# Theoretical Study of Multi-Coordinated Xe(AuF)n (n = 2-4): Intriguing Bond-bending Isomerism

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#### Abstract

This work reports a theoretical study of a novel family of multi-coordinated noble gas (Ng) complexes, Xe(AuF)n (n = 2-4). Geometrical optimization at the LC- $\omega$ PBE-D3/def2TZVPP level locates two types of structures based on the bond-bending isomerism induced by an intramolecular competition between Xe-Au covalent bonding and Au…Au aurophilic interactions. They both comprise a center Xe atom serving as an electron donor binding to AuF moieties, but pronouncedly differ in the Au-Au distance and Au-Xe-Au bending angle. Comprehensive chemical bonding analysis undisputedly demonstrates that aurophilic interactions exist and affect the strength of Xe-Au bonds whose covalent nature is evident. By scanning the potential energy surface of Xe(AuF)2 with arbitrary one atom being substituted by its analogue, we found only Xe(AuF)2 and Xe(AuCl)2 feature bond-bending isomerism, due to the highly electronegative F/Cl atom inducing strongly covalent Xe-Au bond via electron donation-feedback mechanism. The present work predicts multi-coordinated Ng-metal complexes and demonstrates the bond-bending isomerism, which could be an interesting addition and call out more attentions to the research field of Ng chemistry.

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# Theoretical Study of Multi-Coordinated $Xe(AuF)_n$ (n = 2-4): Intriguing Bond-bending Isomerism

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Abstract This work reports a theoretical study of a novel family of multi-coordinated noble gas (Ng) complexes, Xe(AuF),

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## 1 | INTRODUCTION

Noble gas (Ng) atoms have proven capable of forming chemical interactions ranging from weak van der Waals forces to strong covalent bonds and ionic bonds, though they are traditionally considered to feature chemical inertness arising from the fully occupied valence shell. In fact, since  $XePtF_6$  was first synthesized by Bartlett in 1962<sup>[1]</sup> numerous Ng complexes have been discovered and investigated, triggering ongoing and growing attentions. Ng complexes are important in understanding and developing the bonding theory and related chemistry, as well as in various research and industrial applications. For instance,  $XeF_2$  and  $XeF_4$ are exploited as key agents to remove impurities in alloy smelting,<sup>[2]</sup> while  $XeO_3$  and  $XeO_4$  serve as useful explosive components.<sup>[3]</sup>From a chemical bonding perspective, the Ng complexes uncovered so far can be generally divided into two types according to the formation mechanism differentiated by how the Ng atoms donating electrons. The former refers to those formed from that Ng atoms interact with highly electronegative atoms (F, Cl, Br, O, N) or groups (C[?]CH), constituting traditional covalent or ionic bonds.<sup>[4-12]</sup> At present, Ng atoms have been found to bind to electronegative parts with a coordination number up to 6 and Ng atom itself is  $\ln sp^3 d^2$  hybridization, as in both inorganic XeF<sub>n</sub>  $(n = 2, 3, 4, 6)^{[2, 13, 14]}$  and organic Xe(CCH)<sub>n</sub>(n = 1, 4, 6).