

X-ray powder study of *cis*-dichlorido-bis(methylamine)platinum(II)

Sergei D. Kirik* and Aleksandr K. Starkov

Institute of Chemistry and Chemical Technology, 660049 Krasnoyarsk, Russian Federation

Correspondence e-mail: kirik@icct.ru

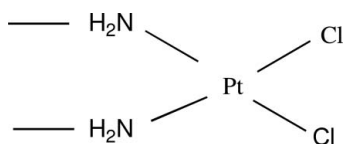
Received 28 August 2007; accepted 2 October 2007

Key indicators: powder X-ray study; $T = 293$ K; mean $\sigma(N-C) = 0.019$ Å; R factor = 0.059; wR factor = 0.080; data-to-parameter ratio = 26.3.

The title compound, *cis*-[PtCl₂(CH₃NH₂)₂], was obtained from the reaction of K₂PtCl₄ with CH₃NH₂·HCl and CH₃COOK. The single-crystal structure has been reported previously [Wimmer, Wimmer, Jaud, Johnson & Castan (1988). *Inorg. Chim. Acta*, **144**, 25–30], but no three-dimensional coordinates are available. We have carried out an *ab initio* crystal structure determination using X-ray powder diffraction techniques. The crystal structure consists of discrete molecules, with the Pt^{II} atom in a slightly distorted square-planar coordination environment. The methyl groups lie on the same side of the plane defined by the two N and two Cl atoms. Molecules are connected *via* intermolecular N—H···Cl hydrogen bonds to form two-dimensional layers perpendicular to the *b* axis. The methylamine groups protrude from these layers, forming organic interlayers.

Related literature

The title compound was previously reported by Watt *et al.* (1967) and Wimmer *et al.* (1988). For related compounds, see: Arpalahiti *et al.* (1988); Clere (1974); Clere & Hoechele (1973); Dhara (1970); Gildengershel (1956); Grinberg & Gildengershel (1951); Kirik & Starkov (2007); Kirik *et al.* (1996); Wells (1984). Searches were conducted using the Cambridge Structural Database (Version 5.28; Allen, 2002) and the Inorganic Crystal Structure Database (Version 2007-1; ICSD, 2007). X-ray powder diffraction data have been deposited in the JCPDS-ICDD PDF-2 database (ICDD, 2005). For analysis techniques, see: Kirik (1985); Kirik *et al.* (1979); Le Bail *et al.* (1988); Rietveld (1969); Visser (1969); Wiles & Young (1981).



Experimental

Crystal data

[PtCl₂(CH₃N)₂]
 $M_r = 328.10$
 Monoclinic, $P2_1/n$
 $a = 7.4512$ (1) Å
 $b = 15.7995$ (2) Å
 $c = 6.3015$ (1) Å
 $\beta = 99.930$ (3)°
 $V = 730.73$ (2) Å³
 $Z = 4$

Cu $K\alpha$ radiation
 $T = 293$ K
 Specimen shape: circular flate plate
 $20.0 \times 20.0 \times 0.5$ mm
 Specimen prepared at 293 K and
 101 kPa
 Particle morphology: thin powder,
 yellow

Data collection

NPO (Burevestnik, USSR) DRON-4 powder diffractometer
 Specimen mounting: packed powder pellet

Specimen mounted in reflection mode
 Scan method: $\theta/2\theta$
 $2\theta_{\min} = 9.0$, $2\theta_{\max} = 115.0^\circ$
 Increment in $2\theta = 0.02^\circ$

Refinement

$R_p = 0.059$
 $R_{wp} = 0.080$
 $R_{exp} = 0.056$
 $R_B = 0.035$
 $S = 1.43$
 Wavelength of incident radiation:
 1.54056 Å
 Excluded region(s): none

Profile function: Pearson VII (Wiles & Young, 1981)
 1001 reflections
 38 parameters
 H-atom parameters not refined
 Preferred orientation correction:
 March–Dollase (Dollase, 1986)

Table 1

Selected geometric parameters (Å, °).

Pt1—Cl1	2.303 (5)	Pt1—N1	2.083 (14)
Pt1—Cl2	2.343 (4)	Pt1—N2	2.088 (12)
Cl1—Pt1—Cl2	92.5 (2)	Cl2—Pt1—N1	88.0 (2)
Cl1—Pt1—N2	89.5 (2)	N1—Pt1—N2	90.0 (4)

Symmetry code: (i) $-x + 2, -y, -z + 2$.

