of Teo[12-14] on the average of 12 nickel and eight iron EXAFS spectra, truncated at 10 and 12 Å^{-1}, respectively.[15,18] Single scans of the nickel[16] and iron[17] models were used.

The first and second peaks of the Fourier transform of the iron EXAFS (data not shown) fit to sulfur and iron, respectively (Table I). Analyses of iron EXAFS could not distinguish iron–nickel interactions among the average three iron–iron interactions per scatterer observed. These data are consistent with but do not rigorously prove the presence of Fe_4S_4 clusters.

The Fourier transform of the nickel EXAFS is shown in Figure 1. The Fourier filtered data was best fit to sulfur (Figure 1b, dashed line) at 2.16 Å. A reasonable fit to oxygen/nitrogen could only be obtained by setting the ΔE_0 to 40 and the Debye–Waller term to 5×10^{-4} Å. A reasonable Ni–S fit was also obtained by assuming two Ni–S bond lengths at 2.22 and 2.11 Å, respectively. Addition of a Ni–M (M = Fe, Ni, Zn) term at 3.25 Å also improved the fit (Figure 1b, dotted line) although a high ΔE_0 (19 eV) was required to obtain a reasonable fit. Similar behavior was observed with the nickel model compound where a Ni–Ni distance could be best fit by setting the ΔE_0 to 21 eV. The calculated χ^2 for various models tested are given in Table II. The nickel in the model compound is a square-planar,[16] and the environment of nickel in CODH may be square planar was well. This would leave open axial coordination sites for CO, methyl, or acetyl CoA.[20]

In summary, the iron EXAFS indicates the presence of iron–sulfur centers, likely Fe_4S_4 clusters. The dominant scatters in the nickel EXAFS are approximately four sulfurs at 2.16 Å. The finding of ^{61}Ni and ^{57}Fe hyperfine splitting in the EPR of the CO complex suggest that both nickel and iron are present in the paramagnetic species produced by CO binding in the enzyme. A nickel–iron interaction at 3.25 Å is plausibly fit to the data but cannot be unequivocally assigned in the present analysis. We emphasize that the present EXAFS results refer to the CO-form of the enzyme. If a Ni–S–Fe complex is present in this form of the enzyme, one would expect, given Fe–S and Ni–S bond lengths of about 2.2 Å, that when the angle of the Fe–S–Ni complex varies between 75° and 180°, the Fe–Ni interaction would vary between 2.7 and 4.4 Å. For thiol bridged Fe–S clusters the angle is found[19] to be about 75°. If the nickel is part of a mixed-metal, cubane-type cluster, one would expect to see an iron atom at about 2.7 Å in the nickel EXAFS, where none in fact is found in the present analysis. Assuming normal bonding strength in the metal–sulfur bonds we conclude that either the Ni–S–Fe angle is larger than 90° or in fact that no direct linkage exists in the CO-free form of the enzyme. If the CO complex can be produced in quantitative yield with respect to the nickel content of the enzyme, further EXAFS measurements may resolve whether CO addition establishes an iron–nickel linkage, perhaps by forming a CO-bridged complex. We also should emphasize that since the enzyme contains two nickel atoms per $\alpha\beta$ dimer, it is possible that the two nickel sites are different in geometry and ligand environment. However, as a minimal working hypothesis, we suggest that the nickel in the EPR inactive state of this enzyme has four sulfurs in an approximately square-planar geometry with a nearby FeS cluster. Further work aimed at characterizing other states of the enzyme and at determining the nature, if any, of the nickel–iron interaction is in progress.

Registry No. $Ni_2(TTH)_2$, 36488-62-7; $(NEt_4)_2[Fe_4S_4(SPh)_4]$, 55663-41-7; carbon monoxide dehydrogenase, 64972-88-9; nickel, 7440-02-0; iron, 7439-89-6.

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[12] Teo, B. K. In *EXAFS Spectroscopy: Techniques and Applications*; Teo, B. K., Joy, D. C., Eds.; Plenum Press: New York, 1981; pp 13–58.

[13] Teo, B. K. *Acc. Chem. Res.* **1980**, *13*, 412–419.

[14] Teo, B. K.; Lee, P. S. *J. Am. Chem. Soc.* **1979**, *101*, 2815–2832.

