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# The Absence of a Titanyl Oxygen in the Ti(IV)-edta$^{4-}$ Complex: [Ti(edta)($H_2O$)]

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The crystal structure of the Ti(IV) complex of edta$^{4-}$, which may be isolated at pH <1.0, has been found to contain no titanyl moiety. The structure is compatible with the formulation [Ti(edta)($H_2O$)] in which the coordinated water is located in a pentagonal plane at 2.082 (3) Å from Ti(IV), as compared to the Ti=O distance of 1.619 Å in the porphyrin complex. The remainder of the pentagonal plane donors are the two ethylenediamine nitrogens at 2.292 (2) and 2.311 (2) Å and two carboxylate oxygens at 1.926 (2) and 1.922 (2) Å. The axial carboxylates that complete the 7-coordinate pentagonal-bipyramid structure are at 1.977 (2) and 1.983 (2) Å. The structure is similar to that of the Li[Fe(edta)($H_2O$)]·$2H_2O$ salt as shown by the axial bond angle of 156.4° and the strain shown by the angle sums of the E ring (515.3°), R rings (534.1 ± 1.4°), and G rings (527.1 ± 1.3°). The influence of electronic configuration and ligand field strength on first-row transition metal-edta$^{4-}$ complexes is discussed. The crystal structure was determined from 2980 reflections (Mo K$\alpha$) to $R = 0.043$ ($R_w = 0.045$); the space group is $P2_1/a$. The unit cell constants for $a$, $b$, and $c$ are 13.237 (4), 7.037 (2), and 13.899 (2) Å with $\beta = 90.85$ (2)°. The number of molecules per cell, $Z$, is 4.

## Introduction

Interest in transition-metal ion complexes of ethylenediaminetetraacetate, edta$^{4-}$, dates back many years. However, little crystallographic work has been done since the pioneering work of J. L. Hoard's group with Co(III),[2] Ni(II),[3] Fe(III),[4] Mn(II),[5] and Mg(II).[6] Two structural types have been found in this series, 6- and 7-coordinate complexes. Of the 7-coordinate species, one is the distorted monocapped trigonal prism, while the other is a pentagonal bipyramid (Fe(III) system).[4] A water molecule occupies a site in the pentagonal plane as the seventh ligand for the Fe(III) complex, together with two N and two O donors from edta$^{4-}$. In more recent times the structures of the Mn(III) complex, K[Mn(edta)]·$2H_2O$[7] and the Ca(II) salt Ca[Ca(edta)]·$7H_2O$[8] were reported. Eight-coordination is observed for the Ca(II) complex; the Mn(III) complex is the normal 6-coordinate complex. Higher coordination numbers such as 9 are observed for the lanthanide +3 ions[20] as would be anticipated for the larger central ions, but for the first transition series including the alkaline-earth ion $Ca^{2+}$, only the spherically symmetric $d^0$($Ca^{2+}$) and the high-spin $d^5$($Fe^{3+}$ and $Mn^{2+}$) cases have been observed to depart from coordination number 6.[23] The edta$^{4-}$ complexes are frequently isolated with one or more of the carboxylate positions protonated and therefore freed from coordination. The vacated site is filled by a $H_2O$ molecule with the protonated carboxylate pendant to the central metal complex.[2] This geometry yields a quinquedentate contribution for the monoprotonated salts. Their structures are analogous to the *N*-(hydroxyethyl)ethylenediaminetriacetate (hedta$^{3-}$) complexes such as the Cr(III) complex, Cr(hedta)($H_2O$),[9] and its isomorphous Ga(III)[10] and Rh(III)[10] complexes. When oxo groups are present on the parent transition-metal ion as in the case of the $d^0$ pervanadyl cation, $VO_2^+$, the site of protonation remains at the carboxylate positions as shown by the structure of ($NH_4$)[$VO_2$(edtaH$_2$)]·$3H_2O$.[11]

