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Dimalonate[C_{60}]fullerene protonation and complexation with uranyl in aqueous solution. Spectrophotometric study

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Abstract

Protonation of water-soluble *e*-dimalonate[C_{60}]fullerene (L^{4-}) was investigated using UV spectrophotometry and data analyzed using a general least-squares minimization approach. The protonation constants determined were ($L^{4-} + rH^{+} \Leftrightarrow LH_r^{r-4}$, log $*\beta_{01r}$; log $*\beta_{011} = 6.19 \pm 0.02$; log $*\beta_{012} = 10.57 \pm 0.01$; log $*\beta_{013} = 13.68 \pm 0.02$; log $*\beta_{014} = 15.85 \pm 0.02$; 25 °C). Complex equilibria study proved the formation of UO_2LH^- and $(UO_2)_2L$ complexes ($pUO_2^{2+} + qL^{4-} + rH^{+} \Leftrightarrow (UO_2)_pL_qH_r^{2p-4q}+^{r}$, log $*\beta_{pqr}$; log $*\beta_{111} = 11.0 \pm 0.2$; log $*\beta_{210} = 14.35 \pm 0.09$; 25 °C). The stability constant for the binding of the first uranyl ion with the dimalonate fullerene ligand is log β_{11}(ML) 4.81 and the second one log K_{21} ($ML + M = M_2L$) = 3.35, thus, uranyl complexation with the second malonate is much lower. The first value (4.81) is near to log $K_1 = 4.88$ for uranyl–malonate 1:1 complex.

Keywords: Dimalonate[C_{60}]fullerene protonation; Uranyl; Complexes; Stability constants

1. Introduction

Fullerene chemistry grew very rapidly during the last decade. The remarkable redox properties and energy storage capacity of pristine fullerene [1], together with its pronounced susceptibility to react with radicals [2,3], have attracted great interest. Furthermore, fullerene derivatives can be used as biologically active compounds in medicinal chemistry [4–7]. Fullerene derivatives inhibit human immunodeficiency virus-1 protease [8], have a role as neuroprotective agents in living systems [9] and can cause photo-induced DNA cleavage [10].

Much effort has been invested in the preparation of solutions in polar solvents of Buckminsterfullerene (C_{60}) in order to study and apply its properties, ultimately, in aqueous solutions. The different approaches consider incorporation of C_{60} in micelles [11–13], encapsulation of C_{60} in γ-cyclodextrin [14–16], and chemical functionalization with hydrophilic addends [17,18]. Monofunctionalization of C_{60} with hydrophilic groups, such as malonate ($C_{60}C(COO^-)_2^{4-}$), promotes the water solubility of the fullerene core, although per se it is not effective enough to prevent irreversible formation of clusters in aqueous solution [19,20]. On the other hand, bis-functionalized C_{60} carrying negatively charged carboxyl groups, $C_{60}[C(COO^-)_2]_2^{4-}$ (L^{4-}, Fig. 1), has been shown to exhibit high water-solubility without cluster formation [21]. This renders L into an interesting coordinating agent for various metal ions in aqueous solution.

Functionalized fullerene derivatives are called buckyligands [22] when they form coordination compounds. The metal-chelating capacities of fullerenes are further discussed elsewhere [23].

The aim of this paper is to investigate (i) the acid–base equilibria of dimalonate[C_{60}]fullerene in aqueous solution, and (ii) its complexation equilibria with uranyl (known to be preferably complexed by hard, O-donor chelating ligands [24]) by UV spectrophotometry.

2. Definitions

Let M be uranyl, UO_2^{2+}, and L fully deprotonated *e*-dimalonate[C_{60}]fullerene (*e* = equatorial), *e*-$C_{60}[C(COO^-)_2]_2^{4-}$ (displayed in Fig. 1).

