

Utilization of a Cobalt Carbonyl Cluster Carboxylic Acid in the Isolation of Novel Titanium(IV) Oxo Alkoxy Carboxylates

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Summary: The reaction of $(\text{CO})_9\text{Co}_3(\mu_3\text{-CCOOH})$ with $\text{Ti}(\text{OR})_4$ results in the formation of $\text{Ti}(\text{IV})$ oxo alkoxy carboxylates exhibiting new structural forms: $R = \text{Et}$, $\text{Ti}_6(\mu_3\text{-O})_4(\mu\text{-OEt})_4(\text{OEt})_8\{\mu\text{-}(\text{CO})_9\text{Co}_3(\mu_3\text{-CCO}_2)\}_4$ (**1**); $R = \text{Pr}^i$, $\text{Ti}_4(\mu_3\text{-O})_4(\text{OPr}^i)_4\{\mu\text{-}(\text{CO})_9\text{Co}_3(\mu_3\text{-CCO}_2)\}_4$ (**3**); $R = \text{Ph}$, $\text{Ti}_4(\mu_3\text{-O})_4(\text{OPh})_4\{\mu\text{-}(\text{CO})_9\text{Co}_3(\mu_3\text{-CCO}_2)\}_4$ (**5**); reaction with $\text{Ti}(\text{OPr}^i)_2(1,2\text{-O}_2\text{C}_6\text{H}_4)$ yields $\text{Ti}_6(\mu_3\text{-O})_2(\mu\text{-O})_2(\mu\text{-OPr}^i)_2(\text{OPr}^i)_2(\text{O}_2\text{C}_6\text{H}_4)_4\{\mu\text{-}(\text{CO})_9\text{Co}_3(\mu_3\text{-CCO}_2)\}_4$ (**4**). Observed stoichiometries and structures reflect the effects of a metal cluster relative to organic substituents.

Metal alkoxides serve as precursors for the formation of oxide networks via inorganic polymerization reactions.^{1,2} Ongoing efforts to elucidate the fundamental chemistry taking place have resulted in the isolation of compounds that define possible molecular models for the sol–gel process, e.g., the structural characterization of $\text{Ti}_{16}\text{O}_{16}(\text{OEt})_{32}$.³ Solution spectroscopic studies, particularly ¹⁷O NMR, in combination with structural studies have permitted the direct investigation of this polymerization process relative to the role of discrete oxo alkoxides in the growth pathways.^{4–9} This network formation, which lies at the heart of the sol–gel process, can be modified by the addition of compounds such as acetic acid or acetylacetone. The additives perturb network formation and permit the isolation of new species such as $\text{Ti}_6\text{O}_4(\text{OR})_8(\text{O}_2\text{CMe})_8$ ^{10–14} and related compounds.

As the equilibria leading to these species should be sensitive to the properties of the acid, we have now

explored the effects of a cluster-substituted^{15,16} acid, $(\text{CO})_9\text{Co}_3(\mu_3\text{-CCOOH})$, on the stoichiometry and structure of $\text{Ti}(\text{IV})$ oxo alkoxy carboxylates that can be isolated from the reaction of the cluster acid with $\text{Ti}(\text{OR})_4$. Previous work with this cluster ligand has provided cluster metal carboxylate coordination compounds with new properties^{17,18} and new structures^{19,20} that serve as precursors for new heterogeneous catalysts^{21,22} with unusual activities and selectivities for demanding hydrogenations.²³

The reaction of $(\text{CO})_9\text{Co}_3(\mu_3\text{-CCOOH})$ with $\text{Ti}(\text{OEt})_4$ proceeds smoothly, and a single product, **1**, is isolated by crystallization from $\text{CH}_2\text{Cl}_2/\text{EtOH}$ in good yield.²⁴ The compound is soluble in THF, toluene, and CH_2Cl_2 , and the infrared spectrum exhibits bands characteristic of the CO ligands of the cluster substituent, bridging carboxylates,²⁵ and alkoxide groups.²⁶ The ¹H and ¹³C solution NMR spectra show only a single type of ethyl group.