**Table I**

| | |
|---|---|
| formula | $C_{10}H_{14}N_2O_9Ti$ |
| cryst syst | monoclinic |
| space gp | $P2_1/a$ |
| $a$, Å | 13.237 (4) |
| $b$, Å | 7.037 (2) |
| $c$, Å | 13.899 (2) |
| $\beta$, deg | 90.85 (2) |
| $V$, Å$^3$ | 1294.5 (5) |
| mol wt | 355.1 |
| $Z$ | 4 |
| $d$(calcd), g/cm$^3$ | 1.822 |
| $d$(obsd), g/cm$^3$ | 1.818 |
| cryst size | 0.68 × 0.56 × 0.34 |
| color | colorless |
| radiation | Mo K$\alpha$ |
| monochromator | graphite |
| $\mu$, cm$^{-1}$ | 7.086 |

Recently an interest in the solution species containing the $d^0$ Ti(IV) center, coordinated with polyamino polycarboxylate ligands has arisen. Weighardt et al. have reported a tetrameric structure for $Cs_4$[TiO(nta)]$_4$·$6H_2O$.[12] In this complex no titanyl or terminal oxo ligands are found, but rather the Ti(IV) centers are all oxo bridged. Shepherd et al. have studied the Ti(IV)-edta$^{4-}$ complex in solution.[13] It is known that $H_2O_2$ will react with the complex in solution to form a peroxo complex, Ti($O_2$)(edta)$^{2-}$, providing the basis of an analytical procedure for $H_2O_2$.[14] It has been assumed that the Ti(IV) complex is that of a coordinated titanyl (Ti=$O^{2+}$) moiety. Indeed, the replacement of the inferred oxo ligand in TiO(edta)$^{2-}$ by $H_2O_2$ obeys associative reaction kinetics that preclude a simple displacement of a solvent molecule in the pH range above 2.[13] A solid may be isolated by mixing a freshly prepared $TiO^{2+}$ solution with a stoichiometric amount of $Na_2$(edta)$H_2$·$2H_2O$, followed by lowering the pH below 1.5. The analysis is compatible with the formulation TiO(edtaH$_2$) as would be anticipated on the basis of the other $d^0$ case of the $VO_2^+$ complex.[11] The structure reported here establishes that in an isolated crystal the site of protonation is on the oxo group with retention of all six edta$^{4-}$ donors in a 7-coordinate [Ti(edta)($H_2O$)] complex. The result is also contrary to what has been presumed parallel chemistry of the $TiO^{2+}$ and $VO^{2+}$ species. Although the vanadyl complexes have been shown to hydrogen bond to the vanadyl oxygen, no net conversion of the oxo group to a coordinated $H_2O$ is known for its polyamino polycarboxylate complexes.[15]

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**Table II.** Atom Coordinates (×10) and Temperature Factors (Å × 10)

| atom | *x* | *y* | *z* | $U^a$ |
|---|---|---|---|---|
| | | A. Non-Hydrogen Atoms | | |
| Ti | 370 (1) | 5529 (1) | 2501 (1) | 16 (1)* |
| O(1) | 360 (1) | 4302 (2) | 1220 (1) | 24 (1)* |
| C(1) | 1133 (2) | 4301 (3) | 642 (2) | 23 (1)* |
| O(6) | 1256 (2) | 3150 (3) | 7 (2) | 39 (1)* |
| C(2) | 1885 (2) | 5864 (4) | 844 (2) | 27 (1)* |
| O(2) | −343 (1) | 5575 (2) | 3748 (1) | 26 (1)* |
| C(3) | −312 (2) | 7000 (3) | 4357 (2) | 22 (1)* |
| O(7) | −912 (1) | 7224 (3) | 4997 (1) | 32 (1)* |
| C(4) | 512 (2) | 8411 (3) | 4173 (2) | 24 (1)* |
| N(1) | 1249 (1) | 7559 (3) | 3496 (1) | 19 (1)* |
| C(9) | 1779 (2) | 9085 (3) | 2966 (2) | 26 (1)* |
| C(10) | 2247 (2) | 8217 (4) | 2086 (2) | 25 (1)* |
| N(2) | 1437 (1) | 7233 (3) | 1522 (1) | 19 (1)* |
| O(3) | 1564 (1) | 4090 (2) | 2832 (1) | 24 (1)* |
| C(5) | 2236 (2) | 4556 (3) | 3500 (2) | 23 (1)* |
| O(8) | 2988 (1) | 3624 (3) | 3681 (1) | 35 (1)* |
| C(6) | 1976 (2) | 6333 (4) | 4040 (2) | 26 (1)* |
| O(4) | −401 (1) | 7758 (2) | 2176 (1) | 22 (1)* |
| C(7) | −180 (2) | 8999 (3) | 1506 (2) | 20 (1)* |
| O(9) | −718 (1) | 10361 (2) | 1316 (1) | 30 (1)* |
| C(8) | 780 (2) | 8587 (3) | 979 (2) | 25 (1)* |
| O(5) | −731 (2) | 3413 (3) | 2481 (2) | 39 (1)* |
| | | B. Hydrogen Atoms | | |
| H(21) | 2048 | 6498 | 255 | 29 (7) |
| H(22) | 2488 | 5328 | 1125 | 49 (11) |
| H(41) | 861 | 8720 | 4768 | 24 (6) |
| H(42) | 238 | 9544 | 3895 | 23 (7) |
| H(91) | 1305 | 10052 | 2775 | 17 (6) |
| H(92) | 2296 | 9635 | 3370 | 58 (11) |
| H(101) | 2759 | 7321 | 2278 | 19 (6) |
| H(102) | 2544 | 9197 | 1702 | 52 (11) |
| H(61) | 2584 | 7044 | 4158 | 31 (8) |
| H(62) | 1683 | 5984 | 4643 | 54 (10) |
| H(81) | 1141 | 9756 | 891 | 64 (12) |
| H(82) | 612 | 8049 | 362 | 28 (7) |
| H(51) | −732 (31) | 2645 (63) | 2092 (28) | 66 (13) |
| H(52) | −1003 (28) | 3150 (52) | 2963 (25) | 44 (10) |

