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# A Coupled-Cluster Study on the Noble Gas binding Ability of Metal Cyanides Versus Metal Halides (Metal = Cu, Ag, Au)

Sudip Pan,<sup>[a]</sup> Ashutosh Gupta,<sup>[a,b]</sup> Ranajit Saha,<sup>[a]</sup> Gabriel Merino,<sup>\*,[c]</sup> and Pratim K. Chattaraj<sup>\*,[a]</sup>

A coupled-cluster study is carried out to investigate the efficacy of metal(I) cyanide (MCN; M = Cu, Ag, Au) compounds to bind with noble gas (Ng) atoms. The M—Ng bond dissociation energy, enthalpy change, and Gibbs free energy change for the dissociation processes producing Ng and MCN are computed to assess the stability of NgMCN compounds. The Ng binding ability of MCN is then compared with the experimentally detected NgMX (X = F, Cl, Br) compounds. While CuCN and AgCN have larger Ng binding ability than those of MCl and MBr (M = Cu, Ag), AuCN shows larger efficacy toward bond formation with Ng than that of AuBr. Natural bond

orbital analysis, energy decomposition analysis in conjunction with the natural orbital for chemical valence theory, and the topological analysis of the electron density are performed to understand the nature of interaction occurring in between Ng and MCN. The Ng—M bonds in NgMCN are found comprise an almost equal contribution from covalent and electrostatic types of interactions. The different electron density descriptors also reveal the partial covalent character in the concerned bonds. © 2015 Wiley Periodicals, Inc.

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## Introduction

The so called “shyness” of noble gas (Ng) atoms toward the formation of a chemical bond originates from their completely filled valence shell electronic configuration, which keeps them away from participating in the electron sharing or electron transfer phenomena with another atom. Although based on the knowledge of the ionization potential and polarizability values of the Ng atoms, the possible existence of xenon and krypton fluorides was predicted,<sup>[1,2]</sup> earlier experimental attempts could not verify it.<sup>[3,4]</sup> As a result, during a long phase before the reporting of the first noble gas compound, xenon hexafluoroplatinate,  $\text{Xe}^+[\text{PtF}_6]^-$ , by Bartlett<sup>[5]</sup> in 1962, the inertness of Ng atoms was considered to be insurmountable. In fact, in 1924 renowned chemist Friedrich Paneth<sup>[6]</sup> wrote from his knowledge that “the unreactivity of the noble gas elements belongs to the surest of all experimental results,” which clearly represents the general view of the scientists regarding the reactivity and the possibility of synthesizing Ng compounds during that period. However, Bartlett’s accidental success to isolate a stable xenon compound broke this long lasting thought about Ng atoms. It created so much frenzy in the related field that in the same year few more xenon compounds were prepared experimentally.<sup>[7,8]</sup> Since then, the field related to Ng chemistry has been passing through rapid phase of development as both experimental<sup>[9–13]</sup> and theoretical chemists<sup>[14–20]</sup> find synergy in their complementary roles in predicting, isolating, synthesizing, characterizing, and analyzing the new Ng compounds.<sup>[21]</sup>

Less reactivity of coinage metals has also been a matter of curiosity, which in fact has resulted in crowning them as “precious metals.” The effort of combining two low reactive species, noble metal and noble gas, is even more challenging.

In 1995, Pyykkö<sup>[22a]</sup> predicted the stability of  $\text{NgAu}^+$  and  $\text{NgAuNg}^+$  through a coupled-cluster method (CCSD(T))-based study, which were detected in mass spectroscopy three years later.<sup>[22b]</sup> It was also argued that there exists significant degree of covalent character in between gold and heavier Ng atoms.<sup>[22]</sup> However, this argument was then challenged by Buckingham and coworkers,<sup>[23]</sup> who expressed that the bonds between Ng and Au originate from the long-range effects of polarization and dispersion. It was in the year 2000, Gerry and coworkers<sup>[12a]</sup> detected  $\text{ArAuCl}$  and  $\text{KrAuCl}$  via rotational spectroscopy whereas in the same year while attempting to isolate  $\text{AuF}$ , Seidel et al.<sup>[24]</sup> discovered a reddish solid that turned out to be  $\text{AuXe}_4^{2+}$ . Their findings helped in the discovery of more Ng-transition metal compounds wherein Ng atoms were found to act as weak ligands. In subsequent years, Gerry and coworkers<sup>[12]</sup> spectroscopically characterized a series of  $\text{NgMX}$  (Ng = Ar, Kr, Xe; M = Cu, Ag, Au; X = F, Cl, Br) compounds

[a] S. Pan, A. Gupta, R. Saha, P. K. Chattaraj  
Department of Chemistry and Centre for Theoretical Studies, Indian Institute of Technology, Kharagpur, 721302, India  
E-mail: pkc@chem.iitkgp.ernet.in

[b] A. Gupta  
Department of Chemistry, Udai Pratap Autonomous College, Varanasi, Uttar Pradesh, 221002, India

[c] G. Merino  
Departamento de Física Aplicada, Centro de Investigación y de Estudios Avanzados Unidad Mérida, km 6 Antigua carretera a Progreso. Apdo. Postal 73, Cordemex, 97310, Mérida, Yuc., México  
E-mail: gmerino@mda.cinvestav.mx

