Capturing a Tetratomic Nitrogen Ring *cyclo-N₄* inside an Aza[82]fullerene

Yuanyuan Wang

Peking University

Ziqi Hu

Universidad de Valencia

Wangqiang Shen

Huazhong University of Science and Technology <https://orcid.org/0000-0002-8711-3934>

Tonghui Zhou

Peking University

Shinobu Aoyagi

Nagoya City University

Yihao Yang

Peking University

Zhiyong Wang

Nagoya University

Pengwei Yu

Huazhong University of Science and Technology

Jie Su

College of Chemistry and Molecular Engineering, Peking University

Eugenio Coronado

University of Valencia <https://orcid.org/0000-0002-1848-8791>

Xing Lu

Huazhong University of Science and Technology

Zujin Shi (✉ zjshi@pku.edu.cn)

Peking University

Article

Keywords: tetratomic nitrogen ring, cyclo-N₄, polymeric nitrogen compounds synthesis

Posted Date: August 31st, 2021

DOI: <https://doi.org/10.21203/rs.3.rs-816416/v1>

Abstract

Synthesis of polymeric nitrogen compounds is a formidable task due to the proneness of nitrogen to the formation of $\text{N} \equiv \text{N}$ triple bond, one of the strongest chemical bonds known. Here, we report an arc-discharge approach to successfully stabilize the elusive four-membered nitrogen ring (*cyclo*- N_4) in an unprecedented endohedral metallofullerene $\text{Dy}_2\text{N}_4@\text{C}_{81}\text{N}$ (**Dy-I**). Its molecular structure has been unambiguously determined by X-ray crystallography to show a covalently bonded *cyclo*- N_4 plane bridging two dysprosium ions inside an aza[82]fullerene cage, highlighting the stabilization of *cyclo*- N_4 as a concurrent result of fullerene encapsulation and metal coordination. Our computational results further reveal a six-center-one-electron ($6c-1e$) bond delocalized over the inverse-sandwich $\text{Dy-N}_4\text{-Dy}$ cluster. This chemical peculiarity stems from the diffuse radical character of the highly anionic *cyclo*- N_4^{3-} ligand, which is confirmed by electron paramagnetic resonance (EPR) spectrum of $\text{Y}_2\text{N}_4@\text{C}_{81}\text{N}$ (**Y-I**).

Introduction

Strikingly distinct from carbon that features well-established chemical diversity of chain or ring structures, nitrogen has been commonly recognized as inert with the ease of dinitrogen (N_2) formation, owing to the unparalleled stability of the homonuclear triple bond over single and double bonds¹. This chemical peculiarity disfavors the synthesis of any larger complex or ion composed exclusively of nitrogen. Nitrogen-only materials are thus inherited with high energy density and have attracted much attention for decades²⁻⁴. Extensive searches for non-molecular nitrogen frameworks have been attempted under harsh conditions using high temperatures and high pressures, leading to a semiconducting nitrogen phase⁵ and a crystalline allotropic form of nitrogen with a single-bonded diamond-like network⁶. On the other hand, linear and cyclic polynitrogen molecules, apart from the well-known azide ion (N_3^-), are of particular interest in the forefront of nitrogen chemistry^{7,8}. In this context, gaseous tetranitrogen (N_4) has been detected from neutralization of the N_4^+ cation in mass spectrometry, indicating an open-chain geometry with a weak bond between two N_2 units⁹. Recently, such a goal of N_2 catenation was achieved through organoboron-mediated coupling, characteristic of a N_4^{2-} chain bridges two boron centers¹⁰. Aromatic five-membered nitrogen ring *cyclo*- N_5^- has also been synthesized by direct cleavage of the C–N bond in a multisubstituted pentazole, which shows reasonable stability in both metal-free and metal-coordinated forms¹¹⁻¹³.

As a homologue of *cyclo*- N_5^- , the existence of a molecular ring consisting of four nitrogen atoms (*cyclo*- N_4) remains bewildering. Previous calculation suggested that its unsubstituted neutral form, isoelectronic with cyclobutadiene, presents a rectangular structure while it is more labile than the metastable single-bonded tetrahedron $T_d\text{-N}_4$ ⁸. Alternatively, alkylated tetrazetidine (N_4R_4) has received substantial interests. A conceivable photo-cycloaddition synthetic strategy was proposed by introducing rigid bisazo scaffolds¹⁴, yet it has been proven unsuccessful due to the propensity of N_2 extrusion¹⁵. To this end, a

substituted tetrazetidine radical cation $[\text{N}_4(\text{CO}_2^-\text{Pr})_4]^{*+}$ was detected in solution by electron paramagnetic resonance (EPR) spectroscopy upon oxidation¹⁶. Similar to this strategy, the phosphorous containing analogues P_4 and P_2N_2 rings, have been synthesized in the form of substituted radical cations¹⁷. However, there is no report to date of the solid-state synthesis of the extremely reactive *cyclo*- N_4 complex. To confirm its absolute structure, an alternative synthetic pathway is ultimately inevitable.