In the solid state **1** is a hexanuclear titanium species, i.e., a dimer of Ti_3 fragments (Figure 1, Chart 1a)²⁷ with a molecular formula $\text{Ti}_6(\mu_3\text{-O})_4(\mu\text{-OEt})_4(\text{OEt})_8\{\mu\text{-}(\text{CO})_9\text{Co}_3(\mu_3\text{-CCO}_2)\}_4$.²⁸ Two Ti_3O_4 units, each of which can

(15) Penfold, B. R.; Robinson, B. H. *Acc. Chem. Res.* **1973**, *6*, 73.

(16) Seyferth, D. *Adv. Organomet. Chem.* **1976**, *14*, 97.

(17) Cen, W.; Lindenfeld, P.; Fehlner, T. P. *J. Am. Chem. Soc.* **1992**, *114*, 5451.

(18) Cen, W.; Haller, K. J.; Fehlner, T. P. *Inorg. Chem.* **1993**, *32*, 995.

(19) Cen, W.; Haller, K. J.; Fehlner, T. P. *Organometallics* **1992**, *11*, 3499.

(20) Lei, X.; Shang, M.; Patil, A.; Wolf, E. E.; Fehlner, T. P. *Inorg. Chem.* **1996**, *35*, 3217.

(21) Bañares, M. A.; Dauphin, L.; Calvo-Perez, V.; Fehlner, T. P.; Wolf, E. E. *J. Catal.* **1995**, *152*, 396.

(22) Bañares, M. A.; Dauphin, L.; Lei, X.; Cen, W.; Shang, M.; Wolf, E. E.; Fehlner, T. P. *Chem. Mater.* **1995**, *7*, 553.

(23) Bañares, M.; Patil, A. N.; Fehlner, T. P.; Wolf, E. E. *Catal. Lett.* **1995**, *34*, 251.

(24) A 0.22 mL amount of $\text{Ti}(\text{OEt})_4$ (1 mmol) was added to a solution of $(\text{CO})_9\text{Co}_3(\mu_3\text{-CCOOH})$ (2 mmol; 0.97 g) in 30 mL of THF via syringe with rapid stirring. The solution was stirred for 12 h at room temperature to give a purple solution. THF was removed under vacuum. The solid obtained was dissolved in 20 mL of CH_2Cl_2 to yield a purple solution. To the solution was added 10 mL of EtOH. The flask was kept at 4 °C for 1 week. Black columnlike crystals were obtained. The crystals collected and washed with ethanol to afford 180 mg of the product. The mother solution was kept at –20 °C. The second crop gives 150 mg of product. The crystals are soluble in THF, toluene, and CH_2Cl_2 but insoluble in hexane. The yield is around 70% based on total Ti. Spectroscopic and elemental analytical data of **1**: Anal. Calcd for $\text{Ti}_6\text{Co}_{12}\text{O}_{60}\text{C}_{68}\text{H}_{60}$: C, 28.84; H, 2.14. Found: C, 29.00; H, 1.98. ¹H NMR (C_6D_6 , 20 °C, δ): 4.493 (quartet, 2H, CH_2CH_3); 1.374 (triplet, 3H, CH_2CH_3). ¹³C{¹H} NMR (C_6D_6 , 20 °C, δ): 199.0 (CO), 188.6 (COO), 73.9 (CH_2CH_3), 18.1 (CH_2CH_3). IR (KBr, cm^{-1}): 2110 m, 2054 vs, 2045 vs, sh, 1513 w, 1490 w, 1378 m, 1340 w, sh, 1123 m, 1101 w, sh, 1073 w, 723 m, 620 m, 612 m, sh, 553 w, 530 m, 499 m. Solution IR (CH_2Cl_2 , 20 °C, cm^{-1}): 2110 s, 2069 vs, 2044 vs, 1510 w, 1505 w, 1485 w, 1379 s, 1338 w.

(25) Mehrotra, R. C.; Bohra, R. *Metal Carboxylates*; Academic Press: New York, 1983; pp 396.

(26) Bradley, D. C.; Mehrotra, R. C.; Gaur, D. P. *Metal Alkoxides*; Academic Press: London, 1978.

* Abstract published in *Advance ACS Abstracts*, August 15, 1996.

(1) Chandler, C. D.; Roger, C.; Hampden-Smith, M. J. *Chem. Rev.* **1993**, *93*, 1205.