Table 2

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N1—H1A···Cl2 ⁱⁱ	0.90	2.80	3.517 (13)	138
N1—H1B···Cl2 ⁱⁱⁱ	0.90	2.48	3.311 (10)	154
N2—H2A···Cl2 ⁱⁱⁱ	0.90	2.70	3.569 (9)	163
N2—H2B···Cl2 ⁱ	0.90	2.83	3.462 (15)	128

Symmetry codes: (i) $-x + 2, -y, -z + 2$; (ii) $-x + 1, -y, -z + 2$; (iii) $x, y, z - 1$.

Data collection: DRON-4 data collection software; cell refinement: *POWDER* (Kirik *et al.*, 1979); data reduction: DRON-4 data collection software; program(s) used to solve structure: modified *DBWM* (Wiles & Young, 1981); program(s) used to refine structure: modified *DBWM*; molecular graphics: *SHELXTL* (Siemens, 1989); software used to prepare material for publication: *SHELXTL*.

The preparation of the X-ray powder diffraction data was supported by the ICDD (Grant-in-Aid 9310) and structure solution by grant RFBR-KSF 07-0396805.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: LH2492).

References

- Allen, F. H. (2002). *Acta Cryst.* **B58**, 380–388.
- Arpalahti, J., Lippert, B., Schollhorn, H. & Thewalt, U. (1988). *Inorg. Chim. Acta*, **153**, 45–49.
- Clere, M. J. (1974). *Coord. Chem. Rev.* **12**, 349–405.
- Clere, M. J. & Hoeshel, J. D. (1973). *Bioinorg. Chem.* **2**, 187–210.
- Dhara, S. C. (1970). *Indian J. Chem.* **8**, 193–200.
- Dollase, W. A. (1986). *J. Appl. Cryst.* **19**, 267–272.
- Gildengershel, H. I. (1956). *Zh. Neorg. Khim.* **1**, 400–405.
- Grinberg, A. A. & Gildengershel, H. I. (1951). *Izv. Sekt. Platiny Drugikh Blagorodn. Met. Inst. Obshch. Neorg. Khim. Akad. Nauk USSR*, **26**, 115–123.
- ICDD (2005). PDF-2. International Centre for Diffraction Data, Newtown Square, Pennsylvania, USA. <http://www.icdd.com>
- ICSD (2007). Inorganic Crystal Structure Database. FIZ-Karlsruhe, Germany, and the National Institute of Standards and Technology (NIST), USA. <http://www.fiz-karlsruhe.de/icsd.html>
- Kirik, S. D. (1985). *Kristallografiya*, **30**, 185–187.
- Kirik, S. D., Borisov, S. V. & Fedorov, V. E. (1979). *Zh. Strukt. Khim.* **20**, 359–364.
- Kirik, S. D., Solovyov, L. A., Blokhin, A. I., Yakimov, I. S. & Blokhina, M. L. (1996). *Acta Cryst.* **B52**, 909–916.
- Kirik, S. D. & Starkov, A. K. (2007). *Acta Cryst.* **E63**, m1705–m1706.
- Le Bail, A., Duroy, H. & Fourquet, J. L. (1988). *Mater. Res. Bull.* **23**, 447–452.
- Rietveld, H. M. (1969). *J. Appl. Cryst.* **2**, 65–71.
- Siemens (1989). *SHELXTL*. Version 5.1. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
- Visser, J. W. (1969). *J. Appl. Cryst.* **2**, 89–95.
- Watt, G. W., Hutchinson, B. B. & Kett, D. S. (1967). *J. Am. Chem. Soc.* **89**, 2007–2011.
- Wells, A. F. (1984). *Structural Inorganic Chemistry*, 5th ed., Russian translation, **3**, 236–242. Oxford: Clarendon Press.
- Wiles, D. B. & Young, R. A. (1981). *J. Appl. Cryst.* **14**, 149–151.
- Wimmer, S., Wimmer, J., Jaud, J., Johnson, N. P. & Castan, P. (1988). *Inorg. Chim. Acta*, **144**, 25–30.

supplementary materials

Acta Cryst. (2007). E63, m2685-m2686 [doi:10.1107/S1600536807048428]

X-ray powder study of *cis*-dichloridobis(methylamine)platinum(II)

