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Induced Optical Activity in $Co(NH_3)_6^{3+}$ by Outer-sphere Association with Chiral Anions

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The formation of outer-sphere 1:1 complexes $[Co(NH_3)_6^{3+}]L$ has been studied with the optically active divalent anions, L = (*R*)-tartrate (I), (*S*)-glutamate (II), (+)camphorate (III) and the monovalent anions, L = (+)10-camphorsulphonate (IV), (*S*)-leucinate (V), (*S*)-alaninate (VI), (*S*)-prolinate (VII), (*S*)-lactate (VIII), (*S*)-mandelate (IX). The stability constants for the complexes were determined at 25.0°C in 0.1 M $NaClO_4$ by UV spectrophotometry:[1]

$\beta_1(M^{-1}) =$

20.3 ± 1.5	(I)	4.0 ± 0.3	(V)
16.1 ± 1.6	(II)	5.4 ± 0.4	(VI)
11.9 ± 1.3	(III)	4.5 ± 0.3	(VII)
[14.6	(IV)]	5.2 ± 0.6	(VIII)
		6.1 ± 0.7	(IX)

In all these complexes optical activity is induced in the magnetic dipole allowed $d-d$-transition ${}^1A_{1g} \rightarrow {}^1T_{1g}$. Only one circular dichroism band was observed but as it appears at a wavelength (480 – 484 nm) slightly shifted from that of the absorption maximum (476 nm) an oppositely directed weak component at shorter wavelength is presumably present. The molar circular dichroism peak values for the complexes were calculated using the above stability constants:

$\Delta\varepsilon_{ML}(M^{-1}\ cm^{-1}) \times 10^2 =$

−1.57	(I)	−0.47	(V)
−0.30	(II)	−0.23	(VI)
−0.09	(III)	−0.41	(VII)
−0.61	(IV)	−0.39	(VIII)
		+0.62	(IX)

For the ${}^1A_{1g} \rightarrow {}^1T_{2g}$ transition, without magnetic moment, no significant circular dichroism was observed ($|\Delta\varepsilon| < 10^{-4}\ M^{-1}\ cm^{-1}$).

The circular dichroism is explained by a chelatic fixation of the outer-sphere ligand to two adjacent ammonia molecules by hydrogen bonding.

In previous papers,[1] it was concluded that a negative circular dichroism (CD) band could be associated with the formation of a 1:1 outer-sphere complex $[Co(NH_3)_6]$ (*R*)-tartrate$^+$, at the wavelength of the $d-d$ transition ${}^1A_{1g} \rightarrow {}^1T_{1g}$. Attempts to use other chiral ligands were also made but it was not then possible either to detect any definite effects or to relate them to any defined complex. Later, a more sensitive CD spectrophotometer has become available and the interference of strong competitive complex formation became obvious, when using perchlorate as an ionic medium, so it was considered worthwhile to make a new attempt, *e.g.* by using the sensitive CD instrument to study the very weak resulting CD at a high constant ionic strength.

The present expansion of the earlier study has been made to examine the validity of the earlier suggestion that the CD was conformationally induced by a type of chelate ring (adjacent ammonia molecules joined by hydrogen bonding *via* the bidentate anion). It should also be very pertinent to try to find a correlation, in a series of such outer-sphere complexes, between the chirality and structure of the ligand and the sign and the magnitude of the induced CD.

The chosen ligands have been mono- and divalent anions derived from amino and hydroxy acids with different complexing capabilities, and with similar chirality with respect to an asymmetric carbon atom (*cf.* footnote of Table 1). Further, two derivatives of camphor with more rigid structures have been studied.

