Experimental Section

8: A solution of diyne **7** (121 mg, 0.43 mmol) and $[W(\equiv CCMe_3)(OCMe_3)_3]$ (12 mg, 6 mol %) in chlorobenzene (20 mL) was stirred under Ar at 80 °C for 2 h. The solvent was removed in vacuo, and the residue purified by flash chromatography (Merck silica gel, hexane/ethyl acetate 4/1). This led to the recovery of some unchanged starting material **7** (12 mg, 10 %) and afforded the desired cycloalkyne **8** as colorless crystals (70 mg, 73 %). M.p. = 106–107 °C; ^{1}H NMR: $\delta = 4.14$ (t, 4H, $J = 5.5$ Hz), 2.53 (t, 4H, $J = 5.6$ Hz), 2.40 (m, 4H), 1.76 (m, 4H); ^{13}C NMR: $\delta = 173.0$, 77.8, 62.4, 34.8, 24.9, 19.0. MS: *m*/*z* (rel intensity): 224 (< 1, $[M^+]$), 179 (< 1), 166 (1), 152 (1), 137 (1), 129 (3), 111 (7), 101 (4), 78 (100), 66 (21), 55 (10), 41 (8); elemental analysis calcd for $C_{12}H_{16}O_4$ (224.3): C 64.24, H 7.18; found: C 64.14, H 7.15.

Received: February 9, 1998 [Z 11453 IE]
German version: *Angew. Chem.* **1998**, *110*, 1758–1760

Keywords: alkylidyne complexes · alkynes · macrocycles · metathesis · tungsten

[1] K. J. Ivin, J. C. Mol, *Olefin Metathesis and Metathesis Polymerization*, Academic Press, New York, **1997**.

[2] a) M. Schuster, S. Blechert, *Angew. Chem*. **1997**, *109*, 2124; *Angew. Chem. Int. Ed. Engl*. **1997**, *36*, 2036; b) R. H. Grubbs, S. J. Miller, G. C. Fu, *Acc. Chem. Res.* **1995**, *28*, 446; c) A. Fürstner, *Top. Catal*. **1997**, *4*, 285.

[3] a) A. Fürstner, K. Langemann, *J. Org. Chem*. **1996**, *61*, 3942; b) A. Fürstner, K. Langemann, *Synthesis* **1997**, 792; c) A. Fürstner, N. Kindler, *Tetrahedron Lett*. **1996**, *37*, 7005; d) A. Fürstner, K. Langemann, *J. Org. Chem.* **1996**, *61*, 8746; e) A. Fürstner, K. Langemann, *J. Am. Chem. Soc*. **1997**, *119*, 9130; f) A. Fürstner, D. Koch, K. Langemann, W. Leitner, C. Six, *Angew. Chem*. **1997**, *109*, 2562; *Angew. Chem. Int. Ed. Engl*. **1997**, *36*, 2466; g) A. Fürstner, T. Müller, *Synlett* **1997**, 1010. h) A. Fürstner, T. Müller, *J. Org. Chem*. **1998**, *63*, 424.

[4] a) S. J. Miller, H. E. Blackwell, R. H. Grubbs, *J. Am. Chem. Soc*. **1996**, *118*, 9606; b) T. D. Clark, M. R. Ghadiri, *J. Am. Chem. Soc*. **1995**, *117*, 12364; c) B. König, C. Horn, *Synlett* **1996**, 1013; d) M. A. McKervey, M. Pitarch, *Chem. Commun*. **1996**, 1689; e) A. F. Houri, Z. Xu, D. A. Cogan, A. H. Hoveyda, *J. Am. Chem. Soc*. **1995**, *117*, 2943; f) S. F. Martin, Y. Liao, H.-J. Chen, M. Pätzel, M. N. Ramser, *Tetrahedron Lett*. **1994**, 6005; g) B. Mohr, M. Weck, J-P. Sauvage, R. H. Grubbs, *Angew. Chem*. **1997**, *109*, 1365; *Angew. Chem. Int. Ed. Engl*. **1997**, *36*, 1308; h) S. H. Kim, I. Figueroa, P. L. Fuchs, *Tetrahedron Lett*. **1997**, *38*, 2601.

