New Synthesis and Crystal Structures of Platinum(II) L-Ascorbate Complexes

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The reaction of *cis*-[$Pt^{II}(OH)_2L_2$] [L_2: chelating diamines or $(PMe_3)_2$] with L-ascorbic acid (H_2asc) in an aqueous solution produces a new platinum(II) ascorbate complex, *cis*-[PtL_2(asc)], whose structure determination reveals the ascorbate ligand coordinates to Pt through O2 and O3 atoms as the first example. ^{1}H NMR results show that the steric relation between the ascorbate and the other ligand L dominates whether or not the O2,O3-chelate is rearranged to the C2,O5-chelate.

One of the present authors and others have developed aqueous chemistry of water-soluble platinum(II) compounds with trimethylphosphane,[1] trimethylarsane,[2] and trimethylstibane,[3] and demonstrated that each of the dihydroxoplatinum(II) complexes, *cis*-[$Pt(OH)_2L_2$] [L: am(m)ines, PMe_3, $AsMe_3$ or $SbMe_3$], behaves as a diacidic base to give an electrically neutral compound with many kinds of organic or inorganic acids.

L-Ascorbic acid (H_2asc) is one of the most important biomolecules, and have been studied from various viewpoints: chemistry, biochemistry, metabolism, and application.[4] Hollis et al. reported a platinum(II)-ascorbate complex [Pt(*cis*-dach)(asc-C^2,O^5)]·$3H_2O$ **1'** (dach = 1,2-diaminocyclohexane), which involves the Pt–C bond, being crystallized from an aqueous solution containing [Pt(*cis*-dach)$(H_2O)_2$]$(NO_3)_2$ and sodium ascorbate.[5] They proposed intricate reaction mechanism in the solution based on the investigation using ^{195}Pt NMR spectroscopy. We considered that the complex might be given by the dibasic acid and the diacidic base, *i.e.* H_2asc and [Pt(*cis*-dach)$(OH)_2$]. Then we examined the reactions between the dihydroxo-platinum(II) complexes, *cis*-[$Pt(OH)_2L_2$] (L: amines or PMe_3), and H_2asc in a 1:1 molar ratio using ^{1}H NMR and X-ray structure determination.

According to the following procedures, the crystals of the platinum(II)-ascorbate complexes were obtained. An aqueous solution of H_2asc was poured into a pale yellow solution of [Pt(*R*,*R*-dach)$(OH)_2$], the mixed solution gradually getting deeper coloration. After overnight standing the solution quantitatively yielded brown precipitate which was recrystallized from water as pale yellow blocks of [Pt(*R*,*R*-dach)(asc-C^2,O^5)]·$3H_2O$ **1**. Although similar procedures were applied to a colorless solution of *cis*-[$Pt(PMe_3)_2(OH)_2$], the mixed solution immediately turned light yellow and have not yielded any precipitate for longer standing. Evaporation of the mixed aqueous solution only gave yellow gummy residue, which afforded quantitative yellow plate-like crystals of *cis*-[$Pt(PMe_3)_2$(asc-O^2,O^3)]·H_2O **2** by recrystallization from 1,4-dioxane-acetonitrile mixture. Anal. **1**. Found: C, 26.7; H, 4.71; N, 5.16%. Calcd for $C_{12}H_{26}N_2O_9Pt$: C, 26.8; H, 4.88; N, 5.21%. **2**. Found: C, 26.8; H, 4.81%. Calcd for $C_{12}H_{26}O_7P_2Pt$: C, 26.7; H, 4.86%.

The molecular structures of **1** and **2** are shown in Figure 1.[6] Compound **1** is analogous with **1'**; the ascorbate dianion coordinates to the Pt atom at the C2 carbon of the five-membered ring and the O5 oxygen of the deprotonated hydroxyl group.

