Co$_{13}$O$_8$—Metalloxocubes: A New Class of Perovskite-like Neutral Clusters with Cubic Aromaticity

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ABSTRACT

Exploring stable clusters to understand structural evolution from atoms to macroscopic matter and to construct new materials is interesting yet challenging in chemistry. Utilizing our newly developed deep-ultraviolet laser ionization mass spectrometry technique, here we observe the reactions of neutral cobalt clusters with oxygen and find a very stable cluster species of Co$_{13}$O$_8$ that dominates the mass distribution in the presence of a large flow rate of oxygen gas. The results of global-minimum structural search reveal a unique cubic structure and distinctive stability of the neutral Co$_{13}$O$_8$ cluster which forms a new class of metal oxides that we named as "metalloxocubes". Thermodynamics and kinetics calculations illustrate the structural evolution from icosahedral Co$_{13}$ to the metalloxocube Co$_{13}$O$_8$ with decreased energy, enhanced stability and aromaticity. This class of neutral oxygen-passivated metal clusters may be an ideal candidate for genetic materials because of the cubic nature of the building blocks and the stability due to cubic aromaticity.

Keywords: Metalloxocube, Oxygen-passivated metal cluster, Cubic aromaticity, Cluster materials, Magnetic property.

INTRODUCTION

Building materials with well-defined components and stable structures is one of the foremost challenges in chemistry and cluster science. Extensive efforts have been made to explore new clusters with highly symmetrical regular structures, and occasional success has been achieved, such as the discovery of fullerene C$_{60}$[1], Au$_{13}$[2], etc[3, 4]. In particular, a few "magic" metal clusters possessing special stability, such as Al$_{13}$[5], have been found to be inert towards oxygen reactions due to the coincident closure of both electronic and geometric shell effects[6-8], embodying the near free electron gas (NFEG) theory of metals and epitomizing the jellium model of clusters within a symmetric potential function[9]. In view of this, the reactivity of metal clusters towards oxygen is often studied to explore the stability of these materials in the gas phase[10]. However, not all clusters are subject to this fundamental constraint. In some cases, cluster stability can be associated with aromaticity or superatom property[8, 11, 12], a large HOMO-LUMO energy gap (the Highest Occupied Molecular Orbital to the Lowest Unoccupied Molecular Orbital), and a large spin excitation energy[13]. In particular, the metal cluster stability can be reinforced by ligand protection. In recent years, various ligand-protected metal clusters have been synthesized via wet chemistry[14-18], where diverse thiols are employed as stabilizers and ligands, allowing for electron transfer and hence balanced charge distribution, occasionally exhibiting superatom characteristics of the core[11, 19].

For gas-phase naked metal clusters, especially those of main group elements, a few previous studies have illustrated that cluster stability can be altered by doping hydrogen or halogen ligands, which may induce formation of active sites on the cluster surface or passivate the metal cluster[20, 21]. There are on-going efforts devoted to exploring stable clusters for new materials, and to understanding atomically precise properties of metals. For example, Ervin et al.[22] studied the reactivity of small cobalt cluster anions Co$_n^-$ (n=2-8) with O$_2$, and noted rapid rate coefficients allowing fragmentation of the clusters (with a removal of Co$_{2^-}$) independent of the cluster size. Bernstein et al.[23] studied 118-nm laser ionization of neutral cobalt oxides Co$_{2n}$O$_m$ (n = 2-11) formed by laser ablation in plasma atmosphere, and have identified a series of Co$_{2n}$O$_m$ clusters showing size-dependent mass abundances. Gutsev et al.[24] performed an systematic investigation on small (FeO)$_n$, (CoO)$_n$, and (NiO)$_n$ clusters, where the 3d-metal oxides preferred oxygen bridge linked Co$_{2n}$ sites. Riley et al.[25] studied the reactions of cobalt clusters with water and ammonia, and found addition reactions to be dominant channels. Besides, Andersson et al.[26] studied the reactivities of neutral Fe, Co, and Cu clusters at single-collision conditions and determined their reaction probability in a single collision. Among these studies, few-collision conditions are convenient to study size-selective cluster reactivity, and sufficient collision conditions are necessarily important to probe stable species in the gas phase. However, the reactivity and reaction-determined stability of preformed cobalt clusters and oxides, especially neutrals, have not been fully unveiled so far.

