this smaller basis set on the enthalpy correction terms was checked, and found to be less than 0.3 kcal mol^{-1}.

[12] a) A. D. Becke, J. Chem. Phys. **1993**, *98*, 5648; b) C. Lee, W. Yang, R. G. Parr, *Phys. Rev. B* **1988**, *37*, 785.

[13] a) T. H. Dunning, P. J. Hay in *Modern Theoretical Chemistry*, *Vol. 3* (Ed.: H. F. Schaefer III), New York, **1976**, p. 1; b) P. J. Hay, W. R. Wadt, *J. Chem. Phys.* **1985**, *82*, 299.

[14] a) R. Krishnan, J. Binkley, R. Seeger, J. Pople, *J. Chem. Phys.* **1980**, *72*, 650; b) A. McLean, G. Chandler, *J. Chem. Phys.* **1980**, *72*, 5639.

[15] G. Frenking, I. Antes, M. Böhme, S. Dapprich, A. W. Ehlers, V. Jonas, A. Neuhaus, M. Otto, R. Stegmann, A. Veldkamp, S. F. Vyboishchikov in *Reviews in Computational Chemistry*, *Vol. 8* (Eds.: K. B. Lipkowitz, D. B. Boyd), VCH, New York, **1996**, p. 63.

[16] S. Köstlmeier, V. A. Nasluzov, W. A. Herrmann, N. Rösch, *Organometallics* **1997**, *16*, 1786.

[17] All transition states were checked by a vibrational analysis at the LanL2DZ level.

[18] K. B. Sharpless, J. M. Townsend, D. R. Williams, *J. Am. Chem. Soc.* **1972**, *94*, 195.

[19] H. Mimoun, I. S. d. Roch, L. Sajus, *Tetrahedron* **1970**, *26*, 37.

[20] a) D. A. Singleton, S. R. Merrigan, J. Liu, K. N. Houk, *J. Am. Chem. Soc.* **1997**, *119*, 3385; b) R. D. Bach, C. M. Estévez, J. E. Winter, M. N. Glukhovtsev, *J. Am. Chem. Soc.* **1998**, *120*, 680.

[21] Internal reaction coordinate analysis carried out at the LanL2DZ level; see C. Gonzalez, H. B. Schlegel, *J. Chem. Phys.* **1990**, *94*, 5523.

The First Organically Templated Layered Uranium(IV) Fluorides: $(H_3N(CH_2)_3NH_3)U_2F_{10}\cdot 2H_2O$, $(H_3N(CH_2)_4NH_3)U_2F_{10}\cdot 3H_2O$, and $(H_3N(CH_2)_6NH_3)U_2F_{10}\cdot 2H_2O$**

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Hydrothermal chemistry in the presence of organic structure-directing agents has been demonstrated to be a highly versatile technique for the synthesis of new layered and three-dimensional framework materials.[1, 2] The versatility of the technique derives from the exquisite control over the detailed topology of the inorganic framework that can be achieved by the systematic variation of the synthesis conditions and the template employed, and over recent years a vast range of novel open-framework and layered materials have been reported. All these materials contain the common structural feature of an inorganic anionic framework within which the cationic organic structure-directing agent is occluded. The continued interest in the synthesis of new materials in this class stems from their suitability for a range of materials chemistry applications including heterogenous catalysis,[3] molecular sieving, ion-exchange,[4] and as host materials for nanochemical applications.[5] Although to date the vast majority of compounds have been derived from main group elements such as silicon and aluminum,[2] over recent years there has been increasing interest in incorporating transition metals within three-dimensional and layered framework structures.[6] Such materials have the potential of combining the shape selectivity demonstrated by framework materials with the catalytic, magnetic, optical, and redox properties associated with d-block elements.

