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STUDIES ON POLYFUNCTIONAL *O*-LIGANDS. SOLUBILITY AND THERMAL STABILITY OF 1,2,4,5-BENZENETETRACARBOXYLATE COMPLEXES WITH ALKALI AND ALKALINE EARTH METAL IONS

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ABSTRACT

A solubility and thermoanalytical study of alkali and alkaline earth solid complexes of pyromellitic acid (1,2,4,5-benzenetetracarboxylic acid, H_4L) is reported. The insoluble Na^+ species is Na_2LH_2. K^+, Rb^+ and Cs^+ form MLH_3. The stoichiometry of precipitation of H_4L with Ca^{2+}, Ba^{2+} and Sr^{2+} depends on pH: at $pH < 4$, MLH_2 is formed; in the range $4 < pH < 4.5$, we found a mixture of MLH_2 and M_2L; and at $pH > 4.5$, only M_2L is formed. The pK_{s0} of all the species were determined. The insoluble compounds were also characterized by thermogravimetric analysis.

INTRODUCTION

The benzenepolycarboxylic acids represent an interesting class of compounds, in that they are the simplest constituents of larger molecules, such as fulvic and humic acids. Despite their remarkable interest, however, there are few studies of these compounds in the literature, and most of those that are available are concerned with their protonation constants. Difficulties which have discouraged a systematic analysis of the complexing ability of the benzenepolycarboxylic acids include the low solubility of the ligands and the very low solubility of the cation complexes. In addition, the great number of charges on the ligand makes it difficult to study these complexes at low ionic strengths, while a large concentration of salts used as background can result in precipitation of the complexes with alkali cations. For instance, in the case of 1,2,4,5-benzenetetracarboxylic acid, only lithium salts can be used to obtain background concentrations higher than 0.5 mol dm^{-3}.

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These difficulties notwithstanding, in consideration of the great interest of this class of ligands, we have undertaken a systematic study, involving: (a) determination of the protonation constants, at different temperatures and ionic strengths, of the various benzene hexa-, tetra-, tri- and bicarboxylic acids in tetraethylammonium iodide medium; (b) determination of the formation constants of the complexes of these acids with alkali, alkaline earth and transition cations; (c) determination of the solubilities of the precipitates.

The techniques employed were: (i) potentiometric titrations with selective electrodes for protonation and complexation studies in homogeneous phase; (ii) spectrophotometric UV analysis to determine the composition of the insoluble compounds; (iii) thermogravimetry for complete characterization of the insoluble compounds.

In the present work, we report solubility and thermoanalytical results for alkali and alkaline earth solid complexes of pyromellitic acid (1,2,4,5-benzenetetracarboxylic acid, H_4L).

EXPERIMENTAL

Materials

The 1,2,4,5-benzenetetracarboxylic acid was purified by recrystallization from water [1]; a solution (40 mmol dm^{-3}) was prepared and standardized using KOH. Alkali chloride solutions were prepared by weighing pure salts previously dried in a stove at 110 ° C. Alkaline earth chloride solutions were prepared using pure p.a. salts and standardized using EDTA [2]. Alkaline hydroxides and hydrochloric acid solutions were prepared either by diluting C. Erba or Merck ampoules, or directly from the solids, and standardized using potassium hydrogenphthalate. Alkaline earth hydroxides were employed without further purification. Grade A glassware and twice-distilled water were used in the preparation of all the solutions.

Precipitation experiments

The pH of the solution was measured using a Metrohm Model 654 potentiometer, coupled with a Ross Model 8102 glass–calomel electrode, supplied by Orion. The electrode system was standardized in terms of hydrogen ion concentration, under the same ionic strength conditions as the solution under study.

The spectrophotometric measurements were carried out using a Beckman model DU 50.

Appropriate quantities (see tables) of H_4L, hydroxide and chloride solutions (or solid reagents) were placed into glass ampoules (length 20 cm and diameter 3 cm) with a Teflon screw plug located in the middle of their length. The ends of the ampoules were hemispherical in shape, to allow uniform shaking of the mixture. The final volume of all the solutions was 120 cm^3. An ultrasound apparatus was employed as necessary, to dissolve the solid reagents.

Precipitation occurred almost immediately, but in any case the solution was stored for 24 h at 25 ± 0.5 °C. The pH was then measured at 25 °C. Separation was carried out by filtration of the mixture, and the solution was collected in a 100 cm^3 volumetric flask in which had previously been placed distilled water (to prevent precipitation) or HCl (to prevent carbonation of the alkaline solutions). A small part of the insoluble compound, well washed, was dissolved in water and placed in a volumetric flask. We then proceeded to analyze the solution and the precipitate. H^+ was titrated with standard KOH solution using phenolphthalein as indicator; Ca^{2+} was determined by EDTA titration at pH = 12 using murexide [2]; Ba^{2+} and Sr^{2+} were titrated with EDTA in ammonia buffer using methyl timole blue [2] *. L^{4-} was determined spectrophotometrically. The UV spectrum of a solution of the ligand, made alkaline up to pH 12, shows a shoulder at 252 nm and a large, well defined plateau at 285 nm. It was useful to utilize the absorption at 285 nm, where the deprotonated ligand L^{4-} has $\epsilon = 1363 \pm 1$ dm^3 mol^{-1} cm^{-1}. At this wavelength we did not find any spectral interference between L^{4-} and other species present in the solution. The concentration of the ligand was determined by measuring the absorption of samples prepared by diluting appropriate aliquots of the solution under study (normally 1 or 10 cm^3 in 100 cm^3) and made alkaline by KOH 2M (2 cm^3 in 100 cm^3).

