entation of the CD receptor have been observed. These findings are of special relevance to the general area of cyclodextrin complexation because they suggest that threaded CD inclusion complexes, such as those formed by α-CD with alkyl tails, might actually be a mixture of two isomers having different CD orientations. Finally, it is also noteworthy that the presence of the ferrocene subunit affords electroactivity to these rotaxanes.[8]

This work demonstrates a simple, step-by-step, synthetic approach to complicated CD-based rotaxanes which is essentially based on the limited size selectivity provided by CD receptors. Yields are higher than expected for rotaxane synthesis owing to the use of aqueous reaction mixtures to maximize CD–substrate interactions. This method is rather general and is likely to produce a diversity of rotaxane structures having threaded CDs.

Acknowledgment. R.I. gratefully acknowledges the Malaysian Petroleum Company (PETRONAS) for a graduate fellowship. Support of this research by the National Science Foundation (CHE-9000531) is gratefully acknowledged. The purchase of the NMR and MS spectrometers was made possible by grants from the NIH (RR-03351 and RR-04680, respectively).

Supplementary Material Available: Experimental details for the synthesis of **2**–**6** and ^1H NMR spectra of **4** and **6** (5 pages). Ordering information is given on any current masthead page.

---

[8] For other recent examples of electroactive rotaxanes, see: Anelli, P. L.; Ashton, P. R.; Ballardini, R.; Balzani, V.; Delgado, M.; Gandolfi, M. T.; Goodnow, T. T.; Kaifer, A. E.; Philip, D.; Pietraszkiewicz, M.; Prodi, L.; Reddington, M. V.; Slawin, A. M. Z.; Spencer, N.; Stoddart, J. F.; Vicent, C.; Williams, D. J. *J. Am. Chem. Soc.*, in press. Stoddart, and co-workers have also recently synthesized a fascinating rotaxane in which a tetracationic "bead" moves back and forth between two identical "stations", thus behaving as a molecular shuttle: Anelli, P. L.; Spencer, N.; Stoddart, J. F. *J. Am. Chem. Soc.* **1991**, *113*, 5131.

Solution Structure Elucidation of Early-Transition-Metal Polyoxoalkoxides Using ^{17}O Nuclear Magnetic Resonance Spectroscopy

V. W. Day,*[,1a] T. A. Eberspacher,[1a] W. G. Klemperer,*[,1b] C. W. Park,[1b] and F. S. Rosenberg[1b]

Department of Chemistry, University of Nebraska
Lincoln, Nebraska 68588
Beckman Institute of Science and Technology and
Department of Chemistry
University of Illinois, Urbana, Illinois 61801

Received June 17, 1991

Early-transition-metal d^0 alkoxides have been known for over a century, but the formulas and structures of polyoxoalkoxides formed in solution upon hydrolysis are unknown despite extensive investigation.[2] All investigations have been frustrated by the absence of a technique capable of characterizing complex mixtures of polynuclear metal oxoalkoxides in solution. As a result, little is known about the principles governing hydrolysis/condensation pathways, an issue of both scientific and technological interest.[3] We have developed a simple technique for characterizing early-transition-metal polyoxoalkoxides in solution that involves ^{17}O NMR spectroscopy[4] of these species selectively enriched in ^{17}O at their oxide (as opposed to alkoxide) oxygen sites. Here, we describe the application of this technique to Ti(IV) polyoxoalkoxides.