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whereas a number of theoretical studies<sup>[25]</sup> on them were also carried out exploring the stability and nature of bonding therein. Recently, NeAuF was also detected via matrix infrared spectroscopy by Wang et al.<sup>[26]</sup> The Ng binding ability of MOH (M = Cu, Ag, Au) was also investigated theoretically.<sup>[27]</sup> The possibility of insertion of Ng atoms within M-F or M-OH (M = Cu, Ag, Au) was also explored by Ghanty.<sup>[28]</sup>

In this article, we have carried out a coupled-cluster-based study to assess the Ng binding ability of experimentally available metal(I) cyanide (MCN)<sup>[29]</sup> where M being Cu, Ag, and Au. Note that the free monomeric MCN molecules were also detected in gas phase.<sup>[29e,29j]</sup> Furthermore, we have compared the Ng binding ability of MCN with those of MX (X = F, Cl, Br). Dissociation energy and thermochemical parameters such as enthalpy change ( $\Delta H$ ) and Gibbs free energy change ( $\Delta G$ ) are computed to assess the efficacy of Ng binding ability of the studied systems. The nature of bonding between M and Ng centers is analyzed through an energy decomposition analysis (EDA)<sup>[30]</sup> and a detailed analysis of the electron density.<sup>[31]</sup>

## Computational Details

NgMCN and NgMX compounds along with their respective bare moieties are optimized at the CCSD(T)/def2-TZVPPD level.<sup>[32,33]</sup> Characterizations of the nature of stationary points as well as the zero-point vibrational energy (ZPE) corrections are done by the computation of harmonic vibrational frequencies. All the structures studied here are local minima on the corresponding potential energy surfaces as indicated by the real values of all the harmonic vibrational frequencies. To check whether the present single reference-based electron correlation procedure is adequate to represent these systems properly, we have computed  $T_1$  diagnostic<sup>[34]</sup> (see Table S1 in Supporting Information). Except for He-Ar bound CuCN and He/NeAuCN compounds, for the other systems it is less than the limiting value, 0.02. As the  $T_1$  values for the above mentioned compounds are not significantly large compared to 0.02, we believe that the presently chosen level of theory provides reliable results for these systems. For the core electrons of the Xe, Rn, Ag, and Au atoms, a quasi-relativistic pseudopotential is used.<sup>[35]</sup> Natural population analysis (NPA) is performed to compute the charge ( $q$ ) at each atomic center. The standard counterpoise method proposed by Boys and Bernardi<sup>[36]</sup> is adopted for the correction of basis set superposition error (BSSE). In the present article, we have only discussed M-Ng dissociation energy corrected from both ZPE and BSSE ( $D_0^{\text{BSSE}}$ ).  $\Delta H$  and  $\Delta G$  are computed at 298 K and one atmospheric pressure. Wiberg bond index (WBI)<sup>[37]</sup> is computed to evaluate bond orders. All the CCSD(T) computations, NPA and WBI calculations are performed using Gaussian 09 program package.<sup>[38]</sup> EDA<sup>[30]</sup> in conjunction with the natural orbital for chemical valence (NOCV)<sup>[39]</sup> is carried out at the PBE-D3/QZ4P//CCSD(T)/def2-TZVPPD level<sup>[40]</sup> using ADF2013.01 program package.<sup>[41]</sup> The scalar zero-order regular approximation, ZORA,<sup>[42]</sup> is included for the heavier atoms. In this energy partitioning scheme, the total interaction energy ( $\Delta E^{\text{total}}$ ) is divided into three attractive terms and one

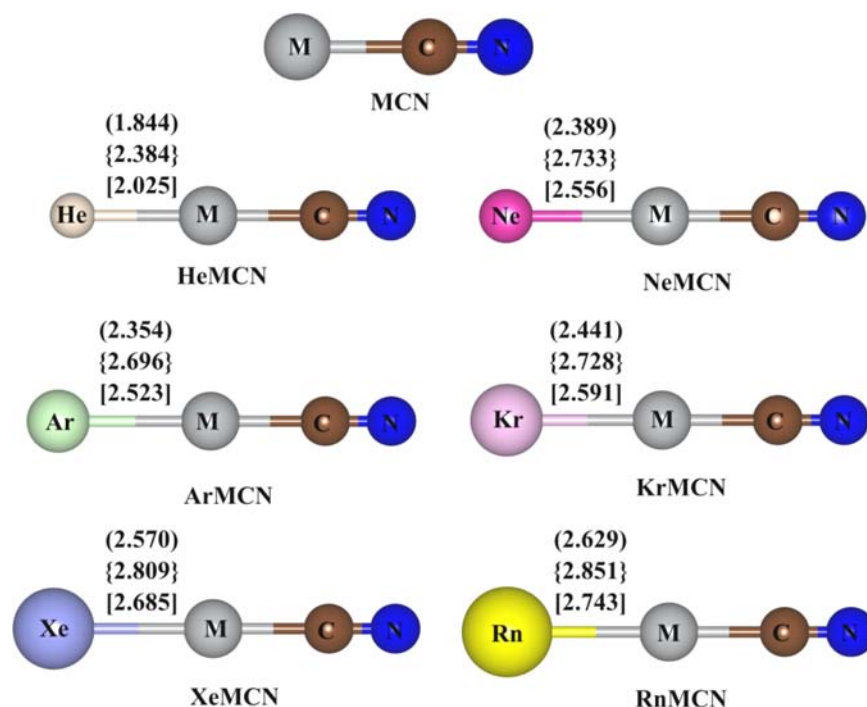
repulsive term, viz., (1) electrostatic term,  $\Delta E^{\text{elstat}}$ , which represents the classical electrostatic interactions between two fragments having the frozen charge distribution as that in the "super-molecule," (2) orbital term,  $\Delta E^{\text{orb}}$ , which accounts for the interactions between occupied molecular orbitals of one fragment with the unoccupied molecular orbitals of another fragment, termed as charge transfer, as well as the mixing between empty and occupied orbitals on the same fragment, termed as polarization, (3) dispersion term,  $\Delta E^{\text{disp}}$ , which describes the dispersion interaction between two fragments, and (4) Pauli repulsion,  $\Delta E^{\text{Pauli}}$ , which represents the repulsive Pauli interaction between the occupied orbitals of the interacting fragments.