S. D. Kirik and A. K. Starkov

Comment

The title complex, *cis*-[Pt(CH₃NH₂)₂Cl₂], has attracted attention due to its biological activity especially in connection with cancer chemotherapy (Clere & Hoechele, 1973; Clere, 1974). Reports on *cis*-[Pt(CH₃NH₂)₂Cl₂] can be found in the literature as early as the nineteen fifties (Grinberg & Gildengershel, 1951; Gildengershel, 1956). X-ray diffraction data were published by Watt *et al.* (1967) and a single-crystal structure was determined by Wimmer *et al.* (1988). This group found the existence of two forms A and B. Concisely the form A is build from molecules *cis*-[Pt(CH₃NH₂)₂Cl₂] in the conformation where both methyl groups lie on the same side of the plane delimited by the two chloride and the two nitrogen atoms (motif A). The form B consists of molecules of two possible conformations: above mentioned motif A and a motif B where methyl groups are on the both side of "platinum" plane. Unfortunately the publication (Wimmer *et al.*, 1988) does not present the 3-D coordinates of the structures, and that hinders the detailed analysis of reasons for the different types of conformations. Here we present the results of crystal structure determination of *cis*-[Pt(CH₃NH₂)₂Cl₂] in form A obtained applying another synthetic approach without using AgI as it was done by Wimmer *et al.* (1988) following Dhara (1970). Another important feature follows from application of the X-ray powder technique that allows ascribing the structure to bulk sample of the substance.

The crystal structure of *cis*-bis(methylamine) dichloro platimun(II) consists of discrete molecules. The geometry of the molecule is presented in Fig. 2. The Pt atom has slightly distorted square-planar coordination enviroment consisting of two N and two Cl atoms. The torsion angle Cl2—C11—N1—N2 = 177.5°. The distances Pt1—N1, Pt1—N2, Pt1—Cl1 and Pt1—Cl2 are 2.083 (14) Å, 2.088 (12) Å, 2.303 (5) Å and 2.343 (4) Å respectively and these correspond well to known in literature values (Arpalahti *et al.*, 1988; Wimmer *et al.*, 1988; Kirik *et al.*, 1996; Wells, 1984; Allen, 2002; ICSD, 2007). Methylamine as a ligand does not induce essential distortions of the molecule. The N1—Pt1—N2 angle is 90.0 (4)°. The N...Cl contacts in the molecule are of 3.081 (16) Å and 3.095 (15) Å. Methyl-groups are oriented to one side of the PtN₂Cl₂plane. Molecules conjugate in pairs due to (Cl...H—N) intermolecular bounding with centrosymmetric orientation respectively each other. N...Cl contacts between nearest molecules are of 3.296 (16) Å and 3.462 (16) Å. The shortest (Pt...Pt) distance in pairs equals to 3.372 (2) Å. The pairs comprise double layers stretched along (*ac*)-plane with methylamine ligands protruding from layers forming organic interlayers (Fig. 3). This type of packing is also typical for other methylamine containing compound (Kirik & Starkov, 2007).

Experimental

For the preparation of *cis*-[Pt(CH₃NH₂)₂Cl₂] the salt K₂PtCl₄ in amount of 4 g was dissolved in 20 ml of water. Then 3 g of CH₃NH₂·HCl and 4 g CH₃COOK were added to the solution. The mixture was slightly heated until solution became colorless and then cooled down to room temperature. The solution was kept during 3 h at room temperature, pH was adjusted close to 8 by KOH solution. The light yellow precipitate was filtered, washed and dried. Elemental chemical analysis confirmed the chemical formula of the substance.

