Molecular Structure of Seven-Coordinate *trans(O_6)*-(Ethylenediamine-*N,N'*-diacetato-*N,N'*-di-3-propionato)(aqua)titanate(III), *trans(O_6)*-$[Ti(eddadp)(H_2O)]^-$

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X-ray crystal analysis revealed that the title complex anion has an approximately pentagonal-bipyramidal (PB) structure in which a water molecule and two five-membered glycine chelates lie in an equatorial plane and two propionate groups occupy *trans*-axial sites. This complex anion is the unprecedented seven-coordinate eddadp complex which moreover has a *trans(O_6)* structure.

Stereochemistry of transition-metal complexes with edta-type ligands has been extensively studied,[1] and it has been established that octahedral edta complexes have equatorial ethylenediamine and glycine rings (referred to as E- and G-rings, respectively) more constrained than axial glycine rings (referred to as R-rings); these five-membered E- and G-rings are not sufficiently large to encircle usual metal ions cozily in an octahedral environment. As a result, some large metal ions such as Ti^{3+},[2] V^{3+},[3] and Fe^{3+} [4] form a seven-coordinate edta complex, with a water molecule as an additional ligand. When the diamine part or carboxylate arms are expanded by one CH_2 group, the resulting complex has a normal, octahedral structure. Typical examples are $[V(1,3\text{-pdta})]^-$,[5] $[V(eddadp)]^-$,[6] $[Fe(1,3\text{-pdta})]^-$,[7] and *trans(O_5)*-$[Fe(eddadp)]^-$ [7] (1,3-pdta = 1,3-propanediamine-*N,N,N',N'*-tetraacetate and eddadp = ethylenediamine-*N,N'*-diacetate-*N,N'*-di-3-propionate). In addition, the *trans(O_5)* isomer[8] is predominantly formed for the octahedral $[M(eddadp)]^-$ complexes (M = Cr^{3+},[9] Fe^{3+},[7] Co^{3+},[10] and Rh^{3+} [11]); the two six-membered β-alanine chelates occupy the equatorial plane preferentially to relieve the constraint which would be imposed if the five-membered glycine chelates occupied it. These observations are all in favor of the view that the five-membered E- and G-rings, both lying in the equatorial plane, suffer considerable steric strains in the octahedral edta complexes.

In the present study, X-ray structure analysis has been performed on the Ti^{3+}-eddadp complex, to ascertain whether it has an octahedral *trans(O_5)* structure like other eddadp complexes, or the Ti^{3+} ion persists in adopting a seven-coordinate structure even with eddadp capable of forming two six-membered chelate rings.

The blue complex salt was crystallized from an aqueous mixture of $TiCl_3$ and $H_4eddadp$[10a] neutralized with $NaHCO_3$ under an N_2 atmosphere. A total of 5617 unique reflections ($2.8° < 2\theta < 59.9°$) were measured on an Enraf-Nonius CAD4 diffractometer with graphite-monochromated Mo-Kα radiation; 4768 reflections with $I \geq 3\sigma(I)$ were used for the subsequent structure analysis. The structure was solved by the direct methods and refined by the full-matrix least-squares method. The final agreement factors R and R_w were 0.047 and 0.038, respectively. Crystal data for $Na[Ti(eddadp)(H_2O)]\cdot 6H_2O$: $C_{12}H_{30}N_2NaO_{15}Ti$, M = 513.26, triclinic, space group $P\bar{1}$(#2), a = 7.265(2), b = 8.495(6), c = 19.038(9) Å, α = 98.08(5), β = 95.02(3), γ = 111.62(5)°, V = 1068(1)$Å^3$, Z = 2, D_c = 1.60 g cm^{-3}, μ (Mo-Kα) = 4.97 cm^{-1}, F (000) = 538, and T = 298 K.

