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Alkali-metal fullerides MC_{60} $(THF)_x$ ($M = Li$, Na, K): a new solution-phase method for the preparation and characterization with ESR, UV–NIR and IR spectroscopy

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Abstract

Alkali-metal fullerides $MC_{60}(THF)_x$ ($M = Li$, Na, K) ($0 < x < 1$), prepared in THF–H_2O solution, were characterized by UV–NIR, ESI MS, IR and ESR spectroscopy. ESR spectra of MC_{60} ($M = Li$, Na, K) in THF are temperature dependent: the linewidth increases abruptly at about the melting point of THF and the ESR signal diminishes gradually below 170 K. A possible explanation for this is that THF crystallization results in the exclusion of solute from the lattice and leads to C_{60}^{-} aggregation, which promotes line broadening and the formation of a diamagnetic dimer $(C_{60})_2^{2-}$. The oxidation of MC_{60} ($M = Li$, Na, K) in THF was monitored by UV–NIR spectroscopy. The oxidation rate of C_{60}^{-} was found to depend on the countercation. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Alkali-metal fullerides; Synthesis; ESR spectroscopy

1. Introduction

Considerable interest has focused on alkali-metal fullerides as a result of the discovery of the high conductivity and high-T_c superconductivity in the alkali-metal intercalated fullerides [1,2]. In addition to the superconducting A_3C_{60} ($A =$ alkali metal) fullerides, an intriguing conducting phase A_1C_{60} has been described in detail, including the quasi-one-dimensional character [3], the formation of dimers [4], one-dimensional polymers [5], the variation in dimensionality and its effect on the change in electronic properties of A_1C_{60} [2,6]. The alkali-metal-doped fullerides have commonly been prepared by the vapor transport method at high temperature and ultrahigh vacuum [7]. A solution-phase route to alkali-metal fullerides has several potential advantages over the vapor-phase routes, and some solution routes to alkali-metal fullerides have been reported [8–21]. We have recently developed a new method for facile and selective generation of C_{60}^{n-} in aqueous caustic–THF (or DMSO) [22,23]. Here, we try to synthesize alkali-metal fullerides by a similar method.

Generally the identification of fullerene anions was established by visible–near IR spectroscopy with characteristic bands [8–11,24–28] and by ESR spectroscopy, but it is a difficult task to assign the observed ESR single lines to the individual ions [24–26,29–32]. The description of C_{60}^{1-} with a wide line (up to a few mT) and a g-value in the range 1.997–2.000 is considered to be well established [8,10,24–26,28–31]. The narrow ESR lines, frequently superimposed on the wide lines, are assumed to originate from impurities, from some consecutive unrelated products [24], from various solvation states and associates [33,34]. These results should stimulate the reconsideration of the ESR lines of C_{60}^{1-}.

2. Experimental

All manipulations were performed under argon atmosphere with the rigid exclusion of air. Chemicals were handled with Schlenk vacuum-line techniques.

The C_{60} with purity 99.9% was purchased from Tianan Company (PR China). Tetrahydrofuran (THF) and hexane were distilled from sodium-benzophenone under

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argon in the Schlenk system. Water was distilled and bubbled with argon under reflux for 10 min before use. NaH, Al–Ni alloy, LiOH, NaOH and KOH were chemically pure and were used as purchased.

ESR spectra were recorded on a Bruker ER 200-D-SRC 10/12 spectrometer. UV–NIR spectra were recorded on a Shimadzu UV-3100. Mass spectra were recorded on a Finnigan mat API SSQ-710 and LCQ Mass Spectrometer. IR spectra were recorded on a Bruker IFS66V FT-IR spectrometer. Thermogravimetric analysis (TGA) spectra were obtained on a Perkin–Elmer thermal analyzer.

2.1. NaC_{60} $(THF)_x$ $(0<x<1)$

To a suspension of 36.0 mg C_{60} powder (0.05 mmol) and 120 mg NaH powder(5 mmol, excess) in 25 ml THF in the Schlenk system with stirring, 3 ml of degassed water was added, and the reduction reaction proceeded immediately with gas bubbling, the THF solution gradually turning red. After reacting for 1 h, the dark red solution was separated from the water phase. 20 ml of fresh distilled hexane was added to 20 ml of the dark red solution to precipitate the solid $NaC_{60}(THF)_x$, which was isolated, washed with hexane, dried under vacuum and used for measurements. TGA was used to ascertain further the THF content: TGA (THF weight loss%). Calc. for NaC_{60} (THF): 8.83; Found: 2.32. λ_{max} (THF) 1075, 1032, 994 nm. ν_{max} (KBr) 527(s), 576(m), 1182(w), 1427(m) cm^{-1}. ESI MS (negative ion mode) m/z 720.