However, with the exception of two organically templated uranium(VI) phosphate phases which we recently reported,[7] we are not aware of any syntheses of organically templated materials in which actinide elements such as uranium are incorporated into a layered or microporous framework. We have been interested in the synthesis of these materials for a number of reasons. First, the high coordination numbers and variety of coordination geometries adopted by actinide elements could be expected to result in the formation of new, complex framework architectures when the syntheses are performed in the presence of bulky organic templates. Clearfield and co-workers have demonstrated that in the synthesis of uranyl phosphonates the presence of sterically demanding organic groups on the phosphonate ligands leads to the formation of novel structure types, including porous structures.[8–10] Second, these materials can also be envisioned to exhibit useful catalytic, ion-exchange, and intercalation properties. For example, hydrogen uranyl phosphate (HUP) is a fast hydrogen ion conductor and a versatile ion-exchange reagent,[11–13] and uranium oxide based materials have recently been shown to be effective halocarbon oxidation catalysts.[14] Finally, the existence of a number of stable oxidation states of actinides offers the possibility of synthesizing materials with useful optical and magnetic properties.

The addition of fluoride ions in hydrothermal syntheses has been shown to be a particularly effective method for the synthesis of novel structure types.[15] The fluoride appears to play a role both in aiding the crystallization of the product, and in stabilizing the increased coordination of the metal atoms thus leading to new and more complex framework architectures. We have been exploring the hydrothermal synthesis of new uranium based materials in the presence of both organic templates and fluoride ions, and we report here the synthesis and structural characterization of the first organically templated layered uranium(IV) fluorides to be isolated, namely **1**–**3**.

$(H_3N(CH_2)_3NH_3)U_2F_{10}\cdot 2H_2O$ **1**

$(H_3N(CH_2)_4NH_3)U_2F_{10}\cdot 3H_2O$ **2**

$(H_3N(CH_2)_6NH_3)U_2F_{10}\cdot 2H_2O$ **3**

The fluorides **1**–**3** are synthesized in a one-step process by the reaction of UO_2 under autogenous hydrothermal conditions at 180 °C in the presence of aqueous orthophosphoric acid, aqueous hydrofluoric acid, and the organic structure-directing agent. The materials are isolated as phase pure rhomboid-shaped single crystals in high yield (ca. 70% based

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on uranium). Compounds **1**–**3** form a structurally related series of layered materials, which contain negatively charged uranium fluoride sheets separated by charge balancing organic cations and occluded water molecules.[16] Figure 1 shows the structure of a single uranium fluoride layer of **1** viewed perpendicular to the layer (along the [100] direction). The local geometry around each uranium atom is shown in Figure 1b. Each uranium atom is bonded to nine fluorine atoms in a tricapped trigonal-prismatic coordination. A similar uranium coordination geometry has been previously observed in condensed uranium fluorides such as β-NH_4UF_5,[17] $LiUF_5$,[18] and KU_2F_9.[19] Equivalent UF_9 polyhedra share three edges with three adjacent polyhedra and share two corners with two additional polyhedra to form uranium fluoride sheets. The ninth fluorine atom of each polyhedra is terminal and projects out of the layers and towards adjacent sheets, but does not connect them. Thus the connectivity within the layers can be described as $[UF_{8/2}F_{1/1}]^-$. The U–F bond involving the terminal fluorine atom is significantly shorter than the bridging U–F bonds; the U–F distance for the terminal fluorine is 2.17(1) Å, whereas for the bridging fluorine atoms the average U–F distance is 2.35 Å (with a range of 2.32(1) to 2.39(1) Å). The uranium fluoride sheets stack along the [100] direction and are separated by charge balancing $[H_3N(CH_2)_3NH_3]^{2+}$ ions and occluded water molecules. Figure 2 shows the structure of **1** viewed along the [010] direction and shows the location of the occluded template.

