

emerges from the synthesis of quite varied types of indirect structural evidence.<sup>2</sup> Proof of seven-coordination is now provided by the direct structural analysis of spectrometrically recorded  $\{hkl\}$  X-ray data from a single crystal of the salt,  $\text{RbFe}(\text{OH}_2)\text{Y}\cdot\text{H}_2\text{O}$ .

The monoclinic unit containing  $4\text{RbFe}(\text{OH}_2)\text{Y}\cdot\text{H}_2\text{O}$  has  $a = 14.17$ ,  $b = 7.73$ ,  $c = 14.63$  Å.,  $\beta = 90.44^\circ$ . Calculated and experimental densities agree at 1.93 g./cc. The space group is  $P2_1/a$ . A crystal specimen small enough to obviate the need for absorption corrections has given 2983  $\{hkl\}$  intensities measurable with  $\text{MoK}\alpha$  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.<sup>2</sup>, that Fe-O and Fe-N bond distances are known already to within 0.01 Å. 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 coordination group, and (3) permitting quasi-equivalence of ligands, the evident choice for a seven-coordinate  $\text{Fe}(\text{OH}_2)\text{Y}^-$  containing sextet Fe(III) with its five unpaired electrons<sup>3</sup> is<sup>2</sup> the  $\text{NbF}_7^-$  configuration<sup>4</sup> 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 sextadentate octahedral  $\text{CoY}^-$ , with which (a presently hypothetical)  $\text{FeY}^-$  containing doublet Fe(III) should be virtually isodimensional, the corresponding bond lengths are<sup>5</sup> 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  $\text{Fe}(\text{OH}_2)\text{Y}^-$  make it easier for two nitrogen and three oxygen atoms (one from  $\text{H}_2\text{O}$ ) 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  $\text{H}_2\text{O}$ , Fe, and the center of the C-C bond of the ethylenediamine ring. The ring bond angles at the central atom in  $\text{Fe}(\text{OH}_2)\text{Y}^-$  are uniformly smaller ( $11$ – $15^\circ$ ) than in  $\text{CoY}^-$ ; apart from the angles and bonds which involve

(2) Cf. J. L. Hoard, Gordon S. Smith and Maurice Lind, in "Advances in the Chemistry of Coordination Compounds," © Stanley Kirschner, 1961, The Macmillan Company, New York, N. Y., in press.

(3) W. Klemm, *Z. anorg. allgem. Chem.*, **252**, 225 (1944).

(4) J. L. Hoard, *J. Am. Chem. Soc.*, **61**, 1252 (1939).

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

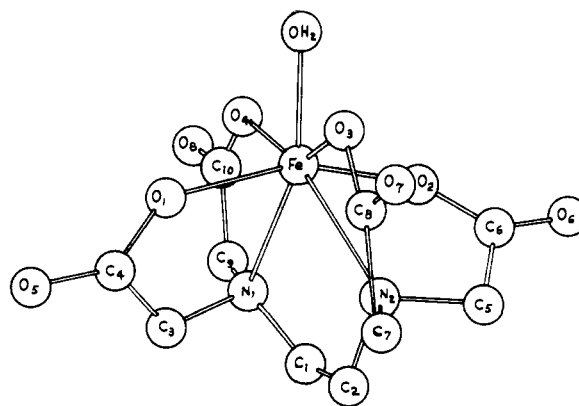


Fig. 1.—Skeleton model in perspective of  $\text{Fe}(\text{OH}_2)\text{Y}^-$ : the short Fe-O bonds involve  $\text{O}_1$  and  $\text{O}_2$ .

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  $\text{Fe}(\text{OH}_2)\text{Y}^-$  is not dismissed readily. A configuration rather more like that of  $\text{NbF}_7^-$  is indicated for an analogous  $\text{Mn}(\text{II})$  complex now under study in this laboratory.

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#### A GENERALIZATION OF THE OCTANT RULE<sup>1</sup>

Sir:

During the past decade a considerable amount of experimental data has been accumulated by Cookson<sup>2</sup> and others that indicates a marked heightening of the long-wave length carbonyl transition in certain  $\beta, \gamma$ -unsaturated ketones, such as the santonides.<sup>3</sup> Recently, Labhart and Wagnière<sup>4</sup> 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. I,III in the series "Optical Rotatory Dispersion Studies" by C. D. For paper LI1 see *Tetrahedron Letters*, 237 (1961).

(2) R. C. Cookson and N. S. Wariyar, *J. Chem. Soc.*, 2303 (1956); H. Birnbaum, R. C. Cookson and N. Lewin, *ibid.*, 1224 (1961).

(3) R. B. Woodward and E. G. Kovach, *J. Am. Chem. Soc.*, **72**, 1009 (1950).

(4) H. Labhart and G. Wagnière, *Helv. Chim. Acta.*, **42**, 2219 (1959). For a recent application of these views see S. Winstein, L. de Vries and R. Orloski, *J. Am. Chem. Soc.*, **83**, 2020 (1961).

