On the Stability of the Mandelate Complexes of Bivalent Zinc, Cobalt and Nickel

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The complex formation between zinc, cobalt, nickel, and mandelate ions has been studied with polarimetric and potentiometric methods. The measurements have been performed in a perchlorate medium of the ionic strength $I = 2.0$ M and at a temperature of 20.0°C. The zinc mandelate system has been investigated earlier with a polarimetric method.[1] The stability constants of the complexes in the three investigated systems are collected in Table 9.

The two methods give consistent values of the stability constants, except for the second constant, for which the potentiometric method yields a greater value. The stability constants of the complexes have been found to decrease in the following order: zinc > nickel > cobalt. The molar rotations of the cobalt and nickel complexes have been calculated (Table 8), and the results indicate the existence of anomalous dispersion curves.

In a previous paper,[1] polarimetric measurements of the complex formation between zinc and mandelate ions have been reported. That investigation gave evidence for the existence of at least three complexes within the used range of ligand concentrations. It was also tentatively suggested that there was a change in coordination number of the central atom, when the third complex was formed. It was therefore of interest to investigate how other metal mandelate systems behave. The intention was to study the mandelate complexity of the bivalent transition metals preceding zinc in the periodic system. The Cu(II) system, however, was not accessible, as even for small values of metal ion and mandelate ion concentrations, a precipitate was formed. For this reason the investigation was limited to the Co(II) and Ni(II) systems only. These two systems are expected to give weaker complexes than Cu(II)[2] and consequently the amount of the second complex, liable to precipitation, will be low for not too high values of the ligand and metal ion concentrations. As these metal ions have absorption bands in the used spectral range, Cotton effects may be expected, which must make it difficult to apply the Drude treatment used in the previous work.

It would also be of great value to investigate the above-mentioned complex systems by another method of measuring than the polarimetric one. Potentiometric measurements are known to give good results if suitable electrodes can be found. The potentiometric measurements can be performed either by measuring the central ion concentration by means of a metal-amalgam electrode or by measuring the free ligand concentration by a pH-electrode. The last mentioned method is to prefer if the complex system is strong, as the difference between total and free concentration of ligand, $C_L - [L]$, will be great and the mean ligand number, $\bar{n}$, can be determined accurately. It seems, however, to be difficult to prepare metal-amalgam electrodes of cobalt and nickel, and therefore the method of measuring the free ligand concentration has been used even if the complex systems must be considered as weak.

THE POLARIMETRIC INVESTIGATION

The notations and general formulae used in this work are exactly the same as those given in Ref. 1, but for the exchange of A for L as a symbol of the ligand. As in Ref. 1 mandelate-mandelic acid buffers with concentration ratio 100:1 were used, so that the pH of the solutions was kept $\simeq 5$. At this pH-value the amounts of hydrolytic products should be very small.[3] All solutions investigated have also the same general composition as in Ref. 1, and therefore the numerical treatment of the experimental results is identical with that of the earlier paper. From the observed angle of rotation, ϑ', and the values of C_M and C_L' one can easily calculate the function φ (cf. eqn. (3), Ref. 1), and from this function the mean ligand number $\bar{n}$ is determined as a function of the free ligand concentration $[L]$.

Hence the stability constants can be determined from the expression: [4,5]

$$\ln X\,([L]_i) = \int_0^{[L]_i} \frac{\bar{n}}{[L]}\ d[L]$$

Experimental

All measurements were made with the same technique as described before.[1]

Chemicals. The preparation of sodium mandelate and sodium perchlorate has been described earlier.[1] Cobalt perchlorate was prepared from analytical grade cobalt carbonate and perchloric acid. From the recrystallized salt a stock solution was made, the concentration of which was determined by a gravimetric oxine-analysis. Nickel perchlorate was made from analytical grade nickel carbonate and perchloric acid. The salt was recrystallized and a stock solution was made. To check the concentration, the nickel content was determined gravimetrically as dimethylglyoximate. The cobalt- and nickel perchlorate solutions were checked for any excess of free acid by means of a cation exchange and alkalimetric titration. The excess of free acid was found to be very small, but later potentiometric measurements with a glass electrode showed that the excess of free acid in the cobalt perchlorate solution was of such magnitude that C_L' and C_{HL} values must be corrected before the numerical treatment. The excess of free acid in the nickel perchlorate solution could be neglected, however.

Table 1. Calculation of the stability constants for the cobalt mandelate system. The following values are obtained: $\beta_1 = 17 \pm 2$ M^{-1}, $\beta_2 = 14 \pm 8$ M^{-2} and $\beta_3 = 570 \pm 100$ M^{-3}.

[L] mM	$\bar{n}$				$\bar{n}_{mean}$	$\dfrac{\bar{n}}{[L]} M^{-1}$	X	$X_1 M^{-1}$	$X_2 M^{-2}$	$X_3 M^{-3}$	$\bar{n}_{calc}$
	589 nm	578 nm	436 nm	365 nm							
5	0.09	0.09	0.07_5	0.07_5	0.08	16.0	1.08_4	16.8			0.08
10	0.16	0.16	0.14	0.15	0.15	15.0	1.17_1	17.1			0.15
15	0.22	0.22	0.20	0.21	0.21	14.0	1.26	17.3			0.21
20	0.28	0.27	0.26	0.27	0.27	13.5	1.35	17.5			0.27
25	0.33	0.32	0.31	0.32	0.32	12.8	1.44_2	17.7			0.32
30	0.38	0.37	0.36	0.37	0.37	12.3	1.53_6	17.9			0.37
35	0.43	0.42	0.41	0.43	0.42	12.0	1.63_2	18.1			0.42
40	0.47	0.47	0.46	0.48	0.47	11.8	1.73_2	18.3	37.5	590	0.47
45	0.51	0.52	0.51	0.53	0.52	11.6	1.83_7	18.6	40.0	580	0.53
50	0.56	0.58	0.56	0.59	0.57	11.4	1.94_6	18.9	42.0	560	0.58
55	0.61	0.63	0.61	0.64	0.62	11.3	2.06	19.3	45.5	570	0.63
60	0.66	0.68	0.66	0.70	0.67	11.2	2.18	19.7	48.3	570	0.68
65	0.71	0.74	0.71	0.75	0.73	11.2	2.31	20.1	50.8	570	0.73
70	0.77	0.80	0.76	0.81	0.78	11.1	2.44	20.5	52.9	560	0.78
75	0.83	0.85	0.81	0.86	0.84	11.2	2.58	21.0	56.0	560	0.83
80	0.88	0.91	0.86	0.92	0.89	11.1	2.73	21.6	60.0	580	0.88
85	0.94	0.96	0.92	0.98	0.95	11.2	2.88	22.1	62.4	570	0.93
90	0.99	1.02	0.98	1.04	1.01	11.2	3.05	22.8	66.7	590	0.98
95	1.05	1.07	1.04	1.10	1.06	11.2	3.22	23.4	69.5	580	1.03
100	1.10	1.13	1.10	1.15	1.12	11.2	3.41	24.1	73.0	590	1.08

Measurements

The quantity δ_{HL} (*cf.* Ref. 1, p. 56) was found to be almost constant, independent of C_M, and equal to the values given in Table 1 (Ref. 1). Hence there is no complexity between M and HL. The same values of δ_{HL} have been used in this work as in the previous one.