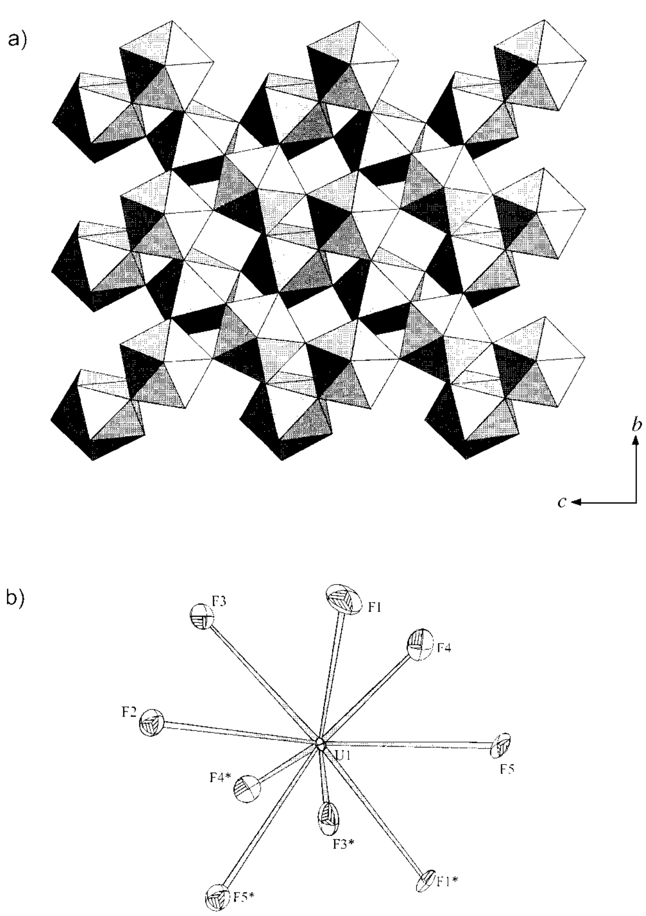

Figure 1. a) The structure of a single uranium fluoride layer in **1** viewed perpendicular to the layers (along the [100] direction), showing how the layers are constructed from corner-sharing $[UF_9]$ tricapped trigonal prisms. Compounds **2** and **3** contain essentially identical layers. b) A view of the local coordination around each uranium atom.

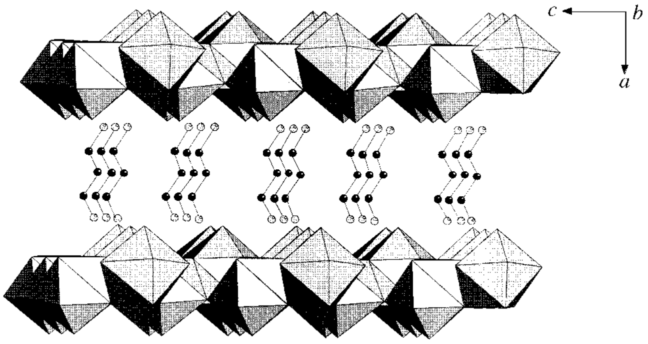

Figure 2. The structure of **1** viewed perpendicular to the uranium fluoride layers (along the [010] direction), showing the location of the organic template. The $(H_3N(CH_2)_3NH_3)^{2+}$ ion lies on an inversion center and the end carbon atom is disordered around this position. For clarity this disorder is not represented in the figure and only one orientation of the template is shown.

The structure of the uranium fluoride layers in compounds **2** and **3** is essentially identical to that seen in compound **1**, which is reflected in two of the lattice parameters, b and c, being almost identical for each compound. In all three materials the $[H_3N(CH_2)_nNH_3]^{2+}$ ions lie almost perpendicular to the uranium fluoride layers, at angles of about 90, 85, and 75° for $n = 3$, 4, and 6, respectively. Hence, as the size of the organic cation increases the separation between uranium fluoride layers also steadily increases. The layers in each compound are bound together through a complex network of strong hydrogen bonds between the substituted ammonium groups and the fluorine atoms of the layers, the oxygen atoms of the water molecules and the fluorine atoms, and the ammonium groups and the water molecules.

