Molecular Magnets

# Magnetic Moments of the Endohedral Cluster Fullerenes $Ho_3N@C_{80}$ and $Tb_3N@C_{80}$: The Role of Ligand Fields

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The electronic and magnetic properties of endohedral fullerenes $M_k@C_{2n}$ for different metals M (such as lanthanides R, Group 3 and Group 2 metals) is a current area of endohedral fullerene research.[1] The influence of the electron transfer from M to the carbon cage, the geometric structure of the $M_k@C_{2n}$, as well as the location of the metal ion(s) in the cage on the magnetic properties are commonly studied. As shown by ESR spectroscopy, photoemission or Mössbauer spectroscopy, R ions are trivalent in most cases as in $Er_k@C_{82}$ for $k = 1$ and 2[2,3] and $Dy@C_{2n}$ ($2n = 80, 82, 84$).[4] Detailed studies of the fullerene magnetization versus applied field and temperature have confirmed these results.[5–11] On the other hand europium was found to be divalent in fullerenes for $2n = 74$ or

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82.[9,10] The formal valency of an ion M depends also on the number of the ions encaged: For $Sc_k@C_{82}$ ($k = 1, 2, 3$) Takata et al.[12] reported scandium to be divalent for $k = 1$ or 2, whereas for $k = 3$ the whole trimer has a charge of +3, $(Sc_3)^{3+}$, that is, the formal valency of scandium is +1. Endohedral thulium is divalent in $Tm@C_{82}$,[13,14] whereas a +3 state is discussed for $Tm_2@C_{82}$.[15,16] Structural studies on $Sc_2@C_{84}$,[17] $Sc_3@C_{82}$,[12] $La@C_{82}$[18] and $Er_2@C_{82}$[3] show the metal ions in an off-center position in the cage causing a low symmetry of the fullerene. In $Sc_3@C_{82}$ the scandium ions form a (nearly) equilateral triangle.[12]

A new type of endohedral fullerene was introduced with the nitride cluster fullerenes such as $Sc_3N@C_{80}$ which are stable endohedral structures of carbon cages, and are almost as stable as empty cages. In $Sc_3N@C_{80}$, the nitrogen atom is bonded to the three scandium atoms in a triangular planar configuration.[19,20] The entire $Sc_3N$ cluster is bonded to the $C_{80}$ cage, the shortest Sc–$C_{80}$ distances being of the order of 2.3 to 2.5 Å.[19,20] This bond configuration which is measured in a short-time-scale experiment may be hidden in experiments with a longer time scale. For example, $^{13}C$ NMR spectroscopy indicated a time-averaged structural picture of a non-interacting $I_h$-$C_{80}$ cage and an isotropic $Sc_3N$ cluster.[19] More detailed investigations revealed a complex diffusion dynamics of the encaged cluster at room temperature.[21]

The interest in endohedral fullerenes encapsulating lanthanide ions is related to the unfilled 4f shell of the lanthanide ions, which gives rise to large magnetic moments and a variety of interesting magnetic properties. Also, these materials have a great potential for applications as contrast agents for magnetic resonance or X-ray investigations, biological tracing agents, and radiopharmaceuticals.[22,23] Some of these applications are closely related to the unique magnetic properties of these materials. For the first time, we present herein a new magnetic structure for the $R_3N$ clusters (R = Ho, Tb) in the systems $Ho_3N@C_{80}$ and $Tb_3N@C_{80}$, and explain the unexpected values observed for the magnetic moments of the encapsulated nitride clusters. These results provide information on the interaction between the magnetic moments of rare-earth metals encapsulated in the fullerene cage. The magnetic properties are used to determine the oxidation state of R in $R_3N@C_{80}$.

