ACS OMEGA

http://pubs.acs.org/journal/acsodf

Article

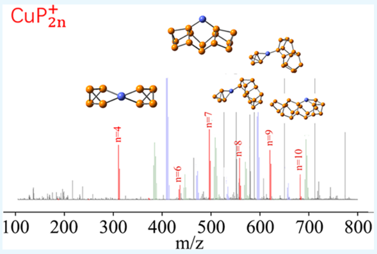
Geometrical Structures and Dissociation Channels of CuP_{2n}^{+} (n = 2−11): Studied by Mass Spectrometry and Theoretical Calculations

Yicheng Xu, Mengying Du, Luyang Jiao, and Xianglei Kong*

Cite This: *ACS Omega* 2022, 7, 7134−7138

Read Online

ABSTRACT: Transition metal phosphorus cluster cations CuP_{2n}^{+} ($2 \le n \le 11$) were studied by laser ablation mass spectrometry and collision-induced dissociation (CID). The magic-numbered cluster ion of CuP_{8}^{+} was identified experimentally, and cluster ions of CuP_{14}^{+} and CuP_{18}^{+} were also found to be generated with high abundance. CID results show that the dissociation channels of CuP_{2n}^{+} (n = 4 and 6−10) are all characterized by the loss of the P_4 unit. Theoretical calculations combining global minima searching with the basin-hopping method and density functional theory (DFT) optimizations were performed for these clusters. Among them, the magic-numbered cluster CuP_{8}^{+} was characterized by a D_{2d} symmetry, with the Cu atom bridging two P_4 units. The most stable isomer of CuP_{14}^{+} was found to be characterized by a C_{2v} symmetry. Calculations also reflect that the dissociation channels of the loss of the P_4 unit are more energetically favorable than those of the loss of the P_2 unit for CuP_{2n}^{+} (n = 4 and 6−10), which are in good consistent with the experimental results.



INTRODUCTION

Due to their remarkable structural characteristics and possible applications, binary cluster ions composed of transition metal and non-metal elements have attracted much attention.[1,2] Among them, related phosphorus clusters doped with transition metals have been studied by laser ablation mass spectrometry for a long time.[3−10] For example, Han *et al.* have detected chromium/phosphorus binary cluster ions with time-of-flight (TOF) mass spectrometry by laser ablation on a tablet of well-mixed chromium and red phosphorus powder.[7] Among the observed ions, the peaks of CrP_{4}^{+} and CrP_{8}^{+} were especially prominent, and the odd−even oscillation in the intensity of the CrP_{m}^{+} series was observed. They have also generated binary cluster ions composed of Fe/P, Co/P, and Ni/P by laser ablation of the mixtures of metal powders and red phosphorus.[8] Abundant peaks of MP_{2}^{+}, $M_2P_{4}^{+}$, and $M_nP_{8}^{+}$ (M = Fe, Co, Ni, n = 2−4) were observed. The odd−even oscillation rule was observed too. Further photodissociation experiments indicated that, for those clusters, the main channels are the loss of the units of P_2 or P_4.[7] For Ti/P and Mn/P binary cluster ions, similar results have been observed.[6]

On the other hand, to better understand these results, theoretical calculations have been also applied.[11−17] The geometrical structures and dissociation channels of MP_{2n}^{+} (M = Fe, Co, Ni, n = 1−4) have been studied by Kuang *et al.*[12] It has been found that the lowest energy structures of these cluster ions are constructed by a two- or four-fold M atom with P_4 or P_2 units. For clusters of same sizes but with different metals, their most stable structures are still different in many cases. Other clusters, including MnP_{m}^{+} (m = 2−8) and TiP_{m}^{+} (m = 2−4, 6), have been also studied.[11,13,14]

However, for some reason, the binary cluster ions composed of Cu/P have not been studied by now. For theoretical studies, due to their structural diversity and complexity, larger-sized transition metal phosphorus clusters MP_{m}^{+} ($m > 8$) have been rarely studied.[17] Thus, in the present work, we investigate the formation of CuP_{2n}^{+} with the method of laser ablation mass spectrometry using a Fourier transform ion cyclotron resonance (FT ICR) mass spectrometer. The tandem mass spectrometric method has been also applied to study the dissociation channels of selected cluster ions. The global structural minima of these clusters and relative dissociation pathways have been theoretically studied too.