For the molar rotation of the mandelate ion (δ_L) used in the calculations the values of Table 2, Ref. 1, have been used. In the main series of measurement C_M was kept constant and equal to 10, 25, 50, and 75 mM, respectively, for the cobalt system. For the two smallest values of C_M it was possible to measure up to C_L about 200 mM, before a precipitation was formed. As the change of rotation was never very pronounced, especially for $C_M = 10$ mM, a great scattering in the φ-values was found, when they were plotted against C_L. For this reason the measurements for $C_M = 10$ mM have been omitted in the calculation of $\bar{n}$. At 546 nm, solutions with $C_M = 50$ and 75 mM, respectively, absorbed too strongly for the polarimeter to give a reliable reading. The other four wavelengths 589, 578, 436, and 365 nm, respectively, seemed to lie well outside the region of strong absorption ($\lambda_{max} = 515$ nm) and the measurements could be performed without complications. As precipitation occurred when a certain value of C_L was reached, the measurements for $C_M = 50$ and 75 mM, respectively, could not be performed longer than to C_L about 150 and 135 mM, respectively. Every solution was carefully checked for any presence of turbidity before and after each measurement. From the

Table 2. Calculation of the stability constants for the nickel mandelate system. The following values are obtained: $\beta_1 = 24 \pm 2\ M^{-1}$, $\beta_2 = 110 \pm 20\ M^{-2}$ and $\beta_3 = 920 \pm 200\ M^{-3}$.

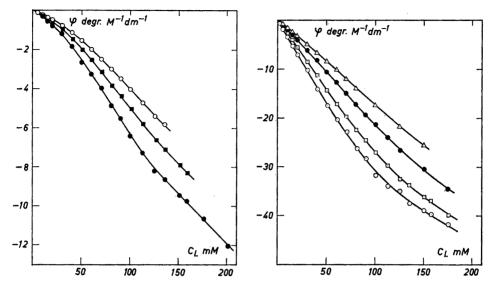| [L] mM	$\bar{n}$ 589 nm	578 nm	546 nm	436 nm	365 nm	$\bar{n}_{mean}$	$\frac{\bar{n}}{[L]}\ M^{-1}$	X	$X_1\ M^{-1}$	$X_2\ M^{-2}$	$X_3\ M^{-3}$	$\bar{n}_{calc}$
5	0.11	0.10	0.11	0.11	0.10	0.11	22.0	1.12_4	24.8			0.11
10	0.22	0.20	0.21	0.21	0.20	0.21	21.0	1.25_3	25.3			0.21
15	0.32	0.30	0.30	0.30	0.29	0.30	20.0	1.38_8	25.9			0.30
20	0.42	0.38	0.38	0.39	0.37	0.39	19.5	1.53_3	26.7			0.39
25	0.50	0.47	0.47	0.47	0.45	0.47	18.8	1.68_7	27.5	124		0.47
30	0.58	0.54	0.54	0.55	0.52	0.55	18.3	1.85_1	28.4	133		0.54
35	0.64	0.61	0.61	0.63	0.59	0.62	17.7	2.02_4	29.3	140		0.60
40	0.71	0.67	0.68	0.70	0.65	0.68	17.1	2.20_8	30.2	145		0.68
45	0.77	0.73	0.74	0.78	0.71	0.75	16.7	2.40_3	31.2	151	910	0.75
50	0.83	0.80	0.81	0.85	0.76	0.81	16.2	2.61	32.2	156	920	0.81
55	0.89	0.86	0.87	0.92	0.82	0.87	15.8	2.83	33.2	160	910	0.87
60	0.95	0.92	0.93	0.98	0.88	0.93	15.5	3.06	34.3	165	920	0.93
65	1.01	0.98	0.99	1.05	0.94	0.99	15.2	3.30	35.4	169	910	0.99
70	1.07	1.04	1.06	1.11	0.99	1.05	15.0	3.56	36.6	174	920	1.05
75	1.13	1.10	1.12	1.16	1.05	1.11	14.8	3.83	37.8	179	920	1.10
80	1.20	1.16	1.18	1.22	1.11	1.17	14.6	4.13	39.1	184	920	1.16
85	1.25	1.21	1.24	1.27	1.16	1.23	14.4	4.44	40.4	188	920	1.21
90	1.30	1.25	1.28	1.31	1.20	1.27	14.0	4.76	41.8	193	930	1.26
95	1.33	1.28	1.31	1.35	1.23	1.30	13.7	5.10	43.2	198	930	1.31
100	1.35	1.30	1.33	1.38	1.26	1.32	13.3	5.46	44.6	202	920	1.35
105	1.37	1.32	1.35	1.41	1.28	1.35	12.9	5.83	46.0	206	910	1.40
110	1.38	1.33	1.36	1.42	1.29	1.36	12.4	6.21	47.3	208	890	1.44
115	1.39	1.34	1.36	1.44	1.30	1.37	11.9	6.60	48.7	211	880	1.49

Fig. 1. The cobalt mandelate system. The function φ as a function of C_L for different values of C_M.
$C_M = 25$ mM ($\bullet$), $C_M = 50$ mM ($\blacksquare$), and $C_M = 75$ mM ($\bigcirc$). $\lambda = 578$ nm.

Fig. 2. The nickel mandelate system. The function φ as a function of C_L for different values of C_M.
$C_M = 10$ mM ($\bigcirc$), $C_M = 25$ mM ($\square$), $C_M = 50$ mM ($\bullet$), and $C_M = 75$ mM ($\triangle$). $\lambda = 436$ nm.

values of optical rotation thus obtained, the φ-values were calculated, and for each wavelength φ was plotted against C_L. Such φ-plots are given in Fig. 1 for $\lambda = 578$ nm. It can be seen from these curves that it is not possible to obtain $\bar{n}$-values for [L] >about 100 mM.

Also for the nickel system C_M was 10, 25, 50, and 75 mM, respectively. In this case the measurements could be performed at all the five wavelengths. The scattering of the φ-values for $C_M = 10$ mM was not greater than that these values could be used for the calculation of $\bar{n}$. Even for this complex system a precipitation occurred, when C_L had reached a certain value. For $C_M = 10$, 25, and 50 mM, respectively, the measurements could be performed up to $C_L = 175$ mM before any turbidity occurred, but for $C_M = 75$ mM the measurements had to be interrupted earlier. In Fig. 2 a typical case of the φ *versus* C_L plot is presented. From these curves it can be seen that $\bar{n}$-values for [L] somewhat >100 mM can be obtained.