Refinement

The structure determination was carried out by the X-ray powder diffraction technique. The experimental data were collected using DRON-4 automatic diffractometer, equipped with a secondary flat graphite monochromator in conjunction with a scintillation detector. Cu $K\alpha$ radiation was used ($\lambda_1 = 1.54056 \text{ \AA}$, $\lambda_2 = 1.54439 \text{ \AA}$). The sample was prepared by top-loading the standard quartz sample holder with cutting the excess of well grained substance. The diffraction pattern was scanned with the step of $0.02^\circ 2\theta$ and counting time of 5 sec./step in the most informative angular range from 9° to $115^\circ 2\theta$ at room temperature. Corundum was used as the external standard. The powder pattern of *cis*-bis(methylamine) dichloro platinum(II) is presented in Fig. 1. X-ray powder diffraction data have been deposited in JCPDS-ICDD PDF2 database (ICDD, 2005). Cell parameters were obtained from d-spaces by indexing and refining using programs described in (Visser, 1969; Kirik *et al.*, 1979). The space group was determined from the analysis of systematic absences. The structural investigations were carried out using a full-profile structure analysis package based on a modified version of the Rietveld refinement program DBWS-9006PC (Wiles & Young, 1981; Kirik, 1985). The intensities of 50 reflections were estimated from the powder pattern by means of the full-profile fitting procedure (Le Bail *et al.*, 1988) and used in the Patterson synthesis. Atoms of Pt and Cl were located directly from the Patterson map. Positions of light atoms N and C were defined from a difference Fourier synthesis. The final refinement was carried out by Rietveld method (Rietveld, 1969; Wiles & Young, 1981). H-atoms were not located, but they were included in the refined structure models and rigidly connected to their C and N atoms with N—H = 0.90 and C—H = 0.96 \AA and $U_{\text{iso}}(\text{H}) = 0.152 \text{ \AA}^2$.

Figures

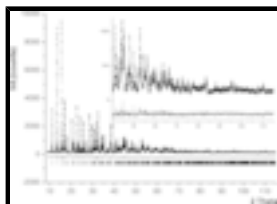


Fig. 1. Observed (dots), calculated (superimposed solid) and difference profiles after the Rietveld refinement. The reflection positions are marked by ticks.

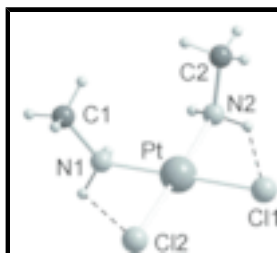


Fig. 2. The molecular structure of *cis*-[Pt(CH₃NH₂)₂Cl₂] shown as a ball and stick representation. Dashed lines indicate intramolecular interactions.

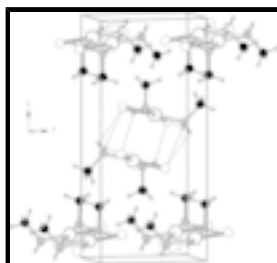


Fig. 3. Part of the crystal structure of *cis*-[Pt(CH₃NH₂)₂Cl₂] with hydrogen bonds shown as dashed lines.

cis-dichloridobis(methylamine)platinum(II)

Crystal data

[PtCl ₂ (CH ₃ N) ₂]	$F_{000} = 592.0$
$M_r = 328.10$	Final cell parameters are obtained from the Rietveld refinement
Monoclinic, $P2_1/n$	$D_x = 2.982 \text{ Mg m}^{-3}$
Hall symbol: -P 2yn	Cu $K\alpha$ radiation
$a = 7.4512 (1) \text{ \AA}$	$\lambda = 1.5418 \text{ \AA}$
$b = 15.7995 (2) \text{ \AA}$	$T = 293 \text{ K}$
$c = 6.3015 (1) \text{ \AA}$	Specimen shape: circular flate plate
$\beta = 99.930 (3)^\circ$	$20.0 \times 20.0 \times 0.5 \text{ mm}$
$V = 730.73 (2) \text{ \AA}^3$	Specimen prepared at 101 kPa
$Z = 4$	Specimen prepared at 293 K
	Particle morphology: thin powder, yellow

Data collection

DRON-4 powder diffractometer	Scan method: ?
Monochromator: graphite	$T = 293 \text{ K}$
Specimen mounting: packed powder pellet	$2\theta_{\min} = 9.0, 2\theta_{\max} = 115.0^\circ$
Specimen mounted in reflection mode	Increment in $2\theta = 0.02^\circ$

Refinement

Refinement on F^2	Excluded region(s): none
Least-squares matrix: full	Profile function: Pearson VII (Wiles & Young, 1981)
$R_p = 0.059$	38 parameters
$R_{wp} = 0.080$	H-atom parameters not refined
$R_{\text{exp}} = 0.056$	Weighting scheme based on measured s.u.'s ?
$R_B = 0.035$	$(\Delta/\sigma)_{\max} = 0.1$
$S = 1.43$	Extinction correction: ?
Wavelength of incident radiation: 1.54056 Å	Preferred orientation correction: March–Dollase correction (Dollase, 1986)

