

**RADIOACTIVE METALLOFULLERENES:
HOT ATOM CHEMISTRY ASPECTS.**

Yu.S.Grushko, M.A. Khodorkovski†, V.S.Kozlov, V.A. Shilin,
S.A. Grachev, T.O. Artamonova†

St.-Petersburg Nuclear Physics Institute RAS, 188300 Gatchina, Russia
†RSCAC “Applied Chemistry”, 197198 St.-Petersburg, Russia

Keywords: metallofullerenes, enrichment, neutron activation, Szilard-Chalmers, retention, recoil implosion, radiation stability

The n, γ – reaction of metallofullerenes of Tb, Sm and $\text{Sc}_3\text{N}@C_{80}$ is studied. Unusually high compared to trivalent lanthanofullerenes retention yield is observed for $^{153}\text{Sm}@C_{2n}$. The recoil implosion yield of ^{177}Lu atom in molecularly tight mixture of Lu diphthalocyanine and C_{60} is measured. It is shown that possibly unfavorable geometry of target/projectile system can not explain low implosion yields observed so far. Possible role of chemical properties of recoil atom at hot atom – cage interaction and mechanisms of energy dissipation are discussed.

Introduction.

Soon after discovery of fullerenes [1] and of the method to prepare them in amount [2] a new discovery of complexes of fullerenes with metals [3] and following confirmation of location of metal atom inside the fullerene cage [4] gave us new nice class of molecular structures, so called endohedral metallofullerenes. In these molecules a metal atom (or group of atoms) is confined inside the closed carbon cage and can not leave it at ambient temperature. In an endofullerene molecule a metal atom (ion) is screened from extramolecular chemical environment and interacts with it only mediately via carbon cage. As the metal atoms encapsulated can be in different isotopic forms and, in particular, in radioactive form, endometallofullerenes become the subject of new branch of radiochemistry and materials science. The most important applications of radiometallofullerenes (RMF) are visible at present in tracer studies and monitoring of

chemical properties of metallofullerenes, in technology of radioactive waste encapsulation and especially in nuclear medicine. The metallofullerenes internally doped with radioactive isotopes can be useful for medical diagnostics, therapy of cancer and immunotherapy. Itinerary of these labeled metallofullerenes in vivo could be adjusted via functionalization of carbon cage of metallofullerenes with proper tissue-seeking substituents. Almost half of metals commonly used in nuclear medicine in radioisotopic form (Y, Ho, Sm, Dy etc.) have been encapsulated in metallofullerenes so far [5,6]. As for preparation of RMF and for their use in applications it is necessary to know well their properties and transformations in different radiation fields and in radioactive decay processes. Because the neutron activation is the most accessible method of production of RMF, it is especially important to know how acts irradiation in reactor on metallofullerenes and what is survivability of original chemical form at thermal neutron capture by encapsulated metal atom. The measure of survival of the mother chemical form at neutron capture is retention, percent of capture events which retain the original molecule. The thermal neutron capture results in highly excited daughter nucleus which decays to ground state emitting the prompt γ – rays. Usually this decay is going through cascade of 2 to 4 γ -transitions. At each γ – ray emission the nucleus recoils and the final kinetic energy can be calculated as a vector sum of all recoil momenta of γ – rays emitted in cascade. The recoil energies for n, γ – reaction lie around hundred eV. That is much higher than energy of any chemical bond. This energy is transferred to chemical surrounding of the atom and as a result the daughter atom can change its original chemical form (Szilard-Chalmers reaction) or retain the mother form. At the production of RMF by irradiation of stable metallofullerenes in reactor Szilard-Chalmers reaction is undesirable scenario. On the other hand recoil process can be used for implantation of hot atom into empty fullerene cage to prepare carrier-free RMF. The latter process is studied for the first time by Braun and Rausch [7]. They observed formation of $^{41}\text{Ar}@C_{60}$ due to recoil implosion. Later it was confirmed in n, γ -reaction for Ar [8], for ^{85}Kr , ^{125}Xe [9] and ^{133}Xe [10]. Formation of $M@C_{60}$ due to recoil implosion at n, γ -reaction was observed as well for ^{140}La , ^{142}Pr , ^{166}Ho , $^{65+69m}\text{Zn}$ and ^{64}Cu [11]. The fullerene cage stability in the reactor fields has been studied at irradiation of C_{60} in [12,13]. In [12] it was found that

pure thermal neutrons do not produce noticeable destruction of C_{60} as well as γ -rays of reactor spectrum and ^{60}Co radiation, but epithermal neutrons amorphize fullerenes substantially even at 2 hours in unfiltered neutron flux of $\sim 10^{14} \text{ cm}^{-2}\text{s}^{-1}$. Retention yields in n,γ -reaction for lanthanide metallofullerenes have been studied in [6,14]. In [6] retention yield for $^{153}Sm@C_{2n}$ was evaluated to be more than 70%. In contrary, in [14] for series of $Ln@C_{2n}$ the retention yields were found to be around 19% independent on details of nuclear decay scheme of compound nucleus. Similarly no correlation with recoil energy is found in [11] for yields of nuclear implosion of lanthanides in C_{60} . It looks as some hidden parameter defines recoil interaction of hot atom with fullerene cage both in case of external and internal attack of the cage.

