$[Rh_2(O_2CCH_3)_4(H_2O)_2]^+$ and $[Rh_2(O_2CC_2H_5)_4(PCy_3)_2]^+$ (where Cy = cyclohexyl) are consistent with the present results for L = OH_2 and PH_3, respectively. The assignments are different from those due to the $X\alpha$–SW calculation. The photoelectron spectra of $Rh_2(mhp)_4$, with Hmhp being 6-methyl-2-hydroxypyridine, were also compared with the present result.

We have investigated the charge distributions and the natures of the Rh–Rh and Rh–L bonds. The origin of the Rh–L bond is mainly the transfer of the lone-pair electrons of the axial ligands to the empty nonbonding orbital on the Rh of the DRTC complex. The back-transfer interaction is small. The Rh–Rh bond is a weak single σ bond. This is reflected in the fact that the Σ level is the ground state or next to the ground state in the cations. We guess that the reason of the shortness of the Rh–Rh bond in the DRTC complexes is due to the existence of the bridging carboxylate ligand. As the Rh–Rh bond is weak, the distance is chiefly determined by the coordination distance of the carboxylate cage.

Finally, let us consider the role of electron correlation. Benard[31] has studied the effect of electron correlation for molecules including a metal–metal bond, through the instability of a Hartree–Fock solution. He concluded that, though the electron correlation is very important for the description of a multiple metal–metal bond, it is less important for binuclear complexes that are without a metal–metal interaction or that display a single metal–metal bond.

Acknowledgment. We thank Dr. T. Kawamura for kindly showing us his experimental results on the electronic spectra of the DRTC cations with substituted phosphines prior to publication. The calculations were carried out with M-200 computers at the Institute for Molecular Science and at the Data Processing Center of Kyoto University. Part of this study was supported by a Grant-in-Aid for Scientific Research from the Japanese Ministry of Education, Science, and Culture.

Registry No. **1** (L absent), 33773-07-8; **1**$^+$ (L absent), 71767-77-6; **1** (L = OH_2), 33700-44-6; **1**$^+$ (L = OH_2), 72067-43-7; **1** (L = NH_3), 15005-98-8; **1**$^+$ (L = NH_3), 85185-76-8; **1** (L = PH_3), 77965-51-6; **1**$^+$ (L = PH_3), 85185-75-7.

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Circular Dichroism Study of the Chiral Interaction between Tartrate Ions and Trigonal $[Co(N)_6]^{3+}$ Complexes in Solution[1]

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The effect of *d*- and *l*-tartrate ions upon the circular dichroism (CD) spectra of some trigonal $[Co(N)_6]^{3+}$ complexes has been investigated. The association constants with *d*- and *l*-tartrates, K_d and K_l, for Δ-$[Co(en)_3]^{3+}$, Δ-$[Co(sen)]^{3+}$, Δ-$[Co(sep)]^{3+}$, Δ-*fac*- and Δ-*mer*-$[Co(1\text{-}pn)_3]^{3+}$, and Δ-$[Co(1\text{-}chxn)_3]^{3+}$ are respectively as follows (M^{-1}): 11.70 ± 0.1, 13.4 ± 0.2; 49.6 ± 1.0, 71.7 ± 1.0; 38.3 ± 0.3, 39.3 ± 1.0; 22.5 ± 0.5, 30.3 ± 0.3; 21.2 ± 1.1, 26.7 ± 0.7; 15.4 ± 0.4, 21.4 ± 0.4 (25 °C, μ = 0.1 with sodium perchlorate, en = ethylenediamine, sen = 1,1,1-tris((2-aminoethyl)aminomethyl)ethane, sep = 1,3,6,8,10,13,16,19-octaazabicyclo[6.6.6]eicosane, 1-pn = (−)-1,2-propanediamine, and 1-chxn = (−)-*trans*-1,2-cyclohexanediamine). Raising the temperature from 288 to 318 K has little effect on K_l values for Δ-$[Co(en)_3]^{3+}$ and Δ-$[Co(sep)]^{3+}$ but causes a significant decrease in the CD intensity of the ion pair formed between Δ-$[Co(en)_3]^{3+}$ and *l*-tartrate. The degrees of chiral discrimination of these systems, as well as the CD spectra of ion pairs and the direction of CD changes due to tartrates, are consistent with the proposition that the access of tartrate ions to the cation along the C_3 axis enhances the A_2 rotational strength, while that along the C_2 axis enhances the E_a rotational strength.

