COMPLEXES OF BERYLLIUM WITH FIVE- AND SIX-MEMBERED CHELATE RINGS

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Complexes of Be(II) with malonic and oxalic acids and with NTA, NTP and EDTA were studied using potentiometric acid–base titrations. The stability constants obtained indicate that ligands forming six-membered chelate rings yield more stable complexes with Be(II) than homologous ligands forming five-membered rings. The use of NTP for the alkalimetric determination of Be(II) has been proposed.

The largest contribution of a chelate ring to an increase in complex stability was observed[1] with five-membered chelate rings. The validity of this generally accepted rule[2] is illustrated, for example, by the stability constants for complexes with aminocarboxylic acids $N(CH_2COOH)_3$ (NTA) and $N(CH_2CH_2COOH)_3$ (NTP); Chaberek and Martell[3] found respective values of log K_1 12·7 and 8·8 for Cu(II), 11·3 and 5·8 for Ni(II), 10·6 and 4·8 for Co(II), 9·8 and 3·4 for Cd(II) and 5·4 and 1 for Mg(II). The K_1 value for NTA forming five-membered chelate rings is always several orders of magnitude larger than that for the homologous reagent NTP, that forms six-membered chelate rings. It has been shown that five-membered ring chelates are most stable for central atoms with atomic numbers greater than 11, for which a coordination number of 6 predominates and s-, p- and d-electrons participate in the bonding. The elements of the first short period, among which Be and B readily form complexes, are bonded through s- and p-orbitals, similar to carbon. The examples given below indicate that Be and B prefer six-membered chelate rings, analogous to organic compounds. Chromotropic[4] and salicylic[5] acids (these reagents form six-membered chelate rings) readily form complexes with boric acid in aqueous solutions, with ratios of B : L = 1 : 1 and 1 : 2, even when the reagent concentration (c_L) is smaller than that of boron (c_B). With pyrocatechol and its derivatives (reagents yielding five-membered rings) only 1 : 1 complexes in aqueous solutions are known[6], even when c_L is much larger than c_B. The Be(II) chelates with malonate (six-membered rings, $K_1 = 10^{5·7}$, $K_2 = 10^{3·5}$) were found[7] to be more stable than those with oxalate (five-membered rings, $K_1 = 10^{4·1}$, $K_2 = 10^{1·8}$).

The present paper is directed to comparison of the stability of Be(II) chelates with five- and six-membered rings with dicarboxylic and aminocarboxylic acids and to the use of stable chelates for the alkalimetric determination of Be(II).

EXPERIMENTAL

Instruments, Chemicals and Methods

The automatic titration assembly from Radiometer (Denmark), ABU 12, TTT 11, SBR and PHM 26, with a G 202B glass electrode and a saturated calomel electrode, was used for titrations. The pH-meter was adjusted with a phosphate buffer at pH 6·50 (Radiometer). The solutions titrated had an initial volume of 30—40 ml, a temperature of 20 ± 1°C, $c_{KNO_3} = 0·1M$ and an ionic strength of $I = 0·11 ± 0·01$. The maximum volume of the 0·1M-NaOH titrant added was 2·5 ml. The value of function $\bar{z}$ was calculated from the titration curves using the procedure described elsewhere[8]. Mixed constants were obtained, since the hydrogen ion activity and the concentrations of the other components were employed for their calculation.

P.a. chemicals were used (Lachema, Brno), except for NTA, β-chloropropionic and malonic acids (Lachema, Brno) and β-alanine (Loba-Chemie, Vienna), which were denoted as "pure". A stock solution of 0·1045M-BeSO$_4$ in 0·1070M-HNO$_3$ was prepared by dissolving BeSO$_4$. 4 H$_2$O in dilute nitric acid and its titre was determined by the procedure described elsewhere[9]. The reagent concentration in solution was determined by alkalimetric potentiometric titration.
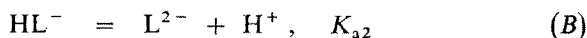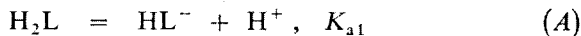
NTP was prepared by the reaction of β-alanine with β chloropropionic acid, using the procedure described earlier[3]: To 0·1 mol sodium β-alaninate in c. 100 ml water were added 0·4 mol sodium β-chloropropionate and the solution was refluxed for 16 hours with gradual addition of 50% NaOH, the overall amount added being 0·4 mol NaOH. The reaction mixture was acidified with 20% HCl to pH 2—3 and gray needle-shaped crystals of NTP separated after several days. After triple recrystallization from hot water, white crystals were obtained, the yield being 25% with respect to β-alanine. NTP can be titrated alkalimetrically (analogous to NTA), as a relatively strong dibasic acid, with the equivalence point at pH $\approx$ 7. $M_r = 235·0$ was determined by potentiometric titration and $M_r = 233·2$ was calculated from the formula, C$_9$H$_{15}$NO$_6$.