As described before,[1] the φ-curves were cut at fixed values of φ and C_L plotted against C_M.[1] In this manner a set of ($\bar{n}$, [L])-pairs was obtained for each wavelength. By graphical interpolation a set of $\bar{n}$-values for a series of suitably chosen values of [L] was then obtained for the different wavelengths. In Table 1 these $\bar{n}$-values are given together with the mean value of $\bar{n}$ for the cobalt system, and in Table 2 the same values for the nickel system can be found. In comparison with the zinc system,[1] where $\bar{n}$ at [L]=100 mM

was about 1.8, it is now only about 1.1 and 1.3 respectively, so that the complex formation studied in this work is less pronounced than that studied before.

Results

When calculating the stability constants the theory [4,5] used before [1] was followed exactly.

The results for the cobalt system are given in Table 1. It can be seen from these data that three complexes exist within the [L]-range investigated. The small β_2-value is reflected by a corresponding inflection of the complex formation curve in the region where the second complex begins to be formed. This may be due to the formation of polynuclear complexes, *e.g.* of the type $(ML_2)_2$, for in such a case $(\delta C_L/\delta C_M)_{[L]}$ will not be equal to $\bar{n}$ for the mononuclear system but somewhat smaller. Another possibility is, of course, that there is actually a very pronounced difference between the formation constants of this system. For this reason the stability constants must be checked by another method. This is so much more the case, as, if this small β_2-value is correct, one gets an unusually great value of the ratio K_1/K_2 ($\simeq 20$).

In Table 2 the results for the nickel system are given. The constancy of the X_3-function indicates that three and not more than three complexes exist. The following values for the consecutive stability constants are obtained: $K_1=24$, $K_2=4.6$ and $K_3=8.4$. This gives $K_1/K_2=5.2$ and $K_2/K_3=0.6$. The K_1/K_2 ratio is somewhat higher than what is common for unidentate ligands, but it is much less than the corresponding ratio for the cobalt system. These values will be dealt with in the later discussion. In both Tables 1 and 2 the $\bar{n}$-values calculated from the stability constants are included. For the cobalt system the agreement with the experimental $\bar{n}$-values is very good, but for the nickel system the calculated $\bar{n}$-values are somewhat greater than the experimental ones for [L]-values >100 mM. This is probably due to the uncertainty of the extrapolations for great values of C_L. Consequently, the X_3-values for [L] >100 mM have not been used in the calculations of the third constant, as these values are mostly influenced by the uncertainty of $\bar{n}$.

THE POTENTIOMETRIC INVESTIGATION

Let C_L' and C_{HL}' denote the total concentrations of sodium mandelate and mandelic acid, respectively, and $[H^+]'$ the hydrogen concentration in a buffer solution without metal ions, then the following expression for the acid dissociation constant, K_a, of mandelic acid at the ionic strength of the experiments is valid

$$K_a = \frac{[H^+]'(C_L + [H^+]')}{C_{HL}' - [H^+]'} \tag{1}$$

When the buffer solution contains metal perchlorate of the concentration C_M and the same total concentration of mandelate buffer as above, we denote by $[H^+]$ the concentration of hydrogen ions, by [L] the concentration of free mandelate ions, and by [HL] the concentration of unprotolyzed mandelic

acid. If the metal perchlorate contains some free acid, its concentration C_H must be accounted for. Then we get

$$[HL] = C_{HL}' + C_H - [H^+]$$

and

$$K_a = \frac{[H^+][L]}{C_{HL}' + C_H - [H^+]} \tag{2}$$

By combining eqns. (1) and (2) we get the concentration of [L].

$$[L] = \frac{[H^+]'}{[H^+]} \cdot \frac{(C_L' + [H^+]')(C_{HL}' + C_H - [H^+])}{C_{HL}' - [H^+]'} \tag{3}$$

As the total mandelate concentration in the complex solution is $C_L = C_L' - C_H + [H^+]$, we can formulate the ligand number, $\bar{n} = (C_L - [L])/C_M$, as

$$\bar{n} = \frac{C_L' - C_H + [H^+] - [L]}{C_M} \tag{4}$$

From the ($\bar{n}$, [L])-values that can be obtained in this way, the calculation of the stability constants may be performed as above.

Experimental

The emf, E, of galvanic cells of the following composition were measured:

Ag,AgCl | 10.0 mM NaCl $I=2$ M NaClO$_4$ | 2 M NaClO$_4$ | C_M M Me(ClO$_4$)$_2$ C_H M HClO$_4$ C_L' M NaL C_{HL}' M HL (2−C_L'−3C_M) M NaClO$_4$ | glass electrode

Here Me means zinc, cobalt, or nickel.

The measurements were performed as titrations, where a known volume of a buffer solution T was added to a known volume of a solution S.

The solutions S and T had the following composition:

S | $C_M°$ M Me(ClO$_4$)$_2$ C_H M HClO$_4$ $I=2$ M NaClO$_4$ T | C_L' M NaL C_{HL}' M HL (2−C_L') M NaClO$_4$

By passing oxygen-free nitrogen through the right half-cell, effective stirring of the solution was obtained.

Two different buffer solutions were used, *viz.* $C_L'/C_{HL}' = 1:1$ and 1:2, respectively. The metal ion concentration was not kept constant during the titrations for the reason that the rate of precipitation was found to increase with increasing C_M and C_L'. Titrations were made by using buffer solutions with different concentrations, to get a great number of experimental points, even for the smallest values of C_L. Tables 4, 5, and 6 present a summary of the titrations.

Titrations were also made at $C_M = 0$. The measured emfs were in this case E'. From titrations with and without any metal ion present, $[H^+]/[H^+]'$ was computed from the following expression:

$$E_A = E - E' = 58.16 \log [H^+]/[H^+]' \tag{5}$$

To get the individual values of $[H^+]$ and $[H^+]'$ it was necessary to measure the emf E'' of the cell, where the right half-cell contained a solution of known hydrogen concentration denoted by $[H^+]''$. The following solution was used:

$$\left\{ \begin{array}{l} 10.04 \text{ mM HClO}_4 \\ I = 2 \text{ M NaClO}_4 \end{array} \right.$$

From the expression

$$E'' - E' = 58.16 \log \frac{[\text{H}^+]''}{[\text{H}^+]'} \tag{6}$$

the $[\text{H}^+]'$ concentration was calculated.

Every titration was repeated at least twice and the reproducibility of the potentials was in general within ± 0.2 mV. Before and after each titration it was checked that the asymmetry potential of the glass electrode had not changed. All the emf measurements were performed with a Radiometer type pH Meter 4 C. The temperature was 20.0°C. The Ag/AgCl electrode was prepared according to Brown.[6] The glass electrode was a Radiometer, type G 202 B.

