Regium Bonds between M_n Clusters (M=Cu,Ag,Au and n=2-6) and Nucleophiles NH_3 and HCN

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Abstract

The most stable geometries of the coinage metal (or regium) atom (Cu, Ag, Au) clusters M_n for n up to 6 are all planar, and adopt the lowest possible spin multiplicity. Clusters with even numbers of M atoms are thus singlets, while those with odd n are open-shell doublets. Examination of the molecular electrostatic potential (MEP) of each cluster provides strong indications of the most likely site of attack by an approaching nucleophile, generally one of two positions. A nucleophile (NH_3 or HCN) most favorably approaches one particular M atom of each cluster, rather than a bond midpoint or face. In the closed-shell clusters, the interaction energies are highly dependent upon the intensity of the MEP, but this correlation fades for the open-shell systems studied in this work. The strength of the interaction is also closely related to the basicity of the nucleophile. Regium bond energies can be more than 30 kcal/mol and tend to follow the Au > Cu > Ag order. These interaction energies are in large part derived from Coulombic attraction, with a smaller orbital interaction contribution.

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1. Introduction

Enormous interest has been building in recent years concerning metal nanoparticles (NPs) due to the wide range of potential opportunities offered by this diverse group of nano-sized metal clusters. Their size, high surface-to-volume ratio, magnetic characteristics,[1] optical, electronic and catalytic properties,[2-4] relatively facile surface functionalization,[5] as well as inhibitory properties against the enlargement of cancer tumors or microbiological diseases[6-12] ignited their scrutiny and spread into many fields of modern science, as distant from each other as searching for new sources to convert solar energy into electricity, heterogeneous catalysis, or targeted anti-cancer treatment.[13-26] Despite the incontestable importance of NPs, the noncovalent interactions in which they participate has only been studied superficially to this point. In fact, it was only very recently, that the highly intriguing idea of the "regium bond" was introduced by Brinck et al.27 The authors computationally characterized sites on coinage metal atoms (also known as regium) copper, silver, and gold nanoparticles that interacted attractively with a variety of electron-donating molecules. They hypothesized that this novel interaction is grounded in the widely discussed σ-hole concept,[28-30] originally used to explain the halogen bond, and later extended to similar interactions such as chalcogen, pnicogen, tetrel or aerogen bonds.[31-38] The σ-hole model is based on the anisotropic electron density distribution[39-40] around the atom in question which is associated with a region of positive electrostatic potential on the extension of each R-X covalent bond (X=halogen, chalcogen, pnicogen, etc). In a more quantitative sense, the numerical value of the maximum on the molecular electrostatic potential (MEP) tends to correlate with the interaction energy[33,41,42] although there are notable exceptions.[43] This overall Coulombic attraction is supplemented by other forces such as charge transfer and dispersion.

The earlier work[27] had extended the idea of the σ-hole and its relation to noncovalent bond strength to metal nanoparticles such as M_9-M_{18} (M=Cu, Ag or Au), suggesting that the regium bond can be characterized as a member of the σ-hole bond family. Other related work[44] extended these ideas to much larger clusters: Au_n (n=13, 55, 147) and Pt_n (n=13, 55), which attributed the origin of the σ-holes to overlap of singly occupied s-orbitals in low-coordinated gold atoms, which ultimately results in catalytic activation of both gold and platinum nanoparticles. Other calculations identified a very uneven charge distribution in homonuclear silver clusters.[45] Propagating some of these ideas to charged systems, the structures and energies of neutral and charged Ag_n clusters (n=1-7)[46] identified all possible isomers of Ag clusters while testing various exchange-correlation functionals, among which, PBE0 appeared to be very accurate and reliable. Larger clusters, Ag_n (n=2-22), have also been considered[47] as well as clusters of Ag interacting with water molecules.[48] Noncovalent interactions were also the focus of another work, in this case between gold nanoclusters (Au_n, n=2, 4, 6, 8, 10 and 20) and imidazole,[49] which highlighted the greater strength of the Au⋯N vs. C-H⋯Au bonds. The computed interactions of Cu, Ag and Au clusters with SO_2 and NO_2[50] were analyzed very recently in terms of the ability of these sorts of clusters to act as air pollution hunters. The biologically relevant glucose molecule was allowed to interact with clusters of Au, Ag and Cu[51] where it was found that silver has the lowest and gold the highest affinity with glucose. The different complexes of general formula FM⋯H_2, MH⋯HF and HM⋯FH (where M was Cu, Ag or Au) were investigated by Grabowski and