RESULTS AND DISCUSSION

Figure 1a and Figure 1b show the laser ablation mass spectra of the samples of CuCl/P and $CuCl_2$/P, respectively. Both spectra are quite similar in the distributions of the identified species. Besides the strong signals of P_{2n+1}^{+} ($5 \le n \le 12$) that have been previously observed in the laser ablation mass spectrum of red phosphorus,[3,18] new cluster ions of CuP_{2n}^{+} (n = 4−10), $Cu_2ClP_{2n}^{+}$ (n = 4−8), and $Cu_3Cl_2P_{2n}^{+}$ (n = 2, 4, 5, and 7) were clearly identified in both spectra. For the observed species of CuP_{2n}^{+} in both cases, the ion of CuP_{8}^{+} has much higher intensities than its adjacent ions and thus can be considered as

Received: December 2, 2021
Accepted: February 7, 2022
Published: February 17, 2022

https://doi.org/10.1021/acsomega.1c06824

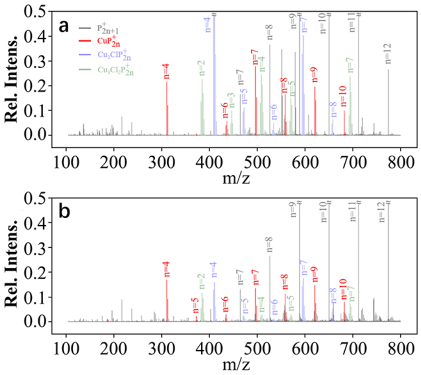


Figure 1. Laser ablation mass spectra of (a) CuCl/P and (b) $CuCl_2$/P.

a magic-numbered cluster. Clusters of CuP_{14}^+ and CuP_{18}^+ also have relatively strong signal intensities in both experiments, although they are less prominent than the ion of CuP_8^+.

The collision-induced dissociation (CID) mass spectra of these ions (except the weak ion of CuP_{10}^+) were performed with the SORI method. The results are shown in Figure 2.

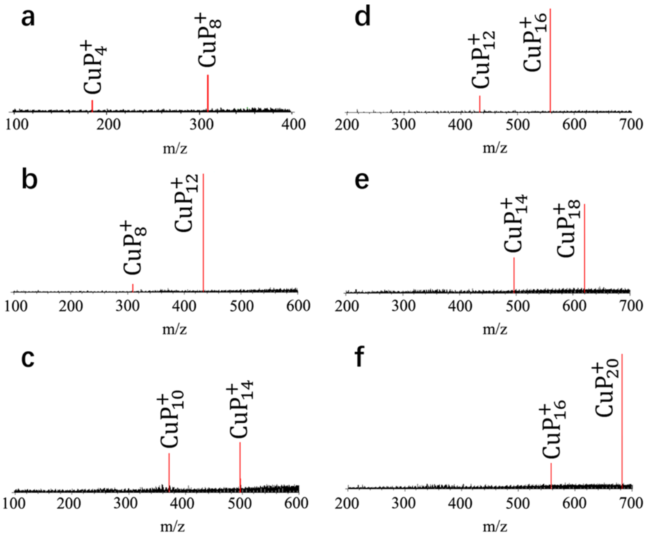


Figure 2. SORI CID mass spectra of (a) CuP_8^+, (b) CuP_{12}^+, (c) CuP_{14}^+, (d) CuP_{16}^+, (e) CuP_{18}^+, and (f) CuP_{20}^+.

