The above interpretation, however, cannot be distinguished from one in terms of a pH-dependent conformational change not linked to the change in the ligand and spin state of the heme Fe^{3+}. Such a possibility is indicated by other probe studies on oxyhemoglobin[15a,33] and must be checked using other ligands. Further experiments should also lead to an adequate explanation of the lower exchange rate constant observed at higher pH. Since the exchange reaction is diffusion limited, and hence sensitive to steric or electrostatic effects, one could expect that either the positions of the C-terminal residues or the ionization of residues in the neighborhood of cysteine F9(93)β should affect the exchange rates.

It is evident that measurement of the exchange rate and correlation time with the bromide probe may yield considerable new information concerning the nature of the conformation at specific sites in macromolecules. Application to the study of the conformational changes near cysteine F9(93)β of hemoglobin has supplied information which apparently is complementary to that previously obtained at that site with esr probes. The smaller mercury bromide nmr probe may not compete with penultimate tyrosine for the tyrosine pocket, as do the esr probes, and thus may give more realistic information on the parent cysteine site. Continued work with this probe, at the least, should provide independent confirmation of the esr probe conclusions, and in addition may indicate the influence of bulky or charged groups near the site on the accessibility of bromide to the mercury.

Potential problems in the application of this probe, as indicated by the present study, may include protein instability at the higher ionic strengths, and dependence of the conformation near the probe on ionic strength or bromide concentration. A more sensitive apparatus, now being tested, should enable future studies to be done at lower concentrations of bromide.

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Communications to the Editor

General Syntheses for New Pentadentate Ligands. The Crystal Structure of α,α'-{2-(2'-Pyridyl)ethyl}-ethylenebis(salicylideniminato)cobalt(II)-Ethanol

Sir:

Some biological systems impose upon a metal a pentacoordinate environment consisting of an unsaturated planar tetradentate group and a heterocyclic base. Notable examples are hemoglobin[1] and myoglobin[2] in which the globin protein provides a pocket for the porphyrin complex in such a way that an imidazole group on the protein is positioned as an axial ligand affording square-pyramidal coordination. Another example of this situation is vitamin B$_{12}$[3] in which the fifth ligand, 5,6-dimethylbenzimidazole, is chemically attached to the corrin affording similar coordination geometry. Synthetic pentadentate ligands capable of assuming this geometry are rare.[4] We wish to report a general scheme for the preparation of such ligands and an X-ray diffraction study of a typical complex.

Our synthetic strategy is based on the observation that vicinal diamines such as 1,2-ethylenediamine (en) and 1,3-propylenediamine (pn) when condensed with carbonyl derivatives (salicyladehyde, 1,3-diketones, oximino ketones, etc.) afford unsaturated tetradentate ligands capable of planar coordination. We, therefore, prepared a series of 1,2-en and 1,3-pn derivatives containing pyridine groups appended by alkyl chains of lengths likely to permit five-coordination (**1** and **2** in Scheme I). These schemes were based on the premise that aldehyde and malonic amide derivatives could serve as antecedents of en and pn groups, respectively. The procedures were cumbersome but uneventful, the only difficulty arising from finding suitable neutral reducing conditions to transform malonic amide derivatives into the pn group without interference from the acidic C–H group. Diborane sufficed.

Condensation of salicylaldehyde with **1a** afforded the expected pentadentate ligand which was transformed (using the divalent metal acetates under N$_2$) into its Co(II) and Fe(II) complexes.[5]

X-Ray structure analysis was used to establish pentacoordination and investigate its stereochemical consequences. The compound α,α'-{2-(2'-pyridyl)ethyl}-ethylenebis(salicylideniminato)cobalt(II)–ethanol, Co-C$_{25}$N$_3$O$_2$H$_{21}$·C$_2$H$_5$OH, was selected for this work. It crystallizes in space group $P\bar{1}$ of the triclinic system with four molecules in a unit cell of dimensions a = 15.049(2), b = 15.127(2), c = 10.258(1) Å; α = 90.53(1), β = 93.53(1), and γ = 105.81(1)°. Least-squares refinement of positional and isotropic thermal parameters for the two independent formula units has led to a conventional R factor of 0.064 for 1237 reflections having $F^2 > 3\sigma(F^2)$.

The two independent, separate, neutral, complex molecules display the same distorted trigonal-bipyr-

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(1) M. F. Perutz, *Nature (London)*, **228**, 726 (1970).

