Fullerides: heterometallic superconductors with composition $M_2M^{\prime}C_{60}$ (M = K, Rb; M^{\prime} = Yb, Lu, Sc)

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One- or two-step reactions of potassium and rubidium fullerides with composition M_kC_{60} (M = K, Rb; k = 3-6) and $K_6C_{60} + m$ K mixtures (m = 1, 3) with anhydrous salts M'Cl₃ (M' = La, Pr, Nd, Sm, Gd, Tb, Yb, Lu, Y, Sc) and YbI₂ in a toluene—THF medium afforded heterometallic fullerides $M_{3-n}M'_nC_{60}$ (n = 1-3). Among these compounds, substituted fullerides with composition $M_2M'C_{60}$ (M' = Yb, Lu, Sc) display superconducting properties with critical temperatures of 14–20 K.

Key words: fullerenes, fullerides, lanthanides, potassium, rubidium, ytterbium, lutetium, scandium, superconductivity.

The insertion of metal atoms into voids of the lattice of C_{60} fullerite leads to successive filling of the t_{1u} electron sublevel of the fullerene molecule and gives rise to fullerides possessing the superconducting properties. These properties have been discovered for the first time in homoand heteronuclear trimetallic fullerides of heavy alkali metals¹⁻⁵ with general composition MM'_2C_{60} (M = K, Rb; M' = K, Rb, Cs) having three electrons in the t_{1u} sublevel of the fullerene molecule. These compounds crystallize in the face-centered cubic (fcc) lattice.

It was hypothesized^{6,7} that fullerides could regain their superconducting properties upon transfer of more than six electrons to the C₆₀ molecule, *i.e.*, upon filling of the next higher-lying t_{1g} sublevel of the lowest unoccupied MO of fullerene, and the rare-earth fullerides could take on even unique superconducting properties.⁸ These expectations were only partially realized. Among alkalineearth fullerides, the maximum superconducting transition temperature (8.4 K) was found for face-centered cubic Ca₅C₆₀⁹ (4, 7, and 5.3 K for body-centered cubic Sr₆C₆₀,¹⁰ Ba₆C₆₀,¹¹ and K₃Ba₃C₆₀,¹² respectively). In a series of rare-earth fullerides, the maximum superconducting transition temperature is 12.5 K for La³⁺_xC₆₀¹³ (6 and 8 K for orthorhombic Yb_{2.75}C₆₀¹⁴ and Sm₃C₆₀,¹⁵ respectively). However, the superconducting transition was not confirmed for Yb_{2.75}C₆₀¹⁶ and Ba₆C₆₀.^{17,18} In the studies,^{16,17} it was suggested that orthorhombic Ba₄C₆₀ serves as the superconducting phase in the Ba– C_{60} system. The superconducting transition temperatures of these compounds having different compositions and structures are lower than the lowest temperature found for K_3C_{60} (19 K).¹⁹

In the present study, we dealt with homo- and heterometallic fullerides of scandium, yttrium, lanthanides, and alkali metals, which were prepared by homogeneousheterogeneous redox reactions of potassium and rubidium fullerides with lanthanide(III) chlorides and ytterbium(II) iodide in a toluene—THF solution at 300—340 K.

Experimental

Toluene and THF were purified and dehydrated according to standard procedures. Anhydrous chlorides M Cl_3 (M' = La, Pr, Nd, Sm, Gd, Tb, Yb, Lu, Y, Sc) were prepared by heating the corresponding crystal hydrates in the presence of ammonium chloride according to a known procedure;²⁰ YbI₂ was synthesized by the reaction of ytterbium metal with iodine in THF²¹ and desolvated by heating *in vacuo*. Potassium and rubidium fullerides were prepared by the reaction of a suspension of C₆₀ in toluene with the calculated amount of the corresponding metal at 120–130 °C according to a procedure described earlier.²² The synthesis of the starting alkali fullerides, mixing of suspensions of the fullerides with suspensions of M Cl_3 or YbI₂ in THF, the exchange reactions, and all intermediate operations were carried out *in vacuo* in all-sealed evacuated devices equipped

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya*, No. 8, pp. 1623–1628, August, 2004. 1066-5285/04/5308-1686 © 2004 Springer Science+Business Media, Inc. with a system of breakable glass valves and metallic anvils. Below, one of procedures is exemplified by the synthesis of K_2YbC_{60} .

