tion. The critical *anti*-selective crotylation reaction was then carried out to establish the relative configuration at the C6 and C7 centers. This double stereodifferentiating[13] reaction was readily accomplished with $TiCl_4$ to afford homoallylic alcohol **11** with high levels of diastereoselectivity (*anti*:*syn* $>30:1$) and in 50–60% yield. This *anti*-bond construction was presumably achieved through simultaneous coordination of the aldehyde oxygen atom and the nitrogen atom in the oxazoline ring. The 1,3-relationship of the heteroatoms ideally predisposes the more Lewis basic nitrogen atom relative to the aldehyde carbonyl group to generate a 5-membered chelate with $TiCl_4$ via the illustrated synclinal transition state (Scheme 3).[14] Oxidative cleavage of (*E*)-olefin **11** under standard ozonolysis conditions and subsequent oxidation with sodium chlorite[15] furnished carboxylic acid **3**.

The completion of (+)-lactacystin was initiated by catalytic transfer hydrogenation of the oxazoline moiety with Pd-black to give the γ-lactam methyl ester after cyclization. Saponification of the methyl ester under mild conditions afforded the dihydroxy acid, which was directly converted into β-lactone **2** by treatment with bis(2-oxo-3-oxazolidinyl)phosphinic chloride (BOPCl). We employed the lactone opening strategy developed by Corey et al. to attach the *N*-acetyl-L-cysteine side chain.[5b] Treatment of **2** with *N*-acetyl-L-cysteine/Et_3N furnished synthetic (+)-**1** identical in all respects to the natural product (^1H and ^{13}C NMR, IR spectroscopies, HR-MS, optical rotation, and TLC).[5b]

Received: October 20, 1998 [Z12551]
German version: *Angew. chem.* **1999**, *111*, 1161–1163

Keywords: asymmetric synthesis · enzyme inhibitors · lactacystin · lactones · total synthesis

[1] a) S. Omura, T. Fujimoto, K. Otoguro, K. Matsuzaki, R. Moriguchi, H. Tanaka, Y. Sasaki, *J. Antibiot.* **1991**, *44*, 113–116. b) S. Omura, K. Matsuzaki, T. Fujimoto, K. Kosuge, T. Furuya, S. Fujita, A. Nakagawa, *J. Antibiot.* **1991**, *44*, 117–118.

[2] E. M. Conner, S. Brand, J. M. Davis, F. S. Laroux, V. J. Palombella, J. W. Fuseler, D. Y. Kang, R. E. Wolf, M. B. Grisham, *J. Pharm. Exp. Therap.* **1997**, *282*, 1615–1622.

[3] a) G. Fenteany, R. F. Standaert, W. S. Lane, S. Choi, E. J. Corey, S. L. Schreiber, *Science* **1995**, *268*, 726–731. b) L. R. Dick, A. A. Cruikshank, L. Grenier, F. D. Melandri, S. L. Nunes, R. L. Stein, *J. Biol. Chem.* **1996**, *271*, 7273–7275. c) J. A. Adams, R. Stein, *Ann. Rep. Med. Chem.* **1996**, *31*, 279–288.

[4] M. Groll, L. Ditzel, J. Löwe, D. Stock, M. Bochtler, H. D. Bartunik, R. Huber, *Nature* **1997**, *386*, 463–471.

[5] a) E. J. Corey, G. A. Reichard, *J. Am. Chem. Soc.* **1992**, *114*, 10677–10678; b) E. J. Corey, W. Li, G. A. Reichard, *J. Am. Chem. Soc.* **1998**, *120*, 2330–2336; c) E. J. Corey, W. Li, T. Nagamitsu, *Angew. Chem.* **1998**, *110*, 1784–1787; *Angew. Chem. Int. Ed.* **1998**, *37*, 1676–1679; d) H. Uno, J. E. Baldwin, A. T. Russell, *J. Am. Chem. Soc.* **1994**, *116*, 2139–2140; e) T. Nagamitsu, T. Sunazuka, S. Omura, P. A. Sprengler, A. B. Smith III, *J. Am. Chem. Soc.* **1996**, *118*, 3584–3590; f) N. Chida, J. Takeoka, N. Tsutsumi, S. Ogawa, *J. Chem. Soc. Chem. Commun.* **1995**, 793–794. See also E. J. Corey, S. Choi, *Tetrahedron Lett.* **1993**, *34*, 6969–6972; E. J. Corey, W. Z. Li, *Tetrahedron Lett.* **1998**, *39*, 7475–7478.