The topological analysis of the electron density<sup>[31]</sup> analysis is performed at the MP2/def2-TZVPPD/WTBS//CCSD(T)/def2-TZVPPD level<sup>[43]</sup> using Multiwfn software.<sup>[44]</sup> All electron WTBS<sup>[45]</sup> basis set is used for Ag, Au, Xe, and Rn atoms.

## Results and Discussion

The ground state geometries of MCN (M = Cu, Ag, Au) compounds and their Ng bound analogues correspond to a  $C_{\infty v}$  point group and  $^1\Sigma_g$  electronic state (see Fig. 1). The related results regarding  $D_0^{\text{BSSE}}$ ,  $\Delta H$ ,  $\Delta G$ , NPA charge on M and Ng centers, WBI, and highest occupied molecular orbital (HOMO)–lowest unoccupied molecular orbital (LUMO) energy gap values of NgMCN are provided in Table 1. The charge on Cu and Ag centers in MCN is found to be same as 0.82 |e| whereas the charge on Au center in AuCN is relatively low (0.63 |e|). In fact, not only in MCN, in cases of MX, the charge on Au center is also found to be less than those on Cu or Ag (see Tables S2–S4 in Supporting Information for the results of MX). It is already known in the literature that due to its very large relativistic effect, Au shows unique and anomalous properties.<sup>[47]</sup> The relativistic effect in Au leads to the contraction of the valence 6s orbital and the expansion of the inner 5d orbital and consequently the overall covalent radius of Au gets reduced (1.36 Å, 0.1 Å less than Ag).<sup>[46]</sup> It further increases its electronegativity. While the electronegativity of Cu and Ag in Pauling scale is around 1.9, the same for Au is relatively high (2.5). This is reflected in the corresponding positive charges on M centers in MCN. Pyykkö<sup>[48]</sup> in his review on gold commented that among the coinage metals, only the chemistry associated with Ag is normal. Anomaly in Cu comes from the compact nodeless d shell resulting in high inter-electronic repulsion.

As He and Ne atoms are quite loosely bound with M center, we have provided the related results in the Supporting Information (see Table S5) and herein we have discussed the results only for the Ar-Rn bound analogues. For NgCuCN and NgAuCN,  $D_0^{\text{BSSE}}$  values range within 5.4–11.0 kcal/mol and 5.8–14.6 kcal/mol, respectively, whereas the same for NgAgCN is found to be relative small ranging from 2.7 to 8.1 kcal/mol. For a given M center,  $D_0^{\text{BSSE}}$  value increases with an increase in the size of Ng atoms, which is further connected with the increased polarizability. Conversely for a given Ng, the Ng binding ability of MCN follows the order of AuCN > CuCN > AgCN. Note that in cases



**Figure 1.** Pictorial depiction of NgMCN (Ng = He-Rn; M = Cu-Au) compounds. The M–Ng bond distances are in Å unit and the values within parentheses, square bracket, and braces are for Cu, Ag, and Au analogues, respectively.

of MX, the same order of the Ng binding ability is always followed except in some cases for He and Ne (see Supporting Information Tables S2–S4).  $D_0^{\text{BSSE}}$  value in NgCuCN is lower by 0.4–0.9 kcal/mol than the corresponding value in NgCuF whereas the same in former cases is found to be higher by 0.5–0.6 kcal/mol and 1.0–1.1 kcal/mol than those in NgCuCl and NgCuBr, respectively. Therefore, based on the  $D_0^{\text{BSSE}}$  values the Ng binding ability of CuCN and CuX can be arranged as  $\text{CuF} > \text{CuCN} > \text{CuCl} > \text{CuBr}$ . Conversely, AgCN has very much similar Ng binding ability as that of AgF and has larger Ng binding ability than those of AgCl (by 0.6–0.7 kcal/mol) and AgBr

(by 0.7–1.0 kcal/mol). Therefore, in this case the order becomes  $\text{AgCN} \approx \text{AgF} > \text{AgCl} > \text{AgBr}$ .  $D_0^{\text{BSSE}}$  value in NgAuCN is found to be lower than the corresponding values in NgAuF (by 2.3–5.0 kcal/mol) and NgAuCl (by 0.2–1.2 kcal/mol) but higher than that in NgAuBr (by 0.3–1.2 kcal/mol) and it makes the order as  $\text{AuF} > \text{AuCl} > \text{AuCN} > \text{AuBr}$ .