Sulphoacetic acid, HO$_3$SCH$_2$COOH, was prepared according to ref.[10] by the reaction of Na$_2$SO$_3$ with ClCH$_2$COONa. On addition of BaCl$_2$ to the neutral aqueous solution a small amount of white precipitate is formed immediately and was filtered off. White crystals of barium sulphoacetate then slowly separate from the solution (the yield is about 80%). The free acid is prepared by suspending the barium salt in water and removing the Ba^{2+} ions with a strongly acidic catex in the H$^+$-cycle; the substance then dissolves. The sulphoacetic acid solution did not contain SO$_4^{2-}$, Cl$^-$ and Ba^{2+}; its concentration was determined alkalimetrically.

RESULTS AND DISCUSSION

Complexes with Malonate and Oxalate

Solutions of malonic and oxalic acids (H$_2$L) with c_L 0·020M were titrated in the presence of Be(II), c_M 0·004M, and in its absence (c_L and c_M are the overall concentrations of the reagent and Be(II) in the solution, respectively). In the systems titrated, dissociation of the reagent, (*A*), (*B*), and complex formation, (*C*), (*D*), take place[7]

$$H_2L = HL^- + H^+, \quad K_{a1} \qquad (A)$$

$$HL^- = L^{2-} + H^+, \quad K_{a2} \qquad (B)$$

$$M^{2+} + L^{2-} = ML, \qquad K_1 \qquad (C)$$

$$ML + L^{2-} = ML_2^{2-}. \qquad K_2 \qquad (D)$$

With systems in which only reactions $(A)-(D)$ occur, equation (1) is employed for the calculation of function $_L\bar{z}$ which gives the average number of protons dissociated from the fully protonated reagent (the ionic charges have been omitted for the sake of simplicity)

$$_L\bar{z} = ([HL] + 2[L] + 2[ML] + 4[ML_2])/([H_2L] + [HL] + [L] + [ML] +$$
$$+ 2[ML_2]). \qquad (1)$$

If $c_M = 0$, expression (1) can be modified to give equation (2), the graphical transformation of which was used for the determination of constants K_{a1} and K_{a2} listed in Table I. For the calculation of the dissociation constants of the reagents were used the data measured at pH $3\cdot2 - 5\cdot8$ and $_L\bar{z}$ $0\cdot77 - 1\cdot77$ for malonic acid and pH $1\cdot9 - 3\cdot1$ and $_L\bar{z}$ $0\cdot22 - 1\cdot30$ for oxalic acid.

$$_L\bar{z}[H]/(1 - _L\bar{z}) = K_{a1} + (_L z - 2) K_{a1}K_{a2}/(_L\bar{z} - 1) [H]. \qquad (2)$$

In solutions with c_M $0\cdot004$M the same $_L\bar{z}$ values are reached in more acidic solution, than at $c_M = 0$. Equations $(3)-(5)$ permit the calculation of the reagent concentration which is not bound in the complex and of the Bjerrum function, $\bar{n}$.

$$[H_2L] = (2 - _L\bar{z}) c_L/(2 + K_{a1}/[H]), \qquad (3)$$

$$[ML] + 2[ML_2] = c_{L-}[H_2L] (1 + K_{a1}/[H] + K_{a1}K_{a2}/[H]^2), \qquad (4)$$

$$\bar{n} = ([ML] + 2[ML_2])/([M] + [ML] + [ML_2]), \qquad (5)$$

$$-\bar{n}/(\bar{n} - 1) [L] = K_1 + (\bar{n} - 2) [L] K_1K_2/(\bar{n} - 1). \qquad (6)$$

From the linear graphical transformation of equation (6), the K_1 and K_2 values given in Table I were obtained. During determination of these constants, the values measured in a pH interval of $2\cdot5 - 3\cdot5$ were used for malonic acid, where function $_L\bar{z}$ attains values of $0\cdot31 - 1\cdot15$ and $\bar{n}$ $0\cdot32 - 1\cdot43$ and pH $3\cdot1 - 3\cdot9$, $_L\bar{z}$ $1\cdot30 - 1\cdot60$ and $\bar{n}$ $0\cdot99 - 1\cdot11$ for oxalic acid.

