_2$Cl$_2$, such that modification **A** is in fact a *trans*-isomer or **B** is contaminated with some *trans*-isomer, the *trans*-isomer was prepared by treating [Pt(MeNH$_2$)$_4$]Cl$_2$ in HCl and the IR spectra compared (m.p. of *trans*-isomer: 228–230 °C). How-

TABLE II. Important Bands in the Infrared Spectra[a] of *cis*- and *trans*-[Pt(MeNH$_2$)$_2$Cl$_2$]

	This work			Literature values			
	Form **A**	Form **B**	*trans*-	Kharitonov [5]		Watt [4]	
				cis-	*trans*-	*cis*-	*trans*-
δNH$_2$	1595(s) 1571(w)	1596(s) 1582(m) 1571(w)	1592(s) 1575(sh)	1598(s) 1577(m)	1596(s)	1596(s) 1581(m) 1575(m)	1594(s)
ν(Pd–N)	518(w) 506(m)	525(w) 510(m)	514(s)	517(m) 505(m)	513(s)	517(m) 506(m)	518(s)
ν(Pt–Cl)	318(br)	329(m) 314(m)	336(s)	Not given		318(s)	334(vs)

[a] w = weak, m = medium, s = strong, vs = very strong, br = broad.

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*There is a slow solvolysis in DMSO over a period of 24 h to give a 1:1 electrolyte such as [Pt(MeNH$_2$)$_2$(DMSO)Cl]Cl.

**In aqueous solutions, Pt(II) complexes are normally inert to isomerization. In aprotic dipolar solvents (DMF, DMSO), pyridine and pyrimidine complexes such as *cis*-[PtL$_2$Cl$_2$] isomerize [12], albeit slowly, for example 65 °C for 3 days. On the other hand, it has been reported that *cis*-complexes of cycloalkylamines (R = butyl, hexyl) isomerize under milder conditions in acetone or chloroform [13]. Meanwhile complexes such as Pt(phosphine)$_2$X$_2$ isomerize in the presence of catalytic amounts of phosphine [14].

ever, it is difficult to use IR spectroscopy to detect the presence of *trans*-[$Pt(MeNH_2)_2Cl_2$] as an impurity in *cis* as the main bands in the spectra of *trans* are not significantly different from forms **A** and **B**. The number of bands in the Pt–Cl stretching region of IR is not always an unambiguous method for differentiating the *cis*- and the *trans*- isomers*. Normally, the frequency of the Pt–Cl stretching vibration for complexes PtL_2X_2 is in the order $\nu_{asym}(trans) > \nu_{asym}(cis) > \nu_{sym}(cis)$. However, for the methylamine complex, there is not a significant difference in the position of the Pt–Cl vibration for the *trans*- isomer and the asymmetric stretching vibration for form **B**.

NMR Spectra

The ^1H spectra of the two forms **A** and **B** in DMSO are identical. The methyl resonance is a well resolved triplet at 2.39 ppm (J(H–H) = 6.2 Hz). The broad NH_2 resonance at 4.86 ppm shows two side bands due to the coupling with platinum (J = 67 Hz). The position of the NH_2 resonance suggests that the forms have a *cis*-geometry; the NH_2 signals for the *trans*-compounds are situated more upfield [17].

For the *trans*-complex, the solvolysis in DMSO is very rapid as two sets of methyl resonances and amine resonances are observed. Conductance measurements for the *trans*-complex in DMSO show that solvolysis to give a 1:1 electrolyte is complete within 40 min.

The ^{195}Pt NMR spectrum of a mixture of **A** + **B** in D_2O exhibits only one signal at −2238 ppm**.

The ^1H NMR spectrum (chemical shifts of ^1H) may not be sufficiently sensitive to the subtle differences in the environment between forms **A** and **B**, but the ^{195}Pt chemical shift is highly dependent on the donor atom, the complex geometry [19] and has also been used to study interconversion of diasteroisomers [20]. We can therefore be confident that the two forms **A** and **B** have the same structure in solution.

In order to gain further insight into the characterization of these complexes, we have undertaken an X-ray structural investigation of the two forms isolated.

Structure Studies

Table I summarizes the crystal data and intensity collection.

Form A

The complex consists of monomeric $Pt(MeNH_2)_2Cl_2$ units which are well separated (a view of the molecule is given in Fig. 1).