Introduction

It has long been known that the circular dichroism (CD) spectra of metal complexes in solution change upon addition of electrolytes. Since the pioneering works of Douglas, Mason, and their co-workers,[2,3] many studies have been done to correlate the observed CD change with the mode of interaction of optically active metal complexes with added ions.[4-7] However, no definite conclusion appears to have been reached on the relationship between the CD change and the mode of interaction. If such a relationship is established, the utility of CD spectra should become invaluable in deducing the stereochemistry of weakly interacting species in solution. The results of our recent experiments seemed to imply that the principal effect of ion association upon the CD spectra of metal complexes is to alter the rotational strength of that transition which is polarized along the direction of access of the anion toward the cation.[6] As part of our program to test this hypothesis, we have studied the chiral interaction of tartrate ions with several $[Co(N)_6]^{3+}$ complexes of trigonal symmetry in solution. If we note that the first ligand field band of the CD spectra of trigonal $[Co(N)_6]^{3+}$ complexes comprises only two transitions, A_2 and E_a, which are polarized along the C_3 and C_2 axes, respectively, the problem here is to confirm which rotational strength, $R(A_2)$ or $R(E_a)$, changes primarily by tartrate ions, providing that the anions approach the cation

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(1) Chiral Recognition in Solution. 3. Part 2: Sakaguchi, U.; Yamamoto, I.; Izumoto, S.; Yoneda, H. *Bull. Chem. Soc. Jpn.* **1983**, *56*, 153.

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(3) (a) Mason, S. F.; Norman, B. J. *Proc. Chem. Soc., London* **1964**, 339. (b) Mason, S. F.; Norman, B. J. *Chem. Commun.* **1965**, 73. (c) Mason, S. F.; Norman, B. J. *J. Chem. Soc. A* **1966**, 307.

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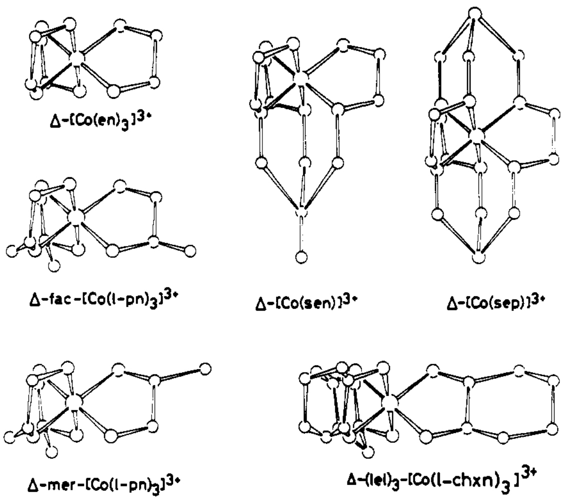

Figure 1. Structures of the Δ complexes investigated in this work.

along, e.g., the C_3 axis. Since the unpolarized absorption spectra of these complexes in the visible region do not change by tartrates,[8] the CD spectra are more convenient and sensitive to probe the chrial interaction in solution.

Experimental Section

Materials. The trigonal complexes used in this work were the perchlorate salts of Δ-$[Co(en)_3]^{3+}$,[9,10] Δ-$[Co(sen)]^{3+}$,[11] Δ-$[Co(sep)]^{3+}$,[12] Δ-*fac*- and Δ-*mer*-$[Co(1\text{-}pn)_3]^{3+}$,[13] and Δ-$[Co(1\text{-}chxn)_3]^{3+}$,[14] which were obtained by the literature methods and had the Δε values of −1.87 at 493 nm (lit.[10c] −1.89), +1.06 at 449 nm (lit.[11a] +1.05), +2.61 at 465 nm (lit.[12b] ca. 2.5), −1.90 at 495 nm (lit.[13d] −1.95), −2.10 at 494 nm (lit.[13d] −1.95), and −1.83 at 500 nm (lit.[11a] −2.15), respectively. The other chemicals were used as supplied.

Measurements. Circular dichroism spectra were measured on a JASCO J-40CS recording spectropolarimeter, and the linearity of the recordings was better than 2%. The sample cell was kept at a constant temperature to ±0.2 °C with a Model FK Haake circulator. The difference CD (DCD) spectra, defined as the CD spectra with tartrates minus the CD spectra without tartrates, were obtained by using the data processor compartment operating at 0.2 nm/step of processor resolution.