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized **U** tensor.

## Experimental Section

The title complex was isolated as reported in ref 12. The density confirms the formula [Ti(edta)($H_2O$)]. The crystals as thin flat plates obtained by this procedure were used without further purification. A crystal was mounted and optically centered on a Syntex $P2_1$ four-circle diffractometer. Fifteen reflections were selected from a $\phi$ rotation photograph and were automatically centered. A total of 5581 reflections was collected, $2° < 2\theta < 55°$, of which 2980 had intensities greater than $3.0\sigma$. Table I summarizes the data collection obtained at room temperature.[21]

The space group was determined from systematic absences. The titanium atom was located by Patterson synthesis and the remainder of the molecule by difference Fourier techniques. The structure was refined with the SHELXTL X-ray crystallographic package to $R = 0.043$, $R_w = 0.045$. The SHELXTL program minimized the function $\sum w_i(|F_o| - |F_c|)^2$, using the $w_i = 1/\sigma_i$ values. $\sigma_i$ values were estimated from the diffractometer intensity measurements, assuming the errors are from counting statistics. SHELXTL programs use the International Tables for scattering factors, $F_o$, $f'$, and $f''$. Corrections for the presence of extinctions were not made as there appeared to be no obvious need for them. Octants collected were ($hkl$, $\bar{h}kl$). The hydrogen atom positions of the coordinated $H_2O$ molecule were located from the difference Fourier listing and refined without constraints. The final difference Fourier listing was featureless, with the maximum observed peaks corresponding to 0.45 e/Å$^3$.