In the present work we carried out experiments to prove data on C_{60} stability in reactor, to confirm unusually high compared to other lanthanofullerenes retention yield of $^{153}Sm@C_{2n}$ [6]. To exclude possible dependence of recoil implosion yield on dispersion of metal oxide / C_{60} mixture, used in [11], probability of implosion of ^{177}Lu was determined at neutron irradiation of cocrystallized lutetium diphthalocyanine ($LuPc_2$) and C_{60} . In such target system each Lu atom is located in close vicinity of C_{60} molecule and possible self-absorption of recoil atom in oxide particle can not interfere implosion yield. For the first time we studied retention yield at neutron capture in $Sc_3N@C_{80}$, the representative of new trimetalnitride class of metallofullerene[15].

Experimentals.

Preparation of metallofullerenes.

Metallofullerenes and C_{60} were prepared by electric arc evaporation method [2].

C_{60} was purified to 99.9% by flash chromatography on activated carbon.

For preparation of Sm metallofullerenes in graphite rods of spectral purity and 6 mm diameter and 200 length were drilled to 3 mm channel, filled with mixture of Sm metal filings and graphite cement, dried and baked at 1000 °C for an hour. Final content of Sm is ca. 1 % at. Evaporation was performed at 70 A DC and He pressure 200 mbar. The wall soot was Soxhlet – extracted with o-xylene in argon to give $^{153}Sm@C_{2n} / C_{2n}$

mixture that was used for irradiation as is. Tb composite electrode was prepared by filling of high purity graphite tube o.d.13/i.d.6 with Tb₄O₇/graphite mixture upto 1,4% at. of final Tb content. It was dried, heated in argon flow at 1000 °C for 2 hours and evaporated in 200 mbar He at 200 A DC. The soot was Soxhlet preextracted with toluene for 10 hours and then extracted with freshly distilled dimethyleformamide (DMF) in argon in Soxhlet for 10 hours. Then DMF was removed in rotary evaporator at 10 torr, the rest was redissolved in o-xylene at sonication and filtered through 0,2 μ Millipor to give finally 29 mg of fullerene mixture . Fig.1 shows LD-TOF spectrum of Tb sample.

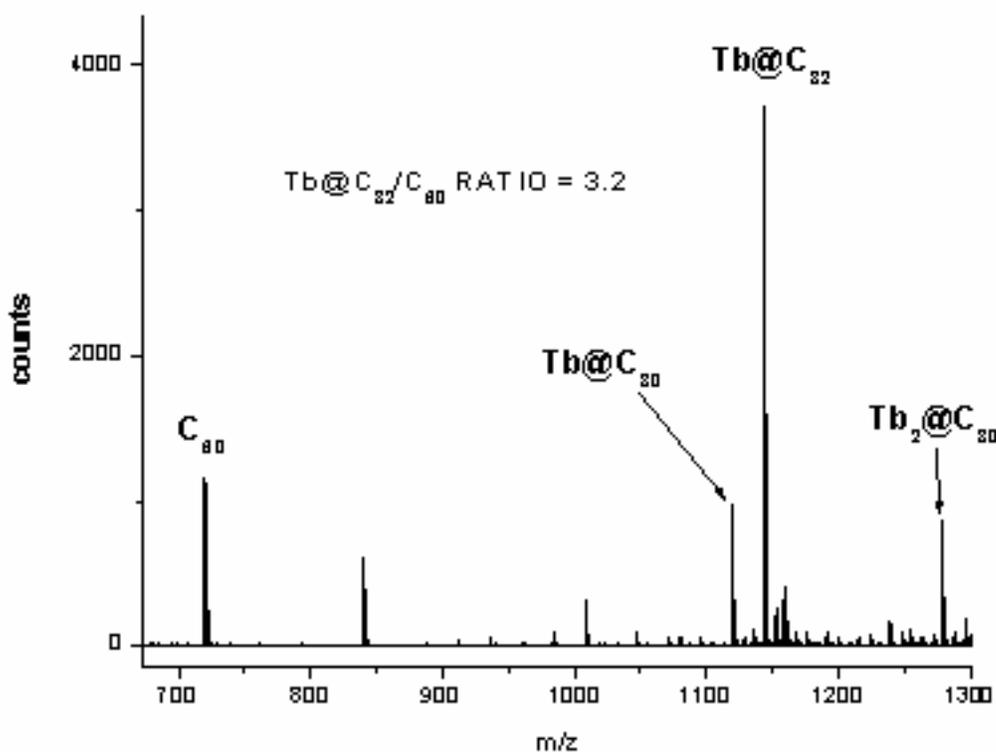


Fig. 1. LD-TOF spectrum of Tb metallofullerenes prepared by two step extraction from rough soot. Second stage DMA extraction gives highly enriched Tb@C₈₂ .

For preparation of Sc₃N@C₈₀ sample we modified the originally proposed method [16]. We refused of continues flow of 99/1 He/N₂ mixture and used stationary atmosphere of He with 6% vol. of N₂ at 180 mbar. The composite electrode was made of 13/6 graphite tube filled with mixture of scandium metal filings, graphite powder and Apiezon K binder. It was dried and backed in dry argon at 1000 °C. Arc evaporation was carried out

at 200A DC . The wall soot was extracted with CS₂ at overnight stirring and then membrane filtered. The solution was dried and the formed crystals were redissolved in o-xylene. The excess of empty fullerenes was separated by selective crystallization from concentrated o-xylene solution. For enrichment of Sc₃N@C₈₀ this procedure was found to be very effective. On Fig.2 LD-TOF spectra of Sc₃N@C₈₀-enriched solution and Sc₃N@C₈₀-depleted crystals are shown.

