

The Reactions of Tetramer Platinum(IV) Complexes, $[\{\text{Pt}(\text{CH}_3)_2\text{X}_2\}_4]$, (X = Cl, Br, and I) with Pyridine

SUTOPO HADI*

Department of Chemistry, Universitas Lampung, Bandar Lampung Indonesia 35145

Abstract: The reactions of tetramer platinum(IV) complexes, $[\{\text{Pt}(\text{CH}_3)_2\text{X}_2\}_4]$ (X = Cl, Br, and I), the final product obtained from the reaction between *fac*- $[\text{Pt}(\text{CH}_3)_2(\text{OCH}_3)(\text{H}_2\text{O})_3]^+$ and halide salts, were investigated. These tetramers were insoluble in many non-coordinating solvents such as acetone, diethylether and chloroform, however they did dissolve in dry pyridine to give $[\text{Pt}(\text{CH}_3)_2\text{X}_2(\text{py})_2]$ complexes. The product obtained was confirmed with NMR spectroscopy [^1H , ^{13}C and ^{195}Pt].

Keywords: cubane structure, NMR, pyridine, tetramer platinum(IV) complexes.

1. Introduction

The platinum complexes containing Pt-CH₃ group are known for Pt(I), Pt(II), Pt(III) and Pt(IV) compounds and the most stable are those with the Pt(IV) [1-9]. The tetramer platinum(IV) containing Pt-CH₃ group was known since 1909 when Pope and Peachy was successfully synthesized the first alkyl platinum(IV) complex with a cubane structure [10]. Since then the attention given to the alkyl platinum(IV) complexes was very intense. But, the first rational synthesis of tetramer platinum complex of the type, $[\{\text{Pt}(\text{CH}_3)_2\text{Br}_2\}_4]$ has only been prepared and reported by Hall and Swile [11]. This compound was prepared by refluxing a suspension of $[\{\text{Pt}(\text{CH}_3)_3\text{I}\}_4]$ in liquid bromine to which several drops of hydrobromic acid were added Hall and Swile [12].

Unlike the reactions of dimethylplatinum(II) and dimethyl-platinum(IV) complexes which have been extensively studied [1-9, 13-15], the reaction of the tetramer platinum(IV) complex was not much reported. According to Hall and Swile [11, 12] the tetramer complex they obtained did not soluble in water and many non-coordinating organic solvents, and it was only soluble in pyridine which they used to purify the tetramer product by removing pyridine by treatment with acid.

In attempt to further understand the reaction of tetramer platinum(IV) complex, in this study, we reported the reactions of tetramer platinum(IV) complexes, $[\{\text{Pt}(\text{CH}_3)_2\text{X}_2\}_4]$ (X = Cl, Br, and I), which were obtained as final product from the reaction of *fac*- $[\text{Pt}(\text{CH}_3)_2(\text{OCH}_3)(\text{H}_2\text{O})_3]^+$ and halide salts with pyridine and was followed by NMR.

2. Materials and methods

2.1. Solvents and starting materials

All Chemicals and solvents used were of A. R. grade or purified by standard techniques.

2.2. Reaction of of $[\{\text{Pt}(\text{CH}_3)_2\text{X}_2\}_4]$ with pyridine

In a small bottle, 10 mg of $[\{\text{Pt}(\text{CH}_3)_2\text{X}_2\}_4]$ was suspended in 0.6 mL of CDCl_3 . A few drops of dry pyridine were added and the mixture was stirred for a few min. After all solids dissolved the N.M.R. spectra (^1H , ^{13}C , ^{195}Pt) were obtained.

2.3. NMR measurements

^1H N.M.R spectra were run with AMX 400 spectrometer operating at 400 MHz. A spectral width of 2,000 Hz - 2,500 Hz was employed together with 16 - 96 scans to obtain the desired F.I.D.

*email: sutopo.hadi@fmipa.unila.ac.id

A recycle time of 4 s was used with a pulse width of 3.6 μs (thus a tilt angle of 45 degrees was used). The number of data points obtained was 16K. Chemical shifts are reported in p.p.m downfield from internal reference, sodium-3-trimethylsilylpropane sulfonate (TSS) ($\delta_{\text{H}} = 0.00$ p.p.m) in aqueous solution and in p.p.m downfield from internal reference tetramethylsilane (TMS) ($\delta_{\text{H}} = 0.00$ p.p.m) in other solvents.

^{13}C N.M.R. spectra were recorded at 100 MHz using a Bruker AMX 400 spectrometer. A Spectral width of approximately 10,600 Hz was utilized. The number of scan used to obtain spectra varied from 500 to 10,000. A recycle time of 3 s was used with a pulse width of 1.8 μs (thus a tilt angle of 30 degrees was used). The number of data points obtained was 32K. Chemical shifts are reported relative to T.M.S., often with the solvent peak as a secondary reference or to internal reference of T.S.S. in aqueous solvent.