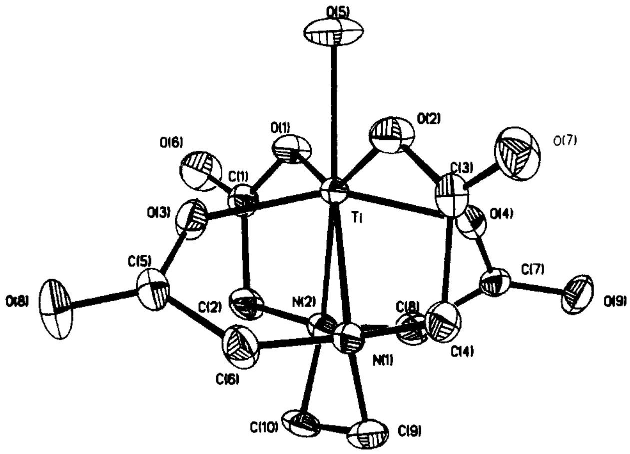

**Figure 1.**

**Table III.** Bond Lengths (Å)

| | | | |
|---|---|---|---|
| Ti–O(1) | 1.979 (2) | Ti–O(2) | 1.985 (2) |
| Ti–N(1) | 2.293 (2) | Ti–N(2) | 2.312 (2) |
| Ti–O(3) | 1.926 (2) | Ti–O(4) | 1.922 (2) |
| Ti–O(5) | 2.084 (2) | O(1)–C(1) | 1.309 (3) |
| C(1)–O(6) | 1.211 (3) | C(1)–C(2) | 1.507 (3) |
| C(2)–N(2) | 1.478 (3) | O(2)–C(3) | 1.312 (3) |
| C(3)–O(7) | 1.211 (3) | C(3)–C(4) | 1.508 (3) |
| C(4)–N(1) | 1.483 (3) | N(1)–C(9) | 1.485 (3) |
| N(1)–C(6) | 1.490 (3) | C(9)–C(10) | 1.508 (3) |
| C(10)–N(2) | 1.490 (3) | N(2)–C(8) | 1.489 (3) |
| O(3)–C(5) | 1.318 (3) | C(5)–O(8) | 1.215 (3) |
| C(5)–C(6) | 1.501 (3) | O(4)–C(7) | 1.312 (3) |
| C(7)–O(9) | 1.221 (3) | C(7)–C(8) | 1.504 (3) |

**Table IV.** Bond Angles (deg)

| | | | |
|---|---|---|---|
| O(1)–Ti–O(2) | 142.7 (1) | O(1)–Ti–N(1) | 144.2 (1) |
| O(2)–Ti–N(1) | 73.0 (1) | O(1)–Ti–N(2) | 72.1 (1) |
| O(2)–Ti–N(2) | 143.9 (1) | N(1)–Ti–N(2) | 73.9 (1) |
| O(1)–Ti–O(3) | 88.8 (1) | O(2)–Ti–O(3) | 101.5 (1) |
| N(1)–Ti–O(3) | 77.1 (1) | N(2)–Ti–O(3) | 84.6 (1) |
| O(1)–Ti–O(4) | 98.5 (1) | O(2)–Ti–O(4) | 86.3 (1) |
| N(1)–Ti–O(4) | 84.1 (1) | N(2)–Ti–O(4) | 76.4 (1) |
| O(3)–Ti–O(4) | 156.4 (1) | O(1)–Ti–O(5) | 71.4 (1) |
| O(2)–Ti–O(5) | 71.4 (1) | N(1)–Ti–O(5) | 143.3 (1) |
| N(2)–Ti–O(5) | 142.8 (1) | O(3)–Ti–O(5) | 101.5 (1) |
| O(4)–Ti–O(5) | 102.2 (1) | Ti–O(1)–C(1) | 123.9 (1) |
| O(1)–C(1)–O(6) | 124.2 (2) | O(1)–C(1)–C(2) | 113.9 (2) |
| O(6)–C(1)–C(2) | 121.8 (2) | C(1)–C(2)–N(2) | 108.9 (2) |
| Ti–O(2)–C(3) | 124.4 (1) | O(2)–C(3)–O(7) | 123.9 (2) |
| O(2)–C(3)–C(4) | 114.2 (2) | O(7)–C(3)–C(4) | 121.8 (2) |
| C(3)–C(4)–N(1) | 108.9 (2) | Ti–N(1)–C(4) | 107.8 (1) |
| Ti–N(1)–C(9) | 113.0 (1) | C(4)–N(1)–C(9) | 109.8 (2) |
| Ti–N(1)–C(6) | 105.3 (1) | C(4)–N(1)–C(6) | 109.4 (2) |
| C(9)–N(1)–C(6) | 111.4 (2) | N(1)–C(9)–C(10) | 108.2 (2) |
| C(9)–C(10)–N(2) | 108.3 (2) | Ti–N(2)–C(2) | 107.0 (1) |
| Ti–N(2)–C(10) | 111.9 (1) | C(2)–N(2)–C(10) | 110.3 (2) |
| Ti–N(2)–C(8) | 105.8 (1) | C(2)–N(2)–C(8) | 109.3 (2) |
| C(10)–N(2)–C(8) | 112.3 (2) | Ti–O(3)–C(5) | 125.5 (1) |
| O(3)–C(5)–O(8) | 123.6 (2) | O(3)–C(5)–C(6) | 113.7 (2) |
| O(8)–C(5)–C(6) | 122.6 (2) | N(1)–C(6)–C(5) | 112.3 (2) |
| Ti–O(4)–C(7) | 125.9 (1) | O(4)–C(7)–O(9) | 122.7 (2) |
| O(4)–C(7)–C(8) | 114.6 (2) | O(9)–C(7)–C(8) | 122.7 (2) |
| N(2)–C(8)–C(7) | 111.6 (2) | | |

