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A New Series of Water-Soluble Platinum(II) Complexes Stabilized with Trimethylarsane. Their Synthesis, Crystal Structures, and Solution Equilibria

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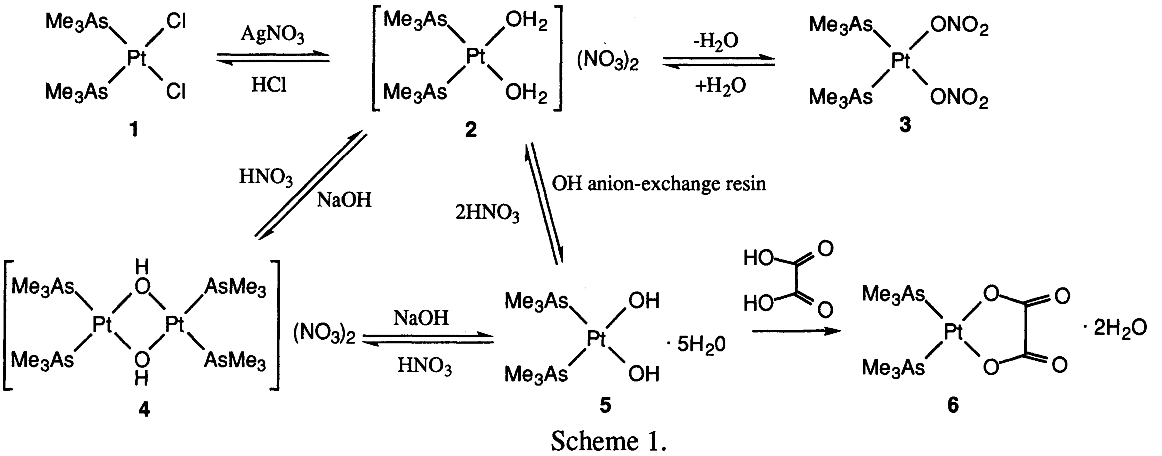
A series of water-soluble platinum(II) complexes stabilized with trimethylarsane were synthesized for the first time. Crystal structures of the complexes, e.g., *cis*-$[Pt(NO_3)_2(AsMe_3)_2]$, *cis*-$[Pt(OH)(AsMe_3)_2]_2(NO_3)_2$, *cis*-$[Pt(OH)_2(AsMe_3)_2] \cdot 5H_2O$ (where Me=methyl; ox=oxalato), were determined by X-ray diffraction method. The ^{13}C NMR spectroscopy demonstrated the solution equilibria among these species.

The aqueous chemistry of platinum(II) complexes with phosphorus and arsenic donors are still scanty and undeveloped whereas that of the am(m)ine complexes are well known as exemplified in spasmodic reports of *cisplatin.*.[1] A series of water soluble phosphane-platinum(II) complexes, such as *cis*-$[Pt(OH)_2(PMe_3)_2] \cdot nH_2O(n=2\text{-}3)$, *cis*-$[Pt(CO_3)(PMe_3)_2] \cdot 3H_2O$, $[Pt(ox)(PMe_3)_2]$ and $[Pt(cbda)(PMe_3)_2] \cdot H_2O$(where ox: oxalate, cbdca: 1,1-cyclobutanedicarboxylate) were synthesized by the elegant use of the anion-exchange resin as reported.[2] For materialization of a copious aqueous chemistry, a further synthesis toward trimethylarsane analogs has been attempted in our laboratory. We report here the successful preparation and the characterization of the new water-soluble bis(trimethylarsane)platinum(II) complexes.

The synthetic procedure is summarized in Scheme 1. The double displacement reaction between *cis*-$PtCl_2(AsMe_3)_2$(**1**) [3] and $AgNO_3$ gave *cis*-$[Pt(OH_2)_2(AsMe_3)_2](NO_3)_2$(**2**) in aqueous solution. Evaporation of the solution yielded *cis*-$[Pt(AsMe_3)_2(NO_3)_2]$(**3**)[4] which was recrystallized from dichloromethane. Its aqueous solution shows low pH value(pH=3; 0.03 mol dm^{-3}). Structure of **3** was determined by the X-ray crystallography(Fig. 1).[5] The nitrato groups lie on opposite sides of the ligand plane in sharp contrast



Scheme 1.