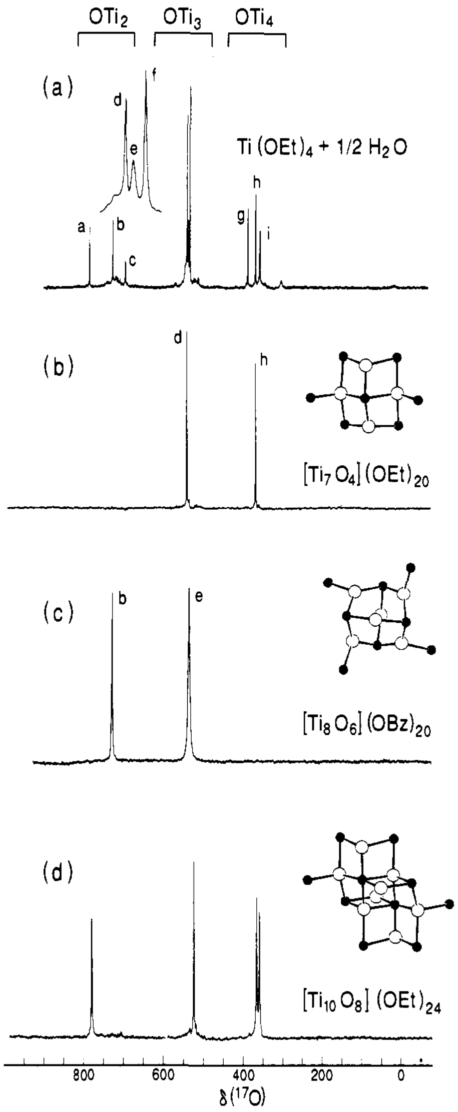

Figure 1. ^{17}O FTNMR (40.7 MHz) spectra of (a) 0.5 M $Ti(OEt)_4$ in $^1/_3$ v/v $CH_3C_6H_5/EtOH$ after addition of $^1/_2$ equiv of 40 atom % ^{17}O-enriched water, (b) selectively enriched $[Ti_7O_4](OEt)_{20}$ in toluene, (c) selectively enriched $[Ti_{10}O_8](OEt)_{24}$ in toluene. The spectral inset in part a is a horizontal expansion of the δ 525–545 region. The structural insets in parts b–d show the metal oxide core structures of the oxoalkoxides under examination, where small filled circles represent titanium centers and large open circles represent oxygen centers. Chemical shifts of principal resonances relative to fresh tap water are as follows: (a) δ 783 (a), 725 (b), 693 (c), 537 (d), 534 (e), 529 (f), 384 (g), 364 (h), 353 (i); (b) δ 537 (d) and 365 (h); (c) δ 726 (b) and 533 (e); and (d) δ 782, 525, 367, and 360.

Hydrolysis of 0.5 M $Ti(OEt)_4$ in $^1/_3$ v/v $CH_3C_6H_5/EtOH$, Et = CH_2CH_3, with $^1/_2$ equiv of 40 atom % ^{17}O-enriched H_2O yielded a clear solution, whose ^{17}O NMR spectrum is shown in Figure 1a. The nine principal resonances labeled a–i in Figure 1a have chemical shifts that are grouped together in three distinct regions, δ 250–450, 450–650, and 650–850. When similar solutions were prepared using slightly different amounts of water, the intensities of certain ^{17}O resonances were observed to vary in a correlated fashion, strongly suggesting their assignment to a single species. Specifically, resonances d (δ 537) and h (δ 364) as well as resonances b (δ 725) and e (δ 534) appeared to arise from distinct complexes that have been identified as $[Ti_7O_4](OEt)_{20}$ and $[Ti_8O_6](OEt)_{20}$, respectively, as outlined below.

Hydrolysis of $Ti(OEt)_4$ in ethanol with $^2/_3$ equiv of H_2O and

---

[1] (a) University of Nebraska. (b) University of Illinois.

[2] Bradley, D. C.; Mehrotra, R. C.; Gaur, D. P. *Metal Alkoxides*; Academic Press: New York, 1978.

[3] Brinker, C. J.; Scherer, G. W. *Sol-Gel Science*; Academic Press: San Diego, 1990.

[4] Kintzinger, J.-P. *NMR: Basic Princ. Prog.* **1981**, *17*, 1.