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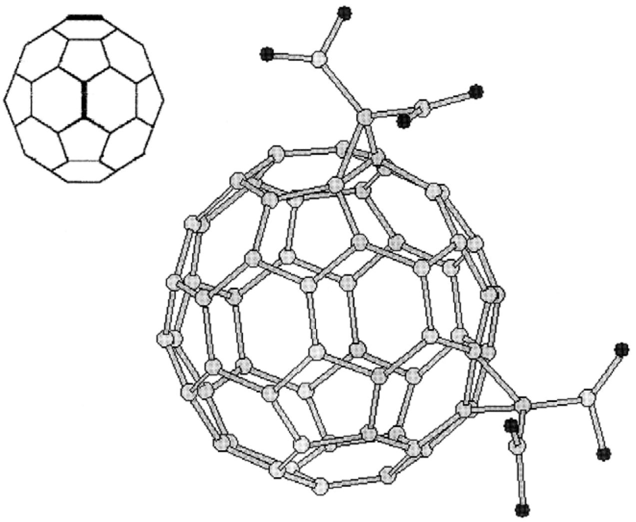

L^{4-}

Fig. 1. Functionalized C_{60} derivative used in this study, *e*-$C_{60}[C(COO^-)_2]_2^{4-}$. Dark balls represent oxygen. In the left upper corner, the relative position of the malonate groups is shown.

The overall formation constants under discussion will be (charges are omitted for the sake of simplicity):

$$pM + qL + rH^+ \rightleftharpoons M_pL_qH_r \qquad (A)$$

with equilibrium constants:

$$*\beta_{pqr} = [M_pL_qH_r][M]^{-p}[L]^{-q}[H^+]^{-r} \qquad (1)$$

In particular, step-wise dissociation constants of the ligand K_a, defined in Eq. (B), are related to ligand protonation constants $*\beta_{01r}$ as given in Eq. (2):

$$LH_r \rightleftharpoons LH_{r-1} + H^+, \quad K_{a(n+1-r)} \qquad (B)$$

$$K_{a(n+1-r)} = [LH_{r-1}][H^+][LH_r]^{-1} = *\beta_{01(r-1)}/*\beta_{01r} \qquad (2)$$

where n is the maximum number of protons that can be accepted by L.

3. Experimental

3.1. Reagents and solutions

Stock solution of uranyl perchlorate was prepared as described elsewhere [25]. The fullerene derivative *e*-$C_{60}[C(COOH)_2]_2$ was kindly donated by Prof. V. Brezová, Slovak Technical University, Bratislava, Slovakia. Its synthesis is described elsewhere [17–19]. A mass of 0.82 mg of *e*-$C_{60}[C(COOH)_2]_2$ (924.69 g mol^{-1}) was dissolved in 10.0 ml of distilled water to form a slightly brown solution (8.87×10^{-5} mol l^{-1}; stock solution). Perchloric acid (70%) was from Merck (Darmstadt, Germany).

3.2. Apparatus

All pH and absorbance measurements were performed at 25.0±0.2 °C. A combined glass electrode GK 2322C of Radiometer (Copenhagen, Denmark) was used to measure the pH with a Radelkis OP-208 Precision Digital pH-meter (Budapest, Hungary). Spectrophotometric measurements were done on a single-beam, diode-array, HP 8452A spectrophotometer of Hewlett Packard (Palo Alto, CA, USA). A quartz cell with 1 cm of path-length was used. Two Biohit (Finland) adjustable volume hand-held pipettors were used to dispense liquid volumes of titrant to a test solution. They covered a volume range of either 20–200 or 100–1000 μl.

Weighing water checked micropipette performance and the errors were found less than 3% rel. Precision of spectrophotometric measurements was about ±0.001–0.003 absorbance unit and pH was measured with accuracy ±0.01 unity.

3.3. Procedure

The experimental information to study the protonation of L was collected as follows. An aliquot of 3.00 ml (2.22×10^{-5} mol l^{-1}, pH 6.323) was titrated with diluted aqueous solution of $HClO_4$ (8×10^{-4}, 8×10^{-3}, 8×10^{-2}, and 8×10^{-1} mol l^{-1}), adding from 20 μl to 1.00 ml to cover a pH-range from 6.323 to 0.560 (40 additions). Dimalonate[C_{60}]fullerene and perchloric acid solutions were mixed in a 25-ml beaker. The mixture was stirred with a magnetic bar. A fraction of the mixture was withdrawn with the help of a syringe and then poured into a 1-cm quartz cell. In the cell, the pH was measured simultaneously with the absorbance measurement.

