

## Circular Dichroism of Co(II) and Ni(II) Complexes with (-)-Mandelate Ions in Aqueous Solution

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Circular dichroism and absorption spectra have been recorded for cobalt and nickel (-)-mandelate solutions in the visible spectral region. From these recordings it was only possible to calculate the spectra of the various complexes for the cobalt system, which have been used for a discussion of the degree of chelation in the complexes. It is suggested that the second cobalt complex is probably chelated, but that the first and third complex are non-chelated or chelated *via* a water molecule. For the nickel system, a detailed analysis could not be made, but it was considered probable that the constitutions of the two systems are alike.

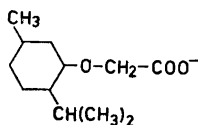
The question of to what degree a ligand molecule, possessing the ability to form chelates with a metal ion, actually does so in solution is a difficult one. In want of the ultimate mean of characterizing the species present in solution — X-ray interference measurements — indirect evidence, such as the comparison of relative magnitudes of the formation constants, or spectroscopic observations, must be used.

The former method<sup>1</sup> has the disadvantage that the formation constants are dependent on the charges of the complexes in ways hard to predict. This holds especially when a high ionic strength is maintained with a neutral electrolyte, which is a necessity if information about all the complexes, and not only about the first one, ML, is to be obtained. Then the formation constants  $K_n$  are determined as concentration constants and, consequently, the dependence of the activity coefficients of the complexes on the charges of these species is included in the ratio  $K_n/K_{n+1}$ . Only for very similar systems one can infer something about the existence of chelates, the ratios  $K_n/K_{n+1}$  being significantly greater if chelate formation occurs than if this is not the case.

On the other hand, spectroscopic techniques, such as infrared absorption measurements<sup>2</sup> or chemical shifts of NMR,<sup>3</sup> require favourable conditions such as rather high solubility of the complexes.

Thus in the present case — the investigation of the mandelate complexes of Co(II) and Ni(II) — the low solubility rules out these methods. However, the optical activity of the mandelate ligand offers a possibility of studying the problem of chelation. It has been proposed<sup>4</sup> that the induction of a rotational strength to the  $d-d$  electronic transitions of a transition metal complex by an optically active ligand can occur only if this ligand is chelated and sufficiently puckered so that one of the possible conformations of the chelate ring should be stabilized. The asymmetric unit is thus regarded to be the metal ion-ligand ring, with one of the enantiomeric conformations represented in larger amounts than the other. This hypothesis must be considered to be empirical, but is supported by the molecular orbital description of rotational strengths of transition metal complexes,<sup>5</sup> as the misalignment of metal orbitals basic to this theory may be caused by the asymmetry of the ring reasonably well. Also, the modified coupled oscillator theory of Mason<sup>6</sup> is consistent with the above-mentioned hypothesis, as this theory certainly demands a fixed geometry of the components of the complex.

It must be mentioned that some exceptions from the rule of Larsen and Olsen<sup>4</sup> have been reported. It seems to us that these are apparent exceptions rather than real ones, however, especially if one expands the concept of chelate to include also interactions of one (or both<sup>7</sup>) of the two donating atoms of the ligand with the metal atom *via* some kind of a second-sphere coordination (*cf.* Ref. 5, p. 3715). Thus, the often quoted results of Bhatnagar and Kirschner<sup>8</sup> on  $\text{Co}(\text{NH}_3)_5(+)$  tartrate and by Fujita *et al.*<sup>9</sup> on  $\text{Co}(\text{NH}_3)_5((-)$ aminoacid) complexes may probably be explained as indicative of the existence of inner-outer-sphere chelates. Similarly, the results of Kirschner and Pearson<sup>10</sup> on the complex  $[\text{Co}(\text{NH}_3)_5(-)$  menac] $^{2+}$ , where "menac" means menthoxyacetate,



can possibly be accounted for by postulating a hydrogen bond from an ammonia ligand to the ether oxygen. A still more intriguing case is presented by Bosnich,<sup>11</sup> reporting circular dichroism for, *e.g.*, *trans*  $[\text{PdCl}_4(-)$  am<sub>2</sub>], where "am" means 1-phenylethylamine. However, as an interaction of the phenyl group with the very "soft"<sup>12</sup> palladium metal ion is possible, it is also possible in this case that a weak outer-sphere type of chelation is present.