Thermal analysis

A Perkin–Elmer thermobalance TGS-2 equipped with data station working at a heating rate of 10 °C min^{-1} was used to characterize the insoluble compounds. The atmospheres used were air or very pure oxygen (99.99%) at a flow rate of 50–100 cm^3 min^{-1}. In air a sublimation process occasionally overlapped the decomposition process, whereas when an oxygen atmosphere was used the decomposition took place at lower temperatures and at the same time the increasing oxidative power of the gas surrounding the sample facilitated the thermal demolition, so that sublimation was avoided. In a very few cases, the oxygen atmosphere was not suitable because the decom-

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* Because of the low concentration of the component in the solution under study, Me^{2+} and H^+ were determined together. This determination was necessary for a correct speciation of the precipitate, where low proton and ligand concentrations might have suggested an incorrect interpretation.

position reaction became explosive in oxygen, but the corresponding samples did not show sublimation in air.

ANALYSIS OF PRECIPITATION DATA

The concentrations of H^+ and L, obtained by analyzing the solution after precipitation, together with the values of initial concentration of the components of the reaction, (C_L^0, C_{OH}^0, C_H^0), allowed us to define the empirical formula of the precipitate. If we indicate with $[M_pLH_q]_s$ the solid obtained, we have

$$H = C_H^0 - C_{OH}^0 - q[M_pLH_q]_s \tag{1}$$

$$H = 4C_L^0 - C_{OH}^0 - q(C_L^0 - L) \tag{2}$$

from which

$$q = (4C_L^0 - C_{OH}^0 - H)/(C_L^0 - L) \tag{3}$$

and then

$$\text{for } M^+, \quad p = 4 - q; \quad \text{for } M^{2+}, \quad p = (4 - q)/2 \tag{4}$$

Quantitative analysis of the solids confirmed the empirical formula of the precipitate.

CALCULATION OF SOLUBILITY

Once the composition of the solution in the presence of insoluble species is known, it is possible to obtain the solubility product

$$K_{s0} = [M^{z+}]^p[L^{4-}][H^+]^q$$

TABLE 1

Formation constants of H^+, Na^+, K^+ and Ca^{2+} pyromellitate complexes at $I = 0$ mol dm^{-3} and $T = 25$ °C [a]

M	pq [b]	$\log \beta_{pq}$	M	pq [b]	$\log \beta_{pq}$
H	01	6.09	K	13	14.33
	02	10.86		20	3.4
	03	13.86		21	8.8
	04	15.81		22	12.8
Na	13	14.22	Ca	10	5.38
	20	3.5		11	10.11
	21	8.7		12	13.55
	22	12.6		20	8.29

[a] See refs. 5 and 6.

[b] The indices refer to the reaction $pM^{z+} + L^{4-} + qH^+ = [M_pLH_q]^{pz+q-4}$.

TABLE 2

Analytical details for the precipitation reactions of H_4L with Na^+

	Initial conditions [a]			Analysis of solution [a]					Analysis of precipitate [b]		
	C^0_L	C^0_{NaOH}	C^0_{NaCl}	pH	H	L	q [c]	p [c]	H	L	H/L
1	20.01	0.0	1000	1.425	46.98	3.91	2.05	1.95	0.1254	0.0640	1.96
2	20.01	0.0	500	1.561	59.14	9.57	2.00	2.00	0.2159	0.1075	2.01
3	20.01	0.0	200								
4	20.01	20.0	1000	1.667	23.06	1.56	2.00	2.00	0.1419	0.0694	2.04
5	20.01	20.0	500	1.801	27.29	4.08	2.06	1.94	0.1172	0.0591	1.98
6	20.01	20.0	200	2.065	42.00	11.01	2.00	2.00	0.1902	0.0948	2.00
7	20.01	40.0	1000	4.151	2.26	1.30	2.02	1.98	0.0646	0.0318	2.03
8	20.01	40.0	500	4.200	2.60	1.37	2.01	1.99	0.0932	0.0469	1.99
9	20.01	40.0	200	4.152	4.91	2.89	2.05	1.95	0.1135	0.0586	1.94
10	20.01	63.0	879	5.05	3.35	13.17	2.00	2.00	0.0867	0.0441	1.97
11	19.50	4.9	96	Mean ($3\sigma = 0.024$)			2.021	1.979	Mean ($3\sigma = 0.034$)		1.985
12	19.50	−41.0	481								
13	19.50	−41.0	291								
14	32.00	0.0	100								
15	32.00	0.0	200								
16	32.00	0.0	29								
17	26.00	0.0	188								
18	20.01	75.0	500								
19	20.01	90.0	500								

[a] Concentrations in mmol dm^{-3}. (Negative C^0_{NaOH} indicates HCl addition.)

[b] Quantities in mmol.

[c] From eqns. (3) and (4), and referring to the species M_pLH_q.

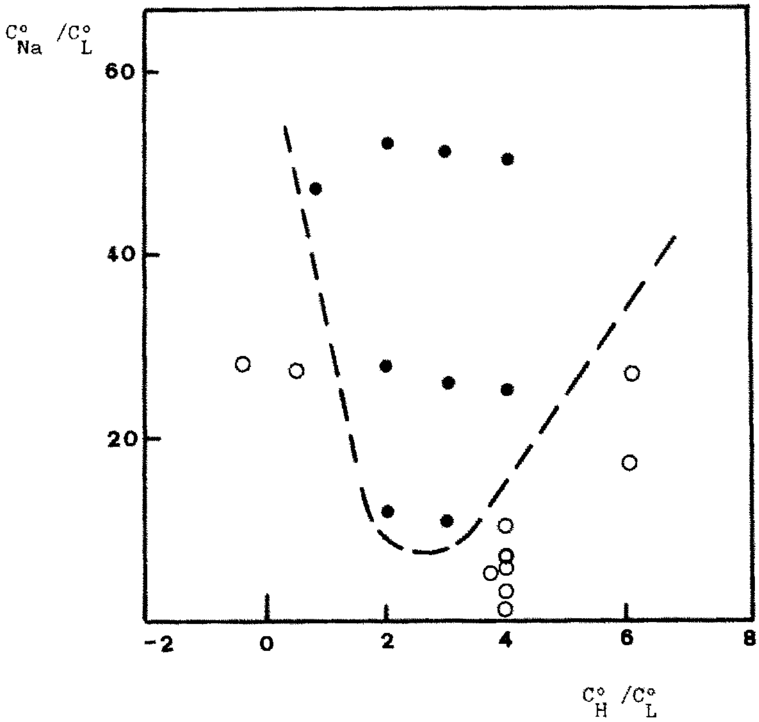

Fig. 1. Analytical conditions for the precipitation of Na_2LH_2: ●, formation of precipitate; ○, complete solubility.