[6] C. E. Masse, J. S. Panek, *Chem. Rev.* **1995**, *95*, 1293–1316.

[7] a) T. Sunazuka, T. Nagamitsu, H. Tanaka, S. Omura, P. A. Sprengler, A. B. Smith III, *Tetrahedron Lett.* **1993**, *34*, 4447–4448; b) E. J. Corey, D.-H. Lee, S. Choi, *Tetrahedron Lett.* **1992**, *33*, 6735–6738; c) C. G. Caldwell, S. S. Bundy, *Synthesis* **1990**, 34–36; d) M. E. Jung, Y. H. Jung, *Tetrahedron Lett.* **1989**, *30*, 6636–6640; e) D. A. Evans, E. B. Sjogren, A. E. Weber, R. E. Conn, *Tetrahedron Lett.* **1987**, *28*, 39–43. For an earlier approach to the hydroxyleucine synthon developed in our laboratories, see J. S. Panek, C. E. Masse, *J. Org. Chem.* **1998**, *63*, 2382–2384.

[8] B. Tao, G. Schlingloff, K. B. Sharpless, *Tetrahedron Lett.* **1998**, *39*, 2507–2510; G. Li, H. H. Angert, K. B. Sharpless, *Angew. Chem.* **1996**, *108*, 2995–2999; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 2837–2841. See also P. O'Brien, *Angew. Chem.* **1999**, *111*, 339–342; *Angew. Chem. Int. Ed.* **1999**, *38*, 326–329.

[9] D. Seebach, E. Hungerbühler, R. Naef, P. Schnurrenberger, B. Weidmann, M. Züger, *Synthesis* **1982**, 138–141.

[10] R. A. Moss, T. B. K. Lee, *J. Chem Soc. Perkin Trans. 1* **1973**, 2778–2781.

[11] D. Seebach, J. D. Aebi, *Tetrahedron Lett.* **1983**, *24*, 3311–3314.

[12] K. E. Pfitzner, J. G. Moffatt, *J. Am. Chem. Soc.* **1965**, *87*, 5661–5669.

[13] S. Masamune, W. Choy, J. S. Peterson, L. R. Sita, *Angew. Chem.* **1985**, *97*, 1–31; *Angew. Chem. Int. Ed. Engl.* **1985**, *24*, 1–30.

[14] For similar bond constructions of the silane reagents with oxazoles, see P. Liu, J. S. Panek, *Tetrahedron Lett.* **1998**, *39*, 6143–6146.

[15] E. J. Corey, A. G. Myers, *J. Am. Chem Soc.* **1985**, *107*, 5574–5576.

Aerobic Oxidation of Primary Alcohols by a New Mononuclear Cu^{II}-Radical Catalyst[**]

Phalguni Chaudhuri,[*] Martina Hess,
Thomas Weyhermüller, and Karl Wieghardt[*]

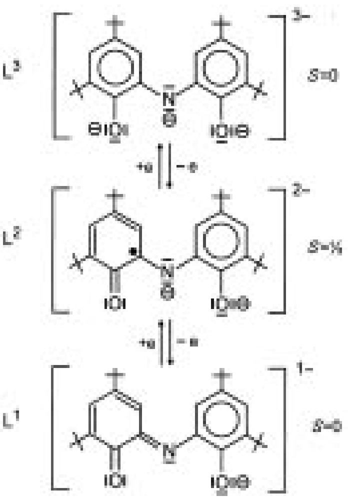
Recently we reported[1] a dinuclear Cu^{II}-phenoxyl radical complex, which catalyzes efficiently the aerobic oxidation of primary and secondary alcohols to the corresponding aldehydes and ketones or to 1,2-glycols by oxidative C–C coupling with concomitant formation of H_2O_2. This complex together with that of Stack et al.[2] are the first reported functional models for the enzyme galactose oxidase (GO).[3] We report here a new mononuclear Cu^{II}-iminosemiquinone catalyst that selectively transforms primary alcohols (e.g. ethanol but not methanol) with O_2 to aldehydes and H_2O_2; secondary alcohols are not at all substrates for the catalyst.