METHOD

Stability constants were obtained by the spectrophotometric method described in earlier

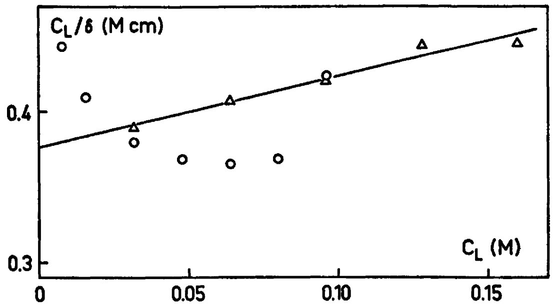

Fig. 1. Typical result indicating interference with perchlorate. L(+)lactate⁻, ○ $I=0.14$ M, $\beta_1=\pm 0$ M^{-1}; △ $I=0.20$ M, $\beta_1=1.2$ M^{-1}. The result can be interpreted by a serious perchlorate ion complexation. The stability constant for the complex $[Co(NH_3)_6]ClO_4^{2+}$ should be $1-10$ M^{-1}, with a β_1 of about 5 M^{-1} for the lactate complex.

papers[1] and the notation from there will be used also here.

At a first attempt to keep a constant "ionic strength",

$$I=6C_M+0.5(|z|^2+|z|)[L^z]+[NaClO_4],$$

deviations were obtained, which could be explained by a competitive outer-sphere complex formation with perchlorate ions.* Fig. 1 thus indicates the unreliability of using a low formal ionic strength; *e.g.* with $I=0.14$ M no reasonable result was obtained. The use of much higher ionic strengths was not possible due to precipitation of $Co(NH_3)_6(ClO_4)_3$ and to a lower accuracy in the absorbance differences as a result of the quenched complexation.

By compromising, using a low constant perchlorate concentration, we have obtained stability constants which fulfil our demands. Thus, though the absolute accuracy can be discussed of a stability constant obtained with 0.1 M $NaClO_4$ as a medium buffer, due to considerable activity coefficient variations, the reexamination in this medium of the complex formation with tartrate gave a result which was in acceptable agreement with the earlier values.[1]

On the basis of an assumed analogy between the case of tartrate, where only the 1:1 complex is of any importance, the investigation was made with a fixed C_M, $C_M \ll C_L$. This restriction was moreover necessary as with $C_M > C_L$ the δ values obtained were of a questionably low precision and the variations of the activity coefficients more serious.

From the determined β_1 values and measured CD, on a few solutions with different concentrations of ML, molar circular dichroism coefficients were calculated.

EXPERIMENTAL

Chemicals. Analytical grade chemicals were used, when available. (The lactic acid and the 10-camphor sulphonic acid were of *puriss.* quality.) The ligand stock-solutions were prepared by adding one or two equivalents of sodium hydroxide to the commercial acids. The $Co(NH_3)_6Cl_3$ (preparation in Ref. 3) was not transformed into the perchlorate salt. This was found unsuitable due to a low solubility of the perchlorate leading to difficulties with the stock-solutions. It was also considered unnecessary, in the light of the discussion on the perchlorate ion as a potent ligand,[2] especially as the complex salt was used in a low and constant concentration in all solutions.

Absorbance measurements. (Notation, see Ref. 1). Solutions with the composition $C_M=6.00$ mM $Co(NH_3)_6Cl_3$, C_L ligand and 0.100 M $NaClO_4$ were prepared and measured within 0.5 h after mixing in a Zeiss PMQII spectrophotometer at 260 nm (273 nm with mandelate), using (when possible) 1, 0.5, and 0.2 cm pathlengths. Mean absorbances, A (normalized to cm^{-1}) were calculated and the difference formed:

$$\delta=A(C_M,\ C_L,\ 0.1\ \mathrm{M\ NaClO_4})-A(C_M,\ C_L=0,\ 0.1\ \mathrm{M\ NaClO_4})-A(C_M=0,\ C_L)$$

The function C_L/δ was plotted *versus* C_L and from the straight line obtained the stability constant was computed, using a least-squares programme, as

$$\beta_1=(\text{slope})/[\text{intercept}-1/(\varepsilon_{ML}-\varepsilon_M)] \text{ and}$$

$$(\varepsilon_{ML}-\varepsilon_M)=1/C_M\times(\text{slope}) \qquad (2)$$

The solutions were tested for Co(II),[3] and it

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* A recent report has focussed interest on the possibilities in different connections for the perchlorate ion to act as a ligand.[2]

was checked that the absorbance maximum at 476 nm had neither shifted nor decreased the day after the measurements. Absorption spectra were recorded on a Hitachi EPS 3T spectrophotometer.

