

Diamagnetic Clusters of Paramagnetic Endometallofullerenes: A Solid-State MAS NMR Study

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Solid powder samples of complexes of the endometallofullerenes (EMF) La@C₈₂ and Y@C₈₂ with hexamethylphosphoramide (HMPA) were studied by magic-angle spinning (MAS) NMR. We have obtained well-resolved ³¹P NMR spectra and ¹³C NMR spectra for both La-EMF/HMPA and Y-EMF/HMPA and ¹³⁹La spectra for the La-EMF/HMPA. The ³¹P measurements on La-EMF/HMPA and Y-EMF/HMPA have revealed considerable chemical shifts of ³¹P signals relative to pure HMPA. Two-dimensional exchange ³¹P experiments revealed that HMPA molecules at different sites in the EMF/HMPA complex do not change positions at a time scale of up to 1 s. Both EMF samples demonstrate a vast chemical shift range for ³¹P of the bound HMPA molecules. In addition, the La-EMF/HMPA exhibits the enormous spreading of the chemical shifts for ¹³⁹La. The experimental results suggest that paramagnetic La@C₈₂ and Y@C₈₂ in the solid state form clusters (nanoparticles) in which the exchange coupling of the EMF takes place with quenching of the most electron spins.

Introduction

Endohedral metallofullerenes are organometallic compounds containing one metal atom (sometimes two or three atoms) inside the fullerene cage C_{2n}.^{1–5} Although endometallofullerenes hold much promise for applications as the basis for novel magnetic materials,^{2–3} contrast agents for NMR imaging,^{6,7} and radionuclide molecular vehicles for nuclear medicine,^{7,8} chemical and physical properties of EMF yet remain poorly studied. In part, little is known either about complexes, which the EMF molecules can form with the solvent molecules, or clusters, which the molecules of EMF can form with each other.

Solid-state NMR spectroscopy with magic-angle spinning (MAS) is commonly used for the determination of molecular structure and dynamics of materials. The application of MAS allows separation of resonances in NMR spectra with overlapping powder patterns so that unique spectral lines can be obtained for chemically distinct sites in the sample.^{9–13} Although many MAS NMR investigations in pristine and doped fullerenes have been published (see, for example, refs 9 and 10), no NMR studies of endometallofullerenes in the solid state have been performed up to now.

Herein, we report the first MAS NMR investigation of the solvent including powder samples of La-EMF and Y-EMF. As the solvent, we used hexamethylphosphoramide (HMPA). Phosphorus contains only one isotope, ³¹P, with a nuclear spin

of $I = 1/2$. This and the high gyromagnetic ratio result in a high sensitivity and provides great probe for NMR experimentation. Additionally, the range of chemical shifts for ³¹P in diamagnetic compounds of pentavalent phosphorus (≈ 100 ppm) is much larger than that for ¹H (≈ 20 ppm) in diamagnetic compounds.¹⁴ In addition, HMPA has an advantage as the effective solvent for EMF. We have acquired well-resolved MAS NMR spectra of ³¹P, ¹³C, and ¹³⁹La, demonstrating, for the first time, that the paramagnetic endometallofullerenes in the solid state form cluster structures (nanoparticles) in which the exchange coupling of the EMF takes place with quenching of the most electron spins.

Materials and Methods

All chemicals used were obtained from the Aldrich Chemical Co. The soots, which contained La-EMF or Y-EMF, were synthesized in the home-built electric-arc reactor. EMF was extracted from the soot by organic solvents under argon atmosphere following the previously developed scheme.¹⁵ In the first step, empty fullerenes (C₆₀, C₇₀, etc.) were removed from the soot by *o*-xylene. Purified EMF was obtained from the soot via a second extraction step with *N,N*-dimethylformamide (DMF).¹⁵