^{195}Pt N.M.R. spectra were recorded at 86.017 MHz using a Bruker AMX 400 spectrophotometer. The spectra obtained were both proton coupled and proton decoupled. A Spectral width used 125,000 Hz. The number of scans used to obtain spectra varied from 1000 to 20,000. A recycle time of 0.066 s was used with a pulse width of 23 μs . The tilt angle was 90 degrees. The number of data points obtained was 16K. The Chemical shifts reported in p.p.m. relative to external standard, Na_2PtCl_6 (0.5 g/mL H_2O) ($\delta_{\text{Pt}} = 0.00$ p.p.m.) [16].

2.4. Microanalyses

C, H, N microanalyses were performed using Fision EA 1108 series CHN analyzer by the Microanalytical Laboratory, Chemistry Department, University of Queensland, Brisbane, Australia.

3. Results and discussions

All the tetramer platinum(IV) complexes obtained as the final product from the reaction of *fac*- $[\text{Pt}(\text{CH}_3)_2(\text{OCH}_3)(\text{H}_2\text{O})_3]^+$ and halide salts formulated as $[\{\text{Pt}(\text{CH}_3)_2\text{X}_2\}_4]$ (X=halide ions). Similar to result reported by Hall and Swile [11], they were insoluble in water and many non-coordinating organic solvents.

The compounds, $[\{\text{Pt}(\text{CH}_3)_2\text{X}_2\}_4]$, must be in the polymeric form in order to maintain their coordination structure as usual six-coordination of platinum(IV). The molecular weights of these complexes were unable to be determined because the compounds were not soluble almost in all non-coordinating solvents. Therefore, the compounds obtained may have tetrameric structures similar to to the known compound which has been reported by Hall and Swile [11]. This compound has a cubane structure and the proposed structure is as in Figure 1.

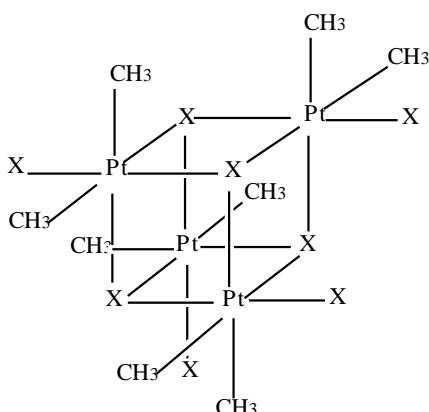


Figure 1. Structure of $[\{\text{Pt}(\text{CH}_3)_2\text{X}_2\}_4]$

The $[\{Pt(CH_3)_2X_2\}_4]$ compounds were not surprisingly only soluble in pyridine and gave $[[PtMe_2X_2py_2]]$ complexes series which were well characterized by multinuclear spectroscopy. The NMR and the analytical data obtained from the reaction are tabulated in Table 1 and 2 respectively and agree to those reported in the literature [1, 11, 12].

Compounds of the type $[[PtMe_2X_2py_2]]$ series which X_2 representing halide ions may have structures/isomers (a), (b) or (c) as in Figure 2. As shown in Table 1, all such complexes obtained show only a single methylplatinum triplet in the NMR, so that isomer (c) may be eliminated as a possible structure for these compounds, as isomer (c) must have two different methylplatinum peaks in the NMR, which are for CH_3 *trans* to X and CH_3 *trans* to pyridine.

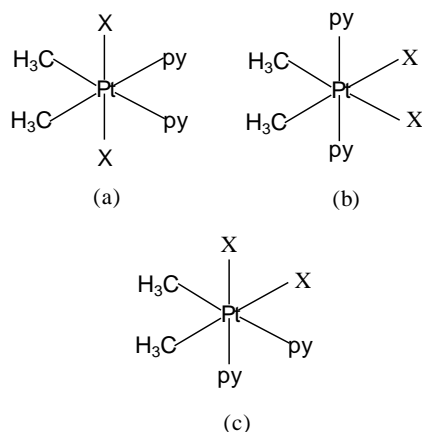


Figure 2. Possible structures of $[[PtMe_2X_2py_2]]$ series

The values of platinum and carbon coupling (Figure 3), $^2J_{Pt-CH_3}$, of $[[PtMe_2X_2py_2]]$ series as in shown Table 1 are in the range from 69 – 73 Hz. The coupling constants reported here were as indication of the presence of CH_3 groups *trans* to either py (isomer (a)) or X (isomer (b)) [17], however based on the discussion below, the NMR spectra recorded are more consistent for the compounds having structure (a) in Figure 2.