(2) Hench, L. L.; Ulrich, D. R., Eds. *Ultrastructure Processing of Ceramic, Glasses and Composites*; Wiley: New York, 1984.

(3) Schmid, R.; Mosset, A.; Galy, J. *J. Chem. Soc., Dalton Trans* **1991**, 1999.

(4) Day, V. W.; Eberspacher, T. A.; Klemperer, W. G.; Park, C. W. *J. Am. Chem. Soc.* **1993**, *115*, 8469.

(5) Day, V. W.; Eberspacher, T. A.; Chen, Y.; Hao, J.; Klemperer, W. G. *Inorg. Chim. Acta* **1995**, *229*, 391.

(6) Chen, Y. W.; Klemperer, W. G.; Park, C. W. *Mater. Res. Symp. Proc.* **1992**, *271*, 57.

(7) Day, V. W.; Eberspacher, T. A.; Klemperer, W. G.; Park, C. W.; Rosenberg, F. S. *J. Am. Chem. Soc.* **1991**, *113*, 8190.

(8) Charnick, S. G.; Klemperer, W. *Abstracts of Papers*, 208th National Meeting of the American Chemical Society, Washington, DC; American Chemical Society: Washington, DC, 1994; I 393.

(9) Chen, Y. W.; Klemperer, W. G. *Abstracts of Papers*, 210th National Meeting of the American Chemical Society, Anaheim, CA; American Chemical Society: Washington, DC, 1995; I 169.

(10) Doeuff, S.; Dromzee, Y.; Taulelle, F.; Sanchez, C. *Inorg. Chem.* **1989**, *28*, 4439.

(11) Doeuff, S.; Dromzee, Y.; Sanchez, C. *C. R. Acad. Sci. Paris, Ser. II* **1989**, *308*, 1409.

(12) Boyle, T. J.; Schwartz, R. W. *Comments Inorg. Chem.* **1994**, *16*, 243.

(13) Gautier-Luneau, I.; Mosset, A.; Galy, J. *Z. Kristallogr.* **1987**, *180*, 83.

(14) Toledano, P.; In, M.; Sanchez, C. *C. R. Acad. Sci. Paris, Ser. II* **1991**, *313*, 1247.

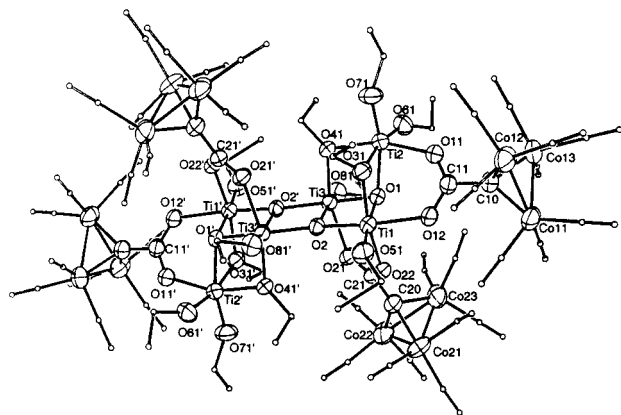
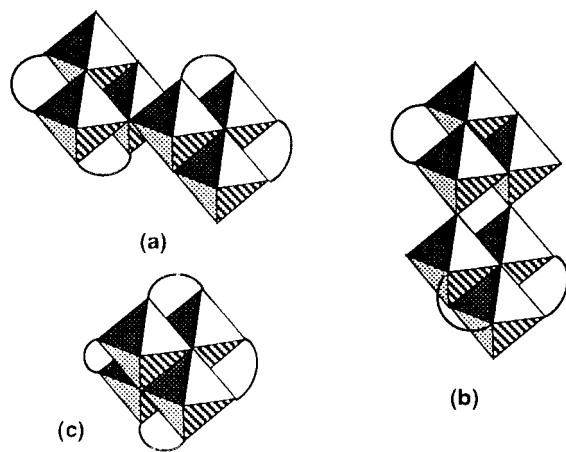


Figure 1. Molecular structure of $\text{Ti}_6(\mu_3\text{-O})_4(\mu\text{-OEt})_4(\text{OEt})_8\{\mu\text{-(CO)}_9\text{Co}_3(\mu_3\text{-CCO}_2)\}_4$ (**1**).