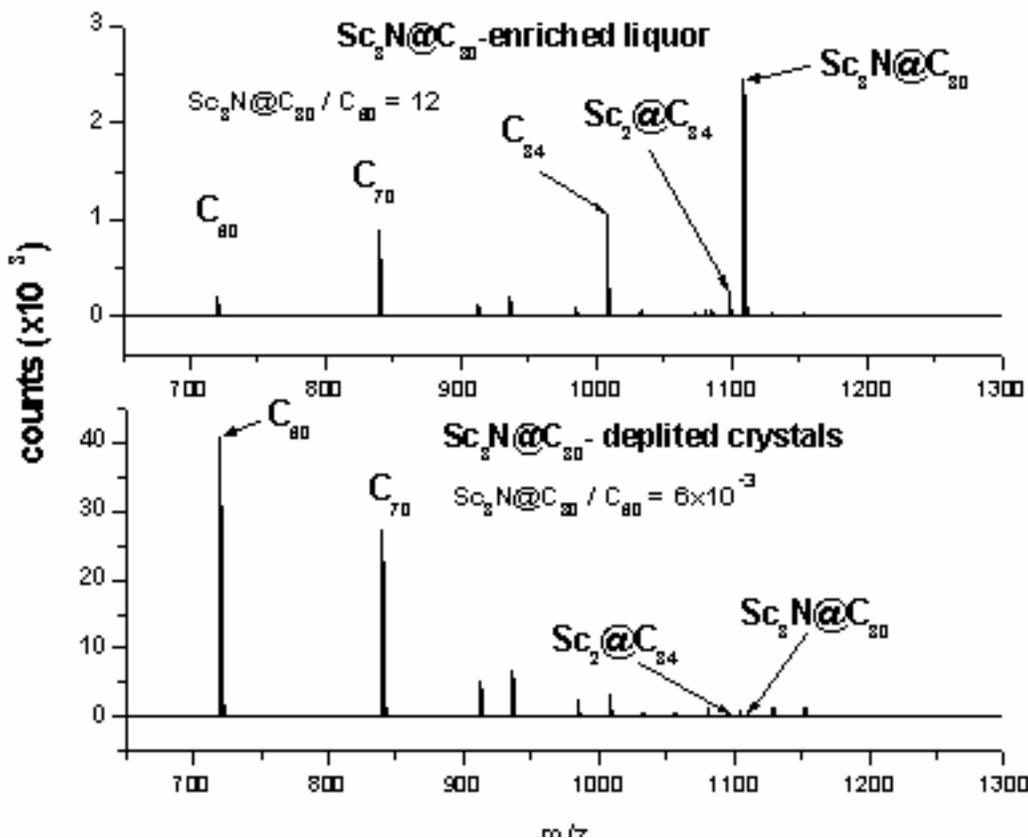


Fig.2. LD-TOF spectra of Sc₃N@C₈₀. enriched by selective crystallization of empty fullerenes. From the comparison of enriched and depleted samples enrichment coefficient derived is ca. 2000.

The one step enrichment coefficient is as large as 2000. Such enrichment is very important because for some purposes the enriched material can be used as is without further HPLC separation, on the other hand being used as a stock material in HPLC procedure it makes possible to increase many times the useful loading of the column.

For the study of recoil implantation of Lu, equimolar amounts of LuPc₂ (Pc – phthalocyanine), purified by sublimation, and C₆₀ were cocrystallized from o-xylene solution.

Neutron activation and treatment of irradiated samples.

Neutron activation of samples was carried out in sealed quartz ampoules in WWR-M research reactor of St.Petersburg Nuclear Physics Institute of RAS. Integrated neutron flux was in the range of 4×10^{17} to 7×10^{17} neutrons and ca. 10% of epithermal neutrons (in following, fast neutrons) was present. To evaluate survivability of metallofullerenes we measured activity distribution between insoluble and aromatics-soluble part of irradiated samples. The part of irradiated samples which is insoluble in aromatic organic solvents (toluene, o-xylene, α -methylnaphthalene) or CS₂ is formed by direct destruction and polymerization of metallofullerenes by fast neutrons and by the damage of fullerene cage at Szilard-Chalmers reaction. To account for contribution of fast neutrons to damage of metallofullerenes we used as a standard C₆₀ samples which were irradiated in the same container as a sample of interest. At the used integrated neutron flux and neutron spectrum the insoluble part of C₆₀ amounts ~10% of a sample weight, Fig. 3.

