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Chelating of Titanium by Lactic Acid in the Water-Soluble Diammonium Tris(2-hydroxypropionato)titanate(IV)

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Stable water-soluble diammonium tris(2-hydroxypropionato)titanate(IV) [ammonium trilactatotitanate(IV)], $(NH_4)_2[Ti(C_3H_4O_3)_3]$, was prepared in the crystalline form. According to the X-ray single-crystal diffraction data, this compound crystallizes in the cubic cell with $a = 11.649(4)$ Å, space group $P2_13$ (no. 198), and has $Z = 4$ molecules per unit cell. The ^{13}C NMR data and Raman and IR spectra support the determined structure. The absence of non-bonded functional groups restricts the formation of oligomers in contrast to the reported speciation of citratoperoxotitanate(IV) complexes.

Recently, we have the reported synthesis and crystal structure of a water-soluble titanium compound[1] that was to be suitable for preparation of different oxide materials containing titanium via a variation of the sol−gel process—the Pechini-type polymerizable complex method.[2,3] Although we were able to synthesize fine powders and thin films of high quality relatively easily compared to the case of titanium isopropoxide utilization,[4] the precursor tends to form Ti-rich intermediate phases at low temperature after the polymer pyrolysis step.[5] We suspected that such behavior could result from the structure of the complex molecule, which contains four Ti atoms. In principle, free carboxylic groups might coordinate other titanium ions, resulting in even larger oligomers. From the viewpoint of materials chemistry, the multidentate nature of citric acid creates an inconvenience in the synthesis, leading to the clustering and segregation of titanium ions in the solution and later in the gel. Therefore, we decided to search for other titanium complex compounds that could be utilized without a glovebox and toxic solvents.

As one can conclude from the structure of citratoperoxotitanate ion,[1] the minimum structural unit of citric acid providing the stability of the complex is a carboxylic group and an α-hydroxo group, yielding a five-member ring together with a Ti atom. For a chemist, it would be natural to attach CH_3- or another bulky group to this fragment to create a steric obstacle for complex ion segregation. In this way, we identified lactic acid $CH_3CH(OH)COOH$ as the primary candidate to form a stable titanium compound. In fact, solutions of “titanium lactate”, bis(ammonium lactato)titanium dihydroxide, are known to be stable in water, and they were successfully used for the synthesis of anatase nanocrystals[6,7] and the fabrication of ultrathin titanium oxide films,[8,9] UV-protective coatings on plastic interfaces,[10] and titania coatings on colloid particles.[11,12] However, to the best of our knowledge, the preparation of titanium lactate single crystals has not been reported, and its assumed structure[7] was proposed from the indirect data. Here, we describe the synthesis and structure of a new titanium−lactic acid complex that is soluble and stable in water: $(NH_4)_2[Ti(C_3H_4O_3)_3]$.

Synthesis of the titanium lactate complex can be summarized by the following chemical equations

$$Ti + 3H_2O_2 + OH^- \rightarrow Ti[(OH)_3O_2]^- + 2H_2O$$

$$Ti[(OH)_3O_2]^- + 3C_3H_6O_3 \rightarrow [Ti(C_3H_4O_3)_3]^{-2} + H_2O_2 + 2H_2O + H_3O^+$$

The description of the synthesis procedures is available in the Supporting Information. The obtained solid product was twice recrystallized for further characterization.

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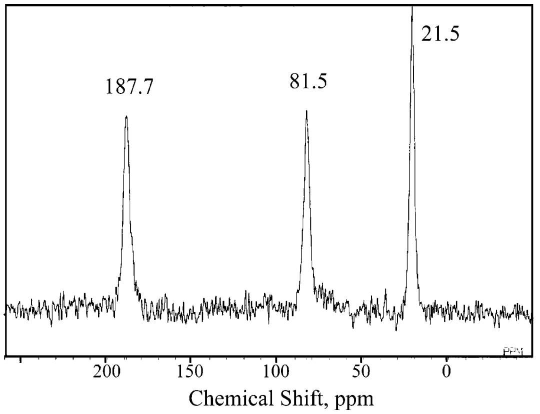

Figure 1. Solid-state ^{13}C NMR spectrum of the $(NH_4)_2[Ti(C_3H_4O_3)_3]$ single crystals.

