

## GLYCINE C<sub>60</sub> ADDUCT AND ITS RARE EARTH COMPLEXES

D.J.Zhou, L.B.Gan\*, L.B.Xu, C.P.Luo, and C.H.Huang

State Key Laboratory of Rare Earth Material Chemistry and Applications,  
Department of Chemistry, Peking University, Beijing 100871, P.R.China

### ABSTRACT

Glycine sodium salt reacts with C<sub>60</sub> to give a water soluble derivative 1, acidification of which produces a less soluble product 2. When compound 2 is treated with Ln(ClO<sub>4</sub>)<sub>3</sub> (Ln=La,Y) in several different molar ratios, insoluble rare earth complexes: C<sub>60</sub>(Gly)<sub>x</sub>Ln<sub>y/3</sub>(OH)<sub>y</sub>(H<sub>2</sub>O)<sub>z</sub> (x=7-8,y=4-6,z=2-6) were obtained. These new compounds have been characterized by IR, TG-DTA and XPS spectra.

### INTRODUCTION

Fullerenes have received intensive interest since the macroscopic production method was reported<sup>1-3</sup> because of its special physical chemical properties and important application respects<sup>4-7</sup>. Although several fullerene metal complexes have been prepared, all these complexes involve the C<sub>60</sub> molecule itself and either direct bonding of C<sub>60</sub> towards the metal center as in the group eight metal complexes<sup>8</sup> or the addition of a metal containing group onto the C<sub>60</sub> as in the case of osmylation<sup>9</sup>. No metal complexes with a fullerene derivative as the ligand have been reported. In this paper, we report a glycine fullerene adduct and its rare earth complexes.

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\* To whom correspondence should be addressed

## EXPERIMENTAL

**Reagents:**  $\text{La}_2\text{O}_3$  (99.98%);  $\text{Y}_2\text{O}_3$  (Luminescence grade); Glycine (Analytic grade);  $\text{C}_{60}$ : prepared by a AC arc method and purified by a absorption method, its purity is more than 99% according to HPLC;  $\text{Ln}(\text{ClO}_4)_3$  solutions were prepared by dissolving  $\text{Ln}_2\text{O}_3$  in equivalent  $\text{HClO}_4$  solution (0.35 M). Other reagents were all analytic grade.

**Instruments:** The IR spectra were collected on a Nicolet 7199 B FT-IR spectrophotometer (KBr pellet); TG-DTA analyses were carried out on a LCT-1 thermal gravimeter with  $\alpha\text{-Al}_2\text{O}_3$  as reference; The XPS spectra were measured on a ESCA LAB-5 Spectrophotometer (Mg K $\alpha$  radiation)

**Synthesis:** glycine  $\text{C}_{60}$  adduct 1 and 2: 2.8 g glycine and 1.55g NaOH in 80 ml of 90% ethanol were added dropwise into a  $\text{C}_{60}$  toluene solution (0.097 g.in 100 ml) under stirring at room temperature. After 24 hours, the reaction mixture separated into two layers, the upper organic layer is almost colorless, and the lower water layer is black brown. The mixture was allowed to react for a week. After that the water layer was extracted with toluene to remove any unreacted  $\text{C}_{60}$ , then 40 ml of ethanol were added to get a black brown precipitate. The precipitate was filtered and washed twice with ethanol and once with diethyl ether, then dried under vacuum to give the dark brown  $\text{C}_{60}$  sodium glycine adduct 1 (breviated as  $\text{C}_{60}\text{-Gly-Na}$ ), it is very soluble in water to produce a red black solution. Upon acidification of 1 with HCl, a brown precipitate began to form at pH 2.8. When the pH reached about 2.0 the precipitate was separated and washed with ethanol, acetone and diethyl ether sequetially, then dried under vacuum at 100°C for 16 hours to give the brown glycine  $\text{C}_{60}$  adduct 2 (breviated as  $\text{C}_{60}\text{-Gly}$ ). Elemental analysis found: C% 57.98, H% 2.56, N% 7.51; calcd. for  $\text{C}_{60}(\text{Gly})_8\text{Na}_4(\text{OH})_6(\text{H}_2\text{O})_6$ : C% 57.99, H% 2.69, N% 7.12. The product is insoluble in common organic solvents such as toluene ethanol, DMF, only slightly soluble in water, and is soluble in NaOH or concentrated HCl solutions.

**Glycine  $\text{C}_{60}$  rare earth complex 3 and 4:** A black brown fibrous precipitate formed when  $\text{Ln}(\text{ClO}_4)_3$  ( $\text{Ln}=\text{La}, \text{Y}$ ) was added to a  $\text{C}_{60}\text{-Gly}$  aqueous solution in different molar ratios, the precipitate was filtered and washed three times with water, twice with acetone and once with diethyl ether, then dried at 100C under vacuum for 16 hours to give the brown rare earth complexes (Breviated as  $\text{C}_{60}\text{-Gly-Ln}$ ). Elemental analysis found that the products are almost the same regardless of

the molar ratios and addition orders. For C<sub>60</sub>-Gly-La: C% 51.60, H% 2.34, N% 5.76; calcd. for C<sub>60</sub>(Gly)<sub>7</sub>(OH)<sub>5</sub>La<sub>7/3</sub>·(H<sub>2</sub>O)<sub>4</sub>, C% 51.69, H% 2.39, N% 5.70; and for C<sub>60</sub>-Gly-Y: C% 54.44, H% 2.54, N% 6.28, calcd. for C<sub>60</sub>(Gly)<sub>7</sub>5(OH)<sub>5</sub>·Y<sub>2</sub>·5·(H<sub>2</sub>O)<sub>4</sub>: C% 54.41, H% 2.60, N% 6.35.

