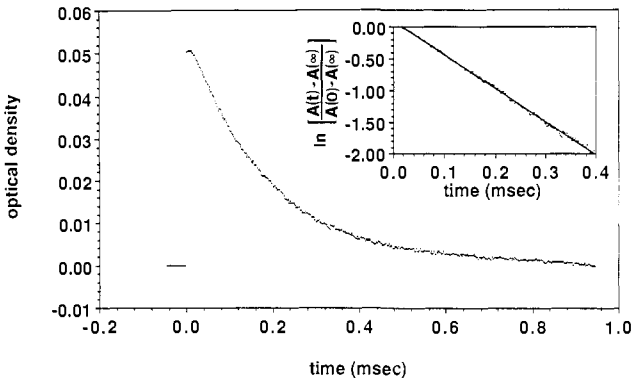


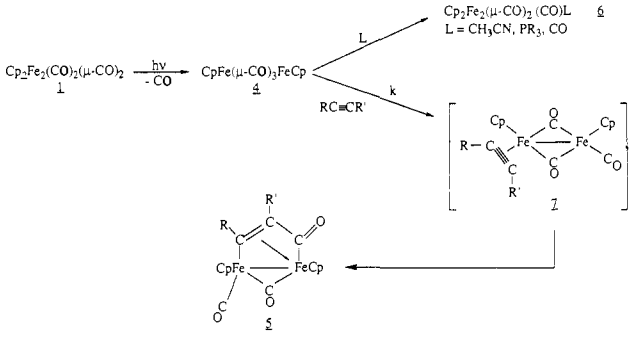
Figure 1. A representative quenching decay between **4** and PHAC (1.785×10^{-1} M) obtained by LFP on a 1.54×10^{-3} M solution of **1** in toluene, monitored at 515 nm. The inset figure shows the pseudo-first-order analysis of the decay curve over more than 1.5 half-lives, with k_{obs} = 5711.6 s^{-1}. The time the laser is fired is set to $t = 0$.

Table I. LFP Rate Constants and Activation Parameters for the Photochemical Reaction of **4** with Alkynes[a] and Several Simple Two-Electron Ligands

quencher	k (M^{-1} s^{-1})	$\Delta H^{\ddagger}$ (kJ mol^{-1})	$\Delta S^{\ddagger}$ (J mol^{-1} K^{-1})
1-hexyne	$(6.24 \pm 0.59) \times 10^4$	25.9 ± 1.0	−69.4 ± 2.6
PHAC	$(3.63 \pm 0.36) \times 10^4$	28.5 ± 1.1	−61.7 ± 3.3
DMAD	$(3.21 \pm 0.28) \times 10^4$	20.8 ± 1.5	−88.6 ± 4.2
CH_3CN[b,c]	7.6×10^5	24.4	−50.0
P(*n*-butyl)$_3$[b]	1.25×10^5	28.1	−52.3
$P(C_6H_5)_3$[b]	2.1×10^5	22.3	−64.8

[a] Toluene solution; rate constants reported are at $T = 24 \pm 2$ °C. Activation parameters were obtained from measurements between 0 and 50 °C. [b] Reference 4c. The rate constants and activation parameters are in cyclohexane solution. [c] We have measured a rate constant of $(3.10 \pm 0.29) \times 10^5$ M^{-1} s^{-1} in toluene.

Scheme I. Proposed Mechanism for the Insertion of Alkynes into **1**



ratios after prolonged irradiation.[9] The photolysis of **1** with an equimolar mixture of 1-hexyne and PHAC yields the corresponding insertion products **5** in the ratio 1-hexyne:PHAC = 1.55 ± 0.15. This is similar to the ratio for the LFP rate constants (1.72 ± 0.14), strong evidence that the observed reaction is under kinetic control. Similar close agreements between the product and kinetic ratios were observed for 1-hexyne/DMAD and PHAC/DMAD competitions. These observations are most consistent with the postulate that the process **4** + alkyne → **5** is irreversible, and that **4** is ultimately responsible for formation of alkyne insertion product **5**. Prolonged irradiation of either the 1-hexyne insertion product with free PHAC or the PHAC insertion product with free 1-hexyne further substantiates this assumption: no crossover of alkynes was observed.