0002-7863/91/1513-8190$02.50/0 © 1991 American Chemical Society

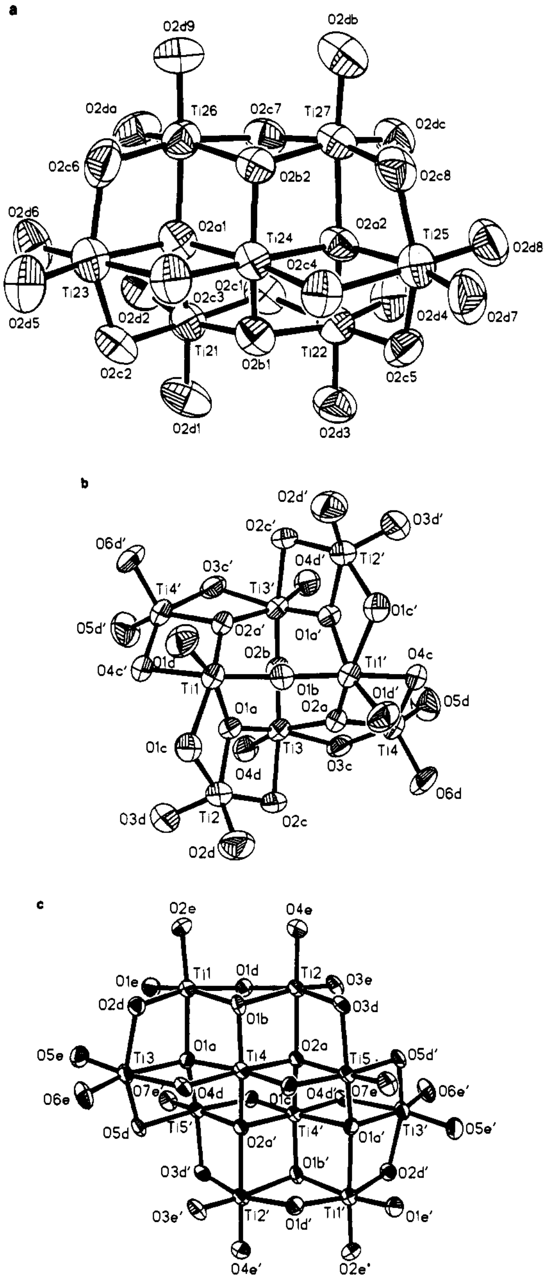

Figure 2. (a) The X-ray crystallographically determined structure of the pseudo-C_{2v} Ti_7O_{24} core in $[Ti_7O_4](OEt)_{20}$ with all atoms represented by 50% probability ellipsoids. The crystal contains two crystallographically independent molecules, which each contain seven six-coordinate Ti(IV) centers and the following ligands: two μ_4-O^{2-}, two μ_3-O^{2-}, eight μ_2-OEt^-, and twelve terminal OEt^- ligands whose oxygen centers are labeled with a, b, c, and d subscripts, respectively. This view shows the second molecule. (b) The X-ray crystallographically determined structure of the pseudo-S_4 Ti_8O_{26} core in $[Ti_8O_6](OBz)_{20}$·OEt_2 with all atoms represented by 50% probability ellipsoids. The $[Ti_8O_6](OBz)_{20}$ molecule possesses rigorous crystallographic C_2 symmetry in the solid state: atoms labeled with primes are related to those without primes by the C_2 axis at ($^1/_4$, y, $^1/_4$) which passes through oxygen atoms O1b and O2b. The molecule contains four five-coordinate and four six-coordinate Ti(IV) centers and the following ligands: four μ_3-O^{2-} two μ_2-O^{2-}, eight μ_2-OBz^-, and twelve terminal OBz^- ligands whose oxygen centers are labeled with a, b, c, and d subscripts, respectively. (c) The X-ray crystallographically determined structure of the $Ti_{10}O_{32}$ core in $[Ti_{10}O_8](OEt)_{24}$·$CH_3C_6H_5$ with all atoms represented by 50% probability ellipsoids. The $[Ti_{10}O_8](OEt)_{24}$ molecule possesses rigorous C_i symmetry in the solid state: atoms labeled with primes are related to those without primes by the inversion center at the midpoint of the $Ti_4 \rightarrow Ti_4'$ vector. The molecule contains 10 six-coordinate Ti(IV) centers and the following ligands: four μ_4-O^{2-}, two μ_3-O^{2-}, two μ_2-O^{2-}, 10 μ_2-OEt^-, and 14 terminal OEt^- ligands whose oxygen centers are labeled with a, b, c, d, and e subscripts, respectively.