The elemental analysis was performed using X-ray fluorescence spectroscopy on a VRA-30 analyzer and showed that the contents of La or Y in the obtained DMF extracts were 11.8–12.3% for La-EMF and 7.9–8.1% for Y-EMF, respectively. These metal contents almost coincide with the theoretical lanthanum content in La@C₈₂ (12.4%) and yttrium content in Y@C₈₂ (8.3%). All the EMF samples were dried until a constant weight was achieved. On the basis of elemental analysis data, the samples contained about 2–3 wt % of nitrogen. Therefore, similar to empty fullerenes, these EMF samples contain a fixed amount of the solvent that is bonded to EMF clusters.¹⁵

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The mass spectroscopic analysis was performed by a laser-desorption ionization (LDI) technique using a time-of-flight mass spectrometer (TOF-1, Bruker).

The powder samples of endometallofullerenes for NMR, EPR, and infrared spectroscopy were prepared from their solutions in HMPA. The solvent was evaporated under vacuum (10^{-2} mm Hg) at 90 °C until a dry solid film without traces of vapors of the volatile compounds was obtained. In the following text, these samples are denoted as La-EMF/HMPA and Y-EMF/HMPA, respectively.

IR spectra were taken on a Specord-M82 spectrophotometer at room temperature. The samples were incorporated into KBr tablets. EPR spectra were recorded on a Varian E-104A spectrometer in the X-band under the conditions precluding the distortion of the line shape. For EPR measurements, the powders were transferred under the argon atmosphere into standard quartz tubes with an inner diameter of 3 mm and deoxygenated before the tubes were sealed in vacuum.

All NMR experiments were performed on a 500 MHz Chemagnetics/Varian spectrometer (static magnetic field 11.7 T, operating frequencies ^1H , 499.7 MHz; ^{31}P , 202.3 MHz; ^{13}C , 125.7 MHz; ^{139}La , 70.6 MHz). Polycrystalline powders of EMF for NMR measurements were ground with an agate mortar and pestle under a nitrogen atmosphere and subsequently transferred to a zirconia rotor and capped under the nitrogen atmosphere. The magic angle was adjusted using an external sample of KBr. MAS NMR spectra were obtained at spin rates from 9 to 20 kHz. The temperature was controlled using a Varian VT-unit. The temperature inside the rotor was calibrated by ^{207}Pb NMR spectroscopy using the chemical shift temperature dependence of $\text{Pb}(\text{NO}_3)_2$.¹⁶ The spatial temperature variation within the spinning rotor was ~ 10 K. Two-dimensional (2D) ^{31}P exchange experiments¹⁷ were performed at a spinning rate 15 kHz.

Results

Typical mass spectra of the final EMF extracts are depicted in Figure 1. In $\text{La}@\text{C}_{2n}$, the most intense line belongs to the molecular cation of $\text{La}@\text{C}_{82}$. This spectrum also shows a less intense line of $\text{La}@\text{C}_{80}^+$ and several minor lines arising from other $\text{La}@\text{C}_{2n}^+$, approximately from $\text{La}@\text{C}_{74}^+$ to $\text{La}@\text{C}_{106}^+$. The mass spectrum of the $\text{Y}@\text{C}_{2n}$ preparation exhibits mainly the line of $\text{Y}@\text{C}_{82}$. There are no peaks of empty fullerenes (C_{60} , C_{70} , or larger) in either mass spectra.

Figure 2 presents high-resolution MAS ^{31}P NMR spectra of the powder samples of La-EMF/HMPA and Y-EMF/HMPA at room temperature. Each spectrum indicates the existence of several magnetically nonequivalent phosphorus sites. In La-EMF (spectrum a), one can distinguish two intense lines which have the chemical shifts $\delta = +0.8$ ppm and -5.1 ppm, respectively, with the ratio of the intensities of approximately 1:1.5. There is also a third line in this spectrum with $\delta = -29.5$ ppm, the intensity of which is about 3% of the integral intensity of the whole spectrum. The most intense line has a shoulder on the low-field side ($\delta \approx -3.7$ ppm). In Y-EMF (spectrum b), there are also three ^{31}P resonances with $\delta = +1.4$, -5.0 , and -29.8 ppm. The intensities of the first two lines are approximately equal to each other, while the intensity of the third line is about 4% of the integral intensity of the whole spectrum.

