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Stereoselectivity in Ion-Pair Formation. The Contribution of the Rotamers to the Interaction of Mono- and Disubstituted Succinate Dianions with Tris(ethylenediamine)cobalt(III)[1]

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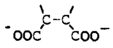
Abstract: The changes in the circular dichroism (CD) spectra of optically active tris(ethylenediamine)cobalt(III) have been measured upon addition of monosubstituted succinate dianions (malate, thiomalate, aspartate, methylsuccinate, phenylsuccinate, chlorosuccinate, bromosuccinate, and succinate ($^{-}OOCCH_2CH(R)COO^{-}$; R = OH, SH, NH_2, CH_3, C_6H_5, Cl, Br, and H)), and upon addition of 1,2-disubstituted succinate dianions (dibromosuccinate, dimethylsuccinate, tartrate (dihydroxysuccinate), and 1,2-cyclohexanedicarboxylate ($^{-}OOCCH(R)CH(R)COO^{-}$; R = Br, CH_3, and OH, and R-R = $CH_2(CH_2)_4CH_2$)). It is found that the resultant CD changes, which are due to the outer-sphere association with these dianions, are similar in shape and magnitude for the monosubstituted succinate dianions, while they vary depending upon the kind of two substituents R for the disubstituted succinate dianions. These findings are examined on the basis of the idea that the substituted succinate dianion interacts with the complex ion through the COO^- group as a mixture of their two rotamers, in which the two COO^- groups are gauche and trans to each other. It is, eventually, concluded that the resultant CD changes are dependent on the fractional populations of gauche and trans rotamers, and the populations of these rotamers are controlled only by the electrostatic repulsion between the two COO^- groups for the monosubstituted succinate dianions, while they are controlled by the interaction between the substituents R as well for the disubstituted succinate dianions. Furthermore, it is proposed that the conformation of the dicarboxylate dianion can be determined by the analysis of the CD change. Actually, the fractional populations of rotamers of *trans*-1,2-cyclohexanedicarboxylate are calculated by this analysis (gauche form 60% and trans form 40%).

Introduction

Several interesting studies have been reported on the stereoselectivity in outer-sphere association of metal complexes. One of the familiar examples of this kind is on the stereoselective association of L-(2*R*,3*R*)-tartrate with Λ- and Δ-$[Co(en)_3]^{3+}$ (en: ethylenediamine) in aqueous solution.[3-6] For the purpose of clarifying the origin of this stereoselectivity, we have investigated the ion-pair structure in solution between the dicarboxylate anion and the complex ion. We have already elucidated by measuring CD changes that the dicarboxylate anion interacts with the complex ion through the carboxyl group (COO^-), and that the skeleton I is essential to a favorable association in this system.[7,8] However, most of the dicarboxylate anions do not exist as only one species in solution but as some rotamers. Therefore, the interaction of the dicarboxylate anion with the complex ion cannot be elucidated until the contribution of each rotamer to the interaction becomes clear. It is, at present, not clear in detail how the rotamers contribute to the interaction with the complex ion. Thus we investigated the interaction of the rotamers of monosubstituted and 1,2-disubstituted succinate dianions with the complex ion by utilizing the CD measurement.



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In solution, the rotational isomerism of dicarboxylate dianions can be investigated by means of the NMR technique. In fact, the fractional populations of rotamers of dicarboxylate dianions, e.g., malate[9,10] and aspartate,[11,12] have been already determined from the NMR coupling constants. This method is applicable to the species showing ABX patterns of ^1H NMR spectra. However, it seems that this method is limited to the monosubstituted succinate dianion. As for the disubstituted succinate dianion, the information on the rotational isomerism is obtained from the comparison with the acid dissociation constants.[13] The result from this method is qualitative but applied to the rotational isomerism between meso and *dl* acids of disubstituted succinate dianions. On the basis of the information on the rotational isomerism obtained in these manners, we attempted to make clear the contribution of the rotamers to the interaction of monosubstituted and 1,2-disubstituted succinate dianions with the complex ion.

Experimental Section

Materials. Tris(ethylenediamine)cobalt(III) Bromide. $[Co(en)_3]Br_3{\cdot}3H_3O$ was prepared and resolved into enantiomers, Λ- and Δ-$[Co(en)_3]Br_3{\cdot}H_2O$, by using silver L-(+)-tartrate. The purity of these complexes was checked by elemental analysis and spectroscopic methods.

Monochlorosuccinic and Monobromosuccinic Acids.[14] The preparation of these compounds was made by passing a stream of N_2O_3 mixed with N_2 into ice-cooled aqueous solutions of (+)-aspartic acid and hydrochloric or hydrobromic acid. Monochlorosuccinic acid: $[\alpha]_D$ −55° (ethyl acetate). Anal. Calcd for $C_4H_5O_4Cl$: C, 31.48; H, 3.30. Found: C, 31.27; H, 3.30. Monobromosuccinic acid: $[\alpha]_D$ −75° (ethyl acetate). Anal. Calcd for $C_4H_5O_4Br$: C, 24.39; H, 2.56. Found: C, 24.38; H, 2.57.

***dl*-Dibromosuccinic Acid.**[15] This compound was prepared by the

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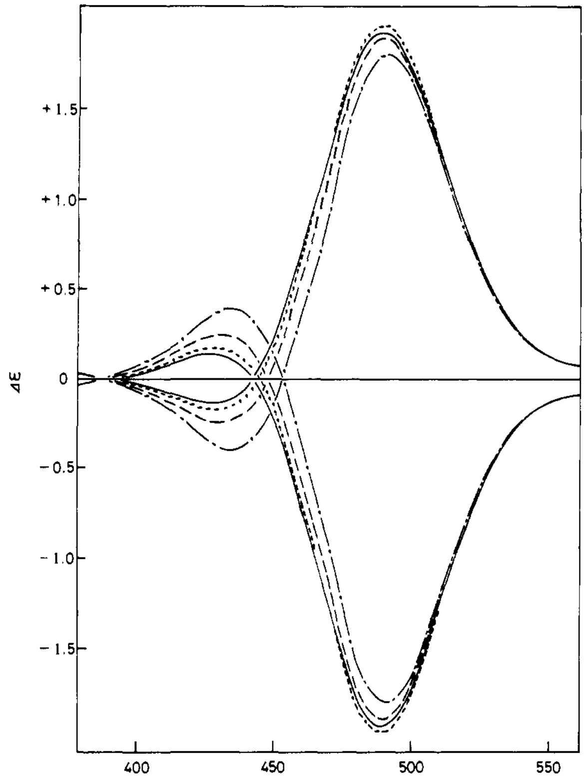


Figure 1. CD spectra of the reference solution (Λ- or Δ-[Co(en)$_3$]$^{3+}$) (——) and the sample solution containing maleate (-·-), malate (- -), and fumarate (···). Λ- or Δ-[Co(en)$_3$]$^{3+}$ and dicarboxylate concentrations were 0.002 and 0.0275 M, respectively, 25.0 °C, μ = 0.1 (NaClO$_4$).

bromination of maleic acid in ether. This racemic compound was resolved into the enantiomers by using an equimolar amount of morphine. Methyl alcohol was used as a solvent. Optical isomer from the less soluble diastereomer: $[\alpha]_D$ −107° (ethyl acetate). Anal. Calcd for $C_4H_4O_4Br_2$: C, 17.41; H, 1.46. Found: C, 17.37; H, 1.44.

