

Methods for Determination of the Stability Constants of Outer-sphere Complexes Using Measurements of Absorbance, Optical Rotation, and Circular Dichroism: A Spectroscopic Study of the Outer-sphere Complex between Trisethylenediamine-cobalt(III) Ion and Ethylenediaminetetraacetate

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The stability constant, β_1 , of the first outer sphere complex between trisethylenediaminecobalt(III) (=M) and ethylenediaminetetraacetate (=H₂Y²⁻=L) has been determined at different ionic strengths, using different spectroscopic methods; measurement of absorbance in the ultra-violet, of circular dichroism, and of optical rotation. The metal compound (M) was kept in excess to assure that only the first complex was formed. At $I=0.1, 0.5, \text{ and } 1 \text{ M}$, $\beta_1=420, 50, \text{ and } 20 \text{ M}^{-1}$, respectively.

The corresponding data obtained with excess of ligand should, according to an often used method, indicate that only one associate was formed, but the " β_1 " values resulting from this method were only 50 % of those obtained from the first mentioned one, and the corresponding molar absorption coefficients of the complex were about two times larger than with M in excess. This discrepancy has been interpreted in terms of a further association. The corresponding stability constant of a second outer sphere complex has been estimated: $\beta_2=3 \times 10^4, 6 \times 10^3, \text{ and } 1 \times 10^2 \text{ M}^{-2}$ at $I=0.1, 0.5, \text{ and } 1 \text{ M}$, respectively. The unreliability has been indicated of taking linearity of the often used function C_L/δ versus C_L (C_L =total ligand concentration, δ =measured spectroscopic difference between the solutions C_M, C_L and $C_M, 0$) as a proof for correct assumptions (*e.g.* one complex only).

The magnitudes of the stability constants and the spectroscopic results are discussed (absorptivity and molar circular dichroism spectra have been computed), and it is suggested that the "ionic" bonding is partly covalent.

Circular dichroism (CD) measurement has proved to be a sensitive tool to detect outer sphere association between dissymmetric transition-metal complexes and polarizable anions in water solution.¹⁻⁷ In view of the recent finding that the change in the CD of cobalt(III)trisethylenediamine (Co(en)_3^{3+})

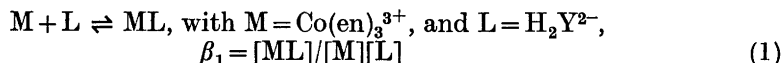
when adding ethylenediaminetetraacetate (H_2Y^{2-}) is *totally* due to the formation of an ordered ion-pair^{1,2} in which the ligand field is modified, it has been considered important to investigate the stability of the complex $Co(en)_3H_2Y^+$. As certain other spectroscopic methods have been considered unreliable (optical rotation,⁷⁻¹⁰ UV-absorbance⁷) when used in this field, this investigation has been performed using on the one hand circular dichroism measurements, and on the other, data from UV-absorbance and optical rotation.

It has recently been reported that a photocatalytic reaction can take place between $Co(en)_3^{3+}$ and H_2Y^{2-} (giving mainly $Co(III)Y^-$),¹¹ and it has been shown¹² that the decreased reaction rate with increasing initial H_2Y^{2-} concentration can in part be explained by a strong ionic strength dependence. The effect can thus to a great extent be cancelled by keeping a constant ionic strength.

The association has been investigated at a few different ionic strengths ($NaClO_4$). Bearing in mind the minimum in the expected general variation of β_1 with I ,¹³ it was considered relevant to extend the ionic strength range, probably at the cost of a large deviation from the more ideal dependence obtained by Posey and Taube¹⁴ in their investigation of $Co(NH_3)_6SO_4^+$.

METHOD AND EXPERIMENTAL

The equilibrium studied may be represented by



A method often used in studies on outer-sphere complexes^{11-17,26} for determining β_1 consists simply of the assumption that only one complex is formed. With $C_L \gg C_M$ (C_L and C_M are the total concentrations of L and M), and C_M constant, the function C_L/δ gives a straight line when plotted *versus* C_L . δ is the measured spectroscopic difference, $X(C_M, C_L) - X(C_M, 0)$, between the solution $C_M + C_L$ and the one with only C_M . If x_M and x_{ML} are the respective molar spectroscopic intensity entities of pure M and ML, the usual approximation is¹⁵⁻¹⁷

$$C_L/\delta = \frac{C_L}{(x_{ML} - x_M)C_M} + \frac{1}{\beta_1(x_{ML} - x_M)C_M} \quad (2)$$

β_1 is obtained as the ratio of slope to intercept of the resulting straight line. A straight line is often taken as a proof that the model and approximations are satisfactory (in this case and that discussed below).^{18,16}

With the concepts introduced above, *i.e.* (1), and $\delta = X(C_M, C_L) - X(C_M, 0)$, it follows that $\delta = (x_{ML} - x_M)[ML]$,* and

$$C_L/\delta = (1 + [L]\beta_1)/\beta_1 C_M (x_{ML} - x_M) + 1/(x_{ML} - x_M),$$

provided that only one complex is formed. With $C_L \gg C_M$, $[L] \approx C_L$, and one obtains