The trifluoroacetate salt of the cation *N*,*N*-bis(2-hydroxy-3,5-di-*tert*-butylphenyl)ammonium $[H_4(L^3)](CF_3CO_2)$ was prepared through the condensation of 3,5-di-*tert*-butylcatechol with NH_3 in *n*-heptane and subsequent acidification with trifluoroacetic acid. It is known[4] that the diamagnetic trianion $(L^3)^{3-}$ (Scheme 1), present as a tridentate ligand in complexes, can be easily oxidized to the radical dianion $(L^2)^{2-}$ and then to the diamagnetic monoanion $(L^1)^{1-}$ in two successive one-electron oxidation steps. Speier and Pierpont et al. have, for example, described the complexes $[Cu^{II}(L^1)_2]$

---

[*] Priv.-Doz. Dr. P. Chaudhuri, Prof. Dr. K. Wieghardt, M. Hess, Dr. T. Weyhermüller
Max-Planck-Institut für Strahlenchemie
Stiftstrasse 34–36, D-45470 Mülheim an der Ruhr (Germany)
Fax: (+49) 208-306-3952
E-mail: chaudh@mpi-muelheim.mpg.de
wieghardt@mpi-muelheim.mpg.de

[**] This work was supported by the Degussa AG, Frankfurt, and the Fonds der Chemischen Industrie.



Scheme 1.

and $[Cu^{II}(L^2)(pyridine)_2]$.[5] In absence of air $[H_4(L^3)](CF_3CO_2)$ reacts with $[Cu^I(NCCH_3)_4]ClO_4$ in CH_3CN in the presence of excess NEt_3 to yield a yellow solution, which upon exposure to air at 20 °C provides the neutral complex $[Cu^{II}(L^2)(NEt_3)]$ (**1**) as green-black crystals.

On the contrary, a solution of Cu^ICl and $[H_4(L^3)](CF_3CO_2)$ (1:1) neutralized by NEt_3 in CH_3OH upon treatment with pure dry O_2 at −50 to −70 °C yields deep red crystals of $[Cu^{II}(L^3H_2)(O_2^{\bullet -})(NEt_3)]$ (**2**). Compound **2** is diamagnetic (2–300 K) due to strong intramolecular antiferromagnetic coupling between the Cu^{II} ion and the bonded superoxide ion. The $Cu^{II}(O_2^{\bullet -})$ moiety exhibits typical charge transfer absorptions at 524 and 650 nm and an infrared stretch $\tilde{\nu}(^{16}O-^{16}O)$ at 964 cm^{-1}, which on ^{18}O-labeling drops[6] to 909 cm^{-1}. Complex **2** can be directly prepared by adding 100-fold excess of H_2O_2 to a green solution of **1** in dry methanol. On the other hand, a solution of **2** in tetrahydrofuran (THF) at 20 °C forms **1** and H_2O_2 due to the equilibrium (1).

$$\mathbf{2} \rightleftarrows \mathbf{1} + H_2O_2 \qquad (1)$$

The X-ray structure[7] of **1** shows that the Cu^{II} ion, coordinated to the tridentate $(L^2)^{2-}$ ligand along with an NEt_3 molecule, is in a slightly distorted square-planar N_2O_2 environment (Figure 1).[8] The metrical parameters of $(L^2)^{2-}$ correspond to those for the reported $[M^{IV}(L^2)_2]$ complexes (M = V, Ti, Sn).[4d, 9] That **1** possesses a diamagnetic ground state ($S = 0$) arising from the intramolecular antiferromagnetic coupling between the spins of radical–ligand ($S_L^2 = 1/2$) and that of the Cu^{II} ion ($S_{Cu} = 1/2$) has been shown by variable-temperature susceptibility measurements (SQUID, 2–400 K)[10] on solid **1**. This behavior is in accordance with that of the active form of GO, in which a Cu^{II} ion is coordinated to a tyrosyl radical.