Recently, we have developed a highly sensitive mass spectrometer combined with a homemade ps-pulsed 177.3-nm (7 eV single-photon energy) deep-ultraviolet laser that has unique advantages of low fragmentation and high ionization efficiency, enabling detailed studies of neutral metal clusters that had been largely unexplored previously. Taking advantages of our optimized cluster source, flow tube reactor and the 177.3 nm laser (Scheme 1), here we are able to prepare and observe well-resolved Co$_n$ (n≤30) clusters and provide insights into their reactivities. Interestingly, a very stable cluster species Co$_{13}$O$_8$ emerges in the mass spectra of...
neutral cobalt clusters reacting with oxygen, and shows dominant mass abundance in the presence of sufficient oxygen. Using first-principles theoretical calculations based on genetic algorithm and basin-hopping strategies, we find a cubic structure and distinctive stability of this neutral cluster Co$_{13}$O$_8$ and show that it possesses unique cubic aromaticity. This new class of metal oxides with a cubic structure and special aromatic stability is named as “metalloxocubes”. Such neutral oxygen-passivated metal clusters with high stability and cubic aromaticity help to expand the chemistry of ligand-protected metal clusters [27], and provide an ideal candidate for genetic materials[19] with a perovskite-like structure.

Results and Discussion

We prepared well-resolved neutral Co$_n$ clusters (n=2-30) via a homemade laser evaporation (LaVa) source, with a typical distribution shown in Fig. 1A. In general, the preparation of pure neutral metal clusters with more than 10 metal atoms is challenging in view of the much lower bond energy for metal-metal bonds than for the metal-nonmetal bonds. Here, the ionization energies of all the Co$_n$ clusters (n=2-30) are slightly smaller than 7 eV (Scheme 1); thus, the 177.3 nm laser happens to be a perfect ionization condition for such neutral Co$_n$ clusters. Single-photon ionization is available for high-efficiency ionization with absence of photo-induced fragmentation. Fig. 1B presents a typical mass spectrum of the neutral Co$_n$ clusters upon reacting with oxygen (for details see Supplementary Fig. 2).

Among the observed Co$_n$O$_m$ clusters and observed their reactions with oxygen; as results, enhanced stabilities of such a class of M$_{13}$O$_{20}$ (M = Fe, Co, Ni) clusters were repeatedly observed (for details see Supplementary Figs 6-8). While this observation is consistent with a few

Scheme 1. Instrumentation. A A sketch of instrument showing the sampling, reaction and DUV-LIMS strategy. B Ionization energies (IEs) of the neutral Co$_n$ (n=1-30) clusters, which are less than 7 eV (except Co atom) suggesting unique advantages of the ps-pulsed 177.3-nm deep-ultraviolet laser available for single photon ionization of these clusters. The values are from refs.[28-30]
previously identified stable species via gas-phase collisional reactions, such as $\text{Al}_{13}^-$ [5, 31], $\text{Al}_{13}^+$ [5], $\text{Al}_{13}^2-$ [32], and $\text{Ag}_{13}^-$ [13], it is a puzzle why such a oxide cluster ($\text{Co}_{13}\text{O}_8$) with significantly low oxidation state can be stable.

Figure 1. Mass spectrometry observation. A Representative size distribution of the naked $\text{Co}_n$ clusters. B/C The mass spectra after reaction of the $\text{Co}_n$ clusters with different amounts of $20\% \text{O}_2/\text{He}$ introduced into the flow tube (200 µs and 250 µs) and with varying pulse widths controlled by the pulse valve (more details in Supplementary materials). The $\text{Co}_n$ and $\text{Co}_n\text{O}_m$ clusters are ionized by a ps-pulsed deep-ultraviolet 177.3 nm laser.