* If in $\delta = x_M[M] + x_{ML}[ML] + x_L[L] - x_M([M] + [ML])$, $x_L[L]$ can be neglected.

$$C_L/\delta = \frac{C_L}{(x_{ML} - x_M)C_M} + \frac{1}{\beta_1(x_{ML} - x_M)C_M} + \frac{1}{x_{ML} - x_M} \quad (3)$$

compared with the general expression (from (1) and $\delta = (x_{ML} - x_M)[ML]$ and $C_M = [M] + [ML]$):

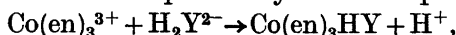
$$C_L/\delta = \frac{C_L}{(x_{ML} - x_M)C_M} + \frac{1}{\beta_1(x_{ML} - x_M)C_M} + \frac{1}{(x_{ML} - x_M)} - \frac{\delta}{(x_{ML} - x_M)^2 C_M} \quad (4)$$

The corresponding expressions, (2'), (3'), (4'), for the case of using M in excess, and C_L constant, are obtained by changing C_M to C_L and C_L to C_M in (2), (3), and (4): *e.g.*

$$C_M/\delta = C_M/(x_{ML} - x_M)C_L + 1/\beta_1(x_{ML} - x_M)C_L \quad (2')$$

is the expression used in the wellknown investigation of Evans and Nancollas¹⁸ on the halide complexes of Co(en)_3^{3+} and $\text{Co}(\text{NH}_3)_6^{3+}$.

After having tested the possibility of a deprotonization,



by pH measurements (*cf.* p. 2520), β_1 was determined by measuring UV-absorbance (A), circular dichroism (CD), and optical rotation (OR) of solutions containing excess of M, and applying (2') and (4'). The value of $x_{ML} - x_M$ obtained from (2') was used in (3') to obtain the function $C_M/\delta + \delta/(x_{ML} - x_M)^2 C_L - 1/(x_{ML} - x_M)$ of (4'). The corresponding procedures were also performed with excess of L.

Experimental. The solutions were made up in 50 ml measuring flasks from stock solutions of *p.a.* reagents (disodium versenate, Merck, sodium perchlorate, Fluka) and (+)trisethylenediaminecobalt(III) perchlorate (prepared in the usual way¹⁹). Only doubly distilled water was used.

The content of Co(II) in the $\text{Co(en)}_3(\text{ClO}_4)_3$ was determined by measuring the absorbance at 660 nm of a solution, 0.15 M $\text{Co(en)}_3(\text{ClO}_4)_3$, 9 M HCl ($\epsilon_{\text{CoCl}_4^{2-}} = 475 \text{ M}^{-1}\text{cm}^{-1}$ at this wavelength²⁰). The sensitivity of the method was tested by adding small amounts of CoCl_2 . The contamination of Co(II) in the sample was thus shown to be less than 0.05 %.

When having M in excess, δ_A was directly measured as the absorbance difference between the sample ($C_M, C_L, x\text{M NaClO}_4$) and ($C_M, 0, x\text{M NaClO}_4$). As δ_A was very small, especially when the ionic strength was high, it was necessary to use a comparatively long cell path-length (*e.g.* 1 cm). This demanded, however, that a large slit width region had to be used (*e.g.* 0.1–1 mm). The slit variation was depressed as much as possible by compensation with different amplification of the photomultiplier signal. In the series with constant low metal concentration, the slit variation was kept equal to zero by using this method.

Two attempts have been made to increase the precision of the spectroscopic measurements. The first concerns the absorbance measurements and serves to minimize the error, just spoken of, due to slit variations; the absorbance differences were measured at different slit values, by using different amplification, and the curve, absorbance *versus* slit width, was extrapolated to a fixed slit value, constant throughout the series. In this way, an artificial "band monochromacy" was obtained.

The second improvement was a more precise CD determination. Instead of reading the absolute CD on a recorded spectrum, the recorder signal was amplified 10 times, and the wavelength was kept constant at a value giving a sufficiently low absolute CD to be in the range of the recorder, but with a strong CD effect due to the outer-sphere association (see, *e.g.*, Ref. 1, Fig. 1, from which 450 nm appears to be a suitable wavelength). The error due to insufficient stability with time of the instrument was minimized by several rapid measurements, alternating between the two samples between which δ_{CD} was to be determined.

Absorbance spectra were recorded with a Cary Model 15 recording spectrophotometer. The differential absorbance measurements were made with a Zeiss PMQ II instrument, the circular dichroism with a Roussel Jouan Dichrograph Model B, and (in the UV) with a Cary 60 OR-CD instrument, and the optical rotation with a Perkin Elmer Servo-polarimeter PE 141, equipped with an He-Ne laser (632.8 nm). The UV-absorbance spectra were recorded using a 0.01 cm cell, the other absorbance measurements and the CD measurements by using 0.5, 1, and 2 cm cells (for CD, also 4 and 5 cm cells were used). The OR measurements were performed in 10 cm cells. All cell-holders were thermostated ($25.00 \pm 0.005^\circ\text{C}$).

The stability constants, β_1 , the actual molar spectroscopic differences and their respective standard deviations (denoted $\pm \sigma$ in the tables) have been computed with a Hewlett Packard desk computer, using a least squares method for a straight line.