Results

The zinc system. E' and the dissociation constant of mandelic acid were determined as a function of C_{L}' and the results are given in Table 3. The measurements show that the emf varies slightly when the perchlorate is gradually exchanged for mandelate buffer. The two different buffer solutions give the same value of K_{a} up to $C_{\text{L}}' \simeq 50$ mM. The reason for the change of emf may be that the medium changes cause variations of the liquid junction potentials and of the activity coefficients of the hydrogen ions. Under the assumption that E' is changed in the same way when metal ions are present in the solutions, the variation of E' does not affect the results, as only E_{A}-

Table 3. Determination of E' as a function of C_{L}'. The values refer to $E'' = 165.2$ mV.

C_{L}' mM	Buffer $C_{\text{L}}'/C_{\text{HL}}' = 1{:}1$			Buffer $C_{\text{L}}'/C_{\text{HL}}' = 1{:}2$		
	E' mV	$[\text{H}^+]'$ mM	$K_{\text{a}} \times 10^4$ (M)	E' mV	$[\text{H}^+]'$ mM	$K_{\text{a}} \times 10^4$ (M)
4.55	82.3	0.377	4.45	98.6	0.719	4.52
8.34	85.5	0.428	4.74	102.0	0.822	4.75
11.54	86.4	0.443	4.78	103.0	0.855	4.77
16.7	87.2	0.458	4.84	104.0	0.890	4.82
20.6	87.6	0.465	4.86	104.3	0.901	4.81
25.0	87.7	0.467	4.85	104.5	0.908	4.79
30.0	87.8	0.469	4.84	104.7	0.915	4.79
37.5	87.8	0.469	4.80	104.6	0.911	4.72
44.4	87.8	0.469	4.79	104.6	0.911	4.70
50.0	87.7	0.467	4.76	104.5	0.908	4.66
60.0	87.7	0.467	4.74	104.3	0.901	4.61
66.7	87.4	0.461	4.67	104.1	0.894	4.56
75.0	87.2	0.458	4.64	103.8	0.883	4.49
88.9	86.9	0.452	4.57	103.3	0.866	4.39
100.0	86.6	0.447	4.51	103.0	0.855	4.33
113.0	86.3	0.442	4.45	102.6	0.842	4.26
120.0	86.0	0.436	4.39	102.3	0.832	4.20
133.3	85.7	0.431	4.34	101.9	0.819	4.13
142.9	85.4	0.426	4.29	101.6	0.810	4.08
150.0	85.2	0.423	4.25	101.4	0.803	4.05
160.0	85.0	0.420	4.22	101.0	0.790	3.98

Table 4. The zinc system. Determination of corresponding values of [L] and $\bar{n}$/[L]. $C_M{}^\circ = 20$ and 40 mM, respectively.

Buffer solution 1:1.

$C_L{'}$ mM	C_M mM	E_A mV	$\dfrac{[H^+]'}{[H^+]}$	[L] mM	$\dfrac{\bar{n}}{[L]}$ M^{-1}	C_M mM	E_A mV	$\dfrac{[H^+]'}{[H^+]}$	[L] mM	$\dfrac{\bar{n}}{[L]}$ M^{-1}
4.55	18.2	9.4	0.689	3.2	31.3	36.4	15.6	0.539	2.5	32.0
8.34	16.7	9.4	0.689	5.9	31.1	33.3	15.4	0.543	4.6	30.1
11.54	15.4	8.8	0.706	8.3	29.9	30.8	14.9	0.554	6.4	29.9
16.7	13.3	7.8	0.734	12.4	29.2	26.7	13.5	0.586	9.8	29.0
20.6	11.8	7.0	0.758	15.8	28.7	23.5	12.3	0.614	12.7	28.6
25.0	10.0	5.9	0.792	20.1	27.5	20.0	10.7	0.654	16.5	28.0
30.0	8.0	4.7	0.830	25.2	26.5	16.0	8.8	0.706	21.4	27.2
37.5	12.5	7.0	0.758	28.7	26.4	25.0	12.8	0.602	22.7	27.5
44.4	11.1	6.1	0.786	35.2	25.1	22.2	11.4	0.637	28.4	26.5
50.0	10.0	5.4	0.808	40.7	24.3	20.0	10.2	0.668	33.6	25.5
60.0	8.0	4.0	0.854	51.6	21.8	16.0	7.9	0.732	44.1	23.4
66.7	6.7	3.3	0.877	58.8	21.4	13.3	6.5	0.773	51.8	22.4
75.0	12.5	5.8	0.795	59.9	20.9	25.0	11.5	0.635	47.7	23.4
88.9	11.1	4.8	0.826	73.7	19.2	22.2	9.8	0.678	60.4	21.7
100.0	10.0	4.1	0.850	85.3	17.8	20.0	8.4	0.717	71.9	20.0
113.0	8.7	3.3	0.877	99.5	16.3	17.4	6.9	0.761	86.3	18.2
120.0	8.0	3.0	0.888	106.9	15.9	16.0	6.2	0.782	94.1	17.6
133.3	6.7	2.4	0.909	121.6	15.1	13.3	5.1	0.817	109.2	16.9
142.9	5.7	2.1	0.920	131.8	15.3	11.4	4.1	0.850	121.7	15.5

Buffer solution 1:2.

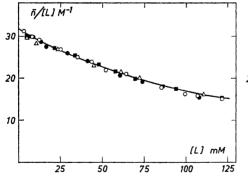| $C_L{'}$ mM	C_M mM	E_A mV	$\dfrac{[H^+]'}{[H^+]}$	[L] mM	$\dfrac{\bar{n}}{[L]}$ M^{-1}	C_M mM	E_A mV	$\dfrac{[H^+]'}{[H^+]}$	[L] mM	$\dfrac{\bar{n}}{[L]}$ M^{-1}
4.55	18.2	9.1	0.697	3.5	31.4	36.4	14.9	0.554	2.7	31.6
8.34	16.7	8.8	0.706	6.3	30.0	33.3	14.6	0.561	4.9	29.7
11.54	15.4	8.5	0.714	8.7	29.9	30.8	14.2	0.570	6.9	29.3
16.7	13.3	7.5	0.743	12.9	28.7	26.7	12.9	0.600	10.3	28.3
20.6	11.8	6.6	0.770	16.4	27.5	23.5	11.8	0.627	13.3	27.9
25.0	10.0	5.8	0.795	20.5	27.3	20.0	10.3	0.665	17.1	27.4
30.0	8.0	4.5	0.837	25.8	25.7	16.0	8.4	0.717	22.0	26.2
37.5	12.5	6.8	0.764	29.2	26.0	25.0	12.4	0.612	23.3	26.9
44.4	11.1	6.0	0.789	35.7	25.0	22.2	11.0	0.647	29.2	25.7
50.0	10.0	5.3	0.810	41.2	24.2	20.0	9.8	0.678	34.4	24.7
60.0	8.0	4.0	0.853	51.9	22.1	16.0	7.7	0.737	44.8	23.0
66.7	6.7	3.2	0.881	59.5	20.7	13.3	6.3	0.779	52.5	21.8
75.0	12.5	5.7	0.798	60.5	20.7	25.0	11.3	0.639	48.3	23.2
88.9	11.1	4.8	0.827	74.1	19.2	22.2	9.7	0.681	61.0	21.5
100.0	10.0	4.0	0.853	86.0	17.5	20.0	8.4	0.717	72.2	20.1
113.0	8.7	3.3	0.877	99.8	16.3	17.4	7.1	0.755	85.9	18.9
120.0	8.0	2.9	0.891	107.6	15.5	16.0	6.4	0.776	93.7	18.3
133.3	6.7	2.3	0.913	122.5	14.4	13.3	4.9	0.824	110.5	16.2