Synthesis of K₂YbC₆₀ from K₅C₆₀ and YbCl₃. A reactor A containing a suspension of K_5C_{60} (0.25 g) in toluene (15 mL) was sealed to a reactor B containing a suspension of YbCl₃ (0.076 g) in THF (10 mL). The system was evacuated and sealed off from the vacuum line. Then all necessary operations associated with the replacement of the solvent, mixing of the reagents, and removal of wastes were performed. Finally, the intermediate reactor B was sealed off. The mixture of the compounds in the reactor A was kept in an oven at 75–85 °C for 15–20 days. The suspension over the crimson-red solution was stirred at regular intervals by shaking. After completion of the synthesis, a special system was sealed to the reactor A. This system made it possible to remove the solvent, dry the precipitate in vacuo, pack the dry substance in tubes, and fill the system with helium (at 350-400 Torr) necessary for thermal exchange between a cryostat and a sample in determining the superconducting properties.

Two-step procedure for the synthesis of K_2YbC₆₀. In the first step, YbC₆₀ was prepared by the reaction of K_3C_{60} with a suspension of YbCl₃ in THF (10 mL). Then the calculated amount of potassium metal was added.

The compounds synthesized according to the above-mentioned two procedures were found to have the same X-ray diffraction patterns and electrophysical properties.

Other heterofullerides of rare-earth metals and alkali metals were synthesized analogously.

The X-ray diffraction spectra of the compounds were recorded on a STADI/P (STOE) diffractometer (Cu-K α radiation) in vacuum-sealed glass capillaries. The structures of the fullerides were refined using the GSAS program.²³ The atomic coordinates published in the study²⁴ were used as the starting models. The background was approximated graphically and refined using polynoms of different degrees. The occupancies of the K atom positions were refined with fixed thermal parameters.

The ¹³C NMR spectra were recorded on a Bruker AC-200 spectrometer according to a single-pulse program (excitation pulse duration was 4 μ s, the pulse interval was 2 s). The number of accumulations was varied from 400 to 4000 depending on the amount and composition of the compounds. The chemical shifts in the ¹³C NMR spectra were determined relative to the signal of Me₄Si.

The superconducting transition temperatures in the fullerides were determined by a standard low-frequency inductive method from the temperature dependence of the magnetic susceptibility in a temperature range of 4.2-300 K (accuracy of the determination of the transition temperature was ± 1 K) using the same tubes as those used for NMR spectroscopy.

Results and Discussion

Heterofullerides of lanthanides and alkali metals were synthesized on the assumption that the reactions (1)-(5)

Spe- cimen	Composi- tion of the	Tentative composition	$T_{\rm c}/{ m K}$	Color of compound	Electronic configuration	¹³ C NMR, δ
	starting	of hetero-			of the	
	mixture ^a	fulleride			metal atom	
1	$5 \text{ K} + \text{ScCl}_3$	K ₂ ScC ₆₀	14	Black	$3d^14s^2$	190
2	$5 \text{ K} + \text{YCl}_3$	K_2YC_{60}	_	Black	$4d^{1}5s^{2}$	189
3	$6 \text{ K} + \text{LaCl}_3$	K ₃ LaC ₆₀	—	Black	5d ¹ 6s ²	190 (br)
4	$5 \text{ K} + \text{LaCl}_3$	K_2LaC_{60}	—	Dark-brown	5d ¹ 6s ²	216 (v.br)
5	$5 \text{ K} + \text{PrCl}_3$	$K_2 PrC_{60}$	b	Black	4f35d06s2	191
6	$5 \text{ K} + \text{NdCl}_3$	K_2NdC_{60}	—	Black	$4f^45d^06s^2$	187
7	$5 \text{ K} + \text{SmCl}_3$	$K_2 Sm^{3+}C_{60}$	_	Black	$4f^{6}5d^{0}6s^{2}$	187
8	$9 \text{ K} + 3 \text{ GdCl}_3$	Gd_3C_{60}	_	Black	$4f^{7}5d^{1}6s^{2}$	194 (v.br)
9	$5 \text{ K} + \text{GdCl}_3$	K_2GdC_{60}	b	Black	$4f^{7}5d^{1}6s^{2}$	196 (v.br)
10	$5 \text{ K} + \text{TbCl}_3$	$K_2 TbC_{60}$	_	Black	4f95d06s2	<i>c</i>
11	$4 \text{ K} + \text{YbI}_2$	$K_2Yb^{2+}C_{60}$	15	Black	4f ¹⁴ 5d ⁰ 6s ²	198
12	$4 \text{ K} + \text{YbI}_2$	$K_{2}Yb^{2+}C_{60}$	16.5	Black	4f ¹⁴ 5d ⁰ 6s ²	193 (br.asymm)
13	$4 \text{ Rb} + Y b \overline{I}_2$	$Rb_2Yb^{2+}C_{60}$	14	Black	4f145d06s2	
14	$5 \text{ K} + \text{YbCl}_{3}$	$K_2 \bar{Y} b^{3+} C_{60}$	13	Black	4f145d06s2	196 (br.asymm)
15	$5 \text{ K} + \text{YbCl}_3$	$\tilde{K_{2}Yb^{3+}C_{60}}$	16	Black	4f145d06s2	_
16	$5 \text{ Rb} + \text{YbCl}_3$	$R\bar{b}_{2}Yb^{3+}C_{60}$	22	Black	4f145d06s2	c
17	$5 \text{ Rb} + \text{YbI}_2$	$Rb_{2}Yb^{2+}C_{60}$	19	Black	4f145d06s2	c
18	$5 \text{ K} + 2 \text{ Yb}\tilde{I}_2$	$K_2 Y b^{2+} C_{60}$	_	Black	4f145d06s2	206
19	$5 \text{ Na} + \text{YbCl}_3$	$Na_{2}Yb^{3+}C_{60}$	_	Black	4f145d06s2	182
20	$5 \text{ K} + \text{LuCl}_3$	$K_2 LuC_{60}$	20	Black	$4f^{14}5d^{1}6s^{2}$	191