***trans*-1,2-Cyclohexanedicarboxylic Acid.**[16,17] The racemic compound was reagent grade. This compound was resolved into the enantiomers by using an equimolar amount of cinchonidine. Optical isomer from the less soluble diastereomer: $[\alpha]_D$ −20.5° (acetone).

All other chemicals were reagent grade and were used without further purification.

Measurements. The circular dichroism (CD) spectra were recorded on a reference solution of optically active [Co(en)$_3$]$^{3+}$ (0.002 M) and on a sample solution of the complex ion (0.002 M) containing a dicarboxylate dianion (0.0275 M). To obtain the association constant the CD intensities at 430 and 455 nm were measured for the reference solution and the sample solution containing the dicarboxylate dianion ranging in concentration from 0.0025 to 0.0275 M. The ionic strength (μ) was set at 0.1 by the addition of an appropriate amount of sodium perchlorate. A JASCO J-40CS recording spectrometer with a 2-cm cell was used for the CD measurements. The cell was kept at 25.0 ± 0.2 °C with a Haake circulator, Model FK. The difference CD spectra between the sample and reference solutions were measured by using the data processor (DP) compartment operating at 0.2 nm/step of processor resolution. The dicarboxylate salts used here were obtained by neutralizing the dicarboxylic acids with LiOH·H$_2$O.

The NMR spectra were recorded on an R-22 Hitachi high-resolution NMR spectrometer operating at 90 MHz. The HDO signal was used as a standard with an internal lock. All the monosubstituted succinate dianions were 0.1 M in concentration in D$_2$O. The three protons of the monosubstituted derivatives yielded typical ABX spectra. Spin-coupling constants and chemical shifts were calculated by a familiar procedure and by an implementation of LAOCN 3.

Cation-Anion Association Constants. The data obtained from CD measurements were analyzed by using the following equation, in which M and X denote [Co(en)$_3$]$^{3+}$ and the dicarboxylate dianion, respectively.

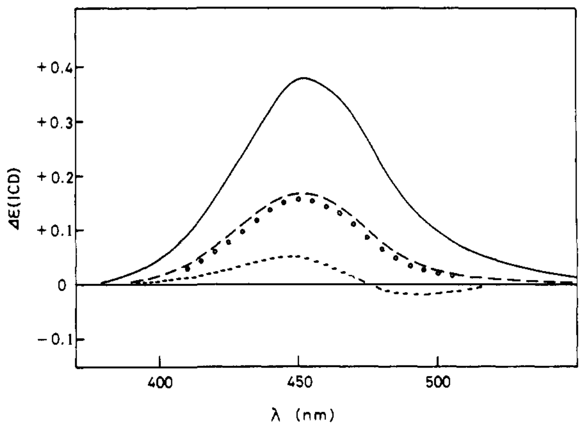
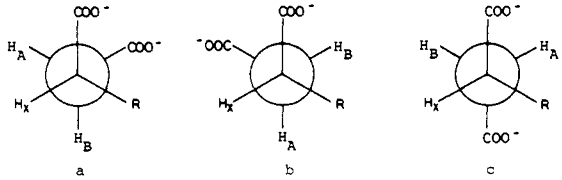


Figure 2. Changes in the CD spectrum of Δ-[Co(en)$_3$]$^{3+}$ (0.002 M) upon addition of the dicarboxylate dianions (0.0275 M): (——) maleate, (- -) malate, (···) fumarate, (○ ○ ○) the calculated curve for malate at 25.0 °C and μ = 0.1 (NaClO$_4$). $\Delta\epsilon(\mathrm{ICD}) = \Delta\epsilon_{\mathrm{sample}} - \Delta\epsilon_{\mathrm{reference}}$.

$$C_M(C_X - C_{MX})/(\Delta CD/2) = (C_X - C_{MX})/(\Delta\epsilon_{MX} - \Delta\epsilon_M) + 1/K(\Delta\epsilon_{MX} - \Delta\epsilon_M) \quad (1)$$

Here ΔCD refers to the difference in the CD between a sample solution and a reference solution and Δε refers to the molar CD of the species indicated by the subscript. The association constant K is obtained through the similar procedure in the previous paper.[8]

Rotamer Populations. It is well-known that monosubstituted succinate dianions exist as an equilibrium mixture of the three staggered rotamers obtained by internal rotation about the α-carbon–β-carbon bond. These rotamers are illustrated in a–c. Since the internal rotation



is rapid, the observed coupling constants are a weighted average over those for the individual rotamers. Therefore, the averaged coupling constants, J_{AX} and J_{BX}, are then given by

$$J_{AX} = (P_a + P_b)J_g + P_cJ_t \quad (2)$$

$$J_{BX} = (P_a + P_c)J_g + P_bJ_t \quad (3)$$

and the fractional populations P_a, P_b, and P_c for each rotamer can be given by the equation $P_c = (J_{AX} - J_g)/(J_t - J_g)$, $P_b = (J_{BX} - J_g)/(J_t - J_g)$, $P_a = 1 - (P_b + P_c)$, in which J_g = 2.60 and J_t = 13.56 Hz for aspartate[18] and J_g = 2.0 and J_t = 13.4 Hz for malate.[9]