values are used for the computations. Titrations were performed at two values of $C_M°$ (20 mM and 40 mM). $C_M°$ indicates the concentration of C_M before any addition of buffer solution.
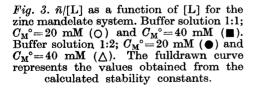
The concentration of free perchloric acid in the pure zinc perchlorate solution was found to be negligible in comparison to the hydrogen concentration in the buffer solution. In Table 4 the experimental values are given together with the calculated values of [L] and $\bar{n}/[L]$. Fig. 3 presents the relation between $\bar{n}/[L]$ and [L]. The fact that no systematic deviation can be observed between the four different titration series indicates that neither polynuclear complexes nor zinc-HL complexes are formed because in the first case $\bar{n}$ should be dependent on C_M, and in the latter case on the ratio between C_L' and C_{HL}'. By graphical integration of the $\bar{n}/[L]$ curve, the function X is obtained, and then the stability constants are obtained as described before. Table 7 gives the various X-functions for different values of [L]. The following results were obtained:

$$\beta_1 = 32 \pm 1 \text{ M}^{-1}$$
$$\beta_2 = 380 \pm 10 \text{ M}^{-2}$$
$$\beta_3 = 2300 \pm 200 \text{ M}^{-3}$$

The full-drawn curve in Fig. 3 is calculated from these stability constants.

The cobalt system. As this system was expected to be weaker than the zinc system, somewhat greater values of $C_M°$ (25 and 50 mM) were used to obtain E_A values of reasonable magnitude. The concentration of free perchloric acid in the cobalt perchlorate solution was of such an order of magnitude that it had to be corrected for (see Table 5). The experimental values are gathered in Table 5. From the close agreement between the experimental points of
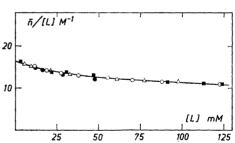
Fig. 3. $\bar{n}/[L]$ as a function of [L] for the zinc mandelate system. Buffer solution 1:1; $C_M° = 20$ mM (○) and $C_M° = 40$ mM (■). Buffer solution 1:2; $C_M° = 20$ mM (●) and $C_M° = 40$ mM (△). The fulldrawn curve represents the values obtained from the calculated stability constants.

Fig. 4. $\bar{n}/[L]$ as a function of [L] for the cobalt mandelate system. Buffer solution 1:1; $C_M° = 25$ mM (○) and $C_M° = 50$ mM (△). Buffer solution 1:2; $C_M° = 25$ mM (●) and $C_M° = 50$ mM (■). The fulldrawn curve represents the values obtained from the calculated stability constants.

Table 5. The cobalt system. Determination of corresponding values of [L] and $\bar{n}$/[L]. $C_M° = 25$ mM $(C_H = 4.8 \times 10^{-3} \times C_M)$ and $C_M° = 50$ mM $(C_H = 10.4 \times 10^{-3} \times C_M)$.

Buffer solution 1:1.

C_L' mM	C_M mM	E_A mV	$\dfrac{[H^+]'}{[H^+]}$	[L] mM	$\dfrac{\bar{n}}{[L]}$ M^{-1}	C_M mM	E_A mV	$\dfrac{[H^+]'}{[H^+]}$	[L] mM	$\dfrac{\bar{n}}{[L]}$ M^{-1}
4.55	22.7	9.2	0.694	3.4	20.6	45.5	17.0	0.510	2.6	19.2
8.34	20.8	7.5	0.743	6.5	16.9	41.7	14.0	0.574	5.1	16.4
11.54	19.2	6.7	0.767	9.2	16.3	38.5	12.6	0.607	7.4	15.9
16.7	16.7	5.6	0.801	13.7	15.2	33.3	10.6	0.657	11.3	15.0
20.6	14.7	4.9	0.824	17.3	14.7	29.4	9.3	0.692	14.6	14.6
25.0	12.5	4.0	0.853	21.7	13.9	25.0	8.0	0.728	18.6	14.6
30.0	10.0	3.3	0.877	26.7	14.2	20.0	6.3	0.779	23.8	13.9
37.5	15.6	4.8	0.827	31.4	13.5	31.3	9.2	0.694	26.4	13.8
44.4	13.9	4.2	0.847	38.0	13.0	27.8	8.1	0.726	32.7	13.4
50.0	12.5	3.7	0.864	43.6	12.6	25.0	7.3	0.749	37.9	13.2
60.0	10.0	2.7	0.898	54.3	11.4	20.0	5.6	0.801	48.5	12.2
66.7	8.3	2.4	0.909	61.0	12.0	16.7	4.9	0.824	55.4	12.7
75.0	15.6	4.5	0.837	63.1	12.5	31.3	8.6	0.711	53.8	12.8
88.9	13.9	3.8	0.861	76.9	11.6	27.8	7.5	0.743	66.5	12.3
100.0	12.5	3.4	0.874	87.8	11.5	25.0	6.6	0.770	77.4	11.8
113.0	10.9	2.8	0.894	101.5	10.9	21.7	5.7	0.798	90.7	11.5
120.0	10.0	2.7	0.898	108.2	11.4	20.0	5.3	0.810	97.6	11.6
133.3	8.3	2.2	0.917	122.7	10.9	16.7	4.1	0.850	113.8	10.5
142.9	7.1	1.8	0.931	133.4	10.4	14.3	3.4	0.874	125.3	10.0
150.0						12.5	3.1	0.885	133.2	10.3

Buffer solution 1:2.