The DCD data were least-squares fitted to the equation

$$C_M/\mathrm{DCD} = 1/(\Delta\epsilon_{MA} - \Delta\epsilon_M) + 1/K(\Delta\epsilon_{MA} - \Delta\epsilon_M)(c_A - x)$$

to obtain the association constant, K, and the CD of the ion pair, $\Delta\epsilon_{MA}$, where c_M, c_A, and x are the initial concentrations of the metal complex perchlorate and sodium tartrate and the concentration of the ion pair, respectively. The subscripts M, A, and MA refer to the metal complex, the tartrate anion, and the ion pair, respectively. Except for Δ-$[Co(1\text{-}chxn)_3]^{3+}$, c_M was kept constant at 3.0×10^{-3} mol dm^{-3} and c_A was changed from 0 to 27.3×10^{-3} mol dm^{-3}. The perchlorate salt of Δ-$[Co(1\text{-}chxn)_3]^{3+}$ was sparingly soluble in water, and c_M of this complex was set to 6.0×10^{-5} mol dm^{-3} and a sample cell of 10-cm length was used. The ionic strength was adjusted to $\mu = 0.1$ with sodium perchlorate.

Table I. Association Constants, K_l and K_d (M^{-1}), at 25 °C and $\mu = 0.1$ ($NaClO_4$)

complex	λ, nm	K_l	K_d	$\Delta\epsilon_{MA}$
Δ-$[Co(en)_3]^{3+}$	450	13.3 ± 0.1		1.15
	475	15.0 ± 0.2		−0.75
	425	13.4 ± 0.2		0.52
	450		11.7 ± 0.1	0.81
Δ-$[Co(sen)]^{3+}$	450		49.0 ± 0.9	1.32
	440		50.1 ± 1.2	1.23
	450	71.7 ± 0.7		1.44
	440	72.3 ± 1.5		1.33
Δ-$[Co(sep)]^{3+}$	490	38.9 ± 0.3		0.03
	470	39.7 ± 0.2		0.81
	490		38.1 ± 0.8	−0.15
	470		38.5 ± 0.4	0.84
Δ-*mer*-$[Co(1\text{-}pn)_3]^{3+}$	450		20.6 ± 0.1	1.34
	440		21.9 ± 0.2	1.40
	450	27.3 ± 0.2		1.66
	440	26.6 ± 0.4		1.73
	430	24.4 ± 2.9		1.70
	475	26.1 ± 0.9		0.96
Δ-*fac*-$[Co(1\text{-}pn)_3]^{3+}$	450		22.5 ± 0.5	1.13
	450	30.3 ± 0.3		1.42
Δ-$[Co(1\text{-}chxn)_3]^{3+}$	475	21.4 ± 0.4		0.54
	475		15.4 ± 0.4	0.14

Results and Discussion

The complexes investigated in this work are Δ-$[Co(en)_3]^{3+}$, Δ-$[Co(sen)]^{3+}$, Δ-$[Co(sep)]^{3+}$, Δ-*fac*- and Δ-*mer*-$[Co(1\text{-}pn)_3]^{3+}$, and Δ-$[Co(1\text{-}chxn)_3]^{3+}$. The structures as well as the absolute configurations of all the complexes have been determined previously by X-ray analyses.[10b,11b,12b,13b,13c,14c] Figure 1 depicts schematically the structures of these Δ cations. In the figure, hydrogen atoms are omitted for clarity. The interaction of tartrate ions with $[Co(en)_3]^{3+}$ and $[Co(pn)_3]^{3+}$ in solution has been studied by several workers. Ogino and Saito[8] found a difference in the association constants of *d*-tartrate with Δ- and Λ-$[Co(en)_3]^{3+}$. Fujita and Yamatera[15] studied qualitatively the CD changes of $[Co(en)_3]^{3+}$ and $[Co(pn)_3]^{3+}$ due to tartrates and related anions and proposed a model for the ion pairs, wherein two hydroxyl and one carboxyl group of the tartrate anion form hydrogen bonds with three axial NH hydrogens of these cations. Our recent crystal structure analyses of Λ-$[Co(en)_3]Br(d\text{-}C_4H_4O_6)\cdot 5H_2O$,[16] Λ-$Li[Cr(en)_3](d\text{-}C_4H_4O_6)_2\cdot 3H_2O$,[17] Λ-$H[Co(en)_3](d\text{-}C_4H_4O_6)_2\cdot 3H_2O$,[18] and Λ-$[Co(sen)]Cl(d\text{-}C_4H_4O_6)\cdot 6H_2O$[11b] pointed to the relevance of such a model in solution.

Association Constants. Figure 2 gives the CD spectra of all the complexes examined here in the first d–d region. The CD peak of lowest energy is assigned to the E_a transition and the higher energy peak to the A_2 transition, except for Δ-$[Co(sep)]^{3+}$, for which the positive $R(A_2)$ dominates over the negative $R(E_a)$.[19] By analyzing the changes in CD intensities caused by *d*- and *l*-tartrate ions, the corresponding association constants, K_d and K_l, were determined (see Figure 3). The linearity of the plots of Figure 3 establishes that only 1:1 association is taking place in our systems. The association constants, K_d and K_l, and the CD intensities of the ion pairs, $\Delta\epsilon_{MA}$, obtained from least-squares analyses are summarized

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(8) (a) Ogino, K.; Saito, U. *Bull. Chem. Soc. Jpn.* **1967**, *40*, 826. (b) Ogino, K. *Ibid.* **1969**, *42*, 447.