[15] After subtraction of a four-segment background spline and multiplication by k^3, the data were Fourier transformed, Fourier filtered (nickel window, 2.3 Å% iron window, 3.0 Å), and fit in k space to the theoretical phase and amplitude functions of Teo and Lee.[14] The model compounds $Ni_2(TTH)_2$ (TTH = 1,4,7-trithiaheptane) and $(NEt_4)_2[Fe_4S_4(SPh)_4]$ were similarly analyzed (Table I) and were used where appropriate to refine distance and coordination numbers according to the fine adjustment based on models (FABM) method.

[16] The nickel model, $Ni_2(TTH)_2$ where TTH = 1,4,7-trithiaheptane, was assigned a dimeric structure, in which each of the nickel ions is coordinated by four sulfurs in an approximately square-planar geometry. The average Ni–S bond length is 2.18 Å while the Ni–Ni distance is 2.74 Å and the Ni–S–Ni angle is 75.6°: Baker, D. J.; Goodall, D. C.; Moss, D. S. *Chem. Commun.* **1969**, 325.

[17] The iron model compound $(NEt_4)_2[Fe_4S_4(SPh)_4]$ was made according to Averill et al. (Averill, B. A.; Herskovitz, T.; Holm, R. H.; Ibers, J. A. *J. Am. Chem. Soc.* **1973**, *95*, 3523).

[18] Teo, B. K.; Antonio, M. R.; Averill, B. A. *J. Am. Chem. Soc.* **1983**, *105*, 3751–3762.

[19] Holm, R. H.; Ibers, J. A. In *Iron-Sulfur Proteins*; Lovenberg, W.; Ed.; Academic Press: New York, 1977; Vol. III, 205–281.

[20] Raybuck, S. A.; Bastian, N. R.; Zydowsky, L. D.; Kobayashi, K.; Floss, H. G.; Orme-Johnson, W. H.; Walsh, C. T. *J. Am. Chem. Soc.* **1987**, *109*, 3171–3173.

Reversible Photodissociation and Thermal Binding of Carbon Dioxide in Oxo-Bridged Copper Dimers

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We report here the reversible sequence of photodissociation and thermal binding of carbon dioxide to a binuclear oxo-bridged copper(II) complex (Scheme I). The carbon dioxide binds the oxo-bridged complex via carbon to μ-oxo and oxygen to copper bonds.[1] The reversible photoexpulsion and thermal binding of carbon dioxide with this type of coordination have not been reported. In general, reversible binding of carbon dioxide to metal complexes is rare. A relatively small number of examples of reversible side-on[2,3] and metal–ligand insertions[2,4] are known.

The (μ-carbonato)dichlorobis(1,10-phenanthroline)dicopper(II) complex (I) and the (μ-oxo)dichlorobis(1,10-phenanthroline)dicopper(II) complex (II) were prepared by using a modification of the literature procedures for similar complexes.[1] For the carbonate complex, a 5 mmol solution of 1,10-phenanthroline (Malincrodt) in 30 mL of anhydrous methylene chloride was flushed with CO_2 for 20 min. Copper(I) chloride[5] (5 mmol) was then added under CO_2, and the mixture was stirred under a stream of CO_2 until all of the copper dissolved. At this point both CO_2 and O_2 were passed through the solution producing a blue-green solution. After an additional 10 min, the gas streams were stopped, and the methylene chloride was removed in a vacuum rotory evaporator leaving a blue-green solid. The oxo complex was prepared in a similar manner except that the system was flushed with nitrogen until the copper dissolved, and then oxygen was passed through the solution to produce a green-brown solution.

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[1] Davis, A. R.; Einstein, F. W. B.; Curtis, N. F.; Martin, J. W. L. *J. Am. Chem. Soc.* **1978**, *13*, 6258. Churchill, M. R.; Davies, G.; El-Sayed, M. A.; El-Shazly, M. F.; Hutchinson, J. P.; Rupich, M. W. *Inorg. Chem.* **1979**, *18*, 2296; **1980**, *19*, 229.

[2] Walther, D. *Coord. Chem. Rev.* **1987**, *79*, 135.

[3] Kharsch, H. H. *Chem. Ber.* **1977**, *110*, 2213. Aresta, M.; Nobile, C. F.; Albano, V. G.; Forni, E.; Marnasie, M. *Chem. Commun.* **1975**, 636. Aresta, M.; Nobile, C. F. *J. Chem. Soc.* **1977**, 708. Jolly, P. W.; Jonas, K.; Krueger, C.; Tsay, Y.-H. *J. Organomet. Chem.* **1971**, *33*, 109. Doehring, A.; Jolly, P. W.; Krueger, C.; Romao, M. J. *Z. Naturforsch.; B: Anorg. Chem., Org. Chem.* **1985**, *40*, 484. Floriani, C.; Fachinetti, C. *J. Chem. Soc., Chem. Commun.* **1974**, 615; *Inorg. Chem.* **1979**, *18*, 3469. Aresta, M.; Nobile, C. F. *Inorg. Chim. Acta* **1977**, *24*, L49.