Clearly, all the precursor ions CuP_8^+, CuP_{12}^+, CuP_{14}^+, CuP_{16}^+, CuP_{18}^+, and CuP_{20}^+ are characterized by the loss of the P_4 unit. No product ions from other dissociation pathways were observed, even under different experimental collision conditions. The results are quite similar to the previously reported CID results of phosphorus cluster cations of P_{2m}^+ (m = 6−11) but are different from those of P_{2m}^-.[18,19]

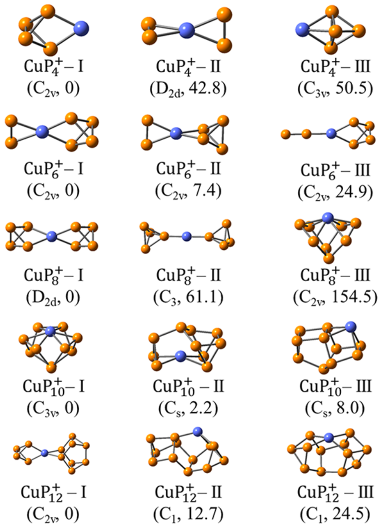


Figure 3. Three most stable structures of CuP_{2n}^+ (n = 2−6) optimized at the level of B3LYP/6-311+G(d). Symmetry groups and relative energies in kJ/mol are shown under the structures.

To better understand the results, theoretical calculations on CuP_{2n}^+ (n = 2−11) have been performed. The three most energetically favorable structures of CuP_{2n}^+ (n = 2−6) are shown in Figure 3 (the other top isomers are shown in Figure S1). For CuP_4^+, the most stable isomer CuP_4^+-I has a C_{2v} symmetry, with the two-coordinate copper atom connected with a folded P_4 unit. The structure is very similar to the previously calculated most stable isomers of MnP_4^+ and CrP_4^+ but is quite different from those of FeP_4^+, CoP_4^+, NiP_4^+, and TiP_4^+. The energies of the second and third stable isomers of CuP_4^+-II (D_{2d}) and CuP_4^+-III (C_{3v}) are found to be 42.8 and 50.5 kJ/mol higher, respectively. The linear structure and pyramidal structures, which exists in the most stable isomer of FeP_4^+ and CoP_4^+, are considered too, and their relative energies are found to be 94.4 and 183.4 kJ/mol higher, respectively (Figure S1). The three most stable structures of CuP_6^+ can be derived from CuP_4^+-I by adding two phosphorus atoms on the other side of the copper atom while keeping the C_{2v} symmetry. Interestingly, the structures of CuP_6^+-I, CuP_6^+-II, and CuP_6^+-III are found to be like those of the most stable isomers of MnP_6^+, CrP_6^+, CoP_6^+, NiP_6^+, TiP_6^+, and FeP_6^+.[11−14,17]

For the magic cluster ion of CuP_8^+, the most stable isomer CuP_8^+-I is characterized by a D_{2d} symmetry, with a four-coordinate Cu atom shared between two folded P_4 units. The structure is very similar to those of MnP_8^+, CrP_8^+, and CoP_8^+ but is different from those of FeP_8^+ and NiP_8^+.[11,12] The second most stable isomer of CuP_8^+-II has a two-coordinate Cu atom shared between two pyramidal P_4 units but with a relative energy of 61.1 kJ/mol higher. This structure is like the most stable structure of FeP_8^+ and the second most stable structure of NiP_8^+.[12] All the three structures of CuP_8^+ were further studied with the method of TPSS/def2-TZVP, and similar results have been obtained. The structure of CuP_{10}^+-I has a C_{3v} symmetry and is similar to the third stable isomer of CuP_8^+-III. Other structures with close energies (2.2 and 8.0 kJ/mol higher) were also found. For CuP_{12}^+-I, a folded P_4 unit and a P_8 cuneane unit are connected by a four-coordinate Cu atom. The structure is also characterized by a C_{2v} symmetry, which is 12.7 and 24.5 kJ/mol more stable than the asymmetry structures of CuP_{12}^+-II and CuP_{12}^+-III, respectively.

