TABLE III

ELECTRONIC SPECTRA FOR TETRAETHYLAMMONIUM BIS(o-CARBORANE-1,2-DITHIOLATO)NICKEL(II)

Solvent	Absorption, cm^{-1}	ϵ	Assignment
Nujol	13,900	...	$^1A_{1g} \rightarrow {}^1A_{2g}$
	20,400	...	$^1A_{1g} \rightarrow {}^1B_{1g}$
	23,300	...	$^1A_{1g} \rightarrow {}^1E_g{}^a$
	29,400	...	$^1A_{1g} \rightarrow {}^1A_{2u}$
	34,500	...	$^1A_{1g} \rightarrow {}^1E_u$
CH_3NO_2	13,700	30	$^1A_{1g} \rightarrow {}^1A_{2g}$
	20,400	70	$^1A_{1g} \rightarrow {}^1B_{1g}$
	22,500	260	$^1A_{1g} \rightarrow {}^1E_g{}^a$
DMF	13,500	49	$^1A_{1g} \rightarrow {}^1A_{2g}$
	20,200	110	$^1A_{1g} \rightarrow {}^1B_{1g}$
	23,300	240	$^1A_{1g} \rightarrow {}^1E_g{}^a$
	30,800	22,000	$^1A_{1g} \rightarrow {}^1A_{2u}$
DMF + pyridine	13,500	54	$^1A_{1g} \rightarrow {}^1A_{2g}$
	20,000	132	$^1A_{1g} \rightarrow {}^1B_{1g}$
	23,300	257	$^1A_{1g} \rightarrow {}^1E_g{}^a$
DMF + KCN	13,600	56	$^1A_{1g} \rightarrow {}^1A_{2g}$
	20,400	132	$^1A_{1g} \rightarrow {}^1B_{1g}$
	22,300	242	$^1A_{1g} \rightarrow {}^1E_g{}^a$

[a] Questionable assignment.

species have their first absorption maximum at higher energies than the comparable bisdithiolate complex. This is consistent with previously reported complexes of this type.[2]

One further point is worthy of note. The substitution of bromine on the carborane nucleus in carboranedithiolate species appears to have some effect on the strength of complexation as indicated by the variation in the respective Δ_1 values. The same type of alteration was not observed in the phosphinocarboranes.

TABLE IV

LIGAND FIELD SPECTRAL DATA

Complex[a,b]	λ_{max}, cm^{-1}	Δ_1, cm^{-1} [c]
$[(C_2H_5)_4N]_2[Ni(DMC)_2]$	13,900	16,690
	20,400	
	23,250	
$[(C_6H_5)_3P)_2Ni(DMC)]$	16,500	19,330
	20,000	
$[((C_6H_5)_3P)_2Ni(DMMBC)]$	18,500	21,320
$[(TPP)Ni(DMC)]$	22,200[d]	
$[(DPPC)Ni(DMC)]$	20,400	23,210
	22,200[d]	
$[Ni(DPPC)_2]Cl_2$	21,500[d]	
$[(DPPC)NiCl_2]$	17,850 sh	20,660
	20,200[d]	
	21,700[d]	
$[Ni(DPMBC)_2]Cl_2$	20,800[d,e]	
	22,700[d]	
$[Ni(DPDBC)_2]Cl_2$	21,300 (ϵ 1640)[d,f,g]	
$[Ni(DPTBC)_2]Cl_2$	21,300 (ϵ 3200)[d,f,g]	

[a] Abbreviations listed in Table I. [b] Spectra obtained on Nujol mulls unless otherwise specified. [c] Δ_1 values calculated using the relationship $F_2 = 10F_4 = 800$ cm^{-1}. [d] The absorption due entirely, or in part, to a charge-transfer phenomenon. [e] Spectrum was also obtained in DMF. One absorption at 21277 cm^{-1} (ϵ 2600) was noted. This absorption arises from a charge-transfer phenomenon. [f] Spectra obtained in DMF. [g] DPDBC = 1,2-bis(diphenylphosphino)dibromo-o-carborane and DPTBC = 1,2-bis(diphenylphosphino)tribromo-o-carborane.