All these ^{31}P resonances arise from different crystallographic sites, probably from molecules of HMPA bound to different topoisomers of La-EMF and Y-EMF after evaporation of the bulk solvent. The interaction of La-EMF and Y-EMF with molecules of HMPA has been supported by the IR spectroscopy data. In both cases, the absorption band of the stretching

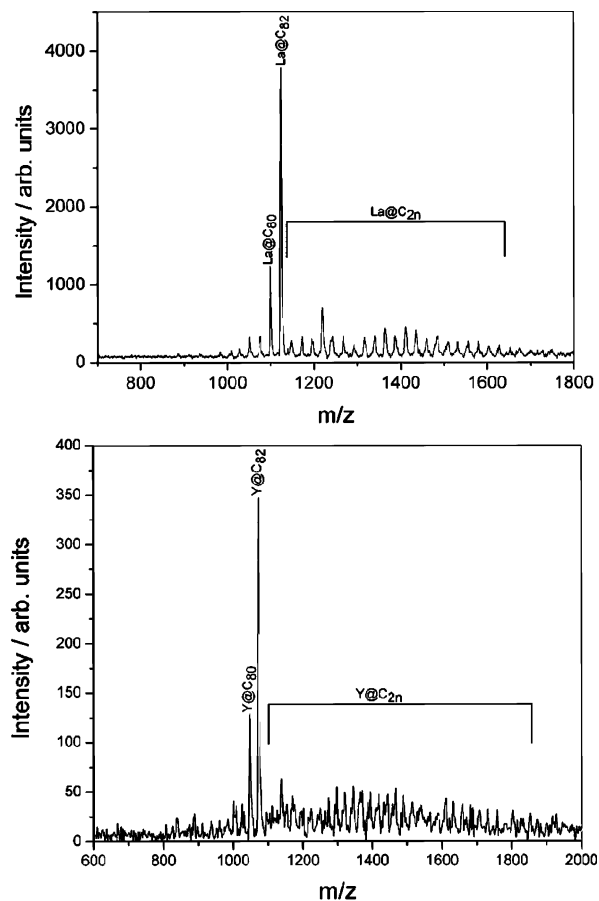


Figure 1. Mass spectra of the preparations of La-EMF (a) and Y-EMF (b).

vibration of P=O bond has occurred to be broadened when compared to the neat solvent. Moreover, this bond has been shifted to 1193 cm^{-1} for La-EMF/HMPA and to 1189 cm^{-1} for Y-EMF/HMPA versus 1209 cm^{-1} for the neat solvent. These changes of the vibration stretching frequency indicate strong interactions between the molecules of HMPA and EMF in the complexes. From the intensity of this absorption band, the composition of the complexes was assessed to be from two to three molecules of HMPA per molecule of EMF.

For both samples, the range of the chemical shifts of ^{31}P lines spreads from approximately 1 to -30 ppm (see Table 1). Meanwhile, for ^{31}P in all different compounds of pentavalent phosphorus, including HMPA, the entire range of tabulated values of the diamagnetic chemical shifts usually does not exceed 100 ppm.¹⁴ In this regard, the spread of the chemical shifts of the ^{31}P for one molecule (HMPA) in La-EMF/HMPA and Y-EMF/HMPA appears rather large in comparison with other diamagnetic pentavalent phosphorus compounds.

To investigate the spatial proximity of different HMPA molecules responsible for two major resonance lines of ^{31}P , 2D phosphorus–phosphorus exchange experiments were performed. Contour plots of these 2D experiments for La-EMF/HMPA and Y-EMF/HMPA are shown in Figures 3 and 4, respectively. If a molecule of HMPA could change its position from one place to another during the exchange time, the spectra would show cross-peaks between the lines of different shifts.¹⁷ The absence of cross-peaks indicates that no exchange takes place on the used time scales. Thus, ^{31}P exchange NMR spectra have revealed that the different HMPA molecules do not change their positions at the time scale of up to 1 s.

