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$[Bi_{12}Ni_7(CO)_4]^{4-}$: Aggregation of Intermetalloid Clusters by Their Thermal Deligation and Oxidation

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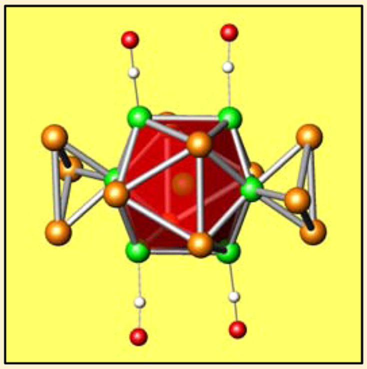
Supporting Information

ABSTRACT: Reported are the synthesis and structure of the anionic intermetalloid cluster $[Bi_{12}Ni_7(CO)_4]^{4-}$. It was synthesized from the known smaller clusters $Bi_3Ni_4(CO)_6{}^{3-}$, $Bi_3Ni_6(CO)_9{}^{3-}$, and $Ni@Bi_6Ni_6(CO)_8{}^{4-}$ by their aggregation as a result of thermal deligation and oxidation. The new cluster is structurally characterized by single-crystal X-ray diffraction in the compound $(K[crypt])_4[Bi_{12}Ni_7(CO)_4]$ (**1**), and its presence in solution is confirmed by electrospray mass spectrometry. It can be viewed as composed of a Ni-centered icosahedral core of $Bi_6Ni_6(CO)_4$ where two diametrically opposed Ni atoms are capped by Bi_3 triangles. However, its electron count is rationalized based on a structure made of fused tetrahedra.



INTRODUCTION

The chemistry of cluster Zintl ions nowadays is a rich field that has come a long way from the early work on isolation and characterization of the naked anionic clusters of groups 14 and 15.[1] In the past couple of decades it has included extensive functionalizations of these clusters with organic and organometallic fragments.[2,3] In addition, novel intermetalloid clusters containing both main-group and transition or lanthanide metals have been pushing the envelop toward more exotic architectures.[3,4] These species often resemble intermetallic structures and can be viewed as cutouts of them, thus the name intermetalloid.[5] Some exhibit partially ligated and well-packed heteroatomic cores, but then others are naked clusters made of two different elements or simple homoatomic cages with an endohedral heteroatom. There are two major classes of intermetalloids, namely, clusters containing at least one main-group element and those made of transition metals only. The structures and electron counts of many of them are nontrivial to rationalize as they often deviate from typical bonding schemes and exhibit mixtures of localized and delocalized bonding.[2−5]

The reported main-group-based intermetalloid clusters have been synthesized primarily by reactions of known Zintl ions, both homo- and heteroatomic, with various transition-metal or lanthanide organometallic compounds.[3] The role of the organometallic reagent is to partially oxidize the Zintl anions leading to their aggregation via oxidative bond formations while at the same time incorporating the transition metal or lanthanide into the cluster, e.g., $Pt_2Sn_{17}{}^{4-}$,[6] $Zn_9Bi_{11}{}^{5-}$,[7] $Ln@Bi_7Sn_7{}^{4-}$ (Ln = La, Ce),[8] etc. A second but less utilized synthetic approach has been the direct extraction of the intermetalloid species from more complex precursors upon dissolving them in appropriate solvents, e.g., $Ni@Sn_9{}^{4-}$ and $(Sn_6Ge_2Bi)_2{}^{4-}$.[9,10]

All known transition-metal intermetalloids, mostly reported by Dahl et al., include noble metals, e.g., $Pd_{157}Pt_8(CO)_{72}(PPh_3)_{20}$,[11] $Au_4Pd_{32}(CO)_{28}(PMe_3)_{14}$,[12] $Au_4Pd_{28}(CO)_{22}(PMe_3)_{16}$,[13] $[Pd_{13}Ni_{13}(CO)_{34}]^{4-}$,[14] $Au_2Pd_{41}(CO)_{27}(PEt_3)_{15}$,[15] $[Au_6Ni_{32}(CO)_{44}]^{6-}$,[16] etc. Unlike the main-group-based intermetalloids, these species are synthesized by thermal deligation of smaller clusters and/or simple coordination compounds in order to generate coordinatively unsaturated metal vertices which, in turn, cause aggregation of the smaller clusters/complexes into larger formations. A good example for such a complex deligation/aggregation reaction is as follows

$$\begin{aligned} &16Pd_{10}(CO)_{12}(PPh_3)_6 + 48Pt(CO)_2(PPh_3)_2 + \text{heat} \\ &\quad \rightarrow Pd_{157}Pt_8(CO)_{72}(PPh_3)_{20} + 120CO\uparrow \\ &\quad\quad + n(Pd/Pt)(PPh_3)_4 \end{aligned} \tag{1}$$