By using a new preparative route[24] for nitride cluster fullerenes, $Ho_3N@C_{80}$ and $Tb_3N@C_{80}$ were synthesized in high yields and with an outstanding selectivity. As demonstrated by HPLC analysis of the holmiumnitride fullerene soot (Figure 1), $Ho_3N@C_{80}$ is the main component in the fullerene soot and can be easily isolated by one HPLC run. Besides $Ho_3N@C_{80}$ small amounts of the endohedral structure $Ho_3N@C_{82}$ and higher cage sizes were produced. The high purity of the isolated samples is confirmed by mass spectrometric data (Figure 1, inset). The fullerenes $C_{60}$ and $C_{70}$ appeared as byproducts of the reaction. $Ho_3N@C_{80}$ and $Tb_3N@C_{80}$ are large-energy-gap fullerenes having optical gaps of approximately 1.75 eV.[24] By Vis-NIR and FTIR analysis both cluster fullerenes were assigned to the carbon cage $C_{80}$:7 with icosahedral symmetry $I_h$.[24] Electron spin resonance experiments revealed that both structures are diamagnetic at room temperature.

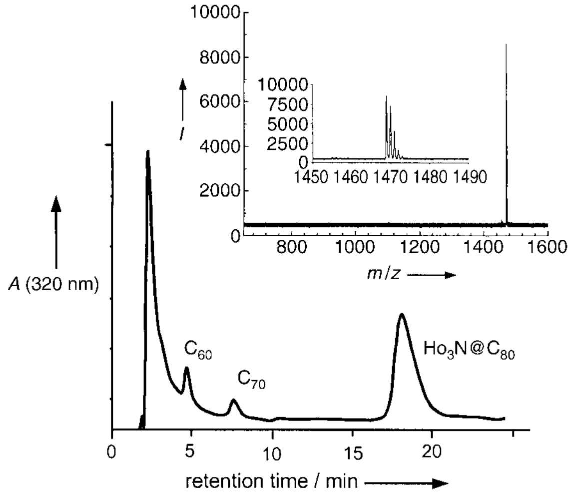

***Figure 1.*** HPLC trace of the $Ho_3N@C_{2n}$ soot on a Buckyprep column with toluene as an eluent. The chromatogram shows the dependence of the optical absorption at $\lambda = 320$ nm on the retention time, which reveals that $Ho_3N@C_{80}$ is the main component of the soot. Inset: LD-TOF mass spectrum confirming the high purity of the $Ho_3N@C_{80}$ sample.

The results of our magnetic studies are presented in Figures 2 and 3. The field dependence of magnetization $M(H,T)$ of $Ho_3N@C_{80}$ and $Tb_3N@C_{80}$ was measured at various temperatures. For both structures the $M(H,T)$ data fit well with a simple dependence on only one variable, $HT^{-1}$, pointing to an ideal Curie paramagnetism. The observed magnetization curves can be described by the Langevin function $M(H/T) = m_s L(\mu H/k_B T)$, with $\mu$ as the moment of the fullerene molecule and $k_B$ as the Boltzmann constant. The as determined values of $\mu$ are 21 $\mu_B$ for $Ho_3N@C_{80}$ and 17 $\mu_B$ for $Tb_3N@C_{80}$ ($\mu_B$ = Bohr's magneton). The large values of $\mu$ justify the neglect of quantum effects, that is, the description of the magnetic behavior by a Langevin function. These moments for the fullerene molecules are quite different from those of non-interacting $Ho^{3+}$ ions (10 $\mu_B$) or $Tb^{3+}$ ions (9 $\mu_B$). Also, they cannot be explained by a linear antiferromagnetic

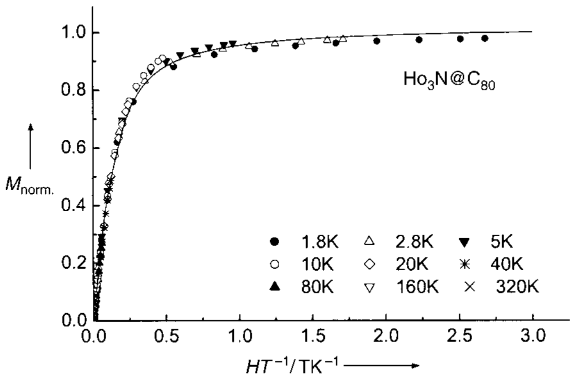

***Figure 2.*** The experimental data $M(H,T)$ for $Ho_3N@C_{80}$ (symbols) corrected for the diamagnetic contribution and normalized to the saturation. The solid line represents the fitted Langevin function with a magnetic moment $\mu = 21\ \mu_B$.