Results and Discussion

Interaction of the Rotamers of Monosubstituted Succinate Dianions with the Complex Ion. The CD spectra of the reference solution containing optically active tris(ethylenediamine)cobalt(III) and the sample solution containing this complex and the dicarboxylate dianions (maleate, malate, and fumarate) are shown in Figure 1. These CD changes in Figure 1 can be observed more clearly by recording the difference CD spectra between the reference and sample solutions, which are presented in Figure 2. (The spectra in the following figures are all the difference CD spectra obtained in this manner.) This figure suggests that maleate and fumarate induce larger and smaller changes in the CD spectra, respectively, than malate does. These CD changes are considered to be due to the outer-sphere association between the complex ion and the dicarboxylate dianion. Therefore, the above result indicates that the complex ion strongly interacts with the dicarboxylate dianion in the order of maleate, malate, and fumarate. In the similar manner, the difference CD spectrum (CD change) for aspartate is shown in Figure 3, in which the CD changes for

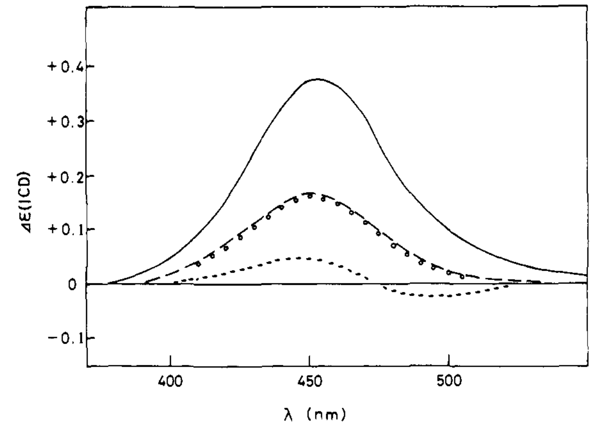


Figure 3. Changes in the CD spectrum of Δ-$[Co(en)_3]^{3+}$ (0.002 M) upon addition of the dicarboxylate dianions (0.0275 M): (——) maleate, (– –) aspartate, (---) fumarate, (o o o) the calculated curve for aspartate, at 25.0 °C and $\mu = 0.1$ ($NaClO_4$). $\Delta\epsilon(ICD) = \Delta\epsilon_{sample} - \Delta\epsilon_{reference}$.

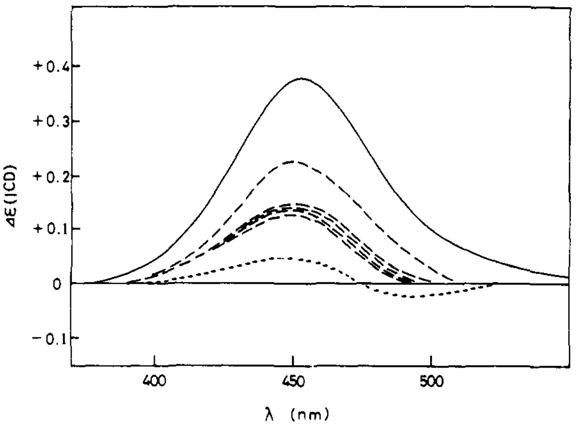
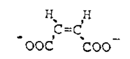


Figure 4. Changes in the CD spectrum of Δ-$[Co(en)_3]^{3+}$ (0.002 M) upon addition of the dicarboxylate dianions (0.0275 M): (——) maleate, (– –) from top to bottom, phenylsuccinate, methylsuccinate, bromosuccinate, succinate, chlorosuccinate, (---) fumarate at 25.0 °C and $\mu = 0.1$ ($NaClO_4$). $\Delta\epsilon(ICD) = \Delta\epsilon_{sample} - \Delta\epsilon_{reference}$.

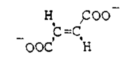
maleate and fumarate are also presented. It is noted in Figures 2 and 3 that the CD changes for malate and aspartate are similar to each other in shape and magnitude. This similarity in the CD change indicates that these CD changes are not dependent on the substituent R other than two carboxyl groups, and both dianions interact with the complex ion to a similar extent. For the purpose of confirming this similarity, the CD changes for other monosubstituted succinate dianions[19] were measured: methylsuccinate, phenylsuccinate, chlorosuccinate, bromosuccinate, and nonsubstituted succinate. All these monosubstituted succinate dianions, except for phenylsuccinate, induce the similar CD changes in shape and magnitude (Figure 4). These curves are also similar to those from malate and aspartate in magnitude. The CD changes[20] for monosubstituted succinate dianions including malate and aspartate are similar to each other, and further to that for succinate which has no substituent other than carboxyl groups. Thus, the CD changes for monosubstituted succinate dianions are not dependent on the substituent R, and these dianions interact with the complex ion to a similar extent.

As shown in Figure 1, the CD spectra of optically active $[Co(en)_3]^{3+}$ have a large peak of an E_a component in the longer wavelength region and a small peak of an A_2 component in the shorter wavelength region. These CD spectra change in magnitude upon addition of the dicarboxylate dianions. As described in a previous paper,[8] these dianions are classified into two groups on the basis of the CD change pattern in the first absorption region of $[Co(en)_3]^{3+}$. In one group the CD intensity largely increases in the A_2 component. Anions in this group strongly interact with the complex ion and behave as doubly charged anions. In another group the CD intensity slightly increases in both E_a and A_2 components. Anions in this group weakly interact with the complex ion and behave as singly charged anions. According to this classification, maleate belongs to the former group, while fumarate to the latter in spite of its divalent charge (Figure 1).

Maleate and fumarate are cis and trans in the position of the two carboxyl groups and they give large and small CD changes, respectively. Therefore, these CD changes seem to be largely



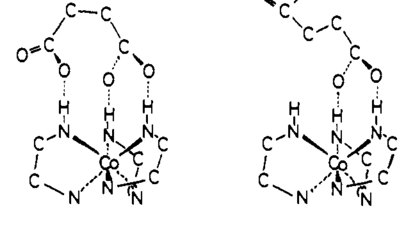
maleate



fumarate

dependent on the relative position of the two carboxyl groups of the added dicarboxylate dianions.

The difference in the CD change between maleate and fumarate is considered to be due to the difference in the association with the complex ion between the cis and trans forms.

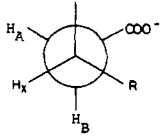


cis form　　trans form

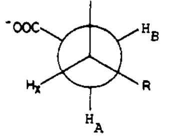
Figure 5. Molecular models for the ion pair between $[Co(en)_3]^{3+}$ and maleate or fumarate.

This difference is interpreted in terms of the idea[8,21] that a preferable association by hydrogen bonding results from the best match of the hydrogen-hydrogen distance of axial amine protons in the complex with the oxygen-oxygen distance of the two carboxyl groups. The cis form can fit the H-H distance of amine protons and this leads to the preferential association. On the other hand, it is impossible that the trans form associates with a complex ion with both carboxyl group oxygens simultaneously hydrogen bonded to amine protons. A glance at Figure 5 makes this clear. As a result, it is natural that maleate strongly associates with the complex ion and has a large CD change, and fumarate weakly associates with the complex ion and has a small CD change, which shows the similar pattern to that for a singly charged anion.