crystallization of the resulting precipitate yielded analytically pure $[Ti_7O_4](OEt)_{20}$ having the structure shown in Figure 2a according to a single-crystal X-ray diffraction study.[5,6] The ^{17}O NMR spectrum of material prepared from ^{17}O-enriched water contained two resonances at δ 537 and 365 having equal intensities corresponding to the two symmetry nonequivalent types of oxide oxygens in the structure (see Figure 1b). The chemical shifts of these two resonances were in good agreement with the chemical shifts for resonances d and h in Figure 1a.

Hydrolysis of selectively ^{17}O-enriched $[Ti_7O_4](OEt)_{20}$ with 1 equiv of ^{17}O-enriched water in heptane/benzene followed by removal of volatiles in vacuo produced a mixture of species whose ^{17}O NMR spectrum in toluene showed $[Ti_7O_4](OEt)_{20}$ oxide resonance plus two resonances at δ 726 and 533 with relative intensities of 1:2.[6] Although the species responsible for these two resonances could not be isolated from this solution, its benzyl analogue $[Ti_8O_6](OBz)_{20}$, Bz = $CH_2C_6H_5$, whose structure is shown in Figure 2b, could be prepared in analytically pure form by hydrolysis of $Ti(OBz)_4(BzOH)$ in toluene/acetonitrile, removal of volatiles in vacuo, and recrystallization.[6] The ^{17}O NMR spectrum of selectively ^{17}O enriched material in toluene showed two oxide resonances at δ 726 and 533 with relative intensities of 1:2, a pattern consistent with this structure (see Figure 1c). The same resonances observed in the ethoxide system were therefore assigned to a $[Ti_8O_6](OEt)_{20}$ analogue (see above and Figure 1a). This assignment was supported by ^{13}C NMR data for pure $[Ti_8O_6](OBz)_{20}$ and $[Ti_8O_6](OEt)_{20}$ mixed with $[Ti_7O_4](OEt)_{20}$: both showed the presence of five symmetry-nonequivalent types of alkoxide groups, consistent with the structure of Figure 2b.[6]

The difficulty of inferring solution compositions from crystal structures is illustrated by the case of $[Ti_{10}O_8](OEt)_{24}$. This material crystallized in analytically pure form from solutions of $[Ti_7O_4](OEt)_{20}$ plus $[Ti_8O_6](OEt)_{20}$ in heptane (see above) and had the crystal structure shown in Figure 2c.[6] The ^{17}O NMR spectrum of selectively ^{17}O enriched material in toluene shown in Figure 1c was consistent with this structure. Note, however, that comparison of this spectrum with the spectrum of hydrolyzed $Ti(OEt)_4$ shown in Figure 1a demonstrates that $[Ti_{10}O_8](OEt)_{24}$ was *not* present among the hydrolysis products, a conclusion supported by spectra of solutions containing $[Ti_7O_4](OEt)_{20}$, $[Ti_8O_6](OEt)_{20}$, and $[Ti_{10}O_8](OEt)_{24}$.

Chemical shift and structural data presented above strongly support the chemical shift scale for titanium(IV) polyoxoalkoxides shown at the top of Figure 1 where doubly bridging oxide oxygen centers (OTi_2 oxygens) have chemical shifts in the δ 650–850 region, OTi_3 oxygens have chemical shifts in the δ 450–650 region, and OTi_4 oxygens have chemical shifts in the δ 250–450 region. Specifically, the resonance observed for $[Ti_8O_6](OBz)_{20}$ in the OTi_2 and OTi_3 regions can be uniquely assigned to the two equivalent OTi_2 and four equivalent OTi_3 oxide oxygens, respectively, in the structure on the basis of relative intensities (1:2), and the equal-intensity resonances observed for $[Ti_7O_4](OEt)_{20}$ and $[Ti_{10}O_8](OEt)_{24}$ all have chemical shift values in the ranges proposed for the types of oxide oxygens present in tl e crystallographically determined structures.