Thermal analysis of each material revealed similar behavior. When heated in air all three undergo a weight loss of 5–8% between room temperature and 200°C due to the loss of occluded water. Between about 220°C and 350°C the materials undergo a more substantial weight loss which can be attributed to the combustion of the template and its loss from the materials. Immediately following this, a further substantial weight loss corresponding to decomposition of the uranium fluoride layers occurs, a weight loss which is associated with a loss in crystallinity of the materials. The initial loss of occluded water is fully reversible; that is, if the materials are heated to 165°C, then cooled back down to room temperature, complete rehydration occurs within an hour. When heated in flowing N_2, the materials showed thermal behavior similar to that in air.

The magnetic behavior of phases **1**–**3** was also investigated. As shown in Figure 3, over the range 20–300 K all three materials displayed magnetic susceptibilities that could be fitted well to the simple Curie–Weiss equation. Below 20 K there is slight levelling off of the magnetic susceptibility, a feature most marked for **3**. This is indicative of either very

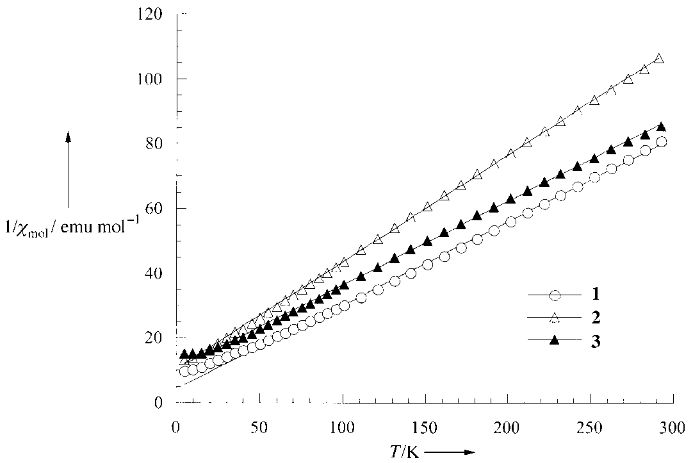

Figure 3. Plot of the variation of inverse molar magnetic susceptibility with temperature for **1**–**3** at a magnetic field of 0.5 T.

weak local antiferromagnetic ordering between U^{4+} ions, or temperature-dependent paramagnetism due to changing populations of atomic energy levels of individual U^{4+} ions. Fitting of the high-temperature (above 20 K) data to the Curie–Weiss equation yielded negative values for the Weiss constant in each case, which is consistent with weak antiferromagnetism. Values of μ_{eff} of 5.66, 4.91, and 5.57 μ_B were obtained for **1**, **2**, and **3**, respectively. These values are somewhat higher than would be expected for U^{IV} ions. However, interpreting effective magnetic moments of uranium compounds is complex because spin–spin, orbit–orbit, spin–orbit, and ligand–field interactions are of a comparable importance and must all be considered in a full treatment.

The negatively charged frameworks and large interlayer separations present in these materials suggested that they may act as good host materials for cationic ion-exchange applications. The ion-exchange properties of these materials were therefore investigated. These experiments revealed that compounds **1**–**3** are extremely robust in their ion-exchange behavior. We were able to fully exchange the organic templates for Na$^+$, K$^+$, or Co^{2+} by stirring suspensions of the compounds in solutions of the appropriate metal salt at room temperature for 48 h. In all cases the exchange was accompanied by a large decrease in the interlayer spacing, and complete exchange was confirmed by the absence of the host 001 reflection and any carbon or nitrogen in the exchanged materials. The ion-exchanged materials were highly crystalline, and powder X-ray diffraction revealed that the exchange of **1**–**3** with any particular cation produced identical products. The diffraction pattern of the potassium exchanged materials matched that of a reported material "$K_7U_6F_{31}$".[20] However, given the synthetic route to the ion-exchanged material we believe the empirical formula is likely to be $KUF_5 \cdot xH_2O$ ("$K_6U_6F_{30}$"). The powder X-ray patterns of the Na$^+$ and Co^{2+}-exchanged materials did not match any known phases. Initial powder X-ray diffraction measurements indicate that the materials are pure and have unit cells that are related to the starting materials. We are currently in the process of determining the structure of these new exchanged phases. Thus, compounds **1**–**3** provide a facile route for the low-temperature synthesis of new alkali and transition metal uranium(IV) fluorides.

