



Au₁₉ Nanocluster Featuring a V-Shaped Alkynyl–Gold Motif

Xian-Kai Wan,[†] Qing Tang,[‡] Shang-Fu Yuan,[†] De-en Jiang,^{*,‡} and Quan-Ming Wang^{*,†}

[†]State Key Laboratory of Physical Chemistry of Solid Surfaces, Department of Chemistry, College of Chemistry and Chemical Engineering, Xiamen University, Xiamen, Fujian 361005, P. R. China

[‡]Department of Chemistry, University of California, Riverside, California 92521, United States

S Supporting Information

ABSTRACT: A novel Au₁₉ nanocluster with a composition of [Au₁₉(PhC≡C)₉(Hdppa)₃](SbF₆)₂ was synthesized (Hdppa = *N,N*-bis(diphenylphosphino)amine). Single crystal X-ray structural analysis reveals that the cluster comprises a centered icosahedral Au₁₃ core hugged by three V-shaped PhC≡C–Au–C≡C(Ph)–Au–C≡CPh motifs. Such motif is observed for the first time in an alkynyl-protected gold nanocluster. The Au₁₉ cluster shows two main optical-absorption bands at 1.25 and 2.25 eV, confirmed by time-dependent density functional theory. Orbital analysis indicates that PhC≡C– groups can actively participate in the frontier orbitals of the whole cluster. The new Au₁₉ cluster and the novel alkynyl–gold motif open the door to understanding the alkynyl–gold interface and discovering many potential members of this new class of gold clusters.

Ligand-protected gold nanoclusters have attracted great interest as promising materials for both fundamental research and applications in catalysis, biosensing, drug delivery, luminescence, molecular electronics, and surface patterning.^{1–5} Their precise compositions and well-defined sizes shed valuable light on understanding the structure–property relationships. Especially, great advances have been made in the structural determination of these nanoclusters, including thiolate-protected Au₂₀, Au₂₃, Au₂₄, Au₂₅, Au₂₈, Au₃₀, Au₃₆, Au₃₈, Au₁₀₂,^{6–15} and phosphine-protected Au₁₄, Au₂₀, Au₂₂, Au₃₉,^{16–20} as well as the mixed-ligand (both thiolate and phosphine) protected Au₂₄, Au₂₅.²¹

Beyond the conventional thiolate and phosphine ligands, one wonders if the ligand space can be further broadened to other types so that new cluster structures, compositions, and interfaces can be discovered. As such, alkynyl groups have emerged as a promising ligand for gold.²² Tsukuda et al. identified several atomically precise alkynyl gold nanoclusters and inferred from their Extended X-Ray Absorption Fine Structure data that the alkynyl groups are terminally bound at the bridge or hollow site.^{22c} Konishi et al. reported a gold nanocluster [Au₈(dppp)₄(C≡CR)₂]²⁺,²³ which is protected by diphosphine and alkynyl ligands, and found that the alkynyl group is terminally bound to one gold atom. Theoretically, Jiang et al. investigated the interfacial binding of PhC≡C– groups on the Au(111) surface and the Au₂₀ cluster and suggested formation of PhC≡C–Au–C≡CPh motif at the interface.²⁴ What these few recent studies found are probably just the tip of an iceberg. What more to be discovered is the

underlying diversity of alkynyl gold nanoclusters and especially their structures.

Herein, we report the synthesis, total structure determination, optical property, and electronic structure of a novel Au₁₉ nanocluster with PhC≡C– ligands: [Au₁₉(PhC≡C)₉(Hdppa)₃](SbF₆)₂ (**1**), where Hdppa is *N,N*-bis(diphenylphosphino)amine. This nanocluster is novel for three reasons: (a) it is the first structurally determined gold nanocluster containing 19 gold atoms; (b) it is the first alkynyl–gold nanocluster with eight free electrons, a magic number, according to superatom complex concept;²⁵ (c) it has RC≡C–Au–C≡C(R)–Au–C≡CR motifs at the interface (C≡C is often shortened as C₂ hereafter), similar to but also different from the RS–Au–S(R)–Au–SR staple motif in thiolate-protected gold nanoclusters.¹¹ The structure and interfacial bonding of this cluster suggests that there may be many analogues between alkynyl- and thiolate-protected gold nanoclusters. In other words, there may be many alkynyl gold nanoclusters remaining to be unearthed, given the large number of Au_n(SR)_m clusters already discovered.