The conclusions of the present studies, i.e. that the alkyne adds to the CO-loss product **4**, run counter to those proposed by us earlier;[5b] our results indicate that **4** (not **3**) is responsible for the alkyne insertion reaction. Experiments are currently in process to better delineate solvent and steric effects and to verify the formation of the proposed η^2-alkyne intermediate **7**.

Acknowledgment. We acknowledge Dr. Karen I. Goldberg for helpful discussions, Dr. James E. Jackson for assistance in obtaining the transient spectrum of **4**, and Mark Glogowski, Kim Lance, and Peter Padolik for assistance with the HPLC apparatus. M.S.P. acknowledges support from the National Science Foundation. B.E.B. is a Camille and Henry Dreyfus Teacher-Scholar (1984–1989).

Registry No. 1, 12154-95-9; **4**, 87985-70-4; PHAC, 536-74-3; DMAD, 762-42-5; CH_3CN, 75-05-8; P(*n*-Bu)$_3$, 998-40-3; $P(C_6H_5)_3$, 603-35-0; 1-hexyne, 693-02-7.

Supplementary Material Available: Experimental details of the laser flash photolysis and alkyne competition experiments (2 pages). Ordering information is given on any current masthead page.

Detection and Assignments of Diastereotopic Chemical Shifts in Partially Deuteriated Methyl Groups of a Chiral Molecule

Frank A. L. Anet* and Max Kopelevich

Department of Chemistry and Biochemistry
University of California
Los Angeles, California 90024
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The three protons of a rapidly rotating methyl group in *any* molecule are homotopic[1] from an NMR point of view and thus give rise to a single chemical shift.[2] On the other hand, the two protons in a rapidly rotating CH_2D group in a *chiral* molecule are diastereotopic[1] and are anisochronous, i.e., they have (in principle) different chemical shifts,[3] but an *observable* shift difference in such a system has not been previously reported to our knowledge.

A significant diastereotopic chemical shift difference is most easily induced by having a strong conformational (rotameric) preference for the CH_2D group,[4] together with having very different magnetic environments at the sites occupied by the CH_2D protons. Because lone pairs of electrons on nitrogens that are adjacent to CHD groups in six-membered rings give relatively large isotope effects on conformational equilibria,[5,6] we have investigated the ^1H NMR spectrum of a chiral molecule, (*RS*)-I-*d*, containing a NCH_2D group. The corresponding undeuteriated compound, (*RS*)-(±)-1,2-dimethylpiperidine, i.e., (*RS*)-I, is known to exist at room temperature to the extent of 95% in the diequatorial chair conformation,[7] viz., structure (*S*)-I-ee for the (*S*)-(+) enantiomer[8] of I. It is sufficient here to use the racemic

(1) Mislow, K.; Raban, M. *Top. Stereochem.* **1967**, *1*, 1–38.
(2) It is assumed that the molecule is in an isotropic medium and tumbles rapidly. All symmetry properties in the present paper refer to a time average suitable for proton chemical shifts. Rotation of methyl groups in very sterically hindered molecules can be slow at low temperatures (−150 to −50 °C). Anderson, J. E.; Rawson, D. I. *J. Chem. Soc., Chem. Commun.* **1973**, 830–831. Nakamura, M.; Ōki, M.; Nakanishi, H. *J. Am. Chem. Soc.* **1973**, *95*, 7169–7171. Nakamura, M.; Ōki, M.; Nakanishi, H. *Bull. Chem. Soc. Jpn.* **1974**, *47*, 2415–2419.
(3) Achiral molecules can also have this property provided that there is no plane of symmetry passing through the CH_2D group.
(4) However, a population difference is not required for the observation of a diastereotopic shift difference (Binsch, G.; Franzen, G. R. *J. Am. Chem. Soc.* **1969**, *91*, 3999–4000).
(5) Anet, F. A. L.; Kopelevich, M. *J. Chem. Soc., Chem. Commun.* **1987**, 595–597.
(6) Forsyth, D. A.; Hanley, J. A. *J. Am. Chem. Soc.* **1987**, *109*, 7930–7932. Forsyth, D. A.; Prapansiri, V. *Tetrahedron Lett.* **1988**, *28*, 3551–3554.
(7) From ^{13}C NMR on several C-dimethylated *N*-methylpiperidines and assuming additivity, Eliel and co-workers deduce a value of 1.9 kcal/mol for the equatorial–axial energy difference of the 2-methyl group in I, the 1-methyl group being almost entirely in the equatorial position (Eliel, E. L.; Kandasamy, D.; Yen, C.; Hargrave, K. D. *J. Am. Chem. Soc.* **1980**, *102*, 3698–3707). They also find that the methyl–methyl interaction energy in the diequatorial form of I is 1.0 kcal/mol. Direct analysis of the ^{13}C NMR spectra of I shows that the diequatorial form is preferred over the 1-equatorial–2-axial form by 1.7 ± 0.1 kcal/mol (Anet, F. A. L.; Dekmezian, A., unpublished work).

