

## Selective Ligand Conversion of Ethylenediamine Tetraacetate to Its Triacetate on Peroxotitanate(IV)

Zhao-Hui Zhou,<sup>\*,†</sup> Yuan-Fu Deng,<sup>†</sup> Qiong-Xin Liu,<sup>†</sup> Hua-Lin Zhang,<sup>†</sup> Thomas C. W. Mak,<sup>‡</sup> and Yuan L. Chow<sup>†</sup>

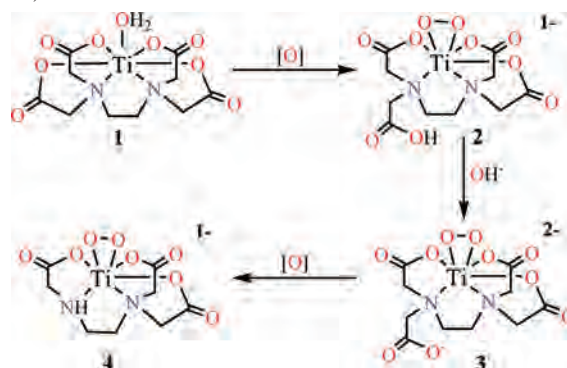
Department of Chemistry, College of Chemistry and Chemical Engineering and State Key Laboratory for Physical Chemistry of Solid Surfaces, Xiamen University, Xiamen 361005, China, and Department of Chemistry, The Chinese University of Hong Kong, Shatin, New Territories, Hong Kong, China

Received June 26, 2007

Ethylenediaminetetraacetate is converted into its triacetate by peroxotitanate(IV), and strong chelation of the triacetate ligand to the metal center facilitates elimination of the pendant acetoxy group. Various species of peroxotitanium(IV) complexes in the reaction sequence are fully characterized.

This Communication is prompted by the discovery that a simple analytical reaction of hydrogen peroxide<sup>1</sup> actually involves a deep-seated oxidative cleavage of side chains to yield a commercially useful product, which otherwise requires a multistep circuitous method to prepare. Ethylenediaminetriacetic acid (H<sub>3</sub>ed3a = C<sub>8</sub>H<sub>14</sub>O<sub>6</sub>N<sub>2</sub>) is commercially synthesized from ethylenediaminediacetic acid via condensation with formaldehyde, addition of cyanide, hydrolysis, cyclization, and ring opening in five steps.<sup>2</sup> It is a widely used industrial chemical to prepare chelating surfactants, such as lauroyl ethylenediaminetriacetate [CH<sub>3</sub>(CH<sub>2</sub>)<sub>10</sub>CON-(CH<sub>2</sub>CO<sub>2</sub><sup>-</sup>)NCH<sub>2</sub>CH<sub>2</sub>N(CH<sub>2</sub>CO<sub>2</sub><sup>-</sup>)<sub>2</sub>], which serves the purpose of chelating multivalent ions.<sup>3</sup> We have exploited the titanium(IV) coordination as a protecting strategy to selectively free an acetoxy coordinating group in ethylenediaminetetracetic acid (H<sub>4</sub>edta = C<sub>10</sub>H<sub>16</sub>O<sub>8</sub>N<sub>2</sub>) and further oxidatively eliminate this group by H<sub>2</sub>O<sub>2</sub> via peroxotitanate

**Scheme 1.** Transformations of Peroxotitanium(IV) Complexes 2–4 (1 to 4)



intermediates, a rarely observed oxidative degradation of a chelated ligand.

[Ti(edta)(H<sub>2</sub>O)] (**1**) is a robust complex in aqueous solution and is used as an analytical reagent for H<sub>2</sub>O<sub>2</sub> through a fast reaction to form peroxotitanate intermediates.<sup>4</sup> The rate process of this rapid reaction has been studied, culminating in a quantity of data in the early 1980s. Unfortunately, because of the fact that the structure of Ti–H<sub>4</sub>edta was wrong at the time of the studies, the peroxotitanate intermediates were not structurally defined correctly, nor was the slower succeeding cleavage reaction discovered.<sup>4,5</sup> We identify the intermediate as well as the final product, (NH<sub>4</sub>)[Ti(O<sub>2</sub>)(ed3a)] (**4** in Scheme 1), and delineate this intriguing reaction.