The experimental information to study the complexation of uranyl by L was collected as follows. The test solution (3.00 ml) was made of L 2.22×10^{-5} mol l^{-1} in distilled water. Uranyl perchlorate ($UO_2(ClO_4)_2$, 3.31×10^{-4} mol l^{-1}) was present in the titrant which was added with a micropipette. The titrant contained L 2.22×10^{-5} mol l^{-1} as well, so that any mixture of test solution and titrant was of the same total L concentration (c_L). Test solution and titrant were mixed and handled following the procedure described above. Number of solutions: 51; pH 3.51 (adjusted with diluted $HClO_4$); $0.10 \leqslant c_M/c_L \leqslant 10.2$. Ionic strength (mol l^{-1}): $0.5 \times 10^{-3} \leqslant I \leqslant 1.2 \times 10^{-3}$. No formation of precipitate was observed during the experiment. The experiments were made with excess of the metal over ligand because the ligand is quite scarce. For pH 3.5 and low uranyl concentration used (max. ~0.2 mM) we have proved that hydrolysis of uranium (VI) is negligible (< 1.5%).

3.4. Computation

The equilibrium constants were calculated and refined with SQUAD [26] and LETAGROP SPEFO [27] least-squares programs. All experimental points were given unit weight in the least-squares refinement. Hence, we had to use approximately the same number of experimental points in the regions where the different species were predominant. The program HYSS [28] was used to perform simulation of experimental data and to calculate distribution diagrams.

4. Results and discussion

4.1. Protonation of L in aqueous solution

Fig. 2 shows a selection of UV-absorption spectra of L in aqueous solution at several pH values. Measured absorption in the visible range was negligible at this order of concentration, 10^{-5} mol l^{-1}. It should be pointed out that under the working conditions, a precipitate was not observed even for the most acid solutions.

The absorbance for some selected wavelengths as a function of pH is shown in Fig. 3. The general least-squares minimization approach was used to analyze the spectrophotometric experimental data and to search for the best model. Results assuming various models are displayed in Table 1. The criteria of goodness of fit ($\sigma(A)$ and $U = \Sigma(A_{exp} - A_{calc})^2$) differ just slightly from model to model, except for Model 2.

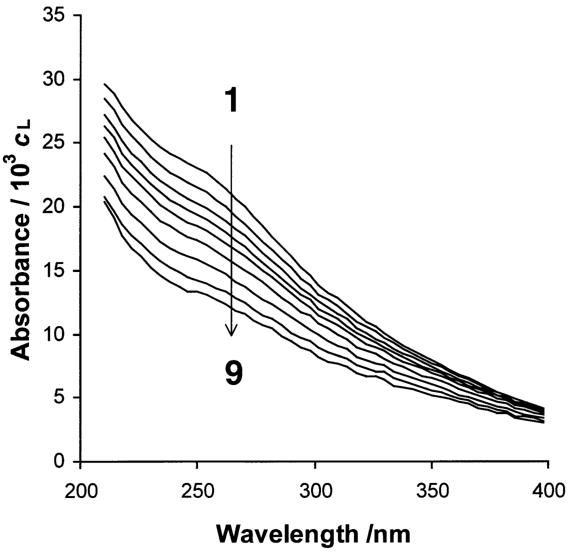

Fig. 2. UV-absorption spectra of L in water. From Solution 1, $c_L = 2.22 \times 10^{-5}$ mol l^{-1}, pH 6.32 to Solution 9, $c_L = 0.86 \times 10^{-5}$ mol l^{-1}, pH 0.87 (41 spectra were collected).

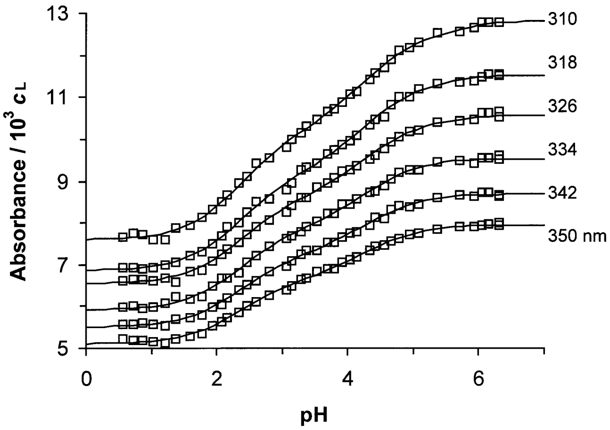

Fig. 3. Apparent molar absorptivity (A/c_L) of dimalonate[C_{60}]fullerene aqueous solutions versus pH. The solid line is calculated according to Model 6, Table 1.