All compounds $[[PtMe_2X_2py_2]]$ exhibit only a single methylplatinum triplet, which provide unequivocal evidence for this compounds having structure (a) (Table 1, Figure 2), Chemical shift values of the methylplatinum proton in these series also support the assignment of structure (a). Besides that based on the *trans* influence theory, the formation of isomer (a) for each compounds in the series is quite consistent, which would predict that the bonds *trans* to CH_3 should be weakened sufficiently to allow attack by incoming ligand if further reaction is undertaken where for X = iodide the *trans* influence would be greater than bromide and chloride.

Insolubility of these tetrameric compound has prevented solution molecular weight determinations. Attempts to grow crystal from the solid tetramer were also unsuccessful, so no crystal structure data are available.

Table 1. NMR data of $[[PtMe_2X_2py_2]]$ series

Compound	Solvent	δ_{Pt} (p.p.m)	δ_H (Me) (p.p.m)	$^2J_{Pt-CH_3}$ (Hz)	δ_C (Me) (p.p.m)	$^1J_{Pt-CH_3}$ (Hz)
$[[PtMe_2Cl_2py_2]]$ (1)	$CDCl_3$	-1823	1.88	69.5	-5.5	525
$[[PtMe_2Br_2py_2]]$ (3)	$CDCl_3$	-2321	2.08	70.6	-9.4	516
$[[PtMe_2I_2py_2]]$ (2)	$CDCl_3$	-2631	2.54	72.8	-19.4	510

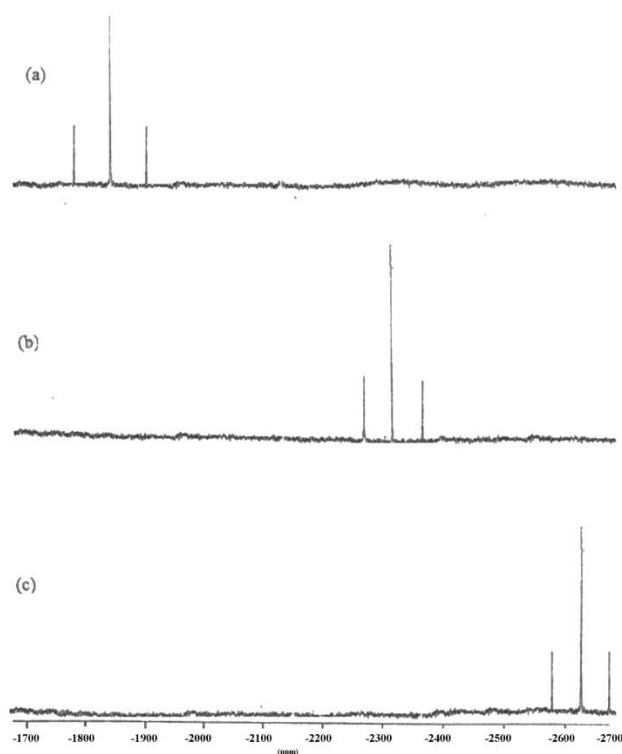


Figure 3. 86.017 MHz ^{195}Pt NMR of (a) $[\text{PtMe}_2\text{Cl}_2\text{py}_2]$; (b) $[\text{PtMe}_2\text{Br}_2\text{py}_2]$; (c) $[\text{PtMe}_2\text{I}_2\text{py}_2]$

Table 2. Analytical Data of $[[\text{PtMe}_2\text{X}_2\text{py}_2]$ series

Compound	Analysis [Found (Calcd.) (%)]	
	$[\text{PtMe}_2\text{Cl}_2\text{py}_2]$	8.77 (8.83)
$[\text{PtMe}_2\text{Br}_2\text{py}_2]$	6.60 (6.66)	1.68 (1.68)
$[\text{PtMe}_2\text{I}_2\text{py}_2]$	5.32 (5.28)	1.35 (1.33)

4. Conclusions

The solid tetramer platinum(IV) complexes obtained as a final product of the reaction between *fac*- $[\text{Pt}(\text{CH}_3)_2(\text{OCH}_3)(\text{H}_2\text{O})_3]^+$ and halide salts were insoluble in many non-coordinating solvents. They did dissolve in dry pyridine to give platinum(IV) dipyridine series, $[[\text{PtMe}_2\text{X}_2\text{py}_2]$ which were well characterized by NMR spectroscopy and having cubane structure.

Acknowledgments: The author would like to thank Universitas Lampung, Indonesia for the funding given so the project was able to be undertaken. Thanks also go to Ms. L. Lambert for her help in NMR experimentation and Mr. G. Blazak for the microanalytical service. Special thanks goes to Prof. Trevor G. Appleton, The University of Queensland, Brisbane Australia who has deceased on June 12, 2013.