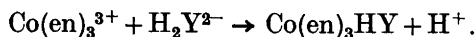
Table 1. Experimental values of δ_A , δ_{CD} , and δ_{OR} , normalised to the dimension of cm^{-1} .

$C_M > C_L$	Absorbance δ_A (cm^{-1}), slit corrected				Circular dichroism $\delta_{CD}(\text{cm}^{-1}) \times (-10^4)$			Optical rotation $\delta_{OR}(\text{deg. cm}^{-1}) \times (-10^4)$		
	C_L (mM)	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00
I (M)	0.100	0.100	0.500	1.000	0.100	0.500	1.000	0.100	0.500	1.000
λ (nm)	265.0	270.0	265.0	265.0	450.0	450.0	450.0	632.8	632.8	632.8
C_M (mM)										
3.00	0.113, 0.120	0.054	0.045	0.021	4.5	1.2	0.49	19	6	2.5, 1.5
6.00	0.184, 0.184	0.089	0.077	0.039	6.7	2.2	1.05	32	8	4.5, 4.0
9.00	0.224, 0.223	0.107	0.103	0.055	7.8	3.1	1.35	38	15	6.0
12.00	0.244, 0.243	0.117	0.126	0.071	9.0	3.8	1.80	41	17	7.0, 7.5
15.00	0.236, 0.227	0.123	0.140	0.083	9.3	4.5	2.17	42	19	8.5
18.00						5.1			20	
24.00						6.0			25	

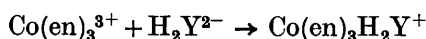
$C_L > C_M$	Absorbance δ_A (cm^{-1}) corrected for absorbance of free L			Circular dichroism $\delta_{CD}(\text{cm}^{-1}) \times (-10^4)$	Optical rotation $\delta_{OR}(\text{deg. cm}^{-1}) \times (-10^4)$
	C_M (mM)	3.00	3.00		
I (M)	0.100	0.500	1.000	0.500	0.500
λ (nm)	265.0	265.0	265.0	450.0	632.8
C_L					
0.40	0.020				
1.00	0.032	0.016			
2.00	0.064	0.026			
3.00	0.094	0.035			
4.00	0.113	0.044	0.019	2.5	8.0
5.00	0.134	0.050	—	—	—
10.00	0.188	0.082	0.041	5.0	19.0
20.00	0.238	0.130	0.075	8.5	33.0
26.00	0.255	—	—	—	—
30.00	—	0.166	0.103	11.1	45.0
40.00		0.190	0.127	13.3	51.0
50.00		0.212	0.149	15.1	59.0
60.00				16.7	66.0
70.00				18.0	71.0

RESULTS

When mixing solutions of $\text{Co(en)}_3(\text{ClO}_4)_3$ and $\text{Na}_2\text{H}_2\text{Y}$ adjusted to identical pH (= 4.5, a pH where approximately all versenate is present as H_2Y^{2-}), and with the same ionic strength, no significant pH change could be detected. An analysis of the accuracy of this determination showed that, e.g., a pH change of at least 2.5 was expected (when considering buffering effect and using a β_1 value from the results below) with a reaction



As the measured difference was less than 0.1, the reaction must be regarded as purely



This is an interesting fact, considering the corresponding reaction between a heavy metal ion and H_2Y^{2-} , which is usually connected with a large pH decrease.

The main results of the spectroscopic measurements are given in Table 1, and partly illustrated in Figs. 1–6. In Fig. 1, a comparison is given between the two results obtained with and without correction by slit value extrapolation—

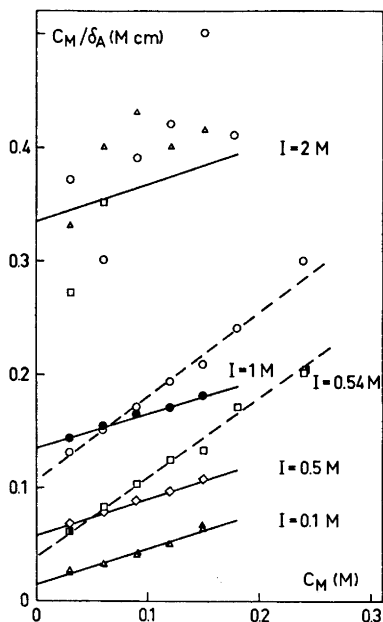


Fig. 1. The function C_M/δ_A at different ionic strengths (0.100, 0.500, 0.542, 1.000, and 2.000 M). — depicts the line obtained when slit value extrapolation is used, - - - without such a correction. δ_A determined at 265 nm. $C_L = 4.00$ mM.

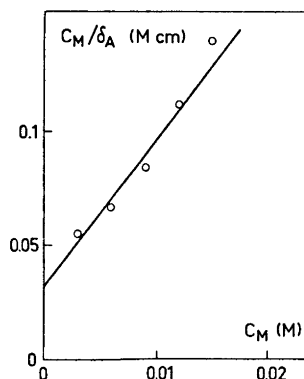


Fig. 2. C_M/δ_A at an ionic strength of 0.100 M and at 270 nm. Slit correction performed. $C_L = 4.00$ mM.

tion (see Experimental). The slopes of the lines C_M/δ versus C_M show a considerably better constancy when using the extrapolated values for δ . The results are generally greatly affected by the correction (except in the $I=0.1$ M case, where the large δ values permitted shorter path-lengths, and therefore a range with low slit values even without performing any extrapolation). It is noteworthy that the error due to slit variation (increasing with C_M) does not appear as a non-linear curve, but gives a new straight line. This may be taken as an instructive warning to those who investigate, *e.g.*, the association between a dye and a polypeptide, using differential absorbance measurements at high absorbances.