Table 1. Tentative compositions and selected properties of heterofullerides of alkali metals and lanthanides

^{*a*} The number of K atoms per C_{60} molecule.

^b The compound contains a superconducting phase, but its amount is too small to allow us to determine the superconducting transition temperature within the framework of the method used for measurements. ^c Polymer.

proceed. The reactions (1) and (3) involve two successive steps.

$$K_{3}C_{60} + M'Cl_{3} \longrightarrow (\{[M'C_{60}] + 3 \text{ KCl}\} + 2 \text{ K}) \longrightarrow K_{2}M'C_{60} + 3 \text{ KCl}$$
(1)

$$K_5C_{60} + M'Cl_3 \longrightarrow K_2M'C_{60} + 3 KCl$$
 (2)

$$K_6C_{60} + 2 \text{ M'Cl}_3 \longrightarrow (\{[\text{M'}_2\text{C}_{60}] + 6 \text{ KCl}\} + \text{K}) \longrightarrow K\text{M'}_2\text{C}_{60} + 6 \text{ KCl}$$
(3)

$$\{K_6C_{60} + K\} + 2 M'Cl_3 \longrightarrow KM'_2C_{60} + 6 KCl$$
 (4)

$$K_4C_{60} + YbI_2 \longrightarrow K_2YbC_{60} + 2 KI$$
(5)

Note. The values in braces and brackets indicate tentative compositions of the mixtures of fulleride with potassium chloride, which formed in the intermediate step of the reaction and were not isolated from the solution.

As in the earlier study,²⁵ alkali fulleride serves as a reducing agent in these reactions, which indicates that the bonds in this compound are of a radically different kind from the purely ionic bond. Taking into account this fact, the charges on the ytterbium atoms and the ionic radii of lanthanides should be considered only as a distinguishing characteristic of the starting state of these atoms (their charge in the halides). Estimation of the degree of charge transfer in fullerides is beyond the scope of the present study.

The bulk chemical compositions of selected compounds synthesized in the present study and the results of their investigation are given in Table 1. It can be seen that only compounds synthesized by the reactions (1), (2), and (5) possess superconducting properties. The tentative composition of these compounds is $M_2M'C_{60}$ (M = K, Rb; M' = Yb, Lu, Sc). This composition assumes that, on the one hand, the fcc lattice is retained and, on the other hand, the t_{1u} sublevel of the fullerene molecule is only partially filled, no more than five electrons being formally transferred from the metal atoms.