References

1. APPLETON, T.G., D'ALTON, C.J., HALL, J.R., MATHIESON, M.T., WILLIAMS, M.A., Synthesis of dimethylplatinum(IV) compounds $[\{\text{PtMe}_2\text{X}_2\}_n]$, $[\{\text{PtMe}_2\text{XY}\}_n]$, and, in solution, *fac*- $[\text{PtMe}_2\text{X}(\text{H}_2\text{O})_3]^+$, where X and Y are anionin ligands, *Can. J. Chem.*, **74**(11), 1996, 2008-2017.

2. HADI, S., APPLETON, T.G., AYOKO, G.A., Reaction of *fac*-[PtMe₂(OMe)(H₂O)₃]⁺ with Halide Ions; Effect of Halide Trans effect on methoxide hydrolysis, *Inorg. Chim. Acta.*, **352**, 2003, 201-207.
3. JENKINS, H.A., KLEMPNER, M.J., PROKOPCHUK, E.M., PUDDEPHATT, R.J., Dimethyl (hydrido)platinum(IV) chemistry related to methane activation: the effect of a tetradentate ligand, *Inorg. Chim. Acta.*, **352**, 2003, 72–78.
4. SHAHSAVARI, H.R., RASHIDI, M., NABAVIZADEH, S.M., HABIBZADEH, S., HEINEMANN, F.W., A Tetramethylplatinum(IV) Complex with 1,1'-Bis(diphenylphosphanyl) ferrocene Ligands: Reaction with Trifluoroacetic Acid, *Eur. J. Inorg. Chem.*, **25**, 2009, 3814–3820
5. HADI, S., APPLETON, T.G., Reactions of cisplatin hydrolytes, *cis*-[Pt(¹⁵NH₃)₂(H₂O)₂]²⁺, with N-acetyl-L-cysteine, *Russ. J. Inorg. Chem.*, **55**(2), 2010, 223-228.
6. PRANTNER, J.D., KAMINSKY, W., GOLDBERG, K.I., Methylplatinum(II) and Molecular Oxygen: Oxidation to Methylplatinum(IV) in Competition with Methyl Group Transfer To Form Dimethylplatinum(IV), *Organometallics*, **33**(13), 2014, 3227–3230.
7. MOMENI, B.Z., EATEZADI, S., Pt–Me bond cleavage in the reactions of dimethylplatinum(II) complexes containing chelating phosphine ligands with organotin(IV) chlorides, *Can. J. Chem.*, **91**(12), 2013, 1288–1291.
8. KLEIN, A., Stayin' Alive—Organoplatinum Complexes, *Inorganics*, **3**(2), 2015, 155-159.
9. MIHAI, S., NEGOIU, M., Synthesis Characterization and Antitumor Activity of Platinum(II), Palladium(II), Gold(III), Silver(I), Copper(II), Rhodium(III) and Ruthenium(III) Complexes with N-Antipirine-N³-Benzoylthiourea, *Rev. Chim.*, **63**(7), 2012, 697-702.
10. POPE, W.J., PEACHY, S.J., LXXIII. - The alkyl compounds of platinum, *J. Chem. Soc., Trans.*, **95**, 1909, 571-576
11. HALL, J.R., SWILE, G.A., Dimethylplatinum(IV) Compounds. II*. Spectra and Reactions of the Compounds [Pt(CH₃)₂X₂]₂ (X = I, Br and Cl), *J. Organomet. Chem.*, **56**, 1973, 419-433.
12. HALL, J.R., SWILE, G.A., Preparation of Some Dimethylplatinum(IV) Complexes, *Aus. J. Chem.*, **24**(2), 1971, 423-426.
13. HADI, S., The Synthesis and NMR Study on The Stability of Dimethylmethoxo-platinum(IV) Complexes, *Indo. J. Chem.*, **5**(1), 2005, 87-91.
14. VOLOVAT, S.R., VOLOVAT, C.C., MIRON, L., SCRIPCARIU, D.V., SEMEN, E.D., CIOCOIU, M., Magnesium Supplementation and Cisplatin-Induced Renal Impairment in Cancer Patients, *Rev. Chim.*, **69** (9), 2018, 2520-2523.
15. NEGREA, S.-C., DIACONU, L.A., NICORESCU V., BACIU, A., POP, A., MANEA, F., Copper-Modified Boron-Doped Diamond (Cu/Bdd) Electrode for the Electrochemical Detection of Paclitaxel and Oxaliplatin in Aqueous Solutions, *Rev. Chim.*, **70** (12), 2019, 4595-4600.
16. PREGOSIN, P.S., Platinum-195 Nuclear Magnetic Resonance, *Coord. Chem. Rev.*, **44**(2), 1982, 247-291.
17. CLEGG, D.E., HALL, J.R., SWILE, G.A., ¹H NMR spectra and characterization of some trimethylplatinum(IV) compounds, *J. Organomet. Chem.*, **38**(2), 1972, 403-420

Manuscript received: 14.03.2020