For larger clusters with $n \geq 7$, the calculations are more difficult and time-consuming. Previous theoretical studies for such kinds of clusters are also insufficient. By increasing the numbers of the randomly built initial structures and program runs, the structures of CuP_{2n}^+ (n = 7−11) were also studied. Figure 4 shows the three most energetically favorable structures of these clusters (and Figure S1 also shows the other top isomers). Except for the most stable isomer of CuP_{14}^+, all these top three stable structures shown in Figure 4 have no symmetry. The structure of CuP_{14}^+-I is characterized by its C_{2v} symmetry, with energies of 1.5 and 22.5 kJ/mol more favorable

https://doi.org/10.1021/acsomega.1c06824
ACS Omega 2022, 7, 7134−7138

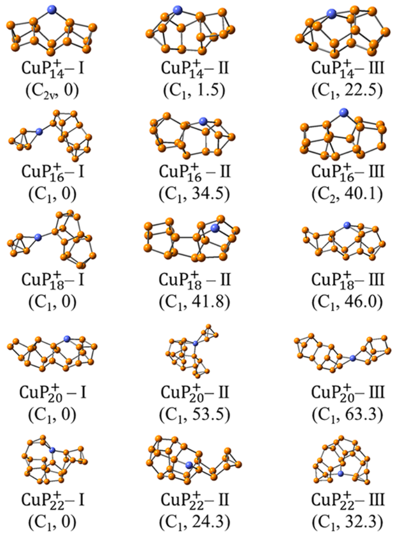


Figure 4. Three most stable structures of CuP_{2n}^+ (n = 7−11) optimized at the level of B3LYP/6-311+G(d). Symmetry groups and relative energies in kJ/mol are shown under the structures.

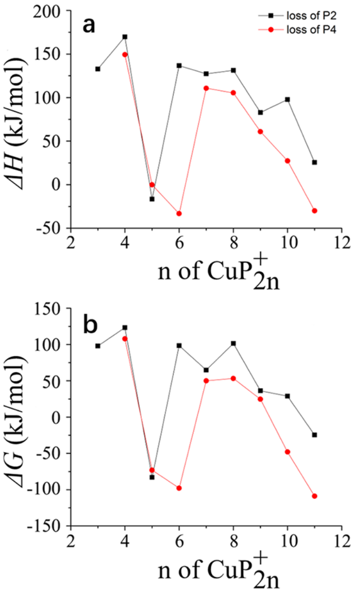


Figure 5. Changes in (a) enthalpy (Δ*H*) and (b) free energy (Δ*G*) of the two dissociation pathways for the ions of CuP_{2n}^+ ($4 \le n \le 11$). The structures of corresponding ions used in calculation are shown in Figure 4.

than those of the second and the third most stable structures, respectively. If the magic number property of this ion shown in Figure 1 is considered, then the suggested highly symmetrical structure of CuP_{14}^+-I is quite reasonable and easy to be accepted. Although more complicated structures have been observed for CuP_{2n}^+ with larger sizes, the most stable isomers of CuP_{16}^+ and CuP_{18}^+ and the second most stable isomer of CuP_{20}^+ are still characterized by the same building block of the P_4 unit. However, for CuP_{22}^+, a curved structure is more energy-favorable.

For understanding the localization of the charge in the clusters, natural bond orbital (NBO) charge distribution analysis[20,21] was applied for the top three structures of CuP_8^+ and CuP_{18}^+. As shown in Figure S2, although the positive charge is mainly localized in the Cu atom in all cases, the P atoms have quite different charge distributions in different structures, reflecting the possible multiple roles of phosphorus atoms in the clusters.