2.2. MC_{60} $(THF)_x$ $(M=Li,\ K)$ $(0<x<1)$

The procedure used for generating LiC_{60} and KC_{60} solutions was similar to that of NaC_{60} in THF [22,23], except that MOH (M = Li, K) was used instead of NaOH. 20 ml of freshly distilled hexane was added to 20 ml of THF solution of MC_{60} to get precipitates of $MC_{60}(THF)_x$ that were isolated, washed with hexane, dried under vacuum and used for measurements. $LiC_{60}(THF)_x$: TGA (THF weight loss%). Calc. for LiC_{60} (THF): 8.94; Found: 2.03. λ_{max} (THF) 1075, 1032, 994 nm. ν_{max} (KBr) 526(s), 576(m), 1182(w), 1428(m) cm^{-1}. ESI MS (negative ion mode) m/z 720. $KC_{60}(THF)_x$: TGA (THF weight loss%). Calc. for KC_{60} (THF): 8.65; Found: 1.66. λ_{max} (THF) 1075, 1032, 994 nm. ν_{max} (KBr) 527(s), 576(m), 1182(w), 1428(m) cm^{-1}. ESI MS (negative ion mode) m/z 720.

3. Results and discussion

3.1. General properties

In the vis–NIR spectra of the red solutions of MC_{60} (M = Li, Na, K) in THF appear absorption bands at 1075 and 994 nm, which is in accord with that previously reported for the monoanion C_{60}^- formed in solution [11,24,27]. The electrospray ionization mass spectra of the THF solution of MC_{60} all showed a very strong peak at $m/z = 720$, which belongs to C_{60} monoanion. There was a minor peak at $m/z = 736$ assigned to $C_{60}O$ that formed by O_2 dissolved in flow phase. The alkali-metal salts of the C_{60} monoanion are soluble in THF, CH_3CN, DMSO and EtOH.

The IR spectra of MC_{60} $(THF)_x$ (M = Li, Na, K) $(0<x<1)$ all exhibit bands at 1427 (1428), 1182, 576, and 526 (527) cm^{-1}, which are similar in frequency to bands in the spectra of C_{60} and many C_{60}-containing materials [35]. Weak bands at 2970, 2844, 1067, 905 and 851 cm^{-1}, correspond to THF absorbances.

Only the C_{60}^- monoanion was generated although the reducing agents used in our experiments were excessive. NaH can reduce C_{60} to C_{60}^- in THF–water with no tendency to form fullerene hydrides being observed, because the reaction medium is alkaline. It is different from the solid-state reaction of C_{60} with NaH or KH [7], which forms either C_{60}^{2-} or C_{60}^{3-}. Due to the fact that MOH (M = Li, Na, K) dissolves in water while MC_{60} is soluble in THF, we can obtain MC_{60} by reducing C_{60} with Al–Ni alloy in a THF–MOH aqueous system and isolate the product from the reaction system easily.

It has been found that C_{60}^- is sensitive to oxygen and the oxidation product in THF is C_{60}. The oxidation process of MC_{60} (M = Li, Na, K) in THF was monitored by NIR spectra and the results are very similar [23]. The oxidation rate of MC_{60} increases in the order of $Li^+ < Na^+ < K^+$, which indicates a countercation dependence and can be rationalized by a mechanism involving superoxide ion being stabilized by the cations [9]. The K^+ has a stronger tendency to bind O_2^- forming a ion pair than Na^+, Li^+, because it has the largest ionic radius.

3.2. ESR spectra

The spectra of $MC_{60}(THF)_x$ (M = Li, Na, K) $(0<x<1)$ in solid state and MC_{60} in solution showed that the ESR signals are similar to those of C_{60}^- in previous reports [25,28–30]. The g-value and peak widths vary slightly with various metal ions and states that are listed in Table 1. The linewidth for solid form is broader than that in THF solution. The anisotropy of the g-factor itself is probably caused [9] by the interaction of C_{60}^- with the crystal field that is formed by the countercations around the C_{60}^-. The different ESR line shape among the various metal ion fullerides might reflect the different environments around the C_{60}^- monoanions.