Fullerene cages, owing to their hollow cavity, are often considered as a templating nanocontainer to capture special atomic clusters to form endohedral fullerenes¹⁸. Starting from the pristine C_{60} , atomic nitrogen¹⁹, ionic lithium²⁰ and small molecule²¹ can be entrapped by plasma implantation, ion-beam and molecular surgical methods. Larger C_{70} cage is able to accommodate unstable homo- and hetero-nuclear dimers such as HeN^{22} and $(\text{H}_2\text{O})_2^{23}$. On the other hand, arc-discharge synthesis²⁴, if incorporated with metal-doped carbon rods, offers more chemical possibilities with respect to cages and encapsulated clusters. Unique structures hence have been discovered, such as $\text{U}_2\text{C}@C_{80}^{25}$ and $\text{Ti}_3\text{C}_3@C_{80}^{26}$ with previously unseen metal-carbon bonding characters, as well as air-stable radicals $\text{Sc}_3\text{C}_2@C_{80}^{27}$ and $\text{M}_2@C_{79}\text{N}$ ($\text{M} = \text{Y}, \text{Gd}, \text{Tb}$ and Dy)²⁸⁻³². Notably, despite that metal coordination is able to promote the stabilization of unusual species in fullerene cages, the kinds of nitrogen-containing clusters are rather limited to metal nitride (M_3N), carbonitride (MCN) and cyanide (MNC)³³.

Motivated by the fullerene-templated and metal-coordination strategy, we aimed to synthesize polymeric nitrogen compounds by introducing melamine ($\text{C}_3\text{H}_6\text{N}_6$) with high nitrogen concentration during the arc-discharging process³⁴. We report herein a successful capture of the long-sought-after tetratomic nitrogen ring anion (*cyclo*- N_4^{3-}) coincident with dimetallic coordination, leading to novel endohedral metallofullerenes $\text{Dy}_2\text{N}_4@C_{81}\text{N}$ (**Dy-I**) and $\text{Y}_2\text{N}_4@C_{81}\text{N}$ (**Y-I**). The molecular structure of **Dy-I** has been confirmed by single-crystal X-ray diffraction (XRD) analysis. This concrete structural evidence makes radical *cyclo*- N_4^{3-} , which is unsupported by any non-metal element and protected inside a fullerene cage, the third air-stable polynitrogen ion after N_3^- and *cyclo*- N_5^- .

Results And Discussion

Synthesis and crystal structure. **Dy-I** and **Y-I** were synthesized using the Krätschmer-Huffman arc-discharge method²⁴. Graphite rods, filled with MNi_2 alloy ($\text{M} = \text{Dy}$ and Y) and melamine powder as solid nitrogen source³⁴, were evaporated under helium atmosphere at high temperatures, resulting in the carbon-based solid. Multi-stage high performance liquid chromatography (HPLC) was then applied to isolate pure **Dy-I** and **Y-I** from the extract of raw soot (see Supplementary Information for detailed information). To determine the molecular structure through single crystal XRD analysis, a black crystal was obtained by co-crystalizing **Dy-I** with $\text{Ni}^{\text{II}}(\text{OEP})$ molecule (OEP is the dianion of octaethyl porphyrin).

The crystal system of the obtained **Dy-I-Ni^{II}(OEP)·C₆H₆** co-crystal falls into the monoclinic *C2/m* space group, where the asymmetric unit cell contains one half of the Ni^{II}(OEP) molecule and two halves of the C_{3v}(8)-C₈₂ cage, regardless of the nitrogen substitution. Note that due to the similar electron density of N and C, direct identification of the exact location of the N atom on the cage is not feasible and will be discussed later. Within the fullerene cage, two fully ordered N atoms are assigned. The other two N are generated by symmetric operation, leading to the unequivocal determination of a planar *cyclo*-N₄ ring (**Figure 1a**). The averaged N-N distance is determined as 1.609(9) Å, which is longer than those of reported polymeric nitrogen compounds with double or aromatic bonds^{10,11}, as well as conventional N-N single bond in hydrazine (1.45 Å)³⁵. However, it is similar to the values of crystalline N₂O₄ (1.64 Å)¹ and metal-triazane cation Ag₂(N₃H₅)₃²⁺ (1.6(1) Å)³⁶, suggesting a weak bonding character between each two adjacent N atoms in the *cyclo*-N₄ unit. This is likely due to the ring strain and metal-ring interaction that weaken N-N bonds, in retrospect to the longer bond length in the silver ion-complexed *cyclo*-N₅⁻ than that of the pristine metal-free anion¹³.

On the other hand, two metals are highly disordered. A total of twenty Dy sites with occupancy varying from 0.03 to 0.27 are widely distributed on two sides of the *cyclo*-N₄ plane. The latter stays in the center of the cage and is almost parallel (dihedral angle: 176.73°) to the Ni^{II}(OEP) molecule (**Figure 1b**). The major sites Dy1 and Dy2, with a Dy-Dy distance of 3.702(5) Å, unexpectedly reside at off-center positions with respect to *cyclo*-N₄, featuring a distorted octahedron with inverse-sandwich Dy-N₄-Dy coordination (**Figure 1c**). This results in a wide range of Dy-N distances from 1.527 Å to 2.828 Å. Despite the fact that such short Dy-N distances are rarely seen in any organometallic complex, it is nevertheless not uncommon for endohedral metallofullerene compounds in which special chemical bond can be found due to severe disorder of metal atoms and confined inner space of fullerene cage. For instance, the C-C distances of M₂C₂ (M = La, Er and Lu)³⁷⁻³⁹ clusters in carbide clusterfullerenes are only about 0.9 Å, much shorter than the average length (1.2 Å) of a C°C triple bond. In addition, Dy1 and Dy2 are located below two hexagon carbon rings, showing a quasi-η⁶ metal-cage coordination mode (**Figure S3.2**). The potential energy surface for metal inside the cage may also be influenced by the existence of porphyrin in the co-crystal.