We have been interested in the main-group-based intermetalloid anions containing bismuth and various transition metals, more specifically nickel. All known Bi/Ni species have been synthesized by reactions of ethylenediamine solutions of the bismuth anions precursor K_5Bi_4 with the nickel complex $Ni(PPh_3)_2(CO)_2$.[17] We were interested in applying the noble-metal intermetalloids synthetic approach to these main-group-based species, namely, using thermal deligation of the existing clusters in order to aggregate them into larger formations.

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Herein, we report the first such large main-group-based aggregate $[Bi_{12}Ni_7(CO)_4]^{4-}$ (**1**) synthesized by this approach.

■ RESULTS AND DISCUSSION

Synthesis. We already reported that ethylenediamine solutions of the intermetallic compound K_5Bi_4 react with $Ni(PPh_3)_2(CO)_2$ to form a number of small intermetalloid clusters such as $Bi_3Ni_4(CO)_6{}^{3-}$, $Bi_3Ni_6(CO)_9{}^{3-}$, and Ni@$Bi_6Ni_6(CO)_8{}^{4-}$.[17] Of these, the first two anions exhibit bent bismuth trimers with an overall charge of 3−, i.e., each bismuth is formally Bi^-. The third cluster is more oxidized with an overall charge of 4− distributed over the chairlike cyclohexane formation of bismuth, making each bismuth atom with a formal charge of 0.66−. The existence of these different bismuth species stabilized by transition-metal fragments as well as the previously isolated double-bonded $Bi_2{}^{2-}$ dimers allude to the possibility that an even greater variety of chain and cyclic oligmers exist and/or can be generated by appropriate oxidation in appropriate solvents.[18] A more recent testament to that has been the isolation of the more oxidized bismuth oligomers $Bi_7{}^{3-}$ and $Bi_{11}{}^{3-}$ that were unknown for bismuth but known for the rest of the pnictogens.[19−21] The oxidation agent in these cases was the pyridine solvent itself which, in turn, is reduced to the 4,4′-bipyridinium anion and hydrogen gas.

We were interested in building larger intermetalloid clusters that could eventually approach nanometer dimensions. One approach is to aggregate the known smaller Bi/Ni/CO clusters $Bi_3Ni_4(CO)_6{}^{3-}$, $Bi_3Ni_6(CO)_9{}^{3-}$, and Ni@$Bi_6Ni_6(CO)_8{}^{4-}$ by applying oxidation and deligation. Both processes can be accomplished by simply elevating the temperature of the reaction mixture. Higher temperatures make the triphenylphosphine that is available from the initial Ni source of $Ni(PPh_3)_2(CO)_2$ a better oxidizing agent (faster).[22] At the same time, the elevated temperature removes some of the CO ligands in the smaller clusters exposing the corresponding Ni vertices for potential aggregation. Both processes are most likely accompanied by various fragmentations and reorganizations. For example, it may be possible for the $Bi_3{}^{3-}$ bent oligomers in the small clusters to get oxidized by PPh_3 to $Bi_3{}^-$ triangles as those found in **1** (see structure below). Similarly, some delegation of the Ni atoms in the small clusters may provide the internal, ligand-free Ni atoms observed in **1**. Thus, in **1** we find only four of the available seven Ni atoms ligated with CO, while the remaining three are internal for the aggregate. This is clearly the result of the thermal deligation and subsequent aggregation caused by the exposure of nickel atoms for interactions with other Ni/Bi species in the solution.

