

that direct anion solvation can be important in the more polar aprotic solvents, at least.<sup>4</sup>

While effects of the kind and magnitude found here may not necessarily persist for less stable anions with less delocalized negative charges, it may be that a change to less polar solvents could promote oxidation of some other carbanions which do not seem to oxidize in polar solvents.

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### Enantiomorphism in the Helical Aggregate of Lithium 12-Hydroxystearate

Sir:

It is been known, by electron microscope study, that some crystalline aggregates of soap from lubricating grease consist of fibers in the form of twisted ribbon or helical rope. However, little attention has been paid to the direction of the twist. Hotten and Birdsall<sup>1</sup> pointed out that fibers of lithium 12-hydroxystearate twist by the same hand, but they did not state the direction.

making a copy of the photograph. Therefore, by taking care of these points, we have made electron micrographs of aggregates of lithium 12-hydroxystearate.

12-Hydroxystearic acid (D-form) was purified from a commercial product by recrystallization of its methyl ester from methanol: m.p. 79.3–79.8°,  $[\alpha]^{15D} -0.3 \pm 0.1^\circ$  (pyridine); lit.<sup>4</sup> m.p. 80.5–81°,  $[\alpha]^{19D} -0.41^\circ$  (pyridine). The preparation of lithium soap was virtually identical with that previously described.<sup>1</sup> A highly refined mineral oil having a viscosity of 89.00 centistokes at 37.8° (100°F.), and containing about 69% paraffinic, 24.5% naphthenic, and 6.5% aromatic carbon atoms, was used as the dispersion medium. The specimens for electron microscopy were prepared by the suspension technique.<sup>2c</sup>

The direction of the twist was, as illustrated in Figure 1a, always right-handed, although the form and size of the aggregate were dependent on the experimental conditions. The same result was also obtained with other 12-hydroxystearate soaps (Na, K, Ca, Ba, and Pb soap). On the other hand, the fibers from hydrated mixtures of calcium oleate and calcium stearate exhibit both right-handed and left-handed twists. These results lead us to suggest that the right-handed twist of the aggregates of 12-hydroxystearate soaps may be related to the optical isomerism of this fatty acid, since the commercial sample of the 12-hydroxystearic acid used was the D-form.

In order to confirm this idea, the DL-form and the L-form of 12-hydroxystearic acid were prepared from the

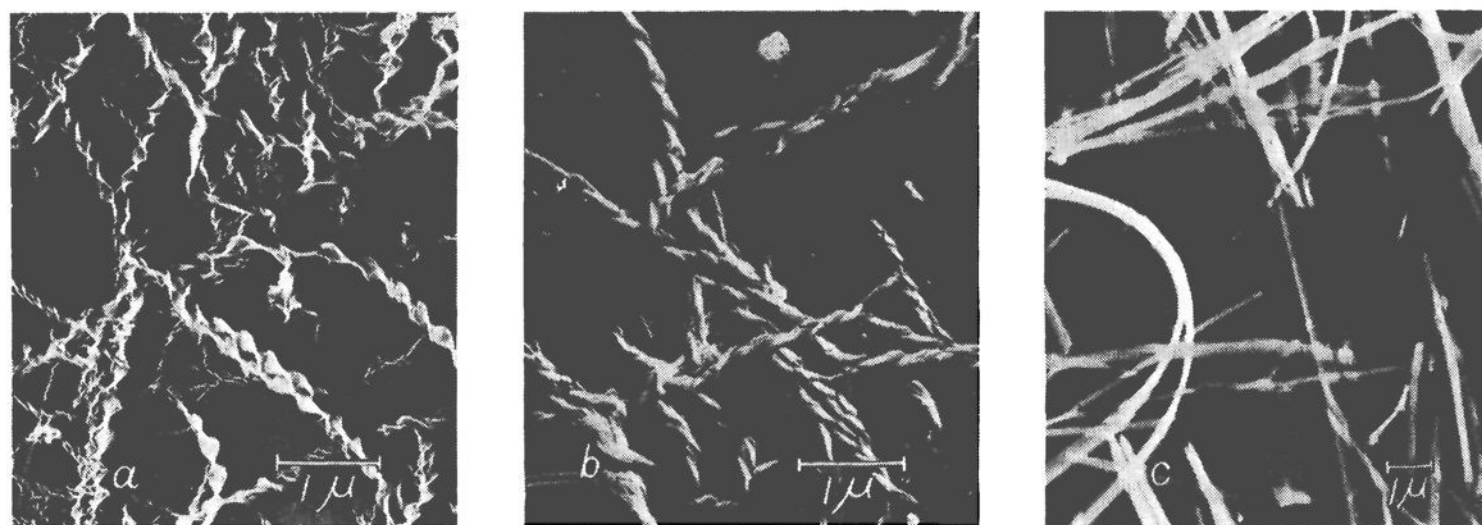


Figure 1. The effect of optical isomerism on the direction of the twist in fibrous aggregates of lithium 12-hydroxystearate: (a) D-form, right-handed twist; (b) L-form, left-handed twist; (c) DL-form, no twist. These photographs were made to show the same direction as that of the twist of the specimen.