[5] For leading references on the synthesis of epothilone and analogues by RCM see a) Z. Yang, Y. He, D. Vourloumis, H. Vallberg, K. C. Nicolaou, *Angew. Chem*. **1997**, *109*, 170; *Angew. Chem. Int. Ed. Engl*. **1997**, *36*, 166; b) K. C. Nicolaou, Y. He, D. Vourloumis, H. Vallberg, Z. Yang, *Angew. Chem.* **1996**, *108*, 2554; *Angew. Chem. Int. Ed. Engl*. **1996**, *35*, 2399; c) D. Schinzer, A. Limberg, O. M. Böhm, M. Cordes, *Angew. Chem*. **1997**, *109*, 543; *Angew. Chem. Int. Ed. Engl*. **1997**, *36*, 523; d) P. Bertinato, E. J. Sorensen, D. Meng, S. J. Danishefsky, *J. Org. Chem*. **1996**, *61*, 8000; e) D. Meng, P. Bertinato, A. Balog, D-S. Su, T. Kamenecka, E. J. Sorensen, S. J. Danishefsky, *J. Am. Chem. Soc*. **1997**, *119*, 10073; f) K. C. Nicolaou, Y. He, D. Vourloumis, H. Vallberg, F. Roschanger, F. Sarabia, S. Ninkovic, Z. Yang, J. I. Trujillo, *J. Am. Chem. Soc*. **1997**, *119*, 7960.

[6] Ene–yne metathesis reactions constitute notable exceptions; see [3 f] and a) A. Kinoshita, N. Sakakibara, M. Mori, *J. Am. Chem. Soc*. **1997**, *119*, 12 388; b) K. Hammer, K. Undheim, *Tetrahedron* **1997**, *53*, 10603; c) A. G. M. Barrett, S. P. D. Baugh, D. C. Braddock, K. Flack, V. C. Gibson, P. A. Procopiou, *Chem.Commun*. **1997**, 1375; d) R. Stragies, M. Schuster, S. Blechert, *Angew. Chem*. **1997**, *109*, 2628; *Angew. Chem. Int. Ed. Engl*. **1997**, *36*, 2518; e) A. Kinoshita, M. Mori, *J. Org. Chem*. **1996**, *61*, 8356; f) S.-H. Kim, W. J. Zuercher, N. B. Bowden, R. H. Grubbs, *J. Org. Chem*. **1996**, *61*, 1073.

[7] T. J. Katz, J. McGinnis, *J. Am. Chem. Soc*. **1975**, *97*, 1592.

[8] a) For the first examples of alkyne metathesis reactions with a defined alkylidyne catalyst see J. H. Wengrovius, J. Sancho, R. R. Schrock, *J. Am. Chem. Soc*. **1981**, *103*, 3932; b) Reviews: R. R. Schrock, *Polyhedron* **1995**, *14*, 3177; c) R. R. Schrock, *Acc. Chem. Res.* **1986**, *19*, 342; d) K. Weiss in *Carbyne Complexes* (Eds.: H. Fischer, P. Hofmann, F. R. Kreissl, R. R. Schrock, U. Schubert, K. Weiss), VCH, Weinheim, **1988** p 205.

[9] a) S. A. Krouse, R. R. Schrock, *Macromolecules* **1989**, *22*, 2569; b) K. Weiss, A. Michel, E-M. Auth, U. H. F. Bunz, T. Mangel, K. Müllen, *Angew. Chem*. **1997**, *109*, 522; *Angew. Chem. Int. Ed. Engl*. **1997**, *36*, 506; c) X.-P. Zhang, G. C. Bazan, *Macromolecules* **1994**, *27*, 4627; d) H. H. Fox, M. O. Wolf, R. O'Dell, B. L. Lin, R. R. Schrock, M. S. Wrighton, *J. Am. Chem. Soc*. **1994**, *116*, 2827.

[10] a) D. Villemin, P. Cadiot, *Tetrahedron Lett*. **1982**, *23*, 5139; b) N. Kaneta, K. Hikichi, S-I. Asaka, M. Uemura, M. Mori, *Chem. Lett*. **1995**, 1055. c) J. Sancho, R. R. Schrock, *J. Mol. Cat*. **1982**, *15*, 75.