All the dissociation processes are found to be endothermic ( $\Delta H$  positive) in nature and for a given M, endothermicity gradually increases in moving from Ar to Rn. For a given Ng,  $\Delta H$  also shows the same trend as that of  $D_0^{\text{BSSE}}$  as we move from Cu to Au. Further insight is obtained from  $\Delta G$  values of

**Table 1.** Both ZPE and BSSE corrected dissociation energy ( $D_0^{\text{BSSE}}$ , kcal/mol) of M–Ng bonds, enthalpy change ( $\Delta H$ , kcal/mol) at 298 K, free energy change ( $\Delta G$ , kcal/mol) at 298 K and equilibrium constant ( $K_{\text{eq}}$ ) for the dissociation process:  $\text{NgMCN} \rightarrow \text{Ng} + \text{MCN}$  (M = Cu, Ag, Au), NPA charge at M and Ng centers ( $q$ , au), Wiberg bond indices of M–Ng bonds (WBI), HOMO–LUMO energy gap (Gap, eV), and M–Ng bond distances ( $r_{\text{M-Ng}}$ , Å) at the CCSD(T)/def2-TZVPPD level.

Clusters	$D_0^{\text{BSSE}}$	$\Delta H$	$\Delta G$	$K_{\text{eq}}$	$q(\text{M})$	$q(\text{Ng})$	WBI	Gap	$r_{\text{M-Ng}}$	$r_{\text{cov}}^{\text{[a]}}$
CuCN					0.82			10.69		
ArCuCN	5.4	6.6	−0.1	$1.18 \times 10^0$	0.68	0.08	0.16	11.58	2.354	2.380
KrCuCN	7.6	9.2	2.7	$1.05 \times 10^{-2}$	0.63	0.11	0.21	11.48	2.441	2.480
XeCuCN	10.1	12.1	5.5	$9.29 \times 10^{-5}$	0.58	0.15	0.29	11.37	2.570	2.720
RnCuCN	11.0	13.7	7.0	$7.39 \times 10^{-6}$	0.57	0.16	0.30	11.24	2.629	2.820
AgCN					0.82			10.55		
ArAgCN	2.7	3.5	−2.5	$6.80 \times 10^1$	0.73	0.04	0.09	11.46	2.696	2.510
KrAgCN	4.5	5.7	−0.7	$3.26 \times 10^0$	0.69	0.07	0.14	11.48	2.728	2.610
XeAgCN	6.9	8.5	2.0	$3.42 \times 10^{-2}$	0.63	0.11	0.21	11.45	2.809	2.850
RnAgCN	8.1	10.2	3.7	$1.94 \times 10^{-3}$	0.62	0.12	0.24	11.31	2.851	2.950
AuCN					0.63			10.96		
ArAuCN	5.8	7.6	0.4	$5.09 \times 10^{-1}$	0.50	0.09	0.16	12.16	2.523	2.420
KrAuCN	8.9	11.2	4.0	$1.17 \times 10^{-3}$	0.46	0.13	0.23	12.05	2.591	2.520
XeAuCN	13.0	15.6	8.4	$6.95 \times 10^{-7}$	0.41	0.19	0.33	11.88	2.685	2.760
RnAuCN	14.6	18.0	10.8	$1.21 \times 10^{-8}$	0.39	0.20	0.35	11.72	2.743	2.860

[a]  $r_{\text{cov}}$  is computed following Ref. 46.



**Table 2.** EDA results of the NgMCN (M = Cu, Ag, Au) clusters considering Ng as one fragment and MCN as another fragment at the PBE-D3/QZ4P//CCSD(T)/def2-TZVPPD level. All energy terms are in kcal/mol.

Clusters	$\Delta E^{\text{total}}$	$\Delta E^{\text{elstat}}$	$\Delta E^{\text{orb}}$	$\Delta E^{\text{Pauli}}$	$\Delta E^{\text{disp}}$
ArCuCN	-8.5	-11.6 (45.5)	-13.7 (53.7)	16.9	-0.2 (0.8)
KrCuCN	-11.0	-15.0 (47.0)	-16.7 (52.4)	20.9	-0.2 (0.6)
XeCuCN	-15.5	-18.7 (45.9)	-21.7 (53.3)	25.2	-0.3 (0.7)
RnCuCN	-16.6	-19.9 (46.2)	-22.9 (53.1)	26.6	-0.3 (0.7)
ArAgCN	-5.2	-7.0 (47.3)	-7.5 (50.7)	9.7	-0.3 (2.0)
KrAgCN	-7.5	-11.2 (49.8)	-10.9 (48.4)	15.0	-0.4 (1.8)
XeAgCN	-11.0	-17.1 (52.0)	-15.4 (46.8)	21.9	-0.4 (1.2)
RnAgCN	-12.4	-19.7 (52.8)	-17.1 (45.8)	24.9	-0.5 (1.3)
ArAuCN	-7.9	-16.1 (48.6)	-16.7 (50.5)	25.2	-0.3 (0.9)
KrAuCN	-11.1	-22.4 (50.7)	-21.5 (48.6)	33.2	-0.3 (0.7)
XeAuCN	-16.1	-32.3 (52.5)	-28.8 (46.8)	45.4	-0.4 (0.7)
RnAuCN	-17.8	-35.2 (53.1)	-30.6 (46.2)	48.5	-0.5 (0.8)

(The percentage values within the parentheses show the contribution toward the total attractive interaction  $\Delta E^{\text{elstat}} + \Delta E^{\text{orb}} + \Delta E^{\text{disp}}$ )

these compounds. Except for KrAgCN, the dissociations of other Kr, Xe, and Rn bound MCN compounds are endergonic in nature at room temperature. While the  $\Delta G$  value for the dissociation of ArCuCN is only slightly negative ( $-0.1$  kcal/mol), ArAuCN is found to be viable as indicated by positive  $\Delta G$  value of the corresponding dissociation process. Nevertheless, ArCuCN, ArAgCN, and KrAgCN might be stable at slightly low temperature as the contribution from favorable  $T\Delta S$  term toward  $\Delta G$  value of the dissociation process would be less at low temperature. Note that we have computed  $\Delta G$  values at standard state, that is, all the components are at 1 atm pressure. As the  $\Delta G$  values are obtained at the standard state, we have further computed equilibrium constant ( $K_{\text{eq}}$ ) using the equation:

$$K_{\text{eq}} = \exp\left(\frac{-\Delta G}{RT}\right) \quad (1)$$

where  $R$ , the ideal gas constant is  $1.987 \text{ cal mol}^{-1} \text{ K}^{-1}$  and  $T = 298.15 \text{ K}$ .