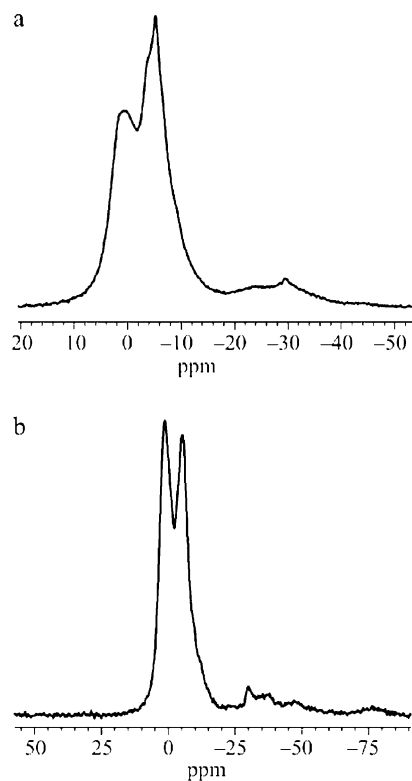


Figure 2. ^{31}P MAS NMR spectra of the powder samples of La-EMF/HMPA (a) and Y-EMF/HMPA (b) recorded at room temperature. The spin rate is 15 kHz. The number of accumulations is 2048 (a) and 512 (b). The spectrum width is 15 kHz (a) and 30 kHz (b). The shifts of the resonances are referenced externally to the position of the ^{31}P NMR of neat HMPA.

TABLE 1: Experimental ^{31}P Chemical Shifts Obtained in MAS NMR Spectra of the HMPA-Solvates of La-EMF and Y-EMF^a

	temperature/K	δ/ppm		
La-EMF	295	+0.8	-5.1	-29.5
	324	+1.4	-5.3	-29.4
Y-EMF	295	+1.4	-5.0	-29.8
	324	+1.3	-5.5	-30.0

^a The shifts of the resonances are referenced externally to the position of the ^{31}P NMR of neat HMPA.

Table 1 presents the values of the chemical shifts measured at two different temperatures. For La-EMF, we can note a slight increase in δ of the first line with temperature while the positions of other lines were almost unchanged. For Y-EMF, the chemical shifts of all lines did not change in this temperature range. Thus, the shifts are not inversely proportional to the absolute temperature, as it should have been in the case of usual paramagnetic shifts.¹⁸ It suggests the strong exchange coupling of unpaired electrons of EMF with the loss of the molecular paramagnetism.

Table 2 presents the results of the EPR measurements. The EPR signal of the powder sample of La-EMF/HMPA occurred as a symmetrical Lorentzian single line with g -factor 2.0015 and line width $\Delta H_{\text{pp}}=0.44$ mT (at 295 K). The powder of Y-EMF/HMPA gave a similar single line with $\Delta H_{\text{pp}}=0.35$ mT at 295 K. The smaller line width of the signal for the case of Y@C₈₂ conforms with the correspondingly smaller value of hyperfine coupling constant, compared to La@C₈₂.^{19–21} The integral intensities of these signals conformed about one spin per 40–50 molecules of M@C₈₂. Hence, the EPR results also

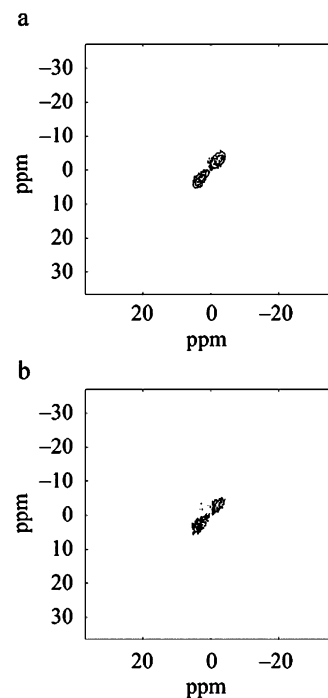


Figure 3. Contour plots of the 2D ^{31}P exchange experiments on the powder samples of La-EMF/HMPA with the exchange time of 500 ms (a) and 1000 ms (b). The record conditions: room temperature, spin rate 15 kHz, two accumulations.