Chart 1



be derived from a Ti_4O_4 cubane by removing one Ti atom, are linked by TiO edges oriented head-to-tail such that the Ti_3O_4 units are related to each other by a center of symmetry. There are two types of $\mu_3\text{-O}$ ligands, planar and pyramidal, with the former constituting the interfragment connections. Each Ti_3O_4 unit is bridged by two cluster ligands and the remaining ligand sites of the approximately octahedral Ti(IV) centers are occupied by 6 ethoxide ligands, two of which are bridging. Comparison of the solid-state and solution infrared spectra provides no evidence of dissociation in the solvents examined, but the ^1H NMR spectrum shows the EtO ligands to be fluxional in solution.

Although the molecular formulas are analogous, the structure of **1** is distinctly different from that of $\text{Ti}_6(\mu_3\text{-O})_2(\mu\text{-O})_2(\mu\text{-OPr}^i)_6(\text{OPr}^i)_6\{\mu\text{-CH}_3\text{CO}_2\}_4$ (**2**).^{11,12} The known compound contains two additional bridging in place of terminal OEt ligands and two μ_2 -bridging in place of μ_3 -bridging oxo ligands. In terms of geometric structure, the difference can be appreciated by comparison of structural representations consisting of linked octahedra, each of which represents the oxygen coordination sphere of a six-coordinate Ti atom (Chart 1a,b). Both

(27) Crystal data for **1**: MW = 2831.72, $\text{C}_{68}\text{H}_{60}\text{Ti}_6\text{O}_{60}\text{Co}_{12}$, monoclinic $P2_1/n$, $a = 15.814(2)$ Å, $b = 16.215(2)$ Å, $c = 21.149(3)$ Å, $\beta = 92.718(12)^\circ$, $V = 5417.0(2)$ Å³, $Z = 2$, $D_c = 1.736$ g/cm³, $T = 293$ K. Full-matrix refinement (based on F_o^2 , SHELXL-93) converged to $R_1 = 0.0527$ for 5286 unique reflections with $I > 2\sigma(I)$.

(28) A hexanuclear titanium oxo alkoxy carboxylate with the same core structure as **1**, $[\text{Ti}_6\text{O}_4](\text{O}_2\text{CCH}_2\text{CMe}_3)_4(\text{OPr}^i)_{12}$, has been recently reported: Boyle, T. J.; Tafaya, C. J.; Scott, B. Presented at the 211th National Meeting of the American Chemical Society, New Orleans, LA, 1996; 062. Boyle, T. J. Private communication.

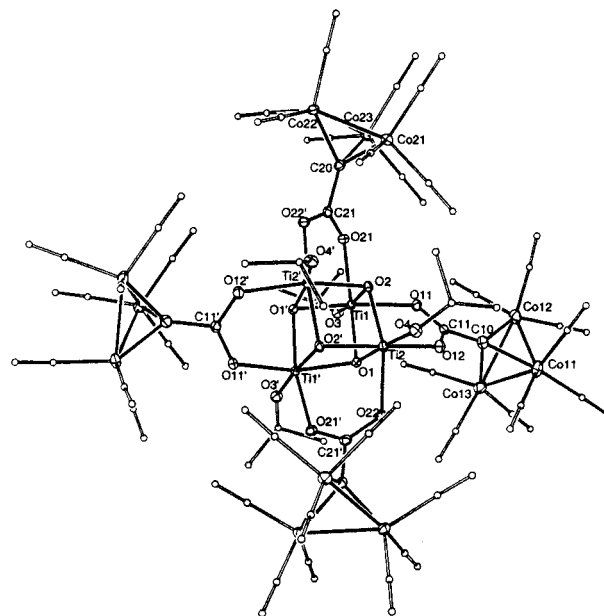


Figure 2. Molecular structure of $\text{Ti}_4(\mu_3\text{-O})_4(\text{OPr}^i)_4\{\mu\text{-(CO)}_9\text{Co}_3(\mu_3\text{-CCO}_2)\}_4$ (**3**).

compounds contain Ti_3O_4 units related by an inversion center of symmetry, but the dimer in the new compound is formed by edge-sharing octahedra whereas in the known compound it is by vertex-sharing octahedra.