[11] a) For example, cycloalkyne **8**, obtained by ring-closing diyne metathesis has been stereoselectively converted into the corresponding *Z*-configured cycloalkene by hydroboration with 9-H-9-BBN and subsequent protonation.[11b] The product thus obtained exhibits the following spectroscopic properties: ^{1}H NMR: $\delta = 5.46$ (t, 2H, $J = 4.5$ Hz); ^{13}C NMR: $\delta = 173.2$, 129.0, 63.3, 34.3, 27.3, 24.5; MS (CI): 244 (100) $[M+NH_4^+]$. Because of the symmetry of this molecule, the stereochemical assignment is based on the characteristic shift of its allylic C-atoms ($\delta = 27.3$). In the case of *Z*-alkenes these positions resonate in the range $\delta = 27-28$; but for *E*-alkenes in the range $\delta = 32-33$; cf.: E. Breitmaier, W. Voelter, *Carbon-13 NMR Spectroscopy*, 3rd ed., VCH, Weinheim, **1987**, 192. b) The hydroboration/protonation sequence is superior to Lindlar hydrogenation in terms of selectivity: A. Fürstner, G. Seidel, *J. Org. Chem*. **1997**, *62*, 2332.

[12] a) R. R. Schrock, D. N. Clark, J. Sancho, J. H. Wengrovius, S. M. Rocklage, S. F. Pedersen, *Organometallics* **1982**, *1*, 1645; b) See also J. H. Freudenberger, R. R. Schrock, M. R. Churchill, A. L. Rheingold, J. W. Ziller, *Organometallics* **1984**, *3*, 1563; c) M. L. Listemann, R. R. Schrock, *Organometallics* **1985**, *4*, 74.

[13] M. Akiyama, M. H. Chisholm, F. A. Cotton, M. W. Extine, D. A. Haitko, D. Little, P. E. Fanwick, *Inorg. Chem*. **1979**, *18*, 2266.

[14] GC and NMR investigations suggest that a single isomer is formed; however, we cannot yet determine whether it is the head–head or the head–tail connected cyclodimeric product.

[15] a) Review: H. Meier, *Synthesis* **1972**, 235. b) For a new synthesis of cycloalkynes and a compilation of the recent literature see J. Boivin, S. Huppé, S. Z. Zard, *Tetrahedron Lett*. **1995**, *36*, 5737. c) The formation of allenes as by-products is reported in A. T. Blomquist, R. E. Burge, A. C. Sucsy, *J. Am. Chem. Soc*. **1952**, *74*, 3636; d) W. R. Moore, R. C. Bertelson, *J. Org. Chem*. **1962**, *27*, 4182; e) W. H. Mandeville, G. M. Whitesides, *J. Org. Chem.* **1986**, *51*, 3257.

Methoxide Coordination at the Pocket of $[Cu^{II}Tp^{Cum,Me}]$ and a Simple Model for the Cu Center of Galactose Oxidase**

Michael Ruf and Cortlandt G. Pierpont*

Functionalized hydrotris(pyrazolyl)borate ligands (Tp^R) have been used to create protected transition metal coordination sites. Pyrazol nitrogen atoms resemble histidine donor groups, and the Tp^R complexes of Fe, Cu, and Zn have

[*] Prof. C. G. Pierpont, Dr. Michael Ruf
Department of Chemistry and Biochemistry
University of Colorado
Boulder, Colorado 80309
Fax: (+1) 303-492-0951
E-mail: cortlandt.pierpont@colorado.edu

[**] Support for this research was provided, in part, by the National Science Foundation and by the Cristol Fund. M.R. would like to thank the Deutsche Forschungsgemeinschaft for a Postdoctoral Research Fellowship

  1433-7851/98/3712-1736 $ 17.50+.50/0

provided both structural and functional models for bioinorganic metal ions.[1] Basic ancillary ligands located in the protected pocket may be displaced by protonation to create a vacancy at the metal center. Hydroxide ions have been used, but alkoxide ions offer advantages as they are stronger bases that lead to superior leaving groups. In this communication we describe the results of a study on methoxide coordination at the pocket formed by the cumenyl-functionalized Tp ligand in $\{Cu^{II}Tp^{Cum,Me}\}$, and the formation of a simple analogue for the copper center of galactose oxidase.