## RESULTS AND DISCUSSION

**IR Spectra** Table 1 shows the C=O stretching frequencies for glycine and the C<sub>60</sub> derivatives. It is well known that glycine exists as a zwitterion and the two bands at 1597 and 1414 cm<sup>-1</sup> are due to the asymmetric (V<sub>as</sub>) and symmetric (V<sub>s</sub>) stretch of the fully dissociated carboxylate ion -COO<sup>-10</sup>. The carboxyl group in 1 is also fully dissociated with V<sub>as</sub> and V<sub>s</sub> at 1597 and 1407 cm<sup>-1</sup>, respectively. However, the carboxyl group is only partially dissociated in compound 2 and two sets of C=O stretching bands appeared. The two bands at 1723 and 1225 cm<sup>-1</sup> is attributed to the undissociated carboxyl group -COOH; the other two at 1633 and 1399 cm<sup>-1</sup> is due to the dissociated carboxylate ion<sup>10,11</sup>. The rare earth complexes exhibit C=O stretching patterns similar to that of 2 but at slightly different positions, suggesting that both the two types of carboxyl groups are coordinated to the lanthanide ion. The four characteristic peaks of C<sub>60</sub> can not be observed in all of these compounds as in the case of fullerenes.<sup>12</sup>

**TG-DTA studies** Unlike the pure C<sub>60</sub><sup>13</sup>, the DTA curves of 2, 3 and 4 all show three exothermic peaks at 272,340,363; 259,414,435; 289,373,396°C, respectively, and they do not gain weight. They all begin to lose weight at about 140°C and then undergo a series of complicated oxidation and decomposition reactions. Finally they all change into their corresponding metal oxides. The total weight loss for 1, 3 and 4 are: (found/calcd.) 91.9(92.1), 79.2(77.9), 84.3 (82.9)%, respectively.

**XPS study** The bonding energy (BE) of each element in the different samples are almost the same (Table 2). The BE of C1s is 284.8 eV which is about 1.1 eV lower than that in pure C<sub>60</sub>, and the full width at half maximum 4 eV is much wider than the 1.5 eV for pure C<sub>60</sub><sup>12</sup>, as a result of the overlapping of carbon peaks with different oxidation states in the derivatives. The BE of other elements are in agreement with references<sup>14,15</sup>. The C, N, O, Na atom ratios in C<sub>60</sub>-Gly is 10.3:1:3.8:0.6 from the XPS analysis, similar to that of the elemental analysis result of 9.5:1:3.3:0.5. The C,N,O atom ratios in C<sub>60</sub>-Gly-La and C<sub>60</sub>-Gly-Y are found to

Table 1 The main absorption peaks ( $\text{cm}^{-1}$ ) and their assignments

Compounds	$\gamma$ (C=O)	
Glycine	1597(vs)	1414(s)
C <sub>60</sub> -Gly-Na 1	1597(vs)	1407(s)
C <sub>60</sub> -Gly 2	1723(vs), 1633(vs)	1399(s), 1225(s)
C <sub>60</sub> -Gly-La 3	1708(s), 1621(vs)	1396(s), 1316(m)
C <sub>60</sub> -Gly-Y 4	1713(s), 1625(vs)	1400(s), 1318(m)

Table 2 The bonding energy (ev) of the samples

Compounds	C1s	N1s	O1s	Na1s	Y3d	La3d5/2	La3d3/2
C <sub>60</sub> -Gly	284.8	399.9	531.7	1071.7	-	-	-
C <sub>60</sub> -Gly-Y	284.8	399.4	531.7	-	157.4	-	-
C <sub>60</sub> -Gly-La	284.8	399.6	531.8	-	-	835.9	852.6

be 9.7:1:3.3 and 9.0:1:3.7, respectively, in agreement with the elemental values, 10.6:1:3.3 and 10:1:3.2, respectively.

## CONCLUSION

The C<sub>60</sub> glycine adduct and its rare earth complexes were synthesized. This is the first report of the metal complexes using C<sub>60</sub> a derivative as the ligand. Elemental analysis, TG-DTA and XPS studies found the average formula can be presented as follows: C<sub>60</sub>(Gly)<sub>x</sub>Ln<sub>y/3</sub>(OH)<sub>z</sub>(H<sub>2</sub>O)<sub>z</sub>, (x=7-8, y=4-6, z=2-6, Ln=La, Y). Because the multi addition property of C<sub>60</sub><sup>11,16</sup>, the compounds we prepared here are very complicated mixtures. Further work is underway to separate these new compounds.

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