In a one-pot reaction, **1** in aqueous solution was transformed to a peroxotitanium(IV) ethylenediaminetriacetate complex (**4**) with H<sub>2</sub>O<sub>2</sub> at pH 6.0. The net elimination of a pentagon ring from **1** under straightforward conditions was shown to involve stepwise peroxotitanate formations to **2** and **3** followed by a slow degradation of the freed pendant

\* To whom correspondence should be addressed. E-mail: zhzhou@xmu.edu.cn. Tel: +86-592-2184531. Fax: +86-592-2183047.

<sup>†</sup> Xiamen University.

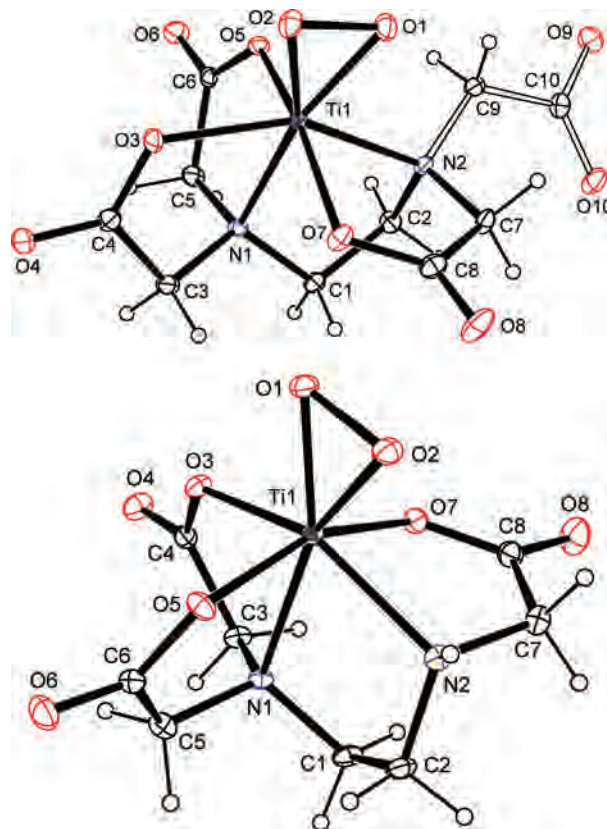
<sup>‡</sup> The Chinese University of Hong Kong.

- (1) (a) Schwarzenbach, G.; Flaschka, H. *Complexometric Titrations*; Methuen: London, 1969; p 200. (b) Fujita, Y.; Mori, I.; Toyoda, M.; Matsuo, T. *Anal. Sci.* **1994**, *10*, 827. (c) Wilkins, D. H. *Anal. Chim. Acta* **1959**, *20*, 113.
- (2) (a) Parker, B. A.; Cullen, B. A.; Gaudette, R. R. (Hampshire Chemical Corp.). U.S. Patent 5,250,728, 1993. (b) Parker, B. A.; Cullen, B. A.; Gaudette, R. R. U.S. Patent 5,449,822, 1995.
- (3) (a) Crudden, J. J.; Lazzaro, J.; Parker, B. A.; Crudden, J. M. U.S. Patent 6,503,873, 2003. (b) Crudden, J. J.; Lazzaro, J.; Parker, B. A. U.S. Patent 6,057,277, 2000. (c) Crudden, J. J.; Lazzaro, J.; Parker, B. A. (Hampshire Chemical Corp.). U.S. Patent 5,821,215, 1998. (d) Pchelintsev, D. (Avon Products, Inc.). U.S. Patent 5,621,008, 1997. (e) Crudden, B. A.; Parker, B. A. *Inform* **1995**, *6*, 1132. (f) Parker, B. A.; Cullen, B. A. U.S. Patent 5,284,972, 1994.

(4) Fackler, J. P.; Kristine, F. J.; Mazany, A. M.; Moyer, T. J.; Shepherd, R. E. *Inorg. Chem.* **1985**, *24*, 1857.