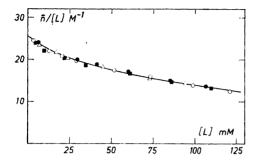| C_L' mM	C_M mM	E_A mV	$\dfrac{[H^+]'}{[H^+]}$	[L] mM	$\dfrac{\bar{n}}{[L]}$ M^{-1}	C_M mM	E_A mV	$\dfrac{[H^+]'}{[H^+]}$	[L] mM	$\dfrac{\bar{n}}{[L]}$ M^{-1}
4.55	22.7	7.5	0.743	3.9	17.9	45.5	13.7	0.581	3.1	16.1
8.34	20.8	6.7	0.767	7.0	15.7	41.7	12.0	0.622	5.7	15.0
11.54	19.2	6.0	0.789	9.7	15.0	38.5	11.1	0.644	8.0	14.7
16.7	16.7	5.2	0.814	14.2	14.5	33.3	9.7	0.681	11.9	14.3
20.6	14.7	4.7	0.830	17.8	14.6	29.4	8.7	0.709	15.2	14.1
25.0	12.5	3.9	0.857	22.2	13.9	25.0	7.3	0.749	19.4	13.5
30.0	10.0	3.0	0.888	27.4	13.0	20.0	5.9	0.792	24.5	13.2
37.5	15.6	4.5	0.837	32.1	12.8	31.3	8.4	0.717	27.5	12.7
44.4	13.9	3.8	0.861	39.0	11.8	27.8	7.6	0.740	33.5	12.7
50.0	12.5	3.5	0.870	44.3	12.2	25.0	6.9	0.761	38.7	12.6
60.0	10.0	2.6	0.902	54.9	11.0	20.0	5.5	0.804	49.0	12.2
66.7	8.3	2.2	0.917	61.9	11.0	16.7	4.4	0.840	56.8	11.4
75.0	15.6	4.0	0.853	64.7	11.1	31.3	8.5	0.714	54.2	12.8
88.9	13.9	3.4	0.874	78.4	10.4	27.8	7.6	0.740	66.4	12.7
100.0	12.5	3.0	0.888	89.5	10.2	25.0	6.7	0.767	77.3	12.2
113.0						21.7	5.6	0.801	91.2	11.4
120.0						20.0	5.3	0.810	97.9	11.7
133.3						16.7	4.3	0.844	113.2	11.1
142.9						14.3	3.7	0.864	124.1	11.0
150.0						12.5	3.2	0.881	132.9	10.8

Fig. 5. $\bar{n}/[L]$ as a function of [L] for the nickel mandelate system. Buffer solution 1:1; $C_M° = 25$ mM (O) and $C_M° = 50$ mM (■). Buffer solution 1:2; $C_M° = 25$ mM (●) and $C_M° = 50$ mM (△). The fulldrawn curve represents the values obtained from the calculated stability constants.

$\bar{n}/[L]$ for the different titrations series (Fig. 4), the existence of polynuclear complexes can be excluded also in this case.

The two different buffer solutions give the same result too within the error of limits. The functions necessary for computing the stability constants are given in Table 7. The following stability constants were obtained:

$$\beta_1 = 16.5 \pm 0.5 \ M^{-1}$$
$$\beta_2 = 55 \pm 5 \ M^{-2}$$
$$\beta_3 = 470 \pm 50 \ M^{-3}$$

The full-drawn curve in Fig. 4, calculated from these constants, shows that these three stability constants describe the measurements.

The nickel system. For this system $C_M°$ was 25 and 50 mM, respectively, for the different titrations. The concentration of free perchloric acid in the nickel perchlorate solution could be neglected. The experimental values from the four titration series are given in Table 6, and Fig. 5 gives the $\bar{n}/[L]$-values as a function of [L]. For this system too no indication of polynuclear complexes was found, nor for any complexes of the Ni—HL type.

The results of computing the stability constants are given in Table 7. The constancy of the X_3-function shows that three complexes exist within the [L]-range investigated. The following values of the stability constants were obtained:

$$\beta_1 = 25.5 \pm 1 \ M^{-1}$$
$$\beta_2 = 180 \pm 10 \ M^{-2}$$
$$\beta_3 = 800 \pm 100 \ M^{-3}$$

In all three systems, the $\bar{n}/[L]$-function calculated from the obtained stability constants (full-drawn curve in Figs. 3—5) agrees well with the experimental points.

THE MOLAR ROTATIONS OF THE COMPLEXES

The calculation of the molar rotations of the complexes is done in the same way as described in Ref. 1. As has been mentioned above the β_2-value for the cobalt system is perhaps not correct, and for this reason the stability constants, determined by the potentiometric method, have been used for

Table 6. The nickel system. Determination of corresponding values of [L] and $\bar{n}/[L]$. $C_M° = 25$ and 50 mM, respectively.

Buffer solution 1:1.

C_L' mM	C_M mM	E_A mV	$\dfrac{[H^+]'}{[H^+]}$	[L] mM	$\dfrac{\bar{n}}{[L]}$ M^{-1}	C_M mM	E_A mV	$\dfrac{[H^+]'}{[H^+]}$	[L] mM	$\dfrac{\bar{n}}{[L]}$ M^{-1}
4.55	22.7	9.4	0.689	3.3	24.5	45.5	16.2	0.527	2.4	26.4
8.34	20.8	8.7	0.709	6.1	22.5	41.7	15.3	0.546	4.6	23.9
11.54	19.2	8.4	0.717	8.5	22.6	38.5	14.6	0.561	6.5	23.2
16.7	16.7	7.4	0.746	12.7	22.0	33.3	13.0	0.598	10.1	22.1
20.6	14.7	6.4	0.776	16.2	20.8	29.4	11.6	0.632	13.1	21.2
25.0	12.5	5.6	0.801	20.3	20.8	25.0	10.2	0.668	16.9	21.0
30.0	10.0	4.4	0.840	25.5	19.7	20.0	8.3	0.720	21.8	20.3
37.5	15.6	6.6	0.770	29.1	19.7	31.3	12.0	0.622	23.4	20.2
44.4	13.9	5.9	0.792	35.5	19.4	27.8	10.5	0.660	29.5	19.1
50.0	12.5	5.2	0.814	41.0	18.7	25.0	9.5	0.687	34.5	18.7
60.0	10.0	4.0	0.853	51.5	17.5	20.0	7.4	0.746	45.0	17.4
66.7	8.3	3.3	0.878	58.9	16.9	16.7	6.2	0.782	52.4	17.0
75.0	15.6	5.8	0.795	59.9	16.8	31.3	11.0	0.647	48.7	17.8
88.9	13.9	5.0	0.820	73.2	16.0	27.8	9.5	0.687	61.2	16.6
100.0	12.5	4.3	0.844	84.7	14.9	25.0	8.2	0.723	72.5	15.5
113.0	10.9	3.5	0.870	98.7	13.9	21.7	6.9	0.761	86.3	14.6
120.0	10.0	3.3	0.877	105.6	14.1	20.0	6.3	0.779	93.7	14.3
133.3	8.3	2.5	0.906	121.2	12.5	16.7	5.0	0.820	109.6	13.3
142.9	7.1	2.2	0.917	131.4	12.8	14.3	4.3	0.844	120.9	13.0
150.0	6.3	1.9	0.928	139.6	12.5	12.5	3.6	0.867	130.4	12.4

Buffer solution 1:2.