<sup>[11, 12]</sup> The latter type, however, represents those where Ng atoms donate electrons to metal atoms (Cu, Ag, Au) to form coordinated structures through van der Waals interactions or covalent bonds with Ng in  $sp^{\bar{s}}$  hybridization. In 2000, by reduction of AuF<sub>3</sub> with elemental xenon, the first complex containing noble gas-noble metal (Ng-Nm) interactions  $(AuXe_4^{2+}[Sb_4F_{11}]_2)$  was synthesized experimentally,<sup>[15]</sup> in which two kinds of noble element, *i.e.*, Au and Xe, formed a strong bonding of the  $\sigma$ -donor type. This unique Ng-Nm bond stimulated further search for similar complexes. Soon after, Gerry et al. observed a series of linear molecules comprising such bonds via laser ablation of metals in explosion of buffer Ng. These species share a general formula of NgNmX (Ng = Ar, Kr, Xe; Nm = Cu, Ag, Au; X = F, Cl, Br)<sup>[16, 17-23]</sup> and comprise Ng-Nm bonds that are short and rigid. In particular, the Xe-Au bond in XeAuF ranked the strongest Ng-Nm bond and was specially characterized with covalent character.<sup>[21]</sup>Given that a Ng atom like Xe owns fully occupied valence shell and can thus afford as many as eight electrons to form four equivalent  $sp^3$  orbitals, it is reasonable to forge multi-coordinated Ng structures via interactions with metals, yet such multi-coordinated complexes have hardly been reported. Gold outstands as a promising role in the study of Ng chemistry and in constructing brand-new multi-coordinated Ng structures. As a heavy atom, gold possesses strong relativistic effects  $^{[24-27]}$  that induce the expanding of 5d orbital and the shrink of the 6s orbital. Accordingly, Au exhibits a higher electron affinity compared to other noble metals like Ag or Cu, which was readily verified in complexes like NgNmX, where Ng-Au bond is saliently stronger than Ng-Ag and Ng-Cu bond. Another unique property of gold is the  $Au(I) \cdots Au(I)$  aurophilic interaction, a special attractive force between Au atoms with closed-shell electronic configuration  $(5d^{10})$  that is thought to be a joint result of strong relativistic effects and dispersion-type electron correlations.<sup>[28-38]</sup> Aurophilic interactions exert profound effects on the configuration of related molecular structures. For example, in a prior synergetic photoelectron spectroscopy (PES) and theoretical study of gaseous  $Au_2I_3$  cluster, aurophilic interaction was found to compete with Au-I covalent bonding, leading to the formation of two "bond-bending isomers" with approximately degenerate energies.<sup>[39]</sup>Therefore, equipped with these peculiar characteristics, Au indubitably proves an ideal candidate for further pursuing novel multi-coordinated Ng-metal structures. However, although many efforts have been devoted to generating and investigating Ng complexes, the understanding of relevant structures and bonding remains controversial and obscure. In fact, it has become one of key issues to search for new Ng complexes, especially the multi-coordinated Ng-metal species, and explore the underlying bonding mechanism. Ng atoms, in particular those having larger radiuses, are capable of coordinating several atoms or groups simultaneously.<sup>[14]</sup> One is nature to wonder, if the strongest Ng-Nm bond, *i.e.* Xe-Au bond, can be extended from already obtained XeAuF to heretofore unknown  $Xe(AuF)_n$ (n [?] 2), in light of the fact that the diameter of Xe atom is large enough to spatially satisfy more AuF