## Results and Discussion

**Structure of [Ti(edta)($H_2O$)].** From the initial refinement of the crystal structure of the Ti(IV)–edta$^{4-}$ salt, which was isolated as described in the Experimental Section, certain features are clear. The best geometric interpretation is that of a pentagonal-bipyramid complex. Atoms O(1), O(2), N(1), N(2), O(5), and Ti(IV) form a nearly planar pentagon (average rms deviation is 0.15 Å). Atoms O(3) and O(4) contribute the axial donors; the numbering scheme is shown in the ORTEP drawing in Figure 1. Positional parameters are given in Tables IIA,B. Bond lengths are given in Table III, and bond angles appear in Table IV. Anisotropic temperature factors (Table VI) and observed and calculated structure factors (Table VII) are available as supplementary material. There is a slight twist to the pentagonal plane, with lines through N(1) and N(2) and through O(1) and O(2) being skewed. The other option of a monocapped trigonal prism requires a plane of O(1), O(2), O(3), and O(4) with a rms deviation of 0.50 Å, which is less preferable than the pentagonal-bipyramid assignment. Protons appear to have transferred to the titanyl functionality, forming a coordinated $H_2O$. The in-plane oxygen atoms from the carboxylate donors have Ti–O bonds of 1.926 (2) and 1.922 (2) Å. The axial carboxylates are at 1.977 (2) and 1.983 (2) Å. The coordinated water molecule oxygen is much further away at 2.08 Å. The Ti=O unit in (α,δ-dimethyl-α,δ-dihydrooctaethylporphinato)oxotitanium(IV) is 1.619 Å.[16] This is very much shorter than any oxygen in the Ti(IV)–edta$^{4-}$ complex. Thus, the crystal chosen from the salt isolated from solution at $\text{pH} \leq 1$ is protonated at the oxo moiety and not at carboxylate. The proper formulation is then [Ti(edta)($H_2O$)]. The water molecule at 2.082 (2) Å is less ionically coordinated than the remaining O(1), O(2), O(3), and O(4) carboxylate oxygens. Bonds to the neutrally charged ligand donors N(1) and N(2) are also longer [2.292 (2) and 2.311 (2) Å] than the ionic Ti(IV)–O bonds. The axial oxygens O(3) and O(4) make an angle of 156.4° through the central titanium. This compares to 165.6° for the Li[Fe(edta)($H_2O$)]·$2H_2O$ and 162.6° from the $Rb^+$ analogue salt, both of the same structure,[4] vs. 173.8° for the K[Mn(edta)]·$2H_2O$[7] and 172.0° in Cr(hedta)($H_2O$),[9] both six-coordinate structures. The only other Ti(IV) complex exhibiting a coordinated $H_2O$ is found in the organometallic complex [π-$(C_5H_5)_2Ti(H_2O)_2$]·3THF, which may be isolated from solution only below pH 1.[17,18] The mean Ti(IV)–$OH_2$ bond distance is 2.01 Å (2.025 Å, 1.987 Å) similar to the Ti–O(5) distance (2.082 (2) Å) observed with [Ti(edta)($H_2O$)]. This further establishes O(5) as a coordinated $H_2O$ as the distance is far too long to be terminal Ti=O.