(5) (a) Mühlebach, J.; Müller, K.; Schwarzenbach, G. *Inorg. Chem.* **1970**, *9*, 2381. (b) Kristine, F. J.; Shepherd, R. E.; Siddiqui, S. *Inorg. Chem.* **1981**, *20*, 2571. (c) Kristine, F. J.; Shepherd, R. E. *J. Chem. Soc., Chem. Commun.* **1980**, 132.

acetoxy group to give **4**, as shown in Scheme 1. The former two steps are known to be fast by prior kinetic studies,<sup>5</sup> but the last cleavage reaction by H<sub>2</sub>O<sub>2</sub> is slow (and, thus, has escaped recognition) and most likely requires a priori formation of a peroxotitanate group (vide infra). Compounds **2–4** were isolated as ammonium salts under the conditions indicated in Scheme 1 and Experimental Section, and their structures were determined by X-ray diffraction analysis.<sup>6</sup> Figure 1 shows the ORTEP plots of the anions of complexes **3** and **4**; that of **2** closely resembles that of **3**. In addition, these peroxotitanates **2–4** were rigorously characterized by physical methods to show compatible data. Their Raman spectra show characteristic bands of coordinated [Ti(O<sub>2</sub>)],<sup>7</sup> a sharp peak near 890 cm<sup>-1</sup> for the  $\nu(\text{O}=\text{O})$  stretching vibration, and one near 630 cm<sup>-1</sup> for the  $\nu[\text{Ti}(\text{O}_2)]$  mode. Thus, the peroxy group O<sub>2</sub><sup>2-</sup> binds to the titanium center in a side-on  $\eta^2$  mode, as in Figure 1. This binding mode is frequently observed in the complexes of early transition metals with O<sub>2</sub><sup>2-</sup> and has also been found in some porphyrin–peroxy complexes<sup>8–10</sup> such as (NH<sub>4</sub>)<sub>4</sub>[Ti(O<sub>2</sub>)(cit)<sub>2</sub>·2H<sub>2</sub>O],<sup>7b</sup> (NH<sub>4</sub>)<sub>6</sub>[Ti<sub>4</sub>O<sub>2</sub>(O<sub>2</sub>)<sub>4</sub>(glyc)<sub>4</sub>(Hglyc)<sub>2</sub>·4H<sub>2</sub>O],<sup>7c</sup> [VO(O<sub>2</sub>)(ida)]<sup>-</sup>, [Mn(O<sub>2</sub>)TPP]<sup>-</sup>,<sup>9</sup> and [Fe(O<sub>2</sub>-



**Figure 1.** ORTEP plots of the anion structures in complexes **3** (top) and **4** (bottom) at the 20% probability levels. Selected bond lengths (Å): **3**, Ti1–O1 1.845(3), Ti1–O2 1.858(3), Ti1–O3 2.058(3), Ti1–O5 1.976(3), Ti1–O7 1.960(3), Ti1–N1 2.286(3), Ti1–N2 2.256(3), O1–O2 1.456(4); **4**, Ti1–O1 1.854(2), Ti1–O2 1.849(2), Ti1–O3 2.045(2), Ti1–O5 1.975(2), Ti1–O7 1.975(2), Ti1–N1 2.280(2), Ti1–N2 2.191(3), O1–O2 1.464(3).

(edta)]<sup>3-</sup>.<sup>10</sup> The <sup>13</sup>C NMR spectra of **2–4** are clean, with simple patterns indicating no dissociation and/or decomposition of these complexes. This also supports the robust nature of these coordination complexes, where titanium(IV) is tightly locked with a multidentate ligand.

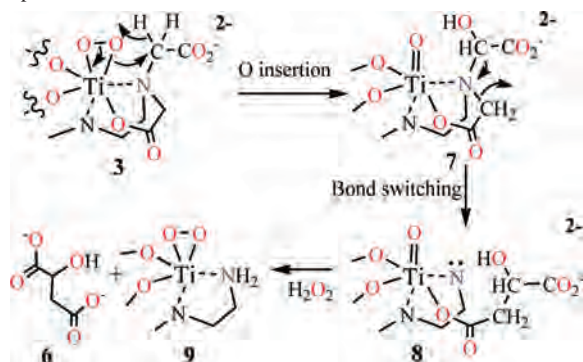
In the allied field, it is reported that in an alkaline solution [Co(edta)]<sup>-</sup> is converted, with PbO<sub>2</sub> or without an oxidizing agent, to [Co(ed3a)(H<sub>2</sub>O)];<sup>11</sup> it is proposed that a specific lactone ring is oxidatively eliminated to an intermediate to relieve steric strain. In the present case, structural features providing a salient driving force for a similar oxidative process can be gleaned from X-ray structures (Figure 1). First of all, as shown by X-ray analysis, these seven-coordinate complexes all possess a stable pentagonal-bipyramidal configuration, where the oxidation-sensitive functions of the ligand are protected by coordination, as stated above. Second, the oxidation is initiated by wedging-in a peroxy group to replace the coordinated H<sub>2</sub>O, which also frees one of four equivalent acetoxy groups as a pendant group, which has a longer N2–C9 bond [1.492(5) Å for **3**] and is susceptible to oxidation. Its oxidative cleavage reaction occurs only when the pH is adjusted to 6.0; i.e., the pendant group is deprotonated and dissociated as an acetoxy anion. Presumably, a carboxylate anion facilitates oxidative electron

