June, 1982] © 1982 *The Chemical Society of Japan* NOTES *Bull. Chem. Soc. Jpn.*, *55*, *1969—1970 (1982)* 1969

Comparison of Association Constants Derived from CD and UV Measurements. The Case of Λ-Tris(ethylenediamine)cobalt(III) and Δ-Tris((1*R*, 2*R*)-1,2-cyclohexanediamine)cobalt(III) with Thiosulfate Ion

Hayami Yoneda,* Katsuhiko Miyoshi, and Hitoshi Matsukawa

Department of Chemistry, Faculty of Science, Hiroshima University, Higashi-senda-machi, Naka-ku, Hiroshima 730

(Received October 9, 1981)

Synopsis. The association constant K_A determined by CD measurement is much smaller than that by UV measurement for the Λ-$[Co(en)_3]^{3+}$–$S_2O_3^{2-}$ system in water, whereas the two kinds of measurements yield almost the same K_A values for the Δ-$[Co(l\text{-chxn})_3]^{3+}$–$S_2O_3^{2-}$ system. These results are discussed in relation to possible interaction modes involved.

Absorption (AB) and circular dichroism (CD) spectra of metal-amine complex cations like $[Co(en)_3]^{3+}$ are changed in shape and/or magnitude upon addition of polarizable oxoanions such as PO_4^{3-}, $S_2O_3^{2-}$, SeO_3^{2-}, and SO_4^{2-}.[1,2] These changes have been utilized to investigate outer-sphere interactions of these complexes with added anions in solution.[3,4] Norden[5] was the first to demonstrate that CD change (in the visible region) gives an appreciably smaller association constant K_A than AB change (in the UV region) for the $[Co(en)_3]^{3+}$–(R,R)-tartrate^{2-} system in water. Taura[6] has recently presented the same trend in K_A values of $[Co(en)_3]^{3+}$ with (R,S)-tartrate^{2-} ion. The anomalous trend pointed out anew by Yamatera[7] remains still unsolved. In the present study, association constants of two chiral complexes, Λ-$[Co(en)_3]^{3+}$ and Δ-$[Co(l\text{-chxn})_3]^{3+}$ (l-chxn$=(1R,2R)$-1,2-cyclohexanediamine), with $S_2O_3^{2-}$ ion were determined by CD and AB measurements under identical conditions, and were compared with each other.

Experimental

Materials. Λ-$[Co(en)_3]^{3+}$ and Δ-$[Co(l\text{-chxn})_3]^{3+}$ prepared as chloride salts[8] were identified by their AB and CD spectra. Optically active $[Co(Hbg)_3]^{3+}$ and $[Co(tri)_2]^{3+}$ (Hbg=biguanide and tri=tribenzo[*b*,*f*,*i*][1,5,9]triazacyclododecine) were also prepared according to the procedures described in the literature.[9,10] All the other chemicals used were of reagent grade.

Measurements. AB and CD changes of aqueous solutions of the chiral complexes (2.0×10^{-3} mol/dm^3) were recorded at 25±0.1 °C on Shimadzu UV-200 and JASCO J-40CS spectrometers, as a function of the concentration of $Na_2S_2O_3$ (2.50×10^{-3} to 2.75×10^{-2} mol/dm^3). Ionic strength I was adjusted with NaCl and not with $NaClO_4$ because of low solubility of $[Co(l\text{-chxn})_3](ClO_4)_3$. Freshly prepared sample solutions were subjected to spectral measurements which were carried out at 460, 315, or 300 nm. No spectral changes with standing time over 1 h were detected, and interference due to Cl^- ion added was found negligible at each wavelength. A standard analysis[5,11] of the data thus obtained gave the association constant K_A.

Results and Discussion

Figure 1 shows AB and CD spectra of Δ-$[Co(l\text{-chxn})_3]^{3+}$ in aqueous solutions with and without $Na_2S_2O_3$. In addition to the usual changes in the AB (UV region) and CD (visible region) spectra, an appreciable CD change is observed in the UV region, which is also attributed to ion association with $S_2O_3^{2-}$ ion.[4] Essentially the same spectral changes are found in the Λ-$[Co(en)_3]^{3+}$ system. Thus, we attempted to determine the association constant K_A by utilizing these CD changes in the UV region as well as the usual spectral changes.