In summary, a simple, high-yield, single-step route for the exclusive synthesis of the first compounds of a new class of organically templated uranium(IV) fluorides has been outlined. The materials have been shown to reversibly dehydrate when heated, display weak antiferromagnetic properties, and undergo facile ion-exchange reactions with a variety of other cations leading to the low-temperature formation of new condensed uranium(IV) phases. The isolation of compounds **1**–**3** is another demonstration of how hydrothermal synthesis can be exploited to synthesize novel hybrid organic–inorganic materials. Of particular interest is the contrasting stoichiometry, coordination, and structure of the uranium(IV) materials reported here, synthesized in the presence of fluoride, and the uranium(VI) materials reported previously. Given the huge variety of possible templates that could be used, and the number of possible reaction variables that could be altered, the scope for the synthesis of new materials displaying interesting structural, catalytic, ion-exchange, magnetic, and redox properties is very large.

Experimental Section

All of the syntheses were performed in 23-mL Teflon stainless steel vessels filled to about 25% volume. The UO_2 was supplied by British Nuclear Fuels Limited and used as received. The H_3PO_4 (85% solution, BDH 99%), HF (40% solution, Fisions 98%), and $H_2N(CH_2)_nNH_2$ ($n = 3$ and 4, Aldrich 99%; $n = 6$, Lancaster 98%) were also used as received.

Compounds **1**–**3** were synthesized by combining UO_2 (0.243 g), H_3PO_4 (1.11 g), HF (0.485 g), H_2O (3.21 g), and either $H_2N(CH_2)_3NH_2$ (0.181 g), $H_2N(CH_2)_4NH_2$ (0.214 g), or $H_2N(CH_2)_6NH_2$ (0.283 g) at room temperature. The respective mixtures were heated to 180 °C for 1 day and cooled at 6 °C per hour over an additional day. In all three instances, pure monophasic crystals were recovered in about 70% yields based on UO_2. Elemental analyses: **1**: found (calcd): C 4.44 (4.63), H 2.05 (2.07), N 3.43 (3.60), U 62.19 (61.17), F 24.20 (24.41); **2**: found (calcd): C 5.86 (5.93), H 2.19 (2.59), N 3.29 (3.46), U 56.73 (58.75), F 23.56 (23.50); **3**: found (calcd): C 7.94 (8.79), H 2.56 (2.70), N 3.10 (3.42), U 56.35 (58.04), F 22.92 (23.17).

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[1] R. Szostak, *Molecular Sieves: Principles of Synthesis and Identification*, Van Nostrand Reinhold, New York, **1989**.
[2] M. E. Davis, R. F. Lobo, *Chem. Mater.* **1992**, *4,* 756.
[3] P. B. Venuto, *Microporous Mater.* **1994**, *2,* 297.
[4] A. Clearfield, *Chem. Rev.* **1988**, *88,* 125.
[5] G. A. Ozin, *Adv. Mater.* **1992**, *4,* 612.
[6] R. C. Haushalter, L. A. Mundi, *Chem. Mater* **1992**, *4,* 31, and references therein.
[7] R. J. Francis, M. J. Drewitt, P. S. Halasyamani, C. Ranganathachar, D. O'Hare, W. Clegg, S. J. Teat, *Chem. Commun.* **1998**, 279.
[8] D. Grohol, M. A. Subramanian, D. M. Poojary, A. Clearfield, *Inorg. Chem.* **1996**, *35,* 5264.
[9] D. M. Poojary, D. Grohol, A. Clearfield, *Angew. Chem.* **1995**, *107,* 1650; *Angew. Chem. Int. Ed. Engl.* **1995**, *34,* 1508.
[10] D. M. Poojary, A. Cabeza, M. A. G. Aranda, S. Bruque, A. Clearfield, *Inorg. Chem.* **1996**, *35,* 1468.
[11] C. H. Johnson, M. G. Shilton, A. T. Howe, *J. Solid State Chem.* **1981**, *37,* 37.