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Circular Dichroism of the Tris[di-μ-hydroxo-bis(ethylenediamine)cobalt(III)]cobalt(III) Ion

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The results and implications of the fractional precipitation of tris[di-μ-hydroxo-bis(ethylenediamine)cobalt(III)]cobalt(III) nitrate with potassium d-antimonyltartrate are reported and the kinetic behavior of the fractions is used to determine their purity. It appears that only four of the eight possible isomers are formed in the synthesis of the complex ion and that only two of these are resolved under the experimental conditions. The circular dichroism is discussed in terms of four adjacent but relatively noninteracting chromophores. However, it is shown that it is impossible to assign uniquely the absolute configurations of the central and peripheral octahedra on the bases of the signs of the rotational strengths from the dominant dichroism maxima.

Werner's[1] polynuclear compound, tris[di-μ-hydroxo-bis(ethylenediamine)cobalt(III)]cobalt(III) nitrate, was only recently resolved by Goodwin, Gyarfas, and Mellor.[2] Of the eight isomers having Werner's proposed structure it was believed that four were obtained by fractional precipitation with d- and l-antimonyltartrate and subsequent conversion to their thiocyanates. The distinct differences between the four, which were designated as D_I, L_I, D_{II}, and L_{II} and thought to consist of two enantiomeric pairs, were established by their specific rotations and their rates of racemization: $[\alpha]^{20}_D$ ±3920° and $t_{1/2}$ = 1.9 hr (40°) for D_I and L_I, while $[\alpha]^{20}_D$ ±3620° and $t_{1/2}$ = 19 hr (40°) for D_{II} and

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[1] A. Werner, *Ber.*, **40**, 2103 (1907).

[2] H. A. Goodwin, E. C. Gyarfas, and D. P. Mellor, *Australian J. Chem.*, **11**, 426 (1958).

L_{II}. When a large quantity of the racemic compound was fractionally precipitated using *d*-antimonyltartrate, a plot of the specific rotation against the number of fractions changed direction no less than 13 times. Since each inflection could not then represent one of the eight isomers, this curious behavior was attributed to the short half-lives of some of the isomers compared to the total time required for their separation.

Our interest in polynuclear metal complexes prompted us to enlarge upon the earlier experimental work in order to investigate more fully the optical activity of this compound.

Experimental Section

Fractionation Scheme.—To circumvent the difficulties encountered by Goodwin, Gyarfas, and Mellor (*vide supra*), the following method was devised. To 5 g of the polynuclear compound in 200 ml of water at 40° was added 10 ml of a near-boiling solution containing 0.30 g of potassium *d*-antimonyltartrate, or $^1/_{32}$ of the amount required to precipitate the total quantity of the complex ion. Crystallization was induced by vigorous scratching on the sides of the vessel. The mixture was then cooled in an ice bath to effect complete precipitation and filtered. The precipitate was washed with water, ethanol, and ether and dried in air. The filtrate was again heated to 40°, whereupon another 0.30 g of the antimonyltartrate was added and a second fraction was obtained in the same manner. To obtain a third fraction, another 5-g portion of the polynuclear compound was treated with 0.60 g of the antimonyltartrate (the sum of the amount used in obtaining the first two fractions), the precipitate was discarded, another 0.30 g of the resolving agent was added to the filtrate, and the third fraction was obtained. This procedure, *viz.*, precipitating the first portion of any fraction using the total quantity of antimonyltartrate from the preceding fraction, followed by the addition of another 0.30 g, was continued until 32 fractions had been collected. Yields were always nearly quantitative, but in the later fractions it was difficult to avoid the formation of intractable tars. Although the procedure was laborious and consumed many days for completion, the total time for the separation of any one fraction was somewhat less than 4 hr, and a great part of this time was at ice-bath temperature.