(9) Abbreviations: en = ethylenediamine, sen = 1,1,1-tris((2-aminoethyl)aminomethyl)ethane, sep = 1,3,6,8,10,13,16,19-octaazabicyclo[6.6.6]eicosane, 1-pn = (−)-1,2-propanediamine, 1-chxn = (−)-*trans*-1,2-cyclohexanediamine, mal = malonate.

(10) (a) Broomhead, J. A.; Dwyer, F. P.; Hogarth, J. W. *Inorg. Synth.* **1960**, *6*, 183. (b) Iwata, M.; Nakatsu, K.; Saito, Y. *Acta Crystallogr., Sect. B* **1969**, *B25*, 2562 and references therein. (c) McCaffery, A. J.; Mason, S. F. *Mol. Phys.* **1963**, *6*, 357.

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(13) (a) MacDermott, T. E. *Inorg. Chim. Acta* **1968**, *2*, 81. (b) Iwasaki, H.; Saito, Y. *Bull. Chem. Soc. Jpn.* **1966**, *39*, 92. (c) Butler, K. R.; Snow, M. R. *J. Chem. Soc., Dalton Trans.* **1976**, 251. (d) McCaffery, A. J.; Mason, S. F.; Ballard, R. E. *J. Chem. Soc.* **1965**, 2883.

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(17) Kushi, Y.; Kuramoto, M.; Yoneda, H. *Chem. Lett.* **1976**, 339.

(18) Tada, T.; Kushi, Y.; Yoneda, H. *Chem. Lett.* **1977**, 379.

(19) See, e.g.: Mason, S. F. In "Optical Activity and Chiral Discrimination"; Mason, S. F., Ed.; D. Reidel Publishing Co.: Dordrecht, The Netherlands, 1979; pp 161–187.

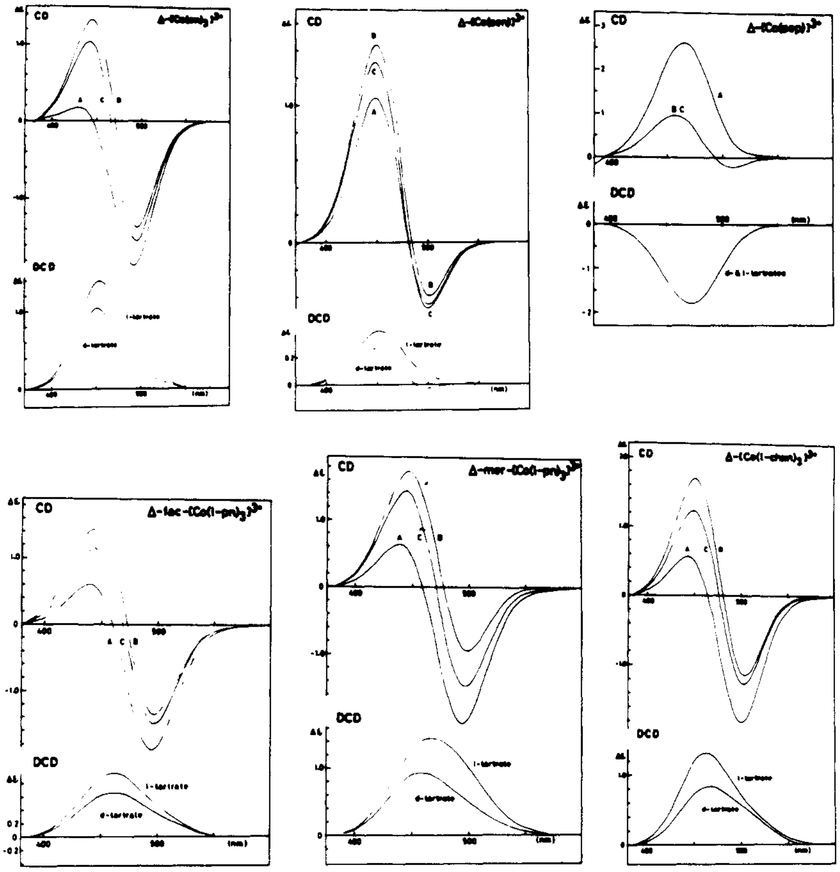

Figure 2. (Upper) CD spectra of the metal complex (A) and of the ion pairs with *l*-tartrate (B) and *d*-tartrate (C). (Lower) DCD spectra due to *l*- and *d*-tartrates.