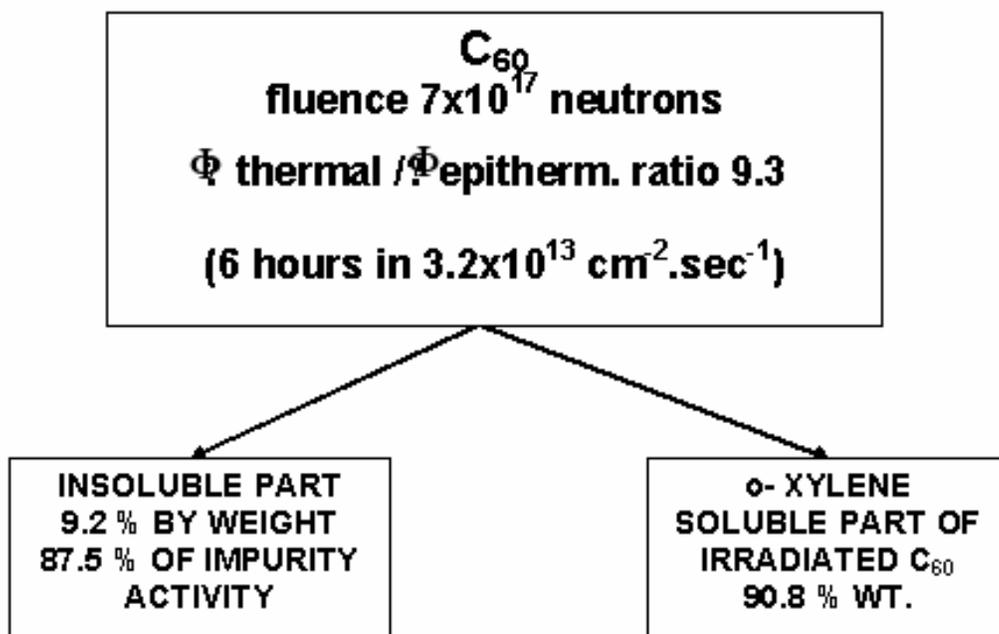


Fig.3. Survivability of pure C₆₀ irradiated together with the samples under study and used as a standard. Only 10 % are damaged by fast neutrons.

The chemical treatment of irradiated samples before measurements of activity is shown in schemes of Fig.4-7. Normally, samples were dissolved in o-xylene or CS₂, filtered through the membrane filter of 0.2 μ porosity, insoluble part was weighted, filtrate was washed with HCl acid to eliminate radiocolloid activity and dried. In case of cocrystallized LuPc₂/C₆₀ (Fig.4) α-methylnaphthalene was used as a solvent. To separate activities of LuPc₂ and C₆₀ the α-methylnaphthalene solution was dried and residue was redissolved in cold concentrated sulfuric acid. LuPc₂ was dissolved and undissolved fullerenes were filtered out on a glass frit and washed on filter with cold water with ice and finally with acetone.

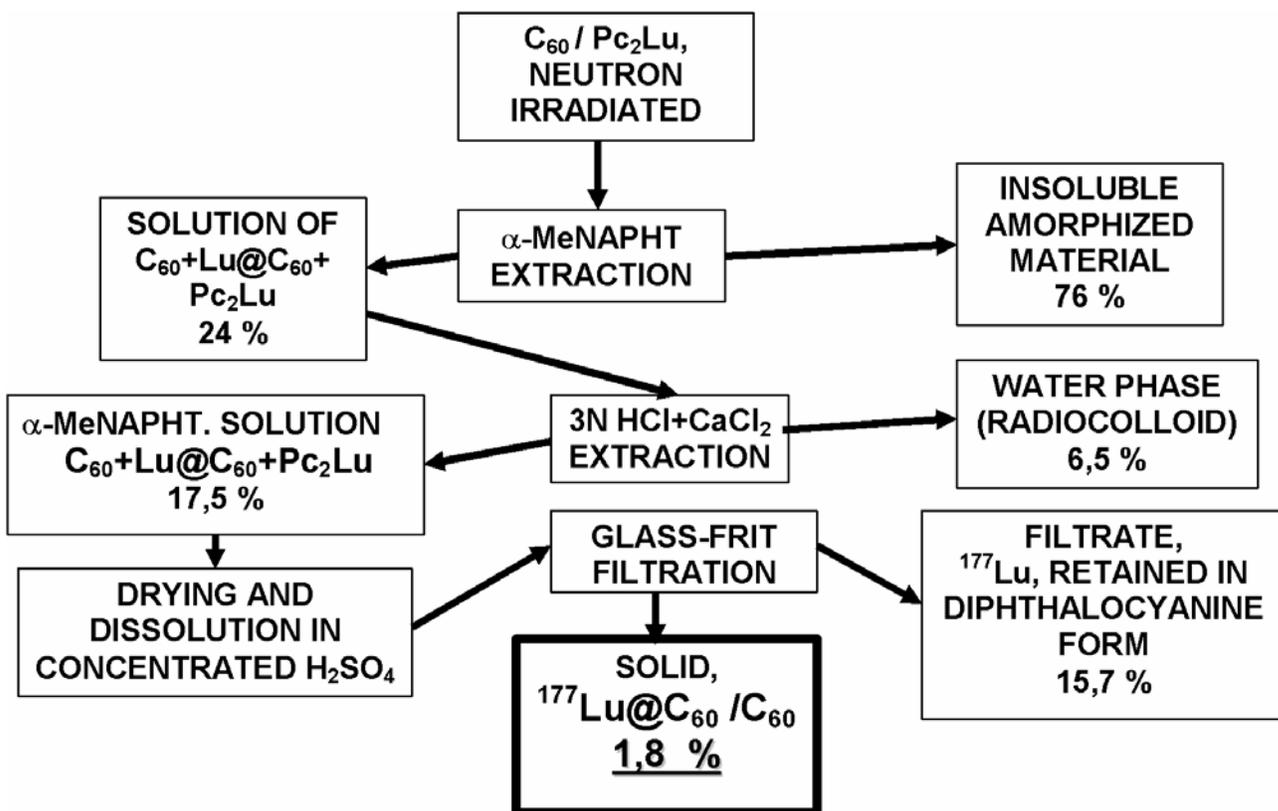


Fig. 4. The scheme of treatment of irradiated sample of cocrystallized LuPc₂ and C₆₀.
See text for details.

The measurements of γ-ray spectra of samples were performed with PC-based spectrometer supplied with HPGe detector and spectroscopic electronics of EG&G

ORTEC. Quantitative evaluation of the spectra was performed with Maestro II ORTEC software. Mass spectra were measured on REFLEX IV “Bruker” LD TOF spectrometer.

Results and discussion.