 $^{\rm at}$ 

groups. To address this question and gain more insights into the Ng-metal bonding nature, this work theoretically predicts and characterizes a series of novel multi-coordinated Ng complexes,  $Xe(AuF)_n$  (n = 2-4), by performing quantum chemical calculations, serving as an essential complement to the research field of Ng chemistry. To the best of our knowledge, such multi-coordinated  $Xe(AuF)_n(n = 2-4)$  complexes have not been reported yet.

# 2 | COMPUTATIONAL DETAILS

In order to select an appropriate theoretical methodology, two key structural and energetic parameters of linear XeAuF molecules, *i.e.*, the length and dissociation energy of Xe-Au bond obtained separately from previous experimental work and CCSD(T) calculations, are employed to benchmark several computational approaches including DFT with different functionals (e.g., PBE,<sup>[40]</sup>B3LYP,<sup>[41]</sup> M06-2X,<sup>[42]</sup>CAM-B3LYP,<sup>[43]</sup>  $\omega$ B97X,<sup>[44]</sup> and LC- $\omega$ PBE-D3 <sup>[45]</sup>) and MP2. During the evaluation, def2TZVPP basis set were used for DFT calculations, while MP2 and CCSD(T) computations are performed with def2-QZVP basis set. All the dissociation energies are acquired based on the LC- $\omega$ PBE-D3/def2TZVPP optimized geometry. According to the comparison results presented in Table S1 and for the sake of balancing the accuracy and cost of calculations, the LC- $\omega$ PBE-D3/def2TZVPP method, whose outputs are very close to the judgment criteria, was chosen for further geometry optimization and single-point energy calculations of  $Xe(AuF)_n$  (n = 2-4). Geometry optimizations were carried out without any symmetry constraints. Vibrational frequency analysis was performed at the same level to ensure that the optimized structures were true minima, and obtained frequencies were used to calculate the zero-point vibrational energies (ZPEs). All the DFT, MP2 and CCSD(T) calculations and natural bonding orbital (NBO) analysis <sup>[46, 47]</sup> were performed with Gaussian 16 suites.<sup>[48]</sup> Basis set superposition error (BSSE) corrections are included when computing dissociation energies.<sup>[49]</sup> To deeper understand the electron structures and chemical bonding characteristics, the electron and bonding analyses including electron localization function (ELF),<sup>[50]</sup> extended transition state-natural orbitals for chemical valence (ETS-NOCV),<sup>[51, 52]</sup> reduced density gradient (RDG)<sup>[53]</sup> and quantum theory of atoms in molecules (QTAIM) methods<sup>[54-56]</sup> were conducted with the aid of Multiwfn codes.<sup>[57]</sup>

