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Measuring Self-Association of Pt Complexes by ^{195}Pt NMR

Alfiya F. Suleymanova,^{[a],[d]} Oleg S. Eltsov,^[a] Dmitry N. Kozhevnikov,^[a] Anastasia O. Lantushenko,^[b] Maxim P. Evstigneev*^[b] and Valery N. Kozhevnikov*^[c]

Abstract: A highly soluble neutral cyclometallated Pt complex of C[^]N[^]N type was prepared and its self-aggregation in CDCl₃ solution was studied by NMR dilution method. It was shown that ^{195}Pt NMR can be used to quantify aggregation and therefore be potentially applied to many other Pt complexes. Two-dimensional HMBC ^1H - ^{195}Pt technique increases sensitivity of experiment and allowed recording ^{195}Pt chemical shift values at concentration as low as 1 mM and it was observed that opposite to shielding of aromatic protons, Pt nucleus is deshielded upon increase of concentration.

One of the key features of square planar Pt(II) complexes, that has been extensively exploited in supramolecular chemistry, is their ability to self-aggregate.^[1] The aggregation is a complex process and involve a variety of intermolecular forces including ligand-based, solvent-based as well as metallophilic Pt-Pt interactions. In the search for new self-associating systems it is desirable to gain information about the magnitude and geometry of interactions. In this regard, one of the most convenient techniques is a NMR dilution experiment that involves monitoring the changes in chemical shift of signals for solutions of different concentration. The method was originally developed for planar organic molecules, but was recently successfully adapted for Pt complexes.^[2] Analysis of literature data shows that ^1H is the most common nuclei monitored during dilution experiments. For Pt complexes, however, ^{195}Pt NMR can potentially be used, and here, for the first time, we report investigation of self-association of neutral cyclometallated Pt(II) complexes using ^{195}Pt NMR.

For our study, we prepared complex **1** depicted in Figure 1. The synthesis is based on previously reported methods and is described in supporting information. The complex incorporates branched aliphatic chain in order to improve solubility in CDCl₃, which was the solvent of choice for this study. The solvophobic interactions in CDCl₃ are expected to be weak due to relatively small value of the dipole moment of the chloroform molecule, and are commonly ignored in weakly polar solvents such as chloroform.^[3]

First, we applied classical ^1H NMR to study self-aggregation (Figure 1). The signals of the aliphatic protons are affected very little by concentration changes while aromatic

protons are most strongly affected in the form of up-field shift of all signals on increase of the concentration. Diamagnetic shielding is considered as the main indicator of aggregation and it is induced by delocalized aromatic π -electrons circulating around the aromatic moieties. The obtained average magnitudes of shielding $\Delta\delta$ (supplementary information), are consistent with the ring-current effect in face-to-face orientation of the molecules in aggregates (Figure 2). Indeed, protons 'a', 'b', 'c', 'd' appear to be more shielded on average than the 'i', 'j', 'h' protons of the benzene ring. This observation can be explained by the antiparallel structure of the dimer in which the electron-deficient pyridine ring stacks over the electron-rich benzene ring, and the Pt-Cl moieties of the partner molecules in dimer are also antiparallel to each other (Figure 2). Such a structure also rules out the steric hindrance of the aliphatic side chains in the dimer, which is crucial for aggregate stability. It should be stressed however, that the system is not static and figure 2 is only a schematic representation of the average structure of the dimer. Following the most recent view on the nature of π -stacking in solutions reported^[4] and taking into account the expected ^1H NMR of the dimer, van der Waals dispersive interactions between the overlapping aromatic rings in dimer are likely to be the leading factor stabilizing the aggregates.^[5]

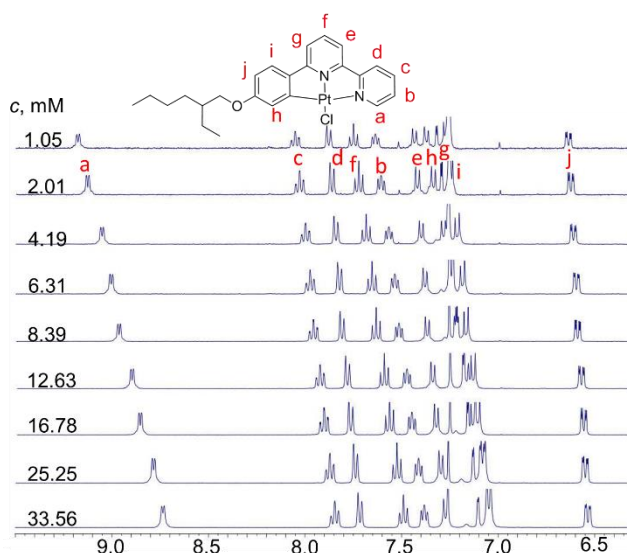


Figure 1. ^1H NMR spectra of **1** at different concentrations in CDCl₃ at 300 K.