In view of the thus accumulating evidence<sup>7-11</sup> one can probably not hold the view anymore that only inner-sphere chelates of optically active ligands confer a rotational strength to the  $d-d$  transitions of transition metal complexes. Inner-outer-sphere chelates have this ability also. All in all, an investigation on the circular dichroism of the  $(-)$ -mandelate complex systems of Co(II) and Ni(II), previously<sup>13</sup> shown to consist of three consecutive complexes seemed well worth its while in order to provide some information on the problem of the constitution and the degree of chelation of these complexes.

## NOTATIONS AND METHOD OF CALCULATION

In the following CD will mean the circular dichroism observed for a given solution of the composition ( $C_M, C_L$ ) and the cell thickness  $b$  cm, and  $\Delta\varepsilon$  will stand for the formal molar circular dichroism. It then holds that

$$\Delta\varepsilon = \text{CD}/bC_M \quad (1)$$

or as CD is the sum of the contributions from the three complexes known to exist from an earlier investigation,<sup>13</sup>

$$\Delta\varepsilon = \frac{\sum_{n=1}^3 \Delta\varepsilon_n \beta_n [\text{L}]^n}{\sum_{n=0}^3 \beta_n [\text{L}]^n} \quad (2)$$

where  $\Delta\varepsilon_n = (\varepsilon_l - \varepsilon_r)_n$  is the molar circular dichroism coefficient for the complex  $\text{ML}_n$ . As  $\Delta\varepsilon$  is a function of  $[\text{L}]$  only, provided that no polynuclear complexes are formed, measurements of  $\Delta\varepsilon$  can be used to determine the stability constants, if the quantities concerned can be determined with sufficient accuracy. Furthermore, if  $\Delta\varepsilon$  is found to be dependent on  $C_M$ , the existence of polynuclear complexes can be inferred. Eqn. (2) can be rewritten in the form

$$\Delta\varepsilon = \sum_{n=1}^3 \alpha_n \Delta\varepsilon_n \quad (3)$$

where  $\alpha_n$  is the fraction  $[\text{ML}_n]/C_M$ .

From these formulae and a knowledge of the stability constants, it is then possible to determine  $\Delta\varepsilon_n$  from a set of ( $\Delta\varepsilon, C_L$ ) pairs.

In the calculation of  $\Delta\varepsilon_n$  eqn. (3) is used.

By forming the expression

$$\Delta\varepsilon/\alpha_1 \quad (4)$$

it is evident that

$$\lim_{[\text{L}] \rightarrow 0} \frac{\Delta\varepsilon}{\alpha_1} = \Delta\varepsilon_1 \quad (5)$$

The expression  $(\Delta\varepsilon/\alpha_1) - \Delta\varepsilon_1$  can then be formed, and one gets

$$\frac{(\Delta\varepsilon/\alpha_1) - \Delta\varepsilon_1}{[\text{L}]} = \Delta\varepsilon_2 \frac{\beta_2}{\beta_1} + \Delta\varepsilon_3 \frac{\beta_3}{\beta_1} [\text{L}] \quad (6)$$

By plotting this quantity against  $[\text{L}]$ , one gets  $\Delta\varepsilon_2$  from the intercept and  $\Delta\varepsilon_3$  from the slope of the straight line. This procedure has been repeated for different wavelengths in the region, where the circular dichroism was measured, and in this way it was possible to get CD spectra of the various complexes.

Absorption spectra, have also been derived for the various complexes, in the same way as described above, from the formulae:

$$\varepsilon = A/bC_M \quad (7)$$

analogous to eqn. (1), and

$$\varepsilon = \sum_{n=0}^3 \alpha_n \varepsilon_n \quad (8)$$

analogous to eqn. (3). In these formulae,  $A$  will mean the absorbance,  $\varepsilon$  the formal molar absorptivity and  $\varepsilon_n$  the molar absorptivity of the complex  $ML_n$ . It must also be pointed out that the summation in eqn. (8) must begin with  $n=0$ , as the absorption of the free metal ion is not negligible.