The temperature dependences of the specific magnetic susceptibility (χ) for potassium-ytterbium, rubidiumytterbium, and potassium-lutetium fullerides are shown in Fig. 1, *a*—*c*. The critical temperatures (T_c) of these specimens were determined from the onset of superconductivity. Their specific magnetic susceptibilities are comparable to the value determined under analogous conditions for individual K₃C₆₀, *i.e.*, the percentage of a superconducting phase in these specimens was at most 50%. For potassium-containing heterofullerides, the maximum T_c (20 K) was observed for K₂LuC₆₀ (see Fig. 1, *c*).

Unfortunately, it is presently impossible to unambiguously answer the question of whether substances with composition $M_2M'C_{60}$ are individual compounds or the reactions (1), (2), and (5) follow another path to form mixtures of phases with partially substituted superconducting



5

10

15

20

25

Fig. 1. Temperature dependences of the specific magnetic susceptibility (χ) for K₂Yb²⁺C₆₀ (*1*) and K₂Yb³⁺C₆₀ (*2*) (*a*); Rb₂Yb²⁺C₆₀ (*1*) and Rb₂Yb³⁺C₆₀ (*2*) (*b*); and K₂LuC₆₀ (*c*).

fullerides K_3C_{60} ($T_c = 18-19$ K) or Rb_3C_{60} ($T_c = 28$ K) containing an impurity of lanthanide fullerides with unknown compositions.

The broadline 13 C NMR spectra of the compounds are indicative of the presence of fulleride in the solid phase (single line at δ 188–190 typical of most compounds of this class) and the absence of free fullerite in the mixture of the products (δ 144–145). Hence, it can be reasoned that the fullerite introduced into the reaction occurs completely in the bound state. However, the fullerite can be both involved in fullerides and consumed for the formation of polymer fullerite phases or X-ray amorphous fulleride phases, whose presence is observed

T/K



Fig. 2. Experimental (1, dotted line), calculated (1, solid line), and difference (2) X-ray diffraction patterns of specimen 11.

in X-ray diffraction patterns as a halo. A phase similar to tripotassium fulleride and, depending on the composition of the starting halide, potassium chloride or iodide were observed as the major crystalline phases in the X-ray diffraction patterns (Figs 2 and 3).

The parameter of the fcc lattice of fulleride K_3C_{60} , which was prepared in the presence of toluene according to a known procedure,²² (Table 2) appeared to be substantially larger than that published in the literature for the fulleride synthesized by the gas-phase method (14.24 Å).²⁴ The refinement of occupancies of the cation positions in this specimen by the Rietveld method gave the composition $K_{2.47}C_{60}$ similar to that calculated in the study²⁴ $(K_{241}C_{60})$, the superconducting transition temperature (18 K) remaining unchanged. By contrast, fullerides, which were prepared according to a procedure described in the study²² but with the use of the reactant ratios K : $C_{60} = (2-2.5) : 1$, do not possess superconducting properties. In the study,²⁶ fullerite was synthesized by pyrolysis of C₆₀D₂₄. Alkali heterofullerides characterized by "expanded" fcc lattices were prepared by intercalation from solutions in ammonia.²⁷ In the latter case, no increase in the superconducting transition temperature was

Table 2. Unit cell parameters (a) and occupancies of the octahedral (8c) and tetrahedral (4b) sites in the structures of homoand heterofullerides of potassium and rare-earth metals

Specimen ^a	<i>a</i> /Å	Occupancy of position		$\frac{A_n C_{60}{}^b}{}$	$A_n C_{60}^b$ KHal ^b	
	-	8 <i>c</i>	4 <i>b</i>	WL.	.%0	
$\overline{K_{3}C_{60}[K_{241}C_{60}]^{c}}$	14.24	0.8	0.81	_	_	
$K_{3}C_{60} [K_{247}C_{60}]^{d}$	14.3110(5)	0.87	0.73	100	_	
$K_2Yb^{2+}C_{60}(11)^d$	14.310(1)	1.26	0.75	88	12	
$K_2Yb^{2+}C_{60}(12)^d$	14.226	_	_	_	_	
$K_2Yb^{3+}C_{60}(15)^d$	14.336(2)	0.75	1.0	85	15	
$K_2 Lu^{3+} C_{60} (20)^d$	14.249(2)	0.75	0.7	87	13	

^{*a*} The specimen number used in Table 1 is given in parentheses. ^{*b*} Estimates of the weight contents of the phases are tentative because of the presence of an amorphous impurity in the specimens (A is the cation in fulleride).