Dissociation channels characterized by the loss of the P_2 or P_4 unit, which have been previously suggested for MP_m^+ (M = Fe, Co, Ni) clusters,[12] were also theoretically considered here

$$\mathrm{CuP}_{2n}^+ \rightarrow \mathrm{CuP}_{2n-2}^+ + \mathrm{P}_2 \quad (1)$$

$$\mathrm{CuP}_{2n}^+ \rightarrow \mathrm{CuP}_{2n-4}^+ + \mathrm{P}_4 \quad (2)$$

To study which dissociation channel is more thermodynamically favored, the changes in enthalpy (Δ*H*) and free energy (Δ*G*) of both pathways were investigated for the ions of CuP_{2n}^+ ($4 \le n \le 11$). For the P_4 unit, the most stable tetrahedral isomer was applied here.[19] For these structures shown in Figures 3 and 4, changes in enthalpies (Δ*H*) and Gibbs free energies (Δ*G*) for both dissociation pathways are shown in Figure 5a and Figure 5b, respectively. The Δ*H* values for both channels of clusters CuP_8^+, CuP_{14}^+, CuP_{16}^+, CuP_{18}^+, and CuP_{20}^+ are positive, indicating that these reaction processes are endothermic. The results shown in Figure 5 also reflect the instabilities of the cluster ions of CuP_{10}^+ and CuP_{22}^+, which are in good consistent with the experimental results. Except for that of CuP_{10}^+, the P_4 loss channels of all clusters have the lower values of both Δ*H* and Δ*G*. The priority of this dissociation channel is in good agreement with the experimental results. The differences between Δ*H* and Δ*G* of the two channels for CuP_{12}^+ are so large that they highlight the stability of the dissociation product—the magic-numbered cluster cation of CuP_8^+.

■ CONCLUSIONS

The Cu/P binary cluster ions were generated by laser ablation on the mixed solid samples of red phosphorus and copper salts. Signals of CuP_{2n}^+ ($4 \le n \le 10$) were observed for both salts of CuCl and CuCl_2. Among them, the intensity of CuP_8^+ is much higher than those of its adjacent ions and thus can be identified as a magic-numbered cluster. Cluster ions of CuP_{14}^+ and CuP_{18}^+ were also generated with higher abundance than other ions. For cluster ions of CuP_{2n}^+ (n = 4 and 6−10), their dissociation pathways are all clearly characterized by the only channel of the loss of the P_4 unit. The most stable isomers of CuP_{2n}^+ ($2 \le n \le 11$) were systematically searched with the self-developed basin-hopping program NKCS followed by the density functional theory (DFT) optimization and calculation on the level of B3LYP/6-311+G(d) for the selected structures. It is found that the magic-numbered cluster ion of CuP_8^+ is characterized by a D_{2d} symmetry, with the Cu atom bridging two P_4 units. The most stable isomers of CuP_{2n}^+ (n = 2, 3, 6, and 7) are all characterized by a C_{2v} symmetry and that of CuP_{10}^+ by a C_{3v} symmetry. However, as the increase in the cluster size, the most stable isomers of CuP_{2n}^+ with large sizes (n = 8−11) show no symmetry. It is also found that the dissociation channels with the loss of the P_4 unit are more energetically favorable than those with the loss of the P_2 unit for most of these observed cluster ions, especially the cluster CuP_{12}^+, which are in good consistent with the experimental results.