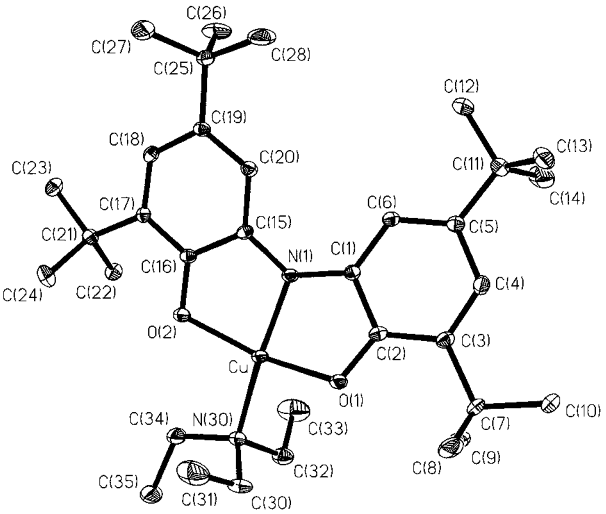


Figure 1. Crystal structure of the neutral complex **1**. Selected bond lengths [Å] and angles [°]: Cu–N(1) 1.906(2), Cu–O(1) 1.926(1), Cu–O(2) 1.959(1), Cu–N(30) 2.010(2), O(1)–C(2) 1.322(2), O(2)–C(16) 1.310(2), N(1)–C(1) 1.384(2), N(1)–C(15) 1.358(2); N(1)-Cu-O(1) 83.83(6), N(1)-Cu-O(2) 83.34(6), O(1)-Cu-O(2) 159.73(6), N(1)-Cu-N(30) 168.13(7), O(1)-Cu-N(30) 96.08(6), O(2)-Cu-N(30) 99.68(6).

The cyclic voltammogram of **1** in CH_2Cl_2 (0.1 M $[(nBu)_4N]PF_6$, glassy carbon electrode, 20 °C) exhibits two reversible one-electron processes at $E^1_{1/2} = -0.14$ V and $E^2_{1/2} = -1.06$ V versus Fc^+/Fc in the potential range +0.2 to −1.3 V. Spectroelectrochemical measurements on the oxidized and reduced forms, generated by coulometry of **1**, show the redox processes to be ligand-centered, as shown in Equation (2). In the absence of protons the Cu^{II} ion is reduced at even more negative potentials.

$$[Cu^{II}(L^1)(NEt_3)]^+ \underset{-e,\,E^1_{1/2}}{\overset{+e}{\rightleftharpoons}} [Cu^{II}(L^2)(NEt_3)]^0 \underset{-e,\,E^2_{1/2}}{\overset{+e}{\rightleftharpoons}} [Cu^{II}(L^3)(NEt_3)]^- \qquad (2)$$

Under anaerobic conditions at 20 °C, a solution of **1** in THF oxidizes stoichiometrically benzyl and ethyl alcohol—but not isopropyl alcohol or methanol—to the corresponding aldehydes [Eq. (3)], while **1** itself undergoes a two-electron reduction process forming most probably $[Cu^I(L^3H_2)(NEt_3)]$.

$$RCH_2OH + \mathbf{1} \rightarrow RCHO + [Cu^I(L^3H_2)(NEt_3)] \qquad (3)$$

On the other hand, as $[Cu^I(L^3H_2)(NEt_3)]$ in THF or CH_2Cl_2 reacts with molecular O_2 to yield at first **2** and subsequently slowly **1** and H_2O_2 [Eq. (4) and (5)], the combination of Equations (3)–(5), in principle, leads to the homogeneously catalyzed oxidation of primary alcohols [Eq. (6)].

$$[Cu^I(L^3H_2)(NEt_3)] + O_2 \xrightarrow{\text{fast}} [Cu^{II}(L^3H_2)(O_2^{\bullet -})(NEt_3)] \qquad (4)$$

$$\mathbf{2} \xrightarrow{\text{slow}} [Cu^{II}(L^2)(NEt_3)] + H_2O_2 \qquad (5)$$

$$RCH_2OH + O_2 \xrightarrow{\text{[catalyst]}} RCHO + H_2O_2 \qquad (6)$$

This is, indeed, the case. A THF solution of **1** (or $[Cu^I(L^3H_2)(NEt_3)]$) ($[Cu]_t = 2.65 \times 10^{-5}$ M) mixed with benzyl alcohol or ethanol (0.125 M) as substrate, provides after stirring in open air at 20 °C for 20 h the corresponding aldehyde in an overall yield of about 55 %. The catalysis can also be performed in neat alcohols without any additional solvent. The gas chromatographic product analysis established aldehydes as the sole oxidation product; no formation of carboxylic acid or oxidative C–C coupling[1] products (> 1 %)

was observed. The catalyst does not show any catalase activity: disproportionation of H_2O_2 does not occur.