^c According to the published data.²⁴

^d Based on the results of the present study.

also observed in spite of an increase in the *a* parameter, which is in contrast with the assumption made earlier^{28,29} based on the linear dependence of T_c on *a*.



Fig. 3. X-ray diffraction patterns of pure $K_3C_{60}(a)$ and specimens 15 (b), 11 (c), and 12 (d).

The partial replacement of the K atoms, which occupy the tetrahedral and octahedral voids of the lattice of the fulleride structure, with rare-earth metals should be accompanied by redistribution of the intensities of reflections (in particular, for pairs of the reflections 111, 200 and 311, 222). However, it should be noted that the results of refinement of the occupancies of atomic positions based on powder X-ray diffraction data cannot provide unambiguous evidence of whether rare-earth metals are involved or not in the heterofulleride structure.

The results of calculations of the occupancies of the 8*c* and 4*b* positions by metal atoms and the unit cell parameters of fullerides with composition $K_2M'C_{60}$ are given in Table 2. The occupancies of these positions for most of the heterofullerides under study and for the above-considered K_3C_{60} compound are lower than those expected for the stoichiometric compositions. At the same time, the parameter of the cubic unit cell of the hetero-metallic specimen 15 is even more increased compared to the value published in the study²⁴ for tripotassium fulleride. This fact can be attributable to an increase in the occupancy of the tetrahedral site and, as a consequence, to an increase in the size of the tetrahedral void. However, the type of atoms inserted into this void is not clear.

The most substantial changes in the occupancies of the positions were observed in the specimen 11. The occupancy of the 8c position increased to 1.26 (calculated for the K atoms) and the intensity of the 200 reflection increased by a factor of more than two, the unit cell parameter being the same and the occupancy of the 4b position being virtually unchanged. This result can be attributable to the insertion of Yb atoms, which are substantially smaller than the K atoms, into the position 1/4; 1/4; 1/4. In spite of the fact that the specimens 11 and 12 were synthesized under similar conditions, the X-ray diffraction pattern of the latter was substantially different. The parameter of the cubic unit cell given in Table 2 is approximate and was calculated from the interplanar distances of two reflections. Most likely, the lattice of the fulleride 12 undergoes orthorhombic distortion (one parameter is 14.23 Å). This assumption is supported by the difference in the half-widths of the reflections and the appearance of a large number of additional reflections compared to those observed for the cubic phase.

The unit cell parameter of the specimen 20 is again close to that of $K_{2.41}C_{60}$. The distribution of the K atoms over the octahedral and tetrahedral sites is virtually identical to that published in the literature, although the superconducting transition temperature for this specimen is maximum in the series of the compounds under consideration and is higher than that determined for K_3C_{60} .

Therefore, analysis of the occupancies of the K atom positions in the fullerides synthesized in the present study demonstrates that rare-earth metals can be involved in these compounds (most probably, in the octahedral sites). This process is accompanied by redistribution of the cations in the voids of the lattice and, as a consequence, by changes in the unit cell parameters and, in some cases, by lowering of the symmetry of the starting cubic unit cell. However, the available data did not allow us to estimate the precise amount of the heteroatoms of rare-earth metals in the fulleride lattice. These data also leave unexplained the differences between, on the one hand, the mechanisms of the reactions (1), (2), and (5) involving the Yb, Lu, and Sc atoms and, on the other hand, the mechanisms of the analogous reactions performed under similar conditions but with the participation of other rareearth chlorides. The role of the inserted atoms in the changes in the electrophysical properties of heterofullerides remains unclear.

The main and evident difference between these metal atoms and the atoms of other rare-earth metals used in the present study is their electronic structure. The highest superconducting transition temperatures were observed for K₂LuC₆₀, in which the Lu atom has the 4f¹⁴5d¹6s² configuration ($T_c = 20$ K, $r(Lu^{3+}) = 0.84$ Å), and for isoelectronic K₂Yb²⁺C₆₀ (average $T_c \approx 16$ K, $r(Yb^{2+}) = 1.05$ Å), *i.e.*, for fullerides in which the completely filled 4f sublevel of the lanthanide atoms remains unchanged.