The study of recoil implosion of some lanthanide atoms in C_{60} [11] put the question on possible mechanisms of recoil energy dissipation at collision of recoil atom with fullerene cage wall. In fact at the recoil implosion the more probability of cage opening the more yield of carrier-free RMF. Oppositely at the radionuclide formation inside the cage the more percent of events with cage opening the less is retention yield of metallofullerene. Schematic process for these two cases is shown in Fig. 8. It is clear that both two processes on molecular scale are very similar and should be defined by similar dynamic mechanisms. The only difference is in that in one case the atom hits the fullerene cage from outside and in other one – from inside the fullerene molecule. The possible difference in details can originate from higher density of π -electrons at outer surface of fullerene cage. Interestingly it was observed for implosion of ^{142}Pr into C_{60} in $^{141}\text{Pr}(n,\gamma)^{142}\text{Pr}$ the yield is 31,1%, but for ^{166}Ho in $^{165}\text{Ho}(n,\gamma)^{166}\text{Ho}$ the yield is only 3,6% [11]. For both reactions Q values and maximal possible recoil energies are almost the same. One can suppose that explanation of that difference could be in different size of metal oxide particles in two cases and corresponding difference in probability for hot atom to leave the oxide particle and to hit C_{60} molecule. Our result on ^{177}Lu implosion into C_{60} with *molecularly tight* target system reveals that it is not the explanation. The yield of $^{177}\text{Lu}@C_{60}$ is only 2% (Fig.4) comparably to Pr oxide/ C_{60} mechanical mixture which yields 31% of $^{142}\text{Pr}@C_{60}$ [11]. The retention yield for $\text{Sc}_3\text{N}@C_{80}$ 19% (Fig.5) was found to be in the range observed in [14] for trivalent lanthanides.

For $^{153}\text{Sm}@C_{2n}$ (Fig.6) unusually high retention was observed 88%. It confirms our earlier measurement for this system [6] where retention lower limit was determined as 70%. In contrary to Sm system for $^{160}\text{Tb}@C_{2n}$ metallofullerenes (Fig.7) the retention was observed to be only 5,9 %. It is clear that at present time is not enough data on

retention yields and recoil implosion probability to understand mechanisms and relevant parameters. Radioactive atom beam implantation in the range of 100 eV could be especially useful in clarification of the problem. Nevertheless one can speculate now on importance of chemical properties of recoil atom for final chemical forms of stabilization of hot recoil system. It looks as if lanthanide recoil atom can potentially be 4-valent then it is favorable for cage wall penetration. In case of Pr high probability of implosion into

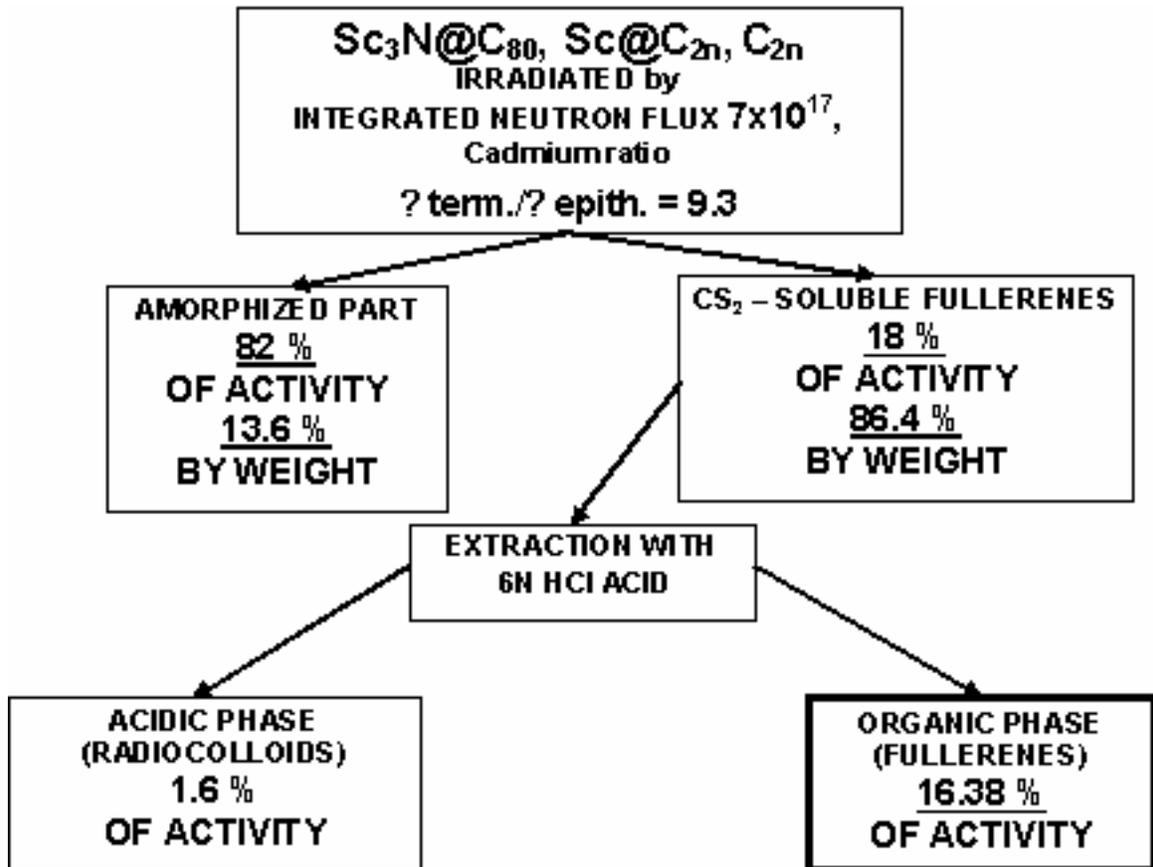


Fig. 5. The scheme of treatment of irradiated sample of $\text{Sc}_3\text{N}@C_{80}$. The retention yield for $\text{Sc}_3\text{N}@C_{80}$ 19% was found to be in the range observed earlier [14] for trivalent lanthanides.

