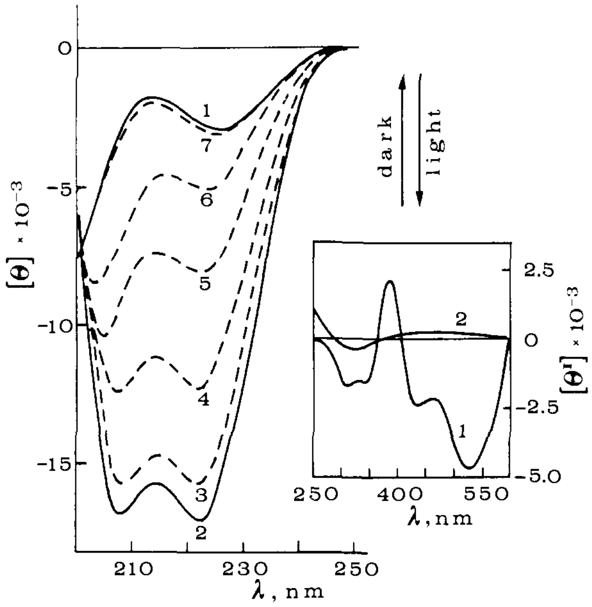

Figure 3. Spiropyran-containing poly(L-glutamic acid) (41 mol %) in HFP ($c = 6.28 \times 10^{-2}$ g/L). Effect of irradiation and dark adaptation on CD spectra: 1, dark adapted solution (colored form); 2, after exposure to sunlight or photostationary state at any wavelength in the range 350–570 nm (bleached form); 3–7, thermal recovery of the colored form at 25 °C, after 36 min (3); 98 min (4); 198 min (5); 324 min (6); 24 h (7). Below 250 nm, CD data are expressed in terms of molar ellipticity *[Θ], based on the mean residue molecular weight. Above 250 nm, the* molar ellipticity [Θ'] is referred to one spiropyran-glutamyl residue.

The negative photochromic behavior is likely to be due to the high polar solvent HFP which stabilizes the zwitterionic merocyanine more than the apolar spiro form. This is confirmed by the ^{13}C NMR spectra. In the colorless solution the resonances of 3,3-dimethyl groups appear as two separate peaks, at 27.0 and 21.0 ppm, as a consequence of the presence of the chiral C(2) spiro carbon atom. In the colored solution, by contrast, the two methyls appear as one singlet at 28.7 ppm, suggesting that the spiro carbon atom has lost its dissymmetry assuming a planar structure.

The CD spectra show that the polypeptide chain adopts an essentially random coil conformation in the dark, where the photochromic side chains are in the merocyanine form. Weak CD bands are also present in the visible range of the spectrum (Figure 3). The bleached solution after exposure to visible light displays the typical CD pattern of the α-helix, indicating that the isomerization of the side chains from the cyanine to the spiro form causes the spiralization of the polypeptide chain. The back-reaction to the colored form in the dark is accompanied by the progressive decrease of the helix content and recovery of the original disordered conformation (Figure 3). The reactions are fully reversible.

The key factor responsible for the photoresponse effects is likely to be the interactions among the photochromic side chains, which are different when they are in the charged merocyanine form or in the apolar spiro form. Actually addition of increasing amounts of 1,2-dichloroethane (DCE) to the HFP solution shifts the equilibrium toward the spiro form (Figure 2). Of course, the spiro species content in the dark-adapted solution changes with the HFP/DCE composition, so irradiation at selected solvent compositions makes it possible to control the intensity of the photoresponse. At HFP/DCE v/v ratios 100/0, 70/30, and 50/50, the photoinduced helix contents are respectively 45%, 35%, and 30%.[19]

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[19] Values are estimated on the basis of the ellipticity at 222 nm, assuming for 100% α-helix $[\Theta]_{222} = -31\,000$ [Parrish, J. R.; Blout, E. R. *Biopolymers* **1971**, *10*, 1491-1512].

Neutron Diffraction Structure Analysis of a Hexanuclear Copper Hydrido Complex, $H_6Cu_6[P(p\text{-tolyl})_3]_6$: An Unexpected Finding