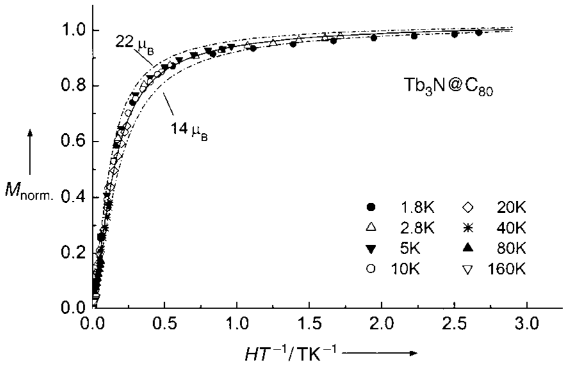

***Figure 3.*** The experimental data $M(H,T)$ for $Tb_3N@C_{80}$ (symbols) corrected for the diamagnetic contribution and normalized to the saturation. The solid line represents the fitted Langevin function with a magnetic moment $\mu = 17\,\mu_B$. The broken lines correspond to the normalized magnetization for $\mu = 14\,\mu_B$ and $\mu = 22\,\mu_B$.

or ferromagnetic alignment of the three moments in the cages. A ferromagnetic linear alignment would result in 30 $\mu_B$ for $Ho_3N@C_{80}$ and 27 $\mu_B$ for $Tb_3N@C_{80}$.

The field and temperature dependence of the magnetization of $Ho_3N@C_{80}$ and $Tb_3N@C_{80}$ can be understood by assuming a stable configuration of the magnetic moments the three atoms R, which is unchanged in the temperature and field range under investigation. These net magnetic moments $\mu$ do not experience any significant magnetic anisotropy. Otherwise the field and temperature dependence of magnetization would deviate from that shown in Figure 2 and Figure 3.[25,26]

A comparison with the literature data on $Sc_3@C_{82}$,[12] $Er_xSc_{3-x}@C_{80}$,[29] $Lu_3N@C_{80}$,[23] and $Sc_3N@C_{80}$[20] allows the following conclusions to be drawn: 1) the three Ho or Tb ions form a nearly equilateral triangle with one $N^{3-}$ species in its center as shown in Figure 4a, and 2) both in $Ho_3N@C_{80}$ and $Tb_3N@C_{80}$ each of the rare-earth ions is in the +III state. Such a charge distribution is supported by HPLC, Vis-NIR, and FTIR data.[23] On taking up six electrons the $C_{80}$ cage attains a closed-shell like that found for $Sc_3N@C_{80}$.[19,20,27,28] No contributions of $N^{3-}$ and $[C_{80}]^{6-}$ to the magnetic moment are expected and the magnetic behavior is governed only by the cluster $(Ho^{3+})_3N^{3-}$ or $(Tb^{3+})_3N^{3-}$. As the cage has no spin, contrary to the case of endohedral monometallofullerenes,[30] no coupling between the R magnetic moments and the cage has to be taken into account.

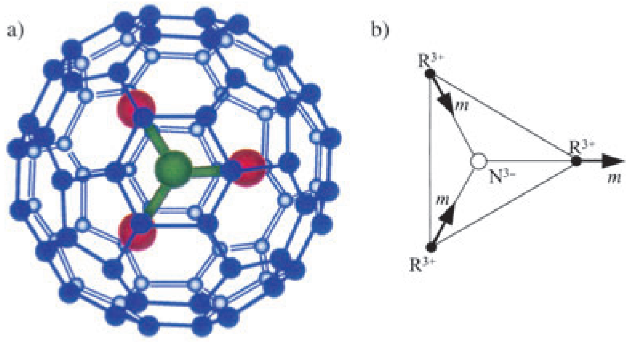

***Figure 4.*** a) Structure of a $R_3N@C_{80}$ molecule according to ref. [18], blue: carbon, green: nitrogen, and red: rare earth atoms; b) orientation of the individual R magnetic moments $m$ (arrows) in the $R_3N$ cluster in $R_3N@C_{80}$ (R = Ho, Tb).