The coordination around platinum is square planar with a Cl–Pt–Cl angle of 93.55° and an N–Pt–N angle of 91.4°. The Pt–Cl and Pt–N distances are comparable with values found in related complexes.

However, more interestingly, it may be underlined that in this complex the two methyl groups lie on the same side of the plane delimited by the two chloride and the two nitrogen atoms. This structure could conform with the C_s point group.

Moreover, if hydrogen bonding in methylamine complexes is frequently invoked in order to interrelate the vibrational assignments, the structure here resolved evidenced a great number of such bonds, *viz.* between the N–H of one molecule and the chlorine of another one. All these hydrogen bonds imply N–H···Cl distances shorter than 2.7 Å and N–H···Cl angles close to 180°. Bond distances and bond angles are reported in Table III.

Form B

This complex consists of three types of monomeric $Pt(MeNH_2)Cl_2$ units. In each case, the coordination around platinum is square planar. However, two units look like form A with the two methyl groups lying on the same side of the square delimited by platinum and its four coordinated atoms. In the third unit, one of the methyl groups is above the plane while the other one is located below. In this case, the network of hydrogen bonds is more complex than in structure A. However, it may be underlined that no hydrogen bond exists between units

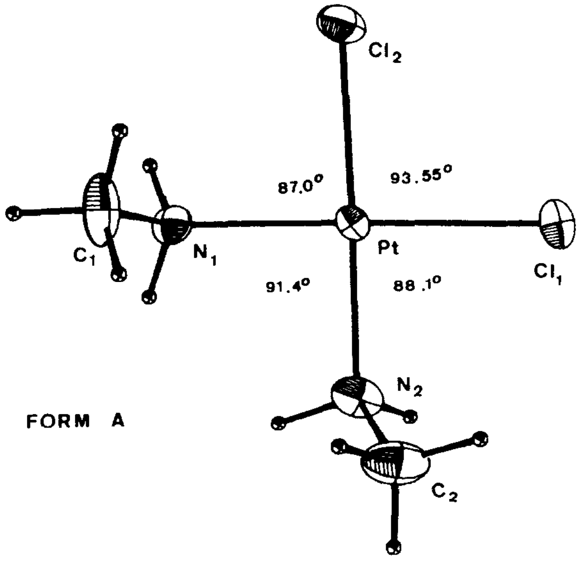

Fig. 1. View of the only molecule implied in Form **A**.

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*For example, only one Pt–Cl stretching vibration is observed for $Pt(NH_3)_2Cl_2$ [15], the red form of [Pt(bipy)-Cl_2] [10] and for several cycloalkylamine complexes, *cis*-[$Pt(RNH_2)_2Cl_2$] [16]. This usually comes about when the symmetrical and unsymmetrical bands have similar frequencies and therefore not well resolved in the spectra.

**The ^{195}Pt chemical shift compares quite well, after allowing for solvent effects, with that of *cis*-$Pt(NH_3)_2Cl_2$ in DMSO (2097 ppm upfield from Na_2PtCl_6 [18]).

TABLE III. Interatomic Distances (Å) and Angles (°)

Form A			
Pt–Cl(1)	2.306(2)	Cl(1)–Pt–Cl(2)	93.55(8)
Pt–Cl(2)	2.308(2)	Cl(1)–Pt–N(2)	88.1(2)
Pt–N(1)	2.027(7)	N(1)–Pt–N(2)	91.4(3)
Pt–N(2)	2.040(7)	Cl(2)–Pt–N(1)	87.0(2)
N(1)–C(1)	1.390(11)		
N(2)–C(2)	1.430(11)		

	Motif_I(A')	Motif_II(A')	Motif_{21}(B')
Form B			
Pt–Cl(1)	2.334(2)	2.307(2)	2.319(2)
Pt–Cl(2)	2.295(2)	2.316(2)	2.284(2)
Pt–N(1)	2.064(6)	2.058(6)	2.048(6)
Pt–N(2)	2.052(6)	2.084(6)	2.034(6)
N(1)–C(1)	1.458(10)	1.455(12)	1.452(12)
N(2)–C(2)	1.459(11)	1.467(10)	1.495(11)
Cl(1)–Pt–Cl(2)	93.30(7)	93.88(7)	91.68(8)
Cl(1)–Pt–N(2)	88.4(2)	89.1(2)	87.3(2)
N(1)–Pt–N(2)	89.5(2)	91.2(3)	93.7(2)
Cl(2)–Pt–N(1)	88.8(2)	85.9(2)	87.4(2)

