Inorganica Chimica Acta, 153 (1988) 45–49

Crystal Structures of Two Pt(II) Diamine Compounds: *trans*-Pt(CH_3NH_2)$_2$Cl$_2$ and *cis*-Pt[(CH_3)$_2$NH]$_2$Cl$_2$

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(Received February 4, 1988)

Abstract

The structures of two Pt(II) diamine compounds, *trans*-Pt(CH_3NH_2)$_2$Cl$_2$ (**1**) and *cis*-Pt[(CH_3)$_2$NH]$_2$Cl$_2$ (**2**), have been determined by X-ray diffraction and refined to $R = 0.051$ for 371 reflections (**1**) and $R = 0.038$ for 1888 reflections (**2**). Compound **1** crystallizes in the space group $C2/m$ and has cell dimensions $a = 8.569(2)$, $b = 8.578(2)$ and $c = 5.393(1)$ Å; $\beta = 98.08(2)°$, $Z = 2$. Compound **2** crystallizes in the space group $P2_12_12_1$ and the cell dimensions are $a = 21.028(5)$, $b = 11.334(3)$ and $c = 8.194(2)$ Å; $Z = 4$. The unit cell of **1** contains only one type of molecule while that of **2** is formed from two independent molecules. Both compounds show only one IR-active Pt–Cl stretching vibration at 336 cm^{-1} (**1**) and 326 cm^{-1} (**2**). The Pt–N stretching bands appear at 516 cm^{-1} (**1**) and 531 cm^{-1} and 503 cm^{-1} (**2**).

Introduction

A wide variety of platinum(II) diamine compounds have been synthesized and tested against tumor cells after the discovery of the antitumor activity of *cis*-Pt(NH_3)$_2$Cl$_2$ by Rosenberg *et al.* [1]. The factor common to all active compounds is two monodentate anionic ligands (or one bidentate) of moderate leaving ability in *cis*-positions [2]. However, the corresponding *trans*-isomers show only marginal activity, if any. The firmly bound amine ligands appear to play an important role in the action of these compounds. For example, the antitumor activity of *cis*-Pt(A)$_2$Cl$_2$ decreases as A is varied along the series $NH_3 > CH_3NH_2 > (CH_3)_2NH$ [3]. The synthesis of these compounds may, however, result in mixtures of *cis*- and *trans*-isomers. Moreover, isomerization from *cis* to *trans* has been reported to take place under certain conditions [4]. Although IR spectroscopy is frequently employed to distinguish a *cis*-isomer from the corresponding *trans*-isomer, this method does not always give unambiguous results. According to group theory, *trans*-Pt(A)$_2$X$_2$ has only one IR-active Pt–N and Pt–X stretching vibration, whereas the *cis*-compound has two active vibrations of this type. However, the two IR-active modes are frequently not resolved: for example, in *cis*-Pt(NH_3)$_2$Cl$_2$ [5] and in the red form of Pt(bipy)Cl$_2$ [6], only single Pt–Cl modes are observed. In addition, Castan *et al.* [7] have very recently reported that *cis*-Pt(CH_3NH_2)$_2$Cl$_2$ crystallizes in two forms which have different IR spectra; form A has only one Pt–Cl band while form B displays two.

In this paper we wish to extend the general characterization of these Pt(II) diamine compounds by reporting the crystal structures of *trans*-Pt(CH_3NH_2)$_2$Cl$_2$ (**1**) and *cis*-Pt[(CH_3)$_2$NH]$_2$Cl$_2$ (**2**). In addition, IR spectra of the *cis*- and *trans*-isomers of both Pt(II) diamine compounds are briefly discussed.