Table 1
Results of spectrophotometric data analysis concerning $L = e\text{-}C_{60}[C(COO^-)_2]_2^{4-}$ protonation equilibria

Model	Species	Log β_{01n}	pK_a	Goodness of fit	
				$\sigma(A) \times 10^3$	$U \times 10^3$
1	LH	4.31±0.01		0.8695	0.3795
	LH_2	6.70±0.02			
2	LH_2	8.68±0.03		2.1520	2.3247
	LH_4	13.73±0.04			
3	LH	4.49±0.04		0.7781	0.2888
	LH_2	8.1±0.1			
	LH_3	10.4±0.1			
4	LH	4.36±0.01		0.8068	0.3105
	LH_2	7.06±0.05			
	LH_4	10.5±0.1			
5	LH_2	11.80±0.01		0.8160	0.3176
	LH_3	16.10±0.01			
	LH_4	18.48±0.01			
6	LH	6.19±0.02	6.19	0.7573	0.2592
	LH_2	10.57±0.01	4.38		
	LH_3	13.68±0.02	3.11		
	LH_4	15.85±0.02	2.17		

Data: 24 solutions; $0.560 \leqslant \text{pH} \leqslant 6.323$; 9.4×10^{-6} mol l^{-1} $\leqslant c_L \leqslant 2.2 \times 10^{-5}$ mol l^{-1}; selected 24 wavelengths: 306, 310,..., 398 nm; $\sigma(A)$ is the standard deviation of absorbance; U is the sum of squares of deviations, $U = \Sigma(A_{exp} - A_{calc})^2$, where A_{exp} are experimental and A_{calc} calculated values of absorbances.

The structural symmetry of L is a reason to suggest a possible equivalency between the two malonates in L.

4.1.1. Hypothesis 1

The acceptance of protons might occur by pairs, two protons being accepted simultaneously, with negligible formation of LH and LH_3. Model 2 (Fig. 4(a)) was proposed to test this hypothesis, which turned out to

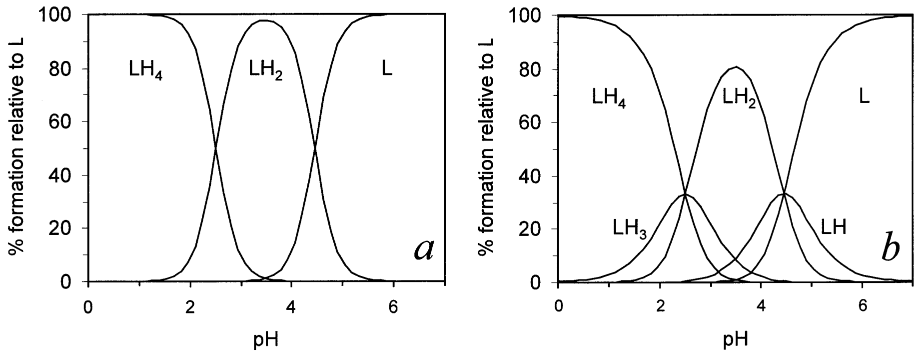

Fig. 4. Distribution diagram of L as a function of pH according to (a) Model 2 (Table 1), and (b) Eqs. (3) and (4); log $^*\beta_{011} = 4.34$; log $^*\beta_{012} = 8.68$; log $^*\beta_{013} = 11.20$; log $^*\beta_{014} = 13.73$.

lead to the highest $U = \Sigma(A_{\mathrm{exp}} - A_{\mathrm{calc}})^2$ and therefore was considered erroneous.

4.1.2. Hypothesis 2

Another way trying to define the possible equivalency of the malonates in L is given by the Eq. (3) (note that the acidity dissociation constants are defined as usual, Eq. (2), and should not be confused with the acidity dissociation microconstants):

$$\mathrm{p}K_{\mathrm{a1}} = \mathrm{p}K_{\mathrm{a2}} \text{ and } \mathrm{p}K_{\mathrm{a3}} = \mathrm{p}K_{a4} \tag{3}$$

or, equivalently, in terms of overall protonation constants

$$2 \log {}^*\beta_{011} - \log {}^*\beta_{012} = 0$$
$$\text{and } \log {}^*\beta_{012} - 2 \log {}^*\beta_{013} + \log {}^*\beta_{014} = 0 \tag{4}$$

This does not mean that LH and $\mathrm{LH_3}$ are absent (as in Model 2); it means simply that LH and $\mathrm{LH_3}$ do not predominate (see Fig. 4(b)). Model 6 works with the four-protonated species but it was found that Eq. (4) are not fulfilled; therefore Hypothesis 2 is considered erroneous, as well.