The origin of the differences in the two structures must be related to the differences between the cluster vs a methyl group and an ethyl vs an isopropyl group, i.e., a metal cluster substituent effect. To reduce the number of additional variables in the comparison, we have explored additional reactions. First, the reaction of the cluster acid with $\text{Ti}(\text{OPr}^i)_4$ yields $\text{Ti}_4(\mu_3\text{-O})_4(\text{OPr}^i)_4\{\mu\text{-(CO)}_9\text{Co}_3(\mu_3\text{-CCO}_2)\}_4$ (**3**),²⁹ which exhibits a single, complete Ti_4O_4 cubane core (Figure 2, Chart 1c).³⁰ Second, the reaction of the cluster acid with $\text{Ti}(\text{OPr}^i)_2(1,2\text{-O}_2\text{C}_6\text{H}_4)$, prepared *in situ*, yields $\text{Ti}_6(\mu_3\text{-O})_2(\mu\text{-O})_2(\mu\text{-OPr}^i)_2(\text{OPr}^i)_2(\text{O}_2\text{C}_6\text{H}_4)_4\{\mu\text{-(CO)}_9\text{Co}_3(\mu_3\text{-CCO}_2)\}_4$ (**4**) (Figure 3) with a structure similar to that of **2** including the positions of the bridging carboxylates.³¹ The catechol ligand has one oxygen bridging and the other terminal. Finally, $\text{Ti}_4(\mu_3\text{-O})_4(\text{OC}_6\text{H}_5)_4\{\mu\text{-(CO)}_9\text{Co}_3(\mu_3\text{-CCO}_2)\}_4$ (**5**) was prepared and shown to have the cubane structure of **3**.³²

A comparison of the syntheses and structures of the cluster derivative with those of related compounds reveals aspects of the cluster substituent effect. All of

(29) **3** was prepared with a similar procedure as for **1**; the yield is 74% based on total Ti. Crystal data for **3**: MW = 2431.54, $\text{C}_{56}\text{H}_{28}\text{Ti}_4\text{O}_{52}\text{Co}_{12}$, monoclinic $C2/c$, $a = 15.197(1)$ Å, $b = 19.139(1)$ Å, $c = 29.006(2)$ Å, $\beta = 92.073(4)^\circ$, $V = 8300(2)$ Å³, $Z = 4$, $D_c = 1.736$ g/cm³, $T = 130$ K. Full-matrix refinement (based on F_o^2 , SHELXL-93) converged to $R_1 = 0.0413$ for 7108 reflections with $I > 2\sigma(I)$.

(30) A tetranuclear titanium oxo alkoxy carboxylate with the same core structure as **3**, $[\text{Ti}_4\text{O}_4](\text{O}_2\text{CPr}^i)_4(\text{O}^i\text{Bu})_4$, has been structurally characterized: Charnick, S. G.; Day, V. W.; Klemperer, W. J. Private communication.

(31) The yield is 45% based on Ti. Crystal data for **4**: MW = 2959.71, $\text{C}_{80}\text{H}_{44}\text{Ti}_6\text{O}_{60}\text{Co}_{12}$, triclinic, $a = 11.6126(9)$ Å, $b = 14.482(2)$ Å, $c = 17.865(3)$ Å, $\alpha = 109.39(1)^\circ$, $\beta = 94.873(6)^\circ$, $\gamma = 106.59(1)^\circ$, $V = 2661.7(6)$ Å³, $Z = 1$, $D_c = 1.846$ g/cm³, $T = 130$ K. Full-matrix refinement (based on F_o^2 , SHELXL-93) converged to $R_1 = 0.0489$ for 10 160 reflections with $I > 2\sigma(I)$.

(32) The yield is 60% based on Ti. Crystal data for **5**: MW = 2656.76, $\text{C}_{74}\text{H}_{26}\text{Ti}_4\text{O}_{53}\text{Co}_{12}$, monoclinic $P2_1/c$, $a = 13.560(3)$ Å, $b = 48.679(4)$ Å, $c = 16.031(3)$ Å, $\beta = 111.28(2)^\circ$, $V = 9860(6)$ Å³, $Z = 4$, $D_c = 1.793$ g/cm³, $T = 293$ K. Full-matrix refinement (based on F_o^2 , SHELXL-93) converged to $R_1 = 0.0596$ for 7753 reflections with $I > 2\sigma(I)$.