Sulphoacetic acid can be derived from malonic acid by replacing a carboxylic group with a sulphonic group; this replacement causes a substantial decrease in the ligand affinity for Be(II). The titrations were carried out for this reagent using similar

concentrations as for malonic and oxalic acids but no complex formation with Be(II) was observed.

Complexes with NTP and NTA

The first two steps of the dissociation of NTP and NTA (H_3L), (E) and (F), take place in acidic solutions, while the proton from the ammonium group is dissociated by reaction (G) only in alkaline media[20]
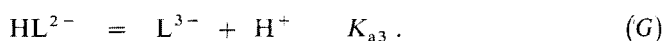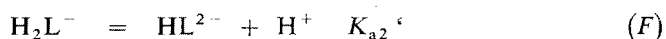
$$H_3L \;=\; H_2L^- \;+\; H^+ \quad K_{a1}, \qquad (E)$$

$$H_2L^- \;=\; HL^{2-} \;+\; H^+ \quad K_{a2} \text{`} \qquad (F)$$

$$HL^{2-} \;=\; L^{3-} \;+\; H^+ \quad K_{a3}. \qquad (G)$$

TABLE I

A Survey of the Dissociation Constants of the Reagents and of the Stability Constants of the Be(II) Complexes

$t = 20°C, I = 0.11.$

Reagent	pK_{a1}	pK_{a2}	pK_{a3}	pK_{a4}	$\log K_1$	$\log K_2$	Reference
Malonic acid	2·70	5·40			5·30	3·26	this paper
					5·73	3·55	7
					5·15	3·33	13
	2·61	5·27					14
Oxalic acid	1·05	3·92			4·08	1·30	this paper
					4·08	1·83	13
					4·12		15
Sulphoacetic acid		3·82					this paper
NTA	1·61	2·74	9·82		7·64		this paper
	1·89	2·49	9·73		7·11		15
NTP	3·79	4·33	9·60		7·90		this paper
	3·67	4·42	9·30				3
EDTA	2·10	2·77	6·30		9·7		this paper
					10·2		16
					10·8		16
					9·27		15
					8·2		19
					8·4		17
	1·99	2·67	6·16	10·26			18

The first two dissociation constants of the reagents were determined from the measurements in acid solutions with $c_M = 0$, c_L 0.0016M in a pH region of $3.8 - 5.8$ for NTP and c_L 0.0035M and pH $3.3 - 3.9$ for NTA; the $_L\bar{z}$ function attains values of $0.67 - 1.95$ and $1.79 - 1.93$, respectively. It follows from K_{a1} and K_{a2} values determined by means of graphical transformation of equation (2) that the carboxylic groups in NTP are less acidic than those in NTA.

The dissociation constant of the least acidic hydrogen was obtained from titration of alkaline solutions with a c_L value identical to that employed for the determination of the former two constants. The pK_{a3} value was found from the linear dependence, $\log \left(_L\bar{z} - 2\right)/(3 - _L\bar{z}) = f(pH)$. In regions of pH of $9.0 - 11.0$ and of $_L\bar{z}$ of $2.18 - 2.97$ for NTP and pH $9.0 - 10.60$ and $_L\bar{z}$ $2.15 - 2.98$ for NTA, the dependence is linear with unit slope and intersects the pH-axis in the point at which $pH_{_L\bar{z}=2.5} = pK_{a3}$. The pK_{a3} values (Table I) were determined in a medium 0.1M in K^+. With NTP, the effect of lithium ions on the dissociation of the ammonium proton was followed in solutions in which $\left[K^+\right] + \left[Li^+\right] = 0.1M$. The dependence found is $pH_{_L\bar{z}=2.5} = K_{a3} + 1.5 \cdot 10^{-9}[Li]$. The $1.5 \cdot 10^{-9}$ value is the equilibrium constant of reaction (H), provided that potassium ions do not form the analogous complex KL^{2-}. As the formation of poorly stable complexes[11] with the alkali metal ions has been found for most substances related to EDTA, it is probable that this value for the constant of the LiL^{2-} complex is also subject to some error. However, the value found indicates clearly that the stability of the lithium complex with NTP is low.

$$Li^+ + HL^{2-} = LiL^{2-} + H^+ \qquad (H)$$
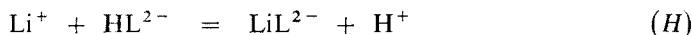
The formation of complexes with Be(II) is manifested in an increased consumption of the base required for attaining the same pH in a weakly acidic region, when solutions with the same c_L value (0.0032M) and values of $c_M = 0$ and $c_M = 1.74 \cdot 10^{-3}$M are compared. In weakly acidic solutions the formation of the complex (reaction (I)) takes place in addition to reagent dissociation (reactions (E) and (F)). The $_L\bar{z}$ quantity is then characterized by equation (7)

$$M^{2+} + HL^- = ML^- + H^+ \quad *K_1 , \qquad (I)$$
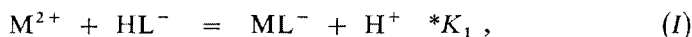
$$_L\bar{z} = ([H_2L] + 2[HL] + 3[ML])/([H_3L] + [H_2L] + [HL] + ML]) . \qquad (7)$$