C_{60} is observed [11], similarly we found that the recoiling Tb atom can leave easy the cage at (n,γ) reaction. For divalent ^{153}Sm in $\text{Sm}@C_{2n}$, in contrary, retention yield is very

high, much more than for trivalent lanthanides[14], it can mean that recoiling Sm atom (or maybe another divalent lanthanide) can hardly penetrate the cage wall.

For discussion of hot chemical process at neutron activation of metallofullerenes it is necessary to evaluate the possible range of kinetic recoil energy. For calculation of recoil energy distribution for a prompt γ -ray cascade the exact cascade branching data should be available. In most cases such data are absent and therefore it is reasonable to use some qualitative estimation. Systematics of neutron capture prompt γ – cascades reveals that first γ -quantum in cascade is in the range of 5 to 7.5 MeV. It means that the rest of excitation energy is less than 3 MeV. Fig.9 shows recoil energy dependence on emitted γ -ray energy for typical lanthanide mass 150. If at the first transition in cascade 6 MeV quantum is emitted then the atom receives ca. 130 eV kinetic energy.

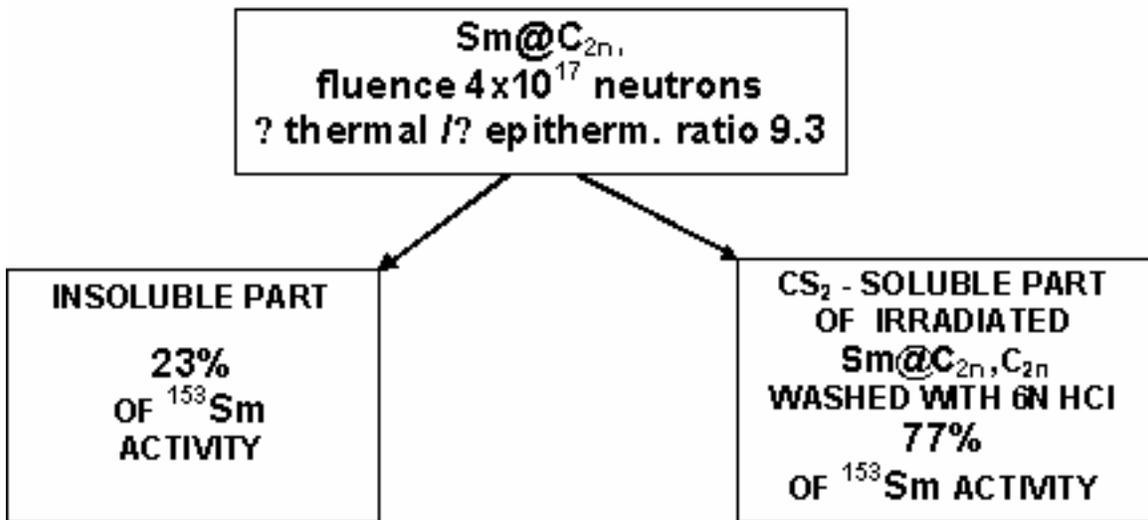


Fig. 6. Unusually high retention yield 88% for $^{153}\text{Sm}@C_{2n}$ confirms our earlier measurement for this system [6].

At any possible following cascade branching the maximal decrease of kinetic energy of recoil atom can not be more than 20 eV. It means that typical recoil energy is around 100 eV. If to distribute smoothly this energy throughout the 123 C-C bonds of C_{82} cage then bond excitation will be less than bond energy and the cage in principle can survive (at least, temporarily). But for such transfer of recoil energy from the place of collision all over the cage the mechanism of energy dissipation must be very fast and

effective. Phonon mechanism seems to be too slow to “cool” collision zone. If to consider an endohedral metallofullerene molecule as a superatom then it seems reasonable to suppose some electronic mechanisms which could be fast enough “to shake off” excess of energy from the hot zone of the cage similarly to electron shake-off and shake-up effects in atom at β - decay.