To prepare the alkynyl-protected gold nanoclusters, we use the bidentate phosphine Hdppa as a second ligand to enhance the crystallization. Typically, a freshly prepared solution of NaBH₄ (0.95 mg in 1.0 mL of ethanol) was added dropwise to 4.0 mL dichloromethane suspension of 0.15 mmol PhC≡CAu and 0.025 mmol HdppaAu₂(SbF₆)₂ under vigorous stirring. The color changed from orange to pale brown and finally dark brown. The reaction continued for 18 h at room temperature in the dark. The mixture was then dried by evaporation to give a dark solid, which was dissolved in 2.2 mL CH₂Cl₂. This crude solution was centrifuged for 3 min at 10000 rpm, and the supernatant was subjected to the diffusion of mixed solvents (ether/*n*-hexane, v/v = 1). Brown-red crystals formed after 2 weeks in 20.3% yield (13.4 mg, based on Au).

The sample was first characterized by electrospray ionization time of flight mass spectrometry (ESI–TOF–MS) in positive mode (Figure 1). The spectrum is very clean, showing the dication [Au₁₉(PhC≡C)₉(Hdppa)₃]²⁺ at *m/z* = 2904.03. The observed isotopic pattern of the dication cluster is in perfect agreement with the simulation.³¹P NMR shows one singlet at 76.44 ppm, indicating that the phosphines are in equivalent environments (Figure S1). IR spectrum (Figure S2) shows the C≡C stretching band red-shifted to 2030 cm^{–1} relative to 2108

Received: December 3, 2014

Published: December 29, 2014



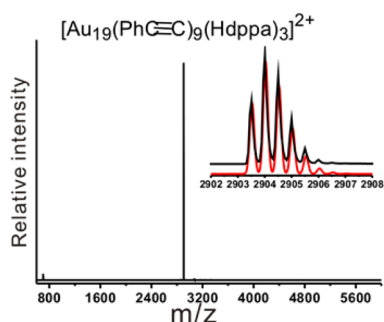


Figure 1. Mass spectrum of the Au_{19} cluster. Inset: The measured (black trace) and simulated (red trace) isotopic patterns of $[\text{Au}_{19}(\text{PhC}\equiv\text{C})_9(\text{Hdppa})_3]^{2+}$.

cm^{-1} of the phenylacetylene molecule, indicating that the $\text{C}\equiv\text{C}$ bond is weakened due to the binding of $\text{C}\equiv\text{C}$ to gold atoms.^{22c,26}

Single crystal structural analysis²⁷ revealed that the dicationic cluster $[\text{Au}_{19}(\text{PhC}\equiv\text{C})_9(\text{Hdppa})_3]^{2+}$ has C_3 symmetry (Figure 2a) and a centered icosahedral Au_{13} core surrounded by an exterior shell consisting of three diphosphines (Hdppa) and three V-shape $\text{PhC}_2\text{-Au-C}_2\text{Ph-Au-C}_2\text{Ph}$ “staple” motifs