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The exact structures of hexameric copper(I) hydrido species have been the subject of considerable debate, particularily with regard to the location of the spectroscopically elusive hydride ligands.[1-5] In the original work on $H_6Cu_6(PPh_3)_6$, neither the NMR nor the IR exhibited features identified with the H ligands.[1] Indeed, it has been speculated that, in solution, this complex (and related species) probably exists as a mixture of various oligomeric forms.[5] At any rate, the solid-state structure of $H_6Cu_6(PPh_3)_6$ showed a central Cu_6 octahedron with six long (average 2.655 (17) Å) and six short (average 2.542 (44) Å) Cu–Cu distances, and it was concluded that the unlocated H ligands were probably situated on the six long Cu–Cu edges.[1] Some years later, we examined the structure of the closely related $H_6Cu_6[P(p\text{-tolyl})_3]_6$ cluster and reached the same conclusion.[2] In the meantime, it was suggested by Stucky and co-workers[3] that the H ligands might be located on the faces rather than the edges of the octahedron, and this was found to be the case in a different hexameric cluster, $H_6Cu_6[P(NMe_2)_3]_6$, by Caulton, Huffman, and co-workers using low-temperature X-ray techniques.[4] In the present communication we report a single-crystal neutron diffraction analysis of $H_6Cu_6[P(p\text{-tolyl})_3]_6$ which shows that, contrary to our earlier expectations,[2] the six H atoms in that cluster are situated at face-bridging positions rather than edge-bridging ones.

In our early attempts to grow large crystals of $H_6Cu_6(PPh_3)_6$ for a neutron diffraction analysis, we quickly became aware of a major obstacle: Namely, the triphenylphosphine derivative[1] tended to crystallize out in thin flat plates, unsuitable for neutron diffraction studies. However, the structurally similar $P(p\text{-tolyl})_3$ complex[2] crystallized in a prismatic habit, more suitable for the growth of large specimens, and by a variation of solvents and crystallization techniques we were able to achieve the crystal size and quality required for a neutron diffraction analysis. The crystal used in the present study was grown from a benzene/toluene/tetrahydrofuran solution (approximately 2:1:1) with pentane as precipitant and utilizing standard drybox techniques.

Neutron diffraction data were collected on an automated four-circle diffractometer[6] at the Brookhaven High Flux Beam Reactor, at room temperature, with a crystal of approximate dimensions 3.0 × 4.0 × 2.0 mm.[7] Four main factors arising

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[7] Crystal data for $H_6Cu_6[P(p\text{-tolyl})_3]_6$: $Cu_6P_6C_{126}H_{126}$, fw = 2213.6, triclinic, space group $P\bar{1}$, $a = 20.248$ (5) Å, $b = 22.985$ (6) Å, $c = 15.869$ (6) Å, $\alpha = 104.06$ (2)°, $\beta = 112.52$ (3)°, $\gamma = 83.43$ (3)°, $U = 6616$ (6) Å^3, $Z = 2$, $d_{calcd} = 1.13$ g/cm^3. The structure was refined with SHELX76[8] using rigid groups for the *p*-tolyl groups. Initial positions of non-hydrogen atoms were obtained from our earlier X-ray study.[2] The capping H ligands were then located from a difference Fourier map. Final least-squares refinement yielded $R(F) = 0.124$ and $R_w(F) = 0.165$, for 279 variable parameters and 1407 unique absorption-corrected observations with $I > 3\sigma(I)$. The neutron wavelength was 1.15930 (12) Å.

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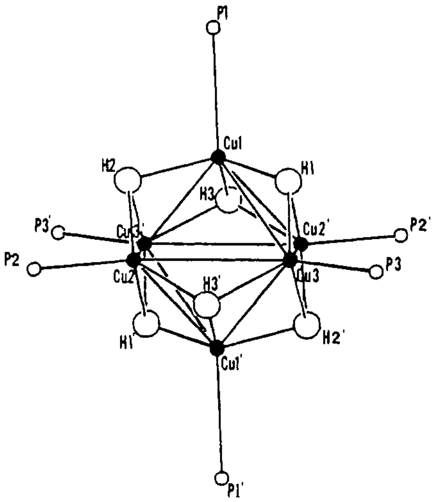

Figure 1. Molecular structure of the $H_6Cu_6P_6$ core of the $H_6Cu_6[P(p\text{-tolyl})_3]_6$ cluster. Thermal ellipsoids are at the 50% probability level.[11] Average pertinent distances: Cu–Cu(long) = 2.68 (4) Å, Cu–Cu(short) = 2.52 (3) Å, Cu–H = 1.76 (3) Å. Primed atoms are related to unprimed ones by a crystallographic inversion. The drawing shows one of the two independent clusters in the unit cell.

during data collection and refinement limited us to a low resolution analysis: (i) Data were collected at room temperature due to a destructive phase transition occurring at approximately 265 K. (ii) Because of the crystal's lack of diffracting ability beyond $2\Theta = 75°$, $\lambda = 1.15930$ (12) (partially due to the relatively high data collection temperature), a comparatively small amount of data (2808 reflections) was obtained, given the size of the unit cell ($U = 6616(6)$ Å^3). (iii) Due to the limited amount of data available and the large number of independent atoms (270), rigid body refinement was employed in which the *p*-tolyl groups were held rigid, and only the rotational angles about the P–C_{ipso} bond lengths were refined.[8] (iv) In order to further reduce the number of parameters and increase the data/parameter ratio, the isotropic temperature factors for groups of atoms also were constrained equal to one other.