# **3 | RESULTS AND DISCUSSION**

#### 3.1 | Geometries and Binding Motifs

Multiple optimized structures of Xe(AuF)<sub>n</sub> (n = 2-4) were theoretically located at the LC- $\omega$ PBE- $D_3/def 2TZVPP$  level and alphabetically labeled from na to nc according to their relative energies, as shown inFigure 1. The key geometrical parameters for all these predicted structures along with XeAuF were summarized in Table S2. For  $Xe(AuF)_2$ , two near-degenerate isomers, 2a and 2b, were found to adopt a common bent geometry with  $C_{2v}$  symmetry, in which the center Xe atom binds to both AuF units but with different sizes of Au-Xe-Au angle. A prior case study of Au<sub>2</sub>I<sub>3</sub><sup>-</sup> shows similar bond-bending isomerism that was characterized by an intramolecular competition between aurophilic interaction and Au-I covalent bonds.<sup>[39]</sup> Here, the slightly high-lying isomer 2b simply contains two strong covalent Xe-Au bonds with a length of 2.56 Å, almost identical to that in linear XeAuF.<sup>[21]</sup> This covalent bonding favors a obtuse Au-Xe-Au bent angle of 104.4°, a value that resembles the angle of water molecules and supports the water-like bent configuration. Isomer 2a is more stable with 0.077 eV lower in energy due to the additional intramolecular Au. Au aurophilic interaction arising from the saliently smaller Au-Au distance of 2.82 Å compared to that of 4.05 Å in**2b**. From **2b** to **2a**, the bond angle of Au-Xe-Au pronouncedly shrinks from 104.4° to 64.9°, the bond length of Xe-Au is mildly elongated from 2.56 Å to 2.63 Å, while the length of Au-F bonds maintains almost unchanged. **FIGURE 1** The optimized structures of  $Xe(AuF)_n$  (n = 2-4) at the level of LC- $\omega$ PBE-D3/def2TZVPP with key bond lengths (Å) and angles (°) noted in black. The natural population analysis (NPA) charges on Xe, Au and F are shown in red. The structural symmetries and relative energies (in eV) are given under each structure (Xe, pink; Au, dark cyan; F, purple). The structures framed by dotted lines have imaginary frequencies at this level. The n = 3 complex presents three triangular conical geometries. The lowest-lying **3a** isomer features  $C_{3y}$  symmetry and three intense aurophilic interactions between every

two of the three Au atoms but is calculated to have an imaginary frequency of  $-29.05 \text{ cm}^{-1}$ . The  $C_s$  symmetric **3b** structure lies 0.241 eV higher in energy and contains one single aurophilic interaction between the Au1 and Au2 atoms that are separated by 2.81 Å and exhibit a bending angle of  $64.5^{\circ}$  with respect to the center Xe atom. The other Au3 atom resides 4.05 Å apart from each of these two Au atoms, with two Au-Xe-Au angles equaling to 102.7°. The rest **3c** structure devoid of aurophilic interactions has a  $C_{3v}$  symmetry, displaying three identical Au-Au distances (4.02 Å) and bending angles (104.0°). By comparing **3b** and **3c**, the absence of one intramolecular aurophilic interaction raises the energy of **3c**by nearly 0.1 eV. It is also worth mentioning that the Au-Au distance corresponding to the aurophilic interaction keeps almost identical for 2a  $(2.82 \text{ \AA})$  and **3b**  $(2.81 \text{ \AA})$ , hinting that these aurophilic interactions are considerably close in intensity. For n = 4, the 4a ( $C_{\rm s}$ ) and 4c ( $D_{\rm 2d}$ ) structures are both calculated to have imaginary frequencies albeit featuring aurophilic interactions, while  $4b (T_d)$  is determined as the stable local minima, which may be attributed from the synergistic effect<sup>[58]</sup> that all eight outer electrons of Xe participate in interacting with four AuF ligands in a perfectly symmetrical manner, forming a regular tetrahedral configuration like that of well-known methane. Overall, these predicted structures informally fall into two types based on whether intramolecular aurophilic interactions exist. One type is that Au simply forms conventional covalent bonding patterns to Xe and that different AuF moieties are connected through a central Xe atom via Xe-Au interactions. The calculated Au-Xe bond length for **2b**,**3c**, and **4b** structures equal to 2.56, 2.55 and 2.53 Å, respectively, appreciably shorter compared to the sum of covalent radii of bare Au and Xe atoms, suggesting the covalent Xe-Au bonding nature. By comparison, the other type features both Xe–Au covalent and Au…Au aurophilic interactions. The isomers of this type, e.g., 2a and 3b, shows a much closer Au-Au distance (2.82 and 2.81Å), in contrast to the former type with Au-Au distance up to 4.0 Å. The lengths of Xe-Au bonds for the Au involved in aurophilic interaction are also slightly elongated, while the Au-F bonds maintain basically identical in length. For the sake of simplicity of discussion, these two types of isomers are each named as traditional and aurophilic structures. FIGURE 2 Electron and bonding analysis of  $Xe(AuF)_n$  (n = 2-4). The left shows results of the extended transition state (ETS) method combined with the natural orbitals for chemical valence (ETS-NOCV), while the right visualizes the electron localization function (ELF) pictures.