The following assumption was made in calculating the $*K_1$ value: In a reagent solution with $c_M = 0$ the $_L\bar{z}$ function has a value of $_L\bar{z}_0$ and the reagent is present in variously protonated forms in dependence on the pH and the acidity constants of the reagent. On addition of ions of metal M and adjustment of the pH to the original value, the $_L\bar{z}$ value increases from $_L\bar{z}_0$ to $_L\bar{z}_m$ owing to the formation of complex ML.

If the portions of the individual forms of the reagent bound in complex ML are denoted as $[H_3L]'$, $[H_2L]'$ and $[HL]'$, then equation (8) is valid. Since the reaction of ion M with H_3L, H_2L and HL leads to liberation of 3, 2 and 1 proton, respectively, equation (9) is also valid.

$$[ML] = [H_3L]' + [H_2L]' + [HL]' = [HL]'(1 + [H]/K_{a2} + \\ + [H]^2/K_{a1}K_{a2}). \tag{8}$$

$$\left(_L\bar{z}_m - {}_L\bar{z}_0\right) c_L = [HL]' \left(1 + 2[H]/K_{a2} + 3[H]^2/K_{a1}K_{a2}\right), \tag{9}$$

$$[M] = c_M - [ML]. \tag{10}$$

$$c_L - [ML] = [HL] \left(1 + [H]/K_{a2} - [H]^2/K_{a1}K_{a2}\right). \tag{11}$$

From equation (9) auxiliary quantity $[HL]'$ is calculated as the only unkown value in the equation. Then $[ML]$ is calculated from equation (8), $[M]$ from (10) and $[HL]$ from (11), thus obtaining all the quantities required for the calculation of constant $*K_1$.

From 8 points on the titration curve of solutions with c_M 0·00174M and c_L 0·00324M, in a pH range of $3·8 - 5·2$, where $_L\bar{z}_0 = 0·67 - 1·87$ and $_L\bar{z}_m = 0·73 - 2·36$, $*K_1 = = 1·74 . 10^{-2}$ was calculated for NTP with a relative standard deviation of $s_r = 5\%$ $(s_r = 35·12 \, R/*K_1$, where R is the difference between the largest and the smallest constant value found). The calculation for NTA was also carried out using 8 points, with c_M, 0·00182 M, c_L 0·0035M, pH $3·5 - 4·2$, $_L\bar{z}_0 = 1·85 - 1·96$, $_L\bar{z}_m = 1·88 - 2·09$, $*K_1 = 6·65 . 10^{-3}$ and $s_r = 7\%$. The equilibrium constants were simultaneously calculated employing the Tesla 200 computer and the POT 3 program (ref.[12]); the values obtained, $*K_1$ 1·86 . 10^{-2} for NTP and 6·70 . 10^{-3} for NTA agree with the manually calculated values. Using the formula, $K_1 = *K_1/K_{a3}$, the equilibrium constants were recalculated to give stability constants (Table I).

In agreement with the above assumption of the greater stability of six-membered chelate rings for central atoms from the first short period, NTP yields a complex with Be(II) with a K_1 value larger than that for the corresponding NTA complex; the reverse stability order has been found[3] for the complexes of NTP and NTA with the transition metals. The numerical difference in $\log K$ for the beryllium(II) complexes with NTP and NTA is not very large. The difference in the stabilities of the complexes is more pronounced in neutral and alkaline media. Turbidity of beryllium(II) hydroxide appears in NTA solutions on increasing their basicity and an amount of base equal c. to the sum $3c_L + 2c_M$, is required in order to reach pH ≈ 11 (i.e. pH $\approx pK_{a3} + 2$). On the contrary, NTP alkaline solutions with Be(II) remain transparent, hydrolysis of Be(II) is suppressed and amount of base corresponding to $3c_L$ is sufficient for attaining pH ≈ 11. These differences also affect the shape of the titration curves:

with NTP the titration curves for the reagent alone and for a solution containing the same c_L and Be(II) with $c_L > c_M$ are virtually identical at pH $\approx$ 11; with NTA an alkaline solution containing Be always requires a higher base consumption than a solution of the reagent alone with the same c_L.