Special details

Refinement. R_prof-backgr = 0.059

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Pt1	0.8950 (2)	0.0946 (1)	0.9978 (2)	0.0121*
Cl1	1.1570 (6)	0.1223 (4)	1.2400 (6)	0.0197*
Cl2	0.7322 (5)	0.0594 (3)	1.2720 (6)	0.0186*

supplementary materials

N1	0.6610 (13)	0.0672 (10)	0.7760 (14)	0.0234*
H1A	0.6022 (13)	0.0245 (10)	0.8290 (14)	0.152*
H1B	0.6954 (13)	0.0484 (10)	0.6543 (14)	0.152*
C2	1.0380 (12)	0.2250 (11)	0.7050 (12)	0.0226*
H2C	1.1018 (12)	0.2353 (11)	0.5875 (12)	0.152*
H2D	0.9164 (12)	0.2470 (11)	0.6698 (12)	0.152*
H2E	1.1007 (12)	0.2525 (11)	0.8324 (12)	0.152*
N2	1.0300 (11)	0.1280 (10)	0.7460 (10)	0.0231*
H2A	0.9738 (11)	0.1028 (10)	0.6245 (10)	0.152*
H2B	1.1446 (11)	0.1078 (10)	0.7751 (10)	0.152*
C1	0.5240 (12)	0.1410 (9)	0.7160 (10)	0.0237*
H1C	0.4220 (12)	0.1214 (9)	0.6134 (10)	0.152*
H1D	0.4823 (12)	0.1606 (9)	0.8432 (10)	0.152*
H1E	0.5831 (12)	0.1865 (9)	0.6543 (10)	0.152*

Geometric parameters (\AA , $^\circ$)

Pt1—C11	2.303 (5)	Cl2—H2B ⁱ	2.829 (16)
Pt1—Cl2	2.343 (4)	N1—H1A	0.90 (1)
Pt1—N1	2.083 (14)	N1—H1B	0.90 (1)
Pt1—N2	2.088 (12)	N2—H2A	0.90 (1)
N1—C1	1.553 (18)	N2—H2B	0.90 (1)
N2—C2	1.557 (25)	C1—H1C	0.96 (1)
Pt1—Pt1 ⁱ	3.372 (2)	C1—H1D	0.96 (1)
Cl1—H2A ⁱⁱ	2.995 (4)	C1—H1E	0.96 (1)
Cl1—H1A ⁱ	3.010 (15)	C2—H2C	0.96 (1)
Cl1—H2B	2.924 (4)	C2—H2D	0.96 (1)
Cl1—H1B ⁱ	2.945 (16)	C2—H2E	0.96 (1)
Cl1—H2B	2.924 (4)		
Cl1—Pt1—Cl2	92.5 (2)	Pt1—N2—H2A	108.6 (6)
Cl1—Pt1—N2	89.5 (2)	Pt1—N2—H2B	108.6 (6)
Cl2—Pt1—N1	88.0 (2)	N1—C1—H1C	109.4 (14)
N1—Pt1—N2	90.0 (4)	N1—C1—H1D	109.4 (6)
Pt1—N1—C1	116.5 (6)	N1—C1—H1E	109.4 (6)
Pt1—N2—C2	114.3 (6)	N2—C2—H2C	109.4 (16)
Pt1—N1—H1A	108.1 (6)	N2—C2—H2D	109.4 (15)
Pt1—N1—H1B	108.1 (6)	N2—C2—H2E	109.4 (14)

Symmetry codes: (i) $-x+2, -y, -z+2$; (ii) $x, y, z+1$.

Hydrogen-bond geometry (\AA , $^\circ$)

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N1—H1A \cdots Cl2 ⁱⁱⁱ	0.90	2.80	3.517 (13)	138
N1—H1B \cdots Cl2 ^{iv}	0.90	2.48	3.311 (10)	154
N2—H2A \cdots Cl2 ^{iv}	0.90	2.70	3.569 (9)	163
N2—H2B \cdots Cl2 ⁱ	0.90	2.83	3.462 (15)	128

Symmetry codes: (iii) $-x+1, -y, -z+2$; (iv) $x, y, z-1$; (i) $-x+2, -y, -z+2$.