For the case of $I=0.1$ M, there appears a slight deviation from linearity (Fig. 1). In Fig. 2, which depicts C_M/δ_A at 270 nm, this deviation is confirmed.

It can be due to the fact that the approximation (2') (or 3') does not hold at lower C_M , either depending on the inequality of C_M and $[M]$, or that the assumption of one complex only is insufficient at this ionic strength. From the result presented in Table 2 it will emerge that the errors in the slopes of the lines (inversely proportional to $x_{ML} - x_M$) are in fact reduced, and the first mentioned explanation is thus satisfactory. This has been further confirmed by using the same C_M range, but a ten times lower C_L (Fig. 3, Table 2).

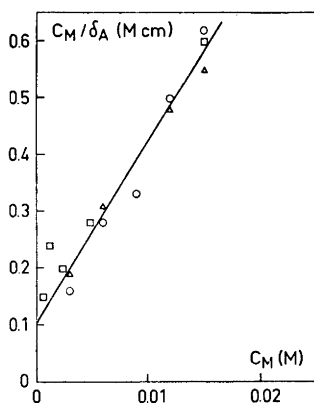


Fig. 3. C_M/δ_A at an ionic strength of 0.100 M. δ_A at 265 nm without slit correction. $C_L=0.400$ mM.

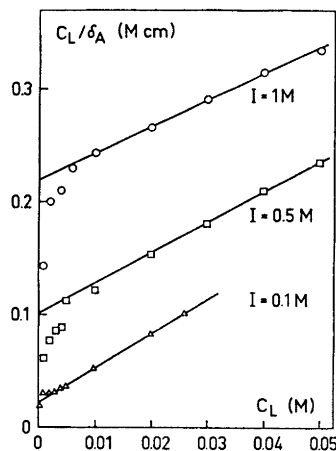


Fig. 4. C_L/δ_A at different ionic strengths (0.100, 0.500, and 1.000 M). δ_A determined at 265 nm. $C_M=3.00$ mM.

Though the measured differences were very small, approximately the same respective values of β_1 and $\epsilon_{ML} - \epsilon_M$ resulted (without slit correction), and there was no longer any marked tendency for the points to form a curved line.

The corresponding absorbance measurements on samples with low constant C_M and high varying C_L are given in Table 1 and Fig. 4. The absorbance data have been corrected for the small absorbance contributions from L. The results are given in Table 2.

Table 2. Computed values of β_1 and $x_{ML} - x_M$ (in parenthesis). Values

Method		$C_M > C_L, C_L = 4.00 \text{ mM}$			
		$I = 0.100 \text{ M}$	$I = 0.100 \text{ M}$ $C_L = 0.400 \text{ mM}$	$I = 0.500 \text{ M}$	$I = 0.542 \text{ M}$
A b s o r b a n c e	$\lambda = 265 \text{ nm}$	220 ± 50	$253 \pm 71 (83 \pm 6)$		$166 \pm 20 (37 \pm 1)$
	$\lambda = 265 \text{ nm}$ slit extrapolated to 0.40 mm	$223 \pm 55 (79 \pm 5)$ $580 \pm 200 (71 \pm 3)$		$56 \pm 3 (77 \pm 3)$ $78 \pm 5 (70 \pm 2)$	
	$\lambda = 270 \text{ nm}$ slit extrapolated to 0.40 mm	$160 \pm 22 (44 \pm 2)$ $320 \pm 30 (40 \pm 1)$			
CD	$\lambda = 490 \text{ nm}$	$157 \pm 106 (-0.32 \pm 0.07)$			
	$\lambda = 430 \text{ nm}$	$119 \pm 47 (-0.17 \pm 0.09)$			
CD difference $\lambda = 450 \text{ nm}$		$180 \pm 17 (-0.322 \pm 0.011)$ $407 \pm 72 (-0.287 \pm 0.009)$		$31.0 \pm 1.1 (-0.355 \pm 0.009)$ $37.5 \pm 1.1 (-0.33 \pm 0.01)$	
OR $\lambda = 632.8 \text{ nm}$		$175 \pm 39 (-15 \pm 1)$ $390 \pm 80 (-13 \pm 1)$		$40 \pm 16 (-13 \pm 3)$ $51 \pm 20 (-12 \pm 3)$	
$\beta_{\text{mean}} (\text{M}^{-1})$		420 ± 50		50 ± 10	

All CD and OR measurements are given in Table 1, and the results in Table 2. Figs. 5 and 6 illustrate the good accuracy when using the differential CD method (see Experimental).