Experimental

cis-Pt(CH_3NH_2)$_2$Cl$_2$

This was made from K_2PtCl_4 (Degussa) via *cis*-Pt(CH_3CN)$_2$Cl$_2$ through the action of 40% methylamine (E. Merck AG, zur Synthese) according to the procedure described in the literature [8]. *Anal.* Calc. for $C_2H_{10}N_2Cl_2Pt$: C, 7.32; H, 3.07; N, 8.54; Cl, 21.61. Found: C, 7.41; H, 2.98; N, 8.58; Cl, 21.48%.

trans-Pt(CH_3NH_2)$_2$Cl$_2$ (1)

To the solution of 0.5 g K_2PtCl_4 in 10 cm^3 of water was added 5 cm^3 of 40% methylamine and the mixture was kept in a stoppered flask overnight at 50 °C, during which time the [Pt(CH_3NH_2)$_4$][PtCl$_4$] precipitate dissolved. The solution was filtered and the excess of amine was evaporated from the filtrate on a water bath. The addition of 5 cm^3 of concentrated HCl and subsequent heating of the mixture on a water bath for 1 h gave 360 mg (91%) of compound **1** as pale yellow crystals. *Anal.* Found C, 7.37; H, 2.97; N, 8.56; Cl, 21.89%.

0020-1693/88/$3.50

cis-Pt[(CH$_3$)$_2$NH]$_2$Cl$_2$ (2)

The solutions of 4.0 g K_2PtCl_4 (9.6 mmol) in 40 cm^3 of water and 4.3 g $(CH_3)_2NH_2Cl$ (52.8 mmol, E. Merck AG, zur Synthese) and 2.1 g NaOH (52.5 mmol) in 20 cm^3 of water were combined and the resulting solution was stirred at room temperature for 6 h. The yellow crystals of **2** that began to form after 30 min were collected by filtration, after cooling the reaction mixture on an ice bath. The obtained filtrate was used for the preparation of the corresponding *trans*-compound, since the action of excess amine on K_2PtCl_4 also produces $[Pt((CH_3)_2NH)_4]Cl_2$ [8]. The crystals were washed with 30 cm^3 of acetone to remove traces of the *trans*-isomer, after which they were dissolved in 75 cm^3 of hot water and the solution was filtered while hot. After cooling to room temperature, 5 cm^3 of concentrated HCl was added to the filtrate and the product was allowed to crystallize in a refrigerator. Yield, 1.12 g (33%) of yellow–green crystals. *Anal.* Calc. for $C_4H_{14}N_2Cl_2Pt$: C, 13.49; H, 3.96; N, 7.87; Cl 19.91. Found: C, 13.33; H, 3.94; N, 7.81; Cl, 19.69%.

trans-Pt[(CH$_3$)$_2$NH]$_2$Cl$_2$ (3)

The acetone washings obtained in the preparation of compound **2** were evaporated to dryness and the residue was combined with the filtrate mentioned above. The mixture was made slightly alkaline with NaOH and the excess amine was evaporated on a water bath (hood), after which 10 cm^3 of concentrated HCl was added and the mixture heated for 2 h. After cooling in a refrigerator, yellow crystals of **3** were filtered off, washed with water and dried in air. Yield, 700 mg (21%). *Anal.* Found: C, 13.49; H, 3.91; N, 7.87; Cl, 19.93%.

The geometry and purity of the prepared compounds were checked as previously described [9]. IR spectra were recorded as KBr disks and Nujol mulls using CsI windows on a Perkin-Elemer 783 IR spectrophotometer. The scale of the instrument was calibrated with 0.005 mm polystyrene film (Perkin-Elmer).

The X-ray data were collected at room temperature on a Philips PW-1100 single-crystal diffractometer by using graphite monochromated Mo Kα radiation ($\lambda = 0.71069$ Å). The unit cell dimensions in both structures were calculated from 12 reflections ($1{:}10° < \theta < 15°$; $2{:}15° < \theta < 20°$). Crystal and structure determination data are summarized in Table I. Lp and, at a later stage, an empirical absorption correction were applied [10]. The positions of the metals were obtained from a Patterson map. Subsequent ΔF syntheses provided the positions of the non-hydrogen atoms. Hydrogens were ignored. All atoms were refined with anisotropic thermal parameters. Final atomic coordinates and equivalent isotropic thermal parameters are given in Table II. Complex scattering factors for neutral atoms were taken from refs. 11 and 12. For calculations, the SHELX program package was used [13].