Calculation of the aggregation parameters was accomplished by means of standard procedure, which minimizes the sum of square deviations of the theoretically calculated chemical shifts from the experimental titration curve. The experimental data (supplementary information) was acquired in wide concentration range, which is high enough to expect the formation of aggregates beyond the dimer stage. Therefore, in

[a] A.F. Suleymanova, Dr. O.S. Eltsov, Prof. Dr. D.N. Kozhevnikov
Department of Technology for Organic Synthesis
Chemical Technology Institute of Ural Federal University
620002, Mira str., 19, Yekaterinburg, Russian Federation

[b] Dr. A.O. Lantushenko, Prof. Dr. M.P. Evstigneev
Department of Physics
Sevastopol State University
Sevastopol, Russian Federation. E-mail: max_evstigneev@mail.ru

[c] Dr. V.N. Kozhevnikov
Department of Applied Sciences
Northumbria University
Ellison Building, Newcastle upon Tyne, NE1 8ST, UK
E-mail: valery.kozhevnikov@northumbria.ac.uk

[d] A.F. Suleymanova, I. Postovsky Institute of Organic Synthesis,
620990, S. Kovalevskoy str., 22, Yekaterinburg, Russian Federation

order to evaluate the theoretical δ we used three common aggregation models^[6]: (i) indefinite isodesmic model (the EK-model), which assumes that on each aggregation step the equilibrium aggregation constant, K , is independent of the number of molecules in aggregate; (ii) indefinite nucleation model (or cooperative model) assuming that starting from trimer the K is different from that for dimer by the cooperativity factor, σ ; (iii) indefinite aggregation model (the AK-model), assuming the intrinsic attenuation of K on aggregate growth due to loss of degrees of freedom. (Table 1)

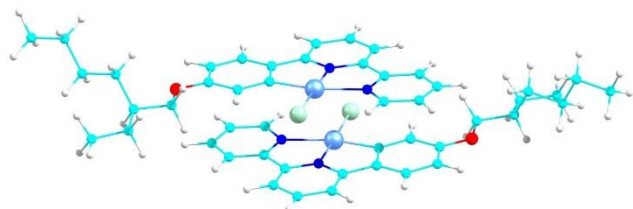


Figure 2. Schematic representation of the dimer

Equipped with initial assessment of the aggregation by ^1H NMR, we then carried out dilution experiments using ^{195}Pt NMR. Although it is possible to monitor ^{195}Pt nucleus directly (natural abundance 33.8%), the method demands very long acquisition time and for the 400MHz machine is limited to concentration of approximately 3 mM. However, if there are protons that couple with Pt through several bonds, two-dimensional HMBC ^1H - ^{195}Pt experiment (Figure 3) can be used to increase the sensitivity. In our case through 2D HMBC ^1H - ^{195}Pt experiment, we were able to monitor concentrations down to 1 mM. Despite longer acquisition times, ^{195}Pt NMR technique is somewhat easier because only one atom is monitored compared to ten hydrogen atoms in case of ^1H NMR. However, this is also a limitation since by monitoring only one atom, structural arrangement of the molecules in the dimer is not possible to predict and only the magnitude of the interaction can be assessed. To the best of our knowledge, this is the first example of the use of ^{195}Pt NMR to elucidate the strength of self-association.

Another interesting observation is that, in contrast to shielding of aromatic protons upon increase of concentration, Pt nucleus is deshielded. The intramolecular effect of attachment of halogen ligand to Pt atoms on ^{195}Pt chemical shift is a relatively well investigated^[7] whereas the intermolecular effect of Pt-halogen moiety on ^{195}Pt chemical shift in partner molecule in dimer at this stage cannot be interpreted. We consider that the deshielding may be the consequence of a small charge delocalization from the Pt atom due to the action of the large dipole of the Pt-halogen moiety of the partner molecule in aggregate located directly above (see Figure 2). Similar deshielding of ^{195}Pt nucleus was reported previously for stacking of Pt-containing heterocyclic compounds with nucleotides that were also explained by charge delocalization in Pt atom^[8]. Another possibility is the presence of metallophilic interactions corresponding to 'short' Pt...Pt distance of typically 3.45 Å. This is a characteristic feature of the Pt-complexes stacked above each other in both solution and solid state^[9] and is the principle phenomenon underpinning the design of optical stimuli responsive materials.