Figs. 9 and 10 show the absorption coefficient and molar circular dichroism spectra of the species M and ML, computed from recorded spectra, using the obtained values of Table 2. The ligand field absorbance band has not been depicted, as ϵ_M and ϵ_{ML} were found identical in this region. In Table 4, some of the data of the spectra are given.

DISCUSSION

A comparison of the stability constant values obtained with the different methods at an ionic strength of 0.1 M (Table 2) does not indicate any method to be the "best". At this ionic strength, the high absorbance differences to be measured make it possible to work also at a wavelength with lower absorption coefficient (270 nm), apparently giving a lower standard deviation. However, the three rather close β_1 values from 265 nm (uncorrected: 220, 223,

in italics correspond to the correction according to eqn. (4) or (4').

		$C_I > C_M$ $C_M = 3.00$ mM, except for CD and OR values		
$I = 1.000$ M	$I = 2.000$ M	$I = 0.100$ M	$I = 0.500$ M	$I = 1.000$ M
78 ± 8 (31 ± 2)		130 ± 12 (110 ± 4) 208 ± 24 (102 ± 3)	26 ± 2 (125 ± 7) 29 ± 3 (122 ± 6)	10.5 ± 0.2 (144 ± 2)
23 ± 2 (81 ± 7) 26 ± 2 (77 ± 5)	10 ± 2			
18 ± 28 (41 ± 40)				
15.4 ± 8 (0.29 ± 0.2) 18 ± 8 (-0.28 ± 0.1)			16.3 ± 0.3 (-0.563 ± 0.004) $C_M = 6.00$ mM	
12 ± 15 (-16 ± 8)			16.6 ± 0.8 (-22.0 ± 0.6) $C_M = 6.00$ mM	
20 ± 5	10 ± 2	210 ± 20	24 ± 5	11 ± 1

and 253 M^{-1} , *i.e.* corrected, eqn. (4'), about 600 M^{-1}) cannot be neglected. A weighted mean of 450 M^{-1} therefore compares rather well with the values obtained from CD differential or OR measurements.

It is remarkable that the β_1 values obtained from absorbance measurements seem to be larger than the corresponding (CD) or (OR) values. Different stability constants from different methods have sometimes been explained by the fact that different measuring techniques (*e.g.* spectroscopic and conductometrical) may show different ranges of sensitivity around the molecule,^{17,21,22} and therefore should account for different degrees of association. However, such arguments are inaccurate, as long as the special molar entities x_M, x_{ML} (=absorptivity, ion conductivity etc.) do not depend of the actual concentration parameters, because a specific excentricity of the method should of course be included in the molar entity. In Fig. 7 are shown the results from measurements of the absorptivity at 265 nm, the molar CD at 490 nm, and the molar OR at 632.8 nm of $\text{Co}(\text{en})_3^{3+}$ at different perchlorate concentrations. The effects of increasing "ionic strength" on the formal molar entities of absorbance, CD and OR, all have the same signs as the corresponding effects

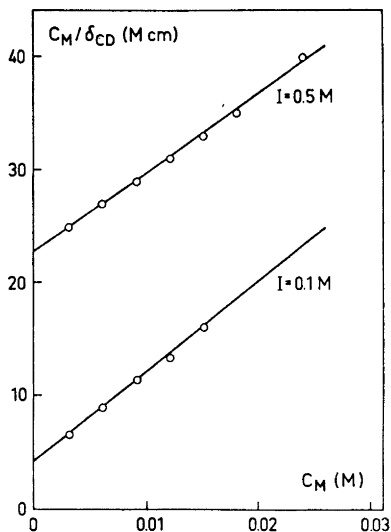


Fig. 5. C_M/δ_{CD} at $I=0.100$ and 0.500 M, $C_L=4.00$ mM. δ_{CD} differentially measured at 450 nm.

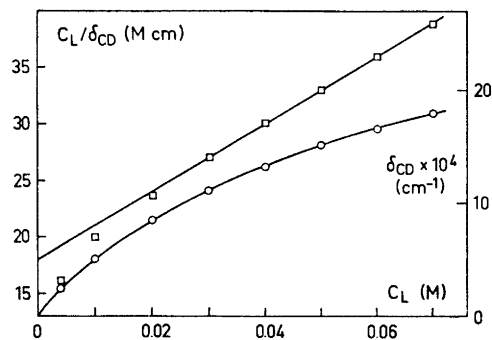


Fig. 6. δ_{CD} (O) at 450 nm, and C_L/δ_{CD} (\square). $I=0.500$ M. $C_M=6.00$ mM.

with increasing C_L . However, in relation to the CD and OR effects, the absorptivity dependence of C_{NaClO_4} appears to be stronger than its dependence of C_L . As the absorptivity at 470 nm is not at all affected by the perchlorate concentration, it is possible that the effect is caused by complex formation with perchlorate. Then it is not impossible that such a competing process,

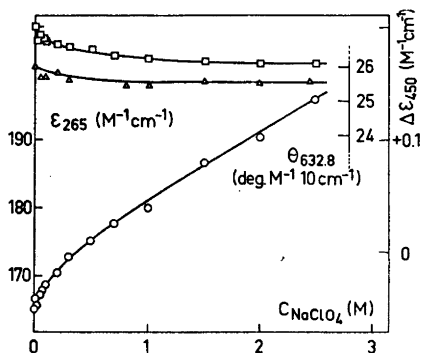


Fig. 7. Dependence of the formal molar entities of absorbance (O), circular dichroism (\square) and optical rotation (\triangle) of $Co(en)_3(ClO_4)_3$ on the $NaClO_4$ concentration (at the wavelengths 265 , 490 , and 632.8 nm, respectively).

neglected in the theoretical treatment, that influences the UV-absorbance only, could cause a difference between the stability constant values obtained from, *e.g.*, absorbance and CD measurements. A corresponding reasoning can also be made from the assumption of a medium effect^{9,23,37} counteracting the OR and CD effects of the M – L association.