Structure. The easiest way to describe the structure of **1** (Figure 1) is as made of an icosahedral core with a central Ni atom, Ni@Bi_6Ni_6, which has two diametrically opposed Ni vertices (the icosahedron's 1,12 positions) capped by bismuth triangles (staggered with respect to each other). The same structural features are observed in the recently reported mixed-stoichiometry anions $[(Pd@Pd_2Pb_{10-2x}Bi_{2x})(Bi_{3-x}Pb_x)_2]^{4-}$ (**2**) in which the two Pd vertices of the core icosahedron (Pd@$Pd_2Pb_{10-2x}Bi_{2x}$) are capped by two external triangles of $(Bi_{3-x}Pb_x)$.[23] These capped Pd vertices, however, are at the 1,11 positions of the icosahedron instead of the axial 1,12 positions for the Ni atoms in **1**. Thus, while the two-capped vertices in **1** are linear with respect to the central Ni atom, they are bent with respect to the central Pd atom in **2**. Furthermore, while the central core in **2** has only three transition-metal atoms (one central and two capped Pd atoms), it contains seven such atoms in **1** (one central, two capped, and four ligated Ni atoms). The latter is rather more similar to the centered icosahedral cluster $[Ni@Bi_6Ni_6(CO)_8]^{4-}$ (**3**), which has the same numbers of transition-metal and main-group atoms.[17] Their positioning, however, is exactly the opposite in the two species. While in **3** the six Bi atoms form a chairlike hexane formation with two staggered Ni triangles on both sides, it is the nickel atoms forming the hexagon in **1**, which has two staggered Bi triangles on its sides.

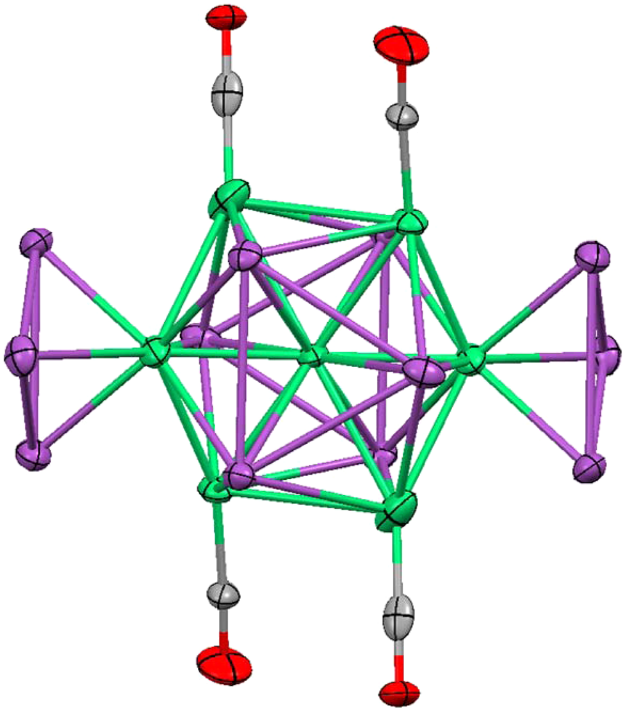

Figure 1. Structure of $[Bi_{12}Ni_7(CO)_4]^{4-}$ (**1**) shown as a Ni-centered icosahedral core being capped by two Bi_3 triangles (Bi, purple; Ni, green; C, gray; O, red).

The most noticeable and important difference between the icosahedral cores of **1** and **3**, however, is in the interatomic distances within the icosahedra, which ultimately leads to a completely different view of the structure of **1**. The latter exhibits noticeably longer and dissimilar distances that suggest significant deviation from a regular icosahedron. The ranges for the Bi−Bi and Ni−Ni distances in **1** are very wide, 3.2273(11)−3.3427(14) and 2.575(3)−3.006(3) Å, respectively, while they are much narrower in **3**, 3.0158(6)−3.0349(5) and 2.540(1)−2.570(1) Å, respectively. The same is true for the distances from the central atom to the peripheral Bi and Ni atoms in **1**, 2.7628(7)−2.8543(8) and 2.408(2)−2.695(2) Å, respectively, compared to the much narrower ranges in **3**, 2.7681(4)−2.7875(4) and 2.525(1)−2.531(1) Å, respectively. A closer look at the positions of the unreasonably long distances combined with the electronic structure of **1** (see below) revealed that it should not be viewed as a capped icosahedron. It is rather made of tetrahedra that are fused via vertices, edges, and faces as shown schematically in Figure 2 (all shared parts shown in orange). Thus, the core is now made of two sets of three Ni_3Bi tetrahedra related by an inversion center. Each set has a pair of tetrahedra fused via a Ni_3 face forming a trigonal bipyramid Ni_3Bi_2. The latter is then edge fused with the third tetrahedron in the set via an equatorial Ni−Ni edge. One of the Ni atoms of that edge is then shared