Ruiperez[52]. For the first type of complexes studied there, they found very strong interactions between hydrogen and metal centers with features of a covalent bond. In the text of Joy and Jemmis[53] one can find the description of X−M···Y interactions (M – transition metal, Y – electron density donor) in comparison with typical model of X−Z···Y (Z – main group elements). The authors confirmed abilities of M atoms to establish complexes with electron-rich molecules by σ-hole based interactions. And in the most recent work to date, [54] complexation between NPs and aromatic surfaces was demonstrated by combining M_9 (M=Cu, Ag and Au) clusters with electron-rich π-systems.

As interest in this field continues to build, it would be timely and worthwhile to develop a full understanding of the fundamental principles involved in the noncovalent bonds between coinage metal clusters and various nucleophiles. How analogous are these interactions involving metal atoms to standard σ-hole bonds, and how predictive of the interaction energies are the various facets of the MEP? In addition to Coulombic forces, how strong are other aspects of noncovalent bonding such as charge transfer and dispersion? Since the metal clusters can in principle occur with various spin multiplicities, it is important to elucidate the relation of the particular spin state to the features and strength of the noncovalent bonding. In the clusters investigated selected Lewis bases are placed at various sorts of binding sites (σ-holes), so it would be useful to know how site position affects the binding. In an effort to construct this set of basic principles, it would be best to start with rather small clusters and then enlarge them gradually. This work thus considers clusters of sizes between two and six atoms, considering all three regium atoms Cu, Ag, and Au. As nucleophiles, both the strong NH_3 base and its weaker HCN cousin are allowed to interact with each cluster. Both open and closed shell clusters are considered for purposes of comparison.

2. Computational Methods

Geometries were fully optimized and molecular electrostatic potentials (MEPs) were calculated for isolated M_n clusters (M = Cu, Ag, Au and n= 2 – 6), as well as for their complexes with NH_3 and HCN at the MP2 level in conjunction with the aug-cc-pVDZ basis set . [55,56] These clusters were taken into consideration as they represent both open-shell and closed-shell model structures of nanoparticles. For the Cu, Ag and Au atoms, the aug-cc-pVDZ-PP basis set was applied so as to incorporate relativistic effects. [57] This level of theory has been demonstrated in numerous works to be reliable for a range of noncovalent interactions. [58-65] All structures were verified as local minima (with no imaginary frequencies) by vibrational analysis within the harmonic oscillator approximation.

The interaction energies, E_{int}, of the complexes were evaluated as the difference in energy between the complex and the sum of monomers within the dimer geometry, and corrected for basis set superposition error (BSSE) via the counterpoise procedure. [66] The energy required to distort the cluster to its geometry within each complex is designated E_{def}. All computations were carried out with the Gaussian 09 program suite. [67] Energy decomposition analysis (EDA) was performed at the PBE0-D3(BJ)/ZORA/TZ2P level by the ADF modeling suite using optimized

DFT geometries. [68-70] The MEPs of the isolated monomers were considered on the 0.001 au electron density isosurface, and its maxima ($V_{s,max}$) were located and evaluated using the MultiWFN and WFA-SAS programs. [71-73] It has been shown previously that the analysis of $V_s(r)$ on this isodensity surface is effective for qualitative and quantitative analysis. [74,75] Charge transfer and second-order interaction energies between the orbitals of interest were assessed by the NBO formalism at the PBE0-D3(BJ)/def2-TVZPP level of theory[76-78] using the 5.0 version of GenNBO program[79] spin density isosurfaces were visualized with Chemcraft software. [80]

3. Results
3.1. Isolated M_n clusters

The MP2 optimized structures of M_n (M = Cu, Ag, Au and n= 2 – 6) clusters of lowest energy are displayed in Fig. 1, along with the labeling of the various interatomic distances. All of these geometries are planar, a characteristic which is confirmed by DFT, as well as available literature data. [46,47,81] In all of these clusters the ground electronic state is that with the lowest possible spin state, viz. singlet for M_n (n= 2, 4 and 6) and doublet for M_3 and M_5. As reported in Table 1, there is a clear separation between the lowest-multiplicity state and those above it.