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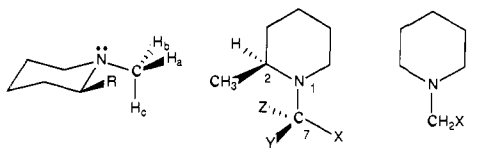


(S)-I-ee : R = CH_3 (S)-I : X = Y = Z = H II : X = H
II-e : R = H (S)-I-d_1 : X = D, Y = H_R, Z = H_S II : X = D
(S)-I-d_2 : X = H, Y = Z = D
(2-S,7-S)-I-d_1t_1 : X = D, Y = T, Z = H

form, (*RS*)-I-*d*[9] (the subscripts *R* and *S* on the hydrogens in the structure (*S*)-I-*d* indicate the *pro-R* and *pro-S* hydrogens of the CH_2D group, respectively). We have made related measurements on (*RS*)-I-d_2 and on 1-methylpiperidine isotopomers (II and II-*d*),[9] which exist virtually completely with the methyl groups in equatorial positions.[10]

As shown in Figure 1a, an AB quartet is clearly observed for the CH_2D group in the $^1H\{D\}$ spectrum of (*RS*)-I-*d* at 500 MHz. The ^1H chemical shift difference in the CH_2D group is 6.9 Hz (0.014 ppm or 14 ppb). Because of the relatively large coupling constant ($|J_{HH}|$ = 11.7 Hz), the inner lines of the AB quartet are separated by only 1.8 Hz, and the outer lines are calculated to have only 7% of the intensity of the inner lines. The chemical shift difference in the CH_2D group increases as the temperature is lowered so that the AB quartet at −95 °C is much less collapsed than at room temperature (Figure 1b). The ^1H spectrum without deuterium decoupling of the CH_2D group at 22 °C consists of the sum of three AB quartets similar to those in (a) above and offset from one other by 1.8 Hz (J_{HD}) (Figure 1c).

The deuterium isotope shifts (Δ_1 and Δ_2) in the CH_2D protons (Figure 1a and 1b at 22 and −95 °C) differ from an expected intrinsic isotope shift of −15 to −19 ppb,[11] especially for Δ_2, which clearly has a large equilibrium contribution.[5,6,11,12] The deuterium isotope shift (Δ_3) in the CH_2D group of II-*d* was measured to be −23 ppb at 22 °C and −27 ppb at −95 °C. Surprisingly, the chemical shift difference (Δ_4) between the 1-methyl groups in I and II is extremely small (12 ppb) and independent of temperature. Finally, the deuteron chemical shift difference (13 ppb) in (*RS*)-I-d_2 was measured at 22 °C (Figure 1d).[13]

In order to analyze the chemical shifts in the 1-methyl groups of I and II, we assume additivity of chemical shift contributions. Let the chemical shifts of H_a, H_b, and H_c of the 1-methyl group in (*S*)-I-ee, relative to those of the corresponding protons in II-e, be $\Delta\delta_a$, $\Delta\delta_b$, and $\Delta\delta_c$, respectively. The gauche arrangement of the CH_3–N–CH–CH_3 moiety in (*S*)-I-ee should deshield the 1-methyl proton (H_a) closest to the 2-methyl group by a steric effect,[7,14] so that $\Delta\delta_a$ is expected to be positive. The electron delocalization from the nitrogen lone pair into the antiparallel