In the case of the reaction of K_5C_{60} with $Yb^{3+}Cl_3$ (4f¹⁴5d⁰6s², $r(Yb^{3+}) = 0.85$ Å), the possible involvement of only one f electron in the bond formation, most likely, changes the reaction mechanism and leads to the formation of partially (or weakly) substituted K_3C_{60} and X-ray amorphous ytterbium fulleride. A further decrease in the number of f electron causes even more substantial changes in the composition of the reaction products. The reactions of all other lanthanide salts listed in Table 1 with K_5C_{60} afforded several compounds, but none of these compounds crystallized in the fcc lattice with the parameter close to that of K_3C_{60} . Therefore, these reactions were accompanied by even more substantial changes in the pathways of the reactions (1) and (2) compared to those observed in the reaction of K_5C_{60} with $Yb^{3+}Cl_3$.

Heterofullerides involving the yttrium and lanthanum atoms, which were prepared according to the above-described procedure and have valence orbitals analogous to those of the Lu atom $(nd^{1}ms^{2})$ but the unfilled f levels, do not possess superconductivity. It is unlikely that this difference is associated exclusively with the difference in the sizes of these metal ions, because the radius of the Y^{3+} ion (0.93 Å) differs only slightly from those of the Yb and Lu ions, and the radius of the La^{3+} ion (1.15 Å) is maximum close (in the series of lanthanides) to that of the K⁺ ion (1.33 Å). Potassium chloride was detected in the precipitates remained after the synthesis. Reduction of halides and the reaction of these metals with a carbon matrix are beyond doubt. However, as mentioned above, the mechanism of this reaction can differ from that of intercalation, and the differences are, presumably, determined by higher Lewis acidity of yttrium and lanthanum halides compared to that of ytterbium and lutetium halides. Judging from the shape and position of the resonance band in the ¹³C NMR spectra, virtually all compounds involving lanthanum are polymeric (see Table 1), *i.e.*, the formation of compounds with La-C covalent bonds is, apparently, more typical of this element. At the same time, the position and shape of the band in the ¹³C NMR spectrum of the product of the reaction between K_5C_{60} and YCl_3 are identical to those in the spectrum of the starting pentapotassium fulleride, *i.e.*, this compound, unlike the La derivative, is not polymeric, but it also does not possess superconducting properties.

By contrast, the reaction of K_5C_{60} with anhydrous and unsolvated ScCl₃, which is characterized by the smallest size of the metal ion ($r(Sc^{3+}) = 0.81$ Å) in the series of Group IIIB metals, afforded a compound with tentative composition K_2ScC_{60} and $T_c = 14$ K. The analogous reaction of K_5C_{60} with ScCl₃·3MeCN was accompanied by a partial change in the composition of the fulleride, as evidenced by the fact that the ¹³C NMR spectrum has a weak band at δ 145, which can be assigned to free fullerite. All the compounds formed in this case are dielectrics. Hence it follows that the presence of a stronger base (compared to THF) in a solution can change either the mechanism of the exchange reaction or the structure of fulleride through solvation of the metal ion, as exemplified by $(THF)K_3C_{60}$.³⁰ Therefore, the smaller radii of the multicharged ions compared to those of the K⁺ and Rb⁺ ions are, apparently, partially compensated by the transfer of additional electrons to the fullerene molecule. However, both the appearance of the superconducting properties of heterofullerides and the value of T_c depend on the nature of these heteroatoms.

Although unexpected, the behavior of scandium in the series of the reagents under consideration is explainable. Many structural and chemical properties of scandium compounds are close to those of lutetium compounds. Some of these compounds are isomorphous. The apparent difference between the electronic structure of the Sc³⁺ ion and the structures of the Y³⁺ and La³⁺ ions is associated with the fact that the Sc^{3+} ion has neither valence d electrons nor the low-lying completely filled d¹⁰ shell. In the Yb^{2+} and Lu^{3+} atoms, the latter is shielded by the compact f shell and, apparently, influences only slightly the electrophysical properties of heterofullerides. If this is the case, one would not expect all heterofullerides involving metals with the completely filled d shell, *i.e.*, all posttransition, late transition, and main-group metals, to exhibit noticeable superconducting properties. Predictions as to metals with the unfilled 3d shell and early maingroup metals having no d electrons are not so unambiguous.

In conclusion, it should be emphasized that the compositions of fullerides found in this study are tentative because they are based exclusively on the stoichiometry of the reactions, which *could* afford these compounds. Hence it also follows that all the above-considered results and conclusions refer only to compounds prepared by exchange reactions. One would expect that other properties, including superconducting properties, will be imparted to these compounds by varying the procedure for the synthesis and taking into account the possibility of the existence of a wide homogeneity region for heterofullerides.

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