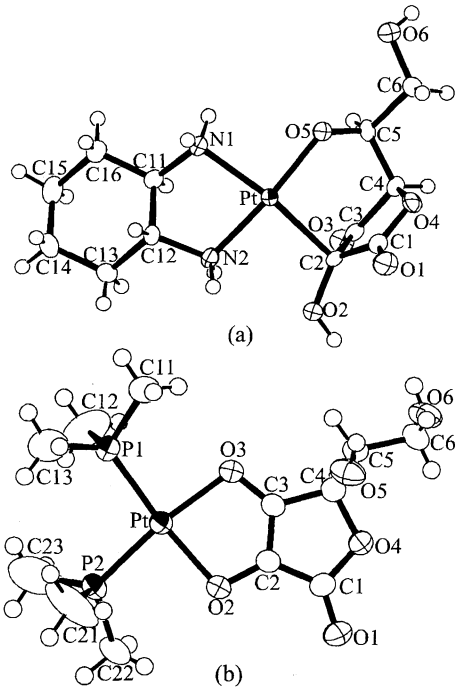

Figure 1. Molecular structures of the platinum(II)-ascorbate complexes. (a) [Pt(*R*,*R*-dach)(asc-C^2,O^5)]·$3H_2O$ **1**, and (b) *cis*-[$Pt(PMe_3)_2$(asc-O^2,O^3)]·H_2O **2**.

On the contrary in **2** the ascorbate ligand is bound to the Pt atom at O2 and O3 of the deprotonated hydroxyl groups. Although the O2,O3-chelating complexes have been proposed as hypothetical models by Martell,[4] compound **2** is the first crystallized example.

The reactions in D_2O solutions were investigated using ^{1}H NMR spectroscopy. As shown in Figure 2 (a), the spectra of the solution containing [Pt(*S*,*S*-dach)$(OH)_2$] and H_2asc was gradually changed as described by Hollis et al.;[5] some signals observed during 1-8 h had been reduced and those due to the C2,O5-chelate had been enlarged. In the final stage of the reaction (after 24 h) the C2,O5-chelating complex was dominant.[7] Thus the signals which were observed during 1-8 h and reduced afterward, should be due to the other species. The spectra of the solution containing *cis*-[$Pt(PMe_3)_2(OH)_2$] and H_2asc almost agree with that of the solution of **2**, and showed no remarkable change for a week.[7]

In addition, ^{1}H NMR spectra of dmen (*N*,*N*-dimethylethylenediamine) and tmen (*N*,*N*,*N'*,*N'*-tetramethylethylenediamine) complexes, [Pt(dmen)$(OH)_2$] and [Pt(tmen)$(OH)_2$], were investigated whether or not the steric repulsion between the hydroxyl group (O2) and the methyl groups of the PMe_3 ligand inhibit the ascorbate ligand from the formation of the C2,O5-chelate. The process of the dmen complex was similar to that of the *S*,*S*-dach complex, but the reaction of the dmen proceeded