The addition of a methanolic solution of $Cu(ClO_4)_2$ to $\{KTp^{Cum,Me}\}$ dissolved in dichloromethane led to the formation of $[Cu\{Tp^{Cum,Me}Cu(\mu\text{-}OMe)_2\}_2]$ (**1**). Structural characterization shows that the complex consists of a linear arrangement of three Cu^{2+} ions.[2] At the center of the molecule, a planar $[Cu(OMe)_4]^{2-}$ anion is bridged to outer square-pyramidal $[CuTp^{Cum,Me}]^{+}$ cations (Figure 1). Basal methoxide oxygen

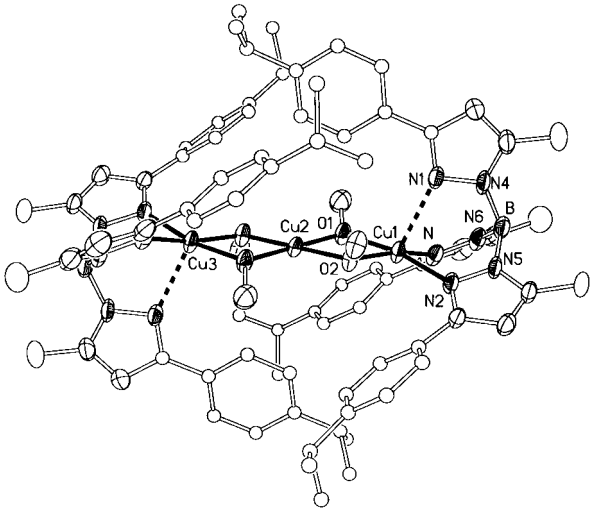
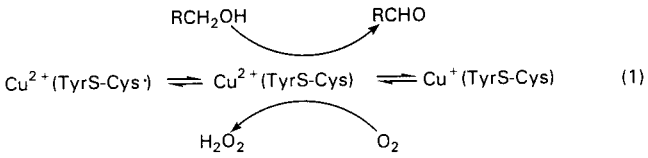


Figure 1. Solid state structure of **1**. Selected bond lengths [Å] and angles (°): Cu1 – O1 1.948(3), Cu1 – O2 1.947(3), Cu2 – O1 1.922(3), Cu2 – O2 1.917(3), Cu1 – N2 2.030(3), Cu1 – N3 2.038(3), Cu1 – N1 2.486(4), O1-Cu1-N2 165.2(1), O2-Cu1-N3 168.8(1).

atoms provide a mechanism for strong antiferromagnetic exchange between the metal centers, resulting in a temperature-invariant $S = ½$ magnetic moment of 1.82 μ_B for the complex. The molecule is EPR-silent at room temperature in the solid state and in toluene solution. In a toluene glass at temperatures below 100 K a weak, featureless signal appears at $g = 2.26$. The strong basicity of the methoxide ligands of (**1**) has been used to form the sulfanyl derivative $[Cu(Tp^{Cum,Me})\{O(MeS)C_6H_4\}]$ (**2**) on reaction with 2-(methylsulfanyl)phenol.

Fungal galactose oxidase (GOase) catalyzes dioxygen oxidation of primary alcohols to aldehydes.[3] It is among an interesting class of metalloenzymes that catalyze a two-electron oxidation process with a single redox active metal ion (copper in this case) at the active site. Crystallographic and EXAFS characterization have revealed that in the partially oxidized inactive ($GOase^{SEMI}$) and fully oxidized active ($GOase^{OX}$) forms of the enzyme the Cu^{II} ion has a square-pyramidal geometry.[4] An unusual cysteinyl-tyrosine ligand (Tyr272, Cys228) that is coordinated to the Cu center through the tyrosine oxygen atom at a basal site provides additional redox activity at the metal ion.[5] Two other basal sites are occupied by histidine nitrogen atoms, and the apical site contains the oxygen atom of a normal tyrosine molecule (Tyr495). The remaining basal site adjacent to the Tyr272 oxygen atom is the site of substrate coordination.[6] Oxidation of $GOase^{SEMI}$ to form active $GOase^{OX}$ occurs at the cysteinyl-tyrosine unit. Sykes has determined that the oxidation potential of this tyrosine molecule is unusually negative, 0.40 V (versus normal hydrogen electrode (NHE), pH 7.5),[5] where tyrosine and phenolate ligands typically undergo oxidation at potentials closer to 1.0 V.[9] Substrate oxidation occurs with dioxygen reduction [Eq. (1)].[10]



Metal coordination and the cysteinyl substituent both contribute to the negative shift in the oxidation potential of Tyr272, placing it at a value that enables reoxidation by dioxygen or superoxide in the activation step.