- (6) Crystal structure analysis: Intensity data were measured on a Bruker Apex CCD diffractometer with graphite-monochromated Mo K $\alpha$  at 296 K. Empirical absorption corrections were applied using the *SADABS* program. All calculations were performed using the *SHELXL-97* and *SHELXS-97* program packages.<sup>17</sup> The structure was solved by direct methods and refined by full-matrix least-squares methods. All of the non-hydrogen atoms were refined anisotropically, while all of the hydrogen atoms were located from differential Fourier maps. Crystal data for **2**: crystal dimensions 0.48 × 0.45 × 0.21 mm, C<sub>10</sub>H<sub>21</sub>O<sub>12</sub>N<sub>3</sub>Ti, *M* = 423.20, monoclinic, *P*2<sub>1</sub>/*c*, *a* = 20.121(1) Å, *b* = 6.9698(3) Å, *c* = 12.4450(6) Å,  $\beta$  = 107.359(1)°, *V* = 1665.8(1) Å<sup>3</sup>, *Z* = 4, *D*<sub>c</sub> = 1.687 g/cm<sup>3</sup>, 18 285 reflections collected, 3974 independent reflections (*R*<sub>int</sub> = 0.0694), *R*<sub>1</sub> = 0.0369, *wR*<sub>2</sub> = 0.0980. Crystal data for **3**: crystal dimensions 0.20 × 0.13 × 0.03 mm, C<sub>10</sub>H<sub>24</sub>O<sub>12</sub>N<sub>4</sub>Ti, *M* = 440.23, triclinic, *P*1, *a* = 6.5678(6) Å, *b* = 7.0325(6) Å, *c* = 20.085(2) Å,  $\alpha$  = 95.202(2)°,  $\beta$  = 96.759(2)°,  $\gamma$  = 107.235(2)°, *V* = 872.1(1) Å<sup>3</sup>, *Z* = 2, *D*<sub>c</sub> = 1.676 g/cm<sup>3</sup>, 5984 reflections collected, 3904 independent reflections (*R*<sub>int</sub> = 0.0749), *R*<sub>1</sub> = 0.0678, *wR*<sub>2</sub> = 0.1552. Crystal data for **4**: crystal dimensions 0.13 × 0.07 × 0.06 mm, C<sub>8</sub>H<sub>15</sub>O<sub>8</sub>N<sub>3</sub>Ti, *M* = 329.13, monoclinic, *P*2<sub>1</sub>/*n*, *a* = 6.5340(5) Å, *b* = 15.145(1) Å, *c* = 12.306(1) Å,  $\beta$  = 99.705(1)°, *V* = 1200.4(2) Å<sup>3</sup>, *Z* = 4, *D*<sub>c</sub> = 1.821 g/cm<sup>3</sup>, 10 345 reflections collected, 2854 independent reflections (*R*<sub>int</sub> = 0.0653), *R*<sub>1</sub> = 0.0526, *wR*<sub>2</sub> = 0.1124. Crystal data for **5**: crystal dimensions 0.48 × 0.42 × 0.25 mm, C<sub>8</sub>H<sub>13</sub>O<sub>9</sub>N<sub>2</sub>NaTi, *M* = 352.09, monoclinic, *P*2<sub>1</sub>/*n*, *a* = 6.8811(3) Å, *b* = 13.4032(6) Å, *c* = 13.7612(7) Å,  $\beta$  = 100.039(1)°, *V* = 1249.8(1) Å<sup>3</sup>, *Z* = 4, *D*<sub>c</sub> = 1.871 g/cm<sup>3</sup>, 7062 reflections collected, 2785 independent reflections (*R*<sub>int</sub> = 0.0865), *R*<sub>1</sub> = 0.0363, *wR*<sub>2</sub> = 0.0975. Crystal data for **6**: crystal dimensions 0.46 × 0.39 × 0.32 mm, C<sub>4</sub>H<sub>6</sub>O<sub>6</sub>Na<sub>2</sub>, *M* = 196.07, orthorhombic, *P*2<sub>1</sub>2<sub>1</sub>2<sub>1</sub>, *a* = 6.2573(4) Å, *b* = 9.6814(6) Å, *c* = 11.1333(7) Å, *V* = 674.45(7) Å<sup>3</sup>, *Z* = 4, *D*<sub>c</sub> = 1.931 g/cm<sup>3</sup>, 3238 reflections collected, 1537 independent reflections (*R*<sub>int</sub> = 0.0793), *R*<sub>1</sub> = 0.0354, *wR*<sub>2</sub> = 0.0914.