The total magnetic moments $\mu$ of $Ho_3N@C_{80}$ and $Tb_3N@C_{80}$ do not experience any detectable magnetic anisotropy. Taking into account the diffusion dynamics of $R_3N$ and that "static" magnetic measurements have a longer time scale than NMR spectroscopy experiments, this situation is in agreement with the current model for $Sc_3N@C_{80}$.[19–21] However, the single R ions are subjected to ligand fields resulting in a magnetic anisotropy of the individual R magnetic moments with respect to local directions within the $R_3N$ cluster. The ligand field of the nitrogen ion in the $R_3N$ cluster causes the preferred direction of the R magnetic moments with respect to the R–N bonds. If these R–N bonds are "magnetically easy directions" and the magnetic anisotropy caused by the ligand fields is relatively strong compared to the exchange interaction between the R magnetic moments, the direction of these moments will be "pinned" along the bond directions. For ferromagnetic exchange the configuration of the three magnetic moments is shown in Figure 4b. A vector addition of the three (classical) R magnetic moments $m$ results in the magnitude $2|m|$, that is, 20 $\mu_B$ for the $Ho_3N$ cluster and 18 $\mu_B$ for $Tb_3N$, which is in good agreement with the results given above. Antiferromagnetic exchange can be excluded as it would result in a vanishing total moment of the $R_3N@C_{80}$ molecule. The charge distribution of these cluster fullerenes can be formally described as $(R^{3+})_3N^{3-}@C_{80}{}^{6-}$. Because the $N^{3-}$ as well as $C_{80}{}^{6-}$ ions do not contribute to the magnetic moment and the R magnetic moments are shielded by a carbon cage which has a filled electron shell, $Ho_3N@C_{80}$ and $Tb_3N@C_{80}$ do not show a finite paramagnetic Curie temperature, and magnetic hysteresis as well as differences between zero field and field cooling conditions do not occur. The vanishing (or very small) magnetic anisotropy is suggested to be related to the closed shell of the $C_{80}{}^{6-}$ ion. This situation is in contrast to results on endohedral monometallofullerenes, for which the contribution of the π electron has to be taken into account.[31]

In summary, the net magnetic moments of the encaged $(R_3N)$ trimer (R = Ho, Tb) can not be explained either by non-interacting magnetic moments from R, nor by a dominant ferromagnetic or antiferromagnetic exchange interaction between the R moments. The net moments of 21 $\mu_B$ ($Ho_3N@C_{80}$) and 17 $\mu_B$ ($Tb_3N@C_{80}$) are explained by a new model for the magnetic structure of $Ho_3N@C_{80}$ and $Tb_3N@C_{80}$, in which strong ligand fields within the $(R_3N)$ cluster act on the ferromagnetically exchange-coupled moments of R. As a result of this combination of different types of interaction the individual R moments are not collinearly aligned but are parallel to the R–N bonds (R = Ho or Tb).

## Experimental Section

The cluster fullerenes were prepared using a modified Krätschmer–Huffman arc burning method. Two modifications of this process were applied: In a first version a solid nitrogen source was used by adding varying amounts of calcium cyanamide to the metal/graphite powder mixture. As the main and second synthetic route the concept of the reactive arc atmosphere[32] was applied to improve the ratio of trimetal nitride fullerenes to empty fullerenes. In general, graphite rods filled with a metal/graphite or metaloxide/graphite powder mixture were used. The soot of the arc burning process was soxhlet extracted with $CS_2$ for 20 h. After extraction non-fullerene products such as polycyclic aromatic hydrocarbons and other low molecular structures were removed from the extract by washing with acetone.