A portion of each fraction was then converted to the soluble acetate,[2] the concentration was measured spectrophotometrically, at 494 mμ, and the rotation was measured at the sodium D line in a 1-dm cell. The results are displayed in Figure 1 where the ratio of the rotation to the absorbancy, $[\alpha]_D/A_{494}$, is plotted against fraction number. Some of the fluctuation noted beyond the 18th fraction can undoubtedly be attributed to small amounts of tars which prevent a clean separation of fractions.

Attempts to Distinguish Isomers.—The remaining portion of each fraction was converted to the thiocyanate.[2] Since the nmr and infrared spectra of each were not measurably different, the rate of loss of optical activity was measured at 40°. Figure 2 contains the results.

Preparation of D_I, L_I, D_{II}, and L_{II} Thiocyanate Monohydrates.—These were prepared according to the published method.[2] The analytical results are given in Table I, wherein the specific rotations for these fractions are also given.

Discussion of Results

Theoretically, eight isomers of the polynuclear ion can be formed during its synthesis. Denoting the helical sense of the central octahedron by the capital Greek letter and those of the peripheral groups by the lower case letters, these are Δδδδ, Δλδδ, Δλλδ, Δλλλ, Λλλλ, Λδλλ, Λδδλ, and Λδδδ.

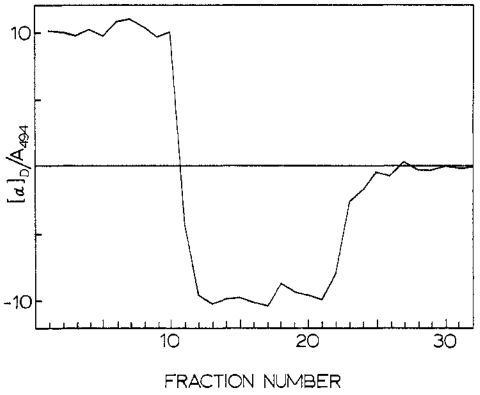

Figure 1.—Results from the fractional precipitation of the $Co_4(en)_6(OH)_6^{6+}$ ion with potassium *d*-antimonyltartrate.

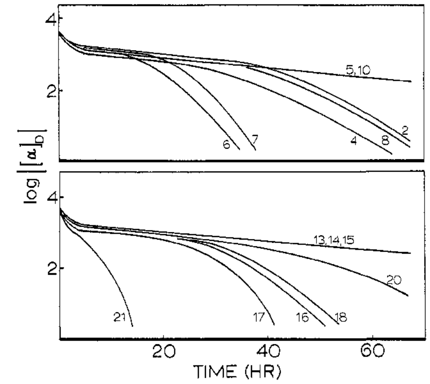

Figure 2.—First-order rate plots for the loss of optical activity at 40° for the various fractions of $[Co_4(en)_6(OH)_6](NCS)_6 \cdot H_2O$. The loss of fractions 1, 3, 9, 12, and 19 prevented the measurement of their kinetic behavior.

TABLE I

ANALYTICAL RESULTS FOR $[Co_4(C_2H_8N_2)_6(OH)_6](NCS)_6 \cdot H_2O$

	% C	% H	$[\alpha]^{20}_D$, deg
Calcd	20.3	5.3	...
D_I	20.1	5.2	3620
L_I	19.8	5.2	−3630
D_{II}	20.3	5.1	3630
L_{II}	20.4	5.0	−3620

The variation of the rotation with fraction number which is shown in Figure 1 indicates the *possibility* of the formation of all eight isomers. Thus, the dextrorotatory fractions comprise very nearly $^3/_8$ of the total number of fractions, as do the levorotatory fractions also. The last fractions which possess essentially no activity make up approximately the remaining $^2/_8$ and must be a racemic mixture. Furthermore, this conclusion would require that all are probably formed in nearly equal amounts. A comparison with the earlier experimental results[2] indicates that D_I includes nearly all of the dextrorotatory fractions while L_{II} consists of approximately the last quarter of the levorotatory fractions (19–22). From the preparative procedure for D_{II} and L_I, we must assume that fractionation using *l*-antimonyltartrate produces results which mirror those of Figure 1.