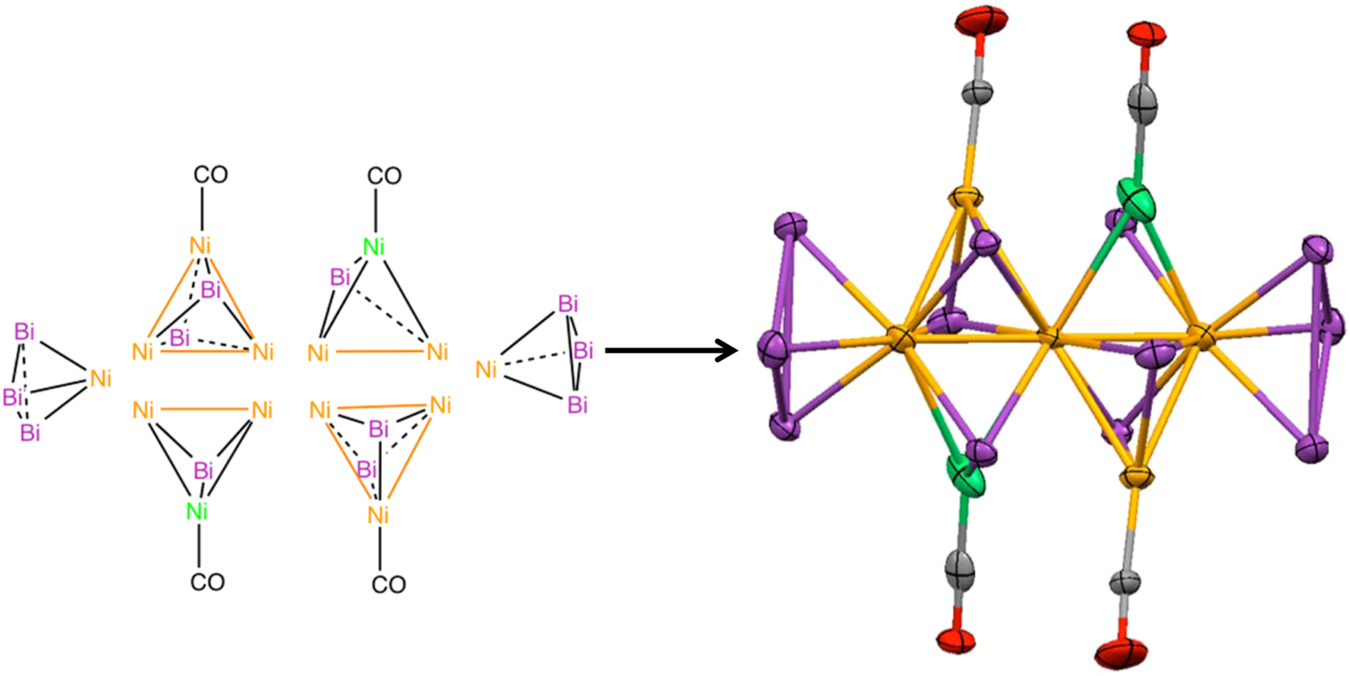

Figure 2. Structure of **1** (right) shown as made of tetrahedra that share nickel vertices, edges, and/or faces (left; shared fragments shown in orange).

between the two sets, that is, the central nickel atom of the whole aggregate. The other Ni atoms of the shared edges in the two sets are shared with the outside Bi_3Ni tetrahedra. It should be pointed out that shapes made of fused and packed tetrahedra are quite common for transition-metal carbonyl clusters, i.e., $Os_7(CO)_{21}$,[24] $Os_8(CO)_{22}$,[25] $Rh_{14}(CO)_{26}{}^{2-}$.[26] They tend to form structures that resemble very much closed-packed structures, i.e., $Ni_{38}Pt_6(CO)_{48}H_{6-n}{}^{n-}$,[27] $Pt_{38}(CO)_{44}{}^{2-}$,[28] and this is definitely true for **1**.