[4] Immirzi, A.; Musco, A. *Inorg. Chim. Acta* **1977**, *22*, L35. Paonessa, R. S.; Trogler, W. C. *J. Am. Chem. Soc.* **1981**, *103*, 3529. Darensbourg, D. J.; Rokiki, A. *J. Am. Chem. Soc.* **1982**, *104*, 349. Slater, S. G.; Lusk, R.; Shumann, B. F.; Darensbourg, M. Y. *Organometallics* **1982**, *1*, 1662. Tsuda, T.; Chujo, Y.; Saegusa, T. *J. Am. Chem. Soc.* **1978**, *100*, 630; *Chem. Commun.* **1975**, 963; *Inorg. Chem.* **1972**, *11*, 2561; *J. Am. Chem. Soc.* **1980**, *102*, 431. Chisholm, M. H.; Rueckert, W. W.; Cotton, F. A.; Extine, M. W.; Murillo, C. A. *J. Am. Chem. Soc.* **1977**, *99*, 1652; **1978**, *100*, 1727.

[5] Keller, R. N.; Wycoff, H. D. *Inorg. Synth.* **1946**, *2*, 1.

0002-7863/88/1510-5582$01.50/0

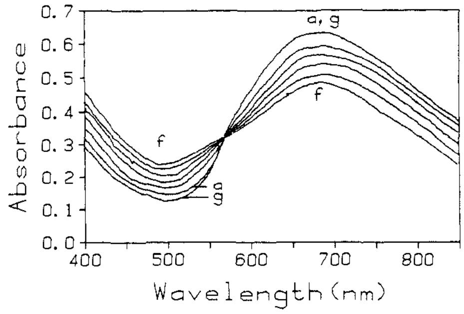
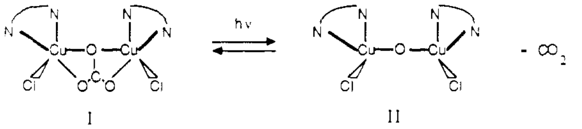


Figure 1. Absorption spectral changes occurring after irradiation of a 1.6×10^{-5} M aqueous solution of I at room temperature. Spectrum a is that of compound I; spectrum f is that of compound II. Spectra g is obtained by flushing photoproduced II with CO_2. Spectra b–e were obtained after irradiation times (min) of 5, 10, 15, and 22, respectively.

Scheme I



Satisfactory elemental analyses were obtained for both of the compounds. The IR spectrum of the carbonato complex contained bands at 1530, 1360, 820, and 750 cm^{-1} characteristic of the bridging "tridentate" carbonate.[1,6]

The electronic absorption spectrum of the μ-carbonato complex in aqueous solution consists of overlapping bands at 250 nm ($\epsilon = 950\ M^{-1}\ cm^{-1}$) and 328 nm ($\epsilon = 1300\ M^{-1}\ cm^{-1}$) and a shoulder at 350 nm. This spectral region contains the chloride-to-copper and the oxo-to-copper charge-transfer bands.[1,6] The electronic absorption spectra of I and II in the 400–850-nm region which are monitored in the photochemical studies are shown in Figures 1 (parts a and f, respectively). Complex I has a broad band at 680 nm with $\epsilon = 162\ M^{-1}\ cm^{-1}$, and complex II has a similar band also at 680 nm with $\epsilon = 140\ M^{-1}\ cm^{-1}$. This similarity suggests that there is no drastic rearrangement of the oxo complex on reaction with CO_2. The 680-nm band is assigned to d–d transitions for two reasons. First, assignment as charge-transfer transitions between the copper and the phenanthroline are eliminated because the analagous μ-carbonato and μ-oxo complexes containing substituted ethylenediammine ligands have a similar absorption band at 700 nm.[1,6] Secondly, d–d bands in the 700-nm region in copper(II) chloride complexes are well known.[1,7] On the basis of breadth of the spectrum, the observed 680-nm band is probably comprised of several closely spaced d–d excited states.