#### 3.2 | Electronic structures and chemical bonding analysis

Noting that some of the structures are computed to be unstable with imaginary frequencies, only the rest stable isomers, namely **2a**, **2b**, **3b**, **3c** and **4b**, were used to in-depth analyze the electronic structure, while the analysis results of the unstable species were simply listed in Figure S1-S3 for necessary reference. As a matter of fact, for all these multi-coordinated structures, Au atoms are in the +1 oxidation state. The  $\delta s$ electron of each Au atom is transferred to the adjacent F atom, forming an intense Au-F $\sigma$  covalent bond with each Au atom in  $5d^{10}$  electron configuration. Meanwhile, the highly electronegative F atom induces a  $\sigma$ -hole of Au atom on the side away from the F atom (Figure S4). The electron on Xe atom will be further pushed to this  $\sigma$ -hole and constitute covalent Xe-Au bonding. This generalizes how the electron donation-feedback mechanism works within the formation of Xe-Au bonds. To better understand the chemical bonding nature and to obtain a qualitative bonding picture, ETS-NOCV analysis and EFL analysis were jointly performed (Figure 2) to elucidate the electronic structures. ELF directly visualize the probability of finding an electron in the vicinity of another reference electron. On the other hand, ETS-NOCV method has been long established useful in investigating orbital interactions by decomposing the orbital interaction energy into the contribution of each NOCV pair. The density of each NOCV pair corresponds to its contribution to the electron density. Here,  $Xe(AuF)_n$  were divided into n+1 groups (Xe and nAuF, n = 2-4) to directly probe the interactions of Xe and Au. Figure 2 shows the dominating NOCV pairs selected to characterize Xe-Au bonding. Apparently, all the Xe-Au bonds are formed upon p electron transferred from Xe to Au (see pair 1) and the feedback from d orbital of Au atom to Xe (see pair 2). No orbital interactions were observed between any two Au atoms in **2b**,**3c** and **4b**, indicating the absence of aurophilic interactions. By contrast, the NOCV pairs in 2a and 3b clearly present the d orbital interaction between the specific Au atoms that forms aurophilic interaction, which was also visually confirmed by the rendered ELF image in Figure 2. Moreover, the ETS-NOCV analysis suggests stronger d orbital feedback of Au in the aurophilic species, interpreting why the Xe-Au bonding intensity differs when aurophilic interactions are engaged. The hyperconjugation of nNg -  $\sigma^*$ Nm, on the other hand, results in electron density transferring from the lone pair electron of Ng to the antibonding orbital of NmX moiety, thereby endowing the Ng atom moderate positive charge with the X atom getting slightly negative, aligning with the NPA analysis in **Figure 1**. When the number of AuF groups increases, the positive charge on Xe atom of traditional structures (2b-**3c-4b**) gradually increases from 0.35 to 0.45 and then to 0.49, implying a rise in the contribution of electron pairs of Xe, while the positive charge on Au and F keeps nearly unchanged.FIGURE 3 Reduced density gradient (RDG) analysis of  $Xe(AuF)_n$  (n = 2-4) with non-covalent interactions (NCI) isosurface set at s = 0.3. In addition, to quantitatively investigate the related chemical bonding strength, Reduced density gradient (RDG) analysis was conducted to obtain the peak spike values of non-covalent interactions (NCI) (seeFigure 3). Generally, the more negative the spike value, the stronger the corresponding interaction. Three types of spike values were captured for  $Xe(AuF)_n$  (n = 2,3,4) from the crossing point of the RDG image with horizontal axis. The two side values approximately equal to -0.140, and -0.045, respectively, whereas the middle value occupies an appreciably broader range from -0.066 to -0.082. Noting that the spike value in neutral AuF was reported as  $-0.138^{[38]}$ , the most negative value of nearly -0.140 was reasonably attributed to the Au-F bond, which is moderately stronger in  $Xe(AuF)_n$  due to the feedback from d orbital of Au to Xe atom. The close spike values of -0.045 and -0.048 respectively in 2a and 3b arise from the isosurface denoting Au…Au interaction on account of they only showing up in these aurophilic structures. Given above, the middle spike value that spans from -0.066 to -0.082 is concluded to represent Au-Xe bonding, in which the smaller values refer to those where Au participates in aurophilic interactions. Obviously, the Xe-Au bonding strength in **2a** is mildly weaker than that in **2b** by comparing the corresponding spike values of -0.070 and -0.078, in good agreement with the bond lengths in **2a** (2.63Å) and **2b**(2.56Å). The **3b** structure comprises two kinds of Xe-Au spike values respectively of -0.080 and -0.066, representing two different Xe-Au interactions classified according to whether the Au atom is involved in aurophilic interactions. Moreover, the spike values of Xe-Au bonding in traditional structures slightly reduce from -0.078 to -0.080 and then to -0.082 as the number of AuF increases, consistent with the decrease in bond length of Xe-Au (from 2.56 to 2.55 and to 2.53 Å) and the enhancement of Xe-Au bonding intensities. Furthermore, by comparing the largest spike value of Xe-Au bond equaling to -0.066 in **3b** with the corresponding value of -0.070 in **2a**, we are convinced the aurophilic interaction is more competitive in 3b than that in 2a.TABLE 1 The Xe-Au bond lengths, along with electron density  $\rho(r_{\rm c})$ , Laplacian of electron density  $V^2 \rho(r_{\rm c})$ , electron local energy density  $H(r_c)$ , local kinetic energy density  $G(r_c)$ , and the ratio of  $G(r_c)$  and  $\rho(r_c)$  at the bond critical points (BCPs) of the Xe-Au bonds in Xe(AuF)<sub>n</sub> (n = 1-4) calculated at the LC- $\omega$ PBE-D3/def2TZVPP level.

