Fig. 1.—Nuclear magnetic resonance spectra: Curve A, 5-*exo*-chloro-6-*exo*-amide (III); curve B, 5-*exo*-chloro 6-*endo*-deuterio-6-*exo*-amide (IV); Curve C, 5-*exo*-chloro-6-*endo*-amide (V); Curve D, 5-*exo*-chloro-6-*exo*-deuterio-6-*endo*-amide (VI).
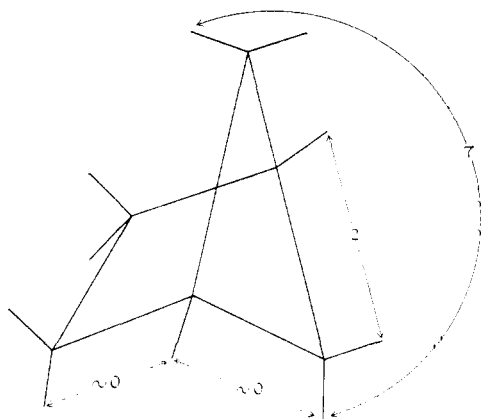

Fig. 2.—Some approximate proton spin–spin coupling constants for bicyclo[2.1.1]hexanes.

more, the deuterated analog (VI) shows remarkable simplicity.

These results, summarized in Fig. 2, suggest rather extensive interactions between a specific pair of protons separated by four single bonds, and smaller interactions between several pairs of adjacent protons. The long-range interaction may be rationalized by assuming fairly extensive overlap between the small lobes of the orbitals directed 180° away from the directions of the *endo* C_5 and C_6 to proton bonds (and consequently pointed *toward* each other). This explanation appears reasonable

when a scale model[4] of the bicyclo[2.1.1]hexane nucleus is examined.

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THE STEREOCHEMISTRY OF THE ETHYLENEDIAMINETETRAACETATOAQUOFERRATE (III) ION[1]

Sir:

A persuasive *a priori* case for a fully chelated (*i.e.*, sexadentate) and *seven*-coördinate formulation, $Fe(OH_2)Y^-$, of the common ethylenediaminetetraacetato (EDTA; Y^{4-}) complex of ferric iron

emerges from the synthesis of quite varied types of indirect structural evidence.[2] Proof of seven-coördination is now provided by the direct structural analysis of spectrometrically recorded $\{hkl\}$ X-ray data from a single crystal of the salt, RbFe-$(OH_2)Y\cdot H_2O$.

The monoclinic unit containing $4RbFe(OH_2)Y\cdot H_2O$ has $a = 14.17$, $b = 7.73$, $c = 14.63$ Å., $\beta = 90.44°$. Calculated and experimental densities agree at 1.93 g./cc. The space group is P2/a. A crystal specimen small enough to obviate the need for absorption corrections has given 2983 $\{hkl\}$ intensities measurable with MoKα radiation in the range, $0 < \sin(\theta/\lambda) < 0.77$. Some 96% of the amplitude data are presently included in a three-dimensional Fourier synthesis which yields both configuration and a structurally consistent set of bond parameters. The remaining amplitudes, mostly for reflections giving counts comparable with background, are gradually being added to the synthesis in conjunction with the refinement (just begun) of thermal parameters. Of present import is the indication from a Fourier synthesis of calculated amplitudes, using a single isotropic B of 3.25 Å.,[2] that Fe–O and Fe–N bond distances are known already to within 0.01 A. on the average. The discrepancy index R for all 2983 forms is presently 0.165 (for the $h0l$ zone, 0.121).