The salient feature of the kinetic data (Figure 2) is that initially all fractions behave similarly. If the rotations measured within the first 5 hr are neglected, only fractions 5, 10, 13, 14, and 15 exhibit continuous first-order behavior with identical half-lives of about 90 hr. Thus, a substance which is far more stable than indicated in the previous results is present. Those results extended only to 3.5 hr and probably correspond to the initial rapid loss of activity which is shown in Figure 2.

If the isomer present in fraction 5 is identical with that in fraction 10 (and presumably the enantiomer of that within fractions 13, 14, and 15), it is difficult to explain the method by which the dextrorotatory isomer appears in fraction 5, apparently disappears, and then reappears in fraction 10. If, on the other hand, fractions 5 and 10 contain different isomers, it is difficult to explain their identical kinetic behavior. Indeed, molecular models indicate that the various isomers have vastly different stereochemical configurations. For example, the $\Delta\delta\delta\delta$ isomer is extremely flat and not unlike four octahedra lying side by side on their trigonal faces. However, in the $\Delta\lambda\lambda\lambda$ isomer the pseudo-threefold axes of the peripheral groups are skewed to the trigonal axis of the central octahedron creating a cylindrical basket. The $\Delta\lambda\delta\delta$ and $\Delta\lambda\lambda\delta$ isomers are gradations of these two extremes. Hence, discernible differences in chemical properties might be expected for each.

Finally, there are no large differences, other than sign, in the rotatory properties of D_I, L_I, D_{II}, and L_{II}. Reference to Figure 2 indicates that this is initially true of all optically active fractions obtained in the fractionation procedure. Similarly, we find that the circular dichroism curves of D_I and D_{II} are identical within experimental error and the mirror images of those of L_I and L_{II} (Figure 3). Optical rotatory dispersion measurements of various fractions obtained in the fractionation procedure have indicated the same phenomenon. Such results for a number of stereochemically different isomers would be unprecedented. For example, in the somewhat more simple case of the isomers of $Co(pn)_3{}^{3+}$, it has been shown[3] that the circular dichroism of (+)-$Co(d\text{-}pn)_3{}^{3+}$ differs appreciably from that of (−)-$Co(d\text{-}pn)_3{}^{3+}$. Douglas[4] has attributed the major differences to vicinal effects of the propylenediamine ligand.

After considering a large number of alternatives, we believe that the most logical explanation is that only four isomers are formed in the approximate ratio of 3:3:1:1. Thus the isomer in D_I is identical with that in D_{II} and the enantiomer of those within L_I and L_{II}. The identical initial kinetic behavior is then readily understood as are the nearly identical specific rotations and the circular dichroism and optical rotatory dispersion measurements. To explain the course of the reactions in their later stages, we are forced to assume that one or more impurities are present which are capable of reacting with the polynuclear ion to produce another substance, which in turn catalyzes the loss of optical activity. Denoting one of these impurities by I and the catalyst by C, one set of reactions would be

$$CoL_3 \xrightarrow{k_1} \text{inactive products}$$

$$CoL_3 + I \xrightarrow{k_2} C + \text{inactive products}$$

$$CoL_3 + C \xrightarrow{k_3} \text{inactive products}$$

from which the following rate expression is obtained

$$\text{rate} = [CoL_3]\{k_1 + k_2[I] + k_3[C]\}$$

With $k_3 > k_1 >> k_2$, the appearance of any nonlinear behavior in Figure 2 can be qualitatively explained. (If the impurity is considered to be a reducing agent, then C could be a species containing the Co(II) ion.) Furthermore, it is not necessary to assume that more than one impurity is actually present.[5] Since the formation of tars was difficult to avoid, the inclusion of the same impurity could have occurred in all of those fractions having nonlinear behavior. Thus with fraction 21, where tar formation was extremely difficult to avoid, there is only a slight indication of linearity. While we are naturally reluctant to accept an argument which necessarily depends on the assumed presence of an unknown substance, we believe it is the only one which simultaneously satisfies all of the experimental data.