Complex	$\mathbf{R_{Xe-Au}}$	$ ho(r_{ m c})$	$V^2(m{r_c})$	$H(r_{c})$	$G(\boldsymbol{r_c})$	$G( ho_{\varsigma})/ ho( ho_{\varsigma})$
1	2.57	0.077	0.178	-0.023	0.068	0.883
<b>2</b> a	2.63	0.068	0.155	-0.018	0.057	0.838
2b	2.56	0.069	0.160	-0.018	0.058	0.841
$3\mathrm{b}^{*}$	2.63/2.55	0.069/0.079	0.159/0.196	-0.018/-0.025	0.058/0.073	0.841/0.924
<b>3c</b>	2.55	0.079	0.197	-0.025	0.074	0.937
4b	2.53	0.082	0.209	-0.027	0.079	0.963

\* The two values in each box for the 3b structure correspond to the Xe-Au1 and Xe-Au3 bonds, respectively.

#### 3.3 | Covalent character investigation of Xe-Au bonds in $Xe(AuF)_n$ (n = 2-4)

The bonding character of Ng-Nm interactions has been one of hot issues of the related research field. To further explore the chemical bonding nature of Xe-Au bonds in Xe(AuF)<sub>n</sub> (n = 2-4), quantum-theory-of-atoms-in-molecules (QTAIM) analysis is performed, aimed at providing extra evidence for a bond path among all bonding interactions with a bond critical point (BCP) and a significant accumulation of electron density within the bond (see electron density  $\rho_{\text{bcp}}$  in **Table 1**). Typically, at the BCP of a certain chemical bond, high electron density  $\rho(r_c)$  and negative Laplacian electron density  $V^2\rho(r_c)$  values define a covalent bond,

but this criterion does not always work especially when heavier atoms are involved. The energy density  $H(r_c)$ , ratio of local kinetic energy density  $G(r_c)$  and electron density  $\rho(r_c)$ , however, are more proper parameters in these cases. Covalent bonds are characterized by BCPs with negative  $H(r_c)$  and  $G(r_c)/\rho(r_c)$  lower than 1, while those with positive  $H(r_c)$  and  $G(r_c)/\rho(r_c)$  exceeding 1 usually denote closed-shell interaction.<sup>[59]</sup> Based on this criterion, the  $H(r_c)$  and  $G(r_c)/\rho(r_c)$  values at all BCPs suggest explicit covalent nature of the Xe-Au bonds for the whole series of predicted structures. Moreover, as mentioned in the RDG analysis, the electron density between Xe and Au atoms are slightly bigger in traditional structures (**2b**, **3c** and **4a**). Topological analysis was additionally performed for linear NgNmX (Ng = He, Ne, Ar, Kr and Xe; Nm = Cu, Ag and Au; X = F, Cl, Br and I) molecules and compared in **Table S3**, revealing that the Ng-Nm bonds are gradually transformed from dispersive to covalent as the Ng atom grows heavier and that the metal and halogen atoms are capable of affecting the Ng-Nm bonding strength without altering the bonding character.



**FIGURE 4** (a) Calculated geometries of **2a** and **2b**. (b) Potential energy curves of  $Xe(MF)_2$  (M = Au, Ag, Cu). (c) Potential energy curves of  $Xe(AuX)_2$  (X = F, Cl, Br). (d) Potential energy curves of  $Ng(AuF)_2(Ng = Xe, Kr, Ar)$ . All geometries used in potential energy curve illustration were obtained by full optimization at each bending angle under the level of LC- $\omega$ PBE-D3/def2TZVPP.

#### 3.4 | Competition between Ng-Nm bonds and metallophilic interactions

A fact should be addressed is that aurophilic interaction can be generalized to a wider range of metals. The concept of metallophilic interaction typically denotes a weak electrostatic attractive force and is encountered mainly between adjacent low-valent closed shell  $[(n-1)d^{10}s^0]$  or pseudo-closed shell  $[(n-1)d^8ns^0]$  metal centers like Cu(I), Ag(I), Hg(II) and so on.<sup>[60]</sup> The competition between Ng-Nm bonds and metallophilic interactions is undoubtedly an interesting issue that induce the bond-bending isomerism. A good way to dig into the competition mechanism is to observe how the molecular structure will respond once any one of the atoms in Xe(AuF)<sub>n</sub> varies. For this purpose, the potential energy curves of Ng(NmX)<sub>2</sub> (Ng = Ar, Kr, Xe; Nm = Cu, Ag, Au; X = F, Cl, Br) were calculated and illustrated in **Figure 4**, by flexibly scanning the potential energy surface via stepwise changing the Nm-Ng-Nm angle. In contrast to Xe(AuF)<sub>2</sub> and Xe(AuCl)<sub>2</sub> that have two minimums on the potential energy curve representing the coexistence of **2a** and **2b**structures, the

rest species exhibit only one minimum at a Ng-Nm-Ng angle of approximately  $60^{\circ}$ , indicative of the sole **2b** isomer. This may be because only Xe(AuF)<sub>2</sub> and Xe(AuCl)<sub>2</sub> have Xe-Au bonds that are strong enough to compete with metallophilic interactions, thereby allowing two types of bond-bending isomers to coexist.

The optimized structures and the key geometrical parameters of Ng(AuF)<sub>2</sub> (Ng = Ar and Kr), Xe(NmF)<sub>2</sub> (Nm = Ag and Cu) and Xe(AuX)<sub>2</sub> (X = Cl and Br) are calculated as well and given in **Figure S5**. RDG analysis of these molecules shows a salient decrease of the Ng-Nm spike value from ~0.08 to ~0.06 (**Figure 3** and S6) once one arbitrary atom of Ng(AuF)<sub>2</sub> is substituted. It is noteworthy that weaker Ng-Nm bonds will lead to an increased instability of the traditional structures while have negligible effects on metallophilic structures, highlighting the significant role of Ng-Nm bonding strength in bond-bending isomerism.

