Argentophilic Interactions, Flexibility, and Dynamics of Pyrrole Cages Encapsulating Silver(I) Clusters

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Streszczenie

Recently,pyrrolecageshavebeensynthesizedthatencapsulateion pairsand silver(I)clustersto formintricatesupramolecularcapsules.We reportherea computationalanalysisof thesestructuresusingdensityfunctionaltheorycombinedwitha semiempiricaltight-bindingapproach.We find that for neutralpyrrolecages,the Gibbsfree energiesofformationprovidereliablepredictionsfor the ratioof boundions.Forchargedpyrrolecages,we find strongargentophilicinteractionsbetweenAgions on the basisof the calculatedbondindicesand molecularorbitals.ForthecagewiththeAg4cluster,we findtwominimum-geometryconformationsthat differby only6.5 kcal/mol,withan energybarrier<1kcal/mol,suggestinga veryflexiblestructureas indicatedby moleculardynamics.The predictedenergiesof formationof[Agn⊂1]n-3+(n= 1−5)cryptandsprovidelow energybarriersof formationof 5−20kcal/molfor allcases,whichis consistentwith the experimentaldata.Furthermore,we also examinedthe structuralvariabilityof mixed-valencesilverclustersto test whetheradditionalgeometricalconformationsinsidethe organiccageare thermodynamicallyaccessible.In thiscontext,we showthat the time-dependentdensityfunctionaltheoryUV−visspectramay potentiallyserveas a diagnosticprobetocharacterizemixed-valenceand geometricalconfigurationsof silverclustersencapsulatedinto cryptands.

Słowa kluczowe

Ethers, Ions, Macrocyclic compounds, Metal clusters, Pyrroles

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