Table 1
g-Values and linewidth for C_{60}^{-} with various metal ions in various states

Sample	T (K)	g	ΔH_{pp} (G)	Reference
LiC_{60} (in THF)	294	2.0016, 2.0009	1.625	This work
NaC_{60} (in THF)	295	2.000, 1.999	1.75	This work
KC_{60} (in THF)	295	2.0011	1.75	This work
LiC_{60} $(THF)_x$	294	2.001	2.75	This work [a]
NaC_{60} $(THF)_x$	295	2.000	30	This work [a]
KC_{60} $(THF)_x$	294	2.0009	16.5	This work [a]
Li_xC_{60} $(THF)_y$	r.t.	2.0021, 2.0006, 1.9986		[15]
Na_xC_{60} $(THF)_y$	r.t.	2.0031, 2.0013, 1.999	30	[13]
NaC_{60} $(THF)_5$	290	1.999	35	[19]
KC_{60} (THF)	300	1.9987	34.1	[17]

[a] $(0<x<1)$.

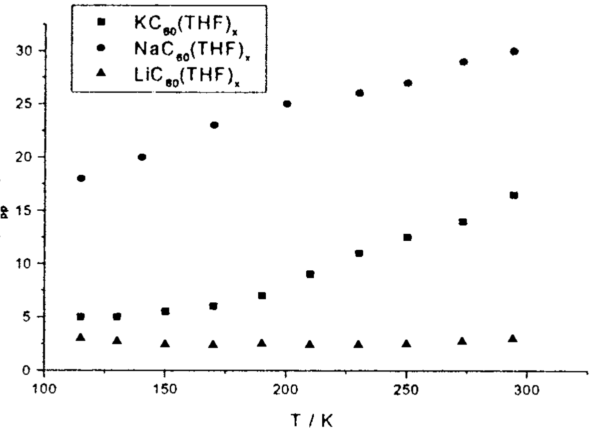

Fig. 2. Plot of ESR spectral linewidth as a function of temperature for $LiC_{60}(THF)_x$, $NaC_{60}(THF)_x$ and $KC_{60}(THF)_x$ $(0<x<1)$ in solid state.

Fig. 1 shows the temperature dependence of ESR spectra of $LiC_{60}(THF)_x$, $NaC_{60}(THF)_x$ and $KC_{60}(THF)_x$ $(0<x<1)$ in solid state over the temperature range 115–295 K. The line patterns among $LiC_{60}(THF)_x$, $NaC_{60}(THF)_x$ and $KC_{60}(THF)_x$ are quite similar. The line width of NaC_{60} and KC_{60} increased with increasing temperature (Fig. 2), which is similar to that previously reported for C_{60}^{-} [29], but these were varied for $LiC_{60}(THF)_x$. The A_1C_{60} phase transformations have not been found, because there is a small amount of THF in MC_{60}, which is different from the stoichiometry A_1C_{60} [2,6].

Figs. 3 and 4 shows the temperature dependence of the ESR spectra of LiC_{60}, NaC_{60}, and KC_{60} in THF. The spectra of three C_{60}^{-} salts in THF are quite similar and are anisotropic in the temperature range 250–150 K. The anisotropy spectra of LiC_{60} in the temperature range of 293 ~ 210 K are close to that for species with axial symmetry, and a third peak appears with $g=2.0004$ between 190 and 165 K. The second feature of the spectra of LiC_{60} is that the intensity of the narrow