C_L' mM	C_M mM	E_A mV	$\dfrac{[H^+]'}{[H^+]}$	[L] mM	$\dfrac{\bar{n}}{[L]}$ M^{-1}	C_M mM	E_A mV	$\dfrac{[H^+]'}{[H^+]}$	[L] mM	$\dfrac{\bar{n}}{[L]}$ M^{-1}
4.55	22.7	8.8	0.706	3.6	24.2	45.5	14.8	0.556	2.7	25.5
8.34	20.8	8.8	0.706	6.3	24.1	41.7	14.8	0.556	4.9	24.1
11.54	19.2	8.3	0.720	8.8	23.2	38.5	14.3	0.568	6.8	23.5
16.7	16.7	7.5	0.743	12.9	22.9	33.3	13.1	0.595	10.3	23.0
20.6	14.7	6.8	0.764	16.3	22.7	29.4	12.0	0.622	13.2	22.8
25.0	12.5	5.8	0.795	20.5	22.0	25.0	10.3	0.665	17.1	21.7
30.0	10.0	4.6	0.833	25.7	21.1	20.0	8.6	0.711	21.8	21.6
37.5	15.6	6.6	0.770	29.5	20.0	31.3	11.9	0.624	23.8	20.4
44.4	13.9	5.8	0.795	36.0	19.3	27.8	10.7	0.654	29.5	19.9
50.0	12.5	5.2	0.814	41.3	18.9	25.0	9.5	0.687	34.8	18.9
60.0	10.0	4.1	0.850	51.7	18.1	20.0	7.7	0.737	44.8	18.3
66.7	8.3	3.1	0.884	59.7	16.1	16.7	6.2	0.782	52.7	17.1
75.0	15.6	5.9	0.792	60.0	17.2	31.3	10.8	0.652	49.3	17.5
88.9	13.9	5.0	0.820	73.5	16.1	27.8	9.4	0.689	61.7	16.6
100.0	12.5	4.3	0.844	85.0	15.0	25.0	8.1	0.726	73.1	15.4
113.0	10.9	3.4	0.874	99.5	13.5	21.7	6.8	0.764	86.9	14.4
120.0	10.0	3.2	0.881	106.4	13.7	20.0	6.3	0.779	94.0	14.4
133.3	8.3	2.5	0.906	121.5	12.6	16.7	4.9	0.824	110.5	13.0
142.9	7.1	2.1	0.920	132.1	12.3	14.3	4.2	0.847	121.6	12.8

Table 7. The functions X, X_1, X_2, and X_3 for the various mandelate systems.

[L] mM	The zinc system				The cobalt system				The nickel system			
	X	X_1 M⁻¹	X_2 M⁻²	X_3 M⁻³	X	X_1 M⁻¹	X_2 M⁻²	X_3 M⁻³	X	X_1 M⁻¹	X_2 M⁻²	X_3 M⁻³
0	1.00	32.0	380	2240	1.00	16.5	55	470	1.00	25.5	180	800
5	1.17_2	34.4			1.08_9	17.8			1.14_1			
10	1.36_2	36.2			1.17_7	17.7			1.27_9	27.9		
15	1.57_4	38.3			1.26_6	17.7			1.42_7	28.5		
20	1.80_9	40.5	425		1.35_9	18.0			1.58_6	29.3	190	
25	2.07	42.8	432		1.45_5	18.2	68.0		1.75_8	30.3	192	
30	2.36	45.4	447	2230	1.55_8	18.6	70.0	440	1.94_2	31.4	197	
35	2.68	48.0	457	2200	1.66_5	19.0	71.4	460	2.14	32.5	200	
40	3.03	50.8	470	2250	1.77_7	19.4	72.5	460	2.35	33.8	208	760
45	3.41	53.6	480	2220	1.89_5	19.9	75.6	455	2.58	35.0	211	780
50	3.83	56.6	492	2240	2.02	20.4	78.0	470	2.82	36.3	216	785
55	4.28	59.7	504	2250	2.15	20.9	80.0	455	3.07	37.7	222	800
60	4.77	62.9	515	2250	2.29	21.5	83.3	460	3.34	39.1	227	800
65	5.30	66.2	526	2250	2.43	22.0	84.6	475	3.63	40.5	231	800
70	5.87	69.6	537	2240	2.59	22.6	87.1	470	3.94	42.0	236	800
75	6.49	73.1	548	2240	2.75	23.3	90.7	475	4.26	43.5	240	800
80	7.14	76.8	560	2250	2.91	23.9	92.5	465	4.60	45.0	244	800
85	7.85	80.5	571	2250	3.09	24.6	95.3	475	4.96	46.6	248	800
90	8.59	84.4	582	2240	3.27	25.2	96.7	470	5.34	48.2	252	800
95	9.39	88.3	593	2240	3.47	26.0	100.0	465	5.73	49.8	256	800
100	10.24	92.4	604	2240	3.67	26.7	102.0	470	6.15	51.5	260	790
105	11.13	96.5	614	2230	3.88	27.4	103.8	470	6.59	53.2	264	790
110	12.08	100.7	625	2230	4.11	28.2	106.4	470	7.04	54.9	267	790
115	13.07	105.0	635	2210	4.34	29.0	108.7	470	7.52	56.7	271	790
120	14.12	109.3	644	2200		29.9	111.7	470	8.02	58.5	275	790
125					4.84	30.7	113.6	470	8.55	60.4	279	790
130					5.10	31.6	116.2	470	9.10	62.3	283	795
135					5.38	32.5	118.5		9.68	64.3	287	800
140					5.67	33.4	120.7		10.30	66.4	292	

Table 8. Molar rotations (degr. M^{-1} dm^{-1}) of the mandelate complexes.

The cobalt system.

Wavelength nm	$-D_1$	$-D_2$	$-D_3$	$-\delta_1$	$-\delta_2$	$-\delta_3$	$-\dfrac{\delta_2}{2}$	$-\dfrac{\delta_3}{3}$	$-\delta_L$
589	4.5	24.0	30.2	23.0	61.0	85.7	30.5	28.6	18.5
578	2.4	26.7	26.0	21.7	65.3	83.9	32.7	28.0	19.3
436	19.0	103.5	110.2	58.8	183	230	91.5	76.7	39.8
365	22.3	141.0	151.0	89.4	275	352	137.5	117.3	67.1

The nickel system.