**Ring Strain in [Ti(edta)($H_2O$)].** Weakliem and Hoard proposed that the sum of angles of the five-membered chelate rings could be used as a measure of the strain in forming the chelate–metal ion bond.[2] The idealized angle sum for the ethylenediamine backbone (E ring) is 527.9° while glycinate rings with no strain would have an angle sum of 538.9°. On the basis of sexidentate complexes of edta$^{4-}$ as in Co(edta)$^-$ and Mn(edta)$^-$, two sets of carboxylate-containing rings are observed. The axial rings are less strained and have been given the designation R (relaxed) vs. the in-plane rings with greater strain, termed G rings. The angle sums obtained from Table IV in [Ti(edta)($H_2O$)] are as follows: E ring, 515.3°; R ring for O(3), N(1) chelation, 533.9°; R ring for O(4), N(2) chelation, 534.3°; G ring for O(1), N(2), 525.8°; G ring for O(2), N(1), 528.3°. These values may be seen to show strain compared to the idealized E, R, and G values above. However, the results may be compared more usefully to the ($NH_4$)[Co(edta)]·$2H_2O$ salt[1] where values are as follows: E, 520.9°; R, 537.8°; G, 523.5°. In this fashion it is seen that the E ring of [Ti(edta)($H_2O$)]·$H_2O$ is more strained than in other polyamino polycarboxylate salts;[19] the R rings are slightly more strained while the G rings in the title complex are less strained. This is compatible with expanding the in-plane rings slightly to tolerate the seventh additional ligand. The values are similar to those of the Li[Fe(edta)($H_2O$)]·$H_2O$ salt: E, 514.1°; R, 535.1 ± 1.6°; G, 524.8 ± 0.6°.[4]

**Structure and $d^n$ Configuration.** It is curious that both the $d^0$ Ti(IV) and high-spin $d^5$ Fe(III) complexes possess the same geometry. This would suggest that a spherically symmetric charge distribution favors the pentagonal-bipyramid geometry if the ion is of sufficient size to tolerate a higher coordination number or if the ligand field splitting does not greatly favor an octahedral arrangement. The monocapped trigonal prism is the lower energy configuration in the absence of these effects. Table V summarizes some relevant bond distances and observed geometries for a number of first-row transition-metal edta$^{4-}$ complexes.

**Table V.** Comparison Data for 7-Coordinate edta$^{4-}$ Complexes

| metal (M) | $d^n$ | geom[a] | M–O[b] | M–N[b] | ref |
|---|---|---|---|---|---|
| Ti(IV) | 0 | 1 | 1.95 | 2.30 | this work |
| Mg(II) | 0 | 2 | 2.17 | 2.38 | 6 |
| Fe(III) | 5 (hs) | 1 | 2.04 | 2.31 | 4 |
| Mn(II) | 5 (hs) | 2 | 2.24 | 2.37 | 5 |
| Ni(II) | 8 (hs) | 2 | 2.10 | 2.11 | 3 |
| Co(III) | 6 (ls) | 2 | 1.90 | 1.93 | 2 |

[a] Key: 1, pentagonal bipyramid; 2, monocapped trigonal prism. [b] Average bond distance (Å).

Obviously, the situation is more complex than indicated above. Ti(IV) and Mg(II) are both $d^0$, yet Mg(II) is best described as a distorted monocapped prism. If one takes into account the difference in the central charge that increases the ligand field strength, it is clear that the Ti ion holds the ligand much more strongly and consequently is able to force the edta$^{4-}$ ligand into the pentagonal bipyramid to bring the ligating atoms closer, ca. 0.22 Å for O donors and 0.08 Å for N donors. The same argument can be used to explain the differences in Fe(III) ($d^5$) and Mn(II) (also $d^5$). Although the difference in charge is only 1, the Fe(III) atom is much smaller (Pauling crystal radii of 0.64 Å vs. 0.80 Å for Mn(II)), thus generating a stronger ligand field and again forcing the ligand into the pentagonal bipyramid to bring them closer. Note also that the differences in the M–O and the M–N distances for geometry 1 vs. geometry 2 for both $d^0$ and $d^5$ configurations are identical (ca. 0.20 Å for M–O and 0.07 Å for M–N). Therefore, the ligand field strength is the overriding factor.

Hoard et al. have pointed out that as the size of the central ion increases or as the difference between the M–N and M–O bond lengths for a complex increase, the favorability of a seven-coordinate structure is greatly increased to fill the "hole" created by expansion of O–M–O bond angles trans to M–N.[6] It may be seen from Table V that the Ti(IV) complex has the greatest difference in the average M–O and M–N bond lengths for any of the 7-coordinate edta$^{4-}$ complexes. Therefore, it is logical that Ti(IV) would become 7-coordinate. The choice of the pentagonal bipyramid is forced on Ti(IV) by means of the highly ionic nature of the Ti(IV)–oxygen bonds.