### EXPERIMENTAL

Chemicals and solutions used in this investigation are identical with those used in earlier works.<sup>13,14</sup> The circular dichroism was measured with a Roussel-Jouan Dichrograph at 20°C using 4 cm cells. The sensitivity of the dichrograph was such that 1 mm recorder deflection corresponded to a circular dichroism of  $1.5 \times 10^{-4}$ . The absorption spectra were obtained with a Beckman Recording Spectrophotometer, Model DK 1. These measurements were also performed at 20°C and using 4 cm cells. In both the CD and the absorption measurements all solutions were carefully checked for any presence of turbidity before and after performing the measurements.

### MEASUREMENTS AND RESULTS

*The cobalt system.* Preliminary measurements of CD for cobalt mandelate solutions of various compositions showed that appreciable instrument recorder deflections were obtained in the spectral region corresponding to the absorption of octahedral Co(II) complexes. A series of CD spectra could consequently

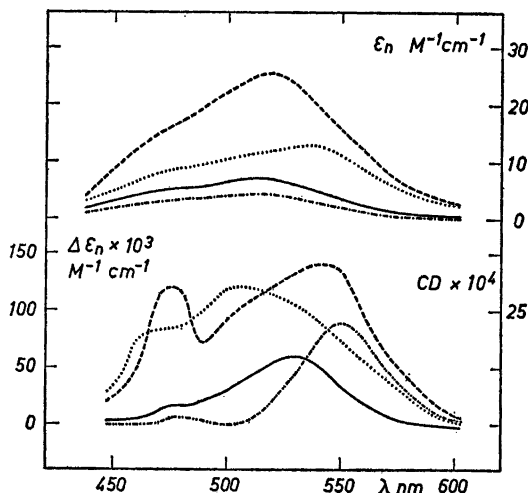


Fig. 1. The calculated circular dichroism (lower curves) and absorption spectra (upper curves) of the cobalt mandelate complexes; (-----)  $n=0$ , (—)  $n=1$ , (---)  $n=2$ , and (···)  $n=3$ . The curve (-·-·-) represents the circular dichroism of the solid  $\text{Co(mandelate)}_2$  in KBr suspension. The concentration is 2.07 mg/300 mg KBr. As the CD spectra of the solid phase did not fit the equation  $\Delta\varepsilon = \text{CD}/bC_M$ ,  $\Delta\varepsilon$  has not been calculated.

Table 1. Experimental values of  $\Delta\epsilon$  (eqn. 1) for the cobalt system and the calculated values of  $\Delta\epsilon_s$  ( $M^{-1} \text{ cm}^{-1}$ ) at different wavelengths (nm).

$C_L$ , mM	$\Delta\epsilon \times 10^3 M^{-1} \text{ cm}^{-1}$															
	450	460	470	480	490	500	510	520	530	540	550	560	570	580	590	600
8	0.7	1.0	1.4	1.7	2.2	3.0	4.1	4.8	5.8	4.8	3.3	1.7	1.0	0.3	0	0
20	1.1	1.6	3.2	4.3	4.8	6.1	9.3	12.1	12.9	11.6	8.9	4.7	2.5	1.1	0.3	0
32	1.6	2.7	6.0	7.3	7.6	10.6	13.7	17.9	20.0	17.8	12.3	7.3	3.5	1.4	0.4	-0.4
40	2.8	4.4	7.8	10.1	10.1	13.8	18.1	22.1	24.2	21.6	16.3	9.5	5.0	2.2	0.7	0.2
60	3.4	6.0	13.1	15.5	15.3	20.4	26.3	30.8	33.9	30.5	22.7	14.6	7.6	4.0	1.4	0.2
80	5.0	9.8	18.8	21.2	19.4	26.8	33.3	40.1	42.6	39.2	30.2	20.0	11.5	6.2	2.0	0.5
100	6.7	13.3	24.2	27.3	25.7	33.3	40.6	47.0	50.5	47.3	37.0	23.7	14.1	7.5	2.9	0
120	7.8	16.4	30.4	33.0	30.4	39.8	47.6	54.2	56.7	52.7	42.1	27.9	17.0	8.9	4.3	0.6
150	12.9	23.4	40.7	43.3	40.0	51.3	59.8	64.9	69.0	62.8	51.4	34.7	22.0	12.2	4.4	0.9
170	11.8	24.2	44.1	46.6	43.5	55.4	64.2	68.9	72.8	67.0	54.0	37.1	23.9	13.6	5.3	1.2
$\Delta\epsilon_s \times 10^3$	3.0	5.0	11.0	16.0	21.0	30.0	42.0	54.0	60.0	52.0	33.0	19.0	8.0	2.0	$\pm 0$	-2.0
$\Delta\epsilon_s \times 10^3$	24	48	114	117	72	93	108	120	132	141	135	96	63	41	19	8
$\Delta\epsilon_s \times 10^3$	33	74	84	84	100	118	119	114	105	91	74	56	42	25	9	2.5