For a given M, in moving from Ar to Rn, the corresponding  $K_{\text{eq}}$  values gradually decrease for the dissociation process indicating increasingly small amount of the dissociated products in the equilibrium along the same (see Table 1). Conversely, for a given Ng the corresponding  $K_{\text{eq}}$  values for the dissociation process follow the order: AuCN < CuCN < AgCN supporting the stability order predicted from the  $D_0^{\text{BSSE}}$  values.

Note that in crystal structures, MCN compounds usually exist as oligomers. Ng attachment with M would be a way to reduce the possibility of dimerization or oligomerization. This is due to the bonding with Ng, the active M center is no longer available for further coordination. For example, in CuCN crystal structure, the Cu center of one CuCN unit interacts with N center of another CuCN. So in Xe bound case (say) for dimerization the interaction exists between Xe center of one XeCuCN unit and N center of another XeCuCN unit. Obviously, the Xe...N interaction would be considerably weaker than the Cu...N interaction. We have checked it at the MP2/def2-TZVPPD level taking the XeCuCN case and have found that

while the interaction energy for dimerization of CuCN is  $-50.8$  kcal/mol, the same is reduced to  $-8.7$  kcal/mol for Xe bound analogues.

The influence of Ng atoms on MCN can be noticed by a decreasing value of positive charge on M in all NgMCN compounds while going down the group from Ar to Rn. This effect is more pronounced in Xe and Rn analogues. Together with increasing positive charges on Ng atoms along Ar to Rn, they clearly highlight the degree of electron transfer from Ng atom to M center. It may be noted that the degree of electron transfer from Ng to M is slightly higher in NgAuCN than those in NgCuCN and NgAgCN. This may be due to the higher electronegativity of Au than those of Cu and Ag. The WBI values for M–Ng bonds in NgMCN gradually increase along Ar to Rn. For Xe and Rn analogues of CuCN and AuCN, the WBI values are found to be around 0.3. Note that in cases of NgMX although the Ng–M bond distance ( $r_{\text{M-Ng}}$ ) is smaller than that of covalent bond distance ( $r_{\text{cov}}$ ), the corresponding WBI values are found to be small ( $< 0.4$ ).

On comparison of  $r_{\text{M-Ng}}$  in NgMCN compounds and the typical  $r_{\text{cov}}$  as computed for M–Ng bonds following the covalent radii of M and Ng atoms proposed by Cordero et al.,<sup>[46]</sup> the Ng–Cu bond distances in NgCuCN are found to be smaller than the corresponding  $r_{\text{cov}}$  values. Conversely, Xe/Rn–M bonds for NgAgCN and NgAuCN have smaller distance than those of corresponding  $r_{\text{cov}}$  values. The Kr–Au bond distance is only slightly larger than the corresponding  $r_{\text{cov}}$  value.

The energy gap between the HOMO and the LUMO, which is a measure of stability and reactivity of a molecule, shows that MCN possesses a quite high HOMO–LUMO energy gap (gap) ranging within 10.55–10.96 eV. Note that the gap in MCN is even higher than those in MCl and MBr. A large separation between HOMO and LUMO energy levels implies that neither it wants to welcome additional electron to its LUMO nor it tends to leave an electron from its HOMO. Given that a chemical reaction usually involves electron transfer and/or electron sharing of one species to/with other interacting species, a high HOMO–LUMO energy gap, which is connected with the maximum hardness principle,<sup>[49]</sup> represents high stability, hence, low reactivity of a molecule. Therefore, the presently studied MCN compounds are highly electronically stable. The stability even increases in Ng bound form as indicated by an increase in HOMO–LUMO energy gap in Ng bound analogues compared to the corresponding bare moieties.

The results of EDA–NOCV taking MCN as one fragment and Ng as another fragment are provided in Table 2 (see Table S6 in Supporting Information for the results of He and Ne). In case of NgCuCN, the contribution from  $\Delta E^{\text{orb}}$  (ca., 52–54%) is slightly larger toward the total attraction than that of  $\Delta E^{\text{elstat}}$  (ca., 45–47%). Conversely, except for the Ar case in NgAgCN and NgAuCN,  $\Delta E^{\text{elstat}}$  (ca., 50–53%) term dominates over  $\Delta E^{\text{orb}}$  (ca., 46–49%). The contribution from  $\Delta E^{\text{disp}}$  toward the total attraction is quite negligible ( $> 2\%$ ). Therefore, the bond between Ng and M in NgMCN is a delicate balance between covalent and electrostatic interactions. In NgMX cases, the EDA–NOCV results show that the Ng–M bonds are of partly electrostatic type and partly as of covalent type, the latter