Electronic Structure. The electronic structure of **1** puzzled us for quite some time, until it was realized that the aggregate is actually made of fused tetrahedra. As already discussed, its central core deviates significantly from an icosahedral shape according to the interatomic distances. DFT calculations of the whole aggregate verified the available electron count and the charge of 4− with a fairly sizable HOMO−LUMO gap of 1.67 eV. However, it was problematic to rationalize that electron count and charge based on the structure of **1**. Initially, we looked at the aggregate as a 16-vertex single-cage arachno species. DFT calculations were carried out on the non-endohedral cage, i.e., the cage without the three internal Ni atoms. The HOMO−LUMO gap of 1.01 eV indicated that the structure could be potentially viewed as such, but there are no missing two vertices in the cage as it should be for arachno clusters. The model used for rationalization of the electron count of **2** (assuming a fixed stoichiometry of $[Pd@Pd_2Pb_{10}Bi_6]^{4-}$) did not work either. The latter exhibits 70 valence electrons, i.e., 10 × 4 (Pb) + 2 × 14 (2 $PdBi_3{}^-$) + 2 (additional charge), while those electrons in **1** are only 68, i.e., 6 × 5 (Bi core) + 2 × 14 (2 $NiBi_3{}^-$) + 4 × 2 (CO ligands) + 2 (additional charge) = 68.

All this indicated that the aggregate should not be viewed as a main-group-based cluster, i.e., as either a single-cage or a capped single-cage cluster, but rather as originating from transition-metal cluster species that typically exhibit fused small clusters, most often tetrahedra. The rules for electron counting in such cases are to add the valence electrons from the small units and subtract the electrons needed for bonding within the shared fragments, i.e., vertices, edges, or faces. Since we have both main-group and transition-metal elements in **1**, however, we have to "translate" the electron count either in all main-group or all transition-metal "language". The former regards Ni atoms and Ni(CO) fragments as providing zero and two valence electrons, respectively. Similarly, following the octet rule, a shared vertex, a shared edge, and a shared face need 1 × 8 = 8, 2 × 7 = 14, and 3 × 6 = 18 electrons for bonding, respectively, assuming normal 2-center−2-electron bonds. With this in hand we can count the number of required electrons for bonding as 8 × 20 (all 8 tetrahedra) − 3 × 8 (3 shared Ni vertices) − 2 × 14 (2 shared Ni−Ni edges) − 2 × 18 (2 shared Ni_3 faces) = 72. The number of available valence electrons is exactly the same, i.e., 12 ×5 (Bi) + 4 × 2 (Ni(CO)) + 4 (charge) = 72. The corresponding rationalization in transition-metal language looks like the following. To begin with, a Ni atom and a Ni(CO) fragment provide 10 and 12 valence electrons, respectively, while a Bi atom donates 5 + 10 = 15 "transition-metal" electrons. A shared vertex, an edge, and a face need 1 × 18 = 18, 2 × 17 = 34, and 3 × 16 = 48 electrons for bonding, respectively. Thus, the number of required valence electrons for bonding is 8 × 60 (8 tetrahedra) − 3 × 18 (shared Ni vertices) − 2 × 34 (shared Ni−Ni edges) − 2 × 48 (shared Ni_3 faces) = 262. The number of available electrons, 12 × 15 (Bi) + 3 × 10 (Ni) + 4 × 12 (Ni(CO)) + 4 (charge) = 262, is also the same.

Solution Studies. The presence of the new anion **1** in solution was confirmed by negative ion electrospray mass-spectrometry (ES-MS) of freshly dissolved crystalline samples in DMF. The spectrum (in the Supporting Information) showed three peaks corresponding to the title anion itself at m/z = 3029, the anion with one cryptated potassium cation $(K[crypt])Bi_{12}Ni_7(CO)_4$ at m/z = 3445, and the same but with two cryptated cations $(K[crypt])_2Bi_{12}Ni_7(CO)_4$ at m/z = 3860, all as singly charged species, which is typical for Zintl ions. It should be noted that the anion decomposes readily during the

ES-MS measurements, often clogging the spray capillary and making its detection difficult.