by calculating the free concentrations of the species using the computer program ES4EC [3,4]. In this calculation, the protonation constants [5] of the ligand and the formation constants of soluble species with alkali [5] and alkaline earth metals [6] were taken into account, as reported in Table 1. For the calculation of the $[RbLH_3]^0$ and $[CsLH_3]^0$ solubilities, the formation constants of the K–L and Na–L systems were taken into account, without significant differences in pK_{s0}. Similarly, for $[BaLH_2]^0$, $[Ba_2L]^0$, $[SrLH_2]^0$ and $[Sr_2L]^0$, the formation constants of the Ca–L system were used.

RESULTS AND DISCUSSION

Insoluble alkali metal species

Table 2 gives analytical details of the precipitation of pyromellitate with Na^+. The concentrations of reactants were chosen so as to give the most complete picture possible of the system under study. Having calculated p and q by eqns. (3) and (4), we can affirm that the only insoluble species formed was Na_2LH_2. Attempts to obtain other insoluble species, and in

TABLE 3

Analytical details for the precipitation reactions of H_4L with K^+

	Initial conditions [a]			Analysis of solution [a]					Analysis of precipitate [b]		
	C_L^0	C_{KOH}^0	C_{KCl}^0	pH	H	L	q [c]	p [c]	H	L	H/L
1	20.06	20.0	1000	2.659	16.62	5.54	3.00	1.00	0.1619	0.0569	2.98
2	20.06	20.0	800	2.598	18.53	6.19	3.01	0.99	0.0642	0.0221	2.91
3	20.06	20.0	650	2.604	21.16	7.30	3.06	0.94	0.1285	0.0426	3.01
4	20.06	20.0	500	2.369	23.92	8.12	3.04	0.96	0.0833	0.0273	3.05
5	20.06	20.0	300	2.492	32.13	10.79	3.03	0.97	0.1049	0.0352	2.98
6	19.81	0.0	1025	1.823	31.98	3.93	2.98	1.02	0.2056	0.0665	3.09
7	20.06	0.0	400	1.810	45.51	8.45	2.99	1.01	0.2734	0.0893	3.06
8	10.04	0.0	1000	2.078	21.47	3.81	3.00	1.00	0.2179	0.0709	3.07
9	37.00	0.0	1003	1.590	50.29	4.82	3.04	0.96	0.1850	0.0625	2.96
10	37.00	0.0	408	1.588	65.83	9.93	3.04	0.96	0.2652	0.0895	2.96
11	10.00	0.0	400								
12	20.01	30.0	500	2.872	39.62	16.57	3.03	0.97	0.1520	0.0510	2.98
13	20.01	45.0	1000								
14	20.01	75.0	1000								
15	20.01	90.0	1000								
16	20.01	20.0	200	2.398	43.38	14.39	2.96	1.04	0.1360	0.0457	2.98
				Mean ($3\sigma = 0.029$)			3.009	0.991	Mean ($3\sigma = 0.035$)		2.994

[a] Concentrations in mmol dm^{-3}.

[b] Quantities in mmol.

[c] From eqns. (3) and (4), and referring to the species M_pLH_q.

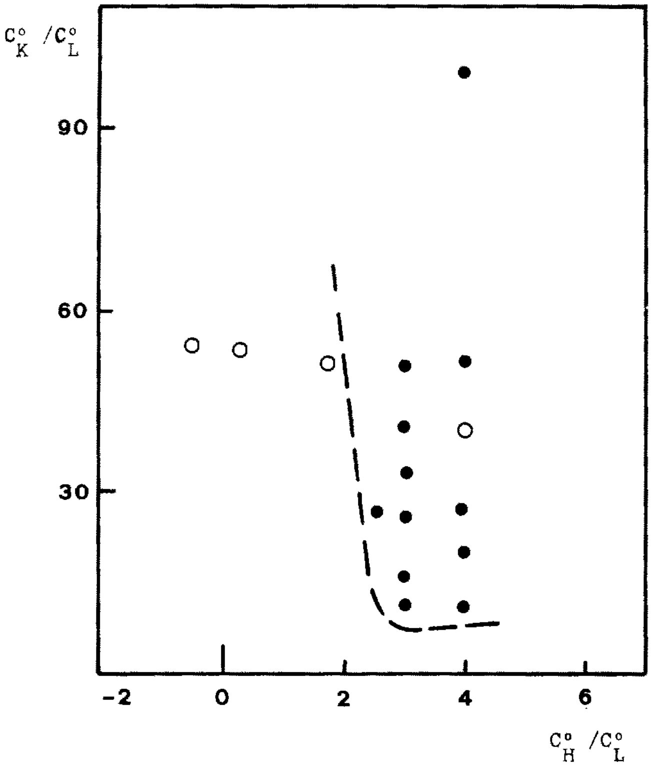

Fig. 2. Analytical conditions for the precipitation of KLH_3: ●, formation of precipitate; ○, complete solubility.

particular $NaLH_3$ (the only one found for the other alkaline cations), were unsuccessful.

In Fig. 1 are represented the quantities C^0_{Na}/C^0_L vs. C^0_H/C^0_L. This allows us to determine the composition of the solution at which precipitation occurs. In fact, we can note a region in which it is possible to achieve the precipitation of Na_2LH_2.