Table 2. Experimental values of  $\epsilon$  ( $M^{-1} cm^{-1}$ ) for the cobalt system and the calculated values of  $\epsilon_n$  ( $M^{-1} cm^{-1}$ ) at different wavelengths (nm).

$C_I$ , mM	$\epsilon$ $M^{-1} cm^{-1}$															
	450	460	470	480	490	500	510	520	530	540	550	560	570	580	590	600
0	1.82	2.50	2.92	3.32	3.62	4.07	4.36	4.20	3.72	2.77	1.95	1.28	0.73	0.48	0.31	0.27
8	1.82	2.50	2.92	3.32	3.62	4.17	4.46	4.35	3.74	2.87	1.96	1.23	0.64	0.39	0.27	0.21
20	1.95	2.66	3.22	3.62	3.96	4.58	4.93	4.86	4.37	3.42	2.47	1.63	0.91	0.59	0.40	0.30
32	2.27	3.12	3.67	4.16	4.50	5.11	5.50	5.50	4.90	3.98	3.00	2.07	1.42	0.87	0.55	0.46
40	2.28	3.14	3.80	4.30	4.65	5.27	5.70	5.70	5.03	4.05	3.00	2.10	1.30	0.84	0.57	0.46
60	2.60	3.55	4.22	4.80	5.30	5.98	6.42	6.44	5.80	4.80	3.60	2.60	1.72	1.08	0.75	0.58
80	2.71	3.78	4.64	5.20	5.75	6.52	7.08	7.14	6.59	5.55	4.26	3.17	2.07	1.42	0.92	0.75
100	2.75	3.88	4.81	5.48	6.06	6.92	7.43	7.59	7.14	6.15	4.81	3.47	2.37	1.58	1.06	0.76
120	2.67	4.08	4.99	5.78	6.36	7.18	7.84	8.00	7.50	6.48	5.25	3.82	2.52	1.67	1.03	0.73
150	2.97	4.38	5.49	6.19	6.84	7.67	8.34	8.75	8.53	7.68	6.40	4.90	3.42	2.22	1.37	0.98
170	3.17	4.63	5.88	6.69	7.40	8.24	9.08	9.38	9.04	8.11	6.72	5.23	3.63	2.50	1.66	1.23
200	4.14	5.68	6.86	7.60	8.34	9.42	10.16	10.50	10.10	9.00	7.56	5.70	4.18	2.88	1.96	1.54
267	4.36	6.08	7.38	8.10	9.06	10.16	11.02	11.42	11.14	10.12	8.36	6.50	4.78	3.32	2.32	1.70
333	4.62	6.44	7.86	8.64	9.56	10.60	11.60	12.16	12.00	11.10	9.46	7.36	5.48	3.88	2.68	2.00
400	4.82	6.68	8.18	9.04	9.96	11.04	12.06	12.64	12.60	11.60	9.86	7.72	5.68	4.00	2.82	2.08
533	4.94	6.68	8.52	9.20	10.20	11.28	12.40	13.06	13.14	12.40	10.68	8.32	6.20	4.40	2.90	2.00
$\epsilon_1$ $M^{-1} cm^{-1}$	2.8	4.0	4.7	5.3	5.6	6.5	6.9	7.0	6.1	5.1	4.0	2.8	2.0	1.2	0.8	0.7
$\epsilon_2$ $M^{-1} cm^{-1}$	8.6	12.0	15.0	16.9	19.7	22.1	24.5	25.5	23.5	19.5	15.8	12.2	8.1	5.7	3.9	2.7
$\epsilon_3$ $M^{-1} cm^{-1}$	4.7	6.5	7.9	8.8	9.5	10.4	11.2	11.9	12.6	12.8	11.1	8.6	6.7	4.7	3.3	2.5