The stability and reactivity of metal clusters are often associated with the nature of both the metal itself and the correlative oxide products, and magic metal clusters could be conclusively determined by $\text{O}_2$ etching reactions [33, 34]. Here, the DFT-calculated binding energies and HOMO-LUMO gaps of $\text{Co}_n$ cluster do not find $\text{Co}_{13}$ as a magic cluster (Supplementary Fig. 12). According to the chemical valence of cobalt, the $\text{Co}_n$ clusters may follow an etching reaction toward the formation of typical bivalent and trivalent cobalt oxide molecules,

$$\text{Co}_n + \text{O}_2 \rightarrow 2\text{CoO} + \text{Co}_{n-2}; \quad \text{Co}_n + 3 \text{O}_2 \rightarrow 2\text{Co}_2\text{O}_3 + \text{Co}_{n-4}$$

On the other hand, the $\text{Co}_n$ clusters and their oxides $\text{Co}_n\text{O}_m$ could undergo successive reactions with oxygen to generate stable species such as $\text{Co}_{13}\text{O}_8$. Based on these reaction channels, it is reasonable to yield distinctive $\text{Co}_{13}\text{O}_8$ clusters; however, it is unclear why $\text{Co}_{13}\text{O}_8$ is “magic” and what kind of structure it is.

Figure 2. Ab-initio molecular dynamics (AIMD) simulations. AIMD simulations of $\text{Co}_{13}\text{O}_8$ at 300K, 600K, 900K and 1200K for 3500 fs, with the average oxygen-oxygen distance on the eight edges indicated in Å.
To determine the structure of Co$_{13}$O$_8$, we have conducted first-principles calculations based on a genetic algorithm strategy. The global lowest energy structures of all the Co$_n$ (3≤n≤16) and Co$_{13}$O$_m$ (m=2, 4, 6, 8) clusters are provided in Supplementary Fig. 10. While bare Co$_{13}$ could have an icosahedral structure [35, 36], it is interesting to find that Co$_{13}$O$_8$ exhibits a body-centered cubic structure (a large HOMO-LUMO gap of 2.14 eV) with 12 cobalt atoms surrounding the inner core and 8 oxygen atoms coherently anchoring the eight triangular facets of the Co@Co$_{12}$. Such a cubic structure is consistent with the previous predicted structures of Fe$_{13}$O$_8$ [37, 38]. It is usual that such a class of M$_{13}$O$_8$ clusters can survive sufficient oxygen etching reactions. In general, sufficient reactions in high-pressure gas collision cells tend to screen out stable clusters of highly degenerate energy states and spherically symmetric structures, such as the previous findings of Al$_{13}$I$_{2n}$ [6], where the doping of iodine which is stretched out of an Al$_{13}$ icosahedron helps to balance the surface charge enabling enhanced stability. Also, we did independent basin-hopping search for Co$_{13}$O$_8$ structure using TGMin code [39], and reproduced the pseudo-O$_h$ global minimum of Co$_{13}$O$_8$. Further, we conducted ab-initio molecular dynamics (AIMD) simulations to identify their relative stability. AIMD simulations indicate that Co$_{13}$O$_8$ has outstanding thermal stability, with the cubic structure undissociated even up to 1200K, as shown in Fig. 2.

**Figure 3.** Chemical reaction dynamics. A The reaction coordinate for “O$_2$ + Co$_{13}$ → Co$_{13}$O$_2$” via an “end-on” coordination orientation, showing readily O-O bond dissociation on Co$_{13}$. The black versus red lines correspond to spin crossing. B The dynamic optimization processes for “O$_2$ + Co$_{13}$” via “side-on” and “face-on” attack orientations, showing spontaneous O-O bond dissociation of Co$_{13}$O$_2$ towards the energy minimum. C Thermodynamic energy changes from Co$_{13}$O$_2$ to Co$_{13}$O$_8$ ($\Delta E = E(\text{Co}_{13}\text{O}_{2n+2}) - E(\text{Co}_{13}\text{O}_{2n}) - E(\text{O}_2)$).