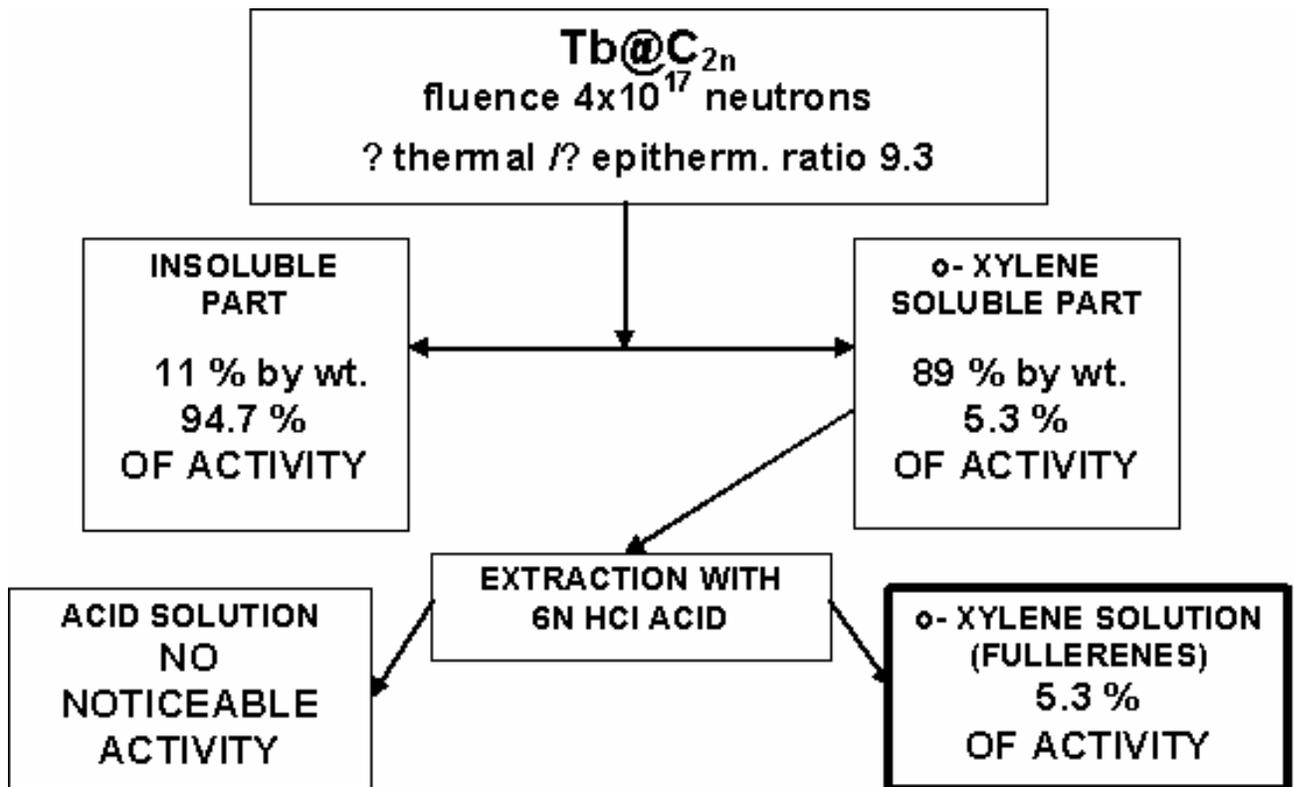


Fig.7. The scheme of treatment of irradiated $^{160}\text{Tb@C}_{2n}$ metallofullerenes. The retention was observed to be only 5,9 %.

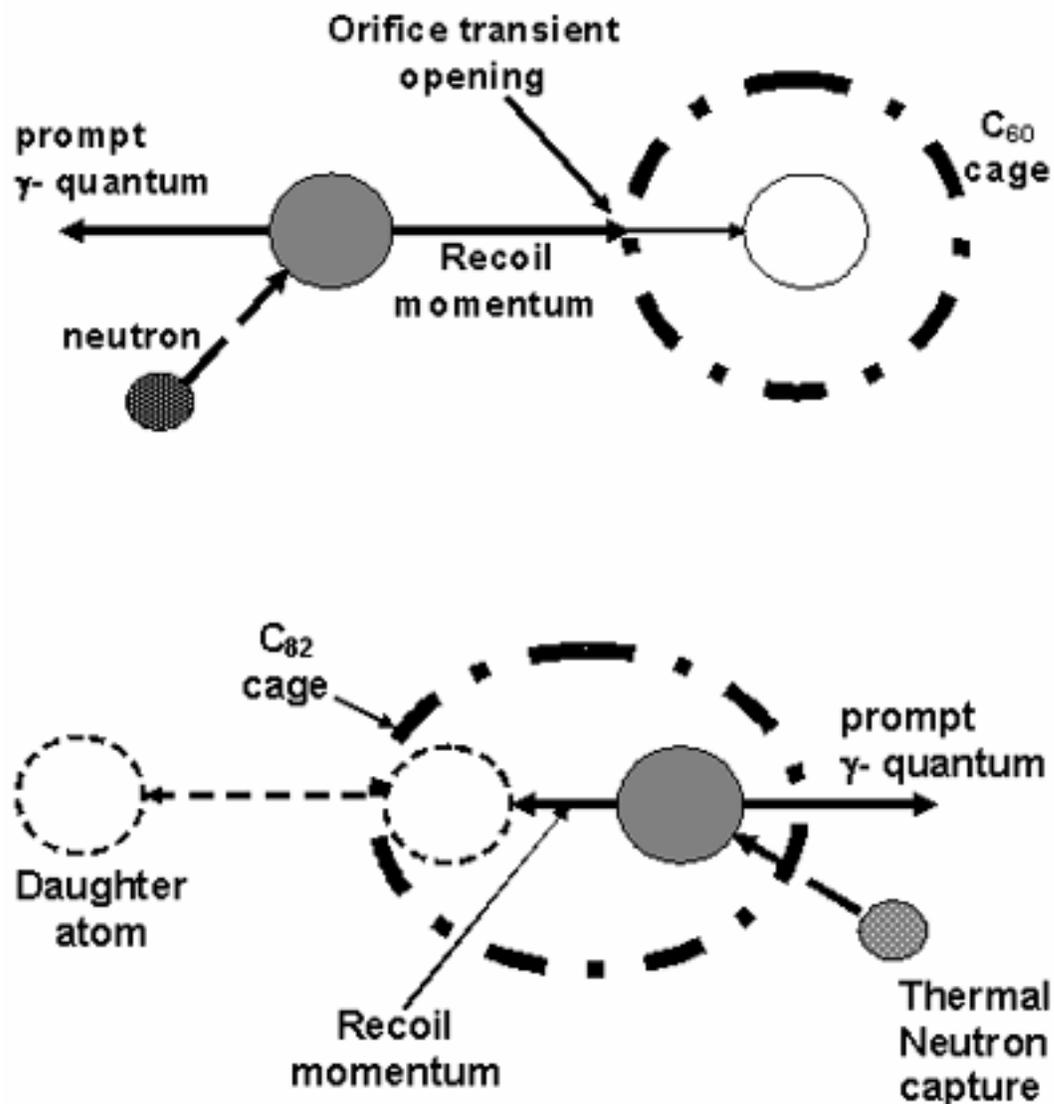


Fig.8. Schematic picture of recoil atom attack of fullerene cage wall for extra and intra cage activation cases.