Computational studies. In order to verify the peculiar structure of **Dy-I** and probe in particular the bonding nature of the *cyclo*-N₄ unit, density functional theory (DFT) calculations were performed starting from the crystal structure. The resulted molecular structure of **Dy-I** is shown in **Figure 2a**. In line with the crystal structure, the planar *cyclo*-N₄ ring is maintained, while they differ in the fact that the calculated *cyclo*-N₄ unit symmetrically complexes to two dysprosium ions. The Dy-N distances fall in the range of 2.28-2.31 Å, rendering an ideally octahedral Dy-N₄-Dy configuration. As discussed above, the crystal structure deviates from this ideal gas phase model as a result of the complicated circumstance in the **Dy-I-Ni^{II}(OEP)·C₆H₆** co-crystal. Concerning the nitrogen location on the fullerene cage, the hexagon/hexagon/pentagon (665) junction substituted structure (**Figure 2a**) is energetically

favorable based on the previous studies of $M_2@C_{79}N$ ($M = Y$ and Gd)^{28,40}; besides, nitrogen tends to reside in the middle of metal ions, thus avoiding short metal-nitrogen distances in $La_3N@C_{79}N$ ⁴¹ and $Y_2@C_{81}N$ ⁴². This is also confirmed by the calculations of **Y-I**, where Dy^{3+} is replaced by diamagnetic Y^{3+} with similar ion radius (**Figure S4.1**). Notably, the configuration of the encapsulated cluster is not affected by the nitrogen locations on the cage.

The bonding nature of **Dy-I** is next illustrated by electron localization function (ELF) mapping on the *cyclo*- N_4 plane. **Figure 2b** shows a salient electron-density accumulation between each nitrogen pair, validating four N-N bonds in *cyclo*- N_4 . On the other hand, nitrogen lone pairs are assigned to areas around four nitrogen atoms with relatively diffuse electron localization, which contributes to the strain relief of the tetranitrogen ring⁴³. Frontier molecular orbital (MO) analysis of this open-shell compound reveals a cluster-based singly-occupied MO (SOMO) (**Figure 2c**). As a consequence, spin density is also distributed within the inverse-sandwich $Dy-N_4-Dy$ cluster and shares the same shape with SOMO (**Figure 2d**), indicating efficient one-electron charge transfer from $C_{81}N$ to Dy_2N_4 , which is similar to the circumstances in $M_2@C_{79}N$ ($M = Y$ and Gd)^{28,40}. In this sense, the fullerene cage stabilizes the enclosed radical, giving rise to moderate SOMO-LUMO gaps of **Dy-I** (1.26 eV) and **Y-I** (1.30 eV) (**Figure 2e**).

As the entrapped six-atom cluster is of significant interest to us, its multi-center bonding motifs in **Y-I** were further elucidated by partially localized orbital analysis using adaptive natural density partitioning (AdNDP) method⁴⁴. Among the cluster-based AdNDP orbitals, **Figure 3a-c** show four N-N single bonds, two Y-N dative bonds and one N-N π bond, respectively; **Figure 3d** presents one half-occupied π^* anti-bonding orbital perpendicular to the tetratomic nitrogen ring, which renders a SOMO-like distribution with substantial $Y(4d)$ contribution from two metals (a $6\sigma-1e$ bond). To sum up, 15 *p*-type electrons have been clearly allocated to the *cyclo*- N_4 ring, yielding a *cyclo*- N_4^{3-} radical anion and a 3+ formal charge of the Y_2N_4 unit, while $C_{81}N$ adopts a 3- ionic model and thus is isoelectronic to the stable $C_{3v}(8)-C_{82}^{4-}$ anion.

Spectroscopic and electrochemical properties. The composition of **Dy-I** and **Y-I** were confirmed by laser-desorption ionization time-of-flight (LDI-TOF) mass spectrum, showing well-matched theoretical and experimental isotopic distributions around the prominent molecular ion peaks accordingly with mass-to-charge ratio of $m/z = 1367.8$ and 1219.7 (**Figure 4a** and **Figure S2.2**). Their visible-near-infrared (vis-NIR) absorption spectra (**Figure 4b**) both feature two characteristic peaks at wavelength of 720 and 910 nm, which resemble those of $C_{3v}(8)-C_{82}$ based metallofullerenes hosting metal carbide (Sc_2C_2 ⁴⁵ and Dy_2C_2) and dimetallic (Sc_2 ⁴⁶ and Er_2 ⁴⁷) clusters. This further verifies that **Dy-I** and **Y-I** possess an identical molecular structure with an azafullerene $C_{81}N$ cage derived from one nitrogen substitution of $C_{3v}(8)-C_{82}$.