Structural characterization of the sulfanyl derivative (**2**) has shown that the Cu center has a square-pyramidal geometry in which the phenolate oxygen atom and two pyrazol nitrogen atoms occupy basal coordination positions (Figure 2).[11] The sulfur atom of the 2-(methylsulfanyl)phenolate ligand

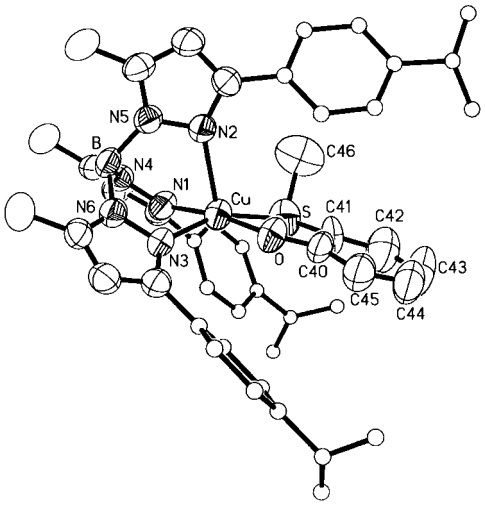


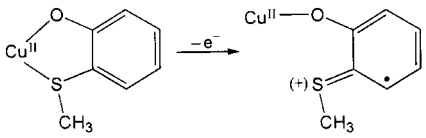
Figure 2. Crystal structure of **2**. Selected bond lengths [Å] and angles (°): Cu – O 1.900(4), Cu-S 2.394(2), Cu – N1 2.023(5), Cu – N3 2.026(5), Cu – N2 2.319(4), C40 – O 1.334(8), C41 – S 1.719(6), S – C46 1.795(8), C40 – C41 1.315(9), C41 – C42 1.456(9), C42 – C43 1.385(11), C43 – C44 1.318(11), C44 – C45 1.367(10), C40 – C45 1.447(9), O-Cu-N1 170.9(2)°, S-Cu-N3 157.7(1).

occupies the fourth basal site with a Cu – S bond length of 2.394(2) Å, a relatively short value for a thioether.[12] In this respect **2** differs from the enzymatic Cu center, but structural features and properties of the complex may provide insights on $GOase^{SEMI}$ and $GOase^{OX}$.

  1433-7851/98/3712-1737 $ 17.50+.50/0

Electrochemical characterization of **2** shows irreversible oxidation of the phenolate ligand at a potential of $+0.61$ V (CH_2Cl_2, vs. ferrocene/ferrocenium (Fc/Fc^+)). This value is more positive than the reduction potentials of pendant phenoxyl ligands that contain electron releasing alkyl substituents.[7, 13–15] Also, it is roughly 0.6 V more positive than the reduction potential of the enzymatic $GOase^{OX}$ tyrosyl group,[5] despite the structural similarity. A feature of the enzymatic site that may contribute to the more negative Tyr272 reduction potential is charge-transfer pairing with the indole ring of tryptophane-290.[6] The cumenyl substituent of the apical pyrazole ring of **2** could potentially form a similar interaction with the phenolate ring.[16] However, as the structure shows, the pairing interaction is blocked by the methyl group bonded to the sulfur atom, and the other isomeric form of the molecule, with the methyl substituent on the opposite face of the plane, is disfavored by interactions with other cumenyl substituents. Model studies indicate that the thiomethyl substituent may shift the coordinated phenolate oxidation potential by roughly -0.2 V.[15] The strong negative shift in the enzymatic reduction potential points to a profoundly important contribution from the tryptophane interaction.

Irreversibility in the oxidation of **2** may result from dissociation of the thioether sulfur atom from the Cu center in the oxidized form of the complex [Eq. (2)]. Oxidation to



(2)

the radical would then place increased positive charge on the sulfur atom. The solid state structure of the (methylsulfanyl)-phenolate unit of **2** shows that even in the reduced form there is considerable double bond character in the $C_{ring}-S$ bond. The distance between S and the ring carbon C41 is 1.719(6) Å, considerably shorter than the distance of 1.795(8) Å to the methyl carbon atom, and the C40–O length of 1.334(8) Å is not significantly different from the values of chelated catecholate ligands. Further, the phenolate ring shows a subtle, but significant, pattern of short and long C–C lengths. The C40–C41 bond and the opposite C43–C44 bond (1.315(9) and 1.318(11) Å, respectively) are nearly the length of localized double bonds. Adjacent C40–C45 and C41–C42 lengths are longer (1.456(9) and 1.447(9) Å,respectively) and the remaining two lengths in the ring are of intermediate values (1.367(10) and 1.385(11) Å).