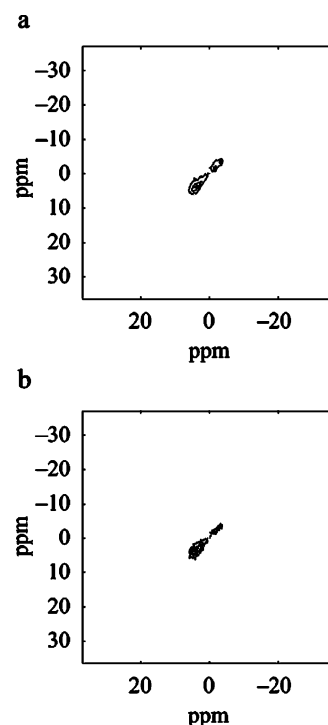


Figure 4. Contour plots of the 2D ^{31}P exchange experiments on the powder samples Y-EMF/HMPA with the exchange time of 500 ms (a) and 1000 ms (b). The record conditions: room temperature, spin rate 15 kHz, two accumulations.

corroborate the spin pairing. The intensity of the EPR signal has essentially no dependence on temperature.

^{13}C NMR spectra of these powder samples of La-EMF/HMPA and Y-EMF/HMPA are shown in Figure 5. Apart from two narrow peaks at 36.5 and 29.3 ppm, which arise from carbons of the HMPA molecules, there is a manifold of signals in the range approximately from 140 to 166 ppm. This range of

TABLE 2: Experimental Parameters Obtained from the EPR Spectra of the HMPA-Solvates of La-EMF and Y-EMF

	temperature/K	<i>g</i> -factor	$\Delta H_{pp}/\text{mT}$	integral intensity/ arbitrary units
La-EMF	295	2.0015	0.44	1
	373	2.0015	0.45	0.87
Y-EMF	295	2.0014	0.35	1
	373	2.0014	0.40	0.94

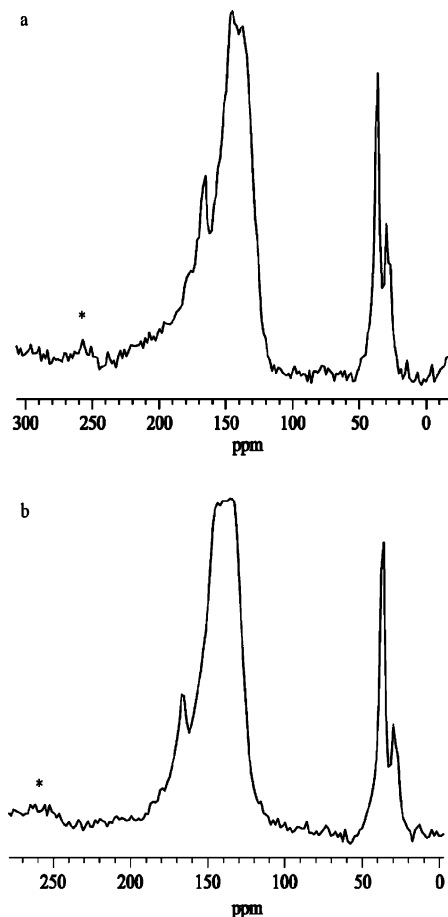


Figure 5. ^{13}C MAS NMR spectra of the powder samples of (a) La-EMF/HMPA and (b) Y-EMF/HMPA recorded at room temperature. The spin rate is 15 kHz. The number of accumulations is 2954 (a) and 4000 (b), respectively. The spectrum width is 200 kHz. The shifts of the resonances are referenced externally to the position of the ^{13}C NMR of tetramethylsilane.

chemical shifts is known for ^{13}C of empty C_{82} (131–151 ppm) as well as for solutions of diamagnetic anions of La@C_{82} , which were reduced electrochemically (131–168 ppm), and for solutions of diamagnetic dimetallofullerenes $\text{La}_2\text{@C}_{80}$.²² Both samples exhibit the well-resolved ^{13}C NMR spectra without being deliberately transformed into diamagnetic monoanions, as it was done in ref 22.