CD measurements. The instrument used was the JASCO model of 1973 ("J – 40"). A slit programme for 8 nm spectral band width was used, 5 cm cells, time-constant: 4 s, and a recording speed of 0.17 nm/s. A few solutions, with $C_M = 6.00$ mM and C_L between 80 and 200 mM, were recorded in the range 300 – 600 nm. The spectrum obtained for water was used as a baseline, but it was also checked that no important "absoption artefact" was obtained with a solution, $C_L = 0$, $C_M = 6$ mM. The molar circular dichroism was calculated from the observed CD (cm^{-1}) by

$$\Delta\varepsilon = \mathrm{CD}(1+\beta_1 C_L)/C_L C_M \beta_1 \qquad (3)$$

RESULTS

The experimental results of the stability study are represented by the C_L/δ values in Figs. 2 – 4; the computed constants are found in Table 1. With respect to the low ionic strength and in comparison with other outer-sphere complexes,[1-3] the majority of the complexes must be considered weak.

Tests with varying $C_M > C_L$ which were performed with prolinate indicated that the 1:2 outer-sphere complexes were most probably not formed to any significant extent. This was as expected at the present low ionic strength.[1] Also the good agreement between the $\Delta\varepsilon$ values shown in Table 2, obtained from opposite limits of the ligand concentration interval, strongly supports the assumption of the absence of higher complexes.

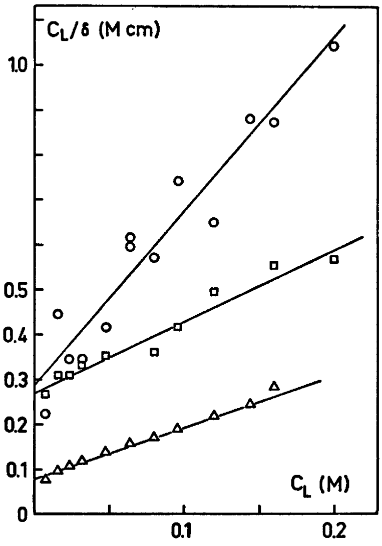

Fig. 2. C_L/δ plotted *versus* C_L for solutions M, L, for determination of β_1 (ML). L = ○ (+)-10-camphorsulphonate, □ (*S*)-mandelate, △ (*S*)-glutaminate.

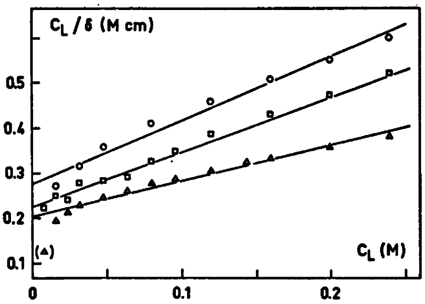

Fig. 3. L = ○ (*S*)-lactate, □ (*S*)-alaninate, △ (*S*)-leucinate.

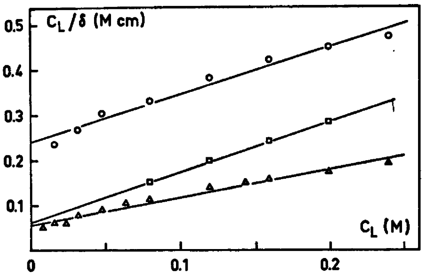

Fig. 4. L = ○ (*S*)-prolinate, □(*R*)-tartrate, △ camphorate.

After having ruled out other more trivial effects, such as CD due to complexation with contaminating species [Co(II), $Co(NH_3)_5L$ by quantitative analysis and from careful inspection of the absorption spectrum in the ligand field range[1]] the calculated molar circular dichroisms could thus be connected with a series of 1:1 outer-sphere complexes. The recorded CD spectra did not at any wavelength show deviation from a linear dependence on the concentration of the outer-sphere complex. Furthermore, the lineshapes $|\Delta\varepsilon(\lambda)|$ appeared very similar and were almost symmetric (Fig. 5) with peaks at about 480 nm. The small shift compared with the position of the absorption

Table 1. Determined stability constants, β_1, for the outer-sphere complexes $[Co(NH_3)_6]L^{+ \text{ or } 2+}$ in 0.1 M $NaClO_4$ at 25.0°C. For comparison, literature values on stability constants ($\beta_{1,i}$) for certain inner-sphere complexes (aqueous solution) [7] have been tabulated. * = at 273 nm.