The best model is Model 6 from which it follows that two malonic groups are not equivalent. Spectra of the individual species calculated according to Model 6 are given in Fig. 5 and the corresponding distribution diagram is shown in Fig. 6.

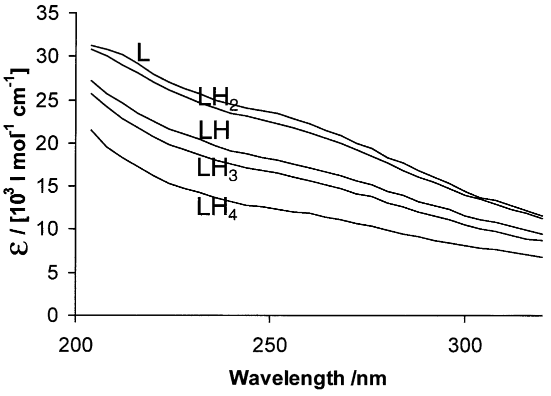

Fig. 5. Dimalonate[C_{60}]fullerene spectrum and the protonated species spectra.

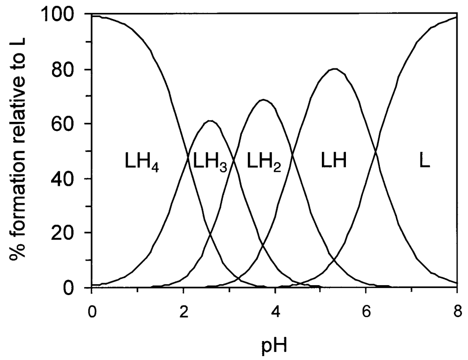

Fig. 6. The distribution of L on different protonated species as a function of pH. Protonation constants were taken from Table 1, Model 6.

If overall protonation constants in Table 1 are expressed in terms of dissociation constants ($\mathrm{p}K_\mathrm{a}$), we will get values 2.17, 3.11, 4.38 and 6.19 (compare with $\mathrm{p}K_{\mathrm{a1}} = 2.62 \pm 0.03$ and $\mathrm{p}K_{\mathrm{a2}} = 5.30 \pm 0.01$, 25 °C, $I = 0.1$ M $\mathrm{NaClO_4}$, for malonate [29]).

The first two values, $\mathrm{p}K_{\mathrm{a1}} = 2.17$ and $\mathrm{p}K_{\mathrm{a2}} = 3.11$, are comparable with $\mathrm{p}K_{\mathrm{a1}} = 2.62$ of simple malonic acid and so are the values $\mathrm{p}K_{\mathrm{a3}} = 4.38$ and $\mathrm{p}K_{\mathrm{a4}} = 6.19$ when comparing with $\mathrm{p}K_{\mathrm{a2}}$ of simple malonic acid (5.30). However, there are also differences and it appears that malonic groups in L are not behaving as completely independent.

4.2. Uranyl complexation with L in aqueous solution

Fig. 7 shows the UV-absorption spectra of uranyl and bucky-ligand L mixtures in aqueous solution. Fig. 8 shows the absorbance for 296 nm as a function of the metal to ligand ratio. This curve per se is a proof of reaction between M and L. If M and L do not react, then this curve should follow a straight line with a slope equal to the uranyl molar absorptivity at the corresponding wavelength, but this is not the case.