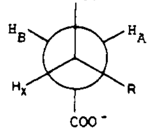
In contrast to maleate and fumarate, monosubstituted succinate consists of rotamers. Possible rotamers are illustrated in II-IV. The two carboxyl groups are in gauche position in the



II



III



IV

rotamers II and III, and are in trans position in the rotamer IV. Therefore, the change in the CD spectra of optically active $[Co(en)_3]^{3+}$ upon addition of monosubstituted succinate is naturally attributed to the contribution of these three rotamers, two gauche and one trans rotamers.

On the other hand, the populations of the above rotamers can be determined from the NMR coupling constants. The NMR data for the monosubstituted succinates are summarized

Table I. Chemical Shifts,[a] Coupling Constants,[a] and Fractional Populations of Monosubstituted Succinate Dianions

	$\lvert\nu_A - \nu_X\rvert$	$\lvert\nu_B - \nu_X\rvert$	J_{AB}	J_{AX}	J_{BX}	P_{II}[b]	P_{III}	P_g	P_{IV} (P_t)
(1) malate	174.7	147.1	−15.3	10.2	3.0	19	9	28	72
(2) malate[c]			−15.5	9.4	3.3	24	11	35	65
(3) malate[d]			−15.4	9.5	3.2	24	10	34	66
(4) malate[e] + $[Co(en)_3]^{3+}$	168.9	147.0	−15.4	9.3	3.7	21	15	36	64
(5) malate[f] + $[Co(NH_3)_6]^{3+}$	167.9	146.8	−15.4	9.2	3.7	22	15	37	63
(6) aspartate	114.7	82.1	−15.4	9.9	3.7	24	10	34	66
(7) aspartate[e] + $[Co(en)_3]^{3+}$	106.4	83.1	−15.3	9.0	4.7	23	19	42	58
(8) phenylsuccinate[g]	111.9	92.5	−15.1	9.8	6.2			34 (32)	66[h] (68)[i]
(9) chlorosuccinate	175.7	145.9	−15.6	10.5	3.9	16 (8)	12 (17)	28 (25)	72 (75)
(10) bromosuccinate	159.4	133.0	−15.8	9.9	4.9	13 (6)	21 (25)	34 (31)	66 (69)
(11) thiomalate	106.4	71.4	−15.4	9.6	5.7	8 (1)	28 (32)	36 (33)	64 (67)

[a] In Hz. [b] Fractional populations in %. [c] Reference 9. [d] Recalculated in ref 10. [e] In the presence of $[Co(en)_3]^{3+}$ (0.2 M). The NMR data was calculated by using ten lines of signals because the methylene signals in $[Co(en)_3]^{3+}$ partially overlapped with those in malate. [f] In the presence of $[Co(NH_3)_6]^{3+}$ (0.2 M). [g] The value of $P_{III} + P_{IV}$ becomes larger than 100%. Therefore, P_g was determined by the equation $P_g = 100 - P_t$. [h] Calculated on the basis of the J_g and J_t values for aspartate. [i] Calculated on the basis of the J_g and J_t values for malate.

Table II. Association Constants for Λ- and Δ-$[Co(en)_3]^{3+}$ at 25 °C (μ = 0.1)

	nm	maleate[a]	malate[b]	fumarate
Λ-$[Co(en)_3]^{3+}$	430	48.8 ± 1.3	10.9 ± 0.4	
	455	48.2 ± 1.3	11.0 ± 0.5	
Δ-$[Co(en)_3]^{3+}$	430	47.0 ± 1.0	11.1 ± 0.5	3.8 ± 0.9
	455 (443)[c]	45.9 ± 0.9	11.2 ± 0.6	3.2 ± 0.6

[a] Reference 8. [b] *l* isomer. [c] The measurements were undertaken at 443 nm for fumarate.

in Table I. J_{AB} and J_{AX} are nearly equal for all the monosubstituted succinate dianions. The fractional population P_{IV} (P_t) of the trans rotamer is determined from the coupling constant J_{AX} by utilizing the equation

$$P_t = P_{IV} = (J_{AX} - J_g)/(J_t - J_g) \qquad (4)$$

where J_g is the coupling constant between the gauche protons and J_t is the coupling constant between the trans protons. Therefore, the sum of the populations P_{II} and P_{III} of the gauche rotamers is determined by the equation

$$P_g = P_{II} + P_{III} = 1 - P_{IV} \qquad (5)$$

Here, the appropriate J_g and J_t values are found in the literature[9-12] for malate and aspartate. However, the corresponding values for other monosubstituted succinate dianions seem not to be found in the literature. Therefore, their fractional populations are calculated on the basis of the J_g and J_t values for malate and aspartate (Table I).

The data for malate are summarized in Table I with the values cited from the literature. The fractional populations of three rotamers (II, III, IV) of malate are found to be 23, 10, and 67% (gauche, 33%; trans, 67%) on the average in the absence of the complex ion. The changes in these populations upon addition of the complex ion are small and may be negligible.

It is considered that maleate and fumarate are appropriate stereochemical models for the gauche and trans rotamers of malate, respectively. Therefore, assuming that the contributions of the gauche and trans rotamers of malate could be replaced by those of maleate and fumarate, respectively, the CD changes for malate are estimated by the equation

$$\Delta\epsilon(\mathrm{ICD})_{\mathrm{malate}} = 0.33\Delta\epsilon(\mathrm{ICD})_{\mathrm{maleate}} + 0.67\Delta\epsilon(\mathrm{ICD})_{\mathrm{fumarate}} \qquad (6)$$

where Δε(ICD) refers to the CD change at each wavelength. The spectrum thus calculated is in good agreement with the observed one as shown in Figure 2. Furthermore, this procedure is applied to the case of aspartate. In this case the observed spectrum is also in good agreement with the curve which is estimated by the equation

$$\Delta\epsilon(\mathrm{ICD})_{\mathrm{aspartate}} = 0.34\Delta\epsilon(\mathrm{ICD})_{\mathrm{maleate}} + 0.66\Delta\epsilon(\mathrm{ICD})_{\mathrm{fumarate}} \qquad (7)$$

These results suggest that each rotamer interacts with the complex ion through the carboxyl group, and that the apparent CD change is additive; the CD changes for malate and aspartate are equal to the sum of the CD changes for their rotamers. Furthermore, it is noted that these dianions interact with the complex ion as a mixture of gauche and trans rotamers, which strongly and weakly associate with the complex ion leading to large and small CD changes, respectively. The association constants also confirm this conclusion (Table II).