On the basis of (1) minimizing ring strain, (2) minimizing steric repulsion within the inner co-ordination group, and (3) permitting *quasi*-equivalence of ligands, the evident choice for a seven-coördinate $Fe(OH_2)Y^-$ containing sextet Fe(III) with its five unpaired electrons[3] is[2] the $NbF_7^=$ configuration[4] of maximum symmetry C_{2v}-mm. In fact, however, the experimentally established configuration is loosely describable as pentagonal bipyramidal, in disregard of the assumptions (2) and (3). Fe–O bond lengths average to 2.055 Å., very nearly the sum of the ionic radii, whereas the Fe–N bonds are 2.30 and 2.32 Å. In the sexadentate octahedral CoY^-, with which (a presently hypothetical) FeY^- containing *doublet* Fe(III) should be virtually isodimensional, the corresponding bond lengths are[5] 1.88 and 1.92 Å., much smaller and much less different from one another than with sextet Fe(III). The very long Fe–N bonds in $Fe(OH_2)Y^-$ make it easier for two nitrogen and three oxygen atoms (one from H_2O) to form a very roughly planar girdle about iron with three not unreasonably long Fe–O bonds at 2.08, 2.09, 2.10 Å. The other pair of Fe–O bonds, closed along the "pentagonal" axis without semblance of steric interference, are compensatingly short: 1.98, 2.02 Å. The free anion may have at most a twofold axis passing through H_2O, Fe, and the center of the C–C bond of the ethylenediamine ring. The ring bond angles at the central atom in $Fe(OH_2)Y^-$ are uniformly smaller (11–15°) than in CoY^-; apart from the angles and bonds which involve

Fig. 1.—Skeleton model in perspective of $Fe(OH_2)Y^-$: the short Fe–O bonds involve O_1 and O_2.

the central atoms, the ring geometries of the two complexes are similar.

The possibility that packing relations in the crystal control the selection of configuration for the bulky and presumably flexible $Fe(OH_2)Y^-$ is not dismissed readily. A configuration rather more like that of $NbF_7^=$ is indicated for an analogous Mn(II) complex now under study in this laboratory.

The machine computations of this paper were carried out at the Cornell Computing Center through the courtesy of Mr. Richard C. Lesser, Director. Our thanks go also to Mrs. Diana Chantry and Dr. Gordon S. Smith for assistance in the early stages of the study.

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(7) Predoctoral Fellow of the Monsanto Chemical Company, 1960–1961.

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A GENERALIZATION OF THE OCTANT RULE[1]

Sir:

During the past decade a considerable amount of experimental data has been accumulated by Cookson[2] and others that indicates a marked heightening of the long-wave length carbonyl transition in certain β,γ-unsaturated ketones, such as the santonides.[3] Recently, Labhart and Wagnière[4] put forth a possible explanation of the phenomenon. We wish to point out that the same electric dipole transition moment responsible for the enhanced intensity of absorption must also give rise to a marked increase in the rotational strength of the same electronic promotion. Briefly, the latter

(1) (a) Financial support was provided by National Science Foundation grants No. G-15746 (to K. M.) and No. G-6579 (to C. D.). (b) This paper represents No. LIII in the series "Optical Rotatory Dispersion Studies" by C. D. For paper LII see *Tetrahedron Letters*, 237 (1961).

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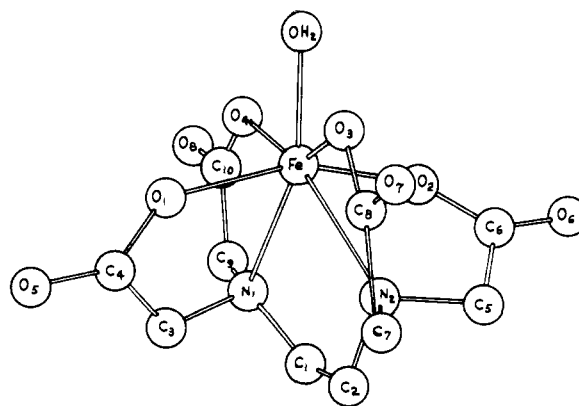(5) H. A. Weakliem and J. L. Hoard, *ibid.*, **81**, 549 (1959).