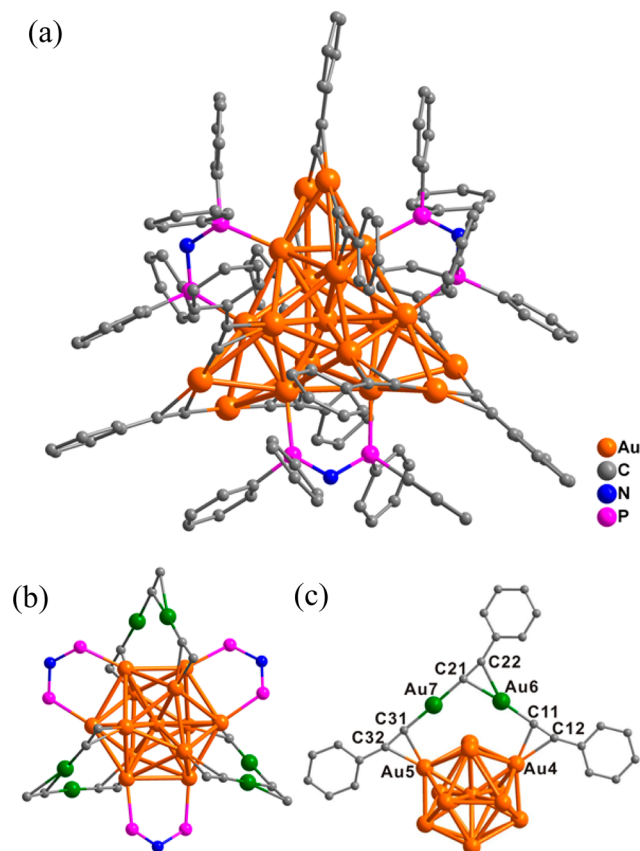


Figure 2. (a) Structure of the dicationic $[\text{Au}_{19}(\text{PhC}\equiv\text{C})_9(\text{Hdppa})_3]^{2+}$ cluster. (b) Three V-shape $\text{PhC}_2\text{-Au-C}_2\text{Ph-Au-C}_2\text{Ph}$ “staple” motifs with six surrounding gold atoms highlighted in green. Phenyl groups omitted for clarity. (c) The $\text{PhC}_2\text{-Au-C}_2\text{Ph-Au-C}_2\text{Ph}$ motif. Selected bond lengths in Å: Au4–C11, 2.225(15); Au4–C12, 2.337(15); Au5–C31, 2.181(13); Au5–C32, 2.271(16); Au6–C21, 2.207(14); Au6–C22, 2.229(14); Au6–C11, 1.991(14); Au7–C21, 1.992(16); Au7–C31, 1.954(14); C11–C12, 1.26(2); C21–C22, 1.25(2); C31–C32, 1.26(2).

(Figure 2b). On the surface of the icosahedron, $\text{Au}\cdots\text{Au}$ distances of the front and back triangles, 2.8192(8)–2.8487(7) Å, are significantly shorter than those of the others (average 2.965 Å). The Au–Au distances from the six exterior Au atoms to the Au_{13} icosahedron are 3.0950(7)–3.2594(7) Å. All the alkynyl ligands participate in the staple motifs, a novel feature very different from the terminally bonding mode in the much smaller $[\text{Au}_8(\text{dppp})_4(\text{C}\equiv\text{CR})_2]^{2+}$ cluster.²³ Interestingly, this Au_{19} cluster is closely related to the famous $\text{Au}_{25}(\text{SR})_{18}^-$.¹¹ They share the same Au_{13} kernel and both have eight free electrons; in **1**, three $\text{RC}_2\text{-Au-C}_2\text{R-Au-C}_2\text{R}$ motifs are connected to six Au vertices of the icosahedron, as the remaining six Au atoms are protected by phosphines (Figure 2b), while six RS-Au-SR-Au-SR staples cap the 12 surface Au atoms of the Au_{13} kernel in $\text{Au}_{25}(\text{SR})_{18}^-$. Another key point is that the $\text{RC}_2\text{-Au-C}_2\text{R-Au-C}_2\text{R}$ motif interacts with the surface Au atoms by π bonding with the $-\text{C}\equiv\text{C}-$ group; inside the motif, one Au atom also has such π bond (Au6 in Figure 2c), while the other (Au7 in Figure 2c) interacts with $\text{PhC}\equiv\text{C}-$ groups via two terminal C atoms through σ bonds.

The present work represents the first structural determination of a ligand-protected Au_{19} nanocluster. Previously, Jin et al. reported a thiolate protected Au_{19} cluster with a composition of $\text{Au}_{19}(\text{SCH}_2\text{CH}_2\text{Ph})_{13}$ based on mass spectrometry,²⁸ and Jiang predicted from density functional theory (DFT) that this cluster has a defective icosahedral Au_{11} core wrapped by two RS-Au-SR and three RS-Au-SR-Au-SR staple motifs.²⁹ But its experimental structure is still unknown.

To understand the electronic structure of the $[\text{Au}_{19}(\text{PhC}_2)_9(\text{Hdppa})_3]^{2+}$ cluster, we examined its optical absorption and frontier orbitals. Figure 3 shows the experimental absorption spectrum in comparison with simulation from time-dependent DFT. One can see that the main absorption peaks from the experiment such as α (1.25 eV) and β (2.25 eV) peaks are well reproduced in the simulated