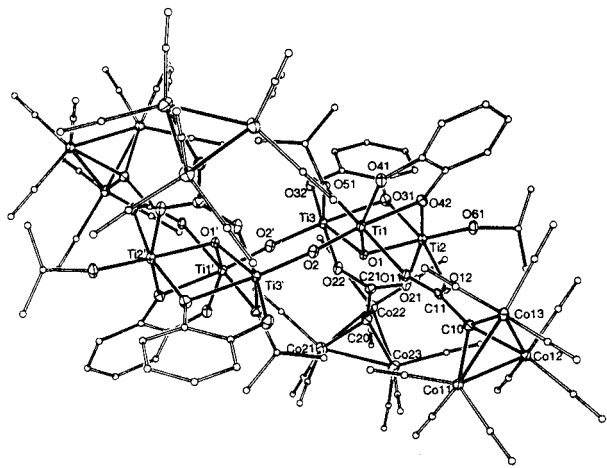


Figure 3. Molecular structure of $\text{Ti}_6(\mu_3\text{-O})_2(\mu\text{-O})_2(\mu\text{-OPr}^i)_2(\text{OPr}^i)_2(\text{O}_2\text{C}_6\text{H}_4)_4\{\mu\text{-(CO)}_9\text{Co}_3(\mu_3\text{-CCO}_2)\}_4$ (**4**).

the cluster-substituted compounds are quite soluble, and **3** and **5** even dissolve in hexane. Unlike derivatives of organic acids,¹² the number of cluster ligands found in a product is independent of whether the Ti/cluster acid reaction stoichiometry is 1:1 or 1:2. The solution- and solid-state IR spectra suggest the cluster-substituted compounds are largely intact in solution.

These phenomenological differences undoubtedly lie in the electronic and/or steric properties of the cluster substituent relative to those of an organic moiety. We have already pointed out the greater ligating ability of the cluster acid vs an organic acid,¹⁸ but these results suggest an important role of steric effects as well. Perhaps this is not surprising as, in the case of oxo alkoxides, Klemperer et al.^{5,33} have suggested the possibility that a decrease of steric repulsion between organic substituents as the degree of condensation

increases might in general lead to a significant increase in stability (degree of condensation is y/x for $[\text{Ti}_x\text{O}_y]\text{-(OR)}_{4x-2y}$).

There is considerable free space in the cubanelike structures **3** and **5**, but in the hexameric structures less room is available. Comparison of **2** vs **3** or **5** suggests that the larger steric demands of the cluster substituent relative to CH_3 fosters the cubane structure. However, if the size of the substituent on the alkoxide is changed from isopropyl to ethyl, then the hexamer is again favored. Alternatively, the same result is achieved if 8 isopropyl groups are replaced with 4 catechol groups. The different connectivity of the Ti_3O_4 units in **1** and **4** is most likely caused by the restricted coordination possibilities of the bidentate catechol ligand forcing an alternate placement of the cluster ligands. As shown in Figure 2, the relative disposition of the bridging cluster ligands in **4** is the same as that of the acetate ligands in **2**, and coupling the two Ti_3O_4 units as in **1** is not possible.

The magnitude of the energy differences between structure types is unknown, and these steric factors, as well as other factors, can only be more quantitatively assessed as more examples of cluster-substituted compounds are examined. Nonetheless, the set of compounds isolated illustrates the unique way a metal cluster can perturb these coordination equilibria.

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Supporting Information Available: Text giving details of the preparations and tables of crystal data, positional and equivalent isotropic thermal parameters, bond distances and angles, and general displacement parameter expressions for **1** and **3–5** (51 pages). Ordering information is given on any current masthead page.

(33) Campana, C. F.; Chen, Y.; Day, V. W.; Klemperer, W. G.; Sparks, R. A. *J. Chem. Soc., Dalton Trans.* **1996**, 691.

OM960326+