From the measurements of the kinetics[11] of these catalytic reactions the rate law [Eq. (7)] has been derived which establishes a mononuclear copper complex to be the active

$$v = k[\mathrm{Cu}]_t[\text{alcohol}] \qquad [\mathrm{NEt_3}] = 2\times10^{-3}\,\mathrm{M} = \text{const.} \tag{7}$$

form of the catalyst, as is found also in the compound described by Stack et al.[2] and in GO.[1] With the selectively deuterated substrates $PhCD_2OH$ and CH_3CD_2OH kinetic isotope effects k_H/k_D of about 8 have been evaluated. As for other functional models[1, 2] and GO,[3] hydrogen abstraction from the α-carbon atom of the coordinatively bound alcoholate is apparently also in this case the rate-determining step. The turnover frequency for **1** in neat alcohol of $0.5\ s^{-1}$ is somewhat bigger than that of the system described by Stack et al. for the oxidation of benzyl alcohol (ca. $0.005\ s^{-1}$); the catalysis proceeds overall relatively slowly.

Figure 2 shows that the rate of aldehyde formation increases with increasing [NEt_3] concentration until a maximum is reached and then starts to decrease. An excess of NEt_3 inhibits the catalysis. Our qualitative (and speculative) interpretation of this behavior is as follows: In absence of excess NEt_3, the monodentate ligand NEt_3 dissociates from **1** in THF [Eq. (8)], while in presence of excess NEt_3 the five-coordinate complex [$Cu^{II}(L^2)(NEt_3)_2$] is formed [Eq. (9)].

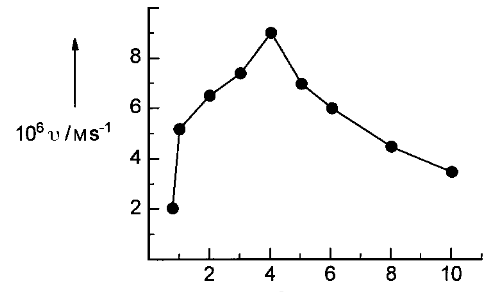


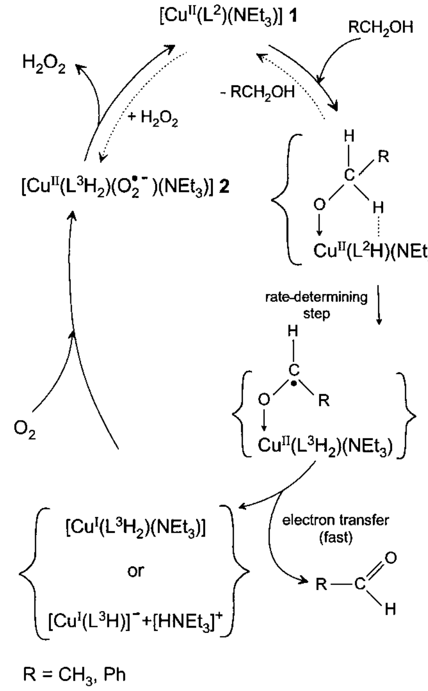
Figure 2. Effect of the concentration of base [NEt_3] on the catalytic rate. Experimental conditions: [Cu^ICl] = 2.5×10^{-4} M (constant), [H_4L^3] = 2.5×10^{-4} M (constant), [benzyl alcohol] = 0.125 M (constant), [NEt_3] = (1.0–10.0) × 10^{-3} M in THF at 20 °C and 1 atm air. Formation of benzaldehyde as a function of time was quantitatively determined.

$$[\mathrm{Cu^{II}(L^2)(NEt_3)}] + \mathrm{THF} \rightleftharpoons [\mathrm{Cu^{II}(L^2)(THF)}] + \mathrm{NEt_3} \tag{8}$$

$$[\mathrm{Cu^{II}(L^2)(NEt_3)}] + \mathrm{NEt_3} \rightleftharpoons [\mathrm{Cu^{II}(L^2)(NEt_3)_2}] \tag{9}$$

As [$Cu^{II}(L^2)(NEt_3)_2$] and [$Cu^{II}(L^2)(THF)$] (or its dimeric form, detected by ESI-MS) are catalytically inactive, there is a particular NEt_3 concentration, at which the catalytically active form **1** is present in the highest concentration. If the experimental concentration of NEt_3 is smaller than that at the maximum, the catalysis becomes slowed down by increasing formation of the monomeric dissociation product (or its dimer); a higher concentration of NEt_3 than that at the maximum results in more adduct formation also causing slow catalysis or even complete inhibition.