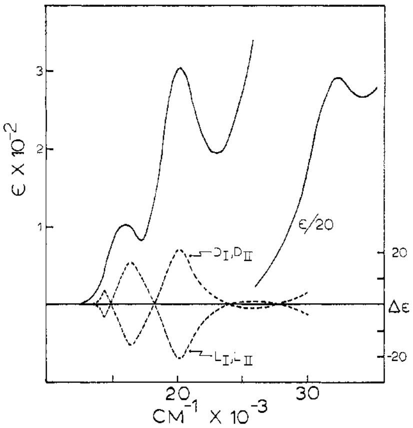

Figure 3.—Absorption spectrum and circular dichroism of the D_I, L_I, D_{II}, and L_{II} fractions of $[Co_4(en)_6(OH)_6](NCS)_6 \cdot H_2O$.

Circular Dichroism

The circular dichroism and absorption spectrum suggest that each polynuclear ion can be represented by four *relatively* noninteracting, adjacent chromophores. In Table II we compare the spectra of the polynuclear ion with those of $Co(H_2O)_6{}^{3+}$ and *cis*-$Co(en)_2(H_2O)_2{}^{3+}$. Neglecting the obvious differences in intensity, the spectrum of the large ion appears to contain transitions predominantly centered upon individual chromophores. Thus, the absorptions at 16,000 and 20,300 cm^{-1} are due to the $^1A_1 \rightarrow {}^1T_1$ transitions within the CoO_6 and

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(3) A. J. McCaffery, S. F. Mason, and B. J. Norman, *Chem. Commun.*, 49 (1965).

(4) B. E. Douglas, *Inorg. Chem.*, **4**, 1813 (1965).

(5) The initial rapid loss of optical activity may not be due to a common impurity but may be due to a mutarotation to yield a long-lived intermediate. The circular dichroism has been followed as a function of time and gave no indication of the appearance of a new species. Thus, the reaction which produces this intermediate would need to be extremely subtle, since the intermediate must be very similar to the original polynuclear ion. Fortunately, however, the cause of the initial rapid loss of activity is not pertinent to the number of isomers present.

TABLE II

ABSORPTION SPECTRA AND CIRCULAR DICHROISM

	Absorption		Circular Dichroism	
	Cm^{-1} × 10^{-3}	ϵ_{max}	Cm^{-1} × 10^{-3}	$\Delta\epsilon_{max}$
$Co_4(en)_6(OH)_6^{6+}$ [a]	8.0	1.5		
	11.5	5[b]		
			14.6	4.9, 5.0, −5.0, −4.8[c]
	16.0	101	16.5	−15.9, −16.0, 16.0, 15.8
	20.3	304	20.2	20.6, 20.4, −20.8, −20.8
			25.6	−1, −1, 1, 1
	32.3	5800		
$Co(H_2O)_6^{3+}$ [d]	8.0			
	12.5			
	16.5			
	24.7			
(+)-$Co(en)_2(H_2O)_2^{3+}$ [e]			17.9	−0.30
	20.2	83	20.6	1.05
	27.7	66	26.5	0.20

[a] Taken as the thiocyanate monohydrate. [b] Shoulder. [c] Multiple values for the polynuclear ion are for D_I, D_{II}, L_I, and L_{II}, respectively. [d] Diffuse reflectance spectra of the alum: D. A. Johnson and A. G. Sharpe, *J. Chem. Soc.*, 798 (1966). [e] A. J. McCaffery, S. F. Mason, and B. J. Norman, *ibid.*, 5094 (1965).