Acknowledgments.

The authors are grateful to V.P. Sedov for supplied $LuPc_2$, S.G. Kolesnik for HPLC analyses, P.N. Moskalev and Yu.E. Loginov for useful discussions and M.E. Emelyanov for technical assistance. This work is supported by Research Program of RAS “Influence of atomic-crystal and electronic structure on properties of condensed matter.” and by

Russian Agency on Science and Innovations project “ Development of technology of preparation of multifunctional materials based on carbon”.

References:

1. H.W. Kroto, J.R. Heath, S.C.O'Brien, R.R. Curl, R.E. Smalley, “C₆₀: buckminsterfullerene” Nature, 318 (1985) 162-163.
2. W.Kraetschmer, L.D. Lamb, K. Fostiropoulos, D.R. Haffman, “Solid C₆₀: a new form of carbon.”, Nature 347, 354-358 (1990).
3. Y. Chai, T. Guo, C. Jin, R.E. Haufler, L.P.E. Chibante, J.Fure, L. Wang, G.M. Alford, R.E. Smalley, “Fullerenes with metal inside.” J. Phys. Chem., 95 (1991) 7564 - 7568.
4. M. Takata, B. Umea, E. Nishibori, M. Sakata, Y. Saito, M. Ohno, H. Shinohara, “Confirmation by X-Ray Diffraction of the Endohedral Nature of the Metallofullerene Y@C₈₂”, Nature, 377 (1995) 46 - 49.
5. T.Guo, R.E.Smalley, G.E.Scuseria, “*Ab initio* Theoretical Predictions of C₂₈, C₂₈H₄, C₂₈F₄, Ti@C₂₈H₄ and M@C₂₈ (M= Mg,Al, Si, S, Ca, Sc, Ti, Ge, Zn and Sn).”, J.Chem.Phys., 99, 352-359 (1993).
6. Yu. Grushko, E.G. Alekseev, V.V. Voronin, S.G. Kolesnik, S.N. Kolesnik, T.M. Pershikova, “Tracer Study of Sm@C_{2n}”, Molecular Materials, v. 7, 115- 118 (1996).
7. T.Braun, H.Rausch, “Endohedral Incorporation of Argon into C₆₀ by Neutron Irradiation”, Chem. Phys. Lett., 237 (1995) 443 - 447.

8. G.E.Gadd, P.J. Evans, D.J. Hurwood, J. Wood, S. Moricca, M. Blackford, M. Elcombe, S. Kennedy, M. James, "Neutron Irradiation of Ar₁C₆₀.", Chem. Phys. Lett. 261 (1996) 221-227.
9. G.E.Gadd, P.J. Evans, D.J. Hurwood, , P. L. Morgan, S. Moricca, G. McOrist, T.Wall, M. Elcombe, P.Prasad, "Endohedral formation From Neutron Activation of Interstitial Rare Gas C₆₀.", Full. Sci. Technol. 5 (1997) 871-902.
10. Gadd, G. E.; Schmidt, P.; Bowles, C.; McOrist, G.; Evans, P. J.; Wood, J.; Smith, L.; Dixon, A.; Easey, J.; " Evidence for Rare-Gas Endohedrel Fullerene Formation From Gamma-Recoil From HPLC Studies.", J. Am. Chem. Soc., 1998, 120(40), 10322-10325.
11. T.Braun, H.Rausch, "Radioactive Endohedral Metallofullerenes Formed by Prompt Gamma-Generated Neuclear Recoil Implosion", Chem. Phys. Lett. 288 (1998) 179-182.
12. K. L. S. Lawrence, G. J. Ehrhardt, D. W. Cagle, T. P. Thrash and L. J. Wilson, "Fullerene Radiopharmaceuticals? High-Flux Neutron Irradiation Study of C₆₀," in Fullerenes: Recent Advances in the Chemistry and Physics of Fullerenes and Related Materials: Vol. 2, K. Kadish and R. S. Ruoff, Eds., The Electrochemistry Society, **1995**, 66-71.
13. T. Braun, I. Konkoly- Thege, H. Rausch, K. Suevegh, A. Vertes, "Dose Effects in Neutron Irradiated C₆₀: A Positron lifetime Spectroscopy and DSC Study", Chem. Phys. Lett., 238 (1995) 290-294.

14. H.Nakahara, K. Sueki, W. Sato, K. Akiyama, "Nuclear Reactions and Radionuclides in the Study of Fullerenes.", *Journal of Radioanalytical and Nuclear Chemistry*, v.243 (2000) 169-179.
15. S. Stevenson, G. Rice, T. Glass, K. Harich, F. Cromer, M. R. Jordan, J. Craft, E. Hadju, R. Bible, M. M. Olmstead, K. Maitra, A. J. Fisher, A. L. Balch, H. C. Dorn, "Small-bandgap Endohedral Metallofullerenes in High Yield and Purity" , *Nature* 401, 55-57 (1999).