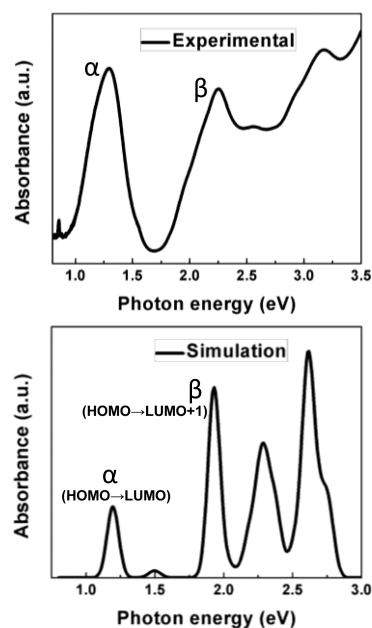


Figure 3. Experimental and simulated optical absorption spectra of the $[\text{Au}_{19}(\text{PhC}_2)_9(\text{Hdppa})_3]^{2+}$ cluster. For the experimental spectrum, a Jacobian factor is used to convert the nm-based to the eV-based absorbance. See Supporting Information for the experimental spectrum in nm and details about the simulation.

spectrum. We found that the α peak corresponds to the HOMO to LUMO transition, while the β peak represents the HOMO to LUMO + 1 transition. Figure 4 illustrates the

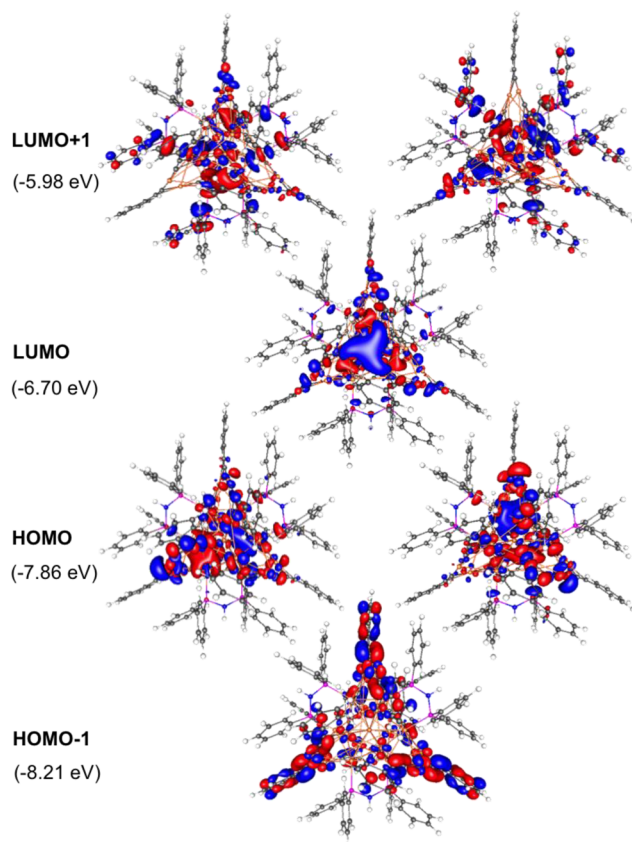


Figure 4. Frontier orbitals of the $[\text{Au}_{19}(\text{PhC}_2)_9(\text{Hdppa})_3]^{2+}$ cluster.

frontier orbitals of the cluster. We found that the electronic structure of the Au_{19} cluster has new features due to its geometry and the phenylethynyl ligands, as we elaborate below.

According to the superatom complex model,²⁵ the $[\text{Au}_{19}(\text{PhC}_2)_9(\text{Hdppa})_3]^{2+}$ cluster has eight free valence electrons, just like $\text{Au}_{25}(\text{SR})_{18}^-$, which normally occupy 1S and 1P orbitals as $(1\text{S})^2(1\text{P})^6$. Under the C_3 symmetry and the triangular shape of the Au_{19} cluster (Figure 1a), the empty 1D orbitals split into a nondegenerate 1Dz^2 (LUMO), doubly degenerate $1\text{Dxy}/x^2 - y^2$ (LUMO + 1), and doubly degenerate $1\text{Dxz}/yz$ (LUMO + 2); the triply degenerate 1P orbitals split into the doubly degenerate $1\text{Px}/y$ (HOMO) and the lower-lying 1Pz . One can see from Figure 4 that the HOMO orbitals show P character, while the LUMO and LUMO + 1 orbitals show D character. Interestingly, we found that the 1Pz orbital is close in energy to the π system of PhCC, leading to a rehybridized HOMO - 1 which spreads along all the PhCC groups (Figure 4). This indicates a distinct difference between RS- and PhCC- groups in that the latter can actively participate in the frontier orbitals of the whole cluster. To clearly demonstrate the participation of the PhCC- group in the frontier orbitals, we also examined the frontier orbitals of the Au_{19} cluster with PhCC replaced by HCC (Figure S3). In this case, one can clearly see that the HOMO - 1 orbital is of the 1Pz character; in other words, the HCC orbital level is deeper and not interacting with the superatomic orbitals.