Acknowledgment. This research was supported by the United States Department of Energy, Division of Materials Science, under Contract DE-AC02-76ER01198. We thank Dr. Scott Wilson of the University of Illinois X-ray Crystallographic Laboratory for carrying out the X-ray crystal structure determination of $[Ti_{10}O_8](OEt)_{20}$·C_7H_8.

Supplementary Material Available: Details of sample preparation and characterization, crystal structure reports, listings of

---

(5) This crystalline form of $[Ti_7O_4](OCH_2CH_3)_{20}$ has previously been characterized, but the limited yield of data prevented unambiguous identification of the compound: Watenpaugh, K.; Caughlan, C. N. *J. Chem. Soc., Chem. Commun.* **1967**, 76.

(6) For preparative analytical, spectroscopic, and X-ray crystallographic data, see the paragraph at the end of the paper regarding supplementary material.

positional parameters, anisotropic thermal parameters, bond lengths and angles, and perspective structural drawings for $[Ti_7O_4](OCH_2CH_3)_{20}$, $[Ti_8O_6](OCH_2C_6H_5)_{20}\cdot O(CH_2CH_3)_2$, and $[Ti_{10}O_8](OCH_2CH_3)_{24}\cdot CH_3C_6H_5$ (86 pages); tables of calculated and observed structure factors for $[Ti_7O_4](OCH_2CH_3)_{20}$, $[Ti_8O_6](OCH_2C_6H_5)_{20}\cdot O(CH_2CH_3)_2$, and $[Ti_{10}O_8](OCH_2CH_3)_{24}\cdot CH_3C_6H_5$ (64 pages). Ordering information is given on any current masthead page.

Computer Software Reviews

SYSTAT/SYGRAPH. Version 5.0 DOS. SYSTAT, Inc.: 1800 Sherman Ave., Evanston, IL 60201-3793. List price $895.00. The package includes four manuals: GETTING STARTED, STATISTICS, DATA, and GRAPHICS. A MacIntosh version is available for $795.00. Single copies of both versions are available to academic users in the U.S. and Canada at a 30% discount. A student version called MYSTAT is available at $5.00 per copy. Site licenses and network versions are available to colleges, universities, and other multiuser organizations.

SYSTAT is a statistics package with extraordinary capability for a non-mainframe package. However, some might argue that its 6 Mb hard disk requirement puts it in a mainframe category. It can be run from floppy disks if two drives are available. The almost 700 page manual on statistics is packed with useful information in a very readable format. Some topics include correlations, factor analysis, multidimensional scaling, analysis of variance, nonlinear estimation, nonparametric statistics, and series analysis including Fourier transformations. Each individual statistical approach (e.g. linear regression, piecewise regression, analysis of covariance, Lilliefors test, exponential smoothing, etc.) is augmented with an example with pre-entered data for a hands-on experience. There are approximately 115 examples in the statistics manual alone. On the computer, the package is extremely easy to use with a well-designed menu system. For those with some computer experience it takes approximately one day to learn one's way around the menu system used in this program. The well-written tutorial in the GETTING STARTED manual provides an excellent and efficient way to learn the system.

Data input and preliminary manipulation is covered in a separate 250 page manual. Data are easily entered manually, from ASCII data files and from data bases such as Lotus 1-2-3, Symphony, and dBase. Data may be transformed, removed, and added to files by some simple BASIC style programming commands. Macros may be written for overall program control and long repetitive processes.

SYGRAPH is the second part of this package, described in its own 500 page manual. The graphics capabilities are excellent. Bar and pie charts, scatter plots, three dimensional and contour plots and many more are all readily generated. Graphs are readily converted between Cartesian and polar coordinates. Maps (USA and world maps are included in the package) in a variety of projections are also easily drawn. Commands for all plots may be made from the menu or from typed command lines. Color may be added to graphics by specifying the name of the color or the desired wavelength in nanometers. There is an interesting and well-documented chapter entitled Cognitive Science and Graphic Design. It presents some important insights on avoiding unintended visual aberrations. Finally, output from SYGRAPH can be formatted for a wide range of printers, plotters, or laser printers, either in the setup program or directly from the menus. No listing of our Okidata Microline 320 was found, but after some trial and error the EPSON 8 pin high density option was found to be a suitable substitute.