High performance liquid chromatography (HPLC) was used for fullerene purification and analysis (BuckyPrep column, Nacalai Tesque). Owing to the high content of the $R_3N@C_{80}$ structure (R = Ho or Tb) in the fullerene extract these fullerenes were isolated by a single separation step using a 4.6 × 250 mm BuckyPrep column. The resulting purity was over 95 %.

The mass spectrometric characterization was by MALDI-TOF mass spectrometry using the Biflex II spectrometer (Bruker, Germany) and 9-nitroanthracene as the matrix. Positive and negative ions of the fullerenes were detected.

The magnetic measurements were performed on a SQUID magnetometer at temperatures $T$ from 1.8 K to room temperature in magnetic fields $H$ up to 5 Tesla. As the mass of the investigated samples was very small (about 60 µg in the case of $Ho_3N@C_{80}$, 40 µg for $Tb_3N@C_{80}$) the as measured magnetization values $M_{exp}(H,T)$ data revealed a remarkable diamagnetic contribution to the susceptibility, $\chi_{dia}$, from the encapsulating glass ampoule and a two-step analysis had to be done. In a first step $\chi_{dia}$ was determined from a fit of $m_s L(\mu H/k_B T) + \chi_{dia} H$ to $M_{exp}$. The magnetization values $M(H,T)$ of the fullerene powder is then given by $M(H,T) = M_{exp} - \chi_{dia} H$. The final values of $m_s$ and $\mu$ were determined by fitting $m_s L(\mu H/k_B T)$ to these $M(H,T)$ values. The very small changes in $m_s$ and $\mu$ demonstrated the consistency of the procedure. Furthermore it is noted, that such small fullerene amounts were "smeared" over the walls of the encapsulating glass ampoule in the SQUID magnetometer. Therefore the absolute value of the magnetization of the sample could not be determined sufficiently precisely. However the dependence of the magnetization $M(H,T)$ normalized to $m_s$ on field and temperature could be determined with an accuracy of typically 1 % as confirmed by repeated measurements. Regarding $\mu$, the fitting results have been verified by a comparison of the fitted magnetization curve with theoretical curves for assumed $\mu$ values of 22 $\mu_B$ and 14 $\mu_B$ in the case of $Tb_3N@C_{80}$ (see Figure 3).