The Au_{19} cluster is quite stable: ESI-TOF-MS confirmed that no decomposition was observed after its solution had been stored under ambient conditions in the absence of light for more than a month (Figure S4). The broad absorption bands cover the range 270–1200 nm (Figure S5) and the low optical gap makes Au_{19} a very good candidate for light-harvesting applications and photosensitive agent.

In summary, we have synthesized a novel Au_{19} cluster protected by phenylethynyl and phosphine groups and determined its crystal structure. The $\text{PhC}_2\text{-Au-C}_2\text{Ph-Au-C}_2\text{Ph}$ motif was experimentally observed for the first time in gold nanoclusters, which could shed light on the investigation of gold-alkynyl nanoclusters and gold-alkynyl interface. It suggests that various gold-alkynyl motifs similar to gold-thiolate cases could exist in gold-alkynyl systems. More importantly, this Au_{19} cluster resembles the status of $\text{Au}_{25}(\text{SR})_{18}^-$ in the $\text{Au}_n(\text{SR})_m$ universe; the success in its synthesis and structure determination opens the door to the discovery of many new members of this class of gold nanoclusters with alkynyl groups in the protective layer.

■ ASSOCIATED CONTENT

📄 Supporting Information

Synthesis, characterization, and computation details. This material is available free of charge via the Internet at <http://pubs.acs.org>.

■ AUTHOR INFORMATION

Corresponding Authors

qmwang@xmu.edu.cn
de-en.jiang@ucr.edu

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was supported by the 973 program (2014CB845603), the Natural Science Foundation of China (21125102, 21390390, 21473139) and the University of California, Riverside.

■ REFERENCES

- (1) Schmid, G. *Chem. Soc. Rev.* **2008**, *37*, 1909.
- (2) Yamazoe, S.; Koyasu, K.; Tsukuda, T. *Acc. Chem. Res.* **2013**, *47*, 816.
- (3) Li, G.; Jin, R. *Acc. Chem. Res.* **2013**, *46*, 1749.
- (4) Daniel, M.-C.; Astruc, D. *Chem. Rev.* **2003**, *104*, 293.
- (5) Parker, J. F.; Fields-Zinna, C. A.; Murray, R. W. *Acc. Chem. Res.* **2010**, *43*, 1289.
- (6) Jadzinsky, P. D.; Calero, G.; Ackerson, C. J.; Bushnell, D. A.; Kornberg, R. D. *Science* **2007**, *318*, 430.
- (7) Qian, H.; Eckenhoff, W. T.; Zhu, Y.; Pintauer, T.; Jin, R. *J. Am. Chem. Soc.* **2010**, *132*, 8280.
- (8) Crasto, D.; Malola, S.; Brososky, G.; Dass, A.; Häkkinen, H. *J. Am. Chem. Soc.* **2014**, *136*, 5000.
- (9) Zeng, C.; Qian, H.; Li, T.; Li, G.; Rosi, N. L.; Yoon, B.; Barnett, R. N.; Whetten, R. L.; Landman, U.; Jin, R. *Angew. Chem., Int. Ed.* **2012**, *51*, 13114.
- (10) Zeng, C.; Li, T.; Das, A.; Rosi, N. L.; Jin, R. *J. Am. Chem. Soc.* **2013**, *135*, 10011.
- (11) (a) Heaven, M. W.; Dass, A.; White, P. S.; Holt, K. M.; Murray, R. W. *J. Am. Chem. Soc.* **2008**, *130*, 3754. (b) Zhu, M.; Aikens, C. M.; Hollander, F. J.; Schatz, G. C.; Jin, R. *J. Am. Chem. Soc.* **2008**, *130*, 5883.