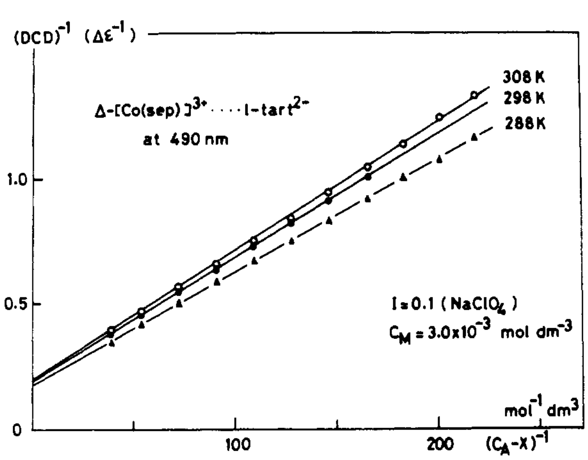

Figure 3. Some final plots for the pair Δ-[Co(sep)]$^{3+}$···*l*-tartrate.

in Table I. The K_d and K_l values obtained here for Δ-[Co(en)$_3$]$^{3+}$ agree very well with those determined previously (K_l = 13.6 ± 0.2, K_d = 11.7 ± 0.4 at 25 °C, 455 nm and μ = 0.1),[4b] which lends credence to the present results. Ogino[8b] reported that, under the same experimental condition as ours, K_d = 28 ± 2 and K_l = 30 ± 2 for Δ-[Co(l-pn)$_3$]$^{3+}$, which was, however, a mixture of *fac* and *mer* isomers in unknown proportions.

Several interesting features emerge from comparison of the association constants. The first point noted is that the association constants for the *d*- and *l*-tartrates differ significantly except for Δ-[Co(sep)]$^{3+}$, for which K_l is equal to K_d within experimental uncertainties. In each complex except Δ-[Co(sep)]$^{3+}$, K_l is larger than K_d, indicating that these Δ complexes favor the association with *l*-tartrate. The degree of chiral discrimination may be defined by $(K_l - K_d)/(K_l + K_d)$. The degrees of chiral discrimination are approximately 7, 18, 0, 15, 11, and 16% for Δ-[Co(en)$_3$]$^{3+}$, Δ-[Co(sen)]$^{3+}$, Δ-[Co(sep)]$^{3+}$, Δ-*fac*- and Δ-*mer*-[Co(l-pn)$_3$]$^{3+}$, and Δ-[Co(l-chxn)$_3$]$^{3+}$, respectively. Thus, chiral discrimination by Δ-[Co(sen)]$^{3+}$, Δ-*fac*- and Δ-*mer*-[Co(l-pn)$_3$]$^{3+}$, and Δ-[Co(l-chxn)$_3$]$^{3+}$ is substantially more efficient than that by Δ-[Co(en)$_3$]$^{3+}$. This may be ascribed to the fact that the first four complexes have ethylenediamine moieties locked in the lel$_3$ conformation, while Δ-[Co(en)$_3$]$^{3+}$ does not.[12b,20] In the lel$_3$ conformation, one of the NH hydrogens of each chelate ring points approximately parallel to the C_3 axis and this will help the tartrate ion to hydrogen bond with these three hydrogens simultaneously. The sen complex with only one face of three axial NH hydrogens exhibits a degree of discrimination similar to that of the l-pn and l-chxn complexes. This result seems to indicate that only one such face is enough for discrimination, which in turn suggests that the chiral discrimination is effected through a 1:1 association. The fact that Δ-[Co(sep)]$^{3+}$, which lacks such axial NH hydrogens, does not discriminate tartrate at all seems to imply that the tartrate ions approach the cation along the C_2 axis of the cation and this mode of access is ineffective for chiral discrimination. An access along the C_3 axis is sterically and electrostatically unfavorable, because the anion cannot come as near to the cation as the anion would if the trimethyleneamino caps were absent. This inference is supported also by the sign of the DCD spectra and the CD of the ion pairs (see below).

Though the Δ-*fac* isomer of the l-pn complex shows larger K_l and K_d values than the Δ-*mer* isomer, the differences in both K_l and K_d values are rather small. This indicates that the spatial disposition of methyl groups has only a small effect on the association constants. This result is quite reasonable if

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(20) (a) Beattie, J. K. *Acc. Chem. Res.* **1971**, *4*, 253. (b) Sudmeier, J. L.; Blackmer, G. L.; Bradley, C. H.; Anet, F. A. L. *J. Am. Chem. Soc.* **1972**, *94*, 757.

