

^{195}Pt AND ^{119}Sn NMR STUDIES OF Pt-Sn COMPLEXES IN THE Pt(II)-Sn(II)-i-C₃H₇OH SYSTEM

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According to ^{195}Pt and ^{119}Sn NMR studies of the interaction of $(\text{C}_3\text{H}_6)\text{PtCl}_2$ with $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ in dehydrated isopropanol solution, three types of complexes with atomic ratios Pt : Sn = 1 : 5, 1 : 2 and 1 : 1, being in a dynamic equilibrium, have been revealed. A removal of the free HCl promotes the formation of the Pt : Sn = 1 : 2 complex.

Методом ЯМР на ядрах ^{195}Pt и ^{119}Sn изучено взаимодействие $(\text{C}_3\text{H}_6)\text{PtCl}_2$ со $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ в растворе абсолютированного изопропанола. Обнаружено три типа комплексов с атомным отношением Pt : Sn = 1 : 5, 1 : 2 и 1 : 1, находящихся между собой в подвижном равновесии. Удаление из раствора свободной HCl способствует образованию комплекса Pt : Sn = 1 : 2.

A previous study [1] of the complex formation of Pt(IV) with Sn(II) in isopropanol solution has revealed a strong effect of the conditions of formation of Pt-Sn complexes on their composition, depending also on the type of the solvent [2, 3]. We have studied the interaction of Pt(II) with Sn(II) in a solution of dehydrated isopropanol.

EXPERIMENTAL

The interaction of a solid, freshly recrystallized $^{119}\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ with 0.05 or 0.01 M solution of Pt(II) propylene dichloride in anhydrous isopropanol was examined. $(\text{C}_3\text{H}_6)\text{PtCl}_2$ (Zeisse acid analog) was prepared via dissolving $\text{PtCl}_4 \cdot 5\text{H}_2\text{O}$ in anhydrous i-C₃H₇OH at room temperature. Before the reaction the Pt(II) solution was evacuated and the reaction was carried out in argon. The molar ratio was: Pt : Sn = 1 : 2 and 1 : 4. Solutions of the compounds of Pt(II) with Sn(II) were prepared in two ways. Samples 1-3 (Table 2) were held in argon. Samples 4 and 5, after the addition of $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ to $(\text{C}_3\text{H}_6)\text{PtCl}_2$, were periodically evacuated

for an hour and then also held in argon. NMR spectra were recorded from the second minute on after the reaction onset at 1 h intervals for 10 h, then at one day's intervals for a week and later periodically for two months, on a Brücker CXP 300 spectrometer at 64.5 and 111.82 MHz for ^{195}Pt and ^{119}Sn , respectively.

RESULTS AND DISCUSSION

The NMR spectra of the initial Pt(II) propylene dichloride solution exhibit a single signal of ^{195}Pt with a chemical shift $\delta = -2709$ ppm with respect to the external standard of the solution $3\text{N H}_2\text{PtCl}_6 + 3\text{N HCl}$. Splitting due to protons was not observed.

Upon adding $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ to the Pt(II) solution, its color becomes bright-red from light-yellow. In 20–30 min the line with $\delta = -2709$ ppm in the NMR spectra vanished and lines appeared whose multiplicities correspond to the Pt-Sn compounds of the composition Pt : Sn = 1 : 5, 1 : 2 and 1 : 1 (Table 1) /1/. The ^{119}Sn -NMR spectra exhibit no lines of uncomplexed Sn(II) or Sn(IV). The relative contents of the Pt-Sn complexes determined from the intensities of ^{119}Sn NMR lines are listed in Table 2. The composition of the Pt-Sn complexes in the isopropanol solution depends on the concentration of the reagents in the solution, their atomic ratio and the reaction conditions (Table 2). The composition of solutions 1–3 is practically independent of time.

Upon adding Sn(II) to Pt(II) (1 : 2), Pt : Sn = 1 : 2 (~60%) and 1 : 1 (~30%) complexes are mainly formed with small amounts of the 1 : 5 complex (Table 2). The increase of the Sn : Pt atomic ratio leads to the predominant formation of the Pt : Sn = 1 : 5 complex. After evacuation of the freshly prepared solution in isopropanol, only the Pt : Sn = 1 : 2 complex (solutions 4 and 5, Table 2) is formed.

Table 1
Parameters of ^{195}Pt and ^{119}Sn NMR spectra

Composition of complexes	^{195}Pt	^{119}Sn	$I^{195}\text{Pt}-^{119}\text{Sn}$
	δ^* (p.p.m.)	δ^* (p.p.m.)	
1 : 5	-5762	-126	15 990
1 : 2	-4235	-391	28 300
1 : 1	-3569	-454	29 200

*Relative to 3 N H_2PtCl_6 in 3N HCl (external standard)

**Relative to $\text{Sn}(\text{CH}_3)_4$ (external standard)

Table 2

Composition of Pt-Sn complexes in isopropanol solution according to ^{119}Sn NMR data

No of solution	Composition of solutions		Relative content of Pt-Sn complexes (%) of the composition:**		
	Pt concentration (mol/l)	Atomic ratio (Pt : Sn)	Pt : Sn = = 1 : 5	Pt : Sn = = 1 : 2	Pt : Sn = = 1 : 1
1	0.05	1 : 2	12	62	26
2	0.1	1 : 2	15	56	29
3	0.05	1 : 4	63	24	13
4*	0.05	1 : 2	—	100	—
5*	0.1	1 : 2	—	100	—

*After evacuation of freshly prepared solutions 1 and 2.

** ^{195}Pt and ^{119}Sn NMR spectra of these complexes in isopropanol and acetone are given in Refs /1, 3/ and /2, 4/, respectively

Thus, the characteristic feature of the given Pt(II)-Sn(II)-i-C₃H₇OH system in comparison with Pt(IV)-Sn(II) in isopropanol /1/ and acetone /2/ is the rapidly attained equilibrium composition that is stable for a long period of time. Evacuation of the solution promotes the formation of Pt : Sn = 1 : 2, apparently due to the removal of free HCl from the solution. According to the stoichiometry, HCl can be suggested to initiate the transformation of Pt : Sn = 1 : 2 to 1 : 5 complexes. A negligible discrepancy between the parameter of ^{195}Pt and ^{119}Sn NMR spectra (Table 1) and those in Refs /1, 2/ can be due to the variations in the ligand environment in the first coordination sphere of platinum with preservation of the SnCl_3^- ligand.

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