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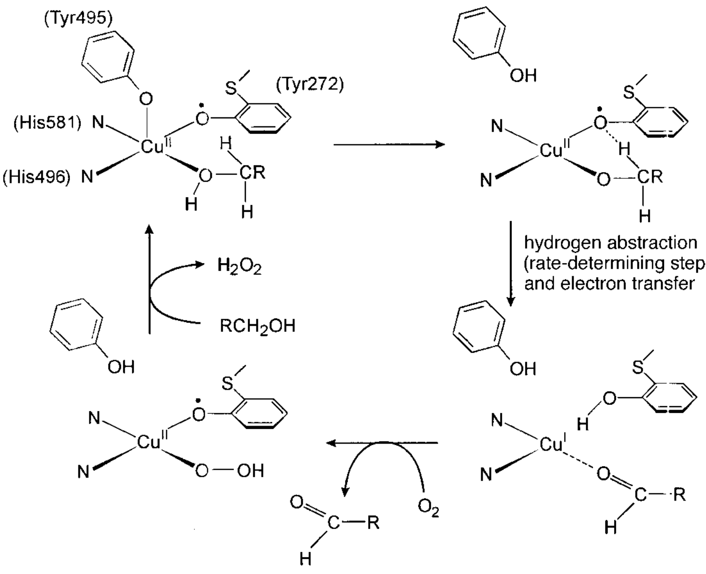
[12] L. Moreno-Real, R. Pozas-Tormo, M. Martinez-Lara, S. Bruque-Gamez, *Mater. Res. Bull.* **1987**, *22*, 19.
[13] D. Grohol, E. L. Blinn, *Inorg. Chem.* **1997**, *36*, 3422.
[14] G. J. Hutchings, C. S. Heneghan, I. D. Hudson, S. H. Taylor, *Nature* **1996**, *384*, 341.
[15] J. L. Guth, H. Kessler, R. Wey, *Stud. Surf. Sci. Catal.* **1986**, *28*, 121.
[16] Crystal data for **1**–**3**: For all three materials the data were collected on an Enraf-Nonius DIP 2000 Image Plate diffractometer using $Mo_{K\alpha}$ radiation. For **1**: monoclinic $P2_1/c$, $a = 10.715(1)$, $b = 7.097(1)$, $c = 8.767(1)$ Å, $\alpha = 93.804(6)^\circ$, $V = 665.21(3)$ Å^3, $Z = 2$, $T = 200$ K. For 1097 observed reflections with $I > 5\sigma(I)$ and 97 variables, $R(R_w) = 0.052(0.060)$. For **2**: triclinic, $P\bar{1}$, $a = 12.024(2)$, $b = 7.149(3)$, $c = 8.765(2)$ Å, $\alpha = 90.063(4)$, $\beta = 107.133(5)$, $\gamma = 92.098(3)^\circ$, $V = 719.46(3)$ Å^3, $Z = 1$, $T = 200$ K. For 1218 observed reflections with $I > 5\sigma(I)$ and 190 variables $R(R_w) = 0.079(0.091)$. For **3**: monoclinic, $P2_1/c$, $a = 13.800(2)$, $b = 7.056(2)$, $c = 8.720(3)$ Å, $\alpha = 108.338(3)^\circ$, $V = 805.97(2)$ Å^3, $Z = 2$, $T = 200$ K. For 892 reflections with $I > 5\sigma(I)$ and 100 variables $R(R_w) = 0.034(0.039)$. Further details on the crystal structure investigations may be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, Germany (fax: (+49) 7247-808-666; e-mail: crystdata@fiz-karlsruhe.de), on quoting the depository numbers CSD-408217, CSD-408218, and CSD-408219.
[17] R. A. Penneman, R. R. Ryan, *Acta Crystallogr. Sect. B* **1974**, *30*, 1966.
[18] G. Brunton, *Acta Crystallogr.* **1966**, *21*, 814.
[19] G. Brunton, *Acta Crystallogr. Sect. B* **1969**, *25*, 1919.
[20] JC-PDF Catalogue No. 10-0150. (Insky, McVay, Thomas, White; Oak Ridge National Lab, USA).