■ METHODS

Experimental Section. Experiments were performed on a Bruker SolariX XR 7.0 T FT ICR mass spectrometer equipped with the commercial MALDI source without any modification. The red phosphorus sample was purchased from Alfa Aesar, and the samples of CuCl and $CuCl_2$ were purchased from the Tianjin Guangfu Fine Chemical Research Institute (Tianjin, China). The fresh suspension of red phosphorus (2 mg/mL) was prepared in a mixed solution of methanol and water (1:1, v/v). Both aqueous solutions of CuCl and $CuCl_2$ were prepared with a concentration of 20 mM. Then, 1 μL of red phosphorus and 1 μL of CuCl/$CuCl_2$ were deposited and mixed onto a metal target and dried at room temperature before analysis. Mass spectra reported here were all measured in positive ion mode. Typically, mass spectra were acquired in the range of m/z 100−800. In the collision-induced dissociation (CID) experiments, the precursor ions of interest were pre-selected before entering the cell and reselected in the FT ICR cell. Sustained off-resonance irradiation (SORI) excitation of the selected isotopic peak was performed here.[22] In the processes, the target ions were excited by a waveform with a frequency that is typically 100−500 Hz off-resonance with their corresponding cyclotron frequency and were caused to undergo many acceleration/deceleration cycles and multiple collisions. In the experiments reported here, the SORI was set with a relative power of 0.8−1.4%.

Computations. To find the minima in their potential energy surfaces, a self-developed program named NKCS, which has been previously reported in detail, was applied here.[23] Briefly, initial structures of CuP_{2n}^+ ($1 \leq n \leq 11$) were randomly generated and optimized with the geometry, frequency, noncovalent, extended tight binding (GFN-xTB) method[24] and then basin-hopping optimization was applied to search for the global structural minima. The initial population size for clusters with N atoms (after the reasonability and similarity check) is set as $N^{2.3-2.8}$. The 50 most stable structures after basin-hopping were picked out for further optimization with DFT calculation at the level of B3LYP/6-31G(d) using the Gaussian 09 program.[25−28] To make sure of the results, the program has been run three and five times for clusters of CuP_{2n}^+ with sizes satisfied $3 \leq n \leq 6$ and $7 \leq n \leq 11$, respectively. On the other hand, to prevent missing some important structures, some highly symmetrical structures were built manually followed by DFT optimization at the same level and comparison with the previously selected structures. Our previous studies on phosphorus clusters show that the method of B3LYP/6-311+G(d) can provide quite reasonable results.[18,19,23] Thus, the top 10 isomers for each cluster were picked out and finally optimized at this level. These structures were further verified by vibrational frequency analysis. For all structures, their electronic energies were calculated at 0 K with zero-point energy (ZPE) corrected, while their free energies were calculated at 298 K. For all the top three isomers of each cluster, both singlets and triplets were considered. It has been found that, in all cases, the singlets have the lower energies than their triplets. Thus, all the structures discussed below are only shown in their singlets. For further comparison, the DFT method of TPSS/def2-TZVP that has been previously suggested for the transition-metal complex geometrical study[29,30] has been also applied here for some of the clusters with small sizes.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.1c06824.

Other top structures of CuP_{2n}^+ (n = 2−11) (Figure S1), the NBO charge distribution of some structures (Figure S2), and the Cartesian coordinates of all the most stable isomers studied here (PDF)

■ AUTHOR INFORMATION

Corresponding Author

Xianglei Kong − *The State Key Laboratory and Institute of Elemento-Organic Chemistry, Collage of Chemistry and Collaborative Innovation Center of Chemical Science and Engineering, Nankai University, Tianjin 300071, China;* orcid.org/0000-0002-8736-6018; Phone: +89 22 23509564; Email: kongxianglei@nankai.edu.cn

Authors

Yicheng Xu − *The State Key Laboratory and Institute of Elemento-Organic Chemistry, Collage of Chemistry, Nankai University, Tianjin 300071, China*

Mengying Du − *The State Key Laboratory and Institute of Elemento-Organic Chemistry, Collage of Chemistry, Nankai University, Tianjin 300071, China*

Luyang Jiao − *The State Key Laboratory and Institute of Elemento-Organic Chemistry, Collage of Chemistry, Nankai University, Tianjin 300071, China*

Complete contact information is available at:
https://pubs.acs.org/10.1021/acsomega.1c06824

Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was supported by the National Natural Science Foundation of China (grant nos. 21627801 and 22174076).