Figure 6 represents the ^{139}La NMR spectrum of the powder sample of La-EMF/HMPA. This spectrum exhibits three resonances at 1650, 900, and -400 ppm, the middle peak being twice as intense as the other two. The chemical shift at -400 ppm is close to the shifts observed previously for diamagnetic $\text{La}_2\text{@C}_{80}$ (at -403 ppm) and for diamagnetic anions of La@C_{82} (at -450 and -520 ppm).²² Two other resonances have never been reported previously, to our knowledge. Furthermore, the scope of the chemical shifts of ^{139}La in diamagnetic complexes is about 1200 ppm spreading from -130 to 1100 ppm.²³ Meanwhile, our sample has given the resonances with the

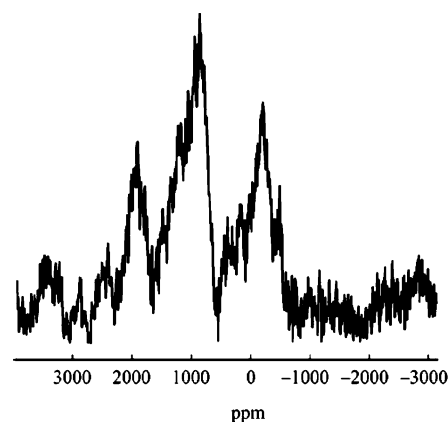


Figure 6. A ^{139}La MAS NMR spectrum of the powder sample of La-EMF/HMPA recorded at room temperature. The spin rate is 15 kHz, the number of accumulations is 80 000, the spectrum width is 500 kHz. The shifts of ^{139}La are externally referenced to an aqueous solution of LaCl_3 .

chemical shifts about -400 , 900, and 1650 ppm (see Figure 6), which are far beyond the scope of the chemical shifts of this nucleus in usual diamagnetic substances.

Discussion

Mono-metallofullerenes of lanthanum and yttrium are paramagnetic molecules. Paramagnetism results from the fact that the La atom donates two 6s-electrons and partially one 5d-electron to its fullerene cage while the Y atom donates two 5s-electrons and partially one 4d-electron to its fullerene cage (see reviews 2–5 and references therein). Correspondingly, these paramagnetic molecules give distinctive EPR signals in solutions, the octet hyperfine structure being observed for La@C_{2n} because of the coupling of the unpaired π -electron with the nuclear magnetic moment of ^{139}La ($I = 7/2$) while the doublet structure being observed for Y@C_{2n} (with $I = 1/2$ for ^{89}Y).^{19–21,24}

However, according to the EPR data, the powders of these molecules only exhibit a residual paramagnetism of less than 3% of the total amount of the EMF molecules. In addition, both samples exhibit well-resolved ^{13}C NMR spectra corresponding to the spectra of the diamagnetic derivatives of EMF. These findings suggest that an important rearrangement of the electronic structure of EMF takes place in the solid with loss of the molecular paramagnetism.

A partial loss of the paramagnetism of EMF in the solvents of high polarity has been already noted in our previous papers.²⁴ The EPR signals of La-EMF and Y-EMF in DMF and DMSO were not as intense as expected, assuming each molecule of EMF has one unpaired electron with $S = 1/2$. Therefore, we suggested that EMF form clusters on dissolving in polar solvents in which the exchange coupling of molecules of EMF with quenching of the electron spins takes place.²⁴