Table 3 gives analytical details concerning the precipitation reactions of H_4L with K^+. For this cation, and for Rb^+ and Cs^+ *, we found only one insoluble species, MLH_3, at different pH values. Figure 2 shows the results obtained for K^+. The ratio $C^0_H/C^0_L = 2$ is a division region between the precipitation conditions and solubility, for concentrations of ligand in the range 20–37 mmol dm^{-3}.

Insoluble alkaline earth metal species

Table 4 reports the analytical details of the precipitation reactions of H_4L with Ca^{2+}, together with the indices of Ca_pLH_q obtained under different

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* Supplementary data are available on request.

TABLE 4

Analytical details for the precipitation reactions of H_4L with Ca^{2+}

	Initial conditions [a]			Analysis of solution [a]					
	C_L^0	$C_{Ca(OH)_2}^0$	$C_{CaCl_2}^0$	pH	H	L	Ca	q [b]	p [b]
1	20.00	0.0	4.92	1.808	72.42	16.34	1.23	2.07	0.96
2	20.00	0.0	9.84	1.707	64.54	12.60	2.58	2.09	0.96
3	20.00	0.0	14.92	1.652	59.75	10.19	4.94	2.06	0.97
4	19.97	1.91	2.03	1.933	70.58	17.32	1.09	2.07	0.97
5	19.97	4.90	4.92	1.881	53.35	11.85	1.55	2.06	0.97
6	19.97	8.29	7.97	1.866	36.98	6.63	2.50	1.97	1.01
7	15.88	5.12	2.54	2.039	40.83	9.60	1.00	1.98	1.01
8	20.08	9.71	4.92	1.986	35.21	6.99	1.67	1.96	1.02
9	20.08	9.95	0.0	2.172	42.41	10.61	0.58	1.90	1.05
10	20.08	14.99	0.0	2.366	22.74	5.81	0.50	1.93	1.03
11	20.08	15.04	4.92	2.157	16.66	2.67	2.19	1.93	1.04
12	20.08	15.28	10.01	2.077	13.22	1.27	6.15	1.94	1.03
13	20.08	30.76	0.0	4.572	2.30	1.43	1.70	1.01	1.49
14	19.62	24.97	10.00	4.130	0.82	0.46	10.37	1.45	1.28
15	19.97	25.07	20.01	3.998	0.64	0.31	20.43	1.48	1.26
16	19.97	25.01	30.02	3.932	0.69	0.27	30.56	1.48	1.26
17	19.97	0.0	24.93	1.557	50.92	5.61	10.88	2.02	0.99
18	19.97	0.0	40.02	1.525	46.18	3.11	24.00	2.00	1.00
19	19.97	21.0	0.0	4.534	2.00	1.37	1.62	1.92	1.04
20	19.97	25.7	0.0	4.539	2.15	1.63	1.94	1.43	1.28
21	10.23	0.0	50.03	1.731	22.75	1.16	41.80	2.00	1.00
22	12.00	9.0	0.0	2.585	12.89	3.88	0.60	2.09	0.95
23	10.23	14.8	0.0	4.205	4.55	2.93	3.14	0.92	1.54
24	20.01	0.0	15.98	1.706	59.60	10.22	5.49	2.09	0.96
25	20.01	25.7	10.08	4.169	1.00	0.51	10.43	1.41	1.30
26	20.01	30.0	0.0	4.559	2.62	1.87	1.89	0.95	1.52
27	20.01	37.1	0.0	4.426	3.75	2.41	2.39	0.12	1.94
28	20.01	39.9	0.0	9.212	0.0	0.31	0.85	0.01	2.00
29	20.01	44.1	0.0	11.39	−5.80	0.09	3.34	−0.12	2.06
30	20.18	10.1	0.0	2.227	42.78	11.67	0.69	2.07	0.96
31	20.18	20.0	0.0	3.106	4.27	1.68	0.62	1.97	1.02
32	20.18	28.2	0.0	4.475	2.33	1.81	1.89	1.19	1.40
33	20.18	34.8	0.0	4.308	3.32	2.54	2.26	0.44	1.78
34	20.18	41.8	0.0	10.85	−1.11	0.22	1.07	−0.10	2.05
35	20.18	47.4	0.0	11.78	−12.91	0.08	6.87	−0.07	2.03

[a] Concentrations in mmol dm^{-3}. (Negative H indicates excess of OH^-.)

[b] From eqns. (3) and (4), and referring to the species M_pLH_q.

experimental conditions. Figure 3 shows the values of q (index of the proton) vs. the pH of the solutions, after precipitation. The stoichiometry of the precipitation depends on pH: at $pH < 4$, only $CaLH_2$ forms, whilst at $pH > 4.5$, we found only the deprotonated species Ca_2L. Mixtures of $CaLH_2$ and Ca_2L in varying proportion form in the range $4 < pH < 4.5$.

TABLE 5

Analytical details for the precipitation reactions of H_4L with Ba^{2+}

	Initial conditions [a]			Analysis of solution [a]					Analysis of precipitate [b]		
	C_L^0	$C_{Ba(OH)_2}^0$	$C_{BaCl_2}^0$	pH	H	L	q [c]	p [c]	Ba	L	Ba/L
1	20.01	0.0	499.7	1.399	42.31	1.14	2.00	1.00	0.0234	0.0239	0.98
2	20.00	10.06	49.97	1.820	21.68	1.68	2.09	0.96	0.0329	0.0326	1.01
3	20.01	0.0	19.99	1.754	59.94	9.92	1.99	1.00	0.0166	0.0168	0.99
4	20.01	0.0	10.27	1.879	66.28	13.30	2.05	0.97	0.0981	0.0100	0.98
5	20.01	0.0	10.24	1.869	66.69	13.24	1.97	1.01	0.0355	0.0354	1.00
6	19.76	0.0	54.88	1.586	47.90	4.56	2.05	0.98	0.0392	0.0396	0.99
7	20.01	0.0	200.14	1.472	43.21	2.11	2.06	0.97	0.0498	0.0508	0.98
8	20.01	10.0	49.9	1.804	24.01	2.03	2.00	1.00	0.0326	0.0323	1.01
9	20.01	40.03	53.48	4.531	0.0	0.0	–	–	0.0054	0.0055	0.98
10	20.01	12.49	49.98	1.919	17.01	1.30	2.03	0.98	0.0311	0.0317	0.98
11	16.92	13.40	0.0	2.664	19.92	6.81	2.07	0.96	0.1127	0.1138	0.99
12	16.92	20.62	0.0	2.688	6.43	7.08	2.03	0.98	0.0316	0.0310	1.02
13	16.92	29.89	0.0	3.065	0.0	0.0	–	–	0.0146	0.0143	0.97
14	16.92	38.14	0.0	11.53	−8.08	0.0	0.0	2.00	0.0826	0.0411	2.01
15	11.84	36.08	0.0	11.94	−23.46	0.0	0.0	2.00	0.0784	0.0388	2.02