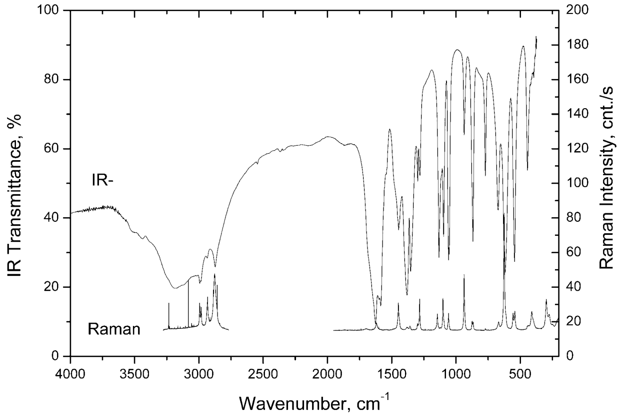

Figure 2. IR (upper) and unpolarized micro-Raman (lower) spectra of $(NH_4)_2[Ti(C_3H_4O_3)_3]$.

The elemental analysis of the prepared single crystals gives H, 5.86%; C, 31.08%; N, 8.22%; O, 34.53%; and ash (percentage from TG), 22.91%. According to the powder X-ray diffraction, the ash contains TiO_2 as a single phase. Judging from the elemental analysis and taking into account the synthesis method, one can conclude the most likely chemical formula of the obtained crystals is $(NH_4)_2[Ti(C_3H_4O_3)_3]$, which contains H, 5.74%; C, 31.05%; N, 8.04%; O, 32.17% (assuming that the rest of the oxygen is consumed for TiO_2 formation); and TiO_2, 22.94%.

The ^{13}C NMR spectrum (JEOL NMR-GSX-270 operating at 67.9 MHz with cross-polarization magic spinning) in Figure 1 allows the assumption that the complex molecule contains three structurally different carbon groups. The absence of a peak at approximately 70 ppm in the ^{13}C NMR spectrum and the peak at ~80 ppm indicate complete deprotonation of the alcoholic −OH group in the lactic acid molecule.[13] Thus, lactic acid should either chelate titanium in a bidentate manner similar to the bis(ammonium lactato)titanium dihydroxide[7] or bridge two titanium atoms.

The Raman spectrum was measured in a backscattering geometry with a Jobin-Yvon T64000 triple spectrometer equipped with Atago Bussan microprobe optics and an Ar laser for excitation (514.5 nm). FT-IR spectrum was recorded on a SYSTEM 2000 FT-IR Perkin-Elmer spectrometer using KBr for dilution (sample/KBr = 0.3:100). The Raman and IR spectra of the obtained single crystals in Figure 2 are different from those of $(NH_4)_2[Ti(C_3H_4O_3)_2(OH)_2]$, a commercial Aldrich product.[14] This fact unambiguously indicates that $(NH_4)_2[Ti(C_3H_4O_3)_3]$ is a novel compound different from bis(ammonium lactato)titanium dihydroxide. Note that all vibrations are active in both the Raman and IR spectra, and their intensities are complementary. The presence of the same vibrations in both spectra well supports the choice of noncentrosymmetric space group. At the same time, the relative complexity of both spectra does not provide unequivocal evidence for the presence or absence of peroxo groups in the prepared single crystals. Depending on the structure of the peroxo complex, one should expect $\nu(O_2^{-2})$ peaks at 800−900 cm^{-1} and $\nu(Ti{-}O_2)$ peaks in the 560−610 cm^{-1} region.[15] We can locate peaks at 545, 623, 860, and 939 cm^{-1}. Although there is no good match for the Ti−O_2 frequency, the interpretation of the spectra should be still carried out with caution. Perhaps the additional evidence against the presence of peroxo group is the white color of the crystals. Peroxo complexes of Ti tend to have from yellow to deep yellow color depending on the pH.