On examining the electron micrographs of fibers of lithium 12-hydroxystearate hitherto published, we found that some micrographs<sup>2a-c</sup> exhibit right-handed twist and others,<sup>1,3a,b</sup> left-handed twist. This may be explained by the fact that the direction of the twist of fibers appearing in the photographs is dependent on (1) whether the specimen shadowed previously with metal was exposed directly to the electron beam, or through the support film, and (2) the process of

D-form of this acid. DL-12-Hydroxystearic acid<sup>5</sup> was obtained by reduction of 12-ketostearic acid derived from D-12-hydroxystearic acid. L-12-Hydroxystearic acid was prepared by the Walden inversion of D-12-hydroxystearic acid according to the procedure shown in Figure 2. The aggregates of their lithium soap were examined as described above for the D-form. The results are illustrated in Figures 1b and 1c, which show that the direction of the twist is left-handed for the L-form in contrast with the right-handed twist for the D-form, and that no twisted fibers are obtained for the DL-form. Although the acids of the L-form and DL-

(1) B. W. Hotten and D. H. Birdsall, *J. Colloid Sci.*, **7**, 284 (1952).  
(2) (a) A. Bondi, *et al.*, *NLGI Spokesman*, **13** (12), 12 (1950); (b) B. W. Hotten, *ibid.*, **19** (1), 14 (1955); (c) G. V. Vinogradov and V. V. Sinitsyn, *J. Inst. Petrol.*, **47**, 357 (1961).  
(3) (a) M. J. Vold, *et al.*, *NLGI Spokesman*, **18** (5), 8 (1954); (b) A. L. McClellan, *J. Chem. Phys.*, **32**, 1271 (1960).

(4) K. S. Hanssen, *Chem. Ind. (London)*, 1554 (1958).  
(5) I. Nakajima and S. Toyama, *J. Chem. Soc. Japan*, **81**, 1598 (1960).

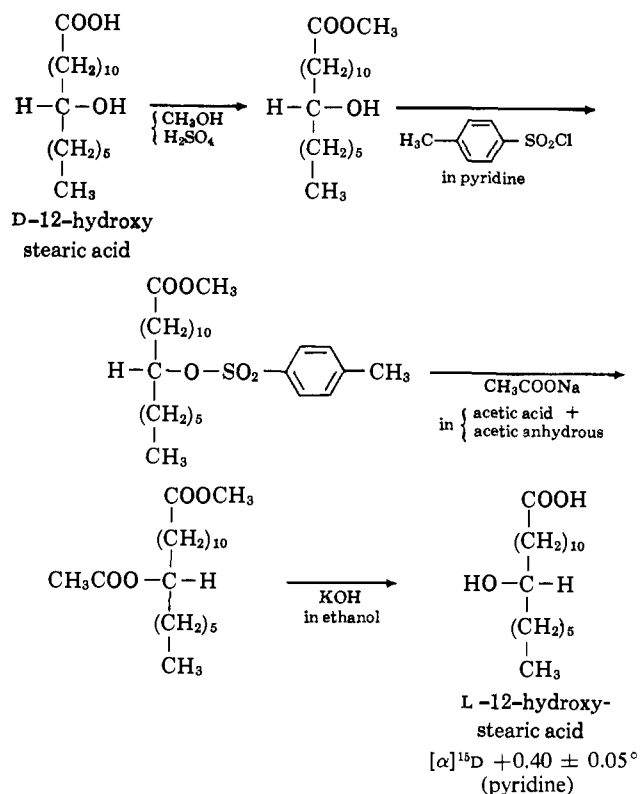


Figure 2. Preparation of L-12-hydroxystearic acid by Walden inversion.

form were used without sufficient purification, this did not affect the result.

As is well known, single crystals of optically active antipodes exhibit the phenomenon of enantiomorphism. It is interesting to note that the enantiomorphism has been found to occur in the crystalline aggregate when the optical isomer aggregates to possess helical symmetry.