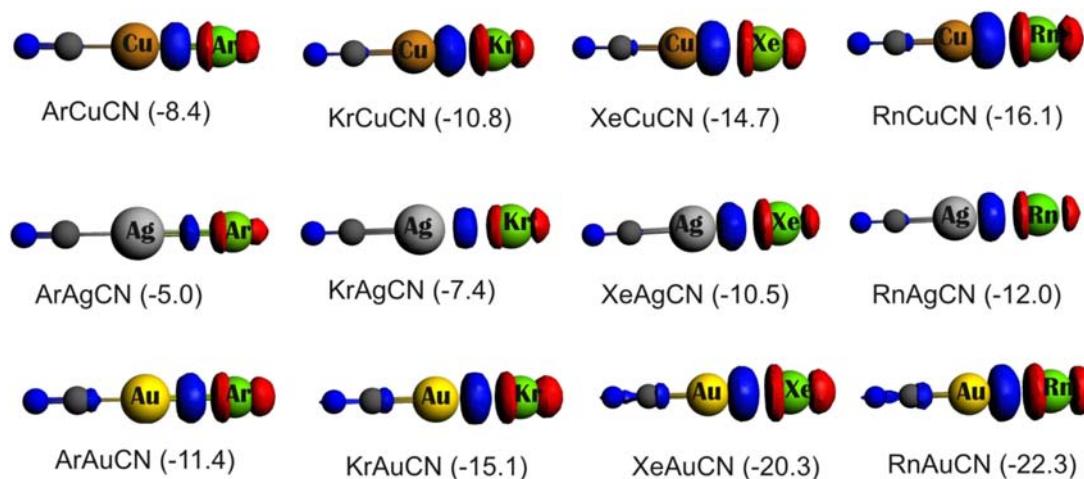


Figure 2. The plots of deformation densities,  $\Delta\rho(\mathbf{r})$ , of the pair-wise orbital interactions in NgMCN at the PBE-D3/QZ4P//CCSD(T)/def2-TZVPPD level. The associated orbital interaction energies are given within parentheses in kcal/mol.

being slightly dominant over the former in NgCuX and former being slightly larger than the latter in NgAgX and NgAuX (see Tables S7–S9 in Supporting Information).

It may be noted that for a long time the bonding situation between Ng and a coinage metal had been a matter of debate. While on the basis of the smaller M–Ng bond lengths than that of  $r_{\text{cov}}$  Pyykkö<sup>[22]</sup> designated the Ng–Au bond in NgAu<sup>+</sup> as of covalent type, Read et al.<sup>[24]</sup> by including higher order linear polarization effects argued the covalency within NgAu<sup>+</sup> as unproven. Gerry and coworkers<sup>[12]</sup> also explored the nature of bonding between M and Ng in their works related to experimental characterization of NgMX (Ng = Ar–Xe; X = F–Br) compounds. They also found the existence of covalent bonds (or at least of some degree) in between M and Ng in these compounds and especially in Ng–Au cases, the covalent part was reported to be larger than the electrostatic part. Furthermore, Belpassi et al.<sup>[50]</sup> investigated the nature of chemical bond in NgAuF and NgAu<sup>+</sup> by adopting an all-electron fully relativistic DC-CCSD(T) level of theory. They showed that the electron density is accumulated in between Ng and Au, via contour plots of the electron density difference between NgAuF and the Ng and AuF fragments. The electron accumulation even gradually increases in moving from Ar to Xe. They termed it as “weak covalent chemical bond,” which certainly becomes stronger down the group. Note that in the present EDA results, the contribution of  $\Delta E^{\text{elstat}}$  term is found to be slightly higher than that of  $\Delta E^{\text{orb}}$  in NgAgX and NgAuX cases.