The fractional populations for the other monosubstituted succinate dianions are similar to each other ($P_g \sim 30\%$ and $P_t \sim 70\%$) and their CD changes are similar in shape and magnitude. This similarity in the population and the CD change indicates that the conformation of these dicarboxylate dianions is not dependent on the substituent R other than two carboxyl groups.

One exceptional case is for phenylsuccinate. The CD change for this dicarboxylate is large in comparison with other monosubstituted succinate dianions. This indicates that the rotamer II or III of gauche form is relatively stabilized. It is reported[12,22] that the strong steric hindrance between the bulky phenyl group and carboxyl group becomes more significant in the conformation of phenylalanine. This is also the case with

Table III. Association Constants for Λ- and Δ-$[Co(en)_3]^{3+}$ at 25 °C (μ = 0.1)

		aspartate[a]	methylsuccinate[b]	phenylsuccinate[b]	chlorosuccinate[c]	bromosuccinate[c]	succinate
Λ-$[Co(en)_3]^{3+}$	430	11.0 ± 0.4			9.5 ± 0.9	12.9 ± 1.1	
	455	12.3 ± 1.2			9.8 ± 0.8		
Δ-$[Co(en)_3]^{3+}$	430	11.9 ± 0.4	10.3 ± 0.3	19.4 ± 0.3	10.0 ± 0.5	12.7 ± 0.4	13.8 ± 0.6
	455	12.0 ± 0.6	10.7 ± 0.5	20.1 ± 0.3	10.3 ± 0.6		13.2 ± 0.4

[a] *d* isomer. [b] Racemate. [c] *l* isomer. The measurement was undertaken as soon as possible (within 0.5 h), because bromosuccinate reacts gradually with water. No significant fluctuation in the CD change was observed at 25 °C during the period required for measurements.

Table IV. Association Constants for Λ- and Δ-$[Co(en)_3]^{3+}$ at 25 °C (μ = 0.1)[a]

		meso-dibromosuccinate	*dl*-dibromosuccinate	*l*-dibromosuccinate
Λ-$[Co(en)_3]^{3+}$	430			16.5 ± 0.7
Δ-$[Co(en)_3]^{3+}$	430	3.3 ± 0.2	16.4 ± 0.6	15.8 ± 0.4
	443	3.8 ± 0.7		

[a] All the measurements were undertaken as soon as possible (within 0.5 h), because dibromosuccinates react gradually with water.

Table V. Association Constants for Λ- and Δ-$[Co(en)_3]^{3+}$ at 25 °C (μ = 0.1)

		meso-tartrate	*dl*-tartrate	*d*-tartrate
Λ-$[Co(en)_3]^{3+}$	430	39.6 ± 0.8		13.0 ± 0.1
	455	39.5 ± 0.5		13.6 ± 0.2
Δ-$[Co(en)_3]^{3+}$	430	40.3 ± 0.7	12.5 ± 0.3	10.5 ± 0.4
	455	39.8 ± 0.6	12.9 ± 0.1	11.7 ± 0.4

Table VI. Association Constants for Λ- and Δ-$[Co(en)_3]^{3+}$ at 25 °C (μ = 0.1)

		cis-1,2-cyclohexanedicarboxylate	*dl*-*trans*-1,2-cyclohexanedicarboxylate	*l*-*trans*-1,2-cyclohexanedicarboxylate	1,4-cyclohexanedicarboxylate
Λ-$[Co(en)_3]^{3+}$	430			45.2 ± 1.3	
	455			44.5 ± 1.5	
Δ-$[Co(en)_3]^{3+}$	430	67.7 ± 1.9	44.7 ± 1.1	43.8 ± 1.9	8.6 ± 0.6
	455 (443)[a]	71.5 ± 2.1	45.6 ± 0.9	43.3 ± 1.5	8.3 ± 0.9

[a] The measurements were undertaken at 443 nm for 1,4-cyclohexanedicarboxylate.

phenylsuccinate. The rotamer III of the gauche form is stabilized because of the trans position of COO^- group to phenyl group, leading to the great CD change. The association constant (K = 20) for phenylsuccinate is also somewhat larger than those for the other monosubstituted succinates, which have similar association constants to each other (K = 10–13, Table III), though the enrichment of P_g for phenylsuccinate does not appear on the NMR data.

Thus, the conclusion is as follows. The substituent R is not significant in controlling the populations of rotamers of monosubstituted succinate dianions, and their populations are determined only by the electrostatic repulsion between two COO^- groups leading to similar CD changes in shape and magnitude. Consequently, the gauche rotamer of about 30% strongly interacts with the complex ion and the trans rotamer of about 70% weakly interacts with the complex ion, leading to a resultant CD change which is smaller than that for maleate and is larger than that for fumarate.

Interaction of the Rotamers of Disubstituted Succinate Dianions with the Complex Ion. Figure 6 shows the CD changes for *meso*- and *dl*-dibromosuccinates. The meso isomer gives rise to a smaller CD change than the *dl* isomer does and to a similar pattern to that usually observed for a singly charged anion. The association constant for the meso isomer is smaller than that for the *dl* isomer to a great extent (Table IV). In contrast to dibromosuccinate, the meso isomer of tartrate gives rise to a larger CD change than the *dl* isomer does.[23] This feature is shown in Figure 7. The association constant for the *meso*-tartrate is also larger than that for the *dl* isomer (Table V). One more example, which shows a CD change behavior similar to tartrate, is provided by 1,2-cyclohexanedicarboxylate (1,2-CHD). *cis*-1,2-CHD (corresponding to a meso isomer) gives rise to a larger CD change than *trans*-1,2-CHD (corresponding to a *dl* isomer) does.[23] The association constant for *cis*-1,2-CHD is larger than that for *trans*-1,2-CHD (Table VI). Thus, the CD changes and the association constants for disubstituted succinate dianions vary depending on the substituent R. These CD changes will now be analyzed on the basis of a consideration of the acid dissociation constants.

The rotational isomerism of the 1,2-disubstituted succinate, for which the conformation is not determined by the NMR technique described before, has been studied on the basis of the acid dissociation constant. This study is based on the idea[13] that the difference in the ratio (K_1/K_2) of the first and second dissociation constants between the meso and *dl* acids is due to the difference in the position of the two carboxyl groups.