Our mechanistic proposal for the catalysis is displayed in Scheme 2. At the beginning **1** binds an alcohol; in the rate-determining step hydrogen-atom transfer from the α-C atom of the alcoholate ligand to the radical–ligand $(L^2H)^-$ occurs, in which it is reduced to $(L^3H_2)^-$. The resulting coordinated ketyl radical anion, a strong one-electron reducing agent, transfers very fast an electron to the Cu^{II} ion, during which the "bad" ligand aldehyde is formed and dissociates. The Cu^I form can now react with O_2 to form the Cu^{II} superoxide complex **2**, which then provides noncoordinated H_2O_2 and regenerates the active form **1**.



Scheme 2. Proposed mechanism for the catalysis.

Experimental Section

N,N-Bis(2-hydroxy-3,5-di-*tert*-butylphenyl)ammonium trifluoroacetate (2.7 g, 48 %) [H_4L^3](CF_3CO_2) was obtained as a violet solid through the condensation of 3,5-di-*tert*-butylcatechol (5 g) with 25 % aqueous ammonia (0.75 mL) in *n*-heptane (50 mL) under an argon atmosphere (48 h stirring at 20 °C) and subsequent addition of trifluoroacetic acid (20 mL) and H_2O (50 mL). The crude product was washed several times thoroughly with *n*-pentane to yield a colorless product, which is slightly light-sensitive but strongly O_2-sensitive. Remark: For the following syntheses and catalysis only the colorless pure product should be used. C, H, N analyses (%; $C_{30}H_{44}F_3NO_4$): calcd (found): C 66.64 (66.34), H 8.39 (8.30), N 2.59 (2.48); EI-MS: m/z: 425 [M^+]; ^1H NMR ($CDCl_3$): $\delta = 7.11$ (s, 2 H), 6.83 (s, 2 H), 5.61 (s, br, 4 H; OH, NH_2), 1.44 (s, 18 H, $C(CH_3)_3$), 1.22 (s, 18 H, $C(CH_3)_3$).

1: A solution of [$Cu^I(NCCH_3)_4$](ClO_4) (0.16 g, 0.5 mmol), [H_4L^3]CF_3CO_2 (0.272 g, 0.5 mmol), and triethylamine (0.5 mL) was refluxed in dry CH_3CN (50 mL) for 0.5 h under argon. Exposure of the resulting pale yellow solution to air at about 20 °C initiated a color change to deep green, from which within 1 h green-black crystals of **1** precipitated (0.21 g, 71 %). C, H, N, Cu analyses (%; $C_{34}H_{55}N_2O_2Cu$): calcd (found): C 69.52 (69.73), H 9.23 (9.22), N 4.77 (4.62), Cu 10.81 (10.63).

2: A solution of Cu^ICl (0.10 g, 1.0 mmol) [$H_4(L^3)$](CF_3CO_2) (0.54 g, 1.0 mmol) and NEt_3 (0.5 mL, 3.5 mmol) in dry CH_3OH (50 mL) was heated to boiling for a short time under argon and then cooled to a temperature in the range of -50 to $-70\,^{\circ}C$ and treated with pure O_2 to yield a deep red solution. Within 5–10 min a precipitation of a deep red microcrystalline substance **2** (0.12 g; 19%) occurred. An alternative method for crystallizing **2** was to add 30% H_2O_2 (0.26 mL) to a solution of **1** (160 mg, 2.23 mmol) in CH_3OH (25 mL) at $-80\,^{\circ}C$. C, H, N, Cu analyses (%; $C_{34}H_{57}N_2O_4Cu$): calcd (found): C 65.72 (65.45), H 9.25 (9.23), N 4.51 (4.52), Cu 10.23 (10.20); UV/Vis (CH_2Cl_2): λ_{max} [nm] (ε [$L\,mol^{-1}\,cm^{-1}$]) = 391 (2.1×10^3), 423 (1.8×10^3), 524 (2.1×10^3), 649 (1.6×10^3); ^1H NMR (CD_2Cl_2, 400 MHz): $\delta = 0.99$ (t, 9H), 1.18 (s, 18H), 1.29 (s, 18H), 1.80 (br. s, 2H), 2.50 (dt, 6H), 7.20 (s, 2H), 7.33 (s, 2H).

Received: November 26, 1998 [Z12714IE]
German version: *Angew. Chem.* **1999**, *111*, 1165–1168

Keywords: alcohols · copper · galactose oxidase · homogeneous catalysis · metalloenzymes

---

[1] P. Chaudhuri, M. Hess, U. Flörke, K. Wieghardt, *Angew. Chem.* **1998**, *110*, 2340; *Angew. Chem. Int. Ed.* **1998**, *37*, 2217.