be recorded for  $C_M=25$  mM and increasing values of  $C_L$  in the region 660—400 nm. This value of  $C_M$  was chosen to give absorbaney values of about 0.5—0.8. Hence the dichrograph readings are quite reliable. To check the reproducibility new solutions were prepared and the measurements were repeated once more. The agreement between two series of measurements was within 2 %. For all these solutions absorption spectra were also recorded. The mean values of  $\Delta\epsilon$  (eqn. 1) were calculated and are reported in Table 1. Analogous values of the absorption measurements are presented in Table 2. The stability constants used in the calculation were those reported earlier from potentiometric measurements<sup>13</sup> ( $\beta_1=16.5$  M<sup>-1</sup>,  $\beta_2=55$  M<sup>-2</sup> and  $\beta_3=470$  M<sup>-3</sup>). From these values the complex formation curve  $\bar{n}=f([L])$  was calculated, and thus from the expression  $\bar{n}=(C_L-[L])\times C_M^{-1}$ , one can obtain  $[L]$  in the solutions, when  $C_M$  and  $C_L$  are known. Then  $\alpha_0$  and  $\alpha_1$  were calculated, and it was possible to get the values of  $\Delta\epsilon_n$  as described above. Fig. 1 represents the calculated CD spectra of the three cobalt complexes. It must be pointed out, however, that the error limits are 5 % for  $\Delta\epsilon_2$  and about 10 % for  $\Delta\epsilon_3$ . As to the absorption spectra, only those of the two first complexes could be obtained by the calculation procedure described above. For this reason absorption spectra were recorded for a series of solutions with  $C_M=5$  mM and high ligand concentrations. Then  $\epsilon_3$  could be determined in the following way:

The expression

$$(\epsilon - \epsilon_0\alpha_0)/\alpha_1[L]^2 \quad (9)$$

was formed.

It then holds from eqn. (8) that

$$\lim_{1/[L] \rightarrow 0} \frac{\epsilon - \alpha_0\epsilon_0}{\alpha_1[L]^2} = \epsilon_3 \frac{\beta_3}{\beta_1} \quad (10)$$

Thus when the equantity (9) was plotted against  $[L]^{-1}$  a curve was obtained, which yielded  $(\epsilon_3(\beta_3/\beta_1))$  as an intercept and  $\epsilon_2(\beta_2/\beta_1)$  as the limiting slope. In this way the value  $\epsilon_2$  determined earlier could be checked. In Table 2 the values of  $\epsilon$  for these measurements are included. The reported values of  $\epsilon_2$  are the mean values of the two calculations. The error limits for all  $\epsilon_n$  were about 5 %. The error limits for  $\Delta\epsilon_n$  and  $\epsilon_n$  do not include the error limits in  $\beta_n$ .

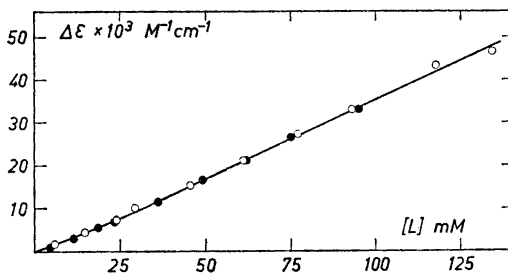


Fig. 2. The cobalt system.  $\Delta\epsilon$  as a function of  $[L]$  for two values of  $C_M$ .  $C_M=25$  mM (○) and  $C_M=50$  mM (●).  $\lambda=480$  nm.