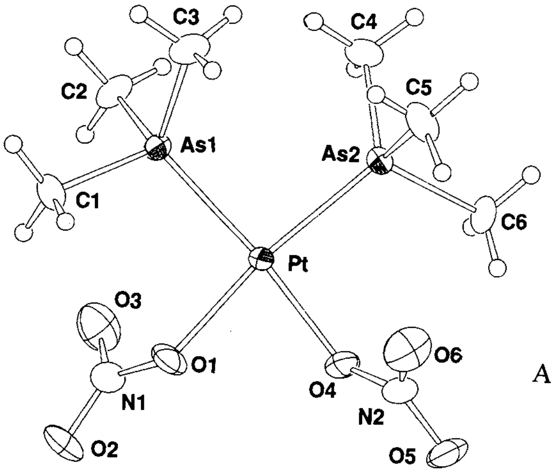


Fig. 1. Molecular structure of **3**. Selected bond distances(Å) and angles(°): Pt-O1=2.10(1), Pt-O4=2.10(1), Pt-As1=2.329(2), Pt-As2=2.335(2), O1-N1=1.30(2), O2-N1=1.30(2), O3-N1=1.22(2), O4-N2=1.29(2), O5-N2=1.24(2), O6-N2=1.24(2), As1-Pt-As2=94.22(6), O1-Pt-O4=83.3(5).

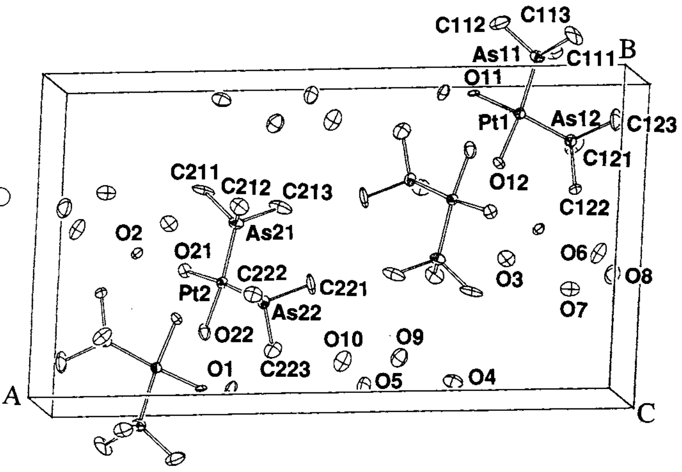


Fig. 2. ORTEP drawing of the unit cell of **5**, with atomic numbering. Hydrogen atoms are omitted for clarity. Selected bond distances(Å) and angles(°): Pt1-O11=2.04(1), Pt1-O12=2.06(2), Pt2-O21=2.02(2), Pt2-O22=2.00(2), Pt1-As11=2.232(5), Pt-As12=2.337(4), Pt2-As21=2.327(5), Pt2-As22=2.341(5), O11-Pt1-O12=87.3(6), O21-Pt2-O22=84.0(7), As11-Pt1-As12=95.3(2), As21-Pt2-As22=95.5(2).

to the corresponding diammine analog, *cis*-$[Pt(NO_3)_2(NH_3)_2]$,[6)] in which the nitrato groups sit on the same side. Bulky trimethylarsane appears cause such a distortion due to the steric repulsion.

Aqueous solution of **2** was passed through an anion exchange resin(DIAION SA10AOH) to give a dihydroxy species in a quantitative yield. The hydroxide, *cis*-$[Pt(OH)_2(AsMe_3)_2]\cdot 5H_2O$ (**5**), is hygroscopic white powder and is readily soluble in water or dichlorometane.[7)] Its aqueous solution shows high pH value(pH=10.4; 0.015 mol dm^{-3}).

Crystals marginally suitable for the X-ray measurements have been obtained by cooling the dichloromethane solution of **5** to -20 °C. The unit cell is shown in Fig. 2.[8)] There are two independent platinum atoms in the asymmetric unit. The Pt-OH distances(2.00(2)-2.06(2) Å) have the values close to the Pt-O distances of the other platinum(II) monohydroxide or alkoxide (in a range of 1.95-2.07 Å).[9, 10)] The As-Pt-As angles show the values larger than 90°, owing to the steric repulsion between the two trimethylarsane ligands in a mutually *cis* position. The 14 crstallographically independent oxygen atom (4 hydroxy groups and 10 water molecules) form a hydrogen bonded network in the solid state.