[2] Y. Wang, J. L. DuBois, B. Hedman, K. O. Hodgson, T. D. P. Stack, *Science* **1998**, *279*, 537.

[3] a) J. W. Whittaker in *Metal Ions in Biological Systems, Vol. 30* (Eds.: H. Sigel, A. Sigel), Marcel Dekker, New York, **1994**, pp. 315–360; b) P. F. Knowles, N. Ito in *Perspectives in Bio-inorganic Chemistry, Vol. 2* (Eds.: R. W. Hay, J. R. Dilworth, K. B. Nolan), Jai, London, **1994**, pp. 207–244; c) H.-J. Krüger, *Angew. Chem.* **1999**, *111*, 659; *Angew. Chem. Int. Ed.* **1999**, *38*, 627.

[4] a) A. Y. Girgis, A. L. Balch, *Inorg. Chem.* **1975**, *14*, 2724; b) E. L. Simpson, S. R. Boone, C. G. Pierpont, *Inorg. Chem.* **1989**, *28*, 4379; c) S. K. Larsen, C. G. Pierpont, *J. Am. Chem. Soc.* **1988**, *110*, 1827; d) S. Bruni, A. Caneschi, F. Cariati, C. Delfs, A. Dei, D. Gatteschi, *J. Am. Chem. Soc.* **1994**, *116*, 1388.

[5] G. Speier, J. Csihony, A. M. Whalen, C. G. Pierpont, *Inorg. Chem.* **1996**, *35*, 3519.

[6] Kitajima et al. have reported the structure of the mononuclear, diamagnetic superoxocopper(II) complex $[Cu^{II}(O_2^{\bullet -})(HB(3\text{-}t\text{Bu-}5\text{-}i\text{Pr-pyrazole})_3)]$ with a coordinated $O_2^{\bullet -}$ ligand in "side-on" mode ($\tilde{\nu}(^{16}O_2)$ 1111 cm^{-1} and $\tilde{\nu}(^{18}O_2)$ 1062 cm^{-1}): K. Fujisawa, M. Tanaka, Y. Moro-oka, N. Kitajima, *J. Am. Chem. Soc.* **1994**, *116*, 12079. We consider **2** to contain an "end-on" coordinated $O_2^{\bullet -}$, which is evident from the isotope labeling of **2** with $^{16}O-^{18}O$. A broad asymmetric band for $\tilde{\nu}(Cu\text{-}^{16}O\text{-}^{18}O)$ at 939 cm^{-1} (due to superposition of two bands at 942 and 932 cm^{-1} for the isotopomers $Cu^{16}O\text{-}^{18}O$ and $Cu\text{-}^{18}O\text{-}^{16}O$, respectively, is observed. a) A. Nakamura, Y. Tatsuno, M. Yamamoto, S. Otsuka, *J. Am. Chem. Soc.* **1971**, *93*, 6052; b) J. E. Pate, R. W. Cruse, K. D. Karlin, E. I. Solomon, *J. Am. Chem. Soc.* **1987**, *109*, 2624. The single structurally characterized hydroperoxocopper(II) complex $[Cu^{II}(bppa)(OOH)]^+$ (bppa = bis(6-pivalamide-2-pyridylmethyl)(2-pyridylmethyl)amine) exhibits a $\tilde{\nu}(^{16}O_2)$ stretch at 856 cm^{-1} ($\tilde{\nu}(^{18}O_2) = 810\ cm^{-1}$): A. Wada, M. Harata, K. Hasegawa, K. Jitsukawa, M. Masuda, M. Mukai, T. Kitagawa, H. Einaga, *Angew. Chem.* **1998**, *110*, 874; *Angew. Chem. Int. Ed. Engl.* **1998**, *37*, 798.