The manufacturer offers unlimited technical support for registered users. SYSTAT has a two day training course costing approximately $550. A bulletin board is available for users which also maintains a list of bugs that have been found (none were found in this review). At least 15 different supplements and map files are available to enhance SYSTAT/SYGRAPH.

This package most likely provides more statistical power than the chemist would typically use. The graphics portion has little capability for chemical structures, as was expected. Four volumes of instructions totalling about 1700 pages is daunting. However, after the tutorial the other manuals can be consulted on a need-to-know basis. All of the methodologies are amply referenced to appropriate texts and primary literature. The DOS version runs on IBM pc's or compatibles with at least 640k RAM and 7.5 Mb free hard disk space, and the license allows for one backup copy and use on only one computer at a time. This program is currently being used with the Perkin-Elmer LS-50 luminescence spectrometer in the generation of three-dimensional fluorescence plots.

Neil D. Jespersen, *St. John's University*

*Book Reviews**

Progress in Colloid and Polymer Science. Volume 83. Interfaces in Condensed Systems. Guest Editor: G. H. Findenegg (Bochum). Springer-Verlag: New York. 1990. viii + 224 pp. $89.00. ISBN 0-387-91369-6.

This book contains a selection of the papers presented at the Kolloid-Tagung 1989 at the Ruhr-Universität-Bochum on October 1–4, 1989. The papers are grouped into the following sections: General (Invited papers); Interfaces; Monolayers; Surfactant Systems; and Dispersed Systems. There is a 1-page preface, an author index, and a subject index.

Progress in Colloid & Polymer Science. Volume 82. Surfactants and Macromolecules: Self-Assembly at Interfaces and in Bulk. Guest Editors: B. Lindman (Lund), J. B. Rosenholm (Abo), and P. Stenius (Stockholm). Springer-Verlag: New York. 1990. viii + 364 pp. $148.00. ISBN 0-387-91367-X.

This book contains a selection of the papers presented at the 10th Scandinavian Symposium on Surface Chemistry held at the Abo Akademi University in Abo, Finland, on June 14–16, 1989. The papers presented are groupd into the following sections: Adsorption from Solution; Emulsions, Foams, Thin Liquid Films; Self Assembling Systems; and Surface Modification and Interactions. There is an author index and a subject index.

Flavour Science and Technology. Edited by Y. Bessière (Borex, Switzerland) and A. F. Thomas (Firmenich SA, Geneva, Switzerland). John Wiley & Sons: Chichester, New York, Brisbane, Toronto, Singapore. 1990. xiv + 370 pp. $150.00. ISBN 0-471-92782-1.

This book is based on the Sixth Weurman Symposium held May 2–4, 1990 in Geneva. It contains most of the contributions presented as oral communications and posters on the following main topics: (1) The Chemistry of Flavours, (2) Energy Application and Food Flavour Systems, and (3) Instrumentation and Data Treatment. There is an author index and a subject index.

Materials Chemistry at High Temperatures. Volume 1: Characterization. Volume 2: Processing and Performance. Edited by John W. Hastie (National Institute of Standards and Technology). Humana Press: Clifton, NJ. 1990. $120.00 each volume. Volume 1: xviii + 446 pp. ISBN 0-89603-186-1. Volume 2: xviii + 522 pp. ISBN 0-89603-187-X.

These books contain selected papers from the Proceedings of the Sixth International Conference on High Temperatures: Chemistry of Inorganic Materials, many of which were originally published in *High Temperature Science, An International Journal*, Volumes 26–28; the plenary papers were originally published by IUPAC in *Pure and Applied Chemistry*

---

*Unsigned book reviews are by the Book Review Editor.