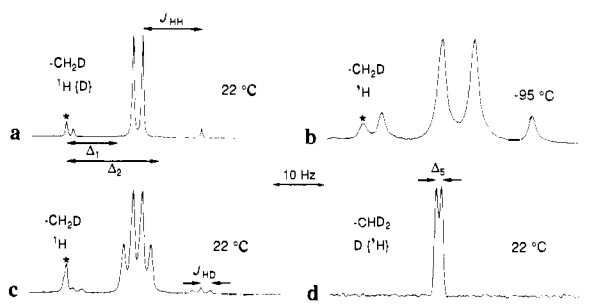
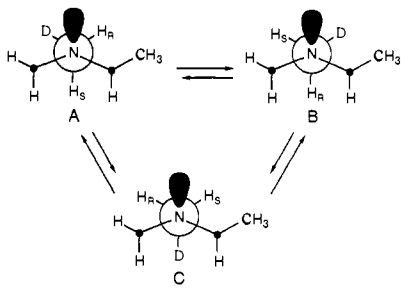


Figure 1. 500-MHz ^1H NMR spectra in CD_2Cl_2 of the CH_2D group in (*RS*)-I-*d* at (a) 22 °C with deuterium decoupling ($^1H\{D\}$), (b) −95 °C with a line narrowing of −1.75 Hz and with the deuterons spontaneously decoupled by quadrupolar relaxation, and (c) 22 °C without deuterium decoupling. In (a) the separation (1.8 Hz) of the two large inner lines of the AB quartet is $[\Delta\nu^2 + J_{HH}^2]^{1/2} - |J_{HH}|$, where $\Delta\nu$ (in Hz) is $(\nu_1 - \nu_2)$; Δ_1 (in ppb) = $2(\nu_1 - \nu^*)$ and Δ_2 (in ppb) = $2(\nu_2 - \nu^*)$, where ν^* is the frequency of the CH_3 signal (marked by an asterisk) in undeuteriated 1,2-dimethylpiperidine ($\delta_{N\text{-}CH_3}$ = 2.17 at 22 °C). 76.77-MHz $D\{^1H\}$ NMR spectrum (d) at 22 °C of the CHD_2 group in (*RS*)-I-d_2.

Scheme I



• = remaining portion of the piperidine ring

methyl-CH σ^* orbital, which weakens this CH bond and creates a partial negative charge on H_c,[15] should give a shielding contribution ($\Delta\delta_L$) to this proton.[16]

The three rotamers in the N–CH_2D moiety of I-*d* are shown as Newman projections in Scheme I, where the longer arrows indicate the preferred equilibrium directions. The lone pair on nitrogen is expected to contribute 60 ± 10 cal/mol (G_L) more toward $H°$ and $G°$ for C than for A or B through a zero-point energy effect.[5,6,17] Also, rotamer B (but not A or C) is expected to be stabilized because steric compression caused by the gauche 2-methyl group should increase the bending frequency involving the C–D bond in B. We estimate that this energy contribution (G_M) is −7 ± 5 cal/mol.[18] Using these parameters[19] and the values of Δ_3 at 22 and −95 °C, we then calculate that the lone-pair effect ($\Delta\delta_L$) and the intrinsic isotope effect (E_I) are −490 ± 80 and −18 ± 0.5 ppb, respectively.

With the previously established relation $\Delta_4 = \Delta\delta_a + \Delta\delta_b + \Delta\delta_c$ = 12 ppb and the values of $\Delta\delta_L$ and E_I determined from Δ_3, the experimental data at −70, −95, and −105 °C for Δ_1 and Δ_2 can be well fitted with $\Delta\delta_a$ = 425, $\Delta\delta_b$ = −150, and $\Delta\delta_c$ = −260 ppb.[20] The reasonableness of the shielding and deshielding parameters deduced here allows us to assign with high confidence the protons in (*S*-)-I-*d* associated with the Δ_1 and Δ_2 shifts to H_R and H_S,

(8) For the assignment of the absolute configuration of (*S*)-(+)-2-methylpiperidine, see: Ripperger, H.; Schreiber, K. *Tetrahedron* **1965**, *21*, 1485–1487. King, F. E.; King, T. J.; Warwick, A. J. *J. Chem. Soc.* **1950**, 3590–3597. Methylation of (*S*)-(+)-2-methylpiperidine gives (*S*)-(+)-1,2-dimethylpiperidine (Leithe, W. *Ber.* **1930**, *63*, 800–805).