[a] Concentrations in mmol dm^{-3}. (Negative H indicates excess of OH^-.)

[b] Quantities in mmol.

[c] From eqns. (3) and (4), and referring to the species M_pLH_q.

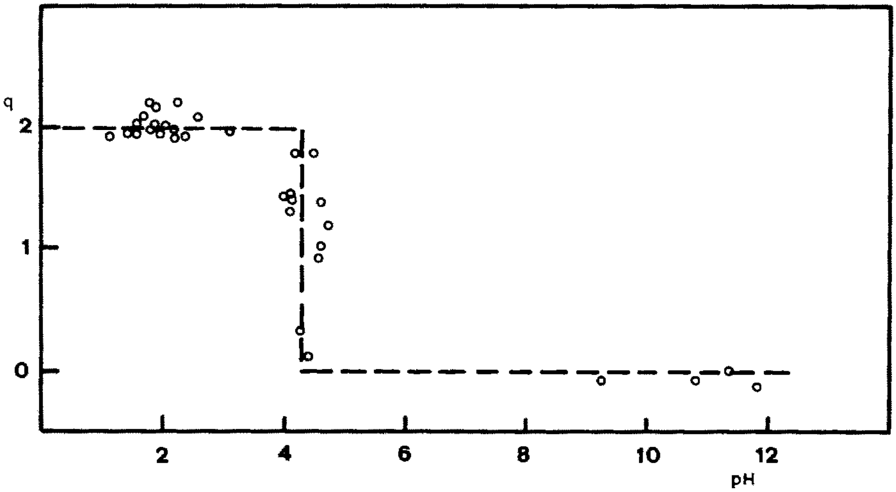

Fig. 3. Values of q vs. pH of solutions after precipitation.

The Ca_2L content of the mixture increases as the solution is neutralized and/or the concentration of Ca^{2+} is increased. The quantities C^0_{Ca}/C^0_L vs. C^0_H/C^0_L are represented in Fig. 4. Three vertical zones may be clearly

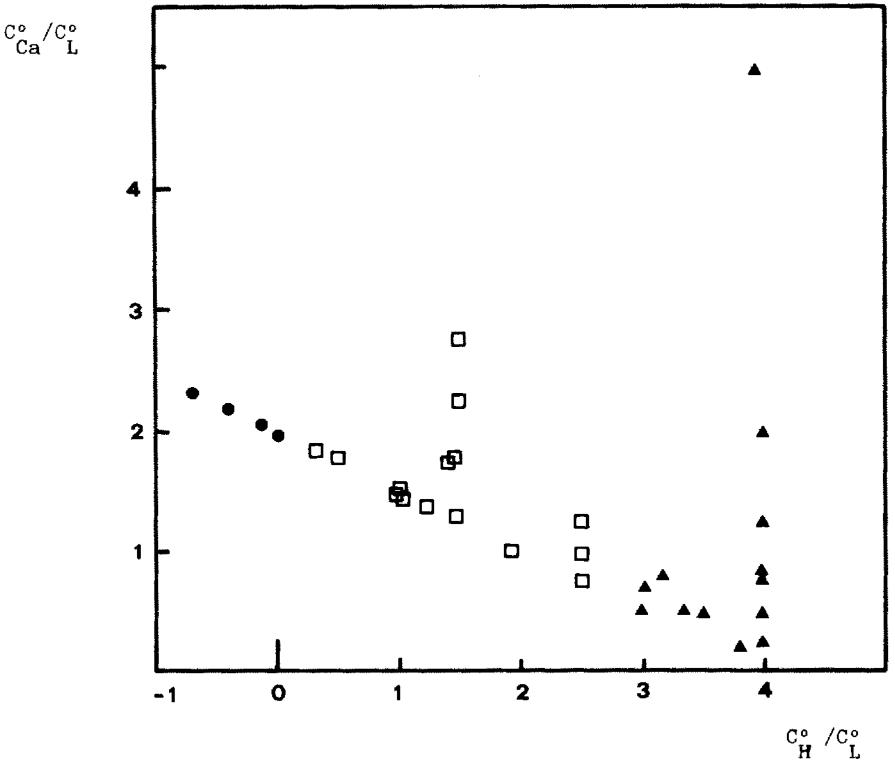

Fig. 4. Analytical conditions for precipitation: ●, Ca_2L; □, $Ca_2L+CaLH_2$; ▲, $CaLH_2$.