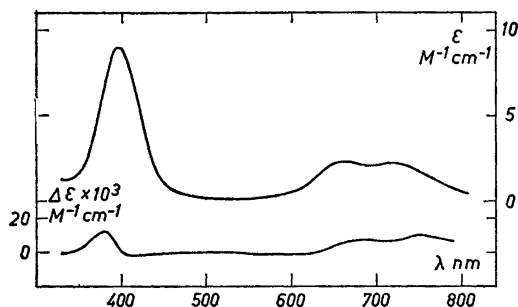


Fig. 3. The experimental circular dichroism (lower curve) and absorption spectrum (upper curve) of a nickel mandelate solution of the composition  $\bar{n}=1.2$  and  $[L]=77$  mM.

As has been mentioned above, CD measurements can be used to test the presence of polynuclear complexes in the system. Therefore, a series of measurements with  $C_M=50$  mM was also undertaken. In the same way as above,  $\Delta\epsilon$  and  $[L]$  were calculated and  $\Delta\epsilon$  was plotted against  $[L]$  for the two values of  $C_M$  at various different wavelengths. The curves were found to coincide, as is shown for  $\lambda=480$  nm in Fig. 2, so it must be concluded that the CD measurements do not give evidence for the existence of polynuclear complexes. The earlier potentiometric measurements<sup>13</sup> gave the same result too.

*The nickel system.* CD measurements of nickel mandelate solutions gave only small recorder deflections even for the greatest ligand concentrations obtainable. This made it impossible to perform a quantitative treatment of this system. Nevertheless, CD spectra as well as absorption spectra were recorded in the region 800–300 nm for a series of solutions with  $C_M=20$  mM and increasing values of  $C_L$ . A representative example of these measurements is given in Fig. 3.

#### DISCUSSION

As has been pointed out above, there seems to be no certain rule correlating the type of chelates present in a complex system and the circular dichroism. However, one may generalize rather safely that there must be some kind of chelate formation, if circular dichroism is actually observed. This generalization offers some help in trying to understand the constitution of the present systems. There are some points that must be stressed, and they are all equally important in this connection:

1) The stability constants of the Co(II) and Ni(II) systems are smaller than those of the zinc system. This is in agreement with what could be expected from the Irving-Williams series.<sup>15</sup> For the latter system, however, the ratio of the consecutive formation constants are such that there seems to be no reason to assume the presence of any great amount of chelates. A first-sphere chelate in the Co(II) and Ni(II) cases should most probably cause not only the  $K_n/K_{n+1}$  ratios to be higher than if unidentate complexes are formed, but also the absolute values of the formation constants to be high (*cf. e.g.*,



the Cu(II) acetate and glycolate systems<sup>16</sup>). Consequently, this type of chelation is not very common in these systems.

2) The increase of the ratio  $K_1/K_2$  in the series Zn < Ni < Co, which has previously<sup>13</sup> been used to justify the existence of increasing amounts of chelates in the three systems in this order, may still be considered to be indicating just this. However, the circular dichroism measurements of the present work indicate that some kind of chelates is present also in the third cobalt complex, CoL<sub>3</sub>, and the ratio  $K_2/K_3$  does not fit in with this description. Probably,<sup>13</sup> the low value of  $\beta_2$  that gives rise to the high value of  $K_1/K_2$  and the low value of  $K_2/K_3$  is caused by a low degree of solvation of the second, neutral complex.