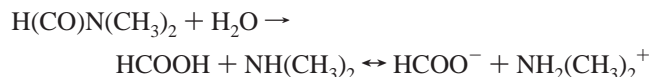
An alternative proposal was made by Solodovnikov et al.²⁵ These authors called attention to the similarity of the electronic absorption spectra of La@C_{82} in DMF and HMPA, which were obtained in their own work, with the UV–vis spectra of the La@C_{82}^- anion, obtained in the work of Akasaka et al.²² On the basis of this similarity, they suggested that the paramagnetic La@C_{82} is reduced by the solvent into the diamagnetic anion, La@C_{82}^- .^{25a} At this point, it is worthy noting that our ^{13}C NMR spectra of La-EMF/HMPA (Figure 5) are similar to the ^{13}C spectrum of La@C_{82}^- from the same paper of Akasaka et al.²²

By themselves, neither the similarity in the UV–vis spectra nor the similarity in the ^{13}C NMR spectra can serve as the basis

for the anion hypothesis as the electronic states and the absorption spectra of fullerenes undergo the dramatic changes with formation of donor–acceptor solvates, complexes, and clusters (for example, see ref 26 and the references therein). The formation of complexes of EMF with DMF was shown by IR spectroscopy in ref 15a. In the present work, we showed the formation of complexes between EMF and molecules of HMPA (see earlier section). Moreover, paramagnetic EMF molecules can form the spin-transfer complexes in which the electron spin density is located partially on atoms of the matrix in which the EMF molecules are embedded.²⁷ By the same reasoning, the finding of the EPR signals in the solutions of Ce@C₈₂ in DMF or pyridine do not prove that Ce@C₈₂, which is EPR-silent at 77–300 K, is indeed reduced to Ce@C₈₂[−] in these solvents.^{25b} In our opinion, the EPR signal discovered in the cited paper may be ascribed to the donor–acceptor solvates of Ce@C₈₂ inside the clusters of EMF (spin-transfer complexes), instead of the hypothetical EMF anions. Furthermore, Akasaka et al. obtained the M@C₈₂[−] anion in an electrochemical cell,²² whereas in the works 25a and 25b, the M@C₈₂[−] anion was proposed to be generated via reduction by the solvent; the nature of the counterion is left unanswered.

Applying electrospray ionization mass spectrometry (ESI-MS) technique in the negative ionization mode, Kareev et al. detected the anions of La@C₈₂ and Y@C₈₂ in the DMF extracts.²⁸ The cathode was the donor of electrons in the experiments of Kareev et al., likewise in the experiments of Akasaka et al.²² Therefore, the finding of the anions in the ESI-MS experiments at the negative ionization mode cannot be considered as the evidence in support of formation of anionic endohedral metallofullerenes during their extraction with *N,N*-dimethylformamide.

Taking into account a rather high electron affinity of endometallofullerenes,²¹ the possibility of reduction of EMF by the solvents cannot be entirely ignored. For example, as far as the presence of admixture of water in the solvent must not be entirely ruled out, it is worthy to consider a possible hydrolysis of DMF into the anion of formate and the cation of dimethylammonium that might proceed during extraction of EMF by DMF:



Then, the formate–anion might reduce EMF into the anion, after which the recombination of the radicals HCOO• would give oxalic acid that breaks down with formation of H₂O, CO, and CO₂ as the final products, along with M@C₈₂[−]. In principle, this hypothetical reaction scheme could solve both problems of the anion hypothesis, the genesis of the anion M@C₈₂[−] and the nature of the counterion. However, if this were so, then all of the EMF should have been reduced into anions by the formate admixture during the extraction process, since the initial amount of EMF in the soot is low. Consequently, we should have observed the total loss of the paramagnetic EMF; however, the EMF extracts always exhibited the EPR signals, the intensity of which was not less than 1 electron spin per 30–50 EMF molecules. Moreover, the EPR spectra of our La-EMF and Y-EMF dissolved in *o*-dichlorobenzene did not differ from the spectra published by other groups, who obtained their EMF without using DMF.²⁴ Furthermore, it is well known that fullerenes can react with amines.^{4,5} Therefore, if the aforementioned reaction scheme had taken place, then the EMF should have reacted with dimethylammonium during the high-temper-

ature extraction procedure giving the final products such as M@C₈₂H_{*n*}R_{*m*}. However, such products were not detected in the mass spectra of our EMF preparations.

