

The Intrinsic Stability of the Noble Gas-Coordinated Transition-Metal Complex Ions

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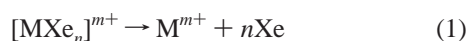
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Abstract: Density-functional-theory and high-level ab initio calculations have been performed on the $[\text{AuXe}_4]^{2+}$ ion and some other hypothetical xenon-, krypton-, and argon-coordinated transition-metal complex cations in the gas phase. Geometry optimization at the QCISD(T) level using a (6s7p4d2f1g) basis set for Au and a (4s4p2d1f) set for Xe predicted Au–Xe bond lengths in good agreement with the $\text{AuXe}_4^{2+}(\text{Sb}_2\text{F}_{11}^-)_2$ crystal structure. The ligand-binding energies of the $[\text{AuXe}_4]^{2+}$, $[\text{AuXe}_4]^{3+}$, and $[\text{PtXe}_4]^{2+}$ ions were predicted to be 229, 565, and 233 kcal/mol, respectively, at the CCSD(T) level. It is found that higher-level correlation effects are important to obtain accurate geometry parameters. The calculated results also indicated that various trivalent, tetravalent, and hexavalent transition-metal complexes of xenon or krypton might also be intrinsically stable.

Introduction

Despite its chemical inertness, the noble gas xenon has been known since 1963¹ to form compounds with fluorine and oxygen atoms, such as XeF_2 , XeF_4 , and XeO_4 , etc. Since 1975,² many organometallic noble gas complexes have been identified, for example, $\text{M}(\text{CO})_5\text{L}$ ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$; $\text{L} = \text{Ar}, \text{Kr}, \text{Xe}$) and $(\eta^5\text{-C}_5\text{R}_5)\text{M}(\text{CO})_2\text{L}$ ($\text{M} = \text{Mn}, \text{Co}, \text{Re}, \text{Rh}$; $\text{L} = \text{Kr}, \text{Xe}$). The stability (or reactivity) of these compounds has been subjected to extensive spectroscopic and kinetics studies in recent years.^{3,4} Khriachtchev et al.⁵ recently identified the first stable neutral argon compound, HArF , in a solid argon matrix. Very recently, the compound $\text{AuXe}_4^{2+}(\text{Sb}_2\text{F}_{11}^-)_2$ was isolated and crystallized by Seidel and Seppelt.⁶ This raised the question of whether other transition-metal ions in various oxidation states can also form stable complex ions of the form $[\text{MXe}_n]^{m+}$. In this article, we report a density-functional-theory (DFT) and high-level ab initio study on the ligand-binding energies (LBEs) of $[\text{AuXe}_4]^{2+}$ and some other hypothetical xenon-, krypton-, and argon-coordinated transition-metal complex cations in the gas phase. The LBE is defined as the classical (or Born–Oppenheimer) energy change of the following reaction:



where the most stable spin states are used for each species. The LBEs of some well-known coordination complexes are also calculated for comparison. The effects of the basis set sizes and the levels of correlation energy calculation are also explored.

Method

The DFT method used was Becke's three-parameter hybrid functional with the LYP nonlocal correlation functional (B3LYP).^{7,8} The quadratic configuration interaction method QCISD(T)⁹ and the coupled-cluster method CCSD(T)¹⁰ were also applied for selected species. Four atomic basis sets of different sizes were used in the current study. The first is the LANL2DZ^{11,12} set, where for heavy atoms the core electrons are represented by Hay and Wadt's effective core potentials (ECPs) and the outer electrons are represented by double- ζ atomic orbitals. The ECP also partially accounts for the relativistic effects. All four basis sets use the same LANL2 ECP to represent the core electrons for heavy atoms. Since the valence basis set of LANL2DZ is relatively small and lacks diffuse and polarization functions, we constructed the second basis set by first uncontracting the LANL2DZ valence set and then adding one set of f polarization functions and one set of diffuse s, p, and d functions for transition metals, and adding one set of d polarization functions and diffuse s and p functions for nonmetals. For example, the LANL2DZ valence set for Au is (5s6p3d) \rightarrow [3s3p2d] and that for Xe is (3s3p) \rightarrow [2s2p], and in the new basis set they are (6s7p4d1f) and (4s4p1d) for Au and Xe, respectively. We call this the B1 basis set. In the third basis set, we added one more set of f functions and one set of g polarization functions for the transition metals and one more set of d functions and one set of f functions for the nonmetals to the B1 set, giving (6s7p4d2f1g) and (4s4p2d1f) for Au and Xe, respectively. We call this the B2 basis set. In calculations using the B2 set, the basis functions for Cl, Cr, and Co were taken directly from the standard 6-311+G(2df) set, where ECPs were not used. The third basis set is identical to B2 except that one more set of d functions is added for both transition metals and nonmetals. We call this the B3 basis set. The B3LYP/LANL2DZ calculation was performed for all species to obtain the general trends. The B3LYP/B2 calculation was performed on selected species for more accurate molecular geometry

(7) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.

