mmoles) of pentacarbonyliron in 20 ml. of ethylcyclohexane was heated in a bath at 130° for 64 hr. The cooled mixture was filtered, and the filtrate was chromatographed. The orange solution eluted by pentane was evaporated, and the residue was dissolved in 20 ml. of pentane. The solution was cooled to −78° and filtered. Evaporation of the filtrate followed by fractional sublimation (product taken at 90° (0.1 mm.)) gave 10 mg. of red-orange solid, m.p. 88°, dec. 145°. Combination of the products from a number of such runs gave sufficient material for analysis and spectroscopic studies. Duplication of the procedure in the literature[3] employing dodecacarbonyltriiron gave the same product.

The infrared spectrum of the material showed carbonyl stretching bands (carbon disulfide solution, NaCl optics) at approximately 2079, 2045, and 2008 cm.$^{-1}$ (lit.[4] 2076, 2044, 2004, and 1992 cm.$^{-1}$). Its n.m.r. spectrum showed bands at τ 0.97, 2.93, and 4.50 (*vs.* external tetramethylsilane), with the relative intensities and coupling constants reported for the bands of hexacarbonyl(thianaphthene)diiron at τ 1.10, 3.05, and 4.60 (*vs.* internal tetramethylsilane).[4]

Anal. Calcd. for $C_{14}H_6O_6SFe_2$: C, 40.61; H, 1.46; S, 7.74; mol. wt., 414. Found: C, 41.64; H, 2.32; S, 7.20; mol. wt , 424.

The Reaction between Anthracene and Dodecacarbonyltriiron.—A mixture of 1.8 g. (10 mmoles) of anthracene with 8.0 g. (16 mmoles) of dodecacarbonyltriiron in 100 ml. of cyclohexane was heated in a bath at 90° for 48 hr. The cooled mixture was filtered, and the filtrate was chromatographed. The orange solution eluted with a 4:1 pentane–dichloromethane mixture was evaporated. After sublimation of the solid product at 90° (0.1 mm.) for 12 hr., the unsublimed portion was crystallized several times from a chloroform–cyclohexane mixture to give 100 mg. (3% yield) of fine orange needles of the complex, dec. 140°. The actual conversion to product was much higher, but freeing the complex from traces of excess anthracene was exceedingly difficult. The infrared spectrum of the compound showed carbonyl stretching bands at 2054 (s), 1993 (s), and 1975 (s) cm.$^{-1}$. Mass spectrometric analysis showed the hydrocarbon moiety of the complex to be anthracene.

Anal. Calcd. for $C_{17}H_{10}O_3Fe$: C, 64.18; H, 3.16; S, 0.0; mol. wt., 318. Found: C, 64.29; H, 3.21; S, 0.05; mol. wt., 357.

The Reaction between 9-Acetylanthracene and Dodecacarbonyltriiron.—A mixture of 2.0 g. (9 mmoles) of 9-acetylanthracene and 5.0 g. (10 mmoles) of dodecacarbonyltriiron in 100 ml. of cyclohexane was heated in a bath at 90° for 21 hr. The cooled mixture was filtered, and the filtrate was chromatographed. The orange solution eluted with a 3:2 pentane–dichloromethane mixture was evaporated. Three crystallizations (pentane–dichloromethane) of the residue gave 100 mg. (3% yield) of orange solid, m.p. 135° dec. Again the complex was formed in more substantial amounts, but freeing it from excess ligand was difficult. The infrared spectrum of the compound showed carbonyl stretching bands at 2061 (s), 2056 (s), 2003 (s), 1995 (s), 1982 (s), and 1698 (w) cm.$^{-1}$.

Anal. Calcd. for $C_{19}H_{12}O_4Fe$: C, 63.36; H, 3.35; mol. wt., 360. Found: C, 63.19; H, 3.28; mol. wt., 354.

The Reaction between 1-Vinylnaphthalene and Dodecacarbonyltriiron.—A mixture of 1.8 g. (14 mmoles) of 1-vinylnaphthalene and 5.0 g. (10 mmoles) of dodecacarbonyltriiron in 100 ml. of cyclohexane was heated in a bath at 90° for 16 hr. The cooled mixture was filtered, and the filtrate was chromatographed. The orange solution eluted by a 4:1 pentane–dichloromethane mixture was evaporated, and two crystallizations (pentane–dichloromethane) of the residue gave 1.25 g. (31% yield) of orange crystals, m.p. 92–95°. A portion was recrystallized to an analytical sample, m.p. 94–96°. The infrared spectrum of the compound showed carbonyl stretching bands at 2048 (s), 1983 (s), and 1973 (s) cm.$^{-1}$.

Anal. Calcd. for $C_{18}H_{10}O_3Fe$: C, 61.25; H, 3.42; mol. wt., 294. Found: C, 61.48; H, 3.56; mol. wt., 278.