The X-ray diffraction data were collected from the single crystal polished to spherical shape. The titanium−lactic acid complex crystallizes in the cubic system and has a relatively large unit cell parameter of 11.649 Å.[16] The crystal structure was solved by the direct method using Sir97[17] after correcting of the diffraction data for the absorption. The guided refinement was carried out with the CRYSTALS[18] software integrated system. After the isotropic refinement of the thermal parameters, the hydrogen atoms of the lactic acid were generated geometrically. During the final stage of the refinement, we located the hydrogen atoms of both NH_4^+ groups. Their positions and thermal parameters were kept constant. Then, we carried out the refinement of the anisotropic thermal parameters of non-hydrogen atoms. Although the parameters-to-reflections ratio decreases to 4.6 in this case, the refinement statistics improved, and the reasonable thermal parameters and only small change of the atomic positions indicate that the refinement stayed within reasonable margins of the obtained model. The full list of atomic parameters is

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(16) Crystallographic data: diffractometer, Rigaku AFC5; chemical formula, $(NH_4)_2[Ti(C_3H_4O_3)_3]$; cubic; space group, $P2_13$ (no. 198); $a = 11.649(4)$ Å, volume = 1580.5(9) Å^3, $T = 296$ K, MW = 348.13, $Z = 4$, Mo Kα, $\lambda = 0.71073$ Å, $\rho_{calc} = 1.459$ g/cm^3, $\mu = 5.83$ cm^{-1}, total reflections = 2616, reflections without Friedel's law =871, $R_{int} = 0.04$, reflections with $I > 2\sigma(I) = 300$, number of parameters = 65, $R_w = 0.0674$, $R = 0.0343$, $R_{all} = 0.1448$, goodness of fit = 0.9443. The structure was solved by the direct method and refined by full-matrix least-squares against F^2. $R_w = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$, and $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$.

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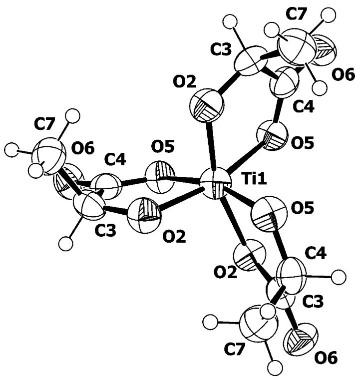

Figure 3. ORTEP view and labeling scheme of the complex anion $[Ti(C_3H_4O_3)_3]^{2-}$. Thermal ellipsoids are displayed for 50% probability.

provided in a separate CIF file available as Supporting Information.

An ORTEP[19] view of the titanium lactate complex is displayed in Figure 3. Note that the titanium is coordinated by six oxygen atoms from three lactic acid molecules, forming a stable five-membered ring composed of Ti, O(2), C(3), C(4), and O(5). The TiO_6 octahedron is slightly distorted, with an O(2)−Ti−O(2) angle of 162.7° and the Ti atom shifted from the center giving, the two sets of Ti−O interatomic distances of Ti−O(5) = 2.071(5) Å and Ti−O(2) = 1.848(5) Å. The lactic acid molecules preserve their chirality. Inspection of the difference Fourier maps did not reveal any residual electronic density that could be interpreted as presence of D-lactic acid. Lactic acid acts as a bidentate ligand, and as we expected, there are no potential free groups for oligomerization. At the same time, tight coordination creates spatial difficulties for nucleophilic attack, the first step of hydrolysis. The bond-valence sum of Ti for the observed interatomic distances is 4.24, which indicates that the titanium coordination might be strained, and the Ti−O(2) distance is particularly short. Nevertheless, such interatomic distances are not outstanding and can be found in a titanium malotolate complex[20] (1.868 and 2.193 Å) and in acetylacetonate complexes[21] (1.796, 1.805, and 2.02−2.08 Å).