TABLE 6

Solubilities of various alkali and alkaline earth pyromellitate compounds at $I = 0$ mol dm^{-3} and $T = 25$ °C

Species	pK_{s0} [a]	Solubility (mol dm^{-3})
Na_2LH_2	15.84 ± 0.06	3.90×10^{-4}
KLH_3	17.18 ± 0.08	1.90×10^{-4}
$RbLH_3$	17.5 ± 0.3	1.69×10^{-4}
$CsLH_3$	18.4 ± 0.3	1.10×10^{-4}
$CaLH_2$	17.71 ± 0.04	2.64×10^{-5}
CaL_2	11.85 ± 0.10	7.07×10^{-5}
$SrLH_2$	16.5 ± 0.3	5.34×10^{-5}
SrL_2	10.8 ± 0.3	16.2×10^{-5}
$BaLH_2$	16.8 ± 0.07	4.38×10^{-5}
BaL_2	13.5 ± 0.1	2.12×10^{-5}

[a] ± standard deviation.

observed, corresponding to three different types of precipitate, the composition of which seems to be a function of the quantity $m = C^0_H/C^0_L$. At $m < 0$, Ca_2L always forms; at $m > 3$ and for any concentration of Ca^{2+}, CaH_2L is found; in the remaining cases, mixtures of the two salts are obtained.

Experimental details for insoluble species of Ba^{2+} are reported in Table 5. Ba^{2+} and Sr^{2+} * behave in similar ways to Ca^{2+}, in that they form insoluble compounds Me_2L and $MeLH_2$.

Solubilities

The solubility of alkali and alkaline earth metal species follows the trends

$Na^+ > K^+ > Rb^+ > Cs^+$

$Ca^{2+} \simeq Sr^{2+} > Ba^{2+}$ for M_2L, and

$Ca^{2+} < Sr^{2+} \simeq Ba^{2+}$ for MLH_2

The solubility products, extrapolated at $I = 0$ mol dm^{-3}, and the theoretical solubilities of different species are reported in Table 6. Values relating to Rb^+, Cs^+ and Sr^{2+} are to be considered only as indicative, in that they are obtained from few experimental data and therefore show high standard deviations.

Thermal analysis

The thermoanalytical curves concerning the insoluble compounds obtained for the alkaline metals show that the only pure sodium insoluble

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* Suplementary data are available on request.

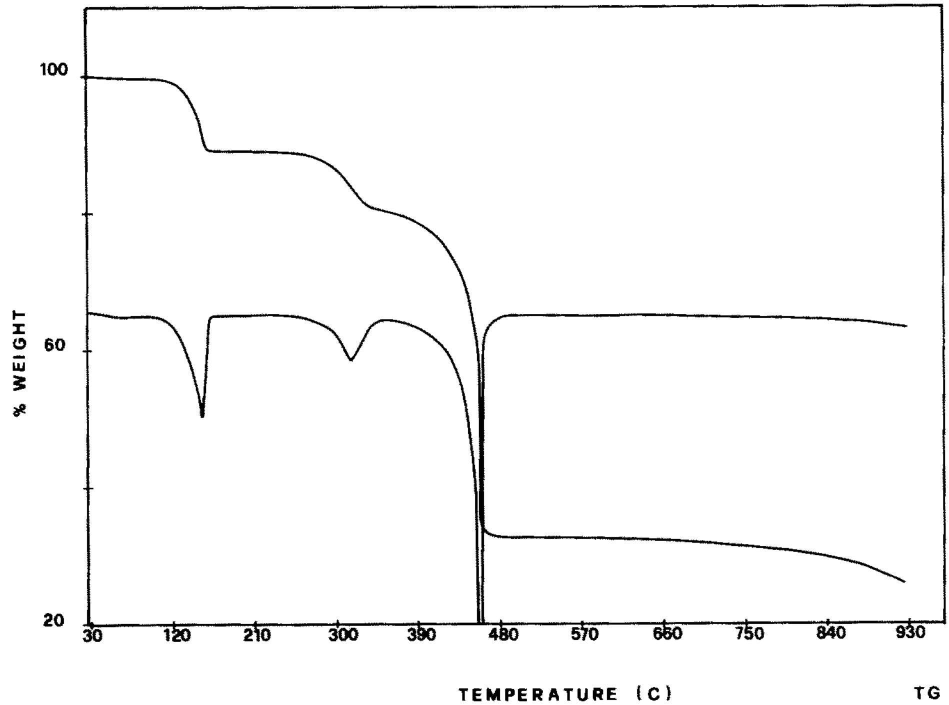

Fig. 5. TG and DTG curves of $Na_2LH_2{\cdot}2H_2O$. Atmosphere, oxygen; heating rate, 10 °C min^{-1}.

species is $Na_2LH_2 \cdot 2H_2O$. As shown by the curve in Fig. 5, the water is lost in one step, and the anhydrous compound decomposes in two steps, corresponding to the beginning of decarboxylation followed by the superimposition of thermal decomposition of the ligand, to give Na_2CO_3. Analogous behaviour for the precipitation of the potassium, rubidium and cesium compounds is confirmed by the TG curves.

The only solid species found for the three alkaline ions was $MeLH_3$, as shown by the curves in Fig. 6.

The potassium compound appears to be anhydrous, while the rubidium and cesium compounds are monohydrate. Their thermal behaviour is similar, and the decomposition always occurs in three steps, to give the corresponding carbonate.

The precipitates obtained by reaction of calcium with 1,2,4,5-benzenetetracarboxylic acid at varying pH give the curves shown in Fig. 7. Curve (a) is that obtained for the compound precipitated at pH 1.7, corresponding to the $CaLH_2$ species. The compound is anhydrous, and decomposes, starting at 338 °C, in three steps, the second of which involves the superimposition of two different thermal reactions, to give calcium oxide. Curves (b)–(e) correspond to the compounds obtained at $4.2 \leq pH \leq 9.2$.