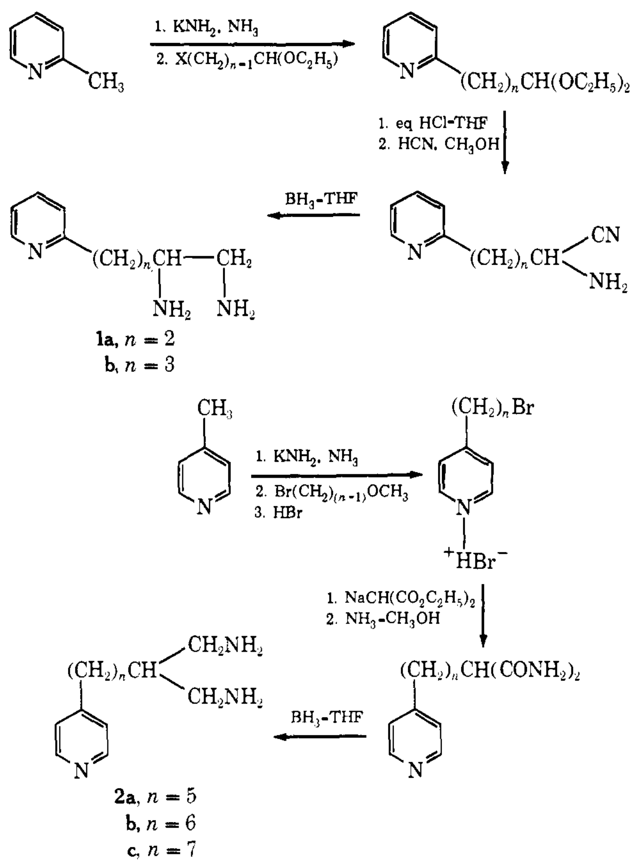
(2) J. C. Kendrew, *Science*, **139**, 1259 (1963).

(3) C. Brink-Shoemaker, D. W. J. Cruickshank, D. C. Hodgkin, M. J. Kamper, and D. Pilling, *Proc. Roy. Soc., Ser. A*, 278, 1 (1964).

(4) W. M. Coleman and L. T. Taylor, *J. Amer. Chem. Soc.*, **93**, 5446 (1971). For this example experimental evidence concerning coordination of the fifth ligand (a secondary amine) is equivocal.

(5) All of these compounds gave acceptable elemental analyses.

Scheme I. Preparation of Triamines



amidal arrangement of nitrogen and oxygen donors about their central cobalt atoms (Figure 1). The basal plane of this bipyramid contains the atoms N(1), O(2), N(3), and Co. One consequence of this ligation is a pronounced twist (dihedral angle 24°) between the six-membered salicylaldehyde rings which include the cobalt atom. Another is a statistically significant difference between Co–N bond lengths which average 2.15 Å for the pyridyl group and 1.96 Å otherwise.

Each molecule is hydrogen bonded to a separate ethanol solvate molecule. The hydrogen bond lengths O(1)–O(3) in both situations are 2.82 Å where O(3) is the oxygen atom in an ethanol molecule. Our calculations and packing diagrams absolutely exclude the possibility of any intermolecular coordination in a sixth position on either cobalt atom.

This five-coordinate Co(II) molecule assumes special interest because its mononuclear dioxygen adduct has been prepared, characterized, and crystallized in the monoclinic space group $P2_1/c$ with four molecules in a unit cell of dimensions $a = 9.566(1)$, $b = 19.466(3)$, $c = 12.773(2)$ Å, and $\beta = 106.03(1)°$. Structure analysis is severely hindered by the presence of disordered solvate molecules but preliminary results ($R = 0.10$) confirm the bent mode of bonding found for one other dioxygen adduct of cobalt[6] and, also, demonstrate significant stereochemical rearrangement of the five-coordinate complex so that the Schiff base adopts a nearly planar arrangement in the six-coordinate product molecule.

Other pentacoordinate ligand systems, and their transition metal complexes, have been prepared from

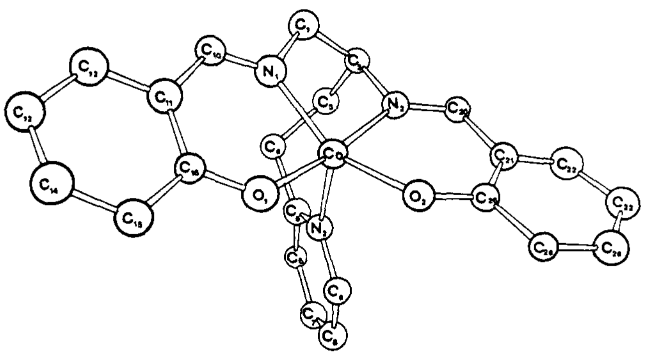


Figure 1. Perspective view of one molecule of $CoC_{25}N_3O_2H_{21}$.

these substituted en and pn derivatives and will be described subsequently.

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[6] G. A. Rodley and W. T. Robinson, *Nature (London)*, **235**, 438 (1972).

The α,α-Difluorobenzyl Radical and Its Analogs. The Question of Planarity[1]

Sir:

The difluorobenzyl cation, $PhCF_2^+$, was shown to be planar by both the ^{13}C and ^{19}F nmr studies of Olah, *et al.*[2,3] Strong back π-bonding from F to C exists in this cation. Conversely, the difluorobenzyl anion, $PhCF_2^-$, is known to be tetrahedral.[4,5] Apparently, this is due to repulsive interactions between the fluorine lone pairs and the π electrons of the sp^2-hybridized carbon of the planar anion.[5,6] What, then, is the geometry of the difluorobenzyl radical, $Ph\dot{C}F_2$ (**1**)? It is well known experimentally and theoretically that radicals $R\dot{C}F_2$ have a tendency to be nonplanar.[7-9] Could the phenyl group provide enough conjugative stabilization to overcome the tendency of $R\dot{C}F_2$ to be nonplanar? We now present esr and theoretical evidence which indicates radical **1** is planar with a shallow out-of-plane energy well.

Radical **1** and its *p*-fluoro analog **2** were obtained

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