■ REFERENCES

(1) Fernando, A.; Weerawardene, K.; Karimova, N. V.; Aikens, C. M. Quantum mechanical studies of large metal, metal oxide, and metal chalcogenide nanoparticles and clusters. *Chem. Rev.* **2015**, *115*, 6112−6216.

(2) Luo, Z.; Castleman, A. W.; Khanna, S. N. Reactivity of Metal Clusters. *Chem. Rev.* **2016**, *116*, 14456−14492.

(3) Kong, X.; Mu, L.; Zhou, M.; Yang, S. M. Phosphorus clusters and quantum dots. *Fundamentals and Applications of Phosphorous Nanomaterial*. 2019, 79−102, DOI: 10.1021/bk-2019-1333.ch005.

(4) Ju, X.; Zhang, N.; Gao, Z.; Shi, C. S.; Kong, F. A. Production and dissociation of Fe/P cluster ions. *Sci. Chin. B* **1995**, *25*, 567−572.

(5) Ju, X.; Shi, C. S. Studies on the stability of iron phosphide cluster ions. *Chem. J. Chin. Univ.* **1995**, *16*, 1325−1328.

(6) Han, C. Y.; Zhang, X.; Zhao, X.; Gao, Z.; Zhu, Q. H. Formation and Photodissociation of Mn/P, Ti/P Binary Clusters. *Chin. J. Chem. Phys.* **2001**, *14*, 19−26.

(7) Han, C. Y.; Zhao, X.; Zhang, X.; Gao, Z.; Zhu, Q. H. Formation, photodissociation and structure of chromium/phosphorus binary cluster ions. *Rapid Commun. Mass Spectrom.* **2000**, *14*, 1255−1259.

(8) Han, C. Y.; Xing, X. P.; Zhang, X.; Gao, Z.; Zhu, Q. H. Formation and Photodissociation of Fe, Co, Ni/P Binary Cluster Ions. *Acta Phys.-Chim. Sin.* **2000**, *16*, 823−824.

(9) Panyala, N. R.; Eladia, M. P. M.; Havel, J. Laser ablation synthesis of new gold phosphides using red phosphorus and nanogold

as precursors. Laser desorption ionisation time-of-flight mass spectrometry. *Rapid Commun. Mass Spectrom.* **2012**, *26*, 1100−1108.

(10) Kubáček, P.; Prokeš, L.; Pamreddy, A.; Peña-Méndez, E. M.; Conde, J. E.; Alberti, M.; Havel, J. Laser ablation synthesis of arsenic−phosphide As_mP_n clusters from As−P mixtures. Laser desorption ionisation with quadrupole ion trap time-of-flight mass spectrometry: The mass spectrometer as a synthesizer. *Rapid Commun. Mass Spectrom.* **2018**, *32*, 789−800.

(11) Kuang, X. J.; Wang, X. Q.; Liu, G. B. Geometrical structures and probable dissociation channels of CrPm+ (m = 2, 4, 6, 8) clusters. *Phys. B* **2010**, *405*, 3328−3333.

(12) Kuang, X. J.; Wang, X. Q.; Liu, G. B. Geometrical structures and dissociation channels of MP_n^+ (M = Fe, Co or Ni; n = 2, 4, 6 or 8) binary cluster ions. *Transition Met. Chem.* **2011**, *36*, 45−51.

(13) Kuang, X.; Wang, X.; Liu, G. Geometrical structures and possible dissociation channels of $MnP_n{}^+$ (n = 2−8) binary cluster ions. *Struct. Chem.* **2012**, *23*, 29−35.

(14) Kuang, X. J.; Wang, X. Q.; Liu, G. B. A density functional theory study on the Ti/P binary cluster ions. *Mol. Simul.* **2012**, *38*, 102−111.

(15) Xu, K. M.; Huang, T.; Wen, H.; Liu, Y. R.; Gai, Y. B.; Zhang, W. J.; Huang, W. A density functional study of phosphorus-doped gold clusters: Au_nP^-(n= 1−8). *RSC Adv.* **2013**, *3*, 24492−24502.