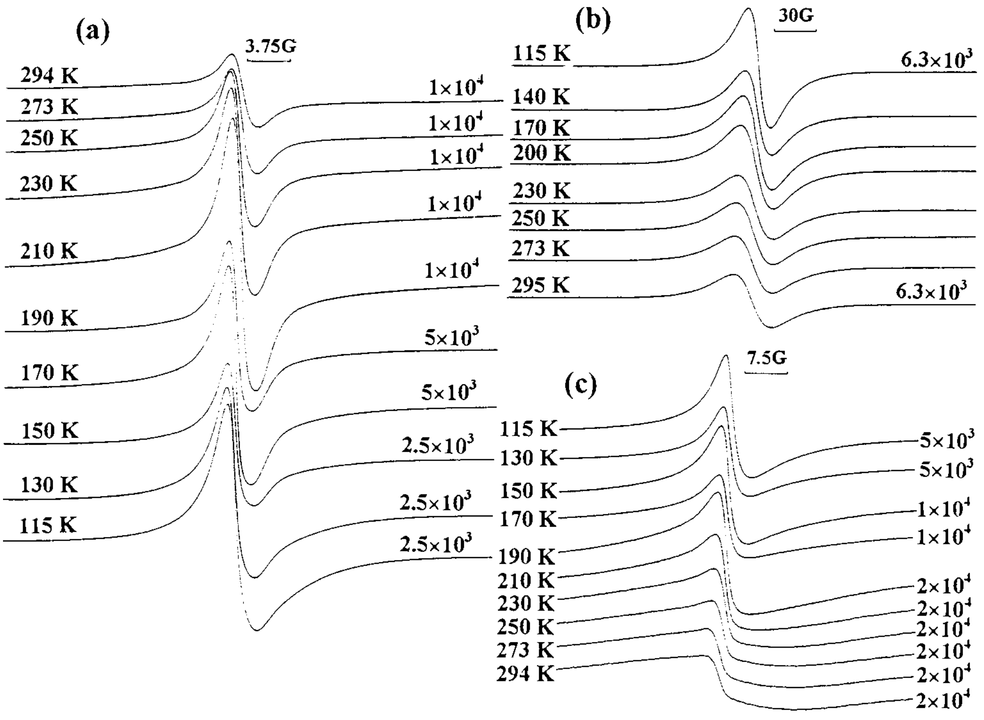

Fig. 1. Temperature dependence of the ESR spectra of (a) $LiC_{60}(THF)_x$ (b) $NaC_{60}(THF)_x$ (c) $KC_{60}(THF)_x$ $(0<x<1)$ in solid state. Temperatures and receiver gains are shown to the left and right of each spectrum, respectively.

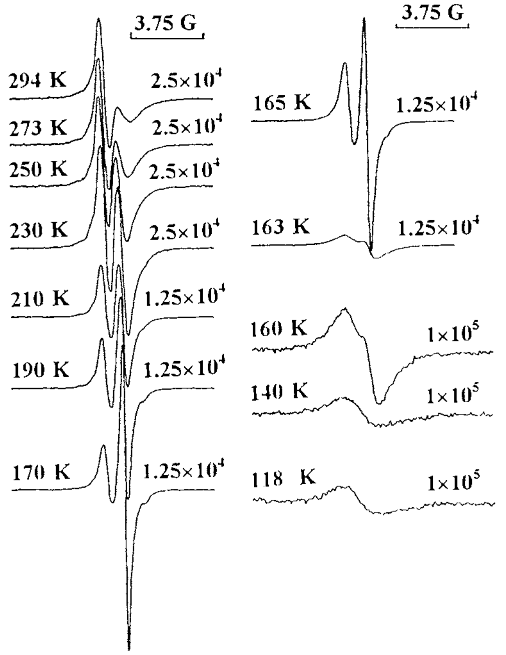

Fig. 3. Temperature dependence of the ESR spectra of LiC_{60} in THF. Temperatures and receiver gains are shown to the left and right of each spectrum.

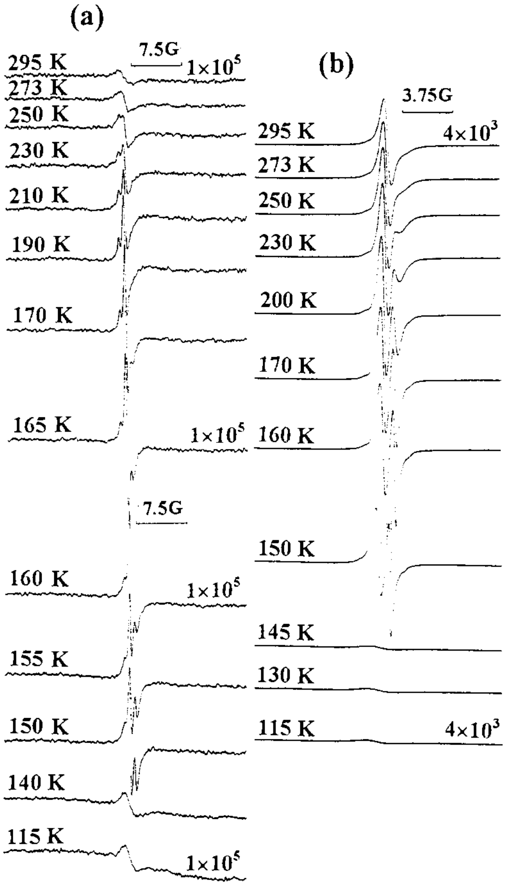

Fig. 4. Temperature dependence of the ESR spectra of (a) NaC_{60}; (b) KC_{60} in THF. Temperatures and receiver gains are shown to the left and right of each spectrum.