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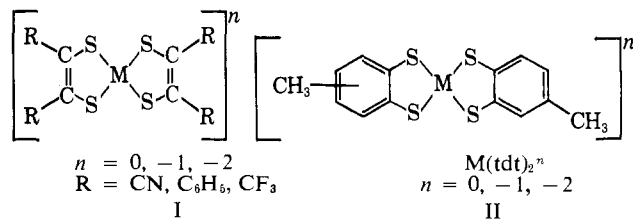
### The Myth of Nickel(III) and Nickel(IV) in Planar Complexes<sup>1</sup>

Sir:

Recent work<sup>2</sup> has firmly established the existence of planar metal complexes of general formulas I and II in which one of the significant features is the stability of the electronically unusual systems with  $n = 0, -1$ . Although the  $n = -2$  complexes can be successfully formulated in the usual fashion as containing dianionic ligands and divalent metal ions, the  $n = -1, 0$  complexes show chemical and physical properties inconsistent with the classical M(III) ( $n = -1$ ) and M(IV)

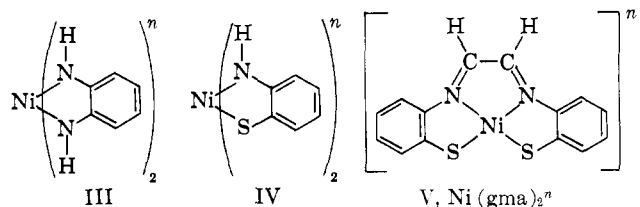
(1) Acknowledgment is made to the National Science Foundation for support of this research.

(2) S. I. Shupack, E. Billig, R. J. H. Clark, R. Williams, and H. B. Gray, *J. Am. Chem. Soc.*, **86**, 4594 (1964), and references contained therein.



( $n = 0$ ) formulations. In fact, evidence indicates that these complexes are more acceptably assigned as "metal-stabilized radical-ligand" systems.<sup>2</sup>

Our interest in the two possible formulations for these systems has led us to investigate the electronic structures of complexes containing nitrogen as well as sulfur as donor atom; certain of these complexes have been cited as authentic examples of Ni(IV).<sup>3</sup> In this communication, we report results on nickel complexes in series II, III, IV, and V.



The  $n = -1$  member of series II is reduced by  $\text{BH}_4^-$  to  $n = -2$  and oxidized by iodine to  $n = 0$ . Both the neutral complex  $\text{Ni}(\text{tdt})_2$  and  $[(n-\text{C}_4\text{H}_9)_4\text{N}]_2[\text{Ni}(\text{tdt})_2]^{4-}$  have been characterized. This demonstrates that electron-transfer reactions occur readily in series II, as they do in series I.

The  $n = 0$  III complex was originally claimed by Feigl and Fürth,<sup>5</sup> but doubt has since been expressed<sup>6</sup> concerning the number of hydrogens attached to nitrogens. Our analytical and molecular weight results, including a mass spectrum with parent peak at  $m/e$  270, on a sample prepared by the published method<sup>5</sup> agree with the original formulation III ( $n = 0$ ). The  $n = 0$  complex undergoes two reversible one-electron reductions to give the  $n = -1$  and  $-2$  complexes.

Complex IV ( $n = 0$ ) was prepared by a published method.<sup>7</sup> Analytical and molecular weight data, including a mass spectrum with parent peak at  $m/e$  304, establish formula IV ( $n = 0$ ) and are inconsistent with the original formulation as a binuclear oxygen-bridged Ni(IV) complex. Complex IV ( $n = 0$ ) shows two reversible reduction waves, indicating the existence of the  $n = -1$  and  $-2$  complexes. Complex IV ( $n = -1$ ), prepared by  $\text{BH}_4^-$  reduction of IV ( $n = 0$ ), shows an e.s.r. spectrum with  $\langle g \rangle = 2.055$  (DMF, DMSO, THF). The behavior of systems III and IV suggests that the electron-transfer reactions common to the sulfur systems may be a more general phenomenon.

Complexes of Zn(II) and Cd(II) with glyoxal bis-(2-mercaptoanil) (gma) have been prepared recently.<sup>8</sup>

(3) See, for example, F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," Interscience Division, John Wiley and Sons, Inc., New York, N. Y., 1962, pp. 744, 745.

(4) R. Williams, unpublished results.

(5) F. Feigl and M. Fürth, *Monatsh.*, **48**, 445 (1927).

(6) Z. Bardoděj, *Collection Czech. Chem. Commun.*, **20**, 176 (1955), prefers two less hydrogens on the nitrogens and formulates this as a nickel(II) species with oxidized ligands.

(7) W. Hieber and R. Bruck, *Z. anorg. allgem. Chem.*, **269**, 13 (1952).

(8) H. Jadamus, Q. Fernando, and H. Freiser, *J. Am. Chem. Soc.*, **86**, 3056 (1964).