Further, we performed DFT calculations to depict chemical reaction dynamics so as to understand how the stable Co$_{13}$O$_8$ cluster was formed (Fig. 3A/B), where the reaction channels for “O$_2$ + Co$_{13}$” via an “end-on”, “side-on” and “face-on” orientation are provided respectively. Note that, the O-O bond lengths increase significantly when an O$_2$ molecule chemisorbed on the cluster surface (Supplementary Fig. 15). The elongated O-O bonds of adsorptive oxygen, followed by the formation of epoxy oxygen, strengthen the subsequent reactivity of O-O bond dissociation. The following oxygen addition reactions on the Co$_{13}$O$_n$ (n = 2, 4, 6) are thermodynamically favorable (Fig. 3C), with O-O bonds elongated to different degrees. We also evaluated the stability of Co$_{13}$O$_8$ by checking the likely decomposition in the presence of excessive oxygen. However, the additional oxygen molecules toward the Co$_{13}$O$_8$ cluster just absorb on the surface but do not break its cubic structure; even at 900 K, Co$_{13}$O$_8$ survives the attack of additional O$_2$ molecules (Supplementary Table 3). It is inferred that four oxygen molecules fully passivate a Co$_{13}$ cluster with the 8 oxygen atoms anchoring eight triangular facets towards the cubic structure.
Further, we calculated the nucleus-independent chemical shifts (NICS) [40-43], which is often used as a criterion to evaluate the aromaticity. The NICS values were computed at a few points along the central axis of a Co$_4$O$_4$ plane of the cubic Co$_{13}$O$_8$. As shown in Fig. 4A, the negative NICS(0) and NICS(1) values (corresponding to the Co$_4$O$_4$ plane center and 1.0 Å above the plane surface) are up to -54.0 and -22.0 ppm respectively, indicating this cluster is aromatic (larger than that of benzene, see Supplementary Table 6). Meanwhile, we have also conducted electron localization function (ELF) analysis [44], which illustrates the bonding and nonbonding areas by measuring the local electron-pair density. As shown in the top-view plane (Fig. 4B), the charge-density distribution value in the central area of square with concave sides is approximately 0.27 e/Å$^3$, pertaining to relatively weak metallic bond interactions between the Co atoms. In addition to covalent interactions, there is electron transfer between Co and O to form ionic bonds. Note that, the electron cloud of oxygen shows obvious polarization towards the centre of each plane, indicative of combined electrostatic interactions pertaining to oxygen passivation of the Co$_{13}$ cluster.