line with $g = 2.0009$ first increases with decreasing the temperature from 293 to 170 K, and reaches a maximum value at 170 K, then decreases with further decreasing temperature. The ESR signal becomes isotropic at 140 K and then vanishes gradually with decreasing temperature, the situations for NaC_{60} and KC_{60} are quite similar, with the maximum value of the signal intensity appearing at 170 K as well, which is close to the melting point of THF (165 K). The temperature dependence of the ESR line width (outer peak to peak) of LiC_{60} in THF is plotted against the temperature (Fig. 5). This shows that the line width varies slightly between 295 and 170 K, but has an abrupt change at about 165. Schell-sorokin et al. [8], Brezová et al. [33] and Moriyama et al. [13] described a similar effect for KC_{60}, fullerene derivative monoanion and $Na_xC_{60}(THF)_y$ in THF and DMSO respectively, but they did not mention why. The phase transition occurs and the physical properties of the THF solution have a sharp change at the melting point (165 K) since THF does not form a glass. THF crystallization at 165 K results in exclusion of solute from the lattice and leads to C_{60}^{1-} anion aggregation, which promotes line broadening.

The organic radical derivatives of C_{60} have a strong tendency to dimerize [36,37]; photopolymerization has also been observed for solid film [38]. It has been found that stoichiometric CsC_{60} has a dimer phase between 160 and 220 K, and the dimer (O' phase) is insulating as is expected from the diamagnetic coupling of the unpaired electrons in the C_{60}^{-} HOMO level upon dimerization. The ESR linewidth variation with the phase transformation can be well understood in terms of the well-established dependence of the spin–lattice relaxation times on dimensionality [2]. We suppose that the aggregation of solvate THF favors C_{60}^{-} anions closing together and leading to the formation of a diamagnetic dimer $(C_{60})_2^{2-}$, which is in agreement with the drastic decrease of the magnetic moment of $NaC_{60}(THF)_5$ be-

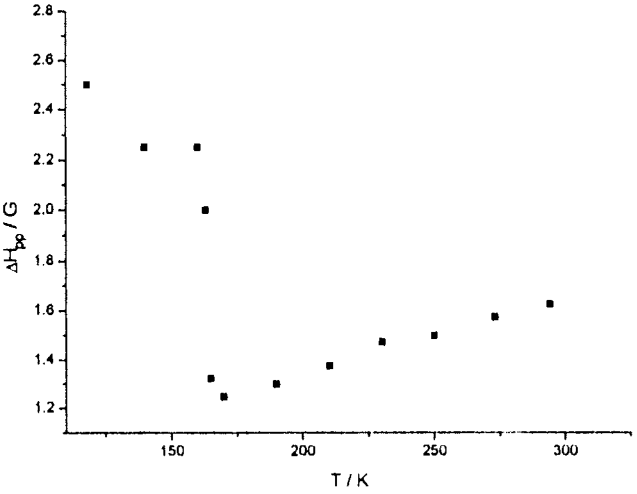

Fig. 5. Plot of ESR spectral linewidth as a function of temperature for LiC_{60} in THF.

low 200 K [27]. The dimerization mechanism also explains the ESR signal diminishing gradually when the temperature falls below 170 K.

By the reaction of C_{60} and NaH or AlNi alloy/MOH in THF–water system, $MC_{60}(THF)_x$ (M = Li, Na, K) ($0 < x < 1$) was prepared without stoichiometric control. The ESR spectra of MC_{60} (M = Li, Na, K) in THF depend on the temperature, the linewidth has an abrupt increase at about the THF melting point and the ESR signal diminishes gradually when the temperature is below 170 K. The proposed explanation for this is that the THF crystallization results in exclusion of solute from the lattice and leads to C_{60} anion aggregation, which promotes line broadening and diamagnetic dimer $(C_{60})_2^{2-}$ formation. The oxidation rate of C_{60}^- depends on the countercations present, which can be rationalized by a mechanism involving superoxide anion being stabilized by cations. The C_{60}^- is oxidized to form C_{60} black powder in dry organic solvent.

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