[Insert Fig. 1 about here]

[Insert Table 1 about here]

The smallest such separation is 10 kcal/mol for Cu_6, and others are considerably higher, as large as 81 kcal/mol for Au_2. It might be mentioned as well that the higher spin states of M_5 and M_6 tend to deviate from planarity. In the particular cases of the Cu_3, Ag_3, and Au_3 trimers, Jashmidi *et al.* [51] had earlier found that increasing multiplicity decreases their stability. CAM-B3LYP computed the doublet-quartet gaps for these three trimers as 54.7, 46.1 and 54.5 kcal/mol, respectively, comparable to our own data.

Regarding certain details of the cluster geometries, the trimers are not equilateral triangles. As indicated in Table 2, the two R1 lengths are less than the remaining R2 for Cu_3 and Ag_3, while the reverse is true for Au_3. Similar geometries have been reported previously for the Ag_3 trimer. [46,47,81] The origin of the structure of the Ag_3 trimer has been explained in terms of the Jahn−Teller effect. [46] The tetramers take the shape of a rhombus with all four peripheral distances equal to one another, and with R2 separating the two vertices of the rhombus, with R2 < R1. Unlike the trimers, M_6 can be described as an equilateral triangle.

[Insert Table 2 about here]

Concerning the doublet nature of M_3 and M_5 the distribution of the spin density may play some role in their interactions with other molecules. The DFT spin densities (ρ_s) are displayed in Fig. 2 for the representative silver trimer and pentamer. There appears to be a preponderance of

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spin density on atoms 1 and 2 in the trimer, which are separated from one another by 2.873 Å, larger than the other two interatomic separations of only 2.592 Å. Likewise in the pentamer where atoms 1 and 2 are further separated than are the remaining Ag atoms. These distinctions are reflected in the spin densities assigned to individual atoms in Table 3.

[Insert Fig. 2 about here]

[Insert Table 3 about here]

The atomic spin densities for Cu_3 resemble those of Ag_3 rather closely. This situation is reversed in Au_3, where the different shape of Au_3 places atoms 1 and 2 closest to one another, leaving the lion's share of spin density on atom 3. In the case of the pentamers, all systems agree that the two atoms 1 and 2 on the top of the diagram encompass more of the spin density than any of the other three atoms.

As two molecular systems approach one another, the first type of interaction they will feel at long range derives from Coulombic forces, which are of longer range than either dispersion or orbital interaction energies. The MEPs of the M_n clusters are illustrated in Fig. 3 where the most positive regions are indicated in red, and negative in blue. These diagrams also depict the locations of the maximum and minimum of the MEP on the isodensity surface, $\rho=0.001$ au. $V_{s,max}$ is located on either end of each dimer. The trimers, as well as the higher-order clusters, contain more than one $V_{s,max}$ point. That of higher numerical value, designated (a) is located above the apex atom for Cu_3 and Ag_3, and the smaller one (b) near the midpoint of the other two atoms. The order of these two is reversed in Au_3, consistent with the geometry change noted above. The locations of the other maxima are also displayed in Fig. 3. The values of these potential maxima are reported in Table 4. In order to compare obtained results with the different level of theory, the additional calculations were performed using PBE0-D3(BJ) functional with def2-TVZPP basis set. The results are collected in Table S1. As is seen from this table, the trimers are not equilateral triangles, as it was predicted by the MP2 method. The MEPs analysis using DFT functional followed the values of maxima obtained earlier with good accuracy. Only in the case of the gold trimer the minor deviation has been found.

To clarify all possible discrepancies concerning the geometry of isolated molecules, the calculations with inclusion of the spin-orbit coupling were carried out with usage of the ADF code at the PBE0-D3(BJ)/ZORA/TZ2P level of theory for all trimer clusters investigated in this work.