	H_nL	L^a	$\varepsilon_{ML} - \varepsilon_M$ at 260 nm (M^{-1} cm^{-1})	β_1 (M^{-1})	M, log $\beta_{1,i}$
I	HOOC–CH(OH)–CH(OH)COOH	(R)-tartrate^{2-}	149 ± 2	20.3 ± 1.5	Co^{2+}, 3
II	HOOC–$CH(NH_2)(CH_2)_2COOH$	(S)-glutamate^{2-}	146 ± 4	16.1 ± 1.6	Ni^{2+}, 5.2; Co^{2+}, 5
III	HOOC–$(C_8H_{14})COOH$	(+)-camphorate^{2-}	269 ± 12	11.9 ± 1.3	–
IV	$O=(C_9H_{13})CH_2SO_3H$	(+)-10-camphor-sulphonate$^-$	43 ± 4	14.6 ± 1.5	–
V	$(CH_3)_2CHCH_2CH(NH_2)COOH$	(S)-leucinate$^-$	211 ± 11	4.0 ± 0.3	Ni^{2+}, 5.6; Co^{2+}, 5
VI	$CH_3CH(NH_2)COOH$	(S)-alaninate$^-$	141 ± 7	5.4 ± 0.4	Ni^{2+}, 6.0; Co^{2+}, 5
VII	$C_4H_7NHCOOH$	(S)-prolinate$^-$	158 ± 11	4.5 ± 0.3	Cu^{2+}, 9
VIII	$CH_3CH(OH)COOH$	(S)-lactate$^-$	119 ± 7	5.2 ± 0.6	Co^{2+}, 3
IX	$C_6H_5CH(OH)COOH$	(S)-mandelate$^-$	618 ± 27*	6.1 ± 0.7	Co^{2+}, 3

[a] For the α-amino acids and α-hydroxy acids the absolute configuration S corresponds to L; for tartaric acid, R corresponds to L, according to the notation of Cahn, Ingold and Prelog.[9]

Table 2. Molar circular dichroism peak values for the outer-sphere complexes $[Co(NH_3)_6]L = ML$ ($C_M = 6.00$ mM). [ML] calculated by means of eqn. (3).

L	C_L (mM)	$-CD \times 10^4$ (cm^{-1})	CD peak (nm)	$-\Delta\varepsilon_{ML} \times 10^2$ ($M^{-1}cm^{-1}$)	mean
I	80.0	0.575	480	1.55	1.57
	200.0	0.758		1.58	
II	80.0	0.102	482	0.30	0.30
	200.0	0.137		0.30	
III	80.0	0.023	482	0.08	0.09
	200.0	0.039		0.09	
IV	80.0	0.167	483	0.52	0.61
	200.0	0.312		0.70	
V	80.0	0.068	483	0.47	0.47
	200.0	0.126		0.47	
VI	80.0	0.039	480	0.21	0.23
	200.0	0.078		0.25	
VII	80.0	0.065	484	0.41	0.41
	200.0	0.114		0.40	
VIII	80.0	0.061	482	0.35	0.39
	200.0	0.133		0.43	
IX	80.0	−0.116		−0.59	
	160.0	−0.191	480	−0.64	−0.62
	200.0	−0.212		−0.64	

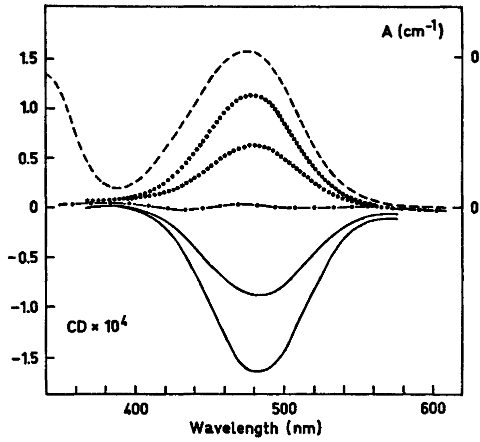

Fig. 5. Some typical recorded spectra ($C_M = 0.006$ M), – – – absorption (1 cm cell, $C_L = 0.080$ M), circular dichroism (5 cm cell, $C_L = 0.080$ and 0.200 M) ··· L = (S)-mandelate, —— L = (+)-10-camphorsulphonate.

maximum can indicate (though not prove) [4] the existence of a band with opposite sign at shorter wavelength.