(16) Wen, X. D.; Cahill, T. J.; Hoffmann, R. Element Lines: Bonding in the Ternary Gold Polyphosphides, Au_2MP_2 with M = Pb, Tl, or Hg. *J. Am. Chem. Soc.* **2009**, *131*, 2199−2207.

(17) Mahtout, S.; Amatousse, N.; Rabilloud, F. Structural, electronic and magnetic properties of P_n^{+1} and FeP_n (n = 1−14) clusters. *Comput. Theor. Chem.* **2017**, *1122*, 16−26.

(18) Mu, L.; Yang, S.; Biao, X.; Yin, H.; Kong, X. Medium-sized phosphorus cluster cations P_{2m+1}^+(6≤m≤32) studied by collision-induced dissociation mass spectrometry. *J. Mass Spectrom.* **2015**, *50*, 1352−1357.

(19) Yang, S.; Mu, L.; Kong, X. Collision-induced dissociation mass spectrometry of phosphorus clusters anions P_{2m+1}^-(3≤m≤20). *Int. J. Mass Spectrom.* **2016**, *399-400*, 27−32.

(20) Carpenter, J. E.; Weinhold, F. Analysis of the geometry of the hydroxymethyl radical by the "different hybrids for different spins" natural bond orbital procedure. *J. Mol. Struct.: THEOCHEM* **1988**, *46*, 41−62.

(21) Reed, A. E.; Curtiss, L. A.; Weinhold, F. Intermolecular interactions rom a natural bond orbital, donor-acceptor viewpoint. *Chem. Rev.* **1988**, *88*, 899−926.

(22) Cody, R. B.; Hein, R. E.; Goodman, S. D.; Marshall, A. G. Stored Waveform Inverse Fourier Transform Excitation for Obtaining Increased Parent Ion Selectivity in Collisionally Activated Dissociation: Preliminary Results. *Rapid Commun. Mass Spectrom.* **1987**, *1*, 99−102.

(23) Zhou, M.; Xu, Y.; Cui, Y.; Zhang, X.; Kong, X. Search for Global Minimum Structures of $P_{2n+1}{}^+$ (n = 1−15) Using xTB-Based Basin-Hopping Algorithm. *Front. Chem.* **2021**, *9*, 694156.

(24) Grimme, S.; Bannwarth, C.; Shushkov, P. A Robust and Accurate Tight-Binding Quantum Chemical Method for Structures, Vibrational Frequencies, and Noncovalent Interactions of Large Molecular Systems Parametrized for All Spd-Block Elements (Z = 1-86). *J. Chem. Theory Comput.* **2017**, *13*, 1989−2009.

(25) Becke, A. D. Density functional exchange energy approximation with correct asymptotic behavior. *Phys. Rev. A: At., Mol., Opt. Phys.* **1988**, *38*, 3098−3100.

(26) Lee, C.; Yang, W.; Parr, R. G. Development of the Colle-Salvetti correlation-energy formula into a functional of the electron density. *Phys. Rev. B: Condens. Matter Mater. Phys.* **1988**, *37*, 785−789.

(27) Becke, A. D. Density-functional thermochemistry. III. The role of exact exchange. *J. Chem. Phys.* **1993**, *98*, 5648−5652.

(28) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G.; et al. *Gaussian 09, Revision C.01*; Gaussian, Inc.: Wallingford, CT, USA, 2010.

(29) Tao, J.; Perdew, J. P.; Staroverov, V. N.; Scuseria, G. E. *Phys. Rev. Lett.* **2003**, *91*, 146401.

(30) Bühl, M.; Kabrede, H. Geometries of Transition-Metal Complexes from Density-Functional Theory. *J. Chem. Theory Comput.* **2006**, *2*, 1282−1290.

https://doi.org/10.1021/acsomega.1c06824