The results revealed that the gold trimer exhibits the distances of the perfect equilateral triangle with R equals 2.65 Å when the spin-orbit effect is taken into account. In the case of the copper and silver trimer even now the R2 distance is elongated significantly, though. With respect to the copper trimer the R2 is 2.605 Å (longer by 0.305 Å than R1) while the silver trimer is characterized by R2 which equals 2.916 Å (longer by 0.258 Å than R1). These Cu_3 and Ag_3 geometries are intact after including spin-orbit effect as the results for them are in agreement

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with those obtained using MP2 methodology. It is worth to mention that the role of spin-orbit effect in determining the final geometry of certain coinage metal clusters was reported in the literature [82-85].

[Insert Fig. 3 about here]

[Insert Table 4 about here]

There is a general tendency of $V_{s,max}$(a) to reach its apex for the trimer, and then diminish gradually with n. There is a small deviation from this pattern for Au_n, where the dimer has a slightly larger MEP maximum than does the trimer.   Note that the secondary $V_{s,max}$(b) is consistently far weaker than its higher intensity counterpart $V_{s,max}$ (a). In the particular case of the pentamers, a third maximum arises, as indicated in Fig. 3, but its magnitude is far smaller than even $V_{s,max}$(b), hovering around a value of 0.

3.2. Closed-shell complexes

The optimized geometries of the closed-shell M_n (M=Cu, Ag, Au and n=2, 4 or 6) complexes with NH_3 and HCN are illustrated in Fig. 4. Although there may be several other local minima, focus was placed on the most important minima wherein the base approaches the maxima in the MEP, both $V_{s,max}$(a) and (b). The N···M distances and M···N-C angles for selected dimers are gathered along with BSSE corrected interaction energies (E_{int}) in Table 5.

[Insert Fig. 4 about here]

[Insert Table 5 about here]

The N···M distances falls into the 1.782-1.997 Å range for the Cu complexes, and are longer, 2.191-2.489 Å and 1.974-2.301 Å for Ag and Au atoms, respectively. These distances are all considerably smaller than the sum of the van der Waals radii of 4.04, 4.19 and 3.98 Å, respectively. [86] The θ(M···N-C) angle for the HCN complexes is linear, or very nearly so. Although the vast majority of complexes are planar, three exceptions were observed. When Cu_6 is combined with both NH_3 and HCN, it adopts a nonplanar geometry, as illustrated in Fig. S1. This particular structure of the isolated Cu_6 cluster is less stable than the planar conformer by 1.06 kcal/mol. However, in rearranging in this fashion, the nonplanar cluster creates an intense $V_{s,max}$ of 33.1 kcal/mol, larger by 7.2 kcal/mol than $V_{s,max}$(a) in the planar geometry. It is this intensified maximum which can attract the bases even more strongly than can the planar cluster, resulting in a lower overall energy. The NH_3···Ag_6(b) complex is deformed from planarity as well (Fig. S2) but its deformation is more subtle and does not lead to significant energetic consequences.

The interaction energies vary over a broad range from -2.97 to -34.20 kcal/mol, and obey a number of systematic trends. For instance, NH_3 consistently binds more strongly than does HCN. As anticipated based on their more intense MEP maxima, a-type complexes are stronger than b (with the Cu exceptions noted above). With respect to the more stable a-dimers, interaction energies climb in the order Ag < Cu < Au, with the exception of the HCN···M_6(a) complexes where Cu and Ag switch places. With respect to cluster size M_4 appears to be bound most strongly, followed by n=2 and then n=6. Also included in Table 5 are the deformation energies required to transition each cluster from its fully optimized structure to the geometry it adopts within the context of the dimer. E_{def} is typically quite small, 2 kcal/mol or less, which generally amounts to less than 6% of the interaction energy. The largest deformations are associated with the secondary MEP maxima, for the Au_4 and Ag_6 complexes, but even these are less than 3 kcal/mol.