3) Indicative of a special type of bonding present in the second cobalt complex, CoL<sub>2</sub>, is also the extraordinarily great increase of the circular dichroism at 475 nm compared to what is found in the spectra of the other two complexes. This CD-peak is probably related to the high-energy component of the  ${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$  transition, split by spin-orbit coupling,<sup>17</sup> present as a shoulder in the absorption spectrum. Now, circular dichroism intensities are thought to be enhanced for a given electronic transition by the coupling with the totally symmetric vibrations of the metal-ligand group,<sup>18</sup> whereas the enhancement of absorption intensities requires the coupling with — if any — the unsymmetrical vibrations.<sup>19</sup> The consequence of this is<sup>18</sup> that the position of the CD maximum is red-shifted compared with the absorption maximum. As it follows from the work of Koide<sup>17</sup> that both the ground state and the highest state arising from the spin-orbit splitting of the  ${}^4T_{1g}(P)$  state are non-degenerate ones in systems of octahedral symmetry, but for the presence of a Kramer's degeneracy, they will certainly remain so even when the symmetry of the ligand field is lowered. The other states originating from the  ${}^4T_{1g}(P)$  state are doubly or threefold degenerate — still omitting the Kramer's degeneracy — and will consequently split up in the low-symmetry field of the present complexes. Thus the circular dichroism related to the transitions to these latter states will be composed by a number of overlapping bands of opposing signs, thus giving rise<sup>20</sup> to observable bands with apparent maxima — and minima — lying in a manner, difficult to predict, more or less away from the position of the maximum of the light absorption related to these transitions. For the first mentioned transition, being one between non-degenerate states, this situation will not appear. Thus it is possible to make a meaningful comparison between the positions of the maxima for circular dichroism and light absorption. One observes from Fig. 1 that the first is found at 475 nm, whereas the latter is found at about 465 nm. From this redshift of the circular dichroism one may conclude<sup>18</sup> that a vibronic interaction is really at hand. Then it also seems reasonable that the intensity of the circular dichroism, characteristic of the second complex, is actually caused just by this effect. Now if this is so, there must obviously be pronounced deformations of the bonding electron system during a vibration period. We should like to suggest that such a strong interaction is more plausible if the ligands are forming chelates (in the usual, inner-sphere sense of the concept), than if only one end of the ligand is directly attached.

Consequently we propose that the second complex is actually an inner-sphere chelate, whereas the other two — especially the first one, for which the 475 nm CD intensity is very low — are chelates of the inner-outer-sphere type discussed above. If this is due to the zero charge of this complex or if it is caused by the presence of heavy and polarizable phenyl groups or by other factors may be the subject of some speculation and of further experimental studies too. It should also be noted that the proposition of Moffitt and Moscovitz,<sup>18</sup> relied upon above, has been questioned in a recent work by Denning.<sup>21</sup>

Another effect, causing some perplexity, is that the CD of the solid Co(mandelate)<sub>2</sub> in KBr suspension (Fig. 1) shows no or very little indication of circular dichroism at 475 nm. This may be due to the non-existence of chelate complexes in the crystals, then probably built by bridging mandelate ions, a possibility that is reasonable because of the unsolubility of this compound in all normally used organic solvents. For this reason it seems desirable that an X-ray structural investigation of this compound could be made.

The general picture of the cobalt mandelate system, emerging from the observations under points 1—3 above, should then be that the ligands in the first complex are predominantly non-chelated and chelated *via* a water molecule, whereas, in the second complex, they are mostly truly chelated. In the third complex, there are probably mostly ligands chelated *via* a water molecule or non-chelated, but also some truly chelated ones. It is interesting to compare the result for the first complex with the cobalt-glycolate system, where infrared absorption measurements<sup>2</sup> seem to indicate that for the first complex chelation occurs *via* a water molecule.

Turning then to the nickel system this cannot be dealt with in any detail. One can make the observation, though, that the anisotropy factors<sup>22</sup>  $g = \Delta\epsilon/\epsilon$ , for the nickel system, measured at the position of absorption maxima, are of about the same order of magnitude as those found for the cobalt complexes. Then, probably, the constitution of the two systems is alike, or at least, the splitting of the energy levels, caused by the decrease of symmetry from the octahedral one, in the complexes is alike.

The conclusions drawn from the present investigation relies mainly on current theories on the origin of circular dichroism of metal complexes, still under debate. Therefore, it should be valuable if other techniques, whether spectroscopic, thermodynamic or others, could be offered that would contribute to the clarification of the problems discussed here, *i.e.* the degree of chelation of various types that is present in a certain metal ion-ligand system in solution.

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