The neutralization of **5** with 1 equivalent of aqueous nitric acid or with $H_2ox\cdot 2H_2O$ gave the new complexes, μ-hydroxo dimer, *cis*-$[\{Pt(AsMe_3)_2\}_2(\mu\text{-}OH)_2](NO_3)_2$ (**4**) [11)] or oxalate, $[Pt(ox)(AsMe_3)_2]$ (**6**)[12)] respectively, in virtually quantitative yield.

X-Ray analysis$^{13)}$ of **4** revealed the dinuclear structure as shown in Fig. 3. The mean Pt-O distance[2.061(1) Å] is longer than that found in *cis*-$[\{Pt(NH_3)_2\}_2(\mu\text{-}OH)_2](NO_3)_2$[2.02(2) Å].$^{14)}$ The mean O-Pt-O angle [78.5(2)°] of **4** is smaller than that of the ammine complex[81.3°]. Steric bulk and strong *trans* influence of trimethylarsane appear cause some distortion of Pt_2O_2 skeleton.

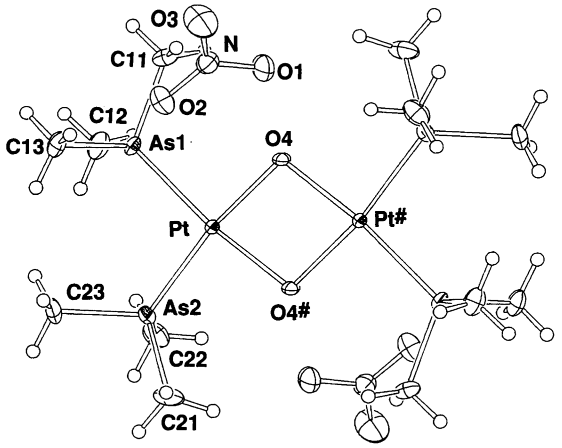


Fig. 3. ORTEP drawing of **4**. Hydrogen atoms(OH) and nitrate groups are omitted for clarity. Selected bond distances(Å) and angles(°): Pt-O4=2.057(5), Pt-O4$^{\#}$=2.064(5), Pt-As1=2.3318(8), Pt-As2= 2.330(1), O4-Pt-O4$^{\#}$=78.5(2), As1-Pt-As2=94.49(3), As1-Pt-O4=93.9(1), As2-Pt-O4$^{\#}$=93.2(1).

Acid-base equilibria of trimethylarsane complexes have been surveyed. Some equivalents of aqueous nitric acid or $NaOD/D_2O$ were added to the solution of **4** (in D_2O; in a molar ratio; 1:1, 1:2 or 1:4). The ^{13}C NMR measurement identified the solution-species, referenced to those of authentic samples; dihydroxide(**5**) and the aqua complex(**2**). Only the signal due to the solution-species of **5** or **2** could be observed when 4 equiv. of acid or base had been added. The addition of 1 equiv. of NaOH to the aqueous solution of **2,** followed by condensation of the reaction mixture, gave **4**. Therefore there are the acid-base equilibria as presented in Scheme 1.

An unidentified solution species was observed in ^{13}C NMR spectra(δ 11.54(D_2O)) when 1-2 equiv. of base was added to the solution of the dimer complex (**4**). It is speculated that the trimer species, cis-$[Pt(AsMe_3)_2(\mu\text{-}OH)]_3{}^{3+}$, would form in aqueous solution as in the case of amine system.$^{15)}$ The formation of the corresponding trimethylphosphine trimer, however, has not been observed at all.$^{2,\ 16)}$

Taken all together, gross features of the trimethylarsane-platinum(II) system resemble closely to those$^{2)}$ of the trimethylphosphane analog. The property peculiar to the former may be the possible trimer formation in aqueous solution. In ethylenediamine-platinum(II) system, even μ-hydroxy tetramer formation was reported.$^{17)}$ The cosiderable efforts to clarify the ligand-influences to μ-hydroxy multinuclear formation are put forth in our laboratory.