Furthermore, we estimated the magnetically induced current density using gauge-including atomic orbitals (GIMIC) [45, 46] of the Co$_{13}$O$_8$ cluster, as displayed in Fig. 4C (more details in supplementary materials). As results, the positive contribution of the induced current is found to be up to 5.83 nA/T, while the negative contribution is only -0.69 nA/T (that is, an integrate net current of 5.14 nA/T with an external magnetic field perpendicular to the Co$_4$O$_4$ plane), suggesting remarkable aromaticity on each Co$_4$O$_4$ plane of the Co$_{13}$O$_8$ cluster. Figs 4D, 4E and 4F depict a few typical orbitals contributing to the delocalization (more details in supplementary materials). The multi-center delocalization of electrons accounts for its aromaticity, which, in turn, promotes cluster stability within Wade-Mingos rules analogous to polyhedral boranes, boron clusters, and all-metal clusters [43, 47].
Having determined the stability, dynamics, and aromaticity of the \( \text{Co}_{13}\text{O}_8 \) cluster, what is the nature of the chemical bonding and aromatic property? In order to elucidate the physical origin of the special stability of this cluster, we performed electronic structure analysis on the pseudo-cubic cluster, which can be viewed as \( \text{Co}_8\text{Co}_{12}\text{O}_8 \) for the sake of bonding analysis. Fig. 5 depicts the Kohn-Sham energy levels from interactions among \( \text{Co}_{12} \), \( \text{O}_8 \) and the central \( \text{Co} \) atom (labeled as \( \text{Co}_c \)). The \( 3d \)-orbitals span a narrow 3d-band with 65 orbitals because of the relatively small orbital overlap between the neighboring \( \text{Co} \) atoms connected with a \( \text{Co-Co} \) distance of \( \sim 2.4 \) Å. This narrow 3d-band allows hosting a large number of magnetically coupled, unpaired electrons on each \( \text{Co} \) center. In contrast, the radially more diffused \( \text{Co} \) 4s-orbitals form a much larger manifold of group orbitals of symmetry \( a_{1g}, t_{1u}, t_{2g}, e_g \) and \( t_{2u} \), respectively. Among them, the \( a_{1g} \) and \( t_{1u} \) orbitals are strongly bonding for \( \text{Co}_{12} \) cage, thus lying in the low-energy end of the 3d-band. The weakly antibonding orbitals \( t_{2u} \) and \( e_g \) of the \( \text{Co}_{12} \) cage are destabilized by the \( \text{Co}_c \) atom (with 3d-orbitals in \( t_{2u}+e_g \) symmetry) so much that they become strongly antibonding orbitals in \( \text{Co}_8\text{Co}_{12}\text{O}_8 \). As a result, the \( \text{Co}_{12} \) cage can only hold 8 electrons in the 4s-based \( a_{1g} \) and \( t_{1u} \) orbitals to form an \( (a_{1g})^4(t_{1u})^4 \) configuration. This scenario is reminiscent to \( [\text{Zn}^{12+}]_8 \) and \( [\text{Mn}^{9+}]_8 \) clusters within a ‘6n+2’ rule of electron counting and have so-called cubic aromaticity [48, 49].

As a metal oxide cluster, \( \text{Co}_{12}\text{O}_8 \) possesses special stability due to the cubic aromaticity from multi-center \( \text{Co-Co} \) meta-metal bonding. The electronic structure analysis shows that the oxidation states of the atoms in this cluster can be formally assigned as central \( \text{Co}^{(7)} \), cage \( \text{Co}^{(4+)}_8 \), and \( \text{O}^{(2-)}_8 \), respectively, which are consistent with the calculated net charges and spin distribution of them (supplementary Table 7). Here the \( \text{Co}_{12} \) cage (in cubic \( \text{Co}_{13}\text{O}_8 \) cluster) with 12 quasi-monovalent \( \text{Co} \) (1, 3d\(^4\)4s\(^1\)) atoms is forced to lose 4 extra electrons because of the antibonding interaction with the 3d orbitals of the central \( \text{Co}_c \) atom (Fig. 5). The calculated spin density populations support this chemical bonding analysis (for details see Supplementary Table 7). Also, we searched for the lowest-energy spin states of \( \text{Co}_8\text{Co}_{12}\text{O}_8 \) and found that a total spin quantum number \( S=29/2 \) corresponds to the lowest energy state. On this basis, we calculated the total magnetic moment of \( \text{Co}_{13}\text{O}_8 \) being up to 30 \( \mu_B \), simply by using \( \mu_s = g_s \sqrt{S(S+1)} \mu_B \) (the Landé factor \( g_s = 2.0023 \)), which is larger than the usual cobalt oxides [50].

CONCLUSION

In summary, utilizing self-developed deep-ultraviolet laser ionization mass spectrometry (DUV-LIMS) technique which takes advantage of high-efficiency photoionization of neutral cobalt clusters, here we observe the reactions of cobalt clusters with oxygen and discover the prominent stability of \( \text{Co}_{13}\text{O}_8 \). Theoretical calculations based on different methods concur with this experimental finding, and unveil its distinctive stability pertaining to a perovskite-like body-centred cubic structure. Thermodynamics and reaction dynamics involving structural evolution from icosahedron \( \text{Co}_{13} \) to the cubic \( \text{Co}_{13}\text{O}_8 \) are addressed. We name this kind of clusters as ‘metallooxocubes’, to stimulate further research interest in exploring such materials with well-defined components and regular structures. This class of neutral oxygen-passivated metal clusters is a reasonable candidate for genetic materials in view of the cubic nature of the building blocks and the special stability from cubic aromaticity.

