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Synthesis of Water-Soluble Platinum(II) Complexes Stabilized with Trimethylstibane. Stibane Transfer in Aqueous Solution

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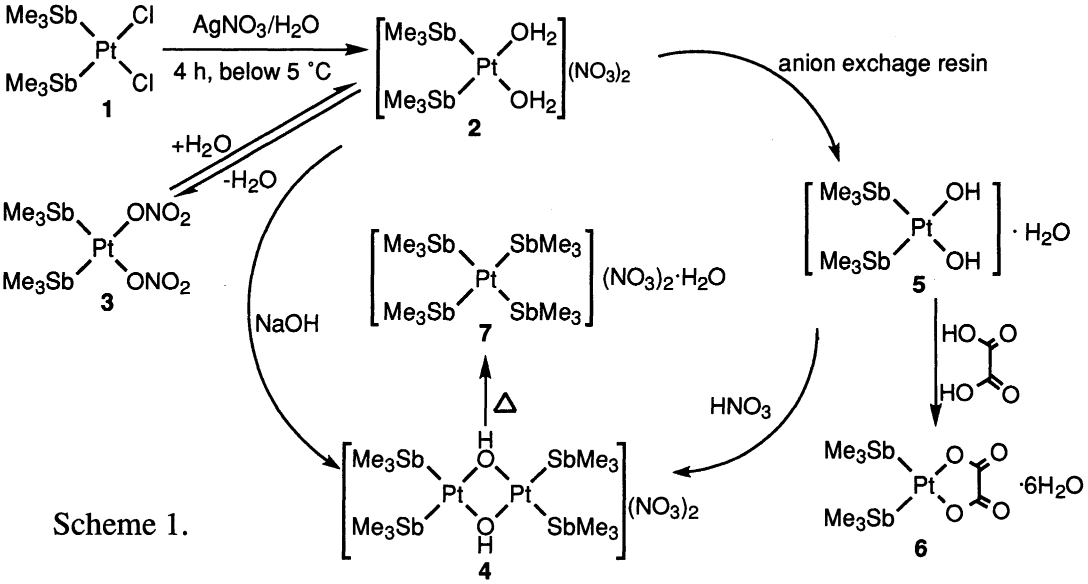
A new series of trimethylstibane-platinum(II) complexes were prepared. They have relatively low thermal stability in solution. The crystal structures of $[Pt(SbMe_3)_4](NO_3)_2$(where Me=methyl) was determined by X-ray analysis.

So far, water-soluble stibane complexes of platinum(II) have not been reported at all. Continued from our research on trimethylphosphane-platinum(II) complexes,1) the synthetic work has been extended to the corresponding stibane analogs. The procedures are summarized in Scheme 1. The reaction temperatures were kept in the range 2-5 °C except for the preparation of **7**.



Scheme 1.

The nitrate (**3**)2) was prepared in a similar way to the phosphane analog.1) The dinuclear complex (**4**) was isolated by "one pot synthesis", without separation of intermediate complexes such as **3** and **5**. The chloride (**1**) was dispersed into water and reacted with silver nitrate. Silver chloride formed was removed by filtration. The filtrate was passed through the column of anion exchange resin(OH-form). To the eluate, an equivalent of nitric acid was added and the resulting solution was reduced to give product (**4**).3)

With heating(80 °C, 5 min), the solution of **4** turned black. After removal of insoluble solid, the filtrate was left standing for 3 hours in a refrigerator to give **7**.4) The structure of **7** determined by X-ray analysis was shown in Fig. 1.5)

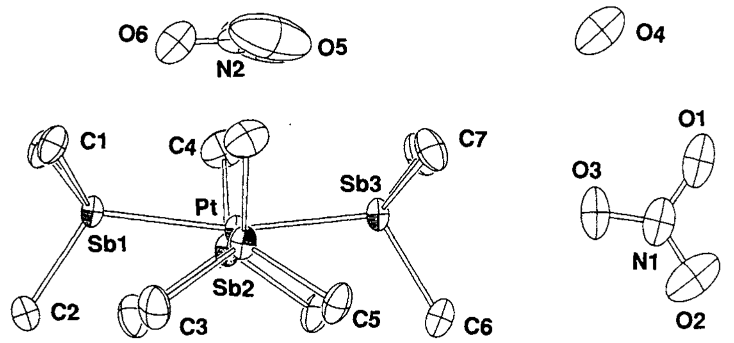


Fig. 1. ORTEP drawing of **7**. Selected bond distances(Å) and angles(°). Pt-Sb1=2.5619(9), Pt-Sb2=2.5579(6), Pt-Sb3=2.5596(9), Sb1-Pt-Sb2=90.89(2), Sb1-Pt-Sb3=166.97(3), Sb2-Pt-Sb2=166.81(3), Sb2-PT-Sb3=90.60(2). The coordination around platinum is distorted square planar.