A feature of **2** that sets it apart from the enzymatic center is the coordination of a sulfur atom at the site that would otherwise serve for enzymatic substrate binding. In fact, **2** is formed by displacement of methanol from this coordination site, and samples of the complex obtained from methanol show that the sulfur atom is not displaced from the metal atom by the alcohol. The plane of the Tyr272 phenyl ring of $GOase^{SEMI}$ is oriented perpendicular to the tetragonal plane of the Cu center.[6] Rotation of the Cys-228 sulfur atom into the substrate binding site would probably deactivate the enzyme. Instead, it is held away by the cysteine link to the protein, and also by the pairing interaction with Trp290.

The principal focus of interest in galactose oxidase has been the copper–(cysteinyl-tyrosine) interaction, but tryptophane-290 is essential for active site function. Molecular modeling has shown that it contributes to substrate selectivity through a hydrogen-bonding interaction with the ring oxygen of D-galactose.[8] Tryptophane-290 restricts rotation of the unique cysteinyl-tyrosine ligand preventing irreversible sulfur coordination at the active site, and the charge transfer interaction with the ring of Tyr272 places the reduction potential at a value that is appropriate for its oxidation by superoxide.

Experimental Section

1. $Cu(ClO_4)_2\cdot 6H_2O$ (429 mg, 15 mmol) dissolved in methanol (20 mL) was added to $\{KTp^{Cum,Me}\}$ (500 mg, 0.77 mmol)[17] dissolved in dichloromethane (15 mL). The mixture was stirred and the green precipitate that formed was separated by filtration. Compound **1** was obtained as a pale green microcrystalline solid in 78 % (460 mg) yield. Crystals suitable for crystallographic characterization were grown by slow evaporation of a saturated dichloromethane/methanol solution and obtained as the unstable dichloromethane solvate, $[Cu\{Tp^{Cum,Me}Cu(\mu\text{-}OMe)_2\}_2]\cdot 2CH_2Cl_2$.

2. Compound **1** (100 mg, 0.065 mmol) was combined with two equivalents of 2-(methylsulfanyl)phenol in a dichloromethane/methanol solution. The green-brown mixture was filtered to remove polymeric $Cu(OMe)_2$, and the filtrate was slowly evaporated to give dark blue-green crystals of **2** in 50 % (53 mg) yield. Elemental analysis calcd: C 68.0, H 6.5, N 10.3; found: C 67.8, H 6.9, N 10.2. UV/Vis (toluene): λ_{max} (ε) = 485 (1530), 756 nm (510); magnetic moment (292 K) 1.81 μ_B.

Received: January 5, 1998 [Z11318IE]
German version: *Angew. Chem.* **1998**, *110*, 1830–1832

Keywords: bioinorganic chemistry · coordination modes · copper · galactose oxidase · metalloenzymes

[1] a) K. Weis, H. Vahrenkamp, *Inorg. Chem.* **1997**, *36*, 5589; b) N. Kitajima, W. B. Tolman, *Prog. Inorg. Chem.* **1995**, *43*, 419.

[2] Crystallographic characterization of **1**: triclinic, space group $P\bar{1}$, a = 11.8856(4), b = 13.9361(5), c = 14.5955(5) Å, α = 72.265(1), β = 68.873(1), γ = 74.359°, V = 2112.9(1) Å^3 for Z = 1 at T = 168(2) K. Data were collected on a Siemens SMART diffractometer equipped with a CCD detection system. The structure was solved with direct methods. Refinement converged with $R(F)$ = 0.059 and $Rw(F^2)$ = 0.147.

[3] a) J. W. Whittaker in *Metal Ions in Biological Systems, Vol 30* (Eds.: H. Sigel, A. Sigel), Marcel Dekker, **1994**, p. 315; b) B. P. Branchaud, M. P. Montague-Smith, D. J. Kosman, F. R. McLaren, *J. Am. Chem. Soc.* **1993**, *115*, 798.

[4] a) N. Ito, S. E. V. Phillips, K. D. S. Yadav, P. F. Knowles, *J. Mol. Biol.* **1994**, *238*, 794; b) N. Ito, S. E. V. Phillips, C. Stevens, Z. B. Ogel, M. J. McPherson, J. N. Keen, K. D. S. Yadav, P. F. Knowles, *Nature*, **1991**, *350*, 87; c) P. F. Knowles, R. D. Brown III, S. H. Koenig, S. Wang, R. A. Scott, M. A. McGuirl, D. E. Brown, D. M. Dooley, *Inorg. Chem.* **1995**, *34*, 3895.