As indicated above, the most stable cluster geometries are planar as are the majority of the complexes. The exceptions are the dimers involving the secondary MEP of the Cu_6 cluster, wherein the latter adopts a nonplanar, cage-like structure, as shown in Fig. S1. This dimerization must therefore overcome a rearrangement energy penalty to form this particular dimer. This penalty amounts to only 1.05 kcal/mol for Cu_6. Cu_5 also has a secondary minimum which is nonplanar, 1.31 kcal/mol higher in energy than the planar conformation, as indicated in Table S2. Note, however, that this penalty rises quickly for heavier regium atoms Ag and Au, amounting to more than 25 kcal/mol for Au_6. It is these large penalties which prevent the formation of complexes involving such nonplanar clusters. In fact, other workers had also noted nonplanar distortions of Cu clusters upon formation of complexes with SO_2.[51]

One might anticipate a direct relation between E_{int} and $V_{s,max}$, and indeed such a relation was observed recently by Brinck *et al.*,[27] for complexes of NH_3 with various binding sites of the particular Ag_9 cluster. This sort of relationship is confirmed here for the closed-shell complexes in Table 5. Of course, due to the differing basicities of NH_3 and HCN, the data must be compared separately for each. These correlations between E_{int} and $V_{s,max}$ are displayed in the six diagrams of Fig. S3 for each of the three metal atoms. The R^2 correlation coefficient varies between 0.890 and 0.956, which supports the notion that Coulombic interactions play an important role in the binding of these complexes.

Another window into the forces responsible for the geometries and energetics of these complexes can be gleaned from a decomposition of the total interaction energy into meaningful physical components. The EDA/PBE0-D3(BJ)/ZORA/TZ2P decomposition results are collected in Table 6 for the complexes involving Ag.

[Insert Table 6 about here]

The total DFT-EDA interaction energies reproduce the MP2 interaction energies rather closely, with RMSD=0.69 kcal/mol. The electrostatic attraction accounts for a large share of the total interaction energy, between 62% and 74%. The second leading component is much smaller

with orbital interaction (which includes charge transfer, polarization and induction effects) amounting to 25-30%. The dispersion contribution is very small less than 5% in most cases. The sum of the Pauli and electrostatic terms can be thought of as a steric term of sorts. This sum is generally quite small, 8 kcal/mol or less for these systems. From this perspective, the orbital interaction term, which is considerably larger, takes on added significance. To summarize, the attractive forces of regium bonded complexes are very much like those observed in other σ-hole bonded species, e.g. aerogen or tetrel bonds. [87,88] An alternate way of looking at orbital interactions considers individual MOs on each molecule via the NBO formalism. The primary interaction involves charge transfer from the N lone pair of the base into a σ* antibonding orbital of the cluster which includes the M atom to which the base is attached. The energetic manifestation of this particular charge transfer is measured as E(2) and is listed in Table 7 for the Ag complexes. The EDA analyses results for the Cu and Au closed-shell complexes with ammonia are presented in Table S3. The distribution of percentage contribution to the total attractive forces is similar to that for Ag complexes. However, in the case of Au complexes it is clearly seen that the influence of orbital interaction raises up to 35% and contribution of electrostatic falls down of about 10 %.

[Insert Table 7 about here]

Like the interaction energies themselves, these energies are larger for NH_3 than for HCN, and the a complexes show more charge transfer than their b counterparts. The total charge transferred from the base to the cluster, regardless of orbital sources, is tabulated in the last column of Table 7. This quantity is rather moderate and ranges from 2 to 72 me, placing them in the same range as in the case of halogen bonded complexes between NH_3 and SCS. [43] The pattern of total charge transfer between subunits mimics the E(2) energies as the latter accounts for a major part of all orbital interactions involved in the stabilization of these complexes.

3.3. Open-shell complexes

The optimized geometries of the open -shell complexes containing 3 and 5 M atoms are depicted in Fig. 5, again for both a and b types of $V_{s,max}$, as well as the less intense c maxima. Their interaction energies are compiled in Table 8, along with relevant geometrical parameters.

[Insert Fig. 5 about here]

[Insert Table 8 about here]

While the θ(M⋯N-C) angles are fully linear for most of the HCN complexes with the trimers, there is some deviation for the pentamers, but still less than 8º. It is interesting to note that the a and b interaction energies are very similar to one another, as are the intermolecular separations, even though the two values of $V_{s,max}$ differ by a great deal (see Table 4). The

footnote to Table 4 had indicated the presence of a third maximum in the MEP for these open-shell systems, albeit of very low intensity, not even necessarily of positive sign. One would thus not anticipate these maxima would be able to attract a nucleophile, but in fact, corresponding minima do appear on the potential energy surface of the pentamers. Even more surprising are the fairly large interaction energies in Table 8, only slightly smaller than the a and b maxima of Ag_5 and Au_5. This interaction is even stronger for Cu_5, although this particular structure profits from a deformation of the cluster from planarity. In any case, it is clear that there is little correlation between interaction energy and $V_{s,max}$ for these open-shell systems. The DFT gained results presented in Table S4 are in line with those obtained at higher level of theory and support the observation of the lack of correlation between energies and electrostatic potential maxima.