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References

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4) Anal. Found: C, 12.89; H, 3.15; N, 4.98%. Calcd for $C_6H_{18}N_2As_2O_6Pt$: C, 12.89; H, 3.24; N, 5.01%. ^{1}H NMR(D_2O) δ 1.63(CH_3, s, 18H). ^{1}H NMR(CD_2Cl_2) δ 1.58(CH_3, s, 18H). ^{13}C NMR(D_2O) δ 11.73(CH_3, s, $^2J_{CPt}$=50 Hz, 6C). ^{13}C NMR(CD_2Cl_2) δ 10.93(CH_3, s, 6C).
5) Crystallographic Data **3**; monoclinic system, space group $P2_1/c$, a=8.687(4) Å, b=14.822(3) Å, c=11.452(3) Å, β=97.79(2)°, V=1410.8(3) Å^3, Z=4, D_{calc}=2.542 gcm^{-3}, D_m=2.54 gcm^{-3}, Mo Kα, $R(Rw)$=0.058(0.060) for 2423 reflections(I>3.00 σ(I)). The structure was solved by direct methods and refined by least squares. Details will be described elsewhere.
6) B. Lippert, C. J. L. Lock, B. Rosenberg, and M. Zvagulis, *Inorg. Chem.*, **16**, 1525 (1977).
7) Anal. Found: C, 12.59: H, 5.33%. Calcd for $C_6H_{30}As_2O_7Pt$: C, 12.89; H, 5.41%. ^{1}H NMR(D_2O) δ 1.46(CH_3, s, 18H). ^{1}H NMR(CD_2Cl_2) δ 1.44(CH_3, s, 18H), δ 2.10(H_2O and OH, s, 12H). ^{13}C NMR(D_2O) δ 11.79(CH_3, s, $^2J_{CPt}$=45 Hz, 6C). ^{13}C NMR(CD_2Cl_2) δ 10.55(CH_3, s, $^2J_{CPt}$=44 Hz, 6C).
8) So far none of the crystal structure has been reported on *cis*- and/or *trans*-dihydroxoplatinum(II) compound. The structure of **7** is the first example. However, bad crystal quality hampered the lucid determination of space groups, i. e., $P\bar{1}$ or $P2_1/n$. So far as our collected data are concerned, the computational results fit better to $P\bar{1}$ than $P2_1/n$. In spite of poor crystal quality and limited data, main tructural features of **7** were thus determined. Until more precise structure becomes available, it seems unsuitable to ascribe any significance to the subtle differences of the bond angles and distances. Crystallographic data **7**; triclinic system, space group $P\bar{1}$, a=22.52(2) Å, b=12.36(2) Å, c=6.24(2) Å, α=89.8(2)°, β=90.0(1)°, γ=92.3(1)°, V=1739(5) Å^3, Z=4, D_{calc}=2.135 gcm^{-3}, D_m=2.12 gcm^{-3}, Mo Kα, $R(Rw)$=0.045(0.047) for 2070 reflections(I>3.00 σ(I)). The structure was solved by direct methods and refined by least squares.
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10) H. E. Bryndza and W. Tam, *Chem. Rev.*, **88**, 1163 (1988).
11) Anal. Found: C, 14.24; H, 3.60; N, 2.70%. Calcd for $C_{12}H_{38}N_2O_8As_4Pt_2$: C, 12.89; H, 3.73; N, 2.72%. ^{1}H NMR(D_2O) δ 1.48(CH_3, s, 36H). ^{13}C NMR(D_2O) δ 11.02(CH_3, s, 12C).
12) Anal. Found: C, 18.32; H, 3.35%. Calcd for $C_8H_{18}O_4As_2Pt$: C, 18.37; H, 3.47%. ^{1}H NMR(D_2O) δ 1.62(CH_3, s, 18H). ^{13}C NMR(D_2O) δ 11.57(CH_3, s, $^2J_{CPt}$=45 Hz, 12C), δ 170.01(CO, s, 2C).
13) Crystallographic data **4**; monoclinic system, space group $P2_1/c$, a=11.526(3) Å, b=10.526(2) Å, c=12.168(3) Å, β=114.30(2)°, V=1345.4(5) Å^3, Z=4, D_{calc}=2.538 gcm^{-3}, D_m=2.51 gcm^{-3}, Mo Kα, $R(Rw)$=0.030(0.035) for 2755 reflections(I>3.00 σ(I)). The structure was solved by direct methods and refined by least squares. Details will be described elsewhere.
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