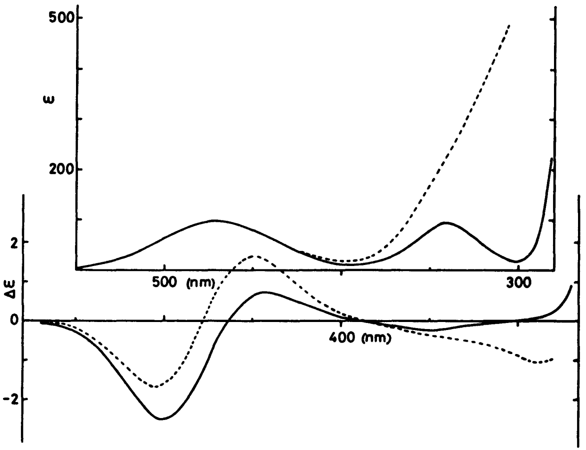

Fig. 1. AB (upper curves) and CD (lower curves) spectra of aqueous Δ-$[Co(l\text{-chxn})_3]^{3+}$ (2.0×10^{-3} mol/dm^3) in the absence (solid curves) and presence (dotted curves) of $Na_2S_2O_3$ (2.5×10^{-2} mol/dm^3).

Table 1. Association constants K_A with $S_2O_3^{2-}$ ion at $I=0.1$ (NaCl) in water at 25 °C

K_A	Λ-$[Co(en)_3]^{3+}$	(λ/nm)	Δ-$[Co(l\text{-chxn})_3]^{3+}$	(λ/nm)
K_{UV}	59.0±0.5	(300)	70.4±0.3	(315)
	59.6±0.7	(300)	70.0±0.5	(315)
$K_{CD(V)}$	43.7±0.4	(460)	69.0±0.4	(460)
	44.5±0.7	(460)	69.1±0.5	(460)
$K_{CD(UV)}$	51.5±0.4	(300)	61.6±0.5	(315)
	51.1±0.5	(300)	62.9±0.4	(315)

In Table 1 are given the K_A values obtained by the two independent measurements, where K_{UV}, $K_{CD(V)}$, and $K_{CD(UV)}$ refer to the association constants derived from the AB (UV region), CD (visible region), and CD (UV region) measurements, respectively. The most striking finding in Table 1 is that $K_{CD(V)}$ is appreciably smaller than K_{UV} for the $[Co(en)_3]^{3+}$ system as already observed with (R,R)-tartrate^{2-} [5] and (R,S)-tartrate^{2-},[6] while the two values are the same within our experimental errors for the $[Co(l\text{-chxn})_3]^{3+}$ system.

In Table 2 are summarized the K_A values of Λ-

TABLE 2. ASSOCIATION CONSTANTS K_A OF Λ-$[Co(en)_3]^{3+}$ WITH SOME ANIONS AT $I=0.1$ ($NaClO_4$) IN WATER AT 25 °C

Anions	K_A		Ref.
(R,R)-Tartrate^{2-}	K_{UV}	26 ± 2	5,14
		22.5 ± 0.4	6
	$K_{CD(V)}$	16 ± 3	5
		13.6 ± 0.2	6,11b
(R,S)-Tartrate^{2-}	K_{UV}	60.7 ± 0.7	6
	$K_{CD(V)}$	39.6 ± 0.5	6,11b
SO_4^{2-}	$K_{UV}$$^{b)}$	49 ± 2	14
	$K_{CD(V)}$	30.3 ± 0.4	a)

a) H. Yoneda *et al.*, unpublished work. b) $K_{UV}=70\pm2$ for the Λ-$[Co(d\text{-}pn)_3]^{3+}$–SO_4^{2-} system at $I=0.1$ (Ref. 14).

$[Co(en)_3]^{3+}$ with some anions reported by earlier workers. It seems a general observation that $K_{CD(V)}$ is smaller than K_{UV} as far as $[Co(en)_3]^{3+}$ is concerned. Here, we assume that the CD change in the visible region is due to the asymmetry around the coordinated N atoms, which is newly generated through the hydrogen-bonding of the N–H protons with added oxoanions along the C_3 axis of the complex.[1a,4b,12] This assumption is supported indirectly by the fact that $[Co(Hbg)_3]^{3+}$ and $[Co(tri)_2]^{3+}$, either having no N–H proton directed parallel to their C_3 axis, do not suffer any CD change in the visible region upon addition of some oxoanions.[9] If the above assumption is valid, it follows that the $K_{CD(V)}$ value reflects predominantly the magnitude of ion-pair formation with anions along the C_3 axis.