The EPR spectrum of **Y-I** solution at room temperature shows rich hyperfine patterns from ^{89}Y ($I = 1/2$) and ^{14}N ($I = 1$) nuclei with significant anisotropy. The hyperfine tensor components $A_\perp$ and $A_\parallel$ of two inequivalent ^{89}Y centers (Y1/Y2) are 208/237 MHz and 213/242 MHz, respectively; four ^{14}N nuclei exhibit an equivalent hyperfine tensor with $A_\perp(^{14}N) = 13.0$ MHz and $A_\parallel(^{14}N) = 19.5$ MHz; the g-tensor components

are determined as $g_{\perp} = 1.9780$ and $g_{\parallel} = 1.9775$. The large $A(^{89}\text{Y})$ values and g factor below 2 indicate that significant spin density is localized on the two Y atoms, which is consistent with the spatial distribution of SOMO fully enclosed inside the cage and is comparable to the single-electron Y-Y bond in $\text{Y}_2@\text{C}_{79}\text{N}$ and $\text{Y}_2@\text{C}_{80}\text{-CH}_2\text{Ph}$ ^{32,48}. The ^{14}N hyperfine splitting is similar to the value of 16.3 MHz (5.8 G) for N_2^{3-} -radical-bridged diyttrium complex⁴⁹. In contrast to the SOMO of the latter which is mainly localized at its N_2 moiety, the highly diffuse radical character of **Dy-I** also suggests noticeable metal- N_4 interaction, which would weaken N-N bonds whereas contribute to the stabilization of this special six-atom cluster inside the fullerene cage.

The redox behavior of **Dy-I** was investigated in an ortho-dichlorobenzene (*o*-DCB) solution by means of cyclic voltammetry to display two reversible oxidation steps and four reversible reduction peaks (**Figure 4d**). Compared with the results of other $\text{C}_{3v}(8)\text{-C}_{82}^{4-}$ based metallofullerenes (**Table 1**), the redox property of **Dy-I** is distinct. The most striking differences lie in the first oxidation ($^{\text{ox}}E_1$) and reduction ($^{\text{red}}E_1$) steps, in which the cluster-based SOMO of **Dy-I** is largely involved. In spite of their very different redox behaviors, the electrochemical gap of **Dy-I** (1.13 V) is still close to those of $\text{M}_2@\text{C}_{3v}(8)\text{-C}_{82}$ ($\text{M} = \text{Sc}$ and Er). A closer analysis (**Figure S4.4**) reveals that one-electron oxidation of **Dy-I** results in an expected transformation of N_4^{3-} to N_4^{2-} . On the contrary, the high-lying unoccupied cluster-based orbital precludes the reduction of N_4^{3-} to N_4^{4-} , where each N obeys octet rule to form four N-N single bonds. Instead, the *cyclo*- N_4^{3-} unit donates the unpaired electron to the cage-based LUMO of **Dy-I** upon reduction, leading to a $[\text{Dy}_2]^{6+}[\text{N}_4]^{2-}@\text{C}_{81}\text{N}$ ⁵⁻ electronic configuration of **Dy-I**⁻ anion. Noteworthy is that this eccentric electronic property of the N_4 ring is in accordance with the fact that the N_4R_4^+ radical cation is more stable than its neutral form in solution⁵⁰, suggesting a unusual bonding tendency in *cyclo*- N_4 which is likely attributed to the strain of the four-membered nitrogen ring.

Table 1. Redox potentials (V vs Fc/Fc^+)^a and electrochemical band gaps (ΔE_{gap})^b of **Dy-I** and related metallofullerenes possessing a $\text{C}_{3v}(8)\text{-C}_{82}$ cage.

Compounds	$^{\text{ox}}E_2$	$^{\text{ox}}E_1$	$^{\text{red}}E_1$	$^{\text{red}}E_2$	$^{\text{red}}E_3$	$^{\text{red}}E_4$	ΔE_{gap}	Ref.
Dy-I	0.85 ^c	0.46 ^c	-0.67 ^c	-1.29 ^d	-1.62 ^c	-2.08 ^d	1.13	this work
$\text{Er}_2@\text{C}_{3v}(8)\text{-C}_{82}$	-	0.11	-1.09	-1.33	-1.76	-2.49	1.20	46
$\text{Sc}_2@\text{C}_{3v}(8)\text{-C}_{82}$	-	0.02	-1.16	-1.53	-1.73	-2.02	1.18	47

^aRedox potentials in V are measured vs. ferrocene couple. ^b $\Delta E_{\text{gap}} = ^{\text{ox}}E_1 - ^{\text{red}}E_1$. ^cHalf-wave potential.

^dPeak potential.

Conclusions And Outlook

In summary, using arc-discharge method, a polymeric nitrogen ring comprising four covalently connected nitrogen atoms (*cyclo*-N₄) has been stabilized in endohedral metallofullerenes **Dy-I** and **Y-I**, thanks to the concerted effect of metal-coordination and fullerene-templated isolation. We thus have been able to obtain a single crystal of **Dy-I** to determine definitively for the first time the exact structure of *cyclo*-N₄, which is the second nitrogen-only ring after *cyclo*-N₅⁻¹¹ and presents as a planar ligand bridging two dysprosium ions inside the fullerene cage. The electronic structure of **Dy-I** was elucidated by DFT calculations as [Dy₂]⁶⁺[]³⁻@[C₈₁N]³⁻, showing a diffuse radical fully delocalized over the whole cluster. This radical nature induces large hyperfine splitting from the two ⁸⁹Y centers for **Y-I** and could be expected to invoke outstanding single-molecule-magnet behavior for **Dy-I**, as has been demonstrated in N₂³⁻-radical-bridged dilanthanide compounds^{51,52} and dimetallofullerene molecules^{31,48,53,54}. Moreover, *cyclo*-N₄³⁻ serves as a good electron donor that can be readily converted to *cyclo*-N₄²⁻ anion in redox processes. Our work opens up a unique route to the synthesis of polynitrogen compounds apart from conventional synthetic strategies.