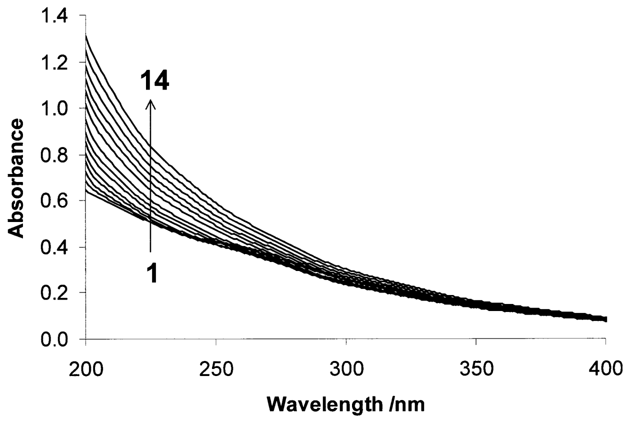

Fig. 7. Spectra of dimalonate[C_{60}]fullerene-uranyl aqueous solutions. $c_L = 2.22 \times 10^{-5}$ mol l^{-1}; 4.4×10^{-6} mol l$^{-1} \leqslant c_M \leqslant 2.27 \times 10^{-4}$ mol l^{-1}; pH 3.51.

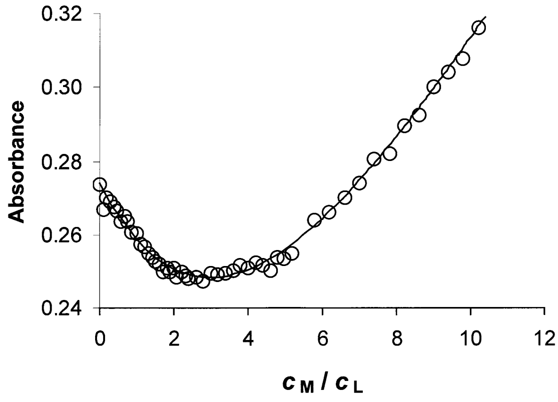

Fig. 8. Absorbance versus metal to ligand ratio. The calculated curve, traced together with the experimental points, assume model C, Table 2. $c_L = 2.22 \times 10^{-5}$ mol l^{-1}; 4.4×10^{-6} mol l$^{-1} \leqslant c_M \leqslant 2.27 \times 10^{-4}$ mol l^{-1}; pH 3.51.

The first step of data analysis was to determine the p, q values in $M_pL_qH_r$, and to do so we have first used the concept of conditional constants [30].

The results of data analysis are summarized in Table 2. Neither Model A nor Model B can sufficiently explain the experiments. At least two complexes are required to fit the data with sufficient accuracy. Model C, with ML and M_2L species appears as the best one since the fit is good enough and the model can be chemically explained without any controversy. Each attached malonate would be 1,5-bidentate to a uranium atom, giving rise to a six-membered ring. The same was observed by crystal X-ray analysis for uranyl malonato [31–33]; uranyl dimethylmalonato [34,35]; and uranyl diethylmalonato [35] salts of different cations.

Furthermore, single-crystal X-ray diffraction study shows that there are five bonding modes of malonate with uranyl [35] in solid state. One of these is the already mentioned bidentate (terminal 1,5-bidentate) complexation. The other bonding modes of malonate in solids involve each carboxylate binding a different uranyl ion. This possibility was examined also during the present speciation study. However, the formation of M_3L and M_4L under the present experimental conditions was not proved and therefore Model C is proposed as the most probable one in aqueous solution.

Table 2
Results of the spectrophotometric analysis concerning generalized chemical equilibria at buffered pH 3.5: $M' + qL' \rightleftharpoons M_pL'_q$

Model	Species	Conditional constant, log β'_{pq}	Goodness of fit	
			$\sigma(A) \times 10^3$	$U \times 10^2$
A	ML'	5.11 ± 0.02	11.495	15.183
B	M_2L'	11.8 ± 0.1	10.948	13.772
C	ML'	4.21 ± 0.03	7.494	6.167
	M_2L'	7.66 ± 0.02		
D	ML'	4.64 ± 0.02	7.513	6.198
	M_4L'	15.04 ± 0.3		
E	M_2L'	10.4 ± 0.1	8.639	8.195
	M_4L'	22.5 ± 0.2		

$M = UO_2^{2+}$ and $L = e\text{-}C_{60}[C(COO^-)_2]_2$. *Data:* 24 solutions; $c_L = 2.22 \times 10^{-5}$ mol l^{-1}; 4.4×10^{-6} mol l$^{-1} \leqslant c_M \leqslant 2.27 \times 10^{-4}$ mol l^{-1}; pH 3.51; selected 50 wavelengths: 194, 196,..., 292 nm; $\sigma(A)$ is the standard deviation of absorbance; U is the sum of squares of deviations, $U = \Sigma(A_{exp} - A_{calc})^2$, where A_{exp} are experimental and A_{calc} calculated values of absorbances.