Fig. 1

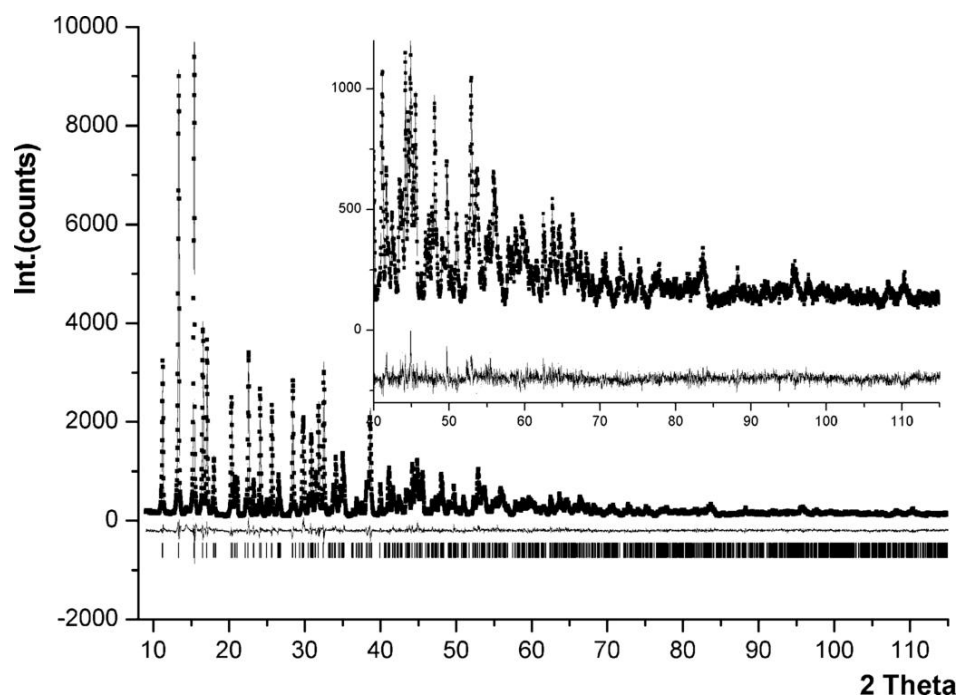


Fig. 2

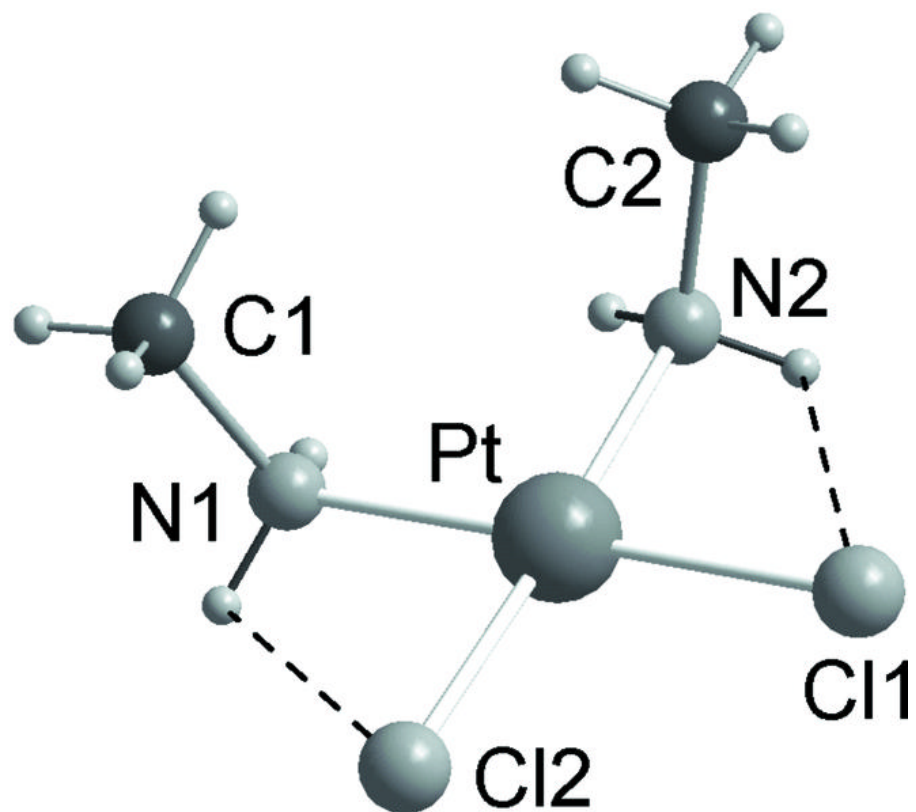


Fig. 3