Methods

Synthesis and isolation. **Dy-I** and **Y-I** were synthesized via the direct current arc-discharge method²⁴. Graphite anode rods, filled with finely mixed MNi₂ alloy (M = Dy and Y), graphite powder and melamine (molar ratio metal:C:N=1:10:0.8), were evaporated at 110 A under a 160 Torr helium atmosphere. The collected raw soot was extracted by refluxing with *o*-dichlorobenzene under a nitrogen atmosphere for 6 h. After replacing the solvent of the extract to toluene, a multi-stage HPLC procedure was performed to separate and purify **Dy-I** and **Y-I** with 5PYE, Buckyprep, and 5PBB columns (Cosmosil, Nacalai Tesque, Japan). Further details of synthesis and isolation are described in the Supplementary Information.

Single-crystal X-ray diffraction. A single black co-crystal of **Dy-I**/Ni^{II}(OEP) was grown by layering the benzene solution of nickel octaethylporphyrin (Ni^{II}(OEP)) onto the CS₂ solution of the **Dy-I** for three weeks. X-ray data were collected at 173 K using a Rigaku Oxford diffractometer equipped with a CCD collector (Bruker AXS Inc., Germany). The multi-scan method was used for absorption corrections. The structure was solved by direct method and refined with SHELXL-2014/7⁵⁵. The intact cage was modeled via the crystallographic mirror plane in refinement. This data can be obtained free of charge from The Cambridge Crystallographic Data Centre with CCDC No. 2005503.

Crystal Data for **Dy-I**·Ni^{II}(OEP)·C₆H₆: C₁₂₄H₅₀N₈NiDy₂, *M* = 2035.35, 0.16 × 0.12 × 0.10 mm³, monoclinic, *C*2/*m*, *a* = 25.300 (3) Å, *b* = 15.215 (2) Å, *c* = 19.830(4) Å, β = 95.644 (15)°, *V* = 7569 (2) Å³, *Z* = 4, ρ_{calcd} = 1.780 g cm⁻³, μ = 2.263 mm⁻¹, θ = 3.017-25.430°, *T* = 173 K, *R*₁ = 0.1358, *wR*₂ = 0.2841 for all data; *R*₁ = 0.1232, *wR*₂ = 2775 for 9045 reflections (*I* > 2.0σ(*I*)) with 838 parameters and 1014 restraints. Goodness of fit indicator 1.093. Maximum residual electron density 2.825 e Å⁻³.

Spectroscopic and electrochemical measurements. Laser desorption ionization time-of-flight (LDI-TOF) mass spectra were measured by positive-ion mode (TOF/TOF 5800, AB Sciex). Visible-near-infrared (vis-NIR) absorption spectra were recorded in toluene solution at room temperature with a Shimadzu UV3600Plus spectrophotometer. EPR spectrum of **Y-I** toluene solution was measured on a Bruker Elexsys E580 spectrometer operating in the X-band ($\omega = 9.47$ GHz). The spectrum was simulated by EasySpin toolbox⁵⁶ (<http://www.easyspin.org/>) based on Matlab. Cyclic voltammetry experiment of **Dy-I** was performed in *o*-dichlorobenzene solution using tetrabutylammonium hexafluorophosphate (0.05 M TBAPF₆) as supporting electrolyte in a CHI-660E instrument. A conventional three-electrode system with a platinum working electrode, a counter electrode and a silver wire reference electrode were used. Potentials were measured by adding ferrocene as an internal standard. The scan rate is 100 mV/s.

Computational methods. All density functional theory (DFT) calculations were carried out with Gaussian 09 package⁵⁷. Optimizations without symmetry restriction were performed using hybrid B3LYP functional. To treat Dy atoms, a 4*f*-in-core effective core potential with ECP55MWB basis set was used. 6-31 G(d) and ECP28MWB basis sets were used for C/N and Y atoms, respectively. Frequency analyses were calculated for all optimized structures to verify that the true local minima were reached. ELF and AdNDP analyses were performed with Multiwfn program⁵⁸. Molecular structures and isosurfaces were visualized using the VMD package.

Additional Information

Supplementary Information

HPLC profiles for the separation process of **Dy-I** and **Y-I** and computational details (PDF)

Additional Crystal data of **Dy-I**-Ni^{II}(OEP) (CIF)

Competing interests

The authors declare no competing financial interest.

Declarations

AUTHOR INFORMATION

Corresponding Authors

*zqi.hu@uv.es

*lux@hust.edu.cn

*zjshi@pku.edu.cn

Author Contributions

Y.W. performed synthesis, separation and crystallographic study of **Dy-I**. T.Z. performed synthesis and separation of **Y-I** with the help of Y.W. W.S. determined the crystal structure of **Dy-I** under the supervision of X.L. Y.Y. helped the synthesis. S.A., Z.W. and J.S. contributed to the crystallographic study. W.S. and P.Y. conducted electrochemical analysis. Z.H. performed theoretical studies, measured EPR spectrum and wrote the paper with the input from W.S., Y.W., X.L. and E.C. Z.S. and Z.H. initiated and led the project. Y.W., Z.H., W.S. and T.Z. contributed equally to this work.

ACKNOWLEDGEMENTS

This work was supported by the National Natural Science Foundation of China (grant no. 21875002), and the National Basic Research Program of China (grant no. 2017YFA0204901). The measurements of (Mass Spectrometry, XRD, and Optical Spectroscopy) were performed at the Analytical Instrumentation Center of Peking University. The help from PKUAIC (Dr. Wen Zhou and Dr. Mingxing Chen) was acknowledged.