Presently, there is no evidence in the available literature in the unambiguous support of the anion hypothesis. On the contrary, the hypothesis that EMF form nanoparticles (clusters) in the solvents of high polarity has been recently proved. Having studied the optical absorption, fluorescence spectra, and dynamic light scattering of solutions of Y-EMF in polar solvents, we demonstrated for the first time that the endometallofullerenes indeed form nanoparticles, the mean size of which ranges up to 100 nm.²⁹ Therefore, we suggest that the dominant bulk of EMF in the solid powders also exists as clusters rather than anions.

The data of EPR spectroscopy as well as the spreading of the shifts of the NMR resonances for ³¹P and ¹³⁹La can be explained on the basis of the cluster structure of the EMF solids. Spectroscopic and structural studies, such as EPR, synchrotron X-ray diffraction, and ultrahigh vacuum scanning tunneling microscopy measurements, have clearly shown evidence for a nearby complete charge transfer from the encaged metal atom to the carbon cage in La@C_{2*n*} and Y@C_{2*n*} that results in the formal electronic structure as M⁺³@C_{2*n*}^{−3} (the “superatom” concept).^{2–5} Additionally, there are experimental data which unambiguously indicate that the electron spin density is partially localized even beyond the fullerene cage.²⁷ This “spin leakage” obviously facilitates a strong exchange coupling of adjacent molecules of EMF with quenching of the electron spins. As another example, the formation of the EPR silent dimers from the C₆₀ monoanions has been described in ref 10b.

One way of explaining the residual paramagnetism of the nanoparticles is to assume that EPR detects paramagnetic defects, such as odd EMF molecules, while most of the EMF electron spins are quenched. Then, the finding that chemical shifts of the NMR resonances are independent of temperature suggests the diamagnetic origin of the observed shifts. The observation of the single Lorentzian EPR line, instead of the signal with the hyperfine structure, can be understood in terms of exchange coupling between the localized spins of the defects and the delocalized spins of the nanoparticles. It is known that the most relevant contribution to the chemical shifts in diamagnetic aromatic compounds arises from ring currents of the π-electrons.¹⁸ Considering the conformational variations of the fullerene cage of EMF and the variability of EMF/HMPA clusters in size and number of molecules, one can suggest that different clusters of EMF should yield different ranks of deshielding for the same nuclei, depending upon specificity of the electron ring current, the direction of circulation of the current, and its proximity to the resonant nuclei. For example, the anomalous shift values of the lanthanum NMR lines may indicate the influence of the cluster delocalized spins on the electrons of the lanthanum.

An alternative explanation is to assume that EPR detects conduction band electrons, the energies of which are above the Fermi level, while other electron spins inside the nanoparticles are quenched. It is well known that the polarization of electrons and holes in magnetic field (spin paramagnetism of the degenerated electron gas) does not depend on temperature.¹⁸ If that is the case, then the large shifts of ¹³⁹La NMR (and ³¹P NMR, possibly, too) may be classified as the Knight shifts caused by the density of unpaired conduction electrons at the position of the NMR observed nuclei. Such shifts are essentially temperature independent.¹⁸ However, further experiments and

appropriate quantum chemical calculations are required to explain the shifts in detail.

Conclusions

The experimental results presented in this paper demonstrate that well-resolved multinuclear (^{31}P , ^{13}C , ^{139}La) MAS NMR spectra can be obtained from powder compounds of EMF. Most likely, the paramagnetic La@C_{82} and Y@C_{82} form clusters (nanoparticles) in which the exchange coupling of the EMF takes place with quenching of the most electron spins. In the nanoparticles, HMPA phosphorus atoms and the central metal atoms strongly interact with the delocalized electrons. Thus, MAS NMR provides a unique means of investigating clusters of EMF in the solids with full details.

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