The compound did not absorb hydrogen at atmospheric pressure over palladium-on-charcoal catalyst in ethanol. It reacted with triphenylphosphine at room temperature in acetone solution to give tricarbonylbis(triphenylphosphine)iron and tetracarbonyl(triphenylphosphine)iron, identified by their infrared spectra.[10]

(10) F. A. Cotton and R. V. Parish, *J. Chem. Soc.*, 1440 (1960).

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
THE UNIVERSITY OF PITTSBURGH,
PITTSBURGH, PENNSYLVANIA 15213

Study of the Relative Solubilities of Diastereoisomers of Cobalt(III) Complexes Containing Optically Active Amino Acids[1]

BY CHONG TAN LIU AND BODIE E. DOUGLAS

Received July 13, 1964

The most generally used method for the resolution of optically active complex ions involves the fractional crystallization or precipitation of diastereoisomers. A solubility rule has been used[2,3] for relating the configurations of octahedral complexes based on the expectation that, for similar complexes resolved with the same resolving agent, the configurations will be the same for all of the complexes with the same relative solubilities of their diastereoisomers. Jaeger[4] at first criticized the solubility rule and later used it in his own work.[5]

The complexes for which the solubility rule has been applied differ in the chirality of the spiral arrangement of the chelate rings formed by the bidentate ligands AA in complexes of the type $[M(AA)_3]^{n+}$ or *cis*-$[M(AA)_2X_2]^{n+}$. The present study was concerned with complexes of the type $[Co(en)_2aa]^{2+}$ (aa = bidentate amino acid anion) using L- and D-alanine (alan), L- and D-leucine (leuc), L- and D-phenylalanine (palan), glycine (gly), and picolinic acid (pic). L and D refer to the absolute configurations of the amino acids.

The preparations of the complexes have been described.[6] The unresolved complexes as the iodide salts (in solution) were converted to the diastereoisomers by adding equivalent amounts of the silver salt of the resolving agent to remove all of the iodide ions as AgI. The diastereoisomers were fractionally separated by either: (1) slow crystallization from aqueous solution by cooling or by evaporation at room temperature, or (2) adding at least an equal volume of an organic solvent followed by slow crystallization. The first method was used for the diastereoisomers which

(1) This work was supported by a research grant (GM10829-06S1) from the Division of General Medical Studies, Public Health Service.
(2) A. Werner, *Ber.*, **45**, 1229 (1912).
(3) M. Delépine, *Bull. soc. chim. France*, [5] **1**, 1256 (1934).
(4) F. M. Jaeger and H. B. Blumendal, *Z. anorg. allgem. Chem.*, **175**, 161 (1928).
(5) F. M. Jaeger, *Bull. soc. chim. France*, [5] **4**, 1201 (1937).
(6) C. T. Liu and B. E. Douglas, *Inorg. Chem.*, **3**, 1356 (1964).

were appreciably soluble in ethanol, methanol, and acetone. These were the bromo-*d*-camphor-π-sulfonates (*d*-Bcs) of the complexes of L- and D-leucine, L- and D-phenylalanine, and picolinic acid. Method 2 using water and acetone was employed for the *d*-Bcs salt of the alanine and glycine complexes. For these compounds the solubilities of the diastereoisomers decreased with increasing temperature. Water only, water and ethanol, or water and methanol were used in the other cases. Procedures for an example of each type of resolution have been given.[6] The resolutions were carried out using 0.5–10 g. of complex. The smaller amounts were used for the more expensive amino acids. All resolutions were repeated at least once and in many cases using appreciably different weights of complex. Where it could be checked it was found that changing the solvent or solvent combination did not reverse the order of solubilities of the diastereoisomers.

The separation of diastereoisomers is usually based on solubility differences. However, in some resolution procedures timing seems to be important, suggesting that in these cases the rate of nucleation may be more important than the solubility differences. No time dependence was observed in the present work. The fractions separated initially were never completely resolved. Many recrystallizations were necessary. Since some of each of the configurational isomers had crystallized in even the first fraction and since enough time—hours, days, or even weeks—had elapsed for crystallization to be complete for the conditions, it is assumed that the separations were determined by solubility differences.

Stereospecific effects can cause significant differences in the stabilities of optically active complexes in the two configurations (Λ and Δ) when they contain an optically active ligand.[7] However, it has been shown that when the complexes of the type $[Co(en)_2L\text{-aa}]I_2$ (or D-aa) are prepared the two isomers are produced in equal amounts.[6] Hence the differences in stability of the two isomers as iodide salts must be small.

