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CALORIMETRIC INVESTIGATION OF COPPER(II) AND LEAD(II) COMPLEXES WITH LACTATE AND 3-HYDROXYPROPIONATE

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ABSTRACT

The enthalpies of ligation of H^+, Cu^{2+}, and Pb^{2+} to lactate and 3-hydroxypropionate ions were determined by calorimetry at 298.15 K in aqueous $NaClO_4$ (2 mol dm^{-3}). The first two (stepwise) ligational enthalpies are of small magnitude (the first usually exothermic, the second endothermic) while the third is strongly exothermic, possibly indicating a change in the kind of bonding.

INTRODUCTION

The stability of metal complexes with monocarboxylate and hydroxymonocarboxylate ligands was systematically investigated in this laboratory using various methods (see e.g. ref. 1). In order to support the stability data with the information from an independent source and to clarify the way of metal–ligand bonding in these complexes a thermochemical investigation was designed.

EXPERIMENTAL

All reagents were of analytical reagent grade; ligands were purified by repeated recrystallisation. Ligand solutions were standardised by alkalimetric titration and the metal ion stock solutions by complexometry. Sodium perchlorate was recrystallised from water (once), and metal perchlorates three times, also from water.

The calorimeter used in the present work was described by Ivičić and Simeon[2]. pH measurements were made by means of a Metrohm E 436 Potentiograph equipped with a combined glass/Ag, AgCl electrode, standardised against a 0.02 mol dm^{-3} $HClO_4$ solution in 1.98 mol dm^{-3} $NaClO_4$; pH is thus defined on the concentration scale: $pH = -\log([H^+]/(\text{mol dm}^{-3}))$.

To determine the ligational heats the calorimeter was charged with 35 cm^3 of half-neutralised ligand solution ($pH_i = pK$) and the ampoule with 0.8 cm^3 of

metal perchlorate solution. Both solutions contained $NaClO_4$ (2 mol dm^{-3}) to maintain an approximately constant ionic strength. After assembling, the calorimeter was left to thermally equilibrate with the thermostat bath kept at 298.15 ± 0.1 K. The bath was controlled to 1 mK by means of a Tronac 1000 A temperature controller. The initial and final rating periods lasted at least 10 min while the duration of the main period was typically 2 to 4 min. Each "chemical" run was followed by an electrical calibration. The corrected temperature rise was evaluated using Dickinson's method. The enthalpies of ligand protonation were determined in much the same way: the ligand solution was contained in the ampoule and the calorimeter was charged with a 2 mol dm^{-3} $NaClO_4$ solution containing an adequate (> 10%) excess of NaOH to suppress the hydrolysis.

The final pH in the ligational-heat determinations (pH_f) was determined in a separate series of experiments in order to ensure a long enough time for the equilibration of the glass electrode and for a very careful calibration. The amounts of various species (HL, ML, ML_2, ML_3) were calculated from the analytical concentrations (C_H, C_L, C_M), initial and final pH values and relevant stability constants which were taken from ref. 1. After computing the composition of the solutions and after allowing for the heats of dilution and protonation (Q_{HL}) a set of three simultaneous equations of the type

$$n(ML)\ \Delta_{01}H + n(ML_2)\ \Delta_{02}H + n(ML_3)\ \Delta_{03}H = -Q_c/n_M \qquad (1)$$

where $Q_c = Q_R - Q_{HL} - Q_{dil}$, was obtained and solved for the cumulative ligational enthalpies, $\Delta_{0n}H$. The species with $n < 0.01\ n_M$ were neglected in the computations.

TABLE 1

LIGATION OF Cu^{2+} AND Pb^{2+} TO LACTATE AND 3-HYDROXYPROPIONATE IONS — CALORIMETRIC DATA

Ligand	*Central ion*	C_L *(mol dm^{-3})*	C_M *(mol dm^{-3})*	pH_f	Q_R*(J)*	Q_{dil}*(J)*	Q_{HL}*(J)*	Q_c*(J)*
Lactate	Cu^{2+}	0.05534	0.04612	2.813	10.13(3)	8.51(17)	−0.40	2.02(24)
		0.09076	0.04612	3.075	10.31(22)	8.51(17)	−0.23	2.03(28)
		0.2912	0.006657	3.325	13.49(16)	9.76(25)	−0.11	3.84(30)
	Pb^{2+}	0.06044	0.05036	2.982	6.70(3)	2.29(5)	−0.26	4.67(6)
		0.1008	0.05036	3.153	5.33(4)	2.29(5)	−0.15	6.22(6)
		0.2521	0.05036	3.596	9.50(13)	2.29(5)	−0.11	7.32(14)
3-Hydroxy-propionate	Pb^{2+}	0.06044	0.05036	3.620	2.12(1)	2.29(5)	0[a]	−0.17(5)
		0.1007	0.05036	3.880	1.78(2)	2.29(5)	0[a]	−0.51(5)
		0.2969	0.05036	4.130	4.31(6)	2.29(5)	0[a]	2.02(8)

[a] $|Q_{HL}| < 0.01$ J.