References

1. Greenwood, N. N. & Earnshaw, A. *Chemistry of the Elements*. (Elsevier, 2012).
2. Alemany, M. & Martins, J. L. Density-functional study of nonmolecular phases of nitrogen: metastable phase at low pressure. *Phys. Rev. B* **68**, 024110, (2003).
3. Janoschek, R. Pentazole and other nitrogen rings. *Angewandte Chemie International Edition in English* **32**, 230–232, (1993).
4. Klapötke, T. M. *Chemistry of high-energy materials*. (Walter de Gruyter GmbH & Co KG, 2019).
5. Eremets, M. I., Hemley, R. J., Mao, H.-k. & Gregoryanz, E. Semiconducting non-molecular nitrogen up to 240 GPa and its low-pressure stability. *Nature* **411**, 170–174, (2001).
6. Eremets, M. I., Gavriluk, A. G., Trojan, I. A., Dzivenko, D. A. & Boehler, R. Single-bonded cubic form of nitrogen. *Nat. Mater.* **3**, 558–563, (2004).
7. Hirshberg, B., Gerber, R. B. & Krylov, A. I. Calculations predict a stable molecular crystal of N₈. *Nat. Chem.* **6**, 52, (2014).
8. Nguyen, M. T. Polynitrogen compounds 1. Structure and stability of N-4 and N-5 systems. *Coordin. Chem. Rev.* **244**, 93–113, (2003).
9. Cacace, F., De Petris, G. & Troiani, A. Experimental detection of tetranitrogen. *Science* **295**, 480–481, (2002).
10. Légaré, M.-A. *et al.* The reductive coupling of dinitrogen. *Science* **363**, 1329–1332, (2019).
11. Zhang, C., Sun, C., Hu, B., Yu, C. & Lu, M. Synthesis and characterization of the pentazolate anion cyclo-N₅ in (N₅)₆(H₃O)₃(NH₄)₄Cl. *Science* **355**, 374–376, (2017).
12. Xu, Y. *et al.* A series of energetic metal pentazolate hydrates. *Nature* **549**, 78–81, (2017).

13. Sun, C. *et al.* Synthesis of AgN 5 and its extended 3D energetic framework. *Nat. Commun.* **9**, 1–7, (2018).
14. Ritter, G., Haefelinger, G., Lueddecke, E. & Rau, H. Tetrazetidine: ab initio calculations and experimental approach. *J. Am. Chem. Soc.* **111**, 4627–4635, (1989).
15. Exner, K. & Prinzbach, H. Highly efficient photometathesis in a proximate, synperiplanar diazene-diazene oxide substrate: retention of optical purity, mechanistic implications. *Chem. Commun.*, 749–750, (1998).
16. Camp, D., Campitelli, M., Hanson, G. R. & Jenkins, I. D. Formation of an unusual four-membered nitrogen ring (tetrazetidine) radical cation. *J. Am. Chem. Soc.* **134**, 16188–16196, (2012).
17. Su, Y. *et al.* Two stable phosphorus-containing four-membered ring radical cations with inverse spin density distributions. *J. Am. Chem. Soc.* **136**, 6251–6254, (2014).
18. Popov, A. A., Yang, S. & Dunsch, L. Endohedral fullerenes. *Chem. Rev.* **113**, 5989–6113, (2013).
19. Weidinger, A., Waiblinger, M., Pietzak, B. & Murphy, T. A. Atomic nitrogen in C₆₀: N@C₆₀. *Appl. Phys. A* **66**, 287–292, (1998).
20. Aoyagi, S. *et al.* A layered ionic crystal of polar Li@C(60) superatoms. *Nat. Chem.* **2**, 678–683, (2010).
21. Komatsu, K., Murata, M. & Murata, Y. Encapsulation of molecular hydrogen in fullerene C₆₀ by organic synthesis. *Science* **307**, 238–240, (2005).
22. Morinaka, Y. *et al.* X-ray observation of a helium atom and placing a nitrogen atom inside He@C-60 and He@C-70. *Nat. Commun.* **4**, (2013).
23. Zhang, R. *et al.* Synthesis of a distinct water dimer inside fullerene C₇₀. *Nat. Chem.* **8**, 435–441, (2016).
24. Krätschmer, W., Lamb, L. D., Fostiropoulos, K. & Huffman, D. R. Solid C₆₀: a new form of carbon. *Nature* **347**, 27, (1990).
25. Zhang, X. *et al.* A diuranium carbide cluster stabilized inside a C₈₀ fullerene cage. *Nat. Commun.* **9**, 2753, (2018).
26. Yu, P. *et al.* Trapping an unprecedented Ti₃C₃ unit inside the icosahedral C₈₀ fullerene: a crystallographic survey. *Chem. Sci.* **10**, 10925–10930, (2019).
27. Iiduka, Y. *et al.* Structural determination of metallofullerene SC₃C₈₂ revisited: A surprising finding. *J. Am. Chem. Soc.* **127**, 12500–12501, (2005).
28. Fu, W. *et al.* Gd₂@C₇₉N: isolation, characterization, and monoadduct formation of a very stable heterofullerene with a magnetic spin state of S = 15/2. *J. Am. Chem. Soc.* **133**, 9741–9750, (2011).
29. Hu, Z. *et al.* Endohedral Metallofullerene as Molecular High Spin Qubit: Diverse Rabi Cycles in Gd₂@C₇₉N. *J. Am. Chem. Soc.* **140**, 1123–1130, (2018).
30. Velkos, G. *et al.* High Blocking Temperature of Magnetization and Giant Coercivity in the Azafullerene Tb₂@C₇₉N with a Single-Electron Terbium-Terbium Bond. *Angew. Chem. Int. Ed. Engl.* **58**, 5891–5896, (2019).