In general, the values of the first dissociation constant (K_1) and the second dissociation constant (K_2) for all 1,2-disubstituted succinates vary with the relative position of the two carboxyl groups. The first and second dissociations are promoted and hindered in the gauche form, respectively, because the monodeprotonated species is stabilized by the hydrogen bonding. Such a hydrogen bonding does not exist in the trans form. As a result, the acid as a whole has relatively large K_1

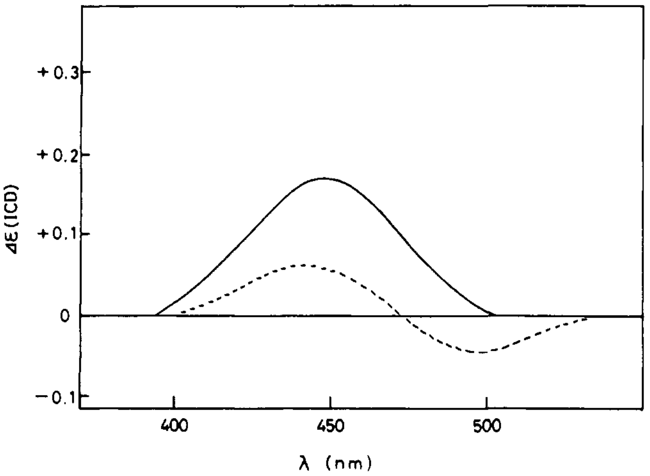


Figure 6. Changes in the CD spectrum of Δ-$[Co(en)_3]^{3+}$ (0.002 M) upon addition of the dicarboxylate dianions (0.0275 M): (——) *dl*-dibromosuccinate, (- - -) *meso*-dibromosuccinate, at 25.0 °C and $\mu = 0.1$ ($NaClO_4$). $\Delta\epsilon(ICD) = \Delta\epsilon_{sample} - \Delta\epsilon_{reference}$. The CD changes for *d* and *l* isomers are the same in magnitude as that for the *dl* isomer.

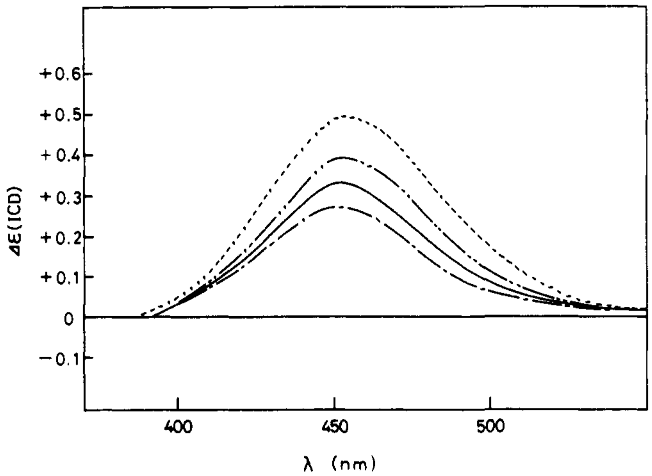
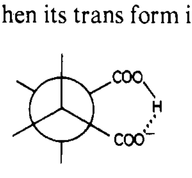
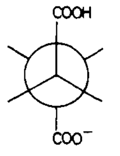


Figure 7. Changes in the CD spectrum of Δ-$[Co(en)_3]^{3+}$ (0.002 M) upon addition of the dicarboxylate dianions (0.0275 M): (——) *dl*-tartrate, (-·-) *d*-tartrate, (- · · -) *l*-tartrate, (- - -) *meso*-tartrate at 25.0 °C and $\mu = 0.1$ ($NaClO_4$). $\Delta\epsilon(ICD) = \Delta\epsilon_{sample} - \Delta\epsilon_{reference}$.

and small K_2 when its gauche form is stabilized and so a large K_1/K_2, while the acid as a whole has relatively small K_1 and large K_2, when its trans form is stabilized and so a small K_1/K_2.



gauche



trans

A typical example of this kind is di-*tert*-butylsuccinic acid. The steric repulsion between two bulky *tert*-butyl groups should stabilize the trans form in the meso acid and the gauche form in the *dl* acid. In fact, the value of K_1/K_2 is smaller for the meso acid and larger for the *dl* acid.[13] This acid is an extreme example. Generally, it is considered that the relative position of the two carboxyl groups in the 1,2-disubstituted succinic acid is controlled by their electrostatic interaction and by the repulsion between the two R groups. It is not clear whether the conformation determined from the acid dissociation constant corresponds to that for the acid or anion. However, it may be a guide to the determination of the conformation of 1,2-disubstituted succinate dianions.

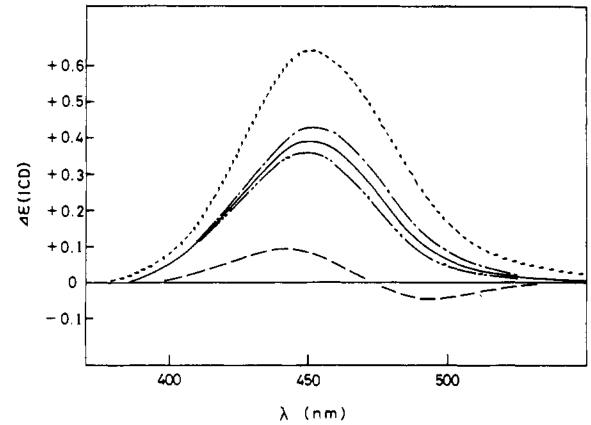
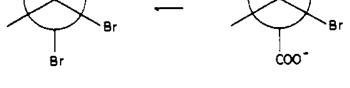


Figure 8. Changes in the CD spectrum of Δ-$[Co(en)_3]^{3+}$ (0.002 M) upon addition of the dicarboxylate anions (0.0275 M): (——) *dl-trans*-1,2-cyclohexanedicarboxylate, (-·-) *d-trans*-1,2-cyclohexanedicarboxylate (this is replaced by the change in the CD spectrum of Λ-$[Co(en)_3]^{3+}$ on addition of *l* isomer), (- · · -) *l-trans*-1,2-cyclohexanedicarboxylate, (- - -) *cis*-1,2-cyclohexanedicarboxylate, (– –) 1,4-cyclohexanedicarboxylate at 25.0 °C and $\mu = 0.1$ ($NaClO_4$). $\Delta\epsilon(ICD) = \Delta\epsilon_{sample} - \Delta\epsilon_{reference}$.