Table II. Temperature Dependence of K_l, $\Delta\epsilon_M$, and $\Delta\epsilon_{MA}$ for Δ-$[Co(en)_3]^{3+}$ and Δ-$[Co(sep)]^{3+}$

T, K	K_l, M^{-1}	$\Delta\epsilon_M$	$\Delta\epsilon_{MA}$
	Δ-$[Co(en)_3]^{3+}$ at 450 nm		
288	13.8 ± 0.6	−0.24	1.30
298	13.3 ± 0.1	−0.23	1.15
308	13.3 ± 0.1	−0.22	1.01
318	13.9 ± 0.1	−0.22	0.85
	Δ-$[Co(sep)]^{3+}$ at 490 nm		
288	38.7 ± 0.2	1.52	0.02
298	38.9 ± 0.3	1.49	0.03
308	37.9 ± 0.1	1.53	0.13
318	36.0 ± 0.5	1.52	0.13

the tartrate ions approach the cations predominantly along the C_3 axis. Molecular models suggest that methyl groups in both isomers will not interfere with the face-to-face contact of the anion to any great extent. A similar discussion has been made by Butler and Snow[13c] to interpret the chiral discrimination mode in the crystal of Δ-*mer*-$[Co(l\text{-}pn)_3]$-Λ-$[Cr(mal)_3]\cdot 3H_2O$. The fact that Δ-*fac*- and Δ-*mer*-$[Co(l\text{-}pn)_3]^{3+}$ and Δ-$[Co(l\text{-}chxn)_3]^{3+}$ exhibited similar degrees of chiral discrimination indicates that the methyl groups have only a minor effect on chiral discrimination as well. This also suggests that chiral discrimination is effected along the C_3 axis of the cation.

The third point noted is that the magnitude of K_l or K_d varies significantly from complex to complex. Except for Δ-$[Co(sep)]^{3+}$, which assumes a different mode of association than the others, both K_l and K_d increase in the order

$$\Delta\text{-}[Co(en)_3]^{3+} < \Delta\text{-}[Co(l\text{-}chxn)_3]^{3+} < \Delta\text{-}mer\text{-}[Co(l\text{-}pn)_3]^{3+} \lesssim \Delta\text{-}fac\text{-}[Co(l\text{-}pn)_3]^{3+} < \Delta\text{-}[Co(sen)]^{3+}$$

At first sight, it might appear that the order parallels the magnitude of the axial component of the dipole moment of the complexes. We consider this coincidence just fortuitous, because the association constants of these complexes with (*d*-tartrato)- and (*l*-tartrato)antimonate(III) ions have no correlation with the above order.[21] Apparently, the prediction based on simple electrostatic theory that the smaller ions should show larger association constants[22] does not hold here. For complexes with lower electric charges, it has been pointed out that the association constants get larger as the sum of the crystallographic radii (rather than the hydrodynamic radii as determined from conductance measurements) of the two ions increases and also as the size of the complex ion increases.[23] However, this trend too cannot be observed here. Also, though it might be expected that the lel_3 conformation of chelate rings contribute to increase K_l and K_d to some extent, it is only a minor factor at best: compare the K_l values of 13.4, 21.4, and 71.7 for Δ-$[Co(en)_3]^{3+}$, Δ-$[Co(l\text{-}chxn)_3]^{3+}$, and Δ-$[Co(sen)]^{3+}$, respectively. The K_l value of Δ-$[Co(sen)]^{3+}$ is markedly larger than that of Δ-$[Co(l\text{-}chxn)_3]^{3+}$, despite the fact that both complexes have ethylenediamine moieties locked in the lel_3 form.

In an attempt to get a clue to this problem we measured the association constants of Δ-$[Co(en)_3]^{3+}$ and Δ-$[Co(sep)]^{3+}$ with *l*-tartrate as a function of temperature between 288 and 318 K. The results, given in Table II, are rather disappointing. No temperature dependence in K_l could be found for the Δ-$[Co(en)_3]^{3+}$ system, though the temperature range covered was very limited. For Δ-$[Co(sep)]^{3+}$, an indication of a very slight decrease in K_l with temperature may be recognized. By using average values of K_l, we obtain $\Delta S^{*} = 5$ eu, $\Delta H^{*} = 0$ and $\Delta S^{*} = 7$ eu, $\Delta H^{*} = 0$ for the ethylenediamine and sep complexes, respectively. The result conforms to the well-known pattern in the formation of ion pairs; outer-sphere association is governed generally by the entropy increase associated with the release of water of solvation as the ions of opposite charges get paired.[24]