- (12) Das, A.; Li, T.; Nobusada, K.; Zeng, Q.; Rosi, N. L.; Jin, R. *J. Am. Chem. Soc.* **2012**, *134*, 20286.
- (13) Song, Y.; Wang, S.; Zhang, J.; Kang, X.; Chen, S.; Li, P.; Sheng, H.; Zhu, M. *J. Am. Chem. Soc.* **2014**, *136*, 2963.
- (14) Das, A.; Li, T.; Nobusada, K.; Zeng, C.; Rosi, N. L.; Jin, R. *J. Am. Chem. Soc.* **2013**, *135*, 18264.
- (15) Zeng, C.; Liu, C.; Chen, Y.; Rosi, N. L.; Jin, R. *J. Am. Chem. Soc.* **2014**, *136*, 11922.
- (16) Teo, B. K.; Shi, X.; Zhang, H. *J. Am. Chem. Soc.* **1992**, *114*, 2743.
- (17) Chen, J.; Zhang, Q.-F.; Bonaccorso, T. A.; Williard, P. G.; Wang, L.-S. *J. Am. Chem. Soc.* **2014**, *136*, 92.
- (18) Wan, X.-K.; Lin, Z.-W.; Wang, Q.-M. *J. Am. Chem. Soc.* **2012**, *134*, 14750.
- (19) Wan, X.-K.; Yuan, S.-F.; Lin, Z.-W.; Wang, Q.-M. *Angew. Chem., Int. Ed.* **2014**, *53*, 2923.
- (20) Gutrath, B. S.; Oppel, I. M.; Presly, O.; Beljakov, I.; Meded, V.; Wenzel, W.; Simon, U. *Angew. Chem., Int. Ed.* **2013**, *52*, 3529.
- (21) (a) Das, A.; Li, T.; Nobusada, K.; Zeng, Q.; Rosi, N. L.; Jin, R. *J. Am. Chem. Soc.* **2012**, *134*, 20286. (b) Shichibu, Y.; Negishi, Y.; Watanabe, T.; Chaki, N. K.; Kawaguchi, H.; Tsukuda, T. *J. Phys. Chem. C* **2007**, *111*, 7845.
- (22) (a) Maity, P.; Tsunoyama, H.; Yamauchi, M.; Xie, S.; Tsukuda, T. *J. Am. Chem. Soc.* **2011**, *133*, 20123. (b) Maity, P.; Wakabayashi, T.; Ichikuni, N.; Tsunoyama, H.; Xie, S.; Yamauchi, M.; Tsukuda, T. *Chem. Commun.* **2012**, *48*, 6085. (c) Maity, P.; Takano, S.; Yamazoe, S.; Wakabayashi, T.; Tsukuda, T. *J. Am. Chem. Soc.* **2013**, *135*, 9450.
- (23) Kobayashi, N.; Kamei, Y.; Shichibu, Y.; Konishi, K. *J. Am. Chem. Soc.* **2013**, *135*, 16078.
- (24) Tang, Q.; Jiang, D.-e. *J. Phys. Chem. C* **2014**, DOI: 10.1021/jp508883v.
- (25) Walter, M.; Akola, J.; Lopez-Acevedo, O.; Jadzinsky, P. D.; Calero, G.; Ackerson, C. J.; Whetten, R. L.; Gronbeck, H.; Hakkinen, H. *Proc. Natl. Acad. Sci. U.S.A.* **2008**, *105*, 9157.
- (26) Kang, X.; Zuckerman, N. B.; Konopelski, J. P.; Chen, S. *Angew. Chem., Int. Ed.* **2010**, *49*, 9496.
- (27) Crystal data for $1 \cdot 3\text{CH}_2\text{Cl}_2$, $\text{C}_{144}\text{H}_{108}\text{N}_3\text{F}_{12}\text{P}_6\text{Sb}_2\text{Au}_{19} \cdot 3\text{CH}_2\text{Cl}_2$ $a = 20.3230(3)$, $b = 20.3230(3)$, $c = 31.8618(9)\text{\AA}$, $\alpha = 90$, $\beta = 90$, $\gamma = 120^\circ$, $V = 11396.6(4)\text{\AA}^3$, space group $R\bar{3}$, $Z = 3$, $T = 173\text{ K}$, 13448 reflections measured, 7555 unique ($R_{\text{int}} = 0.0337$), final $R1 = 0.0335$, $wR2 = 0.0818$ for 7205 observed reflections [$I > 2\sigma(I)$].
- (28) Wu, Z.; MacDonald, M. A.; Chen, J.; Zhang, P.; Jin, R. *J. Am. Chem. Soc.* **2011**, *133*, 9670.
- (29) Jiang, D.-e. *Chem.—Eur. J.* **2011**, *17*, 12289.