A view of the structure of the core of $H_6Cu_6[P(p\text{-tolyl})_3]_6$ is illustrated in Figure 1. Consistent with previous studies,[1,2,4] the geometry of the cluster is that of a distorted octahedron of copper atoms with six short [average 2.52 (3) Å] and six long [average 2.68 (4) Å] Cu–Cu edges, thus resulting in six small and two large faces. The average Cu–Cu distances compare well with those determined by X-ray diffraction:[2] Cu–Cu short = 2.54 (1) Å and Cu–Cu long = 2.66 (1) Å. Two independent clusters are present in the unit cell, and each cluster possesses crystallographic inversion symmetry. All six face-capping hydrides were located on the small faces from a single difference-Fourier map. The average Cu–H bond distance is 1.76 (3) Å, with an average out-of-plane distance of 1.0 (1) Å. These values compare well with Co–H = 1.734 (4) Å and H···Co_3 = 0.978 (3) Å in $(\mu_3\text{-H})FeCo_3(CO)_9[P(OCH_3)_3]_3$[9] and Ni–H = 1.691 (8) Å and H···Ni_3 = 0.907 (6) Å in $(\mu_3\text{-H})_3Ni_3(C_5H_5)_4$.[10] Despite the somewhat low precision of the present analysis, the main conclusions are clear and unambiguous: All six hydrides are definitively found to be face-capping, consistent with the findings of Caulton, Huffman, and co-workers[4] and speculations of Stucky and co-workers.[3]

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Supplementary Material Available: Tables consisting of crystal data and data collection parameters (Table S1), atomic coordinates and thermal parameters (tables S2), and bond distances and angles (Table S3) (8 pages); table of observed and calculated structure factors (Table S4) (8 pages). Ordering information is given on any current masthead page.

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Chemoenzymatic Preparation of *trans*-2,6-Dialkylpiperidines and of Other Azacycle Building Blocks. Total Synthesis of (+)-Desoxoprosopinine

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The aza-Achmatowicz reaction ($1 \rightarrow 2$)[4] has emerged as a practical route to indolizidines, quinolizidines, and piperidines, the latter in the form of oxazolones of the type **6**.[5] Compound **6** may be prepared in either antipodal form (>95 % ee, 10–50 g scale) by the simple chemoenzymatic method summarized in Scheme II,[6] whereas other materials of the type **2** were hitherto available solely in racemic form. Herein, we disclose extension of aza-Achmatowicz techniques to the enantioselective preparation of compounds **2**. In this connection, amidoalkylation reactions of certain derivatives of **6** were examined. Surprisingly, such reactions were found to follow a stereochemical course *opposite to that observed for monocyclic analogues of our substrates.* Consequences of our findings are presented below.[7]

The carbonyl group in **6** may be reduced with complete stereocontrol. Ethanolic $NaBH_4$ (−60 °C) produced an equatorial alcohol, conveniently characterized as the acetate. By contrast, L-selectride in THF (−78 °C) caused formation of the axial alcohol, again characterized as the acetate.[8] Complete stereoselectivity in both cases was apparent within the limits of 300 MHz ^1H NMR spectrometry. No unusual effect[9] interfered with the stereochemical course of these reductions. Hart–Kraus allylation of acetate (+)-**9** occurred rapidly upon treatment with allyltrimethylsilane/$TiCl_4$ (CH_2Cl_2, 25 °C),[10] providing *axially allylated* (+)-***10*** *as the exclusive product* (88% chromatographed yield, $[a]_D = +17.3°$; $c = 1.003$, EtOH). The structure of **10** is firmly established. In addition to extensive NMR studies,[11] an X-ray

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(1) Recipient of a Dow Predoctoral Fellowship, 1987–1988.

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(3) Recipient of a Robert A. Welch Predoctoral Fellowship, 1987–1988.

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(5) The structure of **6** was ascertained by X-ray crystallography. Monoclinic crystals from THF, space group $P2_1/a$; $a = 8.582$ (6) Å; $b = 10.608$ (5) Å; $c = 10.160$ (7) Å; $\beta = 114.92$ (4)°; $Z = 4$; $V = 839$ (2) Å^3. $R = 0.036$, $R_w = 0.052$ for 1515 observed reflections. An ORTEP plot of **3** is provided as Supplementary Material.

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