- (7) (a) Kakihana, M.; Tada, M.; Shiro, M.; Petrykin, V.; Osada, M.; Nakamura, Y. *Inorg. Chem.* **2001**, *40*, 891. (b) Dakanali, M.; Kefalas, E. T.; Raptopoulou, C. P.; Terzis, A.; Voyiatzis, G.; Kyrikou, I.; Mavromoustakos, T.; Salifoglou, A. *Inorg. Chem.* **2003**, *42*, 4632. (c) Tomita, K.; Petrykin, V.; Kobayashi, M.; Shiro, M.; Yoshimura, M.; Kakihana, M. *Angew. Chem.* **2006**, *45*, 2378. (8) (a) Dickman, M. H.; Pope, M. T. *Chem. Rev.* **1994**, *94*, 569. (b) Butler, A.; Clague, M. J.; Meister, G. E. *Chem. Rev.* **1994**, *94*, 6258. (c) Pecoraro, V. L.; Baldwin, M. J.; Gelasco, A. *Chem. Rev.* **1994**, *94*, 807. (d) Vaska, L. *Acc. Chem. Res.* **1976**, *9*, 175. (9) (a) VanAtta, R. B.; Strouse, C. E.; Hanson, L. K.; Valentine, J. S. *J. Am. Chem. Soc.* **1987**, *109*, 1425. (b) Djordjevic, C.; Craig, S. A.; Sinn, E. *Inorg. Chem.* **1985**, *24*, 1281. (10) (a) Ahmad, S.; McCallum, J. D.; Shiemke, A. K.; Appelman, E. H.; Loehr, T. M.; Sanders-Loehr, J. *Inorg. Chem.* **1988**, *27*, 2230. (b) Neese, F.; Solomon, E. I. *J. Am. Chem. Soc.* **1998**, *120*, 12829.

- (11) Yashiro, M.; Mori, T.; Yoshikawa, S.; Shiraishi, S. *Chem. Lett.* **1993**, 1009.

**Scheme 2.** Suggested Pathway of Peroxotitanium Ethylenediaminetetracetate Oxidation and Malate Formation via Oxidative Attack and Bond Switching on the Pendant Acetoxy Group



removal. Third, the peroxotitanate group persists during the oxidative cleavage reaction of the acetoxy pendant group, indicating its participation in the process. Finally, these factors bear similarity in its reaction pattern of lactato-peroxomolybdate to carboxylate-bridged acetate and malato-peroxomolybdate to oxalato-peroxomolybdate by H<sub>2</sub>O<sub>2</sub> oxidation,<sup>12</sup> both recorded by our group while finding no other precedence. These oxidative eliminations are unique and are believed to share some mechanistic commonality.

In the search for mechanistic clues, sodium malate (21% yield) was isolated from the aqueous mother liquor at pH 6.0. The remaining filtrate was shown to contain a significant amount of the malate and **4** by its <sup>13</sup>C NMR spectrum. Sodium malate must be derived from a coupling of two deleted C2 units, which should occur most logically within a titanate complex through intramolecular processes. The necessary redox processes must involve the pendant acetoxy group and the nearest pentagon C7–C8–N2 unit (**3** in Figure 1) around the Ti1–N2 bond. To accommodate the above reaction characteristics, a possible sequence (Scheme 2) is suggested using **3** through **7** → **8** → **9** and **6**. The first step is the insertion of an O atom at C9 followed by the 1,3-bond switch to give **8**, in which the N2 exists as a titanium–nitrene complex. The final release of malate and collapse of the titanium–nitrene complex must give **9**, [Ti(O<sub>2</sub>)(*unsym-ed2a*)], which is unstable, and it is proposed that this intermediate disproportionates with **1** to give **4**. A detailed mechanistic interpretation for each step involves many possibilities and will not be attempted now.