CoN_4O_2 groups, respectively. In the circular dichroism the second and weakest component of this transition which is expected for CoN_4O_2 is presumably buried in the high-energy tail of the dichroism maximum at 16,500 cm^{-1}. While the $^1A_1 \rightarrow {}^1T_2$ transition for each species appears to be masked in the absorption spectrum by the intense band at 32,300 cm^{-1}, a weak dichroism maximum occurs at about 25,600 cm^{-1} and could well contain both transitions. In addition, the weak absorption at 8000 cm^{-1} is assigned to the $^1A_1 \rightarrow {}^3T_1$ transition within the CoO_6 octahedron, but the band at 11,500 cm^{-1} is either due to $^1A_1 \rightarrow {}^3T_2$ within the same group or a composite of that transition and the $^1A_1 \rightarrow {}^3T_1$ transition within the CoN_4O_2 group. A similar approach was used by Chester and Brubaker[6] with the spectrum of μ-amido-decaamminedicobalt(III) ion.

We have not attempted to assign the absolute configurations of the central and peripheral octahedra by interrelating the signs of the trigonal components of the $^1T_1$ excited states within each group to those of (+)-$Co(en)_3^{3+}$, which is known to have the Λ configuration. Generally, the dominant dichroism maximum is assigned to the E_a state, and its sign is presumed to reflect the absolute configuration.[7] Assuming that the dichroism maxima at 16,500 and 20,300 cm^{-1} represent the E_a components within the CoO_6 and CoN_4O_2 octahedra, respectively, we compare in Table III the experimental signs of the rotational strength to those predicted for the eight possible isomers. Each of the latter are based on the sign of the rotational strength of the dominant dichroism maxima found for Λ-$Co(en)_3^{3+}$. It can be seen that the experimental results agree with those predicted for either Δλλλ, Λδδδ or Δλλδ, Λδδλ making a unique solution impossible. However, the extraordinarily high values of Δε indicate that adjacent chromophores do interact to some extent and in an unknown manner. Thus, the traditional arguments employed to assign the absolute configurations of mononuclear complexes may not be applicable. Furthermore and for similar reasons, it does not seem worthwhile at this point to attempt to relate the kinetic behavior[8] noted at the sodium D line to reactions occurring within a particular octahedron.

TABLE III

COMPARISON OF THE EXPERIMENTAL SIGNS OF THE ROTATIONAL STRENGTH TO THE MODEL BASED UPON COMPLETELY NONINTERACTING CHROMOPHORES

	$R(E_a, CoO_6)$	$R(E_a, CoN_4O_2)$ [a]
D_I, L_I	∓	±
D_{II}, L_{II}	∓	±
Δδδδ, Λλλλ	∓	∓ (1)
Δλδδ, Λδλλ	∓	∓ (1/3)
Δλλδ, Λδδλ	∓	± (1/3)
Δλλλ, Λδδδ	∓	± (1)

[a] Values within parentheses refer to relative magnitudes of the rotational strength.

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(6) A. W. Chester and C. H. Brubaker, Jr., to be published. We are grateful to these authors for making a copy of their manuscript available before its publication.

(7) A. J. McCaffery, S. F. Mason, and B. J. Norman, *J. Chem. Soc.*, 5094 (1965).

(8) The assumption that impurities are causing the erratic kinetic behavior of the enantiomers implies that this behavior should be strongly dependent upon the conditions of precipitation of both the diastereoisomer and the thiocyanate. When samples, otherwise identical with fraction 5, were prepared, only the utmost care in the precipitation steps would allow duplication of the results in Figure 2. When this care was not exerted, the kinetic behavior was not reproducible, but in all cases resembled the nonlinear results in the figure.