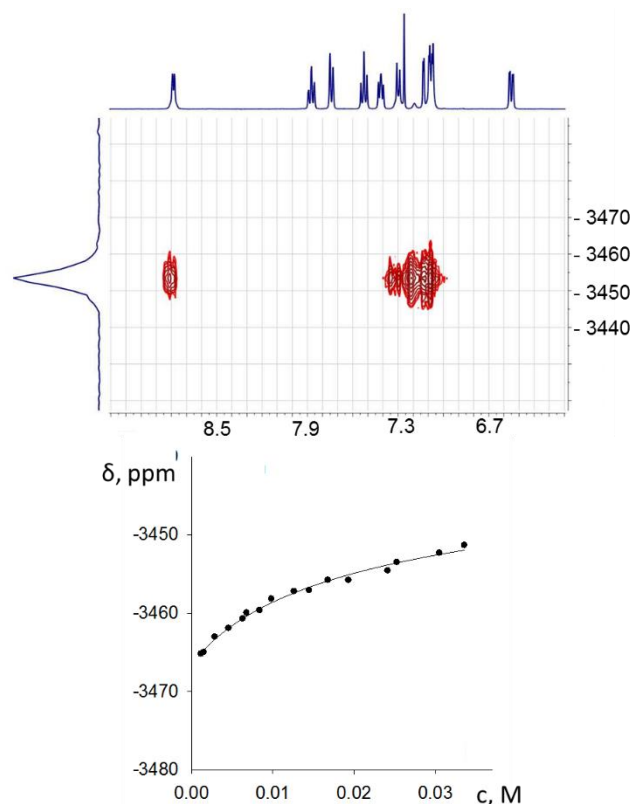


Figure 3. An example of 2D HMBC ^1H - ^{195}Pt spectrum and ^{195}Pt chemical shift values of complex 1 at different concentrations.

Table 1. Calculated aggregation constants, M^{-1}

Nuclei	EK model	Nucleation model, (σ)	AK model
^1H	44	19 (1.8)	30
^{195}Pt	41	17 (1.9)	29

Both ^1H and ^{195}Pt experiments produced the value of the cooperativity parameter σ in nucleation model that is above one, indicating an anticooperative type of the aggregation process (Table 1). This result may be explained by the contribution from aliphatic side chain of the molecules which impedes the formation of high order aggregates, and was previously reported for variety aromatic molecules with branched side chains.^[10] Another anticooperative contribution to σ may arise due to the loss of degrees of freedom (intrinsic attenuation of K on aggregate growth) upon aggregate formation^[6b]. The aggregation parameters calculated using the AK-model taking into account this factor, display slightly better discrepancy as compared with the EK-model (supplementary information), which supports this conclusion. From the data given in Table 1 it may be concluded that the parameters derived from ^{195}Pt nucleus are similar to that obtained from ^1H NMR data for the all three models studied.

In conclusion, ^{195}Pt NMR may be safely used to quantify aggregation of Pt complexes and can potentially be applied to any other Pt complexes and thus serving as a uniform measure of self-aggregation. Further results for other Pt-based systems will be reported in due course.

Acknowledgements

We thank Northumbria University for the support of this project.

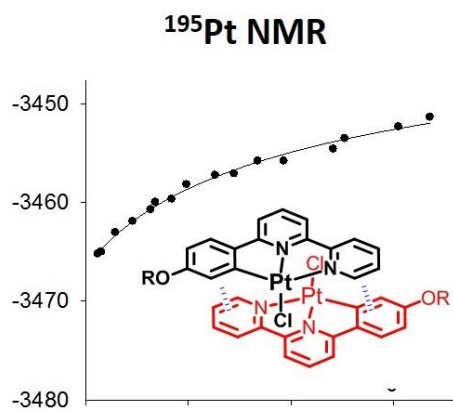
Keywords: Pt complex • ^{195}Pt NMR • self-aggregation

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Entry for the Table of Contents (Please choose one layout)

Layout 1:

^{195}Pt NMR was successfully used to quantify self-aggregation of neutral cyclometallated Pt(II) complexes in non-polar solvent. The method is not dependent on the ligand and can potentially be applied to any Pt(II) complexes.



Alfiya F. Suleymanova, Oleg S. Eltsov, Dmitry N. Kozhevnikov, Anastasia O. Lantushenko, Maxim P. Evstigneev and Valery N. Kozhevnikov**

Page No. – Page No.

Title