Factors which could determine the differences in solubilities of the diastereoisomers are: (1) specific interactions in solution between the resolving agent (an anion) and the optically active complex ion or the coordinated amino acid, (2) differences in crystal energy determined by specific interactions as in (1) occurring in the solid, or (3) differences in crystal energy determined by the efficiency of packing of complex cations containing optically active amino acids with optically active anions.

The optical isomers which were found in the less soluble diastereoisomers are listed in Table I. The most striking pattern is that for either bromo-*d*-camphor-π-sulfonate or *d*-tartrate as the anions, where resolutions were achieved, the complexes with optically inactive or D-amino acids give the less soluble compounds with the $(-)_{546}$ rotation or the Λ configuration.

(7) E. J. Corey and J. C. Bailar, Jr., *J. Am. Chem. Soc.*, **81**, 2620 (1959).

The opposite configuration is encountered in the less soluble diastereoisomer for the complexes of L-amino acids, *i.e.*, the less soluble pairs for each active amino acid are mirror images. There cannot be preferred interactions between the active amino acid in a complex of a given configuration and (specifically) the *d*-anion, since the results with *l*-tartrate ion are identical with those with *d*-tartrate ion. It seemed surprising to find that the same isomers separated with *d*- and *l*-tartrate ion. However, since the $(+)_{546}$-$[Co(en)_2L\text{-leuc}]^{2+}$ ion separated first with *d*-tartrate ion, its mirror image, $(-)_{546}$-$[Co(en)_2D\text{-leuc}]^{2+}$ should be expected to separate before the (+) isomer with *l*-tartrate ion—as observed. The same situation applies to the mirror images $(-)_{546}$-$[Co(en)_2D\text{-leuc}]$ *d*-tartrate and $(+)_{546}$-$[Co(en)_2L\text{-leuc}]$ *l*-tartrate, each of which is the less soluble diastereoisomer. The corresponding pairs could not be completed for the alanine and phenylalanine complexes because of the failure of the resolution procedures in the cases shown in Table I.

TABLE I

CONFIGURATIONS OF THE LESS SOLUBLE DIASTEREOISOMERS[a]

	Resolving agent			
Complex ion	*d*-Bcs	*d*-tartrate	*l*-tartrate	SbO-*d*-tartrate
$[Co(en)_2gly]^{2+}$	− (Λ)	N.r.[c]	N.r.[c]	− (Λ)
$[Co(en)_2L\text{-alan}]^{2+}$	+ (Δ)	N.r.[c]	N.r.[c]	− (Λ)
$[Co(en)_2D\text{-alan}]^{2+}$	− (Λ)*	− (Λ)*	− (Λ)*	+ (Δ)
$[Co(en)_2L\text{-leuc}]^{2+}$	+ (Δ)*	+ (Δ)	+ (Δ)*	+ (Δ)*
$[Co(en)_2D\text{-leuc}]^{2+}$	− (Λ)	− (Λ)*	− (Λ)*	+ (Δ)
$[Co(en)_2L\text{-palan}]^{2+}$	+[b](Δ)	+ (Δ)*	+ (Δ)*	N.r.[c]
$[Co(en)_2D\text{-palan}]^{2+}$	N.r.[c]	N.r.[c]	N.r.[c]	N.r.[c]
$[Co(en)_2pic]^{2+}$	− (Λ)	...	...	...
$[Co(en)_3]^{3+}$	...	+ (Λ)	− (Δ)*	+ (Λ)*

[a] The signs refer to the most prominent CD peak and also to the sign of rotation at 546 mμ for the predominant isomer in the first fraction. The absolute configurations, Λ or Δ using Piper's convention, are those assigned from CD studies,[6] except for $[Co(en)_3]^{3+}$, for which the configuration was established by X-ray methods. The optical isomers were purified and optical rotations reported[6] for all except the complexes marked *. For these compounds the diastereoisomers were fractionally precipitated and the CD curves recorded for the starting solution, the first fraction, and the mother liquor. These were compared with the characteristic curves of the completely resolved complexes. [b] J.-P. Mathieu [*Bull. soc. chim. France*, [5] **6**, 873 (1939)] reported that the $(-)_{546}$ isomer is the less soluble one. The resolution was repeated and also the $(-)_{546}$ isomer was isolated from the more soluble diastereoisomer in this study. [c] No resolution.

The typical behavior of complexes with inactive ligands is shown by $[Co(en)_3]^{3+}$ where opposite configurations are obtained with *d*- or *l*-tartrate ion. It should also be mentioned that the usual method for the resolution of this complex involves the crystallization of $[Co(en)_3]Cl$ *d*-tartrate, but the result is the same—the less soluble salt contains the Λ isomer.

The situation becomes more complicated when one considers the results with the antimonyl-*d*-tartrate ion. The same configurational isomer separates first for both L- and D-leucine, although the pattern for the alanine complexes was the same as that observed earlier with the other amino acids and resolving agents.