The result in Table 2 shows that the stability constant values obtained, using excess of L, are less than half of those obtained with excess of M. As the last mentioned method does not require any one-complex-only condition (it could be assumed that no polynuclear complexes are formed), the values obtained with this method should better account for the stability constant of the first complex, the other values being affected by the formation of two or more complexes. In harmony with this and the lowered " β_1 " with excess of ligand is a corresponding elevation of the obtained difference " $x_{ML} - x_M$ ".

Table 3. β_2 values from absorbance data.

$\varepsilon_{ML} - \varepsilon_M$ ($M^{-1}cm^{-1}$)	$\varepsilon_{ML_2} - \varepsilon_M$ ($M^{-1}cm^{-1}$)	C_L (mM)	C_M (mM)	δ_A (cm^{-1})	I (M)	β_1 (M^{-1})	β_2 (M^{-2})
71	102	10.0	3.00	0.188	0.1	420	2.0×10^4
		26.0	3.00	0.255			2.7×10^4
70	122	30.0	3.00	0.166	0.5	50	6.5×10^2
		40.0	3.00	0.190			6.3×10^2
		50.0	3.00	0.212			6.4×10^2
77	144	40.0	3.00	0.127	1.0	20	1.0×10^2
		50.0	3.00	0.149			1.1×10^2

In Table 3, the β_2 values are given, estimated from the absorbance data with excess of L, the β_1 and $\varepsilon_{ML} - \varepsilon_M$ values with excess of M. With two complexes, the slope of the curve C_L/δ versus C_L should approach $1/C_M(x_{ML_2} - x_M)$,* i.e. the value of " $x_{ML_2} - x_M$ " from the excess of the L method (eqn. (2)) should be, actually, $x_{ML_2} - x_M$. The almost doubled values of " $x_{ML_2} - x_M$ " from this method could thus well fit the theory that with two ligands, the charge transfer transition probability should be doubled. This is, however, based on the assumption of a *superimposed* charge transfer band, arising from the anion association. As will be pointed out below, this is not always the case.

From the observed $\delta_X = X(C_M, C_L) - X(C_M, 0) = (x_{ML} - x_M)[ML] + (x_{ML_2} - x_M)[ML_2]$ at a certain C_L , the equations (1) and $C_M = [M] + [ML] + [ML_2]$ and the estimated β_1 and $(x_{ML_2} - x_M)$ values of $[ML]$ and $[ML_2]$ have been obtained, and $\beta_2 = [ML_2]/[M][L]^2$ computed.**

$$* \lim_{[L] \rightarrow \infty} \frac{d(C_L/\delta)}{d[L]} = \lim_{[L] \rightarrow \infty} \frac{d}{d[L]} \left(\frac{[L] + [ML] + 2[ML_2]}{\beta_1[M][L](x_{ML} - x_M) + \beta_2[M][L]^2(x_{ML_2} - x_M)} \right) =$$

$$= \lim_{[L] \rightarrow \infty} \frac{d}{d[L]} \left(\frac{(1 + \beta_1[L] + \beta_2[L]^2)/C_M + \beta_1 + 2\beta_2[L]}{\beta_1(x_{ML} - x_M) + \beta_2[L](x_{ML_2} - x_M)} \right) = \frac{1}{C_M(x_{ML_2} - x_M)}$$

$$** [ML] = \frac{C_M - \delta/(x_{ML_2} - x_M)}{1 + 1/\beta_1[L] - (x_{ML} - x_M)/(x_{ML_2} - x_M)}$$

First approximation: $[L] = C_L - C_M$

Values of the stepwise association constant, $K_2 = \beta_2/\beta_1$ were about 64, 13, and 5 M^{-1} at ionic strengths of 0.1, 0.5, and 1 M. The corresponding ratios β_1/K_2 were 7, 4, and 4. According to the electrostatic model,^{24,25} with the ion-associate as a result of Coulombic attraction only, $K_2(I=0)$ should be 100 times smaller than β_1 for the ion pair $[\text{Co}(\text{NH}_3)_6]\text{SO}_4^+$. As β_1/K_2 appears to increase with decreasing ionic strength (which is anyhow expected²⁵), at zero ionic strength, 100 seems not to be an unreasonably high value.

An extrapolation of β_1 (Fig. 8) to zero ionic strength gives a value of at least $10^4 M^{-1}$, which may compare rather well with that of Posey and Taube¹⁴ for the sulphate complex (10^3), as they measured with excess of ligand, thus probably obtaining too low a value.