In conclusion, we have shown that analogous to the known noble-metal intermetalloid large aggregates, the main-group/transition-metal Bi/Ni/CO intermetalloids can similarly grow by thermal deligation and partial oxidation to form larger species. While the charge per Bi atom in the small clusters is between 0.66− and 1−, it is only 0.33− in **1**. Clearly, the available PPh_3 from the Ni precursor of $Ni(PPh_3)_2(CO)_2$ plays the role of the oxidizing agent in the reaction at elevated temperature, while the latter is also repsonsible for the deligation.

EXPERIMENTAL SECTION

Materials. All reactions and materials were handled under inert atmosphere or vacuum using standard Schlenk-line or glovebox techniques. K_5Bi_4 was synthesized from the elements (K, Sigma-Aldrich 99.5%; Bi, Alfa Aesar, 99.998%) at high temperature as previous reported.[29] 2.2.2-crypt (4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo [8.8.8]hexacosane, Sigma-Aldrich, 98%), *N*,*N*-dimethylformamide (Anhydrous, EMD Millipore 99.8%), and bis(triphenylphosphine)nickel dicarbonyl (Strem, 98%) were used as received. Ethylenediamine was distilled over sodium metal and stored in a gastight ampule under nitrogen. Toluene (Alfa-Aesar, 99.8+%) was dried by passing over a copper-based catalyst and 4 Å molecular sieves and then stored in a gastight ampule under nitrogen.

Synthesis of $(K[crypt])_4Ni_3@Bi_{12}Ni_4(CO)_4$. K_5Bi_4 (100 mg, 0.096 mmol) and 2.2.2-crypt (181 mg, 0.48 mmol) were weighed out into a test tube and dissolved in 2 mL of ethylenediamine, producing a blue-green solution. This solution was stirred for 10 min, after which $Ni(PPh_3)_2(CO)_2$ (62 mg, 0.097 mmol) was added directly and allowed to stir for 30 min. The blue-green solution was then heated for 6 h at 60 °C and changed color to brown-red. This solution was centrifuged, filtered, and then layered with toluene. Black bars (ca. 40% by crystals) formed after 1 week along with plates of the known phases $(K[crypt])_2Bi_4$ and $(K[crypt])_3Bi_3Ni_4(CO)_6$. The latter two phases were confirmed by single-crystal X-ray diffraction. Analogous yields were achieved by heating for 1 day at 45 °C or 12 h at 60 °C. All heatings lead to some decomposition.

Structure Determination. Single-crystal X-ray diffraction data were obtained on a Bruker APEX-II diffractometer equipped with a curved graphite monochromator and a CCD area detector using Mo $K\alpha$ radiation at 120 K. The crystal was mounted on a Mitegen micromount loop after selection from Paratone-N oil and positioned under a nitrogen cold stream. The structure was solved using SHELXT and refined on F^2 against all reflections using SHELXL2012.[30] Crystal data: monoclinic $P2_1/na$ = 15.7319(17) Å, b = 25.995(3) Å, c = 16.6477(19) Å, β = 118.0610(18)°, V = 6007.7(11) Å^3, Z = 2, R1/wR2 = 0.0632/0.1416 for the observed data, and R1/wR2 = 0.1135/0.1703 for all data. The anion was refined as disordered over two positions with occupancies of 83% and 17%, but only the metrics of the main component are discussed (S4 in Supporting Information for both refined positions).

Mass Spectrometry. ES-MS spectra were collected on a Micromass Quattro-LC triple-quadrupole mass spectrometer (125 °C source temperature, 150 °C desolvation temperature, 2.5 kV capillary voltage, and 15 V cone voltage.) Freshly prepared solutions of **1** dissolved in DMF were introduced using a Harvard syringe pump at 10 μL/min via direct infusion.

Electronic Structure Calculations. DFT calculations were conducted on **1** in order to rationalize its stability. Single-point energy calculations were carried out using Becke three-parameter density functional with the Lee−Yang−Parr correlation (B3LYP) with the LanL2DZ basis set. The calculations were performed using the Gaussian 09 package.[31]

ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorgchem.5b01101.

Electronic structure calculations, figures of the positional disorder, and ES-MS spectra (PDF)
X-ray crystallographic file in CIF format (CIF)

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Notes

The authors declare no competing financial interest.

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