(9) (*RS*)-I-*d* and II-*d* were prepared by methylation of the corresponding secondary amines with formaldehyde and formic-*d* acid-*d*. The NMR measurements were made on a Bruker AM500 spectrometer.

(10) Crabb, T.; Katritzky, A. R. *Adv. Heterocycl. Chem.* **1985**, *36*, 1–173.

(11) The intrinsic isotope effects in RCH_2D are in the range of 15–19 ppb (Batiz-Hernandez, H.; Bernheim, R. A. *Prog. NMR Spectrosc.* **1967**, *3*, 63–85. Hansen, P. E. *Annu. Rep. NMR Spectrosc.* **1983**, *15*, 105–234). The convention for the sign of the isotope shift used by these workers is the opposite of that used in the present paper, which follows the more rational convention of defining the shift as $\delta_D - \delta_H$, where the δ_D refers to the proton shift in the deuteriated molecule (Jameson, C. J. *Nucl. Magn. Reson.* **1986**, *15*, 1–27. Hawkes, G. E. *Nucl. Magn. Reson.* **1986**, *15*, 28–80). For a recent review on equilibrium isotope effects, see: Siehl, H.-V. *Adv. Phys. Org. Chem.* **1987**, *23*, 63–163.

(12) Δ_1 and Δ_2 have the following respective values (ppb): at 22 °C, −21.0 and −34.6; at −70 °C, −22.4 and −45.2; at −95 °C, −22.9 and −50.3; at −105 °C, −23.0 and −52.2.

(13) The 76.8-MHz $D\{^1H\}$ NMR spectrum of (*RS*)-I-d_2, which was prepared by $LiAlD_4$ reduction of the *N*-formyl derivative of the secondary amine, is a doublet split by 1.0 Hz (13 ppb). The calculated coupling constant between the two deuterons is 11.7/6.5[2] or 0.3 Hz and is not resolved.

(14) Winstein, S.; Carter, P.; Anet, F. A. L.; Bourn, A. J. R. *J. Am. Chem. Soc.* **1965**, *87*, 5247–5249 and references therein.

(15) Hehre, W. J.; Pople, J. A. *J. Am. Chem. Soc.* **1970**, *92*, 2191–2197.

(16) The magnitude of the lone-pair shielding effect has been the subject of some controversy, but there seems little doubt that it is a shielding effect.[10]

(17) $\Delta S°$ is expected to be zero (Anet, F. A. L.; Kopelevich, M. *J. Am. Chem. Soc.* **1986**, *108*, 2109).

(18) The bending contribution to the conformational energy difference in cyclohexane-*d* has been estimated to be 6 cal/mol (Anet, F. A. L.; Kopelevich, M. *J. Am. Chem. Soc.* **1986**, *108*, 1355–1356), and molecular mechanics calculations give a similar contribution in *trans*-2-methyl-1-(methyl-*d*)cyclohexane.

(19) The fractional populations at 22 °C of A, B, and C in I-*d* are calculated to be 0.3431, 0.3472, and 0.3097, respectively.

(20) The errors in $\Delta\delta_a$, $\Delta\delta_b$, and $\Delta\delta_c$ depend mostly on the errors in G_L and G_M and are ±100, ±50, and ±100 ppb, respectively); at 22 °C the calculated value of Δ_2 is in error by 3 ppb probably because 5% of the 2-axial form is present.[7]

respectively. These assignments are of course reversed in (*R*)-I-*d*.

The present results show that the configuration of an *intact* stereogenic methyl group,[21] CHDT (so-called "chiral" methyl group[22]), can be determined directly by tritium NMR.[23-27] The diastereomer, (1-*S*,7-*S*)-I-*d*-*t*, is calculated to have a tritium chemical shift at room temperature that is about 15 ppb greater (i.e., less shielded) than that of the other diastereomer, (1-*S*,7-*R*)-I-*d*-*t*. With proton and deuterium decoupling, a mixture of these diastereomers should then give sharp lines separated by 4.8 ± 0.3 Hz at 320 MHz, thus allowing an easy and accurate integration of the two signals on available instrumentation.