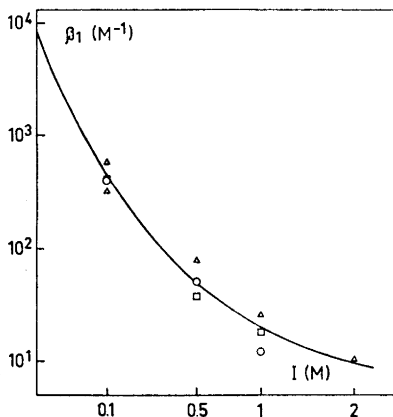


Fig. 8. The β_1 values versus the ionic strength (Δ from absorbance measurements, \square from CD, \circ from OR).

A common conception about the spectral behaviour at an association of outer sphere type is that the visible bands are left unchanged, but there appears a "new" band in the UV, due to charge transfer.⁶ In the typical cases of association between $\text{Co}(\text{en})_3^{3+}$ and thiosulphate, phosphate, or iodide ions, which have suitable high-energy occupied orbitals, an *interionic* charge transfer absorption takes place, connected with the appearance of a corresponding circular dichroism band.^{6,7} As a random orientation should not give rise to any rotational strength, the existence of such a CD band shows that the anion is *stereospecifically* bonded. The accessibility (overlap) of the actual orbitals to charge transfer makes the type of bonding formally close to what is called *covalent* bonding. A suggestion in this direction was first made by Larsson in his work on the outer sphere coordination of cobalt(III) ammine complexes.^{29,28,3}

From Figs. 9 and 10 it appears that there is no interionic charge transfer, as the absorption coefficient (or circular dichroism) spectrum of $\text{Co}(\text{en})_3\text{H}_2\text{Y}^+$ does not show any additional band, when compared with the spectrum of $\text{Co}(\text{en})_3^{3+}$. However, it is remarkable that the absorptivity at the maximum (209 nm) has decreased (though the band has become broader). This means that the anion interferes with the diamine orbitals, either through direct perturbation by its own orbitals, or indirectly *via* steric influence on the positions of diamine molecules.

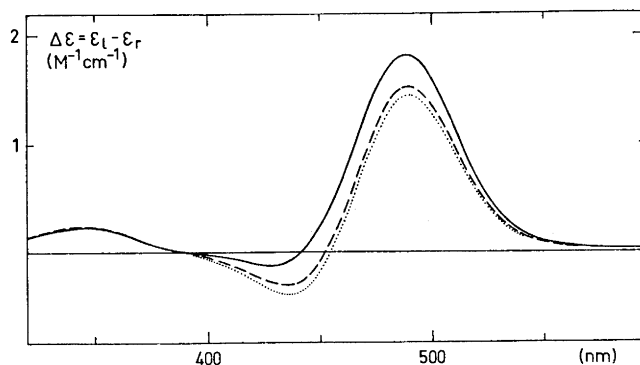


Fig. 9. Calculated molar circular dichroism spectra of Co(en)_3^{3+} (—), and of $\text{Co(en)}_3\text{H}_2\text{Y}^+$ (---, ML_I , ···, ML_{II} ; see Discussion) of the ligand field bands.

In contrast to current work in this field^{30,31,27} we have not only found one negative CD band of (+) Co(en)_3^{3+} , corresponding to the UV absorption, but also a smaller positive band at shorter wavelengths (Fig. 10). Also, the

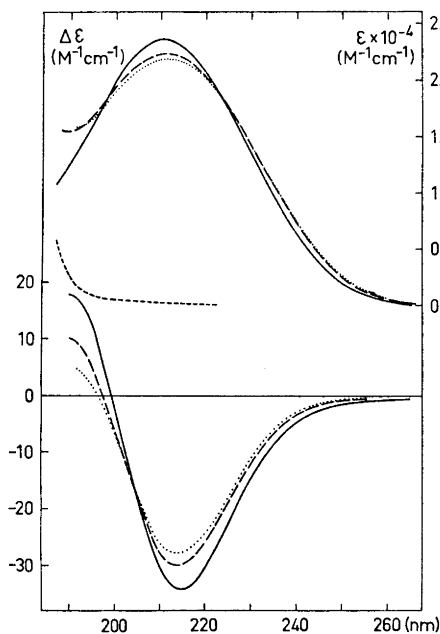


Fig. 10. Calculated absorbance (above) and molar circular dichroism (below) spectra in the UV of Co(en)_3^{3+} (—), and $\text{Co(en)}_3\text{H}_2\text{Y}^+$ (---, ML_I , ···, ML_{II} ; see Discussion), and of free H_2Y^{2-} (---).

absorbance of the CT band does not agree with that reported by Mason³⁰ ($15 \times 10^3 \text{ M}^{-1} \text{ m}^{-1}$), which in part may be due to the fact that different concentrations may have been used (cf. Fig. 7).

The broadening of the absorption band may be regarded as an effect of a splitting into two or more bands, due to a lowered symmetry in the associate. At about 230 nm, there appears in fact a diffuse shoulder. This can, of course, also be the effect of an interionic charge transfer (*cf.* the positive CT CD band of (+)Co(en)₃ phosphate⁶).