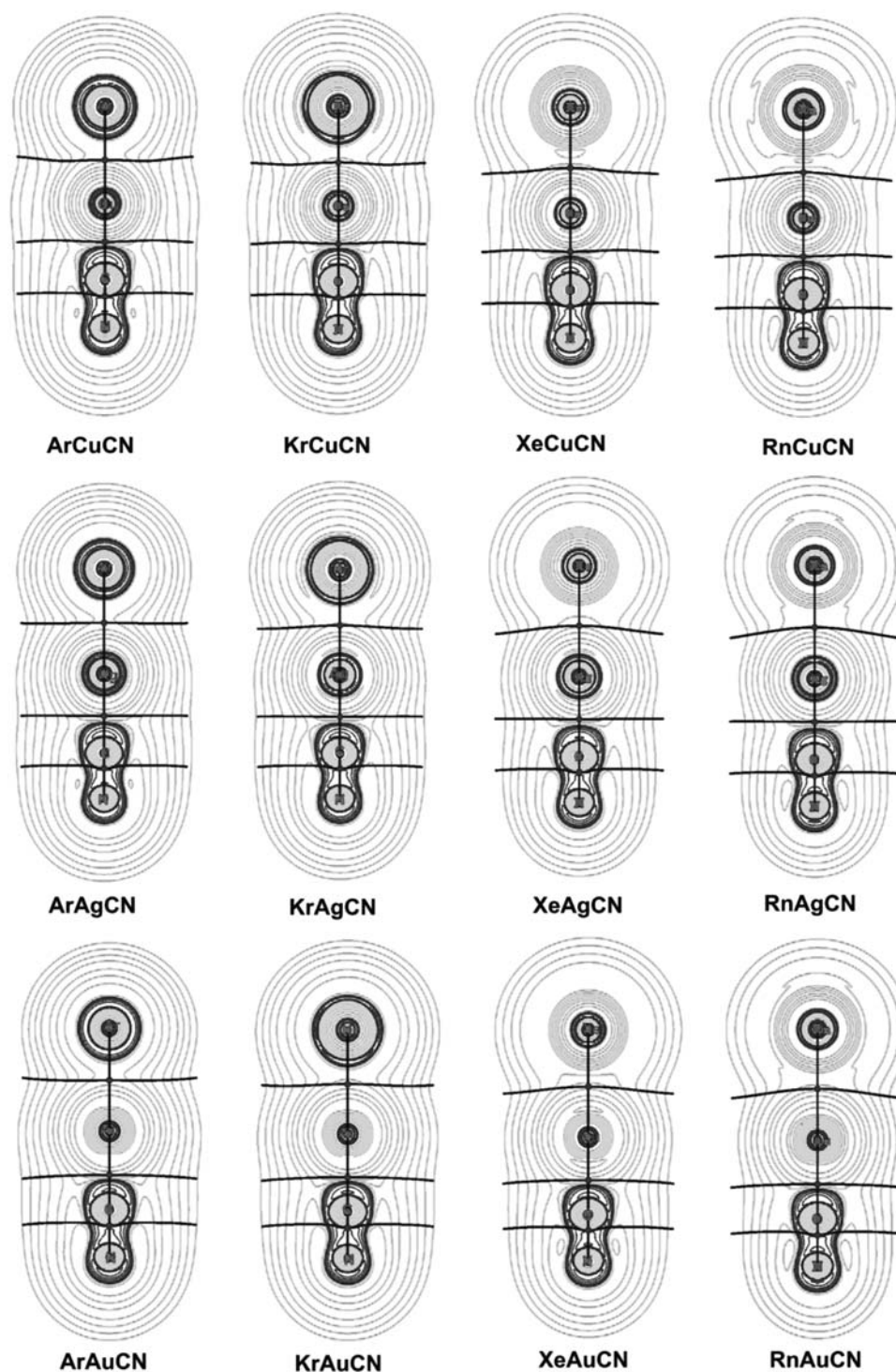
In the EDA–NOCV scheme, we can decompose the differential density,  $\Delta\rho(\mathbf{r})$ , into the deformation densities,  $\Delta\rho^i(\mathbf{r})$ . The direction of flow of electron density within a molecule can be understood from the plot of  $\Delta\rho^i(\mathbf{r})$  (see Fig. 2). Furthermore, corresponding to each  $\Delta\rho^i(\mathbf{r})$  channel,  $\Delta E^{\text{orb}}$  can be decomposed into  $\Delta E_i^{\text{orb}}$ . In Figure 2, the electron flow occurs from red region to blue region as per the present color code. The associated  $\Delta E_i^{\text{orb}}$  term is also provided. Similar to the study of Belpassi et al.,<sup>[50]</sup> the electron density is found to be accumulated in the middle region of M–Ng bond. The associated  $\Delta E_i^{\text{orb}}$  term gradually increases in moving from Ar to Rn implying a larger degree

of covalent character along the same. Therefore, the Ng–M bond in NgMCN compounds is partly covalent and partly electrostatic in type, where in some cases the electrostatic part is slightly dominant over the covalent part whereas in some other cases the reverse is true.

Earlier, Rodrigues et al.<sup>[51]</sup> and Boggs and coworkers<sup>[52]</sup> performed an electron density analysis to investigate the nature of Ng–M bonds in NgMX. While the former group suggested the Ng–Cu bonds in NgCuX as predominantly of covalent type, based on local total energy density ( $H(r_c)$ ), the latter group categorized the Ng–M bonds in NgMF as weak bonding interaction with some degree of covalent character ( $W^c$ ) except in the cases of Xe–Ag and Xe–Au bonds. The Xe–Ag and Xe–Au bonds in XeMF were termed as covalent based on the criterion,  $H(r_c) < 0$  and the ratio of local kinetic energy density ( $G(r_c)$ ) and electron density ( $\rho(r_c)$ ),  $G(r_c)/\rho(r_c) < 1$ . In the present NgMCN compounds, we have computed these electron density descriptors at the bond critical points (BCPs) of M–Ng bonds and the related results are provided in Table 3 (see Table S10 in Supporting Information for the results of He and Ne).

Table 3. Electron density descriptors (au) at the bond critical points (BCP) in between Ng and M atoms in NgMCN obtained from the wave functions generated at the MP2/def2-TZVPPD/WTBS//CCSD(T)/def2-TZVPPD level (All electron WTBS basis set is used only for Ag, Au, Xe, and Rn).

Clusters	BCP	$\rho(r_c)$	$\nabla^2\rho(r_c)$	$G(r_c)$	$V(r_c)$	$H(r_c)$	$G(r_c)/\rho(r_c)$
ArCuCN	Ar–Cu	0.046	0.229	0.063	−0.070	−0.007	1.370
KrCuCN	Kr–Cu	0.049	0.198	0.058	−0.067	−0.009	1.184
XeCuCN	Xe–Cu	0.052	0.132	0.047	−0.061	−0.014	0.904
RnCuCN	Rn–Cu	0.053	0.109	0.042	−0.057	−0.015	0.792
ArAgCN	Ar–Ag	0.028	0.141	0.034	−0.033	0.001	1.214
KrAgCN	Kr–Ag	0.033	0.146	0.038	−0.039	−0.001	1.152
XeAgCN	Xe–Ag	0.034	0.138	0.036	−0.037	−0.001	1.059
RnAgCN	Rn–Ag	0.036	0.130	0.035	−0.038	−0.003	0.972
ArAuCN	Ar–Au	0.046	0.244	0.062	−0.063	−0.001	1.348
KrAuCN	Kr–Au	0.050	0.222	0.060	−0.065	−0.005	1.200
XeAuCN	Xe–Au	0.046	0.195	0.052	−0.056	−0.004	1.130
RnAuCN	Rn–Au	0.046	0.175	0.048	−0.053	−0.005	1.043