Hydrogen atom positions were located as described in the Experimental Section (Table IIB). Hydrogen bonds are established between the coordinated $H_2O$ molecule with atoms O(8′) and O(9′) of the repeat structure. The O(8′)–O(5)–O(9′) angle is found to be 115° with an O(5)–O(8′) distance of 3.08 Å. Assuming the normal O(5)–H distance of 1.0 Å, the 2.08 Å for the hydrogen-bonded distance is somewhat longer than free water to carboxylate H-bonded distances, but still within a reasonable range for interaction. The infrared spectrum taken in KBr exhibits a stretch at 940 $cm^{-1}$. Therefore, the H-bonding between the coordinated $H_2O$ and the repeat units is sufficiently strong to impart significant $O^{2-}$ character to the coordinated $H_2O$. Many oxo-bridged complexes exhibit an intense absorption in the 700–950-$cm^{-1}$ region attributable to the asymmetric MOM′ stretching vibration.[22] In the case of the title complex, strong H-bonding of the hydrogens of $H_2O$ to O(8′) and O(9′) supplies the anchor equivalent to an M′ fragment of an "oxo-bridged" complex. Therefore, the presence of an intense stretch at 940 $cm^{-1}$ is added evidence for strong H-bonding to a coordinated water having rather ionic character in its O–H bonds. The increased oxo character of the coordinated $H_2O$ is also consistent with the H–O–H angle. H-bonds are known to deviate from 180° linearity by as much as 5°. With this uncertainty, the $H_2O$ molecule at

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O(5) has an angle of 115 ± 10°. The lower limit of 105° is that of normal $sp^3$-hybridized oxygen of $H_2O$. Any value higher than 105° suggests increased character toward $sp^2$. The acidity of hydrogens on O(5) will be increased with the s character of the hybrid, and the central oxygen will be available to participate in $\pi$ bonding to the central metal. Thus, the $Ti^{IV}$–$OH_2$ bond appears to be predisposed toward formation of Ti=O as the pH of the solution is raised. This is in concert with the substitution chemistry of $[Ti(edta)(H_2O)]$, which as a species behaves as $TiO(edta)^{2-}$ above pH 2.[13]

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**Supplementary Material Available:** Listings of anisotropic temperature factors (Table VI) and observed and calculated *F* values (Table VII) (20 pages). Ordering information is given on any current masthead page.

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# Preparation and Crystal Structure of the Seven-Coordinate Compound Bis(trifluoroacetato)dicarbonyltris(trimethylphosphine)molybdenum(II)

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The $Mo(CO)_2(PMe_3)_3(CF_3COO)_2$ complex, obtained by stirring $[HMo(CO)_3(PMe_3)_3]^+CF_3COO^-$ in dichloromethane, was characterized by X-ray diffraction and by NMR and IR spectroscopy. The crystals belong to the monoclinic space group $P2_1/c$ with $a = 11.835$ (5) Å, $b = 14.542$ (4) Å, $c = 14.893$ (6) Å, $\beta = 90.29$ (3)°, and $Z = 4$. The structure was solved by the heavy-atom method, and anisotropic refinement of all non-hydrogen atoms on 2067 nonzero Mo K$\alpha$ reflections converged to $R = 0.054$. The Mo(II) atom is seven-coordinated, and its environment is best described in terms of a capped trigonal prism. The capping position is occupied by a monodentate $CF_3CO_2^-$ ion. The quadrangular plane contains two cis $PMe_3$ molecules and one CO ligand, with the remaining $CF_3CO_2^-$ ion also acting as a monodentate group. The remaining edge contains one CO and one $PMe_3$ molecule. In spite of the fact that the present $CF_3CO_2$ complex has a capped-trigonal-prism geometry whereas $MoBr_2(CO)_2(PMe_2Ph)_3$ is a capped octahedron, the structures of these molecules are actually very similar.

## Introduction

The carboxylate ions are known to be highly versatile in binding to metal ions. They can behave as mono- or bidentate donors to a single metal ion or give rise to a variety of more complicated patterns by acting as bridging groups.[2] The specific case of the $CF_3COO^-$ ion has been reviewed by Garner and Hughes.[3]

We have recently undertaken a series of studies on $M(CO)_kL_l(CF_3CO_2)_m$ systems ($M$ = Mo, W; $L$ = $PMe_3$, $PEt_3$, $P(OMe)_3$), in order to assess the influence of the two parameters M and L on the trifluoroacetate binding mode. We present in this report the preparation and X-ray structure determination of $Mo(CO)_2(PMe_3)_3(CF_3CO_2)_2$.