(12) (a) Hou, S. Y.; Zhou, Z. H.; Wan, H. L.; Ng, S. W. *Inorg. Chem. Commun.* **2003**, *6*, 1246. (b) Zhou, Z. H.; Hou, S. Y.; Wan, H. L. *Dalton Trans.* **2004**, 1393.

The selective oxidation of aminopolycarboxylic acids using peroxotitanium complexes with aqueous H<sub>2</sub>O<sub>2</sub> is of both academic and industrial interest as an environmentally benign methodology.<sup>13</sup> The description above shows mechanistic implications of structures of titanium complexes relative to selective oxidative degradation, which is relevant to water purification and environmental renewal technology.<sup>14,15</sup>

In conclusion, serendipitous studies of a well-known analytical reaction for H<sub>2</sub>O<sub>2</sub> lead us to establish the reaction pattern wherein **1** is converted to **4** by an intriguing H<sub>2</sub>O<sub>2</sub> oxidative cleavage of the acetoxy group, most likely aided by the peroxotitanate group, [Ti(O<sub>2</sub>)]. The reaction is related to the preparation of ethylenediaminetriacetic acid and has a strong implication to peroxotitanate in catalysis and their possible role in eliminating important agricultural chemicals from the environment.<sup>14–16</sup>

**Acknowledgment.** Financial contributions from the National Science Foundation of China (Grants 20571061 and 20423002) and the Ministry of Science and Technology of China (2005CB221408) are acknowledged.

**Supporting Information Available:** General methods for the experimental procedures, synthesis of compounds **2–6**, UV, IR, and <sup>1</sup>H and <sup>13</sup>C NMR spectra of compounds **2–6**, figures with representative <sup>1</sup>H and <sup>13</sup>C NMR analyses, crystal data and displacement ellipsoid plots for compounds **2**, **5**, and **6**, and tables of crystal and refinement data, atomic positions and displacement parameters, anisotropic displacement parameters, and bond lengths and angles in CIF format. This material is available free of charge via the Internet at <http://pubs.acs.org>.

IC701256E

- (13) Sheldon, R. A.; Dakka, J. *Catal. Today* **1994**, *19*, 215.  
 (14) (a) Nörtemann, B. *Appl. Microbiol. Biotechnol.* **1999**, *51*, 751. (b) Bohuslavsek, J.; Payne, J. W.; Liu, Y.; Bolton, H.; Xun, L. Y. *Appl. Environ. Microbiol.* **2001**, *67*, 688. (c) Nowack, B. *Environ. Sci. Technol.* **2002**, *36*, 4009.  
 (15) Gledhill, W. E.; Feijt, T. C. J. In *The Handbook of Environmental Chemistry*; Hutzinger, O., Ed.; Springer: Berlin, 1992; Vol. 3, Part F, p 261.  
 (16) (a) Ratnasamy, P.; Srinivas, D.; Knözinger, H. *Adv. Catal.* **2004**, *48*, 1. (b) Katsuki, T.; Sharpless, K. B. *J. Am. Chem. Soc.* **1980**, *102*, 5974. (c) Adam, W.; Mitchell, C. M.; Saha-Moeller, C. R. *J. Org. Chem.* **1999**, *64*, 3699. (d) Mba, M.; Prins, L. J.; Licini, G. *Org. Lett.* **2007**, *9*, 21. (e) Clerici, A.; Pastori, N.; Porta, O. *J. Org. Chem.* **2005**, *70*, 4174. (f) Cui, M.; Adam, W.; Shen, J. H.; Luo, X. M.; Tan, X. J.; Chen, K. X.; Ji, R. Y.; Jiang, H. L. *J. Org. Chem.* **2002**, *67*, 1427.  
 (17) Sheldrick, G. M. *SHELXL97 and SHELXS97*; University of Göttingen: Göttingen, Germany, 1997.