**Figure 3.** The plots of Laplacian of electron density ( $\nabla^2\rho(r)$ ) of NgMCN (Ng = Ar–Rn) at the MP2/def2-TZVPPD level. (Green solid lines show the region with  $\nabla^2\rho(r) > 0$  and blue dotted lines show the region with  $\nabla^2\rho(r) < 0$ ). [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

Generally, covalent and noncovalent nature in a bond can be understood from the negative (electron density concentration) and positive (electron density depletion) values of the Laplacian of the electron density ( $\nabla^2\rho(r_c)$ ), respectively, at the BCPs. However, many shortcomings of this descriptor, especially for heavier atoms were reported.<sup>[53]</sup> Thereafter, the criteria like  $H(r_c) < 0$  and/or  $G(r_c)/\rho(r_c) < 1$  to categorize a bond as

some sort of covalent type were also put forward.<sup>[54]</sup> In our cases, except for Ar–Ag bond  $H(r_c)$  is negative in all cases whereas  $G(r_c)/\rho(r_c)$  is found to be less than 1 only in cases of Xe/Rn–Cu bond and Rn–Ag bond. Therefore, except for Ar–Ag bond, all the bonds can be called of partial covalent type. The  $G(r_c)/\rho(r_c)$  comes closer to its limiting value 1 and even it becomes less than 1 as we move from Ar to Rn. It



indicates that the degree of covalent character increases along the group.

F3

Figure 3 depicts the contour plots of  $\nabla^2\rho(r)$  for Ar–Rn bound MCN compounds. The gradual deformation in the shape of the valence orbitals of Ng atoms in moving from Ar to Rn implies the increased covalent character along the same. Although according to Boggs' classification<sup>[52]</sup> Xe–Rn–Cu bond and Rn–Ag bond can be called as covalent bond, the results from EDA hints that there is significant ionic character as well. Note that the He–Cu bond can also be called as of partial covalent character whereas the remaining M–Ng bonds involving He and Ne are of noncovalent type (see Table S10 in Supporting Information).

## Summary and Conclusion

We have performed a coupled-cluster-based study to assess the Ng binding ability of MCN (M = Cu, Ag, Au) compounds and we have also compared the stability of NgMCN with those of experimentally detected NgMX (X = F, Cl, Br) compounds. Both zero-point energy and BSSE corrected dissociation energy ( $D_0^{\text{BSSE}}$ ) values range within 5.4–11.0 kcal/mol, 2.7–8.1 kcal/mol, and 5.8–14.6 kcal/mol in Ar–Rn bound CuCN, AgCN, and AuCN compounds, respectively, with a gradual increase in  $D_0^{\text{BSSE}}$  value along Ar to Rn. As in MX, for the same Ng, AuCN has the highest Ng binding ability followed by CuCN and then AgCN. In comparison to MX, CuCN has higher Ng binding ability than those of CuCl and CuBr but lower than that of CuF. Conversely, the Ng binding ability in Ag and Au compounds can be written in descending order as AgCN  $\approx$  AgF > AgCl > AgBr and AuF > AuCl > AuCN > AuBr. All the dissociation processes are found to be endothermic in nature and the endothermicity gets gradually larger down the group. The dissociation processes are endergonic in nature at room temperature for Kr–Rn bound MCN compounds, except for KrAgCN. The dissociation of ArAuCN is found to be endergonic in nature as well. For the rest of the systems, lower temperature may be needed to remain in the bound form.

The Wiberg bond indices in Xe and Rn bound CuCN and AuCN are around 0.3 whereas the same in AgCN are approximately 0.2. All the Ng–Cu bond distances and Xe/Rn–Ag/Au bond distances in NgMCN are shorter than the corresponding covalent bond distances. In Ng bound analogues, the HOMO–LUMO energy gap increases compared to that of the bare compounds indicating larger electronic stability.

EDA along with the NOCV theory shows that the Ng–M bonds in NgMCN (Ng = Ar–Rn) may be considered partly as of covalent type and partly as of electrostatic type. Only in some cases one dominates over the other and vice versa. The plot of deformation densities shows the electron cloud is transferred from Ng to the middle of Ng and M centers facilitating a bond formation. The orbital energy term associated with the deformation density increases along Ar to Rn implying a larger covalent character along the same. While the local total energy density is negative at the BCPs of all Ng–M bonds (Ng = Ar–Rn) except for Ar–Ag, the ratio of local kinetic energy density to electron density is less than 1 in cases of Xe/Rn–Cu bond

and Rn–Ag bond. These parameters describe the presence of some degree of covalent character in the bonds.

**Keywords:** coinage metal · noble metal · noble gas bond · dissociation energy · energy decomposition analysis · atoms-in-molecules analysis

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Additional Supporting Information may be found in the online version of this article.

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Noble metal (Cu, Ag, and Au) cyanides are predicted to form stable compounds with noble gas atoms (Ar-Rn) effectively. In some cases, they are predicted to have larger dissociation energies than those of experimentally detected noble gas bound noble metal halides.