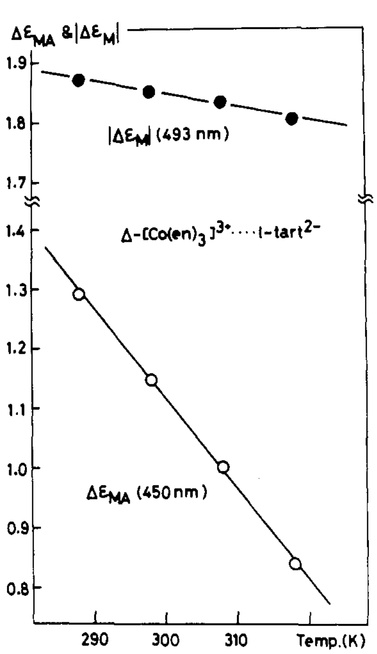

Figure 4. Temperature dependences of $\Delta\epsilon_{MA}$ at 450 nm and $|\Delta\epsilon_M|$ at 493 nm for the pair Δ-$[Co(en)_3]^{3+}\cdots l$-tartrate.

We found, instead, that the CD of the ion pair Δ-$[Co(en)_3]^{3+}\cdots l$-tartrate decreases in intensity significantly as the temperature is raised. Figure 4 plots the CD intensity at 450 nm of this ion pair against temperature, comparing with the CD intensity variation of the complex cation. In Figure 4, $|\Delta\epsilon_M|$ values are plotted at the CD peak (493 nm), where the variations with temperature are proportionately larger than at 450 nm (see Figure 2). As seen from the figure, the decrease in the CD intensity of the ion pair is much more prominent than that of the complex cation. (Unfortunately, the choice of wavelength for the Δ-$[Co(sep)]^{3+}$ system was not proper and $\Delta\epsilon_{MA}$ values are close to zero, rendering the temperature variation less discernible.) A gradual decrease in the CD intensity of a metal complex with rising temperature, which is generally accompanied by the broadening of the CD band, has been found also for other complexes of various metal ions.[25,26] This effect has been ascribed[26] to an increased population in higher energy vibrational levels in the ground state, leading to the broadening of the ground electronic level, from which the transition occurs. This broadening results in the broadening of the CD band and hence in the decrease in the CD intensity. Of more interest is the finding of a rather drastic decrease in the CD intensity of the ion pair. This effect will be seen from Figure 4 to work to nullify the effect of the tartrate ion in the ion-paired species, while keeping the number of ion pairs constant. We cannot attribute this to the formation of the species with, e.g., only one hydrogen bond between the ions, because such species are expected to yield rather different DCD spectra.[27] Though we feel that the effect has also a vibronic origin as the temperature variation of the CD of the

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complex does, the true cause is not apparent. Thus, at present the major factor in the determination of the association constants and the temperature variation of the CD intensity of the ion pair is not clear.

DCD Spectra. As shown in Figure 2, all the DCD spectra due to both *d*- and *l*-tartrates, except for Δ-[Co(sen)]$^{3+}\cdots$*d*-tartrate, are composed of apparently single peaks. The DCD's of the en, 1-pn, and 1-chxn complexes are all positive, whereas they are negative for Δ-[Co(sep)]$^{3+}\cdots$*d*- and *l*-tartrates. If we note that the tartrate anion approaches the former four complexes predominantly along the C_3 axis and the anion approaches Δ-[Co(sep)]$^{3+}$ mainly along the C_2 axis and that $R(A_2)$ and $R(E_a)$ are positive and negative, respectively, for all the complexes, this observation seems to support the idea that an access of an anion along the C_3 axis enhances $R(A_2)$ and that along the C_2 axis enhances $R(E_a)$.[6,28] It may be apparent that the observed DCD is a compromise of two opposing effects: enhancement of $R(A_2)$, which is positive, due to the C_3 access of the anion and enhancement of $R(E_a)$, which is negative, due to the C_2 access. The sign of the observed DCD reflects the dominant mode of these two. The small negative peak observed in the DCD of Δ-[Co(sen)]$^{3+}\cdots$*d*-tartrate is thus assigned to E_a, and the dominant peak is therefore assigned to A_2. From comparison of the DCD spectra in Figure 2 except that of Δ-[Co(sep)]$^{3+}$, it is apparent that the positive DCD's are assigned to A_2.

