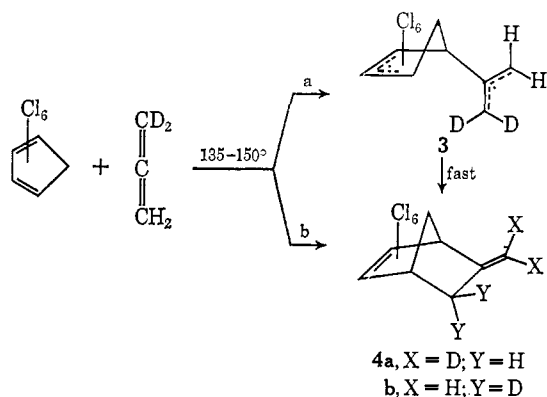


tion conditions.<sup>13</sup> Thus the actual kinetic isotope effect is probably even larger than the largest value observed, 1.21.



In the [2 + 4] cycloaddition reaction of hexachlorocyclopentadiene with 1,1-dideuterioallene to produce adducts **4a** and **4b** in 80% yield,<sup>14</sup> the observed kinetic deuterium isotope effect,  $k_H/k_D$ , was determined to be  $0.90 \pm 0.03$  (see Table II).

This value is entirely consistent with a rate-determining change of hybridization from  $sp^2$  to  $sp^3$  at  $C_1$  or  $C_3$ , and thus is, of course, consistent with a synchronous pathway for the reaction.

The fact that such obvious differences in  $k_H/k_D$  are found for the two different reactions is certainly strong evidence for a difference in mechanisms. The results for the [2 + 2] cycloaddition happily are consistent with past investigations which have shown the reaction to be nonsynchronous.<sup>15</sup> In the case of the [2 + 4] cycloaddition, in spite of the fact that the hypothetical intermediate diradical would be relatively quite stable, the evidence is certainly most consistent with a concerted mechanism. The two conclusions reinforce each other.

Of equal importance is the probability that this technique will prove to be an extremely sensitive probe into the simultaneity of any cycloaddition reaction in which allene may be a reactant.

**Acknowledgments.** We are pleased to acknowledge support of this work by the Petroleum Research Fund (Grant 753-G) of the American Chemical Society and by the National Science Foundation (Grant GP 8320).

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### Model Ligands for Square-Planar and Square-Pyramidal Complexes<sup>1</sup>

Sir:

We wish to report the chelate stereochemistry of an unusual new tetradentate ligand, 1,5-diazacyclooctane- $N,N'$ -diacetate (dacoDA). The stereochemistry of chelated 1,5-diazacyclooctane (daco) and 1,4-diazacycloheptane (dach, homopiperazine)<sup>2</sup> suggested that

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these ligands could be used to design a series of relatively simple tetradentate ligands which would lead to the formation of planar and, in the case of the daco derivatives, square-pyramidal (with an additional ligand) complexes. These ligands,  $daco(N-R)_2$  and  $dach(N-R)_2$ ,  $R = -CH_2CO_2^-$  or  $-CH_2CH_2NH_2$ , should coordinate in a plane since coordination of the two tertiary amines in the eight-membered ring restricts the R groups to such an extent that the two five-membered chelate rings can form only in the plane defined by the metal ion and the two nitrogens (Figure 1). In order to attain axial coordination a great amount of strain has to be introduced into the chelate framework. Furthermore, because of strong nonbonding interactions between the methylene protons on the backbone portions of the tetradentate ligands based on daco when both halves of the chelated eight-membered ring are folded back away from the metal ion, it was expected that one-half of the ring would fold toward the metal ion, placing one of the  $\beta$ -methylene protons over an axial position. This would effectively block coordination at this position as shown in Figure 1. Such appeared to be the case for complexes prepared from the parent daco molecule.<sup>2</sup>

We have now shown these predictions<sup>3</sup> to be correct for the Ni(II)-dacoDA complex. We have determined the structure of  $[Ni(dacoDA)(H_2O)] \cdot 2H_2O$  through X-ray crystallography and have found the solid-state geometry of the complex to be close to square pyramidal. In addition, experimental evidence suggests that this structure is maintained in aqueous solution. This is generally not the case for other five-coordinate complexes.<sup>4</sup>

Three-dimensional X-ray diffraction data were obtained using a Picker diffractometer with Mo  $K\alpha$  radiation. Green  $[Ni(dacoDA)(H_2O)] \cdot 2H_2O$  crystallizes in the space group  $P2_1/c$  with four molecules per unit cell. The lattice constants are  $a = 14.412$ ,  $b = 7.316$ , and  $c = 14.431$  Å with  $\beta = 112.92^\circ$ . A Patterson map was used to locate the positions of the nickel atoms, and a series of Fourier syntheses was then used to locate the remaining atoms. A full-matrix least-squares refinement on 1600 reflections resulted in an  $R$  value of 8%.

The details of the structure determination will be published on completion of the study. Figure 1 gives a perspective of  $Ni(dacoDA)(H_2O)$  with ligand-to-metal bond lengths and some pertinent bond angles. The nickel atom is located out of the plane about  $10^\circ$  toward the coordinated water. The complex is somewhat distorted from the idealized  $C_s$  symmetry expected from molecular models. The two remaining water oxygens (not shown in the figure) are 4.28 and 4.30 Å from the nickel which removes any possibility of coordination to the nickel.