The K_{UV} value, on the other hand, contains all the contributions from the association modes which give rise to the interionic charge transfer (CT) band(s) in the UV region. Since the above-mentioned association mode along the C_3 axis contributes to the CT band,[13] the AB change (UV region) is expected to detect association modes not only along the C_3 axis but also along other directions, K_{UV} thus being greater than $K_{CD(V)}$ for the $[Co(en)_3]^{3+}$ system.

If the same interpretation is applied to the $[Co(l\text{-}chxn)_3]^{3+}$ system, the K_A values given in Table 1 suggest that this complex interacts with $S_2O_3^{2-}$ ion along the C_3 axis only. In fact, the association modes other than that along the C_3 axis are sterically prohibited for this complex owing to the bulky chxn ligands. However, since $[Co(l\text{-}chxn)_3]^{3+}$ adopts a rigid lel_3 conformation with three N–H protons oriented favorably for hydrogen-bonding along the C_3 axis, greater $K_{CD(V)}$ and K_{UV} values are expected for this complex than for conformationally less rigid $[Co(en)_3]^{3+}$. This expectation is actually fulfilled as seen in Table 1. Similarly, a greater K_{UV} value with SO_4^{2-} ion has been reported[14] for Λ-$[Co(d\text{-}pn)_3]^{3+}$ with a lel_3 conformation than for Λ-$[Co(en)_3]^{3+}$. Finally, let us discuss the $K_{CD(UV)}$ values obtained for the first time in the present study. Mason *et al.*[4] proposed for some time that the CD change in the first d-d transition results from the electronic interaction with the interionic CT band, which exhibits an accompanying CD change upon addition of oxoanions (Fig. 1). If their proposal is valid, the CD change in the visible region should be proportional to that in the CT region. In other words, the $K_{CD(UV)}$ value is expected to be equal to the $K_{CD(V)}$ value. Contrary to this expectation, $K_{CD(UV)}$ is in the middle of K_{UV} and $K_{CD(V)}$ for the$[Co(en)_3]^{3+}$ system, whereas it is slightly smaller than K_{UV} or $K_{CD(V)}$ for the $[Co(l\text{-}chxn)_3]^{3+}$ system. As a result, the significance of these $K_{CD(UV)}$ values is not clear at present. Wavelength dependence of the K_A values might give some insight into these problems.

References

1) a) S. F. Mason and B. J. Norman, *Proc. Chem. Soc.*, **1964**, 339; b) S. F. Mason and B. J. Norman, *J. Chem. Soc., Chem. Commun.*, **1965**, 73.

2) H. L. Smith and B. E. Douglas, *Inorg. Chem.*, **5**, 784 (1966).

3) For example, J. Bjerrum, *Adv. Chem. Ser.*, **62**, 178 (1967).

4) a) R. Larsson, S. F. Mason, and B. J. Norman, *J. Chem. Soc., A*, **1966**, 301; b) S. F. Mason and B. J. Norman, *ibid.*, **1966**, 307.

5) B. Norden, *Acta Chem. Scand.*, **26**, 111 (1972).

6) T. Taura, Ph. D. Thesis, Hiroshima University, 1979.

7) H. Yamatera, the 37th National Meeting of the Chemical Society of Japan, Tokyo, April 1978, Abstr. No. 4V2.

8) S. E. Harnung, B. S. Sørensen, I. Creaser, H. Maegaard, U. Pfenninger, and C. E. Schäffer, *Inorg. Chem.*, **15**, 2123 (1976).

9) T. Tada, Y. Kushi, and H. Yoneda, *Bull. Chem. Soc. Jpn.*, **54**, 1538 (1981) and references cited therein.

10) S. C. Cummings and D. H. Busch, *J. Am. Chem. Soc.*, **92**, 1924 (1970).

11) a) H. Yoneda, K. Miyoshi, S. Suzuki, and T. Taura, *Bull. Chem. Soc. Jpn.*, **47**, 1661 (1974); b) H. Yoneda and T. Taura, *Chem. Lett.*, **1977**, 63.

12) J. E. Sarneski and F. L. Urbach, *J. Am. Chem. Soc.*, **93**, 884 (1971).

13) J. K. Beattie, R. A. Binstead, and M. Broccardo, *Inorg. Chem.*, **17**, 1822 (1978).

14) K. Ogino, *Bull. Chem. Soc. Jpn.*, **42**, 447 (1969).