It can be observed that the magnitude of the molar circular dichroisms are of about the same order as those of $[Co(NH_3)_5L\text{-amino acid}]^{2+}$ complexes for which also negative signs have been reported, except for the complex with prolinate.[5]

After a correction for the CD of the ligand no significant CD (less than 10^{-4} M^{-1} cm^{-1}) remained to be associated with the magnetic-dipole forbidden $A_{1g} \rightarrow T_{2g}$ at 340 nm.

DISCUSSION

As expected the strongest complexes are obtained with the divalent anions. The somewhat lower β_1 value for camphorate compared with glutamate is expected, due to a steric hindrance leading to difficulty of coordination with both carboxylate groups. For tartrate the considerably higher value might be referred to a possibility of using the $-$OH groups as well, but can also be explained by this anion being more strongly hydrated.[6]

The high stability constant obtained for the 10-camphorsulphonate complex may probably be considerably in error due to the small difference between ε_M and ε_{ML}. This is also suggested by the large difference between the two estimated molar circular dichroisms (Table 2). From a comparison with the stabilities of the other complexes a β_1 even as low as 5 M^{-1} may be expected, which would also yield more consistent molar circular dichroisms (-0.97×10^{-2} and -1.04×10^{-2} M^{-1} cm^{-1} instead of -0.52×10^{-2} and -0.70×10^{-2} M^{-1} cm^{-1}).

Literature values for some inner-sphere complexes have been included in Table 1. It can be seen that the larger β_1 for glutamate is not due to a coordinating amino group but to the second carboxylate group and the larger negative charge, as leucinate, alaninate and prolinate give much lower constants. The latter are even lower than those for the lactate and mandelate complexes, which, by comparison with corresponding inner-sphere constants, gives evidence for the prevalence of hydrogen bonding or electrostatic bonding in the outer sphere.

With tartrate a lower β_1 should be expected than that from an earlier determination (30 ± 1 M^{-1}) [1] as in average a higher ionic strength range has been used in the present study. Actually a reduction with almost 50 % could be estimated from the dependence on the ionic strength ($NaClO_4$).[1] In view of a certain increase in the yielded β_1, due to the perchlorate ion concentration constancy, the obtained value therefore seems quite reasonable.

In general it is very difficult to correlate a CD effect with a certain molecular structure or even with one of two enantiomeric alternatives, on a purely theoretical basis. Even semi-empirical predictions often hold only within a series of strongly related homologues. As no quantitative data of circularly dichroic outer-sphere complexes have been reported before, the material seems too limited to provide any empirical rules. In other words, as we do not know for certain how the ligands coordinate or how the optical activity is transmitted into the centre of the metal complex, we are in principle incapable of presenting even a qualitative discussion on the sign of the CD. We therefore establish only the "correlation" here * that, with the exception of mandelate, the studied α-amino and α-hydroxy acids (tartrate not included), with the same absolute configurations (*S*) with respect to the moieties $CH(NH_2)COO$ and $CH(OH)COO$, display negative virtually single CD bands positioned in very close connection to the $d-d$ transition ${}^1A_{1g} \rightarrow {}^1T_{1g}$.

The present investigation extends the earlier study of the $[Co(NH_3)_6](R)$-tartrate$^+$ complex, and gives evidence for the existence of 1:1 outer-sphere complexes with a series of other chiral ligands. It further supports the theory of a chelatic bonding correlated to a large stability constant and a strong induced optical activity in the Co(III) magnetic-dipole $d-d$ transition.

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* By assuming that the outer-sphere complexes are well-defined chelates, however, we have found evidence for a tentative correlation between the CD and the positions of the coordinating groups, by means of a regional rule.[8]