Perhaps associated with this surprising similarity of interaction energies is the distribution of spin density within these open-shell structures. As noted in Fig. 2, this spin density is unequally distributed around the M_n clusters. However, as the cluster is attacked by the nucleophile, this density shifts away from the metal atom at the point of attack, and toward the remainder of the cluster. This phenomenon is illustrated graphically in Figures S4 and S5 for the trimer and pentamer of Ag, respectively. A quantitative assessment of this redistribution can be gleaned from the atomic spin densities reported in Tables S5 and S6 where it is apparent that the bonding to the nucleophile completely eliminates any spin density on the interacting metal atom, with its spin density dropping to 0 in the trimer. The spin density is not completely eliminated within the pentamer but is drastically reduced.

Decomposition of the interaction energy in Table 9 (for Ag dimers) and Table S7 (for the Cu and Au complexes with ammonia) confirms the overall finding of little difference between (a) and (b) geometries. Moreover the breakdown is very similar to that obtained for the closed-shell systems in Table 6. and Table S3. Much the same can be said of the NBO analyses of the open-shell systems in Table S8, which are of roughly the same magnitude as the transfers in the closed-shell systems.

[Insert Table 9 about here]

Comparison of the data in Tables 5 and 8 leads to a general trend in terms of how the size of the cluster affects the interaction energy. The M_3 and M_4 clusters generally bind most strongly, which is consistent with the pattern of MEP maxima in Table 4. There does not appear to be any dramatic difference between open and closed-shell clusters.

One may wonder whether this pattern is limited to only planar clusters as neutral silver clusters transition from planar to cage-like structure when the number of atoms is larger than 6. [47] To address this issue, additional calculations were carried out for the larger, nonplanar silver cluster Ag_7. The optimized structure may be termed a pentagonal bipyramid with a pair of apical atoms (denoted Ag6 and Ag7) and 5 atoms in the base. As indicated in Table S9 and presented in Fig. 6, the spin density is located completely on the two apical atoms.

[Insert Fig. 6 about here]

This complex contains two types of $V_{s,max}$, as do most of the planar systems described above. The more intense maximum (a: 17.75 kcal/mol) is located on each of the five equatorial atoms, with no spin density. The secondary MEP maximum (b: 3.34 kcal/mol) is associated with each of the two apical atoms, coincident with the spin density. The former is a bit smaller than its value in the five and six-membered Ag clusters. The latter is comparable to that for Ag_6 but smaller than in the pentamer. The MP2 interaction energies calculated for the $NH_3\cdots Ag_7$(a) and $NH_3\cdots Ag_7$(b) complexes are: -12.78 and -9.99 kcal/mol, respectively, quite similar to their planar Ag_6 analogues (-13.01 and -10.24 kcal/mol, respectively).

3.4. Other Types of Complex

While the MEP maxima of each cluster certainly offer attractive sites for the approach of a nucleophile, there is no guarantee that they represent the only possible locations where a nucleophile might bind. Searches were therefore carried out to explore the possibility of other minima, using the Ag clusters as a testing ground at the DFT level. No other minima were identified for the Ag_2 and Ag_3 clusters with NH_3. The Ag_4 cluster formed an association with NH_3, but rather weakly bound by only 2.65 kcal/mol. Moreover, as indicated in Table S10, there is no regium bond present, as the N lone pair is turned away from the cluster. Further perusal of this table shows a number of other complexes of NH_3 with Ag clusters, but all have the same character, weakly bound and with the same direction of the N lone pair.