31. Wang, Y. *et al.* Dy₂@C₇₉N: a new member of dimetalloazafullerenes with strong single molecular magnetism. *Nanoscale* **12**, 11130–11135, (2020).
32. Zuo, T. M. *et al.* M₂@C₇₉N (M = Y, Tb): Isolation and characterization of stable endohedral metallofullerenes exhibiting M-M bonding interactions inside aza 80 fullerene cages. *J. Am. Chem. Soc.* **130**, 12992–12997, (2008).
33. Yang, S., Wei, T. & Jin, F. When metal clusters meet carbon cages: endohedral clusterfullerenes. *Chem. Soc. Rev.* **46**, 5005–5058, (2017).
34. Svitova, A., Braun, K., Popov, A. A. & Dunsch, L. A platform for specific delivery of lanthanide-scandium mixed-metal cluster fullerenes into target cells. *Chemistryopen* **1**, 207–210, (2012).
35. Shan, H., Yang, Y., James, A. J. & Sharp, P. R. Dinitrogen bridged gold clusters. *Science* **275**, 1460–1462, (1997).
36. Kim, Y., Gilje, J. W. & Seff, K. Synthesis and structures of two new hydrides of nitrogen, triazane (N₃H₅) and cyclotriazane (N₃H₃). Crystallographic and mass spectrometric analyses of vacuum-dehydrated partially decomposed fully silver (1+) ion-exchanged zeolite A treated with ammonia. *J. Am. Chem. Soc.* **99**, 7057–7059, (1977).
37. Zhao, S. *et al.* Stabilization of Giant Fullerenes C₂(41)-C₉₀, D₃(85)-C₉₂, C₁(132)-C₉₄, C₂(157)-C₉₆, and C₁(175)-C₉₈ by Encapsulation of a Large La₂C₂ Cluster: The Importance of Cluster-Cage Matching. *J. Am. Chem. Soc.* **139**, 4724–4728, (2017).
38. Hu, S. *et al.* Crystallographic characterization of Er₂C₂@C-2(43)-C-90, Er₂C₂@C-2(40)-C-90, Er₂C₂@C-2(44)-C-90, and Er₂C₂@C-1(21)-C-90: the role of cage-shape on cluster configuration. *Nanoscale* **11**, 17319–17326, (2019).
39. Shen, W. *et al.* Crystallographic characterization of Lu₂C₂n (2n = 76–90): cluster selection by cage size. *Chem. Sci.* **10**, 829–836, (2019).
40. Zuo, T. *et al.* M₂@C₇₉N (M = Y, Tb): Isolation and Characterization of Stable Endohedral Metallofullerenes Exhibiting M-M Bonding Interactions Inside Aza[80]Fullerene Cages. *J. Am. Chem. Soc.* **130**, 12992–12997, (2008).
41. Stevenson, S. *et al.* Preferential encapsulation and stability of La₃N cluster in 80 atom cages: Experimental synthesis and computational investigation of La₃N@ C₇₉N. *J. Am. Chem. Soc.* **131**, 17780–17782, (2009).
42. Zhang, Z., Wang, T., Xu, B. & Wang, C. Paramagnetic and theoretical study of Y(2)@C(8)(1)N: an endohedral azafullerene radical. *Dalton. Trans.* **43**, 12871–12875, (2014).
43. Nguyen, M. T. Polynitrogen compounds: 1. Structure and stability of N₄ and N₅ systems. *Coord Chem Rev* **244**, 93–113, (2003).
44. Zubarev, D. Y. & Boldyrev, A. I. Developing paradigms of chemical bonding: adaptive natural density partitioning. *Phys. Chem. Chem. Phys.* **10**, 5207–5217, (2008).
45. Iiduka, Y. *et al.* Experimental and theoretical studies of the scandium carbide endohedral metallofullerene Sc₂C₂@ C₈₂ and its carbene derivative. *Angew. Chem. Int. Ed.* **46**, 5562–5564, (2007).