The EDTA Complex

Only 2 protons dissociate from the tetrabasic acid, EDTA, in weakly acidic media. Constants K_{a1} and K_{a2} were obtained from the titration curve for solutions with $c_M = 0$ and c_L 0·0025M in a pH range of 2·7−3·8 and $_L\bar{z}$ 1·27−1·91, in the same manner as previously; constant K_{a3} was also determined in the same way as for NTP and NTA.

In the presence of Be(II) at c_M 0·00104M and c_L 0·0025M, $_L\bar{z}_m$ is larger than $_L\bar{z}_0$ for pH greater than 3·5. Reaction (J) takes place in the solution and function $_L\bar{z}$ is characterized by equation (12).

$$M^{2+} + H_2L^{2-} = ML^{2-} + 2\,H^+ \quad *K_1 \qquad (J)$$
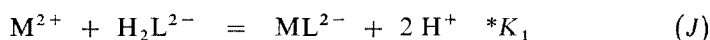
$$_L\bar{z} = ([H_3L] + 2[H_2L] + 3[HL] + 4[ML])/([H_4L] + [H_3L] + [H_2L] +$$
$$+ [HL] + [ML]) . \qquad (12)$$

The $*K_1$ value was calculated analogously as for NTP and NTA; only the different numbers of protons dissociated in reactions (J) and (I) had to be taken into consideration. Evaluation of eight experimental points at pH 4·0−4·7, $_L\bar{z}_0 = 1·94−2·00$ and $_L\bar{z}_m = 1·98−2·26$ gave $*K_1 = 2·32 . 10^{-1}$ and $s_r = 28\%$. The considerable scatter of the K_1 values given in the literature (Table I) and the relatively high s_r value obtained in the present paper indicate that other, probably hydrolytic, processes can simultaneously occur in the solution. The Be(II) complexes with EDTA and NTA are easily hydrolyzed and their equilibrium constants could be determined from the experimental points only in a narrow acidity range $(pH_{max} - pH_{min} < 1)$. The complex with NTP that is not subject to hydrolysis can be evaluated in a broader acidity range $(pH_{max} - pH_{min} > 1)$; the scatter of the calculated values is also smaller than for the NTA and EDTA complexes.

Alkalimetric Determination of Be(II)

An alkalimetric determination of free acid in solutions of beryllium(II) salts has also been described[9]. The titration with a 0·1M standard NaOH solution is performed in a fluoride medium using indicator Phenol Red; the base consumption, v_1, gives the concentration of free acid, $v_1 = k . c_H$. The formation of the fluorocomplex prevents hydrolysis of Be(II). An attempt to replace fluoride with malonate was

unsuccessful. If malonate solutions with c_L 0·1M and c_M 0·02M are titrated using phenolphthalein indicator, $80-90\%$ of the Be present is complexed (reactions (C) and (D)) (only 10% of the Be is complexed in an oxalate medium under the same conditions) and the remainder is hydrolyzed to $Be(OH)_2$. Because of the low acidity of malonic acid, an indicator with a colour change in a more acidic region cannot be employed and if the malonate concentration is substantially increased the colour change of the indicator becomes drawn-out. Hence malonate is unsuitable for suppressing hydrolysis during the determination of acid in solutions of beryllium(II) salts.

If c_H is known, c_M is determined by titration in a sodium salicylate medium with indicator Phenol Red[9]. One mole of Be^{2+} liberates two moles of hydrogen ions on reaction with salicylate; the consumption is $v_2 = k(c_H + 2c_M)$. Be(II) reacts slowly with the disodium salt of NTP. During this reaction, (I), one mole of protons is liberated per mole Be and it can be titrated using Phenol Red or Bromothymol Blue; $v_3 = k(c_H + c_M)$.

Procedure: 20 ml of 0·03M NTP disodium salt is neutralized using the selected indicator, an acidic solution of a beryllium(II) salt is added (> 1 mg Be, $c_L \geqq 2c_M$), the mixture is diluted with water to 40 ml, allowed to stand about 30 min at laboratory temperature $(\approx 20°C)$ and then titrated with 0·1M-NaOH. The composition of the Be(II) solution in dilute acid was obtained simultaneously from the consumptions, v_1 and v_2, $c_M = 51·03$ mM, $c_H = 53·16$ mM, and v_2 and v_3, $c_M = 51·60$ mM, $c_H = 52·40$ mM. The good agreement of the results shows that NTP is suitable for the alkalimetric determination of Be(II). The v_2 and v_3 values were determined with relative standard deviations of 0·5 and 0·6%, respectively.

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