Results and Discussion

Figure 1 shows the molecular structure of **1** and Fig. 2 depicts one of the two independent molecules of **2**. The bond distances and angles are given in Table III. In **1** the Pt coordination sphere is square-planar with bond lengths of 2.287(6) Å (Pt–Cl) and 2.03(2) Å (Pt–N), and bond angles of exactly

TABLE I. Crystallographic Data for *trans*-$Pt(CH_3NH_2)_2Cl_2$ (1) and *cis*-$Pt[(CH_3)_2NH]_2Cl_2$ (2)

	trans-$Pt(CH_3NH_2)_2Cl_2$	*cis*-$Pt[(CH_3)_2NH]_2Cl_2$
Formula weight	328.11	356.17
Space group	$C2/m$	$P2_12_12_1$
a (Å)	8.569(2)	21.028(5)
b (Å)	8.578(2)	11.334(3)
c (Å)	5.393(1)	8.194(2)
β (deg)	98.08(2)	
V (Å^3)	392.5	1952.89
Z	2	4
d_{calc} (g cm^{-3})	2.776	2.423
d_{meas} (g cm^{-3})	2.75	2.42
Crystal size (mm)	0.1, 0.1, 0.1	0.2, 0.2, 0.2
μ (cm^{-1})	177.5	143
θ_{range} (deg)	2–25	2–25
No. unique refl.	371	1986
No. refl. used in the calc.	371	1888^a
No. parameters refined	22	163
R	0.050	0.039
R_w (F)	0.051^b	0.038^c

$^aF_o > 2\sigma F_o$. $^bw^{-1} = \sigma^2(F) + 0.004F^2$. $^cw^{-1} = \sigma^2(F) + 0.0004F^2$.

TABLE II. Atomic Coordinates and Equivalent Isotropic Temperature Factors (Å^2) for **1** and **2**

Atom	*x*	*y*	*z*	*U*
Compound 1				
Pt1	0.5000(0)	0.5000(0)	0.0000(0)	0.029(1)
Cl1	0.5000(0)	0.7666(7)	0.0000(0)	0.054(2)
N1	0.2772(25)	0.5000(0)	−0.1877(35)	0.041(5)
C1	0.2718(51)	0.5000(0)	−0.4676(57)	0.083(14)
Compound **2**				
Pt1	0.2748(1)	0.1974(1)	0.3494(1)	0.034(1)
Cl11	0.3290(2)	0.0540(4)	0.4942(6)	0.054(1)
Cl12	0.3666(2)	0.2418(5)	0.2095(6)	0.057(1)
N11	0.2261(6)	0.3194(12)	0.2139(16)	0.036(4)
N12	0.1924(6)	0.1600(14)	0.4758(18)	0.044(5)
C11	0.2519(10)	0.4458(17)	0.2267(28)	0.060(7)
C12	0.2200(10)	0.2866(20)	0.0371(22)	0.057(7)
C13	0.1991(10)	0.1852(20)	0.6593(23)	0.061(7)
C14	0.1682(12)	0.0373(20)	0.4435(30)	0.080(9)
Pt2	0.0249(1)	0.3334(1)	0.4284(1)	0.036(1)
C121	0.1185(2)	0.4316(5)	0.4764(7)	0.060(1)
C122	0.0707(2)	0.2472(6)	0.2022(7)	0.074(2)
N21	−0.0138(6)	0.4108(11)	0.6325(19)	0.038(4)
N22	−0.0599(7)	0.2494(12)	0.3836(18)	0.043(5)
C21	−0.0173(10)	0.5396(15)	0.6220(25)	0.055(7)
C22	0.0211(11)	0.3716(19)	0.7859(23)	0.060(7)
C23	−0.0851(8)	0.2680(22)	0.2171(27)	0.063(8)
C24	−0.0570(12)	0.1166(18)	0.4127(37)	0.078(10)

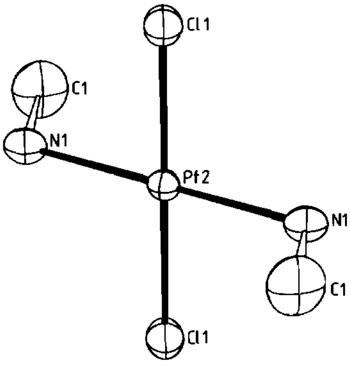

Fig. 1. View of *trans*-$Pt(CH_3NH_2)_2Cl_2$ (**1**).