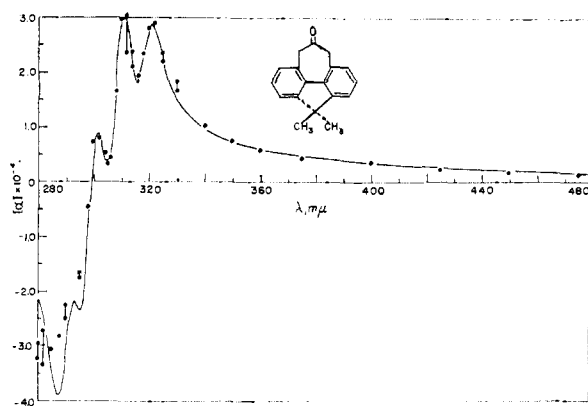


Fig. 1.—Rotatory dispersion of dimethyldibenzsuberone in isoöctane: — calculated; ● experimental. Two dots connected by a vertical line indicate two separate measurements at the same wave length.

phenomenon may be attributed to the formation of a twisted composite chromophore from the carbonyl and ethylenic (or other  $\pi$ -electronic) moieties; there are indications from ultraviolet spectral and optical rotatory dispersion<sup>5</sup> data that in the  $\alpha$ -haloketones, chlorine, bromine and iodine may act in the same manner as the  $\pi$ -electronic groups. As has been noted previously,<sup>6</sup> such *inherently* twisted chromophores (e.g., hexahelicene) will in general be associated with rotational strengths of greater orders of magnitude than are their more symmetric counterparts (e.g., the carbonyl group in saturated ketones).

The above discussion has important implications for structural organic chemistry. It permits a generalization of the octant rule<sup>7</sup> to include  $\beta$ ,  $\gamma$ -unsaturated ketones, although the theoretical principles involved are somewhat different than for the case of the saturated alkyl ketones. Moreover, because the contributions to the optical activity associated with the inherent asymmetry so outweigh those that can be attributed to asymmetrically disposed substituents, such as the ring methylene and alkyl groups, the sign of the Cotton effect of the long-wave length transition will be determined solely by the orientation of the unsaturated group with respect to the carbonyl chromophore.<sup>8</sup> In addition, because of the limitations placed on such orientations by the necessity of satisfying reasonable bond distances and bond angles, the handedness of twist (and hence the sign of the Cotton effect) can be correlated with the four far octants of the previously enunciated octant rule,<sup>7</sup> provided that the relative geometry of  $\pi$ -electronic system and carbonyl group is fixed, as in rigid molecules. Conversely, *conformations may be assigned to flexible molecules of this type on the basis of absolute configuration and Cotton effect curve.*

It is an important corollary to our work that for the type of compound under consideration the

(5) C. Djerassi, "Optical Rotatory Dispersion," McGraw-Hill Book Co., New York, N. Y., 1960.

(6) W. Moffitt and A. Moscovitz, *J. Chem. Phys.*, **30**, 648 (1959).

(7) W. Moffitt, R. B. Woodward, A. Moscovitz, W. Klyne and C. Djerassi, *J. Am. Chem. Soc.*, **83**, August (1961). See also chapter 13 in ref. 5.

(8) K. Mislow and C. Djerassi, *J. Am. Chem. Soc.*, **82**, 5247 (1960).

shape of the partial rotatory dispersion curve is uniquely determined by the shape of the corresponding absorption curve. This means that in a compound such as that depicted in Fig. 1, where the electric dipole and magnetic dipole transition moments must be colinear, it should be possible to *construct the rotatory dispersion curve* (if the background rotation is not too large) *solely from a knowledge of the absorption curve.*<sup>8,9</sup> Our calculations on this point, indicated in Fig. 1, bear out our contentions.

In a later paper the theory will be discussed in detail and examples will be given which point up the utility of the generalized octant rule.

(9) A. Moscovitz, chapter 12 in ref. 5.

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#### EQUILIBRIA BETWEEN LOW-MOLECULAR WEIGHT "LIVING" POLYMERS AND THEIR MONOMER<sup>1</sup>

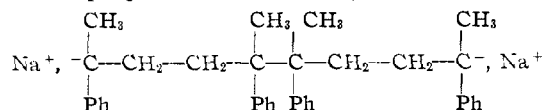
Sir:

Solutions of "living" polymers, *i.e.*, polymeric species retaining indefinitely their ability to grow,<sup>2</sup> must be in equilibrium with their monomer. For a high molecular weight material the equilibrium concentration of the monomer is independent of the degree of polymerization.<sup>3,4</sup> However, this is not the case for a low molecular weight polymer. For each monomer—"living" polymer system there is a minimum degree of polymerization  $n_0$  such that  $P_{n_0}^*$  may grow but not degrade.<sup>5</sup> The equilibrium concentration  $M_e$  is given, therefore, by the equation

$$k_p M_e \sum_{n \geq n_0} P_n^* = k_d \sum_{n > n_0} P_n^* \quad i.e. \quad M_e = K^{-1} (\sum_{n > n_0} P_n^*) / (\sum_{n \geq n_0} P_n^*)$$

where  $k_p$  and  $k_d$  are the rate constants of propagation and depropagation and  $K$  is the equilibrium constant of the polymerization,  $P_n^* + M \rightleftharpoons P_{n+1}^*$ .

It was suggested<sup>5</sup> that  $n_0 = 4$  for the system  $\alpha$ -methylstyrene–poly- $\alpha$ -methylstyrene and this structure was proposed for the "living" tetramer



To show that the action of metallic sodium on diluted THF solutions of  $\alpha$ -methylstyrene produces the tetramer, and not a mixture of polymers of  $\overline{DP} = 4$ , we studied the monomer–tetramer equilibrium. Increasing amounts of the monomer were added to the tetramer solutions and the mixture

(1) This work was supported by the National Science Foundation, Grant No. G14393 and by the Quartermaster Corp Grant No. DA-19-129-QM-1297.

(2) M. Szwarc, *Nature*, **178**, 1168 (1956); M. Szwarc, M. Levy and R. Milkovitch, *J. Am. Chem. Soc.*, **78**, 2656 (1956).

(3) H. W. McCormick, *J. Polymer Sci.*, **25**, 488 (1957).

(4) D. J. Worsfold and S. Bywater, *ibid.*, **26**, 299 (1957).

(5) M. Szwarc, *Makromolekulare Chemie*, **35**, 132 (1960).