Title

Dual spherical-spherical aromaticity in [M(η2-P4)2]+ (M = Cu, Ag, Au) and [P(P4)2]+. Evaluation of bonding nature and spherical aromatic character of the P4 aggregates from DFT calculations

Abstract

The favorable coordination of two P4 units to a coinage metal center, given by [M(η2–P4)2]+ and [P(P4)2]+ clusters, offers an interesting template for evaluating how two spherical aromatic units interact when bridged by either a metal or a main-group element center. Our results indicate a M+–(P4)2 stabilization trend in the order Au > Cu > Ag, involving mainly electrostatic character, followed by a sizable contribution from covalent (orbital) character, with a slight London dispersion type stabilization. The coordination scheme is based on a σ-M+←(η2-P4)2 charge transfer, followed by σ-metal-to-ligand backbonding, in addition to a set of two σ-ligand-to-metal and π-ligand-to-metal charge transfer bonds. Such structural features bring together two spherical aromatic P4 units, leading to the formation of a dual aromatic cluster mediated by a coinage metal center, i.e. two independent aromatic units within the same cluster. However, in [P(P4)2]+ involving stronger covalent P4–P bonds, the spherical aromatic character decreases, owing to the larger distortion of the P4 units, as result of the larger bonding interaction towards the central P atom. Hence, the coordination towards a coinage metal center of the P4 unit incorporates multiple aromatic units into a single molecular entity. This provides a model to envisage larger connected spherical-aromatic species serving as building blocks while retaining their inherent characteristics.

Authors

Olea Ulloa C.; Attia A.A.A.; Lupan A.; King R.B.; Muñoz-Castro A.

Author full names

Olea Ulloa, Carolina (55621919600); Attia, Amr A.A. (55555891500); Lupan, Alexandru (9244824900); King, R. Bruce (35480794100); Muñoz-Castro, Alvaro (18042134900)

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Affiliations

Carrera de Química y Farmacia, Facultad de Ciencias de la Salud, Universidad Autónoma de Chile, Pedro de Valdivia 425, Providencia, Santiago, Chile; Faculty of Chemistry and Chemical Engineering, Babeş-Bolyai University, Cluj-Napoca, Romania; Department of Chemistry, University of Georgia, Athens, 30602, GA, United States; Facultad de Ingeniería, Arquitectura y Diseño, Universidad San Sebastián, Bellavista 7, Santiago, 8420524, Chile

Authors with affiliations

Olea Ulloa C., Carrera de Química y Farmacia, Facultad de Ciencias de la Salud, Universidad Autónoma de Chile, Pedro de Valdivia 425, Providencia, Santiago, Chile; Attia A.A.A., Faculty of Chemistry and Chemical Engineering, Babeş-Bolyai

University, Cluj-Napoca, Romania; Lupan A., Faculty of Chemistry and Chemical Engineering, Babeş-Bolyai University, Cluj-Napoca, Romania; King R.B., Department of Chemistry, University of Georgia, Athens, 30602, GA, United States; Muñoz-Castro A., Facultad de Ingeniería, Arquitectura y Diseño, Universidad San Sebastián, Bellavista 7, Santiago, 8420524, Chile

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Correspondence Address

R.B. King; Department of Chemistry, University of Georgia, Athens, 30602, United States; email: rbking@uga.edu

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