METHODS

Experimental. The experiments were carried out using a customized reflection time-of-flight mass spectrometer (Re-TOFMS) combined with the newly-developed 177.3 nm deep-ultraviolet laser (details in supplementary materials) [51]. The optimized Re-TOFMS, LaVa source and deep-ultraviolet laser ensure highly efficient preparation and detection of well-resolved neutral cobalt
clusters under a normal distribution. Following the generation of cobalt clusters, a tangential deflection electric field (DC 200 V) was designed to remove any charged particles to attain neutral clusters. The homemade LaVa source is coupled with a reaction cell downstream (6 mm diameter, 6 cm long), allowing for sufficient collision reactions (~30 Pa pressure) with varied reactants (e.g., 3-20% O₂ seeded in He), controlled by a pulsed general valve with the on-time duration to be set as 150–250 µs per period of 100 ms (i.e., a frequency of 10 Hz). The neutral cluster beam and reaction products were then collimated into another high-vacuum TOF chamber through a skimmer (φ 2 mm). At the arrival in the ionization zone (i.e., the space between the first and second acceleration plates), the cluster beam meets the deep-ultraviolet laser from the coaxial front direction; simultaneously, the acceleration voltages are triggered so that the instantaneously ionized neutral clusters are analyzed by the Re-TOFMS.

**Theoretical Methods.** Three methods are used to search and identify the global minimum structures of the clusters in this study. The first one is CALYPSO approach based on the particle swarm optimization method.[52] Also, here we have used a homemade code strategy (Supplementary Appendix) based on graph theory method[53] to help find the ground-state structures by taking into consideration of the prototypes of crystal structures of both metal cobalt, rocksalt and spinel cobalt oxides. This is based on chemical knowledge that metal clusters tend to a closest stacking mode. This approach has equivalent efficiency to find energy-minima structure of small clusters (e.g., n<10) as nascent CALYPSO code, but shows faster speed for larger clusters (Supplementary Figure 9). Following density functional theory (DFT) calculations of energetics were performed via a PWmat software package [54, 55] in a plane-wave pseudopotential basis set, with a 20 Å vacuum space set in the x, y and z directions. Spin polarization was considered in all the calculations. Perdew–Burke–Ernzerhof (PBE) exchange correlation functional [56] with SG15 pseudopotential and DFT-D2 van de Waals corrections were applied in the calculations. A Hubbard-U model based on PWmat code was employed to correct the strong-correlation Coulomb interaction between d-orbital electrons on Co atoms.

We also conducted independent basin-hopping global minimum search using TGMind code to conclusively determine the cluster structure of Co₃O₅. Also, DFT calculations were carried out with Gaussian-16 quantum chemical package.[57] Using the standard 6-311G basis set augmented by 3df polarization, the molecular orbitals and ELF patterns are calculated by combining Becke’s exchange and Perdew–Wang’s correlation functionals (denoted BPW91). The program package of Multifmin[58] is utilized to analyze the ELF and orbitals. Further sophisticated calculations of electronic structure and nucleus-independent chemical shifts (NICS) [40-43] were performed via ADF code [59].

**SUPPLEMENTARY DATA**

Supplementary data are available at NSR online.

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**AUTHOR CONTRIBUTIONS**

L. G. and H. Z. conducted the experiments; M. W. conducted the main calculations; X.C., M.H., C.Q.X., H.S.H. and J.L. contributed to the theoretical calculations and analyses; Z.L., F.P. and J.Y. contributed to the design of this project. All authors contributed to analyzing the data and writing the manuscript.

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**Conflict of interest statement.** None declared.

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