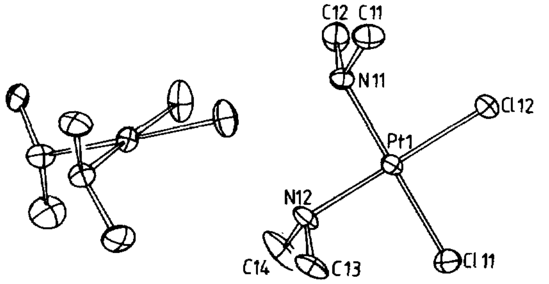

Fig. 2. View of one of two independent molecules of *cis*-$Pt[(CH_3)_2NH]_2Cl_2$ (**2**).

TABLE III. Interatomic Distances (Å) and Angles (deg) of **1** and **2**

Compound 1			
Pt1–C11	2.287(6)	Cl1–Pt1–N1	90.0(0)
Pt1–N1	2.03(2)	Pt1–N1–C1	113.2(2)
C1–N1	1.50(4)		
Compound 2			
Pt1–Cl11	2.312(5)	Pt2–Cl21	2.294(5)
Pt1–Cl12	2.300(5)	Pt2–Cl22	2.306(6)
Pt1–N11	2.05(1)	Pt2–N21	2.06(2)
Pt1–N12	2.06(1)	Pt2–N22	2.06(2)
N11–C11	1.54(2)	N21–C21	1.46(2)
N11–C12	1.50(2)	N21–C22	1.52(2)
N12–C13	1.54(2)	N22–C23	1.48(3)
N12–C14	1.50(2)	N22–C24	1.525(3)
Cl11–Pt1–Cl12	89.8(2)	Cl21–Pt2–Cl22	89.2(2)
Cl11–Pt1–N11	177.7(4)	C121–Pt2–N21	89.6(4)
Cl11–Pt1–N12	90.7(5)	Cl21–Pt2–N22	178.5(4)
Cl12–Pt1–N11	90.1(4)	Cl22–Pt2–N21	178.7(4)
Cl12–Pt1–N12	179.2(5)	Cl22–Pt2–N22	91.3(5)
N11–Pt1–N12	89.5(6)	N21–Pt2–N22	89.9(6)
Pt1–N11–C11	115(1)	Pt2–N21–C21	113(1)
Pt1–N11–C12	114(1)	Pt2–N21–C22	111(1)
C11–N11–C12	109(2)	C21–N21–C22	111(2)
Pt1–N12–C13	112(1)	Pt2–N22–C23	114(1)
Pt1–N12–C14	113(1)	Pt2–N22–C24	113(2)
C13–N12–C14	112(2)	C23–N22–C24	107(2)

90°. The interatomic distances in **1** do not differ significantly from those found in *trans*-$Pt(NH_3)_2Cl_2$: *viz.* 2.32(1) Å (Pt–Cl) and 2.05(4) Å (Pt–N) [14]. The methyl groups in **1** lie on opposite sides of the mean coordination plane and are bent away from the platinum (C–N–Pt = 113.2(2)°). There is intermolecular hydrogen bonding between an amine hydrogen and a coordinated chlorine of two symmetry-related molecules ($0.5 - x$; $1.5 - y$; $-z$): the N–Cl distance is 3.37 Å and Pt–N–Cl angle 120°.

The Pt coordination spheres in both independent molecules of **2** are approximately square-planar with Cl–Pt–Cl and N–Pt–N angles of about 90°. The Pt–Cl bond lengths vary from 2.294(5) to 2.312(5) Å and are significantly longer (*ca.* 11–13 σ*) than the Pt–N distances of 2.05(1) and 2.06(2) Å. The interatomic distances found in **2** do not significantly differ from those observed in other *cis*-$Pt(A)_2Cl_2$ compounds: *viz.* 2.33(1) Å (Pt–Cl) and 2.01(4) Å (Pt–N) in *cis*-$Pt(NH_3)_2Cl_2$ [14] and from 2.284(2) to 2.334(2) Å (Pt–Cl) and from 2.027(6) to 2.084(6) Å (Pt–N) in the two different forms of *cis*-$Pt(CH_3NH_2)_2Cl_2$ [7]. The methyl groups of $(CH_3)_2NH$ moieties lie on opposite sides of the PtN_2Cl_2 coordination plane and they are, as in **1**, slightly bent

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*$\sigma = (\sigma_1{}^2 + \sigma_2{}^2)^{1/2}$.