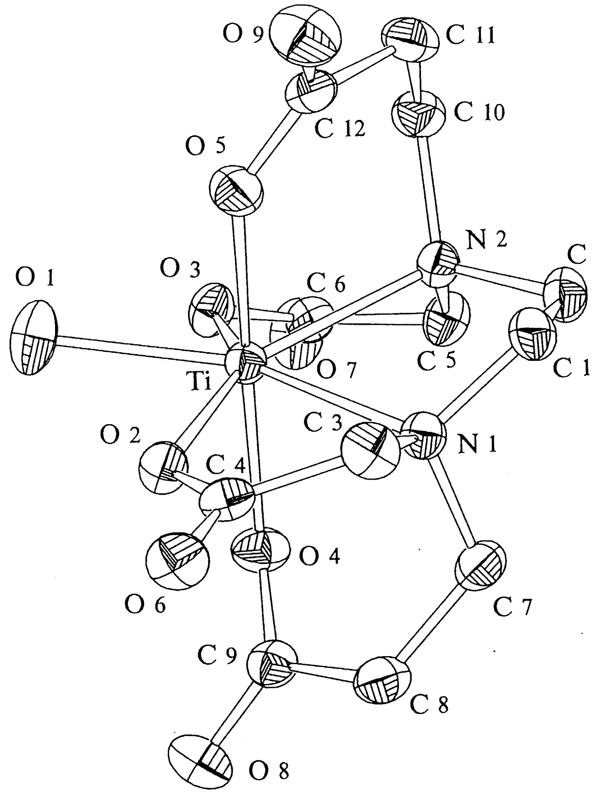

Figure 1. Molecular structure of the complex anion in *trans-(O_6)*-$Na[Ti(eddadp)(H_2O)]\cdot 6H_2O$. Selected bond distances (Å) and angles (°): Ti-O1 2.135(3), Ti-O2 2.078(2), Ti-O3 2.095(2), Ti-O4 2.064(2), Ti-O5 2.022(2), Ti-N1 2.334(2), Ti-N2 2.314(2); O1-Ti-O2 75.74(8), O1-Ti-O3 73.07(8), O1-Ti-O4 97.84(9), O1-Ti-O5 84.87(9), O1-Ti-N1 147.76(8), O1-Ti-N2 137.13(8), O2-Ti-O3 142.61(7), O2-Ti-O4 82.79(8), O2-Ti-O5 90.31(8), O2-Ti-N1 72.51(8), O2-Ti-N2 144.82(7), O3-Ti-O4 81.56(8), O3-Ti-O5 106.75(8), O3-Ti-N1 138.39(8), O3-Ti-N2 71.72(7), O4-Ti-O5 171.69(7), O4-Ti-N1 83.68(8), O4-Ti-N2 100.38(9), O5-Ti-N1 89.84(9), O5-Ti-N2 82.61(9), N1-Ti-N2 73.06(8).

Figure 1 depicts the molecular structure of the complex anion with numbering scheme, which shows that it has a seven-coordinate and approximately pentagonal-bipyramidal (PB) structure in which two five-membered glycine chelates lie with a water molecule in the pentagonal plane to form the G-rings and two propionate groups occupy the *trans*-axial sites to constitute the six-membered R-rings, giving a *trans(O_6)* isomer.[8] To our best knowledge, this complex anion is the unprecedented seven-coordinate eddadp complex which moreover has a *trans(O_6)* structure; all the eddadp complexes known to date are six-coordinate and yet no *trans(O_6)* isomer has been detected for them.[7,9-11]

Recently, some metal complexes have been prepared with edta-like ligands having both of 1,3-propanediamine and propionate groups capable of forming six-membered chelate rings.[1] Notable are 1,3-pddadp complexes with Co^{3+},[12] Cr^{3+},[13] and Rh^{3+} [14] (1,3-pddadp = 1,3-propanediamine-*N,N'*-diacetate-*N,N'*-di-3-propionate). For the former two complexes, the *trans(O_6)* isomer has been characterized as well, making a sharp contrast to the corresponding eddadp complexes. These interesting findings are interpreted as follows. When 1,3-propanediamine is substituted for ethylenediamine in edta to give 1,3-pdta, the constraints of not only the E-ring itself but also the five-membered equatorial G-rings are relaxed to some extent, while that of the axial R-rings is conversely reinforced.[10b] As a result, the two propionate groups are given a chance to occupy the axial sites in the 1,3-pddadp complex, resulting in the strain relief of the R-rings.

The parent Ti^{3+}-edta complex, $[Ti(edta)(H_2O)]^-$ in its sodium salt has a seven-coordinate and approximate PB structure,[2] similar to the present eddadp complex. The strain of each chelate ring may be evaluated on the basis of the deviations of its inner bond angles from respective ideal angles.[1] If an sp^2 hybridization is assumed for the coordinating oxygen[15] and carbonyl carbon atoms, and the ideal O-Ti-N angle is assumed to be 72° and 90° for the equatorial G- and axial R-rings, respectively, in the PB structure, the angle deviations thus calculated reveal that the parent $[Ti(edta)(H_2O)]^-$ has the axial R-rings much more constrained than the equatorial G-rings unlike usual octahedral edta complexes. Consequently, the two propionate groups of eddadp may well occupy the axial sites preferentially in the resulting complex to relieve the severer constraint which would be otherwise present in the R-rings, provided that the PB structure is retained. That is, the *trans(O_6)* structure is highly possible even for the eddadp complex , if the overall structure is PB. If the Ti^{3+} ion does not have a strong propensity to take a PB structure, its eddadp complex will take an octahedral *trans(O_5)* structure predominantly like other eddadp complexes.

The V^{3+} ion (d^2) forms a seven-coordinate edta complex like the Ti^{3+} ion (d^1), both having electron configurations favoring a seven-coordinate structure.[2] However, a recent spectroscopic study suggests that the V^{3+}-eddadp complex is six-coordinate,[6] at variance with the present Ti^{3+}-eddadp complex. The difference is probably due to a smaller ion size of the V^{3+} ion (0.780Å *vs.* 0.810Å) and/or to no adherence of the V^{3+} ion to adopting a PB structure.[3]

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References and Notes

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15 Since the Ti^{3+} ion has only one d-electron, it favors π-donor ligands. It is thus reasonable to assume an sp^2 rather than sp^3 hybridization for the coordinating oxygen atom. In fact, the Ti-O-C(O) angles are all close to 120° in the PB $[Ti(edta)(H_2O)]^-$.[2] Even if an sp^3 hybridization is assumed, the same result is derived.