(8) (a) Stephens, P. J.; Devlin, F. J.; Chabalowski, C. F.; Frisch, M. J. *J. Phys. Chem.* **1994**, *98*, 11623. (b) Stephens, P. J.; Devlin, F. J.; Ashvar, C. S.; Bak, K. L.; Taylor, P. R.; Frisch, M. J. *ACS Symp. Ser.* **1996**, *629*, 105.

(9) Pople, J. A.; Head-Gordon, M.; Raghavachari, K. *J. Chem. Phys.* **1987**, *87*, 5968.

(10) Scuseria, G. E.; Schaefer, H. F. *J. Chem. Phys.* **1989**, *90*, 3700.

(11) Dunning, T. H., Jr.; Hay, P. J. In *Modern Theoretical Chemistry*; Schaefer, H. F., III, Ed.; Plenum: New York, 1976; Vol. 3, p 1.

(12) (a) Hay, P. J.; Wadt, W. R. *J. Chem. Phys.* **1985**, *82*, 270. (b) Wadt, W. R.; Hay, P. J. *J. Chem. Phys.* **1985**, *82*, 284. (c) Hay, P. J.; Wadt, W. R. *J. Chem. Phys.* **1985**, *82*, 299.

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(1) Bartlett, N. *Am. Sci.* **1963**, *51*, 114.

(2) Perutz, R. N.; Turner, J. J. *J. Am. Chem. Soc.* **1975**, *97*, 4791.

(3) Grills, D. C.; Sun, X. Z.; Childs, G. I.; George, M. W. *J. Phys. Chem. A* **2000**, *104*, 4300 and references therein.

(4) Yeston, J. S.; McNamara, B. K.; Bergman, R. G.; Moore, C. B. *Organometallics* **2000**, *19*, 3442.

(5) Khriachtchev, L. K.; Runeberg, N.; Lundell, J.; Räsänen, M. *Nature* **2000**, *406*, 874.

(6) Seidel S.; Seppelt, K. *Science* **2000**, *290*, 117.

Table 1. Calculated Ligand-Binding Energies (LBE, in kcal/mol), Bond Lengths (in Å), and Atomic Charges on the Metal Atoms at the B3LYP/LANL2DZ Level

	Ng = Xe			Ng = Kr			Ng = Ar		
	LBE	R_{M-X}	charge	LBE	R_{M-X}	charge	LBE	R_{M-X}	charge
NiNg ₄ ²⁺	139	2.730	0.24 (−0.02) ^a	96	2.533	0.50 (0.35)	61	2.422	0.75 (0.66)
ZnNg ₄ ²⁺	140	2.877	0.69 (0.53)	108	2.701	0.95 (0.82)	83	2.574	1.17 (1.09)
PtNg ₄ ²⁺	194	2.815	−0.07 (−0.35)	138	2.685	0.26 (0.14)	94	2.589	0.57 (0.52)
AuNg ₄ ²⁺	209	2.979	0.26 (−0.05)	158	2.842	0.56 (0.34)	119	2.733	0.83 (0.67)
HgNg ₂ ²⁺	99	2.913	1.02 (0.91)	68	2.798	1.27 (1.17)	47	2.718	1.49 (1.40)
CrNg ₆ ³⁺	482	2.983	−0.09 (−0.19)	412	2.770	0.41 (0.33)	333	2.628	0.62 (0.76)
CoNg ₆ ³⁺	523	2.818	−0.55 (−0.60)	434	2.627	0.00 (−0.06)	353	2.490	0.09 (0.39)
RhNg ₆ ³⁺	512	2.872	−0.64 (−0.69)	415	2.708	0.16 (−0.14)	410	2.591	0.23 (0.35)
IrNg ₆ ³⁺	493	2.864	−0.71 (−0.91)	394	2.710	−0.21 (−0.28)	381	2.595	0.23 (0.26)
AuNg ₄ ³⁺	535	2.922	0.21 (−0.13)	429	2.806	0.57 (0.39)	342	2.734	0.92 (0.81)
PtNg ₆ ⁴⁺	1086	2.925	−0.96 (−0.88)	920	2.783	0.20 (−0.21)	774	2.694	0.34 (0.38)
MoNg ₆ ⁶⁺	2436	3.169	−0.46 (−0.41)	nf ^b			nf		
WNg ₆ ⁶⁺	2184	3.028	−0.89 (−0.80)	1890	2.956	0.11 (0.26)	nf		

^a Numbers without parentheses are ChelpG charges; numbers in parentheses are Mulliken charges. ^b Stationary point not found.

and LBE. The QCISD(T) and CCSD(T) calculations were performed for most accurate evaluation of the geometry and energies for AuXe₄²⁺, AuXe₄³⁺, and PtXe₄²⁺. Calculations involving the B1 and B3 basis sets were, for the most part, used as convergence checks. The calculations were carried out using the Gaussian 98 program¹³ on several Linux workstations by our research group.