Due to the low accuracy in β_2 , it has not been considered relevant to estimate any ϵ_{ML} , or $\Delta\epsilon_{ML}$, spectra. However, from the recorded spectra of solutions containing high excess of L, ϵ_{ML} and $\Delta\epsilon_{ML}$ spectra have been calculated, using the " β_1 " obtained with excess of L. These spectra ($\epsilon_{ML(II)}$, $\Delta\epsilon_{ML(II)}$, see Table 4) should then in comparison with the first obtained ones

Table 4. Absorption coefficients (ϵ) and molar circular dichroisms ($\Delta\epsilon$) of (+)Co(en)₃³⁺ (=M) and Co(en)₃H₂Y⁺ (=ML) at the band maxima. For ML_I and ML_{II}, see Discussion. I and II represent the cases, 3.00 mM M, 4.00 mM L, $I=0.030$ M, $\beta_1=1.4 \times 10^3$ M⁻¹ (from Fig. 8) and 3.00 mM M, 26.00 mM L, $I=0.096$ M, " β_1 " = 2.2×10^2 M⁻¹, respectively.

Band/assignment	λ_{max} (nm)	x_M	$x_{ML(I)}$	$x_{ML(II)}$	$x =$	$(x_{ML(I)} - x_M) / (x_{ML(II)} - x_M)$
A_2	428	-0.13				0.66
	435		-0.30	-0.39	$\Delta\epsilon$	
	488	+1.83				
LF band	E_a		+1.53	+1.45	(M ⁻¹ cm ⁻¹)	0.81
	$A_2 + E_a$	469	87	87	ϵ (M ⁻¹ cm ⁻¹)	
CT band	A_2	190?	+18		$\Delta\epsilon$	0.69
	$E(T_{1u})$	212		-29.8		
		214	-34.5			
$A_3 + 2E$	209	2.37	2.24	2.19	ϵ (M ⁻¹ cm ⁻¹)	0.71
	235?	0.96	1.05	1.07	$\times 10^{-4}$	

$\epsilon_{ML(I)}$, $\Delta\epsilon_{ML(I)}$) account for stronger spectral differences between ML and ML₂. However, the ratio $(\epsilon_{ML(I)} - \epsilon_M) / (\epsilon_{ML(II)} - \epsilon_M)$ (or the corresponding CD ratio), the change of which should indicate a dissimilarity between the spectra, only exhibits small variations. These might as well be caused by the large medium difference, as by the presence of a second associate.

However, both the values of $\Delta\epsilon_{ML} - \Delta\epsilon_M$ with/without excess of L (Table 2), and the result of comparing $\Delta\epsilon_{ML(I)}$ with $\Delta\epsilon_{ML(II)}$ (Figs. 9 and 10) show that the circular dichroism effect due to the association of one H₂Y²⁻ is not counteracted, but rather reinforced, at a further association. This is interesting, in view of the statement of Larsson^{3,4} that an odd and an even number of anions in the complex should induce converse changes in the rotational strengths.

But let us return to the charge-transfer band at 209 nm (Fig. 10, Table 4). As the circular dichroism of a crystal, 2[(+)Co(en)₃Cl₃]NaCl·6H₂O,³⁴ has been found to increase when the (UV) radiation is propagated along the optic axis (\equiv the C_3 axis), the CT transition (negative CD) has been assigned E sym-

metry^{31,32} The coupling of charge-transfer excitations in the ligands (en)^{33,32} gives rise to four transitions, one with $A_1(T_{2u})$, another with $A_2(T_{1u})$ and two with $E(T_{1u}, T_{2u})$ symmetry (with respective parentages in parentheses). The A_1 transition is forbidden, and the $E(T_{2u})$ transition has only magnetic moment. As the negative CD band (214 nm) is thus due to the $E(T_{1u})$ transition, the positive band at shorter wavelength (190 nm) must be assigned $A_2(T_{1u})$.

According to coupled oscillator theory,³⁵ the corresponding rotational strengths should be related by $R_{A_2(T_{1u})} = -R_{E(T_{1u})} = (4/\sqrt{3})\pi\nu r D$, where ν is the transition frequency, r is the distance between the metal ion and the ligand atom, and D is the dipole strength of each of the six contributing excitations at the ligand atoms. The decrease in rotational strength of both the transitions (Fig. 10) at the association of H_2Y^{2-} may thus suggest either a diminished D or a diminished Co-N distance.

Without closer knowledge of the *absolute* values of the rotational strengths of the transitions (*cf.*, *e.g.*, Ref. 2) it is, however, impossible to draw any selective conclusions. The change (Fig. 10) in the absorption band area (giving the total dipole-strength)³⁶ appears to be small compared with the corresponding change in the band area in CD (giving the rotational strength),³⁶ but as the observed CD bands are probably small rudiments from large rotational components, cancelling each other to a high extent, the relative rotational strength change may be small too, thus being totally explained by the change in dipole-strength.

This investigation gives, besides data on the remarkable association between $Co(en)_3^{3+}$ and EDTA, some information concerning the errors involved in a determination of the stability constant of an outer-sphere complex when using different methods and approximations. It is suggested that UV-absorbance or circular dichroism data, obtained from solutions containing excess of metal, preventing the formation of a second complex, should be used. When approximations in the equilibrium expression are used, these should be carefully controlled.

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