The CD curves of fully ion-paired species are also given in Figure 2. As seen from the figure, the CD spectra of Δ-[Co(en)$_3$]$^{3+}$, Δ-*fac*- and Δ-*mer*-[Co(1-pn)$_3$]$^{3+}$, and Δ-[Co(1-chxn)$_3$]$^{3+}$ tend to be close to the CD of Δ-[Co(sen)]$^{3+}$ upon ion pairing. The CD spectrum of Δ-[Co(sep)]$^{3+}$ tends, upon ion pairing, to mimic the CD spectrum of the ion pair formed between Δ-*fac*- or Δ-*mer*-[Co(1-pn)$_3$]$^{3+}$ or Δ-[Co(1-chxn)$_3$]$^{3+}$ and *d*- or *l*-tartrate. These observations are consistent with the conclusion of Mason et al.[28] that the addition of atoms or groups, whether covalent or hydrogen bonded, to the D_3 polar region of trigonal [Co(N)$_6$]$^{3+}$ complexes enhances generally $R(A_2)$ and that to the D_3 equatorial region enhances $R(E_a)$. Finally, it will be worthwhile to point out that the intensity and the shape of a CD spectrum change, in some complexes, rather drastically by ion pairing. For example, the CD peak of Δ-[Co(sep)]$^{3+}$ diminishes in intensity by about 64% and the shape also changes as illustrated in Figure 2, due to tartrates. A direct consequence of this is that the intensity as well as the shape of the CD spectra taken especially for single crystals is more or less modified by "ion pairing" effects in the solid state.

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Registry No. Δ-[Co(en)$_3$]$^{3+}$, 16569-46-3; Δ-[Co(sen)]$^{3+}$, 85353-30-6; Δ-[Co(sep)]$^{3+}$, 85283-43-8; Δ-*fac*-[Co(1-pn)$_3$]$^{3+}$, 18745-20-5; Δ-*mer*-[Co(1-pn)$_3$]$^{3+}$, 36513-61-8; Δ-[Co(1-chxn)$_3$]$^{3+}$, 60064-15-5; *d*-tartrate, 3715-17-1; *l*-tartrate, 5976-86-3.

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Photoassisted Reduction of Sulfur Dioxide in Nonaqueous Solutions at p-Type Semiconductor Electrodes

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The electrochemical behavior of SO_2 has been investigated at illuminated (632.8 and 514.5 nm) p-type semiconducting Si, WS_2, and InP in CH_3CN/[*n*-Bu_4N]ClO_4 solutions. SO_2 is photoreducible at each of these materials to form $S_2O_4{}^{2-}$, but the electrical power savings efficiencies are variable. The best power savings efficiency, ~11% at 514.5 nm (100 mW/cm^2), is obtained with a p-type InP photocathode modified by photoelectrodeposition of $\sim 5 \times 10^{-8}$ mol/cm^2 of Pt onto the surface. Naked p-InP is considerably less efficient, owing to poor kinetics for the reduction of SO_2. The deposition of Pt onto p-InP forms neither a uniform ohmic contact nor a Schottky barrier; rather, studies of platinized n-InP show directly that the Pt serves as a catalyst for SO_2 reduction. Power savings efficiencies for p-type WS_2 and textured Si are low, owing to small output voltages. Preparative, controlled-potential photoelectrochemical reduction of SO_2 at all three photoelectrodes and Pt in CH_3CN/0.1 M SO_2/0.5 M [*n*-Bu_4N]ClO_4 has been demonstrated to give >90% current efficiency for formation of $S_2O_4{}^{2-}$, which can be precipitated and collected as $Na_2S_2O_4$.

Introduction

There is much interest in demonstrating worthwhile redox reactions that can be driven by illumination of semiconductors immersed in liquid electrolytes.[1] Recently,[2] we showed that the uphill reduction of 2-*tert*-butyl-9,10-anthraquinone in CH_3CN/CH_3COOH/electrolyte solution can be sustained at p-type Si photocathodes and that exposure of the electrolyzed solutions to O_2 results in the formation of synthetically significant quantities of H_2O_2. With the goal of demonstrating a photoelectrochemical route to the known reductant $S_2O_4{}^{2-}$, we have undertaken a study of the electrolysis of nonaqueous solutions of SO_2 using p-type WS_2, Si, and InP photocathodes (eq 1). The light-assisted reduction of SO_2 according to eq

$$2SO_2 + 2e^- \xrightarrow[\text{nonaqueous electrolyte}]{\text{p-type photocathode, } 2h\nu} S_2O_4{}^{2-} \qquad (1)$$

1 is shown to occur at electrode potentials more positive than that when the reduction is carried out at conventional electrodes such as Pt, thereby lowering the electrical energy required for $S_2O_4{}^{2-}$ generation.

The reduction of SO_2 to $S_2O_4{}^{2-}$ is irreversible in the kinetic sense,[3] and complicated electrolyte and SO_2 concentration dependent equilibria make $E°'(SO_2/S_2O_4{}^{2-})$ difficult to de-

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