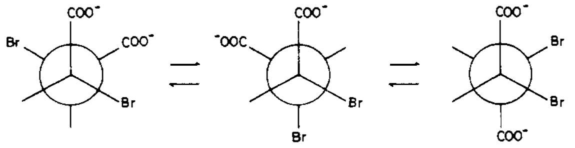
In the case of dibromosuccinate, the consideration from the dissociation constants results in the stabilization of the rotamer which is trans in the position of two Br atoms, because of the repulsive force between the two Br atoms. This suggests that the rotamer VI, which is trans in the position of two carboxyl



V VI

groups, is the most stable in the *meso*-dibromosuccinate dianion. However, the electrostatic repulsion between the two carboxyl groups is one more important factor in controlling the conformation of this disubstituted succinate dianion. This electrostatic repulsion also leads to the stabilization of the rotamer VI, which is trans in the position of the two carboxyl groups. As a result, the effect of the combination of these two factors stabilizes exclusively the trans rotamer. If it is allowed that a trans form interacts weakly with the complex ion, the meso isomer should give rise to a CD change pattern similar to that for a singly charged anion. In fact, the meso isomer gives a similar CD change to that for a singly charged anion, and the association constant is nearly equal to that ($K = 4$) for fumarate (Tables II and IV), in which the two carboxyl groups are trans to each other.[24]

As for the *dl* isomer, the repulsive force between the two Br atoms stabilizes the rotamer VII, which is gauche in the position of the two carboxyl groups. In contrast to this repulsive force, the electrostatic repulsion between the two COO^- groups leads to the stabilization of the rotamer IX, which is trans in the position of the two carboxyl groups. The combination of these two factors gives an equilibrium mixture of rotamers in which the two carboxyl groups are gauche and trans. Therefore, the *dl* isomer interacts with the complex ion as a mixture of gauche and trans forms which can give large

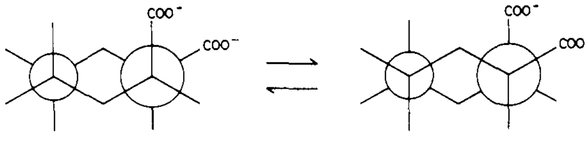


VII VIII IX

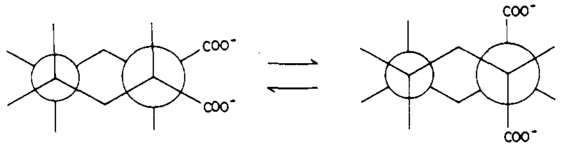
and small CD changes, respectively. As a result, the CD change for the *dl* isomer is larger than that for the meso isomer.

In contrast to dibromosuccinate dianions, tartrate (dihydroxysuccinate) shows a different behavior in the CD change. The CD change for the meso isomer is larger than that for the *dl* isomer (Figure 7). This cannot be interpreted in terms of the repulsion between the two substituents (OH). Here, there is one example which shows the CD change behavior similar to that for tartrate. This example is 1,2-cyclohexanedicarboxylate (1,2-CHD). The CD changes for *cis*-1,2- and *trans*-1,2-CHD are shown in Figure 8. Just like a tartrate, the CD change for *cis*-1,2-CHD (corresponding to a meso-disubstituted succinate) is larger than that for *trans*-1,2-CHD (corresponding to a *dl*-disubstituted succinate). This is interpreted in the following way.

cis-1,2-CHD exists in solution in an equilibrium mixture of the rotamers X and XI because of the restriction of the rotation around the C_α-C_β axis.[25] These two rotamers are gauche in the position of the two carboxyl groups. Both of these rotamers are expected to interact strongly with the complex ion and give rise to a great CD change. In contrast, *trans*-1,2-CHD consists of the rotamers XII and XIII at equilibrium,



X XI



XII XIII

which are gauche and trans in the position of two carboxyl groups. The gauche form can strongly interact with the complex ion and gives rise to a great CD change, but the trans form cannot strongly interact with the complex ion and gives rise to a small CD change. As a result, the CD change for *trans*-1,2-CHD is smaller than that for *cis*-1,2-CHD, which exhaustively consists of the gauche form.

In these dicarboxylates, the positions corresponding to the two Br atoms of dibromosuccinate are fixed by the alkyl chain so that they may be in gauche positions. Therefore, in the case of tartrate, for which the CD change behavior is similar to that for 1,2-CHD, it is concluded that the attractive force but not the repulsive force exists between the two OH groups and that the two OH groups are fixed so as to be in gauche positions, in contrast to dibromosuccinate. This conclusion may be supported by the fact[26,27] that the ratio (K_1/K_2) for *meso*-tartaric acid is larger than that for *dl* acid, in contrast with dibromosuccinic acid.

It is eventually concluded that each rotamer of monosubstituted and 1,2-disubstituted succinate dianions interacts independently with the complex ion through the carboxyl group and that the apparent CD change is additive: the CD change is equal to the sum of the changes for the gauche and trans rotamers. Another conclusion is as follows. In the case of the monosubstituted succinate dianion, the populations of the rotamers are determined by the two COO⁻ groups, and not controlled by the other substituent R than the COO⁻ group. Therefore, the CD changes are similar to each other in shape and magnitude, and these dianions interact with the complex ion to a similar extent. On the other hand, in the case of the disubstituted succinate dianion, the fractional populations of rotamers are markedly controlled by the substituents R as well as the two COO⁻ groups. Therefore, the CD changes for the disubstituted succinate dianions vary depending upon the kind of two substituents R.

A New Method for the Determination of the Conformation of the Dicarboxylate Dianion. One more noteworthy conclusion is as follows. As described before, the rotational isomerism of dicarboxylate dianions has been studied by the measurement of NMR spectra and a consideration of the acid dissociation constant. However, these methods are limited to some cases. That is, the NMR method is effective for only the monosubstituted succinate dianion showing an ABX NMR pattern. The consideration of the dissociation constant gives only information on the conformational relationship between meso and *dl* acids, and, further, qualitative but not quantitative information. In contrast, the analysis of the CD change can give quantitative information on the conformation of the dicarboxylate dianion, even in the case where the conformation cannot be determined by these two methods. For example, in the case of a succinate dianion which has no substituent other than the two COO⁻ groups, the CD change and the association constant are nearly equal to those for the monosubstituted succinate dianion. This implies that the fractional populations are about 30% for the gauche rotamer and 70% for the trans rotamer, similarly to those for malate and aspartate. The conformation of succinate cannot be determined by the NMR method but by the analysis of the CD change. One more case is for dibromosuccinate. Its meso isomer gives a small CD change and a similar pattern to that for a singly charged anion. Therefore, this isomer consists of only the trans rotamer. In contrast, the *dl* isomer gives a slightly larger CD change and association constant than monobromosuccinate does (Tables III and IV). Therefore, the *dl* isomer has a slightly larger population of the gauche rotamer than monobromosuccinate, which has a similar conformation of the two carboxyl groups to malate and aspartate, has. Such quantitative information on the conformation is not obtained by the consideration of the acid dissociation constant, which gives only the qualitative conclusion that the meso isomer has a larger population of the trans rotamer than the *dl* isomer has.