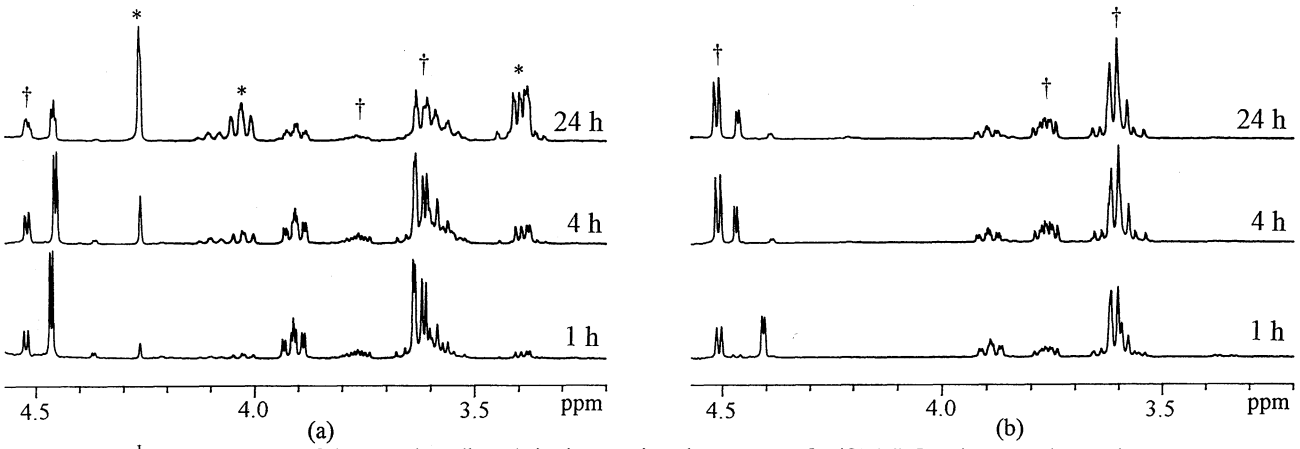

Figure 2. ^{1}H NMR spectra of the ascorbate ligands in the reactions between *cis*-[Pt(OH)$_2$L$_2$] and H$_2$asc observed at 1, 4, and 24 h for the bottom, middle, and, top respectively. (a) L$_2$ = *S*,*S*-dach, and (b) L$_2$ = tmen. The asterisked signals and the daggered ones are due to the C2, O5- and the O2, O3-chelating ascorbate ligands, respectively.

more slowly and completed after a few days. As for the tmen complex, similarly to the *S*,*S*-dach one the signals other than those of the C2,O5-chelating ascorbate complex appeared at 1 h, but differing from the *S*,*S*-dach, no remarkable change have been observed afterward [Figure 2 (b)]. The signals with daggers in Figure 2 seem to be due to the O2,O3-chelating complex, judging from the similarity in the spectral patterns of the tmen and the PMe_3 complexes.[7]

These ^{1}H NMR results mean some 'intermediate' species were formed in each aqueous solution in common with the *S*,*S*-dach, dmen, and tmen complexes at the earlier stage of the reaction. The dominant intermediate species seems to be the O2,O3-chelating ascorbate complex. As for the tertiary amine, tmen, the reaction finished at this stage owing to the steric repulsion. On the contrary in the case of the primary amine, *S*,*S*-dach, the species in the solution appeared to be rearranged into the thermodynamically stable C2,O5-chelating complex. Accordingly the asymmetric dmen ligand possessing the primary amino group along with the tertiary causes the slower rearrangement reaction.

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6 The crystal data are: **1** $C_{12}H_{26}N_2O_9Pt$, M = 537.44, monoclinic, $P2_1$ (No. 4), a = 6.245(2), b = 20.797(2), c = 6.703(2) Å, β = 105.42(2)°, U = 839.3(3) Å^3, Z = 2, D_m = 2.13, D_x = 2.13 g cm^{-3}, 6837 reflections measured, 6068 unique ones used, 319 parameters to R = 0.0327, $wR(F^2)$ = 0.0652; **2** $C_{12}H_{26}O_7P_2Pt$, M = 539.36, orthorhombic, $P2_12_12_1$ (No. 19), a = 10.625(1), b = 19.357(2), c = 9.093(1) Å, U = 1870.1(3) Å^3, Z = 4, D_m = 1.91, D_x = 1.92 g cm^{-3}, 7808 reflections measured, 6760 unique ones used, 269 parameters to R = 0.0360, $wR(F^2)$ = 0.0829. In common for **1** and **2**: Rigaku AFC7R diffractometer, Mo-Kα radiation, 2θ-ω scan method in the range of 4° < 2θ < 65°, SHELXL 93. The authors have deposited atomic coordinates at Cambridge Crystallographic Data Centre. The coordinates can be obtained on the request from The Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK.
7 Conditions in common: Bruker ARX300 (^{1}H: 300 MHz) spectrometer; *ca.* 0.2 mol dm^{-3} in D_2O solutions. ^{1}H NMR spectral assignments for the ascorbate ligand of **1**: δ 4.26 [H(C4), d, 1H], δ 4.02 [H(C5), t, 1H], δ 3.39 [H(C6), d, 2H]; **2**: δ 4.54 [H(C4), d, 1H], δ 3.77 [H(C5), m, 1H], δ 3.66 [H(C6), m, 2H]. The NMR spectra of the *R*,*R*- and *S*,*S*-dach complexes of **1** seem to be so similar that they appear to have common geometries on their molecular structures. Therefore the *S*,*S*-dach complex was used in the NMR investigation because of its higher solubility. Possible assignments for the O2,O3-chelating ascorbate ligand of the tmen complex are: δ 4.48 [H(C4), d, 1H], δ 3.75 [H(C5), m, 1H], δ 3.59 [H(C6), m, 2H].