With its ability to act as proton donor in a H-bond, HCN can act in this role when combined with certain Ag clusters, as illustrated in Table S11. However, the ineffectiveness of these clusters as proton acceptors limits the strength of such H-bonded complexes to 5 kcal/mol or less. On the other hand, much stronger dimers emerge in certain cases. When associated with Ag_3, the HCN becomes nonlinear as its C and N atoms individually approach two Ag atoms, with a total interaction energy of 27.6 kcal/mol. An even stronger complex of similar shape, with E_{int} of 35.1 kcal/mol occurs for the Ag pentamer. With respect to the closed shell tetramer, one sees a weaker complex, 10.9 kcal/mol, wherein both C and N atoms approach the same Ag center. This sort of $Ag\cdots C$ interaction has been observed previously, as in neutral and charged $Ag_n\cdots CO$ complexes. [45] While these sort of complexes are not the principal focus of this study of regium bonding, their strength should stimulate further study.

4. Conclusions and Discussion

The most stable geometries of the clusters are planar, and adopt the lowest possible spin multiplicity. The nucleophile most favorably approaches one particular atom, rather than a bond midpoint or polyhedron face. This point of attack is generally the atom associated with the most intense maximum in the MEP of the cluster. A principal conclusion derived from this work is as follows: while the interaction energy is closely connected with the value of $V_{s,max}$ in the closed shell systems, the same is not true of the open-shell planar counterparts. NH_3 engages in stronger regium bonds than does HCN, due to its higher basicity. The regium bond energies

range between 10 and 36 kcal/mol, and tend to follow the pattern Au > Cu > Ag. There is not a clear correlation between cluster size and interaction energy, but n=3 and 4 appears to engender the strongest bonds. The major contributor to these interaction energies is electrostatic attraction. Orbital interaction is less important, and dispersion makes a negligible contribution.

The results presented in this work can be placed in a wider context by comparison with the literature involving related systems. Adducts between coinage metal clusters and various nucleophiles have been the theme of a number of studies. For instance, complexes between slightly larger Ag_9 NPs and CO, H_2O, NH_3 or H_2S were investigated at the DFT level. [27] With respect to the strongest Ag_9 complex with NH_3, the N···Ag distance was optimized to 2.33 Å, very similar to our own values for the slightly smaller Ag clusters. In overview of all NH_3 complexes, the interaction energies at the seven different binding sites of Ag_9 range from about -7 to -13 kcal/mol, with an average of -10.6 kcal/mol), again in good coincidence with our calculated quantities. The authors found a linear correlation between $V_{s,max}$ and interaction energies, with a correlation coefficient R^2 of 0.961. Similar correlations have also been found[44] for the somewhat larger Au_{13} cluster complexes with CO and H_2O. Our finding of a poor correlation in the smaller open-shell cluster complexes, at both MP2 and DFT levels, is thus a bit surprising. This distinction may reflect on the cluster shapes: It may be perhaps that this correlation is poorest when the open-shell clusters are planar.

Retaining focus on open-shell systems, it was noted above that there is little to distinguish the energetics of the a and b complexes for n=3 and n=5. However, when n increases to 7, the cluster loses its planarity, taking on a trigonal bipyramid shape, and it is here that the binding energy is quite different depending upon whether the NH_3 binds to one of the apical or equatorial Ag atoms. One may speculate that this is a common feature, and that the energetic preference of binding to one site of the cluster over another will rise along with the cluster size. Such a preference makes these systems more like their closed-shell counterparts for which interaction energy is heavily dependent upon binding site, even for planar systems with small *n*.

In summary, the rather strong binding energies of M clusters with bases can be attributed in large part to their uneven charge distributions, resulting in pockets of highly positive MEP that attract the lone pairs of these bases. This uneven charge distribution has been found in a number of prior studies, as in Ag_n clusters with surprisingly large dipole moments[45] that were able to bind CO molecules, or in larger clusters. [27,44,54]

One might think that along with positive regions, there ought to be counterbalancing areas of negative MEP that might attract a Lewis acid. However, when a number of water molecules are placed around Ag_n clusters, it is the O lone pair that is attracted[48] to the positive regions of the cluster MEP, as opposed to the H atoms which could in principle form a strong H-bond with any region of negative MEP. Only the O atoms of SO_2 and NO_2 directly approach the clusters of Cu, Ag, or Au. [50] On the other hand, these negative areas, also called "σ-lumps", do seem capable[54] of attracting the positive regions above certain appropriately substituted aromatic systems. It might be noted parenthetically that the addition of non-metal atoms into the cluster

itself, as in $(TiO_2)_n$, greatly weakens binding with a base like H_2O or NH_3, reducing the interaction energy[89] to less than 2 kcal/mol.