[5] C. G. Saysell, C. D. Borman, A. J. Baron, M. J. McPherson, A. G. Sykes, *Inorg. Chem.* **1997**, *36*, 4520.

[6] Views of the copper coordination sphere derived from crystallographic coordinates, including tryptophane-290, have been reproduced in recent references by Wieghardt et al.[7a] and Wachter and Branchaud (a stereoview).[8]

[7] a) A. Sokolowski, J. Müller, T. Weyhermüller, R. Schnepf, P. Hildebrandt, K. Hildenbrand, E. Bothe, K. Wieghardt, *J. Am. Chem. Soc.* **1997**, *119*, 8889; b) B. Adam, E. Bill, E. Bothe, B. Goerdt, G.

  1433-7851/98/3712-1738 $ 17.50+.50/0

Haselhorst, K. Hildenbrand, A. Sokolowski, S. Steenken, T. Weyhermüller, K. Wieghardt, *Chem. Eur. J.* **1997**, *3*, 308;
[8] R. M. Wachter, B. P. Branchaud, *J. Am. Chem. Soc.* **1996**, *118*, 2782.
[9] a) K. E. Silva, T. E. Elgreen, L. Que, Jr., M. T. Stankovich, *Biochemistry* **1995**, *34*, 14093; b) D. P. Goldberg, S. J. Lippard in *Mechanistic Bioinorganic Chemistry* (Eds.: H. H. Thorp, V. L. Pecoraro) Adv. in Chem. Ser. **1995**, *246* p. 61.
[10] Details of substrate oxidation have recently appeared in a) R. M. Wachter, M. P. Montague-Smith, B. P. Branchaud *J. Am. Chem. Soc.* **1997**, *119*, 7743; b) Y. Wang, J. L. DuBois, B. Hedman, K. O. Hodgson, T. D. P. Stack, *Science* **1998**, *279*, 537.
[11] Crystallographic characterization of **2**: monoclinic, space group $C2/c$, $a = 35.0680(15)$, $b = 11.4263(5)$, $c = 22.8923(10)$ Å, $\alpha = 106.677(1)^\circ$, $V = 8787.1(7)$ Å^3 for $Z = 8$ at $T = 295(2)$ K. Data were collected on a Siemens SMART diffractometer equipped with a CCD detection system. The structure was solved with direct methods. Refinement converged with $R(F) = 0.068$ and $Rw(F^2) = 0.165$. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-101243. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).
[12] Whittaker has described [Cu(pmdt){(methylthio)cresol}]$^+$ (pmdt-pentamethyldiethylenetriamine) as a potential model for the Cu site of GOase^{SEMI}. The coordination geometry is trigonal bipyramidal with a relatively long Cu–S bond length of 2.55 Å. See M. M. Whittaker, Y.-Y. Chuang, J. W. Whittaker, *J. Am. Chem. Soc.* **1993**, *115*, 10029.
[13] a) J. A. Halfen, V. G. Young, W. B. Tolman, *Angew. Chem.* **1996**, *108*, 1832; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 1687; b) J. A. Halfen, B. A. Jazdzewski, S. Mahapatra, L. M. Berreau, E. C. Wilkinson, L. Que, Jr., W. B. Tolman, *J. Am. Chem. Soc.* **1997**, *119*, 8217.
[14] M. M. Whittaker, W. R. Duncan, J. W. Whitaker, *Inorg. Chem.* **1996**, *35*, 382.
[15] S. Itoh, S. Takayama, R. Arakawa, A. Furuta, M. Komatsu, A. Ishida, S. Takamuku, S. Fukuzumi, *Inorg. Chem*. **1997**, *36*, 1407.
[16] See for example the structure of [Cu(Tp^{Ph})(pterin)]: J. Perkinson, S. Brodie, K. Yoon, K. Mosny, P. J. Carroll, T. V. Morgan, S. J. Nieter Burgmayer, *Inorg. Chem.* **1991**, *30*, 719.
[17] M. Ruf, H. Vahrenkamp, *Inorg. Chem.* **1996**, *35*, 6571.

  1433-7851/98/3712-1739 $ 17.50+.50/0