Attempts to isolate the dihydroxo (**5**) gave an impure product, even under low temperatures. However, addition of NaOH (more than 4 equivalents) to the D_2O solution of **4** afforded new ^1H, ^{13}C NMR peaks assignable to solution species of **5** from the analogy with equilibria of the phosphane-system.1, 6) Reaction of **5** with oxalic acid or equivalent nitric acid afforded the oxalate (**6**)7) or the dimer (**4**) respectively.

An unidentified solution species was observed in ^{13}C or ^1H NMR spectra(δ -2.64 or 1.31 respectively) when 1-2 equiv. of base was added to the solution of the dimer complexes (**4**). Speculation leads to the idea that the trimer species would form in the aqueous solution as in the case of the amine system.8)

Thus, all these facts clearly demonstrate that the complexes, (**2**), (**3**), (**4**), (**5**), have relatively low thermal stability to the corresponding ammine- or phosphane-analogs. It is noteworthy that trimethylstibane molecules, which are pyrophoric in air, intermolecularly migrate among platinum atoms in aqueous solution as seen in the reaction **4**→**7** in Scheme 1.

References

1) T. K. Miyamoto, Y. Suzuki and H. Ichida, *Bull. Chem. Soc. Jpn.*, **65**, 3386 (1992).

2) Anal. Found: C, 10.88; H, 2.63; N, 4.15%. Calcd for $C_6H_{18}N_2O_6Sb_2Pt$: C, 11.04; H, 2.78; N, 4.29%. ^1H NMR(D_2O) δ 1.39(CH_3, s, 18H). ^1H NMR(CD_2Cl_2) δ 1.36(CH_3, s, 18H). ^{13}C NMR(D_2O) δ -2.19(CH_3, s, 6C). ^{13}C NMR(CD_2Cl_2) δ -1.48(CH_3, s, 6C).

3) Anal. Found: C, 11.78; H, 3.06; N, 2.28%. Calcd for $C_{12}H_{38}N_2O_8Sb_4Pt_2$: C, 11.86; H, 3.15; N, 2.31%. ^1H NMR(D_2O) δ 1.26(CH_3, s, 36H). ^{13}C NMR(D_2O) δ -3.24(CH_3, s, 12C).

4) Anal. Found: C, 14.21; H, 3.61; N, 2.76%. Calcd for $C_{12}H_{38}N_2O_7PtSb_4$: C, 14.35; H, 3.81; N, 2.79%. ^1H NMR(D_2O) δ 1.59(CH_3, s, $^3J_{HPt}$=13.1 Hz, 36H). ^{13}C NMR(D_2O) δ 2.91(CH_3, s, $^2J_{CPt}$=43 Hz, 12C).

5) Crystallographic data **7**; monoclinic, space group $P2_1/m$, a=6.697(3), b=13.804(1), c=14.540(1) Å, β=94.51°, V=1339.8(8) Å^3, Z=2, D_c=2.490, D_m=2.48 gcm^{-3}, Mo Kα, $R(R_w)$=0.036(0.046) for 2978 reflections($I>3.00\sigma(I)$). The structure was solved by usual heavy-metal methods. Details will be described elsewhere.

6) Anal. Found: C,12.33, H, 3.83%. Calcd for $C_6H_{20}O_2Sb_2Pt{\cdot}H_2O$: C, 12.41; H, 3.82%. ^1H NMR(D_2O) δ 1.25(CH_3, s, 18H). ^{13}C NMR(D_2O) δ -3.08(CH_3, s, $^2J_{CPt}$=54 Hz, 6C).

7) Anal. Found: C, 13.05; H, 3.93%. Calcd for $C_8H_{30}O_{10}Sb_2Pt$: C, 13.26; H, 4.17%. ^1H NMR(D_2O) δ 1.27(CH_3, s, 18H). ^1H NMR(CD_2Cl_2) δ 1.37(CH_3, s, 18H). ^{13}C NMR(D_2O) δ -3.37(CH_3, s, 6C), δ 169.15(CO, s, 2C) . ^{13}C NMR(CD_2Cl_2) δ -2.88(CH_3, s, $^2J_{CPt}$=58 Hz, 6C), δ 167.45(CO, s, 2C).

8) R. Faggiani, B. Lippert, C. J. L. Lock, and B. Rosenberg, *Inorg. Chem.*, **16**, 1192 (1977).

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