On the other hand, there does seem a possibility of this sort of H-bond, but only when secondary to the primary interaction with the MEP maximum. For example, when imidazole molecules are placed in the vicinity of Au_n clusters, [49] it is the basic N atom that is drawn toward the cluster, with longer and weaker CH--Au secondary interactions serving an auxiliary function in certain cases. H_2O, H_2S, and BH_3 all forgo H-bonds with Ag_n clusters in favor of acting as Lewis bases. [27] It is also the basic O atoms that are preferentially bound[51] to M_3 clusters, with only secondary OH··M interactions, when the larger glucose molecule is bound. One can also consider however that negative regions of MEP, so-called σ-lumps, have a role to play in these and other molecular interactions. [27,54]

A pattern emerged in one study[50] that the open-shell clusters with odd numbers of M atoms engaged consistently in stronger interactions with SO_2 and NO_2 than did their closed-shell counterparts, a trend which is not repeated here for the simpler bases NH_3 and HCN. This distinction may have to do with the bifurcated arrangement of the former molecules with respect to the cluster, coupled with their more complicated electronic structure. Another difference for these two particular molecules is that their regium binding energies followed a Cu > Ag > Au order.

There are points of confirmation of other aspects of our results. For example, the optimal shapes of our clusters agree with previous findings[46,47] that also found the state with lowest spin multiplicity to be most stable. Our general range of regium bond energies fit in with earlier calculations, [27,45,49,51] albeit for somewhat different clusters and bases. There have also been correlations noted between the binding energy and the maximum in the MEP. [27] On the other hand the same order as found here emerges when the binding molecule is glucose. [51]

It is worth noting that a very recent work[54] has extended the concept of a base within the context of a regium bond to interaction with the π-system of an aromatic ring. The interaction energy does not suffer from this substitution, with values as high as 30 kcal/mol. On the other hand, these large quantities may be due to the presence of more than one such interaction, as in the case of anthracene with its three aromatic rings and the possibility of three simultaneous regium bonds.

In terms of decomposition of the interaction energy in these regium bonds, the calculations reported above represent the first such analysis. In this context, the nature of the regium bond does not distinctly differ with the general family of noncovalent interactions that include aerogen and tetrel bonds. [87,88] A recent survey[90] examined a wide range of Lewis acid–Lewis base complexes, including the above as well as H-bonds, halogen, pnicogen and chalcogen bonds, and concluded that they have much in common. Based on the results reported above, it appears that regium bonds fall into this same general category.

Conflicts of interest

There are no conflicts to declare.

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Figures captions

Fig. 1 MP2 optimized structures of lowest-energy M_n (M = Cu, Ag, Au and n= 2 − 6) clusters. Calculations performed at the MP2/aug-cc-pVDZ-PP level.

Fig. 2 DFT spin density isosurfaces ($\rho=\pm0.006$ a.u.) calculated in doublet state of Ag_3 and Ag_5. Orange color corresponds to positive values of spin density and purple color to negative values. Calculations performed at the PBE0-D3(BJ)/def2-TVZPP level of theory.

Fig. 3 MEPs of lowest-energy isolated M_n (n= 2 – 6) clusters, computed on the 0.001 au isodensity surface at the MP2/aug-cc-pVDZ-PP level. $V_{s,max}(a)$ and $V_{s,max}(b)$ refer respectively to the larger and smaller maximum. Point groups are given in parenthesis.

Fig. 4 MP2 optimized structures of closed-shell M_n (M = Cu, Ag, Au and n= 2, 4, 6) complexes with ammonia and hydrogen cyanide. MP2/aug-cc-pVDZ /aug-cc-pVDZ-PP level of calculation.

Fig. 5 MP2 optimized structures of open-shell M_n (M = Cu, Ag, Au and n= 3, 5) complexes with NH_3 and HCN. Level of calculations MP2/aug-cc-pVDZ/aug-cc-pVDZ-PP.

Fig. 6 DFT spin densities isosurfaces (±0.006 a.u.) calculated in doublet state of Ag_7. Calculations performed at the PBE0-D3(BJ)/def2-TVZPP level of theory.