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[1] H. Shinohara, *Rep. Prog. Phys.* **2000**, *63*, 843.
[2] M. E. J. Boonman, P. H. M. van Loosdrecht, D. S. Bethune, I. Holleman, G. J. M. Meijer, P. J. M. van Bentum, *Phys. B* **1995**, *211*, 323.
[3] R. M. Macfarlane, G. Wittmann, P. H. M. van Loosdrecht, M. de Vries, D. S. Bethune, St. Stevenson, H. C. Dorn, *Phys. Rev. Lett.* **1997**, *79*, 1397.
[4] Yu. S. Grushko, E. G. Alekseev, V. S. Kozlov, L. I. Molkanov, G. Wortmann, H. Giefers, K. Rupprecht, M. A. Khodorkovskii, *Hyperfine Interact.* **2000**, *126*, 121.
[5] H. J. Huang, S. H. Yang, X. X. Zhang, *J. Phys. Chem. B* **2000**, *104*, 1473.
[6] H. J. Huang, S. H. Yang, X. X. Zhang, *J. Phys. Chem. B* **1999**, *103*, 5928.
[7] B. Diggs, A. Zhou, C. Silva, S. Kirkpatrick, N. T. Nuhfer, M. E. McHenry, D. Petasis, S. A. Majetich, B. Brunett, J. O. Artman, S. W. Staley, *J. Appl. Phys.* **1994**, *75*, 5879.
[8] A. Bartl, L. Dunsch, J. Fröhner, G. Seifert, D. Eckert, M. Wolf, K.-H. Müller, *SPIE J.* **1997**, *3142*, 36.
[9] L. Dunsch, D. Eckert, J. Fröhner, A. Bartl, P. Kuran, M. Wolf, K.-H. Müller, *Electrochem. Soc. Proc.* **1998**, *6*, 955.
[10] K.-H. Müller, L. Dunsch, D. Eckert, M. Wolf, A. Bartl, *Synth. Met.* **1999**, *103*, 2417.
[11] H. Funasaka, K. Sakurai, Y. Oda, K. Yamamoto, T. Takahashi, *Chem. Phys. Lett.* **1995**, *232*, 273.
[12] M. Takata, E. Nishibori, M. Sakata, M. Inakuma, E. Yamamoto, H. Shinohara, *Phys. Rev. Lett.* **1999**, *83*, 2214.
[13] T. Pichler, M. S. Golden, M. Knupfer, J. Fink, U. Kirbach, P. Kuran, L. Dunsch, *Phys. Rev. Lett.* **1997**, *79*, 3026.
[14] T. Pichler, M. Knupfer, M. S. Golden, T. Böske, J. Fink, U. Kirbach, P. Kuran, L. Dunsch, C. Jung, *Appl. Phys. A* **1998**, *66*, 281.
[15] "Nanonetwork Materials" K. Kikuchi, K. Sakaguchi, O. Norio, T. Kodama, H. Nishikawa, I. Ikemoto, K. Kohdate, D. Matsumura, T. Yokoyama, T. Ohta, *AIP Conf. Proc.* **2001**, *590*, 473.
[16] K. Kikuchi, K. Akiyama, K. Sakaguchi, T. Kodama, H. Nishakawa, I. Ikemoto, T. Ishigaki, Y. Achiba, K. Sueki, H. Nakahara, *Chem. Phys. Lett.* **2000**, *319*, 472.
[17] M. Takata, E. Nishibori, B. Umeda, M. Sakata, M. Inakuma, E. Yamamoto, H. Shinohara, *Phys. Rev. Lett.* **1997**, *78*, 3330.
[18] W. Andreoni, A. Curioni, *Phys. Rev. Lett.* **1996**, *77*, 834.
[19] 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, *Nature* **1999**, *401*, 55.
[20] M. Krause, H. Kuzmany, P. Georgi, L. Dunsch, K. Vietze, G. Seifert, *J. Chem. Phys.* **2001**, *115*, 6596.
[21] "Structural and Electronic Properties of Molecular Nanostructures" K. Vietze, G. Seifert, *AIP Conf. Proc.* **2002**, *633*, 39.
[22] M. Mikawa, H. Kato, M. Okumura, M. Narataki, Y. Kanazawa, N. Miwa, H. Shinohara, *Bioconjugate Chem.* **2001**, *12*, 510.
[23] E. B. Iezzi, J. C. Duchamp, K. R. Fletcher, T. E. Glass, H. C. Dorn, *Nano Lett.* **2002**, *2*, 1187.
[24] L. Dunsch, M. Krause, J. Noack, P. Georgi, *J. Phys. Chem. Solids* **2004**, *65*, 309.
[25] H. D. Williams, K. O'Grady, M. El Hilo, R. W. Chantrell, *J. Magn. Magn. Mater.* **1993**, *122*, 129.
[26] M. Respaud, *J. Appl. Phys.* **1999**, *86*, 556.
[27] J. M. Campanera, C. Bo, M. M. Olmstead, A. L. Balch, J. M. Poblet, *J. Phys. Chem. A* **2002**, *106*, 12356.
[28] T. Akasaka, S. Nagase, K. Kobayashi, M. Wälchli, K. Yamamoto, H. Funasaka, M. Kako, T. Hoshino, T. Erata, *Angew. Chem.* **1997**, *109*, 1716; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 1643.
[29] R. M. Macfarlane, D. S. Bethune, S. Stevenson, H. C. Dorn, *Chem. Phys. Lett.* **2001**, *343*, 229.
[30] K. Furukawa, S. Okubo, H. Kato, H. Shinohara, T. Kato, *J. Phys. Chem. A* **2003**, *107*, 10933.
[31] M. Inakuma, H. Kato, A. Taninaka, H. Shinohara, T. Enoki, *J. Phys. Chem. B* **2003**, *107*, 6965.
[32] L. Dunsch, P. Georgi, F. Ziegs, H. Zöller, German patent, DE 10301722A1, **2003**.