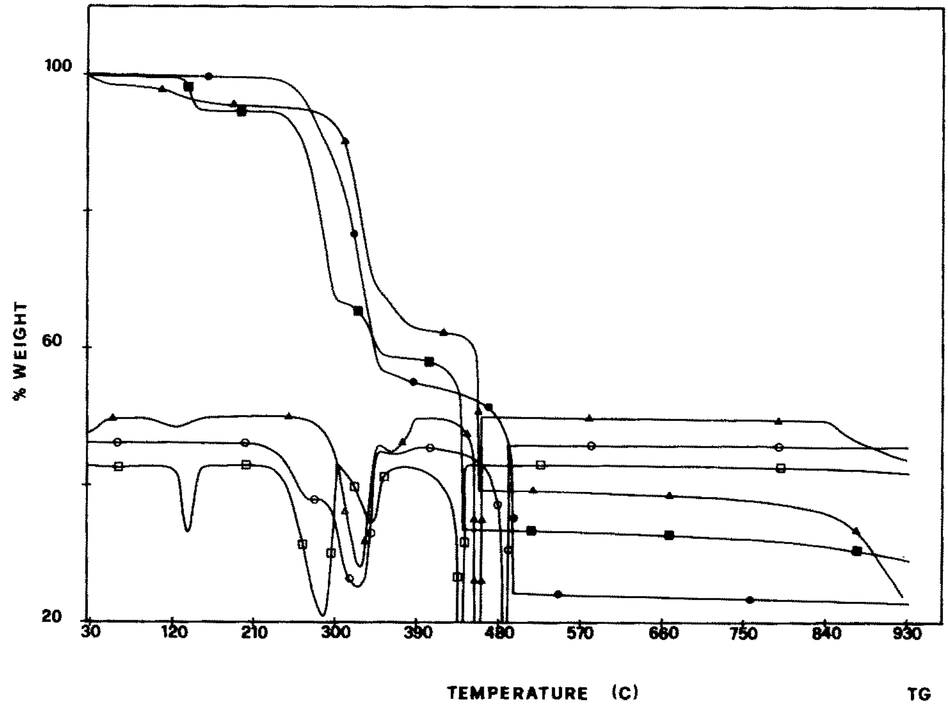

Fig. 6. TG and DTG curves of KLH_3 (●, TG; ○, DTG), $RbLH_3$ (■, TG; □, DTG) and $CsLH_3$ (▲, TG; △, DTG). Atmosphere, oxygen; heating rate, 10 °C min^{-1}.

Curve (f) is that obtained for the compound precipitated at pH 11.4, and corresponds to the species $Ca_2L \cdot 6H_2O$. The water is lost in two steps, the first of four and the second of the two remaining water molecules. The anhydrous compound remains unmodified until 513 °C, and then decomposes in two steps to give calcium oxide.

The intermediate curves from (a) to (e) correspond to mixtures of the two species $CaLH_2$ and Ca_2L, and show how increasing the pH increases the percentage of the form Ca_2L in the mixture, according to the data obtained in solution. It is interesting to note that the simultaneous presence of the two forms results in the very obvious occurrence of a process immediately after the beginning of the second thermal process of the $CaLH_2$ species, and that this phenomenon is strictly influenced by the percentage ratio of the two forms.

Curve (e), corresponding to the compound obtained at $pH = 9.2$, still shows only a very small percentage of the $CaLH_2$ form (about 1.3%), and this does not affect the shape of the curve. At $pH > 12.5$ the precipitate is a mixture of Ca_2L and $Ca(OH)_2$, as shown by the TG curves.

The compounds obtained by reaction of strontium with the ligand are of two types: $SrLH_2$ is obtained in acidic or neutral solution (Fig. 8a), and Sr_2L in an alkaline medium (Fig. 8b). The transition from the $SrLH_2$ to the

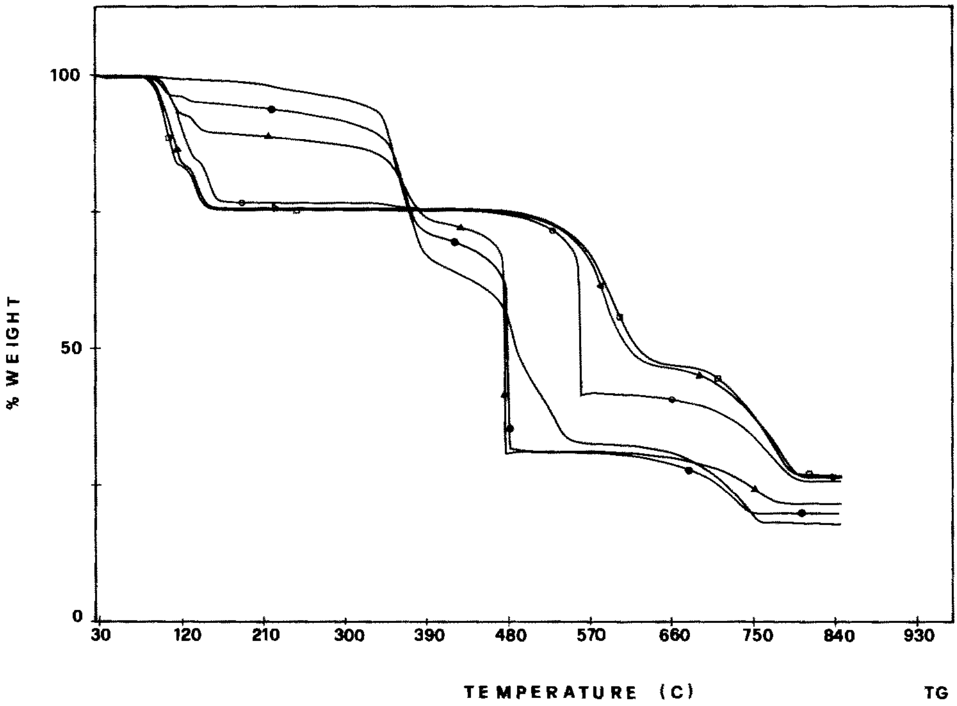

Fig. 7. TG curves of calcium compounds at varying pH: (a) ———, pH 1.7; (b) ●, pH 4.2; (c) ○, pH 4.3; (d) ▲, pH 4.6; (e) △, pH 9.2; (f) □, pH 11.4. Atmosphere, oxygen; heating rate, 10 °C min^{-1}.

Sr_2L species, as a function of pH, occurs via a series of mixtures with increasing percentage of Sr_2L.