[7] Crystal structure determination of **1**: green-black crystal ($0.53 \times 0.40 \times 0.24\ mm^3$); $C_{34}H_{55}CuN_2O_2$, $M_r = 587.3$; orthorhombic space group *I*ba2, $a = 23.151(3)$, $b = 25.143(3)$, $c = 11.747(2)$ Å, $V = 6837(2)$ Å^3, $Z = 8$, $T = 100(2)$ K, $\rho_{calcd} = 1.141\ g\,cm^{-3}$; $\mu_{Mo} = 0.668\ mm^{-1}$; semiempirical absorption correction, full-matrix, least-squares refinement on F^2 with 9397 reflections [$I > 2.0\sigma(I)$] and 348 variables, final R values: $R(F) = 0.036$ and $wR2 = 0.075$. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-109500. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

[8] X-ray analysis reveals an asymmetric electron density distribution in the $Cu(L^2)$ moiety of **1**. The C–N bond lengths are different owing to a substantial portion of double-bond character in N(1)–C(15) (1.358(2) Å). This description is additionally supported by the EPR spectra of the isostructural Zn^{II} complex, $[Zn(L^2)(NEt_3)]$, in which there is significantly different spin density at the two *para* carbon atoms with respect to the imino nitrogens. P. Chaudhuri, M. Hess, K. Hildenbrand, E. Bill, T. Weyhermüller, K. Wieghardt, *Inorg. Chem.* submitted.

[9] A. Bencini, I. Ciofini, E. Giannasi, C. A. Daul, K. Doclo, *Inorg. Chem.* **1998**, *37*, 3719.

[10] The temperature-dependent magnetic moments for **1** were fitted without problem to the theoretical curve based on the exchange Hamiltonian $\boldsymbol{H} = -2J\mathbf{S}_{Cu}\mathbf{S}_{Lig.}$ ($S_{Cu} = S_{Lig} = ½$) for evaluating the exchange coupling constant $J = -137\ cm^{-1}$: In an idealized C_{2v} symmetry a substantial portion of the antibonding effect of the original e_g orbitals is removed to the metal–ligand bond, together with a mixing of metal x and z components in the orbitals of the molecule. Thus the unpaired electron of Cu in **1** residing in a $2a_1$ orbital can overlap with the half-occupied π orbital of the radical ligand resulting in antiferromagnetic coupling. T. A. Albright, J. K. Burdett, M. H. Whangbo, *Orbital Interactions in Chemistry*, Wiley-Interscience, New York, **1985**. Compound **2** is diamagnetic ($S = 0$) in the temperature range 2–300 K.

[11] Kinetic experiments were performed at 20 °C in an open vessel with stirring under air. Formation of aldehydes (GC/^1H NMR) and H_2O_2 (spectrophotometry)[1] was monitored (initial-rate method) as a function of time: $[CuCl] = [\{H_4(L^3)\}(CF_3CO_2)] = 7.5 \times 10^{-4} - 7.5 \times 10^{-3}\,M$; [alcohol] = 0.025–1.25 M; $[NEt_3] = 2.0 \times 10^{-3}\,M$ = constant.

Synthesis, Structure, and Redox Properties of $[\{(\eta^5\text{-}C_5H_5)Co(S_2C_6H_4)\}_2Mo(CO)_2]$, a Novel Metalladithiolene Cluster**

Masayuki Nihei, Takuya Nankawa, Masato Kurihara, and Hiroshi Nishihara*

Dithiolato complexes of late transition metals exhibit interesting physical and chemical properties such as reversible redox activity, deep colors,[1] and various substitution and addition reactions due to the quasiaromaticity and electronic unsaturation of the metalladithiolene ring.[2] However, no reports on metal–metal bond formation by metalladithiolene complexes are available to our knowledge. Here we report the first formation of a cluster from a cobalt dithiolene complex, namely, $[CoCp(S_2C_6H_4)]$ (**1**, Cp = η^5-C_5H_5), by reaction with $[Mo(CO)_3(py)_3]$ and BF_3 to give $[\{CpCo(S_2C_6H_4)\}_2Mo(CO)_2]$ (**2**), which has an almost linear Co-Mo-Co arrangement and four μ-S bridges. It can be regarded as two cobaltadithiolene rings bridged by a molybdenum dicarbonyl moiety. The redox

---

[*] Prof. Dr. H. Nishihara, M. Nihei, T. Nankawa, Dr. M. Kurihara
Department of Chemistry, School of Science
The University of Tokyo
7-3-1 Hongo, Bunkyo-ku, Tokyo 113-0033 (Japan)
Fax: (+81) 3-5800-6890
E-mail: nisihara@chem.s.u-tokyo.ac.jp

[**] We thank Dr. H. Imoto for the DV-Xα calculation and encouraging discussions. This work was partly supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science, Sports and Culture and The Asahi Glass Foundation.