As can be seen in Fig. 6, the predominant ligand species at $3.1 \leqslant pH \leqslant 4.4$ is LH_2 which is the most probably species with one proton on each malonic group. Therefore, there is a high probability that 1:1 complex is protonated MLH complex under the experimental conditions of this study (pH 3.51) while the proton is bound on the free malonic group. Table 3 shows the test of this hypothesis together with the calculation of $^*\beta_{pqr}$. From Table 3 it follows that the species MLH satisfies adequately to fit the data.

Table 3
Results of the spectrophotometric analysis concerning the equilibria $pM + qL + rH^+ \rightleftharpoons M_pL_qH_r$

Model	Species	Log $^*\beta_{pqr}$	Goodness of fit	
			$\sigma(A) \times 10^3$	$U \times 10^2$
I	ML		No convergence	
II	M_2L	13.56 ± 0.06	8.0565	6.2635
III	ML	7.3 ± 0.2	6.7313	4.1822
	M_2L	14.16 ± 0.05		
IV	MLH	11.0 ± 0.2	6.6950	4.1372
	M_2L	14.35 ± 0.09		

$M = UO_2^{2+}$ and $L = e\text{-}C_{60}[C(COO^-)_2]_2$. *Data:* 24 solutions; $c_L = 2.22 \times 10^{-5}$ mol l^{-1}; 4.4×10^{-6} mol l$^{-1} \leqslant c_M \leqslant 2.27 \times 10^{-4}$ mol l^{-1}; $3.0 \leqslant pH \leqslant 3.9$; selected 42 wavelengths: 210, 212,..., 292 nm; $\sigma(A)$ is the standard deviation of absorbance; U is the sum of squares of deviations, $U = \Sigma(A_{exp} - A_{calc})^2$, where A_{exp} are experimental and A_{calc} calculated values of absorbances.

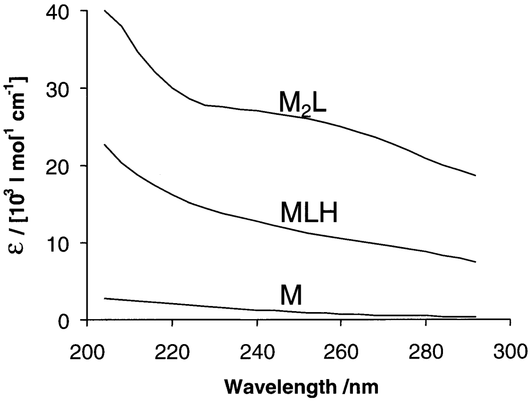

Fig. 9. Spectra of uranyl-dimalonate[C_{60}]fullerene complexes.

Calculated spectra of the individual species are given in Fig. 9.

Remark: There is a possibility of 1:2 (M:L) complex formation. However, because the reagent is quite scarce we were working in solutions in excess of the metal ion and thus no formation of 1:2 complex was observed.

5. Conclusions

The values of protonation constants for water-soluble and truly monomeric *e*-dimalonate[C_{60}]fullerene determined ($\log {}^*\beta_{011} = 6.19 \pm 0.02$; $\log {}^*\beta_{012} = 10.57 \pm 0.01$; $\log {}^*\beta_{013} = 13.68 \pm 0.02$; $\log {}^*\beta_{014} = 15.85 \pm 0.02$; 25 °C) show that attached malonic groups behave slightly different from those of free malonic acid. Uranyl reacts with L forming UO_2LH^- and $(UO_2)_2L$ complexes ($\log {}^*\beta_{111} = 11.0 \pm 0.2$; $\log {}^*\beta_{210} = 14.35 \pm 0.09$; $I = \sim 0.01$, 25 °C). Both malonic groups in L act as bidentate (terminal 1,5-bidentate), while each one is forming a six-membered ring with uranyl.

Step-wise stability constants of uranyl–malonate complex in L are then $\log \beta_{11}$ (ML) 4.81 and $\log \beta_{21} = 3.35$, thus, the stability of uranyl complexation with the second malonate in L is much lower.

Acknowledgements

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