The $SrLH_2$ species is trihydrated, and the water is lost in two steps, of first one and then two molecules. The anhydrous compound decomposes in two steps, the second almost explosive, to give $SrCO_3$. The Sr_2L species is heptahydrated and loses the water molecules in a single step, after which the anhydrous compound decomposes, again in a single step, to give $SrCO_3$. The chemical behaviour of barium in the reaction with 1,2,4,5-benzenetetracarboxylic acid is, as noted previously, similar to that of strontium. Two different species are obtained, depending on the pH. $BaLH_2$ is obtained in acidic or neutral solution, and gives TG curves as shown in Fig. 9a. The compound is anhydrous, and decomposes in two steps, the second almost explosive, to give $BaCO_3$. The Ba_2L obtained in alkaline solution is dihydrated (Fig. 9b). The water is lost in two steps, of one water molecule each, and the anhydrous compound decomposes in one step to give $BaCO_3$.

The Me_2L compounds always decompose at much higher temperatures than the $MeLH_2$ compounds. This behaviour could be due to the divalent ion acting as a bridge between two di-deprotonated ligand molecules, producing a polymeric structure that strongly stabilizes the system.

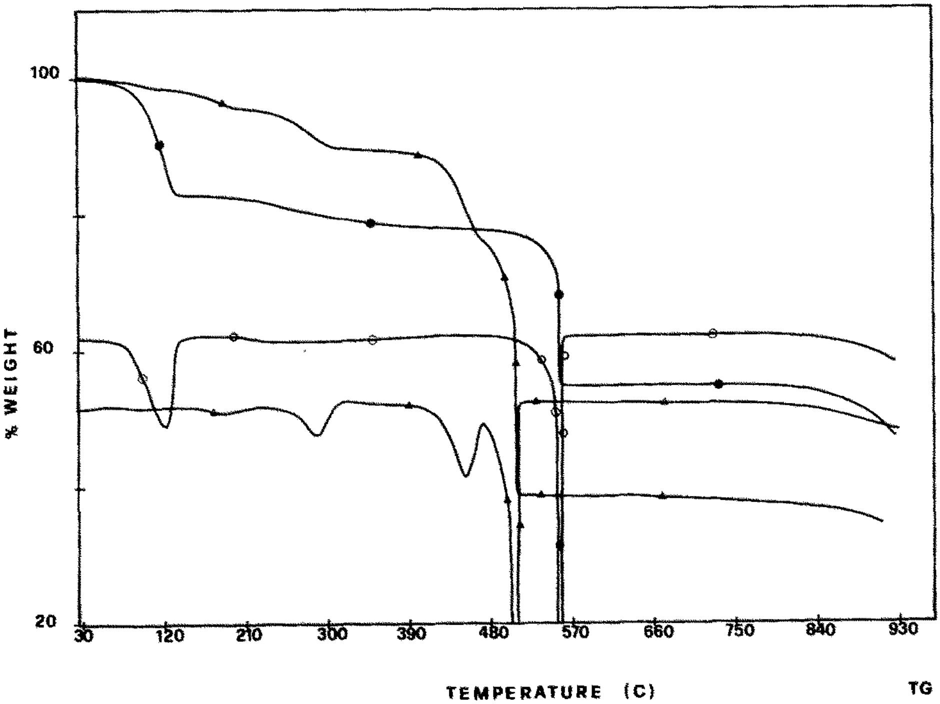

Fig. 8. TG and DTG curves of (a) $SrLH_2$ (▲, TG; △, DTG) and (b) Sr_2L (●, TG; ○, DTG). Atmosphere, oxygen; heating rate, 10 °C min^{-1}.

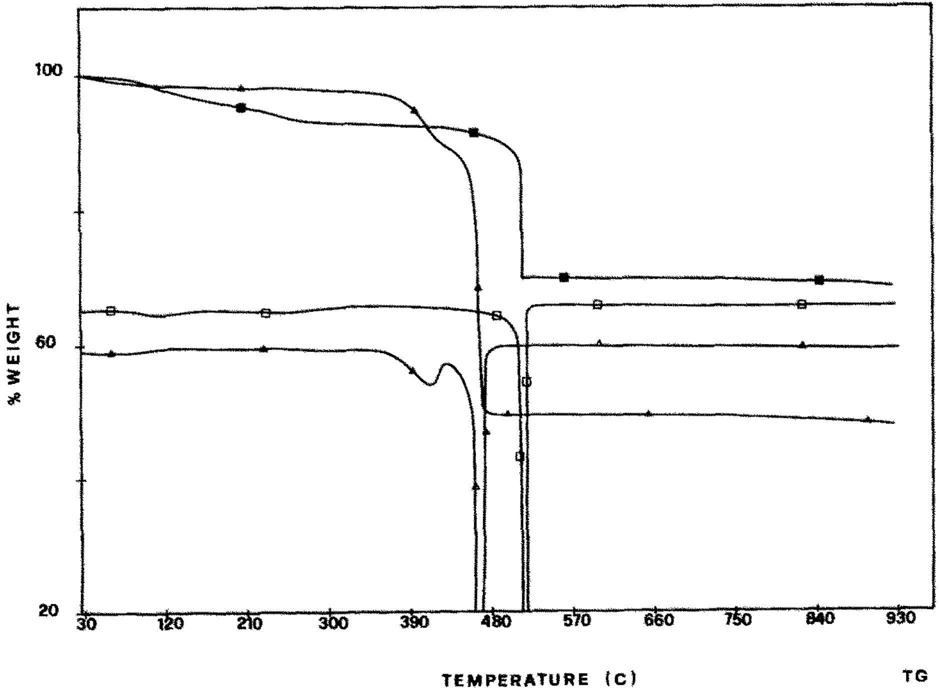

Fig. 9. TG and DTG curves of (a) $BaLH_2$ (▲, TG; △, DTG) and (b) Ba_2L (■, TG; □, DTG). Atmosphere, oxygen; heating rate, 10 °C min^{-1}.

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