Acknowledgment. The NMR spectrometer was purchased through funds provided in part by the National Science Foundation and the National Institutes of Health. We thank the Research Corp. for support.

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(22) Floss, H. G.; Tsai, M.-D. In *Advances in Enzymology and Related Areas of Molecular Biology*; Meister, A., Ed.; Wiley: New York, 1979; Vol. 50, pp 253-302. Floss, H. G.; Tsai, M.-D.; Woodward, R. W. *Top. Stereochem.* **1984**, *15*, 215-320. Floss, H. G. In *Mechanisms of Enzymatic Reactions: Stereochemistry*; Frey, P. A., Ed.; Elsevier: New York, 1986. Frenzel, T.; Beale, J. M.; Kobayashi, M.; Zenk, M. H.; Floss, H. G. *J. Am. Chem. Soc.* **1988**, *110*, 7878-7880.
(23) Altman, L. J.; Han, C. Y.; Bertolino, A.; Handy, G.; Laungani, D.; Muller, W.; Schwartz, S.; Shanker, D.; de Wolff, W. H.; Yang, F. *J. Am. Chem. Soc.* **1978**, *100*, 3235-3237).
(24) For tritium NMR, see: Bloxsidge, J. P.; Elvidge, J. A. *Prog. NMR Spectrosc.* **1983**, *16*, 99-113. Evans, J. A.; Warrell, D. C.; Elvidge, J. A.; Jones, J. R. *Handbook of Tritium NMR Spectroscopy and Applications*; Wiley: New York, 1985. Tritium NMR has been used to determine the configurations of chemical products (e.g., R*CDTX and R*CHTX, where R* is a chiral group, or RR'C=CDT and RR'C=CHT) derived, usually enzymatically, from a compound containing a stereogenic methyl group, XCHDT; if the stereochemistry of the reaction is known, the configuration of XCHDT is established indirectly, whereas if the configuration of XCHDT is known, the stereochemistry of the reaction can be established.[22,23]
(25) It has been thought[22] that such an NMR procedure would require finding conditions where the rotation of the methyl group is slow on the NMR chemical shift time scale,[2] but such conditions are neither necessary nor indeed desirable.
(26) Excess (*S*)-2-methylpiperidine should react[8] with CHDTX, where X is a leaving group; a route to such a CHDTX compound from chiral acetic acid is known.[21]
(27) Investigations of the chemical shift differences in the CHDT groups of diastereomers of I-*d*-*t* and in the CH_2D groups of chiral molecules other than I are planned.

Structure and Properties of a Pterin-Containing Ternary Copper(II) Complex, $[Cu(bpy)(PC)(H_2O)]\cdot 3H_2O$ (bpy = 2,2'-Bipyridine; PC = Pterin-6-carboxylate). Implications for the Active-Site Copper-Cofactor Bonding in *Chromobacterium violaceum* Phenylalanine Hydroxylase

Takamitsu Kohzuma,[1a] Hideki Masuda,[1b] and Osamu Yamauchi*,[1c]

Faculty of Pharmaceutical Sciences
Kanazawa University
Takara-machi, Kanazawa 920, Japan
Coordination Chemistry Laboratories
Institute for Molecular Science
Myodaiji, Okazaki 444, Japan
Department of Chemistry, Faculty of Science
Nagoya University, Chikusa-ku, Nagoya 464, Japan

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Phenylalanine hydroxylase and other aromatic amino acid hydroxylases are metalloenzymes that introduce a hydroxyl group into the side-chain aromatic rings in the presence of the pterin cofactor biopterin (**1a**).[2,3] While the hydroxylases from mammalian and pseudomonas species require iron for their activity, the phenylalanine hydroxylase from *Chromobacterium violaceum* involves 1 mol of type 2 copper per mol of enzyme in place of iron,[4,5] and a reduced pterin ring has been inferred to coordinate to copper through the nitrogen atom from electron spin resonance (ESR) spectroscopic studies by Benkovic and his collaborators.[6] Their electron spin echo studies reported very recently indicated that two imidazole groups from the enzyme are equatorially bound to copper.[7] In the course of the studies on Cu(II)-folic acid interactions, we found that folic acid (FA, **1b**), also a pterin