Wavelength nm	$-D_1$	$-D_2$	$-D_3$	$-\delta_1$	$-\delta_2$	$-\delta_3$	$-\dfrac{\delta_2}{2}$	$-\dfrac{\delta_3}{3}$
589	14.6	45.5	33.0	33.1	82.5	88.5	41.3	29.5
578	13.6	49.9	32.2	32.9	88.5	90.1	44.3	30.0
546	14.0	54.3	34.3	36.2	98.7	100.9	49.4	33.6
436	19.0	75.4	65.1	58.8	155.0	184.5	77.5	61.5
365	22.2	150.8	110.6	89.3	285.0	311.9	142.5	104.0

the calculation of D_n. The result is given in Table 8. Corresponding values for the nickel system can also be seen in Table 8. In this table the molar rotations per ligand of the complexes (δ_n/n) are included. The change of the trend of the δ_n/n-values from the second to the third complex is found to be the same for all three investigated mandelate systems (*cf.* Ref. 1). The numerical values of the rotations are of course dependent on the values of the stability constants actually used, and thus such a comparison is of somewhat limited value. The interesting relations, however, are the variations of δ_n for each complex with the wavelength. An inspection of the δ_1 and δ_3 values for the cobalt system at the different wavelengths shows that the dispersion curves are not "normal" ones, but that a Cotton effect is probably present in the neigbourhood of the Co^{2+} $d-d$ transition (515 nm). For the nickel system it can be seen from Table 8 that the dispersion curve for the first complex at least is not normal, but that there is a Cotton effect in the neighbourhood of the Ni^{2+} $d-d$ transition at 650 nm. Nickel salt solutions have also another rather strong $d-d$ transition at about $\lambda=400$ nm and it is therefore most probable that there is a Cotton effect also in this region. These results show that it is impossible to use the Drude equation [7] to get the far ultraviolet wavelength of the intraligand or ligand-metal electronic transition that is creating the most important part of the rotation of the complexes (*cf.* Ref. 1).

DISCUSSION

The stability constants of the various mandelate complexes are gathered in Table 9. It can be seen that the two methods of measuring give the same

Table 9. The stability constants of the various mandelate complexes determined with polarimetric and potentiometric method.

Central ion	Method	β_1 M^{-1}	β_2 M^{-2}	β_3 M^{-3}	K_1 M^{-1}	K_2 M^{-1}	K_3 M^{-1}	$\dfrac{K_1}{K_2}$	$\dfrac{K_2}{K_3}$
Zn^{2+}	Polarimetric [a]	30 ±2	260±40	3900±700	30	8.7	15	3.4	0.6
	Potentiometric	32 ±1	380±10	2300±200	32	11.9	5.9	2.7	2.0
Ni^{2+}	Polarimetric	24 ±2	110±20	900±200	24	4.6	8.4	5.2	0.6
	Potentiometric	25.5±1	180±10	800±100	25.5	7.0	4.4	3.8	1.6
Co^{2+}	Polarimetric	17 ±2	14±8	570±100	17	0.8	41	21 [b]	0.02 [b]
	Potentiometric	16.5±0.5	55±5	470±50	16.5	3.3	8.5	5.0	0.4

[a] see Ref. 1.   [b] *cf.* the discussion.

value of β_1, the potentiometrically determined ones are perhaps somewhat greater.

On the other hand, the constant β_2, determined with the potentiometric method, is found to be greater for all three complex systems. The reason for this could be the existence of small amounts of a polynuclear complex in the [L] range, where a relatively large amount of the second complex exists. The previous suggestion that the low polarimetrically determined β_2-value was obtained from too low $\bar{n}$-values, may now be extended in the following way: In the polarimetric investigation it has been presupposed that no polynuclear complexes exist, and, of course, if that is not the case, the results could not be entirely correct, since then there must be a new set of terms in eqn. 2 (p. 55 in Ref. 1) *viz.*

$$\sum_{p=2}^{P} \sum_{n=1}^{N} \delta_{pn}[M_p L_n],$$

where δ_{pn} is the molar rotation of the polynuclear complex $M_p L_n$. Even if the concentration of the polynuclear complexes is small, as the results from the potentiometric measurements indicate, δ_{pn} can be great, and therefore this new set of terms can be of certain importance, and consequently φ is no longer dependent only on [L] but also on [M]. The greatest difference between the β_2-values is found for the cobalt system, so it can be concluded that the tendency towards polynuclear complex formation must be greatest, or rather that the parameters δ_{pn} are the greatest, for this system.

The two methods have given consistent β_3-values for the cobalt and the nickel system, but the difference in β_3 for the zinc system is very pronounced. It seems probable that the potentiometrically determined β_3-value is the most correct one, because in the calculation of β_3 from the polarimetric data only two series of measurements with different values of C_M could be used. The uncertainty of the polarimetric measurements is also greatest at high ligand concentrations. The fact that the potentiometric measurements give a

smaller value of β_3 and a greater value of β_2 for the zinc system causes another sequence of the consecutive stability constants, as can be seen from Table 9. Consequently, the interpretation given before,[1] that the coordination number of the central atom has been changed from six to four, when the third complex is formed, and that the increase of entropy from liberation of water should give a large β_3-value, has no longer any motivation. The conclusion regarding this system must be that all ligands occupy one coordination site each, as the ratios K_1/K_2 and K_2/K_3 are of the order of magnitude 2—3.

The potentiometric measurements for the nickel system give a somewhat smaller value of the ratio K_1/K_2 than the polarimetric ones, because of the higher value of β_2. Even so, this ratio is of a magnitude, that makes it probable that some degree of chelation [8] is present at least for the first complex.

For the cobalt system the value of K_1/K_2 is found to be 5.0, with the potentiometric technique, which is higher than the corresponding ratio for the other two complex systems. This fact indicates that the degree of chelation increases from Ni^{2+} to Co^{2+}. An independent method of investigating the formation of chelates in solution of transition metal complexes has been proposed recently.[9] Such measurements have also been performed on the Co^{2+} and Ni^{2+} systems, and will be described later.[10]

The ratio K_2/K_3 for the cobalt system, calculated from the potentiometric results, is of the same order of magnitude as the corresponding ratio for the zinc and nickel systems. In all cases there is definitely a tendency towards low values of K_2/K_3. If the interpretation given before, the change of the coordination number of the central ion from six to four, is correct, an indication of tetrahedral complexes should be found in the absorption spectrum, especially in the cobalt case. Absorption spectra have been recorded for high ligand concentrations, but no absorption peak in the region, where tetrahedral cobalt-oxygen complexes absorb strongly, has been found. For this reason, there must be another explanation of the low value of the ratio K_2/K_3.

It can be suggested tentatively that β_2 is inherently low in the mandelate systems, probably because of low solvating power of the second complex. In conclusion it can be mentioned that the two different methods of measurements give consistent results, on the whole, and that the potentiometric method is preferable, for the above-mentioned reasons.

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