Figure 3 displays the β'-isomer, one of four possible isomers of the Ti−lactic acid complex.[22] Two isomers, β and β', exhibit C_3 symmetry and can be accommodated on the 3-fold axis of the $P2_13$ space group. The other two isomers, α and α′, have C_1 symmetry, and they are inconsistent with the $P2_13$ space group. Analysis of the residual electronic density and low flack parameter of 0.09 suggests that the unit cell contains only the β'-isomer species, which might have the lowest solubility among the four isomers or the crystals of which might have been picked up accidentally. To verify this hypothesis, we collected the ^{1}H NMR spectrum of the solid product recrystallized and dissolved in D_2O (available as Supporting Information). The spectrum contains

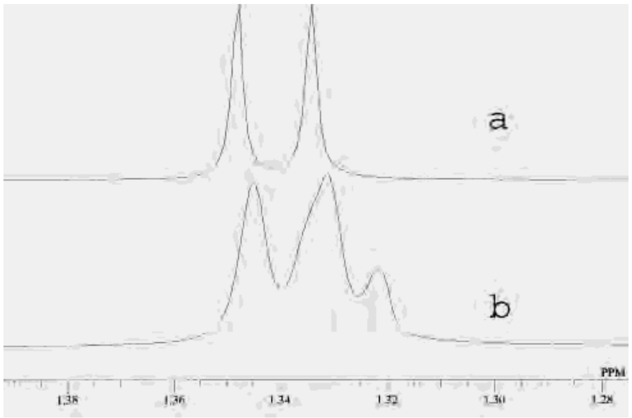

Figure 4. ^{1}H NMR spectrum of the $-CH_3$ doublet of (a) $(NH_4)_2[Ti(C_3H_4O_3)_3]$ single crystals dissolved in D_2O and (b) sporadic powder sample of a similar chemical composition dissolved in D_2O.

a $-CH_3$ doublet (1.3 ppm), a $-CH$ quadruplet (5 ppm), and a weak quadruplet (4.1 ppm, possibly due to the $-CH$ neighboring the protonated $-OH$ group). The $-CH_3$ doublet shown in Figure 4a is of particular interest because it provides evidence of structurally similar groups in the three lactic acid molecules chelating titanium as they are presented in the ORTEP plot in Figure 3. We attempted to prepare the other diasteriomers of the Ti−lactate complex by modifying the preparation conditions. In some instances, we could obtain powder samples having structurally different $-CH_3$ groups (see Figure 4b). However, we could not obtain such compounds in a reproducible way, and after keeping the solution for 24 h, their H NMR spectra always transformed into spectra similar to Figure 4a, suggesting that the formation of β, α, and α′ might be possible, although the β' isomer is thermodynamically the most stable.

In the chiral $P2_13$ space group, the $[Ti(L-C_3H_4O_3)_3]^{-2}$ complex anions form left-handed helixes of 3_2 symmetry (see the stereoview in the Supporting Information). The mirror image of this helix has right-handed direction (3_1 screw rotation) and corresponds to the packing of the similar $[Ti(D-C_3H_4O_3)_3]^{2-}$ complex. One might question whether it is possible to arrange the titanium L-lactate complex ions into a right-handed helix of 3_1 symmetry, yielding one more isomer in the crystalline state. We do not have any experimental evidence that could support or reject this idea.

The described water-soluble titanium lactate complex was successfully utilized for the synthesis of $SrTiO_3$ fine powders and thin films by the spin-coating method.[23]

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Supporting Information Available: Synthesis details and ^{1}H NMR spectrum of the solid product recrystallized and dissolved in D_2O. Atomic positions and selected interatomic bond distances in a separate CIF file. This material is available free of charge via the Internet at http://pubs.acs.org.

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