#### 3.5 | Comparison among multi-coordinated Xe complexes

As mentioned hereinbefore, in inorganic complexes XeF<sub>n</sub>  $(n = 2, 4, 6)^{[2, 14]}$  or organic complexes Xe(CCH)<sub>n</sub>  $(n = 4, 6)^{[12]}$ , Xe tends to bind with an electronegative group via electron donation from both parts. The Xe-F bond in XeF<sub>n</sub> exhibits traditional  $\sigma$ -covalent character with Xe in  $sp^{\beta}d^{n}$ hybridization, forming symmetrical geometries, e.g., linearD<sub>2h</sub> configuration for XeF<sub>2</sub><sup>[2]</sup>, square planarD<sub>4h</sub> structure for XeF<sub>4</sub><sup>[2]</sup>, and square bipyramidalO<sub>h</sub> structure for XeF<sub>6</sub><sup>[14]</sup>. Similar phenomena were observed for the Xe-CCH bond in Xe(CCH)<sub>n</sub> (n = 4, 6), but with slight difference in that this interplay is partially ionic and partially covalent.<sup>[12]</sup> However, the strong covalent Xe-Au bonding in this work was formed via the electron donation-feedback mechanism for the whole family of Xe(AuF)<sub>n</sub> (n = 2-4) with Xe in $sp^{\beta}$  hybridization. The comparison clearly shows the differences regarding the formation mechanism of two types of Ng complexes referred to in the introduction context and gives further evidence to this work serving as an essential complement to the research field of Ng chemistry.

# 4 | CONCLUSION

In summary, the geometrical and electronic structures of a novel family of multi-coordinated Ng complexes,  $Xe(AuF)_n$  (n = 2-4), were theoretically predicted by using LC- $\omega$ PBE-D3/def2TZVPP method. Two types of bond-bending isomers were located with different Au-Xe-Au bond angles as a result of the competition between intramolecular aurophilic interactions and Xe-Au covalent bonds. Thorough potential energy surface scanning of Ng(NmX)<sub>2</sub> (Ng = Ar, Kr, Xe; Nm = Cu, Ag, Au; X = F, Cl ad Br) shows the unique bond-bending isomerism merely exists in Xe(AuF)<sub>n</sub> and Xe(AuCl)<sub>n</sub>, since their Xe-Au bonds are strong enough to compete against aurophilic interactions. Systematic chemical bonding analysis, *e.g.*, ETS-NOCV, EFL, RDG, and QTAIM, between these two types of bond-bending isomers confirms aurophilic interactions indeed exist and pronouncedly affect the intensity of the covalent Xe-Au bonds in these multi-coordinated Ng complexes. This work stands as an essential complement to the research field of Ng chemistry and pave the way for experimental progress in discovering multi-coordinated Ng complexes.

#### SUPPORTING INFORMATION

Comparison of the length and dissociation energy of Xe-Au bond in Xe-AuF at different theoretical levels (Table S1); geometric parameters of  $Xe(AuF)_n$  (n = 1-4) (Table S2); QTAIM topological analysis of linear NgMX (Ng = He, Ne, Ar, Kr, Xe; M = Cu, Ag, Au; X = F, Cl, Br, I) molecule (Table S3); chemical bonding analysis of isomers**3a**, **4a** and **4c**, including ETS-NOCV, ELF and RDG methods (Figure S1-S3); surface electrostatic potential map of AuF molecule (Figure S4); the lowest-energy structures of Ng(MX)<sub>2</sub> (Ng = Xe, Kr, Ar; M = Cu, Ag, Au, X = F, Cl, Br) with geometric and energic parameters; RDG analysis of  $Xe(AgF)_2$  and  $Xe(CuF)_2$  (Figure S6).

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#### CONFLICT OF INTEREST

The authors declare no competing financial interest.

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## **GRAPHICAL ABSTRACT**

This work predicts multi-coordinated Ng complexes  $Xe(AuF)_n$  (n = 2-4) and demonstrates intramolecular bond-bending isomerism that exhibiting two types of isomers due to the competition between Xe-Au covalent bonding and Au-Au aurophilic interactions, with the aid of high-precision theoretical calculations and electron and chemical bonding analysis. The present study serve as an essential complement to the research field of Ng chemistry and pave the way for experimental progress in discovering multi-coordinated Ng-metal complexes.