TABLE 2

STEPWISE EQUILIBRIUM CONSTANTS[a], ENTHALPIES, AND ENTROPIES OF LIGATION OF H^+, Cu^{2+}, AND Pb^{2+} TO LACTATE AND 3-HYDROXYPROPIONATE IONS AT 298.15 K (IN 2 MOL DM^{-3} AQ. $NaClO_4$)

System	*n*	*log* K_n^*	$\Delta_{n-1,n}H^*$ (*kJ mol*$^{-1}$)	$\Delta_{n-1,n}S^*$ (*J K*$^{-1}$ *mol*$^{-1}$)
H^+ + lactate	1	3.82	− 7.1	49
Cu^{2+} + lactate	1	2.66	− 2.6	42
	2	1.62	− 4.4	46
	3	0.61	−17.4	−570
Pb^{2+} + lactate	1	2.16	− 7.5	16
	2	1.07	− 18.3	82
	3	0.44	− 90	−290
H^+ + 3-hydroxypropionate	1	4.56	− 1.4	53
Pb^{2+} + 3-hydroxypropionate	1	2.10	− 0.2	41
	2	1.07	− 2.4	29
	3	0.34	− 54	−170

[a] Taken from ref. 1.

RESULTS

The basic calorimetric and analytical data are collected in Table 1. Each Q term is a mean of at least ten independent calorimetric runs. The figures in parentheses are double standard errors of the mean. Although it is difficult to assess the contribution of the non-calorimetric sources of error to the overall uncertainty in Q_e this is unlikely to exceed some 10%. No data were collected for copper 3-hydroxypropionates because the precipitation occurred at the concentrations high enough to permit the calorimetric measurement.

Standard thermodynamic functions (log K^*, $\Delta_{n-1,n}H^*$, $\Delta_{n-1,n}S^*$), given in Table 2, refer to the stepwise ligation reactions of the general type

$$ML_{n-1} + L = ML_n \qquad (2)$$

As the concentration of any reacting species was considerably lower than the concentration of the background electrolyte the measured enthalpy changes should be very close to the respective standard values. The standard state is defined here for every reacting species as a hypothetical ideal solution of unit concentration ($c^\ominus$ = mol dm^{-3}) in 2 mol dm^{-3} aqueous $NaClO_4$ which is regarded as a solvent. In order to distinguish the so defined standard state from the conventional one ($\ominus$) it is denoted by * superscript.

DISCUSSION

It can be inferred from the data in Table 1 that the net ligational heat effects, Q_e, are essentially differences of two larger numbers and that their reliability is thereby considerably reduced. This especially applies to the data for copper lactates,

and to the protonation enthalpies. Although for the latter case the primary data are not displayed it may be said that here too a difference of two large numbers — the measured heat and the heat of ligation of H^+ to OH^- — is taken. It is a fortunate circumstance, however, that the contribution of Q_{III} term is comparatively small or even nil.

Whatever the uncertainties in the reported data may be, it is not likely that they could alter the basic relationships between the values displayed in Table 2. What justifies such a belief are the magnitudes of the proportions of individual ML_n species in experiments with different C_L/C_M ratios. The experiments were designed in such a way that at the lowest value of C_L almost exclusively ML complex was formed; at the next higher C_L there was a mixture of ML and ML_2 and, finally, at the highest C_L some ML_3 was present, along with quite high amounts of the first two complexes. Because of a low amount of ML_3 complex (4–11%) the $\Delta_{23}H$'s are probably the least reliable of all the values determined.

The first step in the metal ligation is accompanied by a small, usually exothermic, enthalpy change. The second step is endothermic, the magnitude of ΔH being similar as in the first one. The final step is strongly exothermic. This large exothermic enthalpy change is, however, almost compensated by an adequately high negative entropy change.

Although it is difficult to draw any conclusions on the ground of a rather limited body of data it seems that a kind of rearrangement takes place when the third ligand molecule enters the coordination sphere of the metal ion. Such a conclusion is suggested by surprisingly high exothermic $\Delta_{23}H^\circ$ values (and corresponding highly negative $\Delta_{23}S^\circ$). According to Larsson[3] up to three kinds of bonding can be observed in glycolate complexes with a given central ion: (i) the ligand may act as unidentate, coordinating via its carboxylate group only, (ii) chelates with carboxylate and alkoxylate donor groups may be formed, and (iii) a chelate ring may be closed including the carboxylate group, the central ion, a water molecule and finally the alkoxylate group. For a given composition of the complex, ML_n, even a mixture of all the three bonding isomers is possible. It should be mentioned that Larsson's IR spectroscopic work was devoted exclusively to ML complexes which means that an even greater complexity may be expected in the present case. Therefore a more exhaustive study of these kinds of complexes seems to be necessary to clarify their thermochemistry.

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