Finally, the fractional population of *trans*-1,2-cyclohexanedicarboxylate (*trans*-1,2-CHD) will be determined on the basis of this idea. As described before, *trans*-1,2-CHD consists of the trans and gauche rotamers. The CD change for the gauche rotamer of *trans*-1,2-CHD could be replaced by that for *cis*-1,2-CHD. The CD change for the trans rotamer is replaced by that for 1,4-CHD, which behaves as a singly charged anion like a trans rotamer, because the appropriate stereochemical model for the trans rotamer of *trans*-1,2-CHD does not exist. On the basis of this assumption, the CD change for *trans*-1,2-CHD is estimated by the equation

$$\Delta\epsilon(\mathrm{ICD})_{trans\text{-}1,2\text{-CHD}} = P_g\Delta\epsilon(\mathrm{ICD})_{cis\text{-}1,2\text{-CHD}} + P_t\Delta\epsilon(\mathrm{ICD})_{1,4\text{-CHD}} \quad (8)$$

Therefore, when the observed values of $\Delta\epsilon(\mathrm{ICD})_{trans\text{-}1,2\text{-CHD}}$, $\Delta\epsilon(\mathrm{ICD})_{cis\text{-}1,2\text{-CHD}}$, and $\Delta\epsilon(\mathrm{ICD})_{1,4\text{-CHD}}$ are substituted in eq 8, we obtain $P_g = 60\%$ and $P_t = 40\%$. The gauche form is more favored for *trans*-1,2-CHD than for monosubstituted succinates.

Thus, the analysis of the CD change can give quantitative information on the conformation of the dicarboxylate dianion, the conformation of which is not determined by the other methods. It is expected that further information on the conformation is obtained for the various dicarboxylate dianions by utilizing this method.

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(20) The CD changes for Λ- and Δ-$[Co(en)_3]^{3+}$ were the same in magnitude within the limits of experimental errors in the cases of optically active malate, aspartate, chlorosuccinate, and bromosuccinate. Phenylsuccinate and methylsuccinate used were racemates.

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(24) The meso isomer of dimethylsuccinate was examined on the CD change. This dianion should behave like a corresponding meso dibromosuccinate dianion because of the repulsion between the two methyl groups. In fact, the CD change pattern was similar to that for the meso dibromosuccinate, that is, to that for a singly charged anion.

(25) Crystal structure studies have been shown that, in the solid state, *trans*-1,2-CHD acid exists in the diequatorial conformation (gauche conformation). However, the repulsion of two carboxyl groups should partially convert the conformation from diequatorial (gauche) to diaxial (trans) in going from the solid state to solution. See (a) E. Benedetti, P. Corradini, C. Pedone, and B. Post, *J. Am. Chem. Soc.*, **91**, 4072 (1969); (b) *ibid.*, **91**, 4075 (1969); (c) G. Montando and C. G. Overberger, *ibid.*, **91**, 753 (1969).

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Photobehavior of Copper(I) Compounds. Role of Copper(I)-Phosphine Compounds in the Photosensitized Valence Isomerization of Norbornadiene

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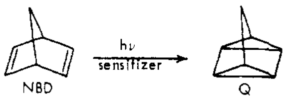
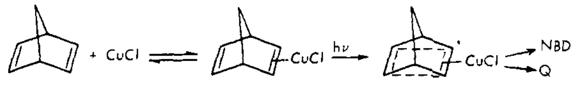
Abstract: The valence isomerization of norbornadiene to quadricyclene can be photosensitized with high quantum efficiency by certain copper(I)-phosphine compounds. Sensitization yields in the presence of $Cu(PPh_3)_2BH_4$ and $Cu(PPh_2Me)_3BH_4$ attain limiting values of 0.76 and 0.54, respectively, at high norbornadiene concentrations. In contrast, $Cu(diphos)BH_4$ (diphos is 1,2-bis(diphenylphosphino)ethane), which contains a bidentate phosphine ligand, is decidely less effective. The mechanism of sensitization by these copper(I)-phosphine compounds is fundamentally different from that exhibited by simple cuprous salts in that no ground-state coordination to the metal center occurs. A pathway involving the bimolecular interaction of the photoexcited Cu(I) compound with a ground-state norbornadiene molecule is better able to accommodate the available data. Electronic absorption and emission studies reveal some interesting differences between the spectral properties of effective vs. noneffective sensitizers.

Previous studies[1,2] from this laboratory have focused upon the use of transition-metal compounds to photosensitize the energy-storing valence isomerization of norbornadiene (NBD) to quadricyclene (Q) (eq 1). Particular attention has been afforded simple copper(I) salts, since their role as sensitizers in a wide variety of olefin photoreactions is well documented.[3,4] Thus we recently reported that cuprous chloride effectively sensitizes the production of Q via a pathway (eq 2) involving a photoactive ClCu-NBD complex.[5] Minimally, complex formation shifts the spectrum of the system to longer wavelengths and thereby enhances absorption of the irradiating light. Moreover, the possibility exists that the complex provides a sterically or electronically favorable path to Q which is inaccessible to the uncoordinated olefin.



(1)



(2)

Our quest for new classes of Cu(I) sensitizers led us to investigate the series $Cu(PPh_3)_2BH_4$, $Cu(PPh_2Me)_3BH_4$, and $Cu(diphos)BH_4$ (diphos is 1,2-bis(diphenylphosphino)ethane). Preliminary studies[6] revealed that the first two members efficiently sensitize the NBD to Q conversion but by a mechanism which appears to be fundamentally different from the complexation pathway noted above. This seminal finding, plus the observation of some intriguing structural and spectral characteristics, prompted us to examine the detailed behavior of these Cu(I) compounds. The results of our investigations are described in the present article.

Experimental Section

A. Reagents. Norbornadiene (Aldrich) was purified by passage through a glass column packed with 8-in. layers of alumina (80-200

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