Photochemical reactivity was studied by irradiating a 1.6×10^{-5} M aqueous solution of I at 351.1 nm with an argon ion laser. The photon flux was 2.47×10^{16} photons/s (14.0 mW) measured with a calibrated power meter. All photoreactions were carried out at room temperature in a constantly stirred quartz cell. Absorption changes were measured by using a HP 8451A diode array spectrophotometer.

The spectral changes resulting from photolysis of I are shown in Figure 1. As irradiation proceeded, the absorbance at 680 nm decreased and that at wavelengths below 575 nm increased with an isosbestic point appearing at 575 nm. The concentration changes of I and II were calculated from the measured absorption spectral changes. A plot of the change of the concentration of I versus time was linear for irradiation times up to 22 min and passed through the origin. After longer irradiation times the plot exhibited curvature, and the isosbestic point in the spectra disappeared, both of which are indicative of secondary photolysis. The quantum yield for the disappearance of I and the appearance of II, calculated from the linear portion of the plot, was 0.44 ± 0.07.

The quantum yield for CO_2 loss is very sensitive to the nitrogen donor ligand. When phenanthroline was replaced by tetraethylethylenediamine, for example, the quantum yield decreased to less than 10^{-2}.

Cessation of photolysis at any time in the reaction sequence when the isosbestic point is maintained followed by flushing of the reaction mixture with CO_2 results in the reformation of the μ-carbonato complex. The spectral change is shown in Figure 1. When the system is flushed with CO_2 after prolonged photolysis which has caused loss of the isosbestic point, the spectra show incomplete regeneration of the μ-carbonato complex.

Photolysis of the μ-carbonato complex causes efficient carbon dioxide loss. The μ-oxo photoproduct binds CO_2 to form the starting material in high yield. The photodissociation of CO_2 from the carbonato complex and the thermal association of CO_2 with the μ-oxo copper dimer form a unique system for reversible carbon dioxide binding.

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(6) Davies, G.; El-Sayed, M. A.; Henary, M. *Inorg. Chem.* **1987**, *26*, 3266. Karlin, K. D.; Curse, R. W.; Gultmeh, Y.; Hayes, J. C.; Zubieta, J. *J. Am. Chem. Soc.* **1984**, *106*, 3372.

(7) Cassidy, P.; Hitchman, M. A. *Inorg. Chem.* **1977**, *16*, 1568; *Inorg. Chem.* **1979**, *18*, 1745.

"Armed" and "Disarmed" *n*-Pentenyl Glycosides in Saccharide Couplings Leading to Oligosaccharides

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Efficient protocols for building oligosaccharides from monosaccharide components present some of the greatest challenges in organic synthesis, one of which is shown in Scheme I. Thus, combination of **1** and **2** requires that the anomeric substituent, Y, of the alcohol donor **2** be less reactive, under the coupling conditions, than substituent, X, of the glycosyl donor **1**, in order to avoid self-condensation of **2**. The consequence of this is that for further elaboration at the reducing end of the product **3**, the stable substituent, Y, must be replaced with a new activated substituent, X′, in **4**. In the present state of the art, if **3** is a glycoside (i.e., Y = OAlk), the conditions for installation of the activated substituent X′ might affect the newly forged intersaccharide bond and/or the protecting groups R_1, R_2, and R_3. This task becomes increasingly daunting as the concatenation of saccharides grows. Therefore, saccharide coupling methodology could profit from a simple protocol for activating and deactivating the anomeric center of a normal, stable glycoside, X = Y = OAlk. In this manuscript, we describe some recent observations which relate to this need.

We recently reported that *n*-pentenyl glycosides undergo chemospecific cleavage, **6** → **9**, with *N*-bromosuccinimide under conditions that leave a wide variety of other protecting groups unaffected.[2] According to our proposed mechanism (Scheme II), replacement of water with an alcohol, SOH, should lead to glycoside exchange, **6** → **10**, a particularly appealing prospect for the synthesis of higher saccharides, where S = sugar.[3] However,

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(1) Financial support of this work was supplied by the National Science Foundation (CHE 8703916) and Glaxo, Incorporated (RTP, North Carolina).

(2) Mootoo, D. R.; Date, V.; Fraser-Reid, B. *J. Am. Chem. Soc.* **1988**, *110*, 2662.

(3) For the use of *n*-pentenyl glycosides in the formation of a wide variety of disaccharides see: Fraser-Reid, B.; Konradsson, P.; Mootoo, D. R.; Udodong, U. *J. Chem. Soc., Chem. Commun.* **1988**, 823.

0002-7863/88/1510-5583$01.50/0