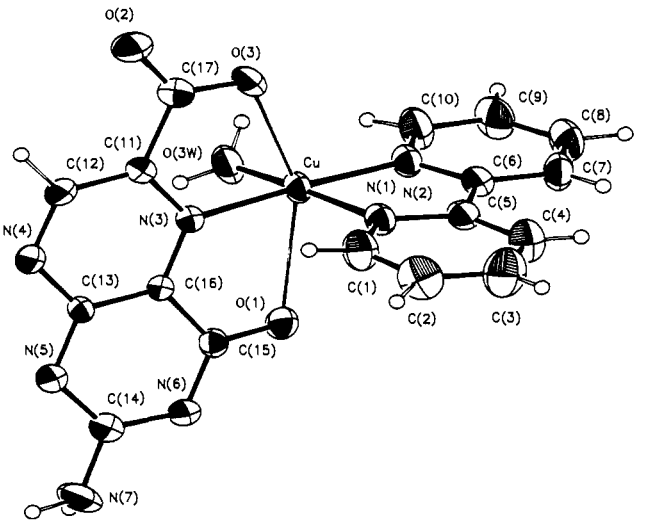
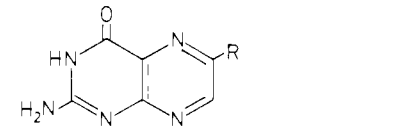


Figure 1. ORTEP view of $[Cu(bpy)(PC)(H_2O)]$ (**2**) showing 50% thermal ellipsoids. Selected bond lengths (Å) and angles (deg) are as follows: Cu-N(1) = 2.005 (3), Cu-N(2) = 1.993 (3), Cu-N(3) = 2.013 (3), Cu-O(1) = 2.499 (3), Cu-O(3) = 2.391 (3), Cu-O(3W) = 1.972 (3); N(1)-Cu-N(2) = 81.1 (1), N(1)-Cu-N(3) = 97.0 (1), N(1)-Cu-O(1) = 83.0 (1), N(1)-Cu-O(3) = 94.7 (1), N(1)-Cu-O(3W) = 171.1 (2), N(2)-Cu-N(3) = 177.1 (1), N(2)-Cu-O(1) = 104.4 (1), N(2)-Cu-O(3) = 108.0 (1), N(2)-Cu-O(3W) = 93.0 (1), N(3)-Cu-O(1) = 73.1 (1), N(3)-Cu-O(3) = 74.3 (1), N(3)-Cu-O(3W) = 88.5 (1), O(1)-Cu-O(3) = 146.7 (1), O(1)-Cu-O(3W) = 92.0 (1), O(3)-Cu-O(3W) = 93.6 (1).



1a; R = $-CH(OH)CH(OH)CH_3$

1b; R = $-CH_2NH-C_6H_4-CONHCH(COOH)CH_2CH_2COOH$

1c; R = $-COOH$

cofactor, suffers oxidative cleavage at the side chain by $Cu(bpy)^{2+}$ (bpy = 2,2'-bipyridine) at pH > 10 under aerobic conditions to give a ternary copper(II) complex involving bpy and pterin-6-carboxylate (PC, **1c**), Cu(bpy)(PC).[8] Since the same oxidation was observed for $Cu(phen)^{2+}$ (phen = 1,10-phenanthroline) but not for $Cu(en)^{2+}$ (en = ethylenediamine), electronic and steric

(1) (a) Kanazawa University. (b) Institute for Molecular Science. (c) Nagoya University.

(2) *Folates and Pterins*; Blakley, R. L.; Benkovic, S. J., Eds.; John Wiley & Sons: New York, 1985; Vol. 2.
(3) Dix, T. A.; Benkovic, S. J. *Acc. Chem. Res.* **1988**, *21*, 101-107.
(4) Nakata, H.; Yamauchi, T.; Fujisawa, H. *J. Biol. Chem.* **1979**, *254*, 1829-1833.
(5) Pember, S. O.; Villafranca, J. J.; Benkovic, S. J. *Biochemistry* **1986**, *25*, 6611-6619.
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