46. Samoylova, N. A. *et al.* Confining the spin between two metal atoms within the carbon cage: redox-active metal-metal bonds in dimetallofullerenes and their stable cation radicals. *Nanoscale* **9**, 7977–7990, (2017).
47. Kurihara, H. *et al.* Sc-2@C-3v(8)-C-82 vs. Sc₂C₂@C-3v(8)-C-82: drastic effect of C-2 capture on the redox properties of scandium metallofullerenes. *Chem. Commun.* **48**, 1290–1292, (2012).
48. Liu, F. *et al.* Single molecule magnet with an unpaired electron trapped between two lanthanide ions inside a fullerene. *Nat. Commun.* **8**, 16098, (2017).
49. Evans, W. J. *et al.* Isolation of dysprosium and yttrium complexes of a three-electron reduction product in the activation of dinitrogen, the (N₂)(3⁻) radical. *J. Am. Chem. Soc.* **131**, 11195–11202, (2009).
50. Camp, D., Campitelli, M., Hanson, G. R. & Jenkins, I. D. Formation of an unusual four-membered nitrogen ring (tetrazetidine) radical cation. *J. Am. Chem. Soc.* **134**, 16188–16196, (2012).
51. Demir, S., Gonzalez, M. I., Darago, L. E., Evans, W. J. & Long, J. R. Giant coercivity and high magnetic blocking temperatures for N₂(3⁻) radical-bridged dilanthanide complexes upon ligand dissociation. *Nat. Commun.* **8**, 2144, (2017).
52. Rinehart, J. D., Fang, M., Evans, W. J. & Long, J. R. Strong exchange and magnetic blocking in N-2(3⁻)-radical-bridged lanthanide complexes. *Nat. Chem.* **3**, 538–542, (2011).
53. Velkos, G. *et al.* High blocking temperature of magnetization and giant coercivity in the azafullerene Tb₂@C₇₉N with a single-electron terbium-terbium bond. *Angew. Chem. Int. Ed. Engl.* **58**, 5891–5896, (2019).
54. Liu, F. *et al.* Air-stable redox-active nanomagnets with lanthanide spins radical-bridged by a metal-metal bond. *Nat. Commun.* **10**, 1–11, (2019).
55. Sheldrick, G. M. Crystal structure refinement with SHELXL. *Acta Crystallogr. C Struct. Chem.* **71**, 3–8, (2015).
56. Stoll, S. & Schweiger, A. EasySpin, a comprehensive software package for spectral simulation and analysis in EPR. *J. magn. reson.* **178**, 42–55, (2006).
57. Gaussian 09 v. Revision D.01 (Gaussian, Inc., Wallingford CT, 2009).
58. Lu, T. & Chen, F. Multiwfn: A multifunctional wavefunction analyzer. *J. Comput. Chem.* **33**, 580–592, (2012).

Figures

Figure 1

Crystallography. a, View showing the positions of the disordered Dy sites relative to the N4 unit in Dy-I. The major Dy sites (Dy1 and Dy2 with occupancies of 0.27 and 0.19) are labelled. Dy1A and Dy2A are generated by symmetric operation from the crystallographic mirror plane (light blue). C is grey and N is blue. b, ORTEP drawing of Dy-I together with Nill(OEP) moiety with 20% thermal ellipsoids. For clarity, only the major Dy sites (Dy1 and Dy2) are shown and the solvent molecules are omitted. c, Configuration of the endohedral Dy₂N₄ cluster considering the major Dy sites. Distances: N1-N2: 1.594(8), N2-N3: 1.656(13) Å, N3-N4: 1.594(8) Å, N4-N1: 1.593(9) Å, Dy1-N1: 1.527(6) Å, Dy1-N2: 1.718(7) Å, Dy1-N3: 2.714(6) Å, Dy1-N4: 2.564(5) Å, Dy2-N1: 2.828(6) Å, Dy2-N2: 2.131(8) Å, Dy2-N3: 1.681(7) Å, Dy2-N4: 2.519(6) Å.

Figure 2

Computational studies. a, Representation of the optimized structure of Dy-I. C is grey, N is blue and Dy is red. b, ELF-plot of Dy-I on the cyclo-N₄ plane, showing electronic accumulations between each nitrogen pair. c, Isosurfaces of SOMO and d, spin density distribution in Dy-I. e, Kohn–Sham MO energy levels (occupied—black, unoccupied—pink) of Dy-I and Y-I. Cluster-based MOs are highlighted in red, while the rest are cage-based MOs.

Figure 3

Bonding analysis. Depictions of the cluster-based AdNDP orbitals in Y-I. The fullerene cage is omitted for clarity. a, Four occupied N-N σ bonds; b, two occupied Y-N dative bonds; c, one occupied N-N π bonds and d, one half-occupied N-N π^* anti-bond with the contribution from Y(4d) (6c-1e). The isosurface values generated here are $\pm 0.04 \sqrt{(e/\text{\AA}^3)}$.

Figure 4

Spectroscopic and electrochemical characterizations. a, Positive-ion mode LDI-TOF mass spectrum of Dy-I with measured and calculated isotopic distributions. b, Vis-NIR spectra of Dy-I, Y-I and Dy₂C₂@C_{3v}(8)-C₈₂ dissolved in toluene. c, Experimental and simulated EPR spectra of Y-I in toluene solution at room temperature. Simulation parameters: $g_{\perp} = 1.9780$, $g_{\parallel} = 1.9775$, $A_{\perp}(14N) = 13.0$ MHz, $A_{\parallel}(14N) = 19.5$ MHz, $A_{\perp}(89Y)1 = 208$ MHz, $A_{\parallel}(89Y)1 = 213$ MHz, $A_{\perp}(89Y)2 = 237$ MHz, $A_{\parallel}(89Y)2 = 242$ MHz; * denotes a $g = 2$ impurity. d, Cyclic voltammogram of Dy-I in a 0.05 M tetrabutylammonium hexafluorophosphate (TBAPF₆)/o-DCB solution (scan rate: 100 mV/s). Each redox step of Dy-I is marked with a solid dot. The peak marked with an asterisk is from impurity. The insets indicate the variation of the formal charge of the cyclo-N₄ unit in different potential regimes.

Supplementary Files

This is a list of supplementary files associated with this preprint. Click to download.

- [1.cif](#)
- [checkcifDy2N4XC81N.pdf](#)
- [Dy2N4Sl.docx](#)
- [floatimage5.png](#)