From Structural Models of Galactose Oxidase to Homogeneous Catalysis: Efficient Aerobic Oxidation of Alcohols[**]

Phalguni Chaudhuri,* Martina Hess, Ulrich Flörke, and Karl Wieghardt*

Dedicated to Professor Achim Müller
on the occasion of his 60th birthday

The fungal enzyme galactose oxidase (GO) catalyzes the aerobic oxidation of primary alcohols to aldehydes and H_2O_2.[1] The structure[2] of this biomolecule and its reaction mechanism[3] are well established (Scheme 1): In its catalytically active form there is an *ortho*-S-modified tyrosyl radical (Tyr 272) coordinated to a single copper(II) ion and a unique radical cofactor. The rate-determining step of this catalysis (k_H/k_D 6–8)[4] upon binding of the alcohol substrate to the Cu^{II} ion is the hydrogen abstraction from the α-carbon atom of the alcohol with formation of a coordinated ketyl radical anion. Rapid intramolecular electron transfer with reduction of Cu^{II} to Cu^{I} then leads to the formation of the unbound aldehyde. The reduced enzyme reacts with dioxygen with formation of H_2O_2 and regeneration of the active radical cofactor .



Scheme 1. Proposed mechanism of catalysis by galactose oxidase (according toWhittaker).[3c]

While structural models for the active form of the enzyme containing Cu^{II}–phenoxyl moieties have been synthesized and characterized spectroscopically,[5] it appears to be much more demanding to model the reactivity of GO.[5a, 6] Stack et al.[7] have reported recently mononuclear functional Cu^{II} model complexes which catalyze the aerobic oxidation of activated benzyl and allyl alcohols with concomitant formation of H_2O_2. We describe here a novel *dinuclear* Cu^{II}–phenoxyl radical species that catalytically oxidizes primary and secondary alcohols with dioxygen (air) to the corresponding aldehyde, ketone, and/or to 1,2-glycol derivatives; the reduction product is in all cases H_2O_2.

The reaction of $Cu^{I}Cl$ with 2,2′-thiobis(2,4-di-*tert*-butylphenol) (LH_2) and triethylamine (1:1:2) in dry methanol under argon produces a yellow solution that becomes deep blue upon controlled exposure to air. From this solution microcrystalline blue $[Cu^{II}L(NEt_3)]$ (**1**) is precipitated. Figure 1 displays the structure of the mononuclear neutral complex **1**: The tridentate dianion L^{2-} is coordinated to a Cu^{II} ion and a fourth coordination site is occupied by an NEt_3 ligand; the resulting coordination polyhedron is intermediate between square planar and tetrahedral. Complex **1** is paramagnetic (1.79 μ_B; 3–300 K). The cyclic voltammogram (CV) of **1** in CH_2Cl_2 (0.10 M $[(n\text{Bu})_4N]PF_6$; glassy carbon working electrode) at 20 °C displays two quasireversible one-electron oxidation processes at $E_{1/2} = 0.52$ and 0.89 V versus ferrocenium/ferrocene (Fc^+/Fc) which are ascribed to two successive oxidations of the coordinated ligand L to generate two phenoxyl radicals.

Passing a stream of dry O_2 through the above yellow solution in tetrahydrofuran (THF) for 1 h induces a color change from deep blue to green and, finally, microcrystalline

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