## Experimental Section

**Preparation of $Mo(CO)_2(PMe_3)_3(CF_3COO)_2$.** $Mo(CO)_3(PMe_3)_3$ was protonated by a method described previously.[4] A 1-g (2.45 mmol) portion of $Mo(CO)_3(PMe_3)_3$ was stirred in 20 mL of $CH_2Cl_2$. To the clear colorless solution was added an excess (0.5 mL, 5.7 mmol) of $CF_3COOH$, whereupon the reaction solution immediately turned blue-green. The solvent was removed under vacuum, and the residue was dissolved in $CH_2Cl_2$ and stirred for 24 h under nitrogen. Filtration gave a yellow solution from which the solvent was removed under vacuum. The residue was dissolved in methanol, and cooling to −20 °C yielded yellow crystals of the title compound (30% yield based on the $Mo(CO)_3(PMe_3)_3$ starting material). Anal. Calcd for $C_{15}H_{27}F_6MoO_6P_3$: H, 4.49; C, 29.72. Found: H, 4.29; C, 30.41.

$^1H$ NMR ($CD_2Cl_2$, 300 K, vs. $Me_4Si$ ($\delta$ 0)): $\delta$ 1.57 (d, $J_{PH}$ = 11 Hz), 1.26 (d, $J_{PH}$ = 8 Hz). $^{31}P\{^1H\}$ NMR ($CD_2Cl_2$, 300 K, vs. 85% $H_3PO_4$ ($\delta$ 0)): $\delta$ 27.60, −8.97. IR wavenumbers ($cm^{-1}$, KBr): 1930 m, 1845 vs, 1720 m, 1660 s.

**Crystal Data:** $C_{15}H_{27}F_6MoO_6P_3$, fw = 606.23, monoclinic, $P2_1/c$, $a = 11.835$ (5) Å, $b = 14.542$ (4) Å, $c = 14.893$ (6) Å, $\beta = 90.29$ (3)°, $V = 2563.1$ Å$^3$, $D_{calcd} = 1.570$ g cm$^{-3}$, $Z = 4$, $\lambda$(Mo K$\bar{\alpha}$) = 0.71069 Å (graphite monochromator), $\mu$(Mo K$\alpha$) = 7.5 cm$^{-1}$, $T = 293$ K, crystal dimensions 0.10 mm (001–00$\bar{1}$) × 0.13 mm (1$\bar{1}$0–$\bar{1}$10) × 0.30 mm (20$\bar{1}$–$\bar{2}$01).

**Crystallographic Measurements and Structure Resolution.** The yellow crystals isolated as described above were suitable for X-ray work. The specimen was mounted in a Lindemann capillary filled with nitrogen. Cell dimensions, space group, and intensity data were determined with an Enraf-Nonius CAD4 diffractometer. A list of 25 reflections was generated by using the automatic search procedure of the CAD4 software. These reflections were centered, and the reduced triclinic cell was calculated. This cell was checked by recording a long-exposure oscillation photograph about each of the axes. They showed the correct layer line spacing and the expected symmetry (mirror for oscillation about *b* only). The Niggli parameters[5] clearly showed that the crystal cannot be described with a lattice of higher symmetry. Space group $P2_1/c$ was uniquely determined by inspection of the full data set ($h0l$, $l \neq 2n$; $0k0$, $k \neq 2n$).

A set of 4516 unique $\bar{h}kl$ and $\bar{h}k\bar{l}$ reflections ($2\theta \leq 50°$, Mo K$\bar{\alpha}$) was collected as described elsewhere.[6] A total of 2067 reflections significantly above background ($I \geq 3\sigma(I)$) was retained for structure resolution. These data were corrected for the effect of Lorentz, polarization, and absorption effects (Gaussian integration, grid 8 × 8 × 8, transmission range 0.82–0.86).

The structure was solved by the heavy-atom method and refined on $|F_o|$ by full-matrix least squares in the early stages. Isotropic refinement

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