TABLE IV. IR-active Pt–N and Pt–Cl Stretching Frequencies (cm^{-1}) of $Pt(CH_3NH_2)_2Cl_2$ and $Pt[(CH_3)_2NH]_2Cl_2$[a]

		ν(Pt–N)	ν(Pt–Cl)	Reference
cis-$Pt(CH_3NH_2)_2Cl_2$	(form A)[b]	517w, 507m	319vs	c
		518w, 507m	320vs	d
		518w, 506m	318br	7
		517m, 506m	318s	17
	(form B)[b]	525w, 512m	333m, 314s	c
		525w, 510m	329m, 314m	7
trans-$Pt(CH_3NH_2)_2Cl_2$		516s	335vs	c
		516s	336vs	d
		514s	336s	7
		518s	334vs	17
cis-$Pt((CH_3)_2NH)_2Cl_2$		530w, 503m	323vs	c
		531w, 503m	326vs	d
trans-$Pt[(CH_3)_2NH]_2Cl_2$		526s	339vs	c
		525s	340vs	d

[a] Relative intensities: vs = very strong, s = strong, m = medium, w = weak, br = broad. [b] According to notation used in ref. 7. In this work, however, the differentiation between forms A and B is based solely on ν(Pt–N) and ν(Pt–Cl) frequencies. [c] This work, KBr disks. [d] This work, Nujol mulls.

away from the platinum (Pt–N–C angle *ca.* 111–115°).

Table IV lists the Pt–N and Pt–Cl stretching frequencies of *cis*- and *trans*-isomers of $Pt(CH_3NH_2)_2Cl_2$ and $Pt[(CH_3)_2NH]_2Cl_2$. According to the IR spectrum, *cis*-$Pt(CH_3NH_2)_2Cl_2$ synthesized in this work seems to correspond to the crystalline form A prepared by Castan *et al.* [7]. The crude product (prior to recrystallization) showed, however, ν(Pt–N) bands at 526(sh) and 513 cm^{-1} and ν(Pt–Cl) bands at 334 and 314 cm^{-1}, which are close to those frequencies reported for the crystalline form B of *cis*-$Pt(CH_3NH_2)_2Cl_2$ [7]. In both Pt(II) diamine compounds the Pt–Cl stretching vibration occurs in *trans*-isomers at higher wavenumbers than in *cis*-isomers. As evident from Table IV, the number of IR active Pt–Cl stretching modes is not necessarily a good indicator of geometrical isomerism. Only in one case (form B of *cis*-$Pt(CH_3NH_2)_2Cl_2$) are two ν(Pt–Cl) modes observed, but it is by no means clear whether the two observed bands indeed correspond to the expected two modes of a *cis*-isomer ($\nu(Pt-Cl)_{asym}$ and $\nu(Pt-Cl)_{sym}$) or rather represent superpositions of single, unresolved ν(Pt–Cl) modes of the three types of monomeric $(CH_3NH_2)_2PtCl_2$ units present in the crystal of form B. It should be noted that by employing an expanded scale, the ν(Pt–Cl) bands of both *cis*-compounds, recorded as Nujol mulls, showed certain asymmetry on the higher wavenumber side. This asymmetry was, however, too weak to allow any firm assignment. Instead, IR-active Pt–N stretching modes appear to be more reliable in differentiating *cis*- and *trans*-isomers, although their IR intensities are usually much weaker [15], which again might pose a problem. Therefore additional methods are needed to ascertain the geometry and purity of an unknown sample. These include, for example, the reaction with thiourea and subsequent chromatographic analysis of the reaction mixture [9, 16].

Supplementary Material

The observed and calculated structure factors and anisotropic thermal factors can be obtained from authors on request.

Acknowledgements

The authors wish to thank Dr. F. Wimmer for providing the manuscript (ref. 7) prior to publication. The Alexander von Humboldt Foundation is gratefully acknowledged for a Fellowship (J.A.) and the Fonds der Chemischen Industrie for financial support.

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