	Dihedral angle (°)
Selected geometric features of the Form **B**	
Pt_I coord plane (A')–Pt_II coord plane (A')	6.5
Pt_I coord plane (A')–Pt_{21} coord plane (B')	132.6
Pt_II coord plane (A')–Pt_{21} coord plane (B')	136.8

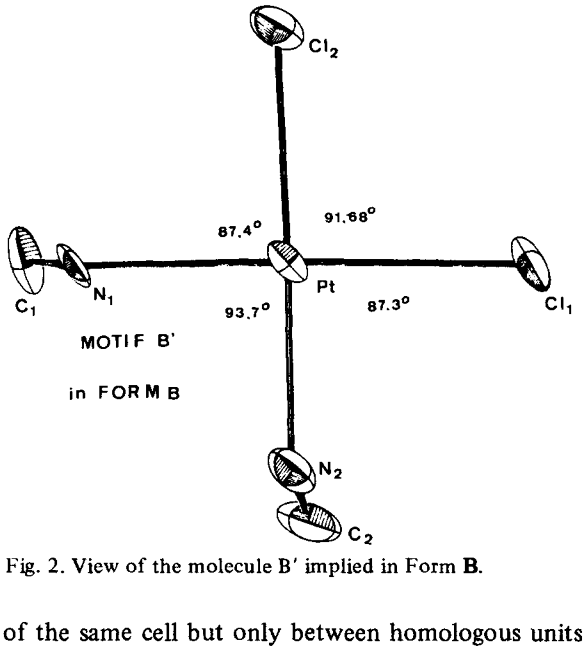

Fig. 2. View of the molecule B' implied in Form **B**.

of the same cell but only between homologous units of non-adjacent cells.

Neutral complexes of stoichiometry PtL_2X_2 generally crystallize in linear stacks unless very bulky ligands hinder the necessary close approach of the platinum atoms.

In form **B**, A' molecules exhibit a columnar framework with the molecular planes perpendicular to the stacking axis, here the A axis; however the platinum chain is distorted from a fully linear arrangement and this results in a zig-zag metal chain. Moreover though in this columnar arrangement all the A' molecules have the methyl groups lying on the same side of the platinum plane, these methyls are alternatively above and below the plane. This order appears different to that found in Wolfram's red salt [21] where all ethyl substituents lie on the same side of platinum atoms.

Between the stack of A' molecules appears the chainlike structure of B' molecules (Fig. 2), the dihedral angle between A' and B' planes being ≈135°. Taking in mind that in B' one methyl lies below the molecule plane and the other above, the Pt–Pt distance is much greater than in the A' stack.

Conclusion

The complex *cis*-$[Pt(MeNH_2)_2Cl_2]$ exists in the solid state in at least two different crystallographic forms. These forms are stabilized by the network of hydrogen bonds. Some years ago, Ducanson and Venanzi [21] interpreted infrared spectra of some amine complexes of platinum(II) in terms of conformational changes which arise from restricted rotation of the amine about the Pt–N bond. In our study, it appears that only intermolecular hydrogen bonding may be responsible for the two forms observed. Upon dissolution, the network is destroyed, facilitating rotation around the Pt–N bonds. Under these conditions, solution spectroscopy such as NMR or UV does not differentiate between forms **A** or **B**.

The differences observed in the infrared spectra of the two forms are caused by different orientations of the methyl group due to different crystal packing effects. The spectrum of form **B** is particularly complex due to the presence of two types of conformers (Fig. 3).

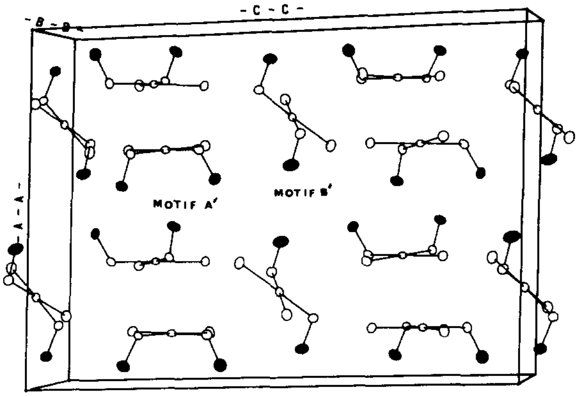

Fig. 3. Drawing of the molecular arrangement in crystal of the two different motifs showing favorable intermolecular interactions.

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