The chelating properties of dacoDA were compared with those of ethylenediamine- $N,N'$ -diacetate (EDDA) which has essentially the same crystal-field strength as dacoDA but should not sterically restrict a metal ion from attaining six-coordination, and it has been found

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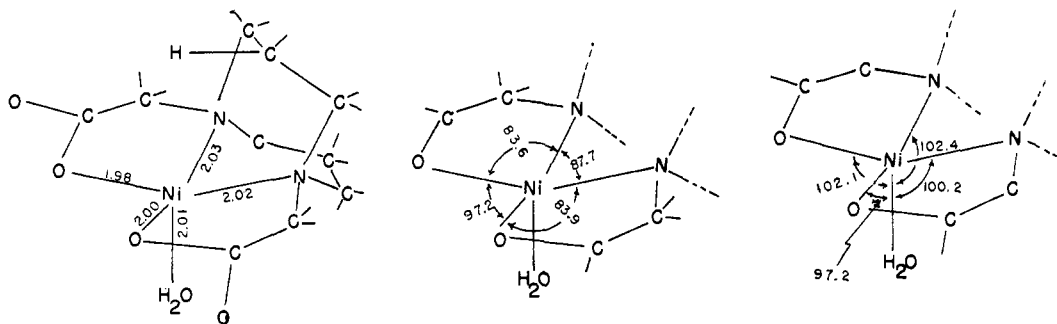


Figure 1. Perspective of Ni(dacoDA)(H<sub>2</sub>O). Bond lengths and bond angles in angstroms and degrees, respectively.

to form normal octahedral complexes with cobalt(III).<sup>5</sup> The blue complex Ni(EDDA)(H<sub>2</sub>O)<sub>2</sub> was prepared and its aqueous absorption spectrum found to adhere closely to that expected for a normal six-coordinate complex. The band at 9900 cm<sup>-1</sup> (<sup>3</sup>A<sub>2g</sub> → <sup>3</sup>T<sub>2g</sub>, O<sub>h</sub> symmetry) corresponding to 10Dq, was used to calculate the energies of the transitions to the <sup>3</sup>T<sub>1g</sub>(F) and <sup>3</sup>T<sub>1g</sub>(P),<sup>6</sup> and these values were within 3% of the experimental energies. Thus the nickel(II) sees an average environment. On the other hand, the spectrum of Ni(dacoDA)(H<sub>2</sub>O) dissolved in water was quite different from that obtained for the octahedral prototype. There was no corresponding band in the region of the <sup>3</sup>T<sub>2g</sub> transition, and the observed bands were considerably more intense than those found for Ni(EDDA)(H<sub>2</sub>O)<sub>2</sub> as might be expected if the Ni(II) were in a severely distorted octahedral or square-pyramidal field where there is no effective center of symmetry. Furthermore, it was found that the positions of the bands of Ni(dacoDA)(H<sub>2</sub>O) in the visible region were the same in the solid state (mull) as in aqueous solution suggesting that the complex has the same stereochemistry in both states.

A very interesting situation has been observed for the Co(II) complex of dacoDA which further substantiates the five-coordinate geometry imposed by this ligand. Whereas the Co(II) complex of EDDA is very easily oxidized to the Co(III) complex (Co(EDDA)(H<sub>2</sub>O)<sub>2</sub> is most easily prepared in an oxygen-free atmosphere), the dacoDA complex is very stable to oxidation. Oxygen and hydrogen peroxide will not oxidize the cobalt(II) complex even in the presence of carbon as evidenced from the lack of change in the absorption spectrum. Furthermore the reaction of H<sub>2</sub>dacoDA with Na<sub>2</sub>[Co(CO<sub>3</sub>)<sub>3</sub>] and [CoCO<sub>3</sub>(NH<sub>3</sub>)<sub>4</sub>]Cl yielded after prolonged heating the cobalt(II) complex of dacoDA as evidenced by absorption spectra. The spectrum of crystalline solid isolated from one of the reaction solutions corresponded quantitatively to that of the Co(II)-dacoDA complex. Since cobalt(III) appears to form exclusively six-coordinate complexes in aqueous solution, it would seem that the ligand is very effective in preventing coordination of the sixth water. It might then be asked how effectively could this ligand stabilize normally very easily oxidized chromium(II) or might it yield a nonoctahedral chromium(III) complex? The answers to these questions are currently being sought.

Both nickel complexes are high-spin with moments of 3.2 BM. Green [Ni(dacoDA)(H<sub>2</sub>O)]·2H<sub>2</sub>O is easily and

reversibly converted to the anhydrous square-planar complex by heating or treating with absolute ethanol. The complex is orange and diamagnetic. The details of the studies of the Co(II), Ni(II), and Cu(II) complexes of dacoDA and EDDA will be reported in the near future. Investigation of the corresponding complexes of other metal ions (*e.g.*, Cr(II), Cr(III), Fe(II), Fe(III), Pd(II), and Pt(II)) is being undertaken.

It is quite clear from our initial studies of the chelating properties of dacoDA that this ligand and its analogs offer a very interesting and unusual system for the investigation of such phenomena as kinetics of ligand exchange at an axial position and electron spin resonance. These studies are planned.

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## Structure and Reactivity of Propyl Ions in Gas-Phase Radiolysis

Sir:

Several years ago, Borkowski and Ausloos<sup>1</sup> irradiated equimolar mixtures of *n*-C<sub>4</sub>D<sub>10</sub> and *n*-C<sub>4</sub>H<sub>10</sub> and examined the isotopic structure of the propane formed in the hydride transfer reaction



They noted that most of the C<sub>3</sub>D<sub>7</sub>H consisted of CD<sub>3</sub>-CDHCD<sub>3</sub> and that, therefore, *n*-propyl ions, if formed in the primary fragmentation, rearranged before or during the hydride transfer reaction to the secondary structure. As was expected only *sec*-propyl ions were seen to react in the radiolysis of isobutane.<sup>2</sup>

Since the time those studies were carried out, considerable advances in our understanding of the gas-phase radiolysis of hydrocarbons have occurred.<sup>3</sup> We now know, for example, that in the earlier studies the straightforward interpretation of the mass spectra of

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