Results and Discussion

The calculated LBE and metal–noble gas bond lengths at the B3LYP/LANL2DZ level are listed in Table 1. We find that the LBE of AuXe₄²⁺ is predicted to be 209 kcal/mol at the B3LYP/LANL2DZ level. The calculation also shows that the Au³⁺ forms a much more stable square-planar complex with Xe than Au²⁺ by more than 300 kcal/mol. Since the binding between the metal ion and Xe is primarily an ion–induced dipole interaction, in general a higher charge density on the metal ion gives a higher binding energy, as is clearly shown in Table 1.

All the trivalent metal–Xe complexes give LBEs of approximately 500 kcal/mol. The LBEs are even much higher for the complexes formed from Pt⁴⁺, Mo⁶⁺, and W⁶⁺ ions.

In Table 1, the calculated M–Xe distances are between 2.7 and 3.2 Å. The Mo–Xe and W–Xe distances in the current study are shorter (by 0.03–0.07 Å at the B3LYP/LANL2DZ level) than those obtained by Ehlers et al.¹⁴ in a theoretical study of M(CO)₅Xe (M = Cr, Mo, W), while the Cr–Xe distances are very similar in both studies. When xenon was replaced by krypton, the calculation showed 13–30% decreases in LBEs and 0.07–0.20 Å decreases in bond lengths. When krypton was replaced by argon, the LBEs were further decreased by 2–40% and the bond lengths were further shortened by 0.07–0.15 Å. The ChelpG¹⁵ and Mulliken atomic charges on the metal atoms are also listed in the table. It can be seen that for each species the charge on the metal increases when the size of the noble

Table 2. Calculated Ligand-Binding Energies (LBE, in kcal/mol), Bond Lengths (in Å), and Atomic Charges on the Metal Atoms at the B3LYP/B2 Level

	Ng = Xe			Ng = Kr		
	LBE	R_{M-X}	charge	LBE	R_{M-X}	charge
PtNg ₄ ²⁺	233	2.619	−0.26 (−0.35)	183	2.528	−0.09(0.70)
AuNg ₄ ²⁺	232	2.842	0.05 (−0.25)	186	2.667	0.27(0.67)
CrNg ₆ ³⁺	503	2.849	−0.99 (2.11)	444	2.608	−0.97(0.76)
CoNg ₆ ³⁺	552	2.742	−2.00 (1.62)	471	2.513	−1.45(0.88)
AuNg ₄ ³⁺	565	2.746	−0.05 (−0.52)	469	2.557	0.28(1.02)
PtNg ₆ ⁴⁺	1108	2.812	−1.96 (−0.41)	961	2.608	−1.51(0.41)
MoNg ₆ ⁶⁺	2424	2.943	−2.01 (0.34)	2157	2.706	−1.40(2.50)
WNg ₆ ⁶⁺	2224	2.885	−1.84 (0.10)	1967	2.650	−1.61(0.61)

gas decreases. Also, for most of the more strongly bound Xe complexes, the metals carry significant negative charges, while in the Kr and Ar complexes most of the metals carry small or positive charges.

Table 2 shows the results of B3LYP/B2 calculations on selected Xe and Kr complexes. Compared with the B3LYP/LANL2DZ results, the calculated LBEs increase by approximately 20–40 kcal/mol for Xe complexes (except for MoXe₆⁶⁺) and by 30–80 kcal/mol for Kr complexes, and the bond lengths decrease by 0.1–0.2 Å for both types of complexes. A better basis set predicts stronger LBEs and more compact structures. At the B3LYP/B2 level the LBE for AuXe₄²⁺ is 232 kcal/mol and the Au–Xe bond length is 2.842 Å, which can be compared to the B3LYP values of 228 kcal/mol and 2.871 Å obtained by Seidel and Seppelt⁶ using a smaller Au basis set, whereas their experimental bond length was 2.728–2.750 Å. (In their MP2 calculation, the bond length was 2.787 Å, but the LBE seemed to be significantly underestimated.) In Table 2, at the same oxidation state, metal atoms with more negative ChelpG charges might correspond to a more covalent character of the M–Ng bonds, as shown in Figures 1 and 2, where the electronic density isosurfaces of PtXe₄²⁺ and AuXe₄²⁺ calculated at the B3LYP/B2 level are plotted. The Pt atom in Figure 1 carries a more negative ChelpG charge than the Au atom in Figure 2. The electronic density isosurfaces of PtCl₄^{2−} are plotted in Figure 3 for comparison. Similar correlation was also found for CrXe₆³⁺ and CoXe₆³⁺, and their isodensity plots are included in the Supporting Information. However, it should be understood that the values of the atomic

(13) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Baboul, A. G.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, Revision A.7; Gaussian, Inc.: Pittsburgh, PA, 1998.

(14) Ehlers, A. W.; Frenking, G.; Baerends, E. J. *Organometallics* **1997**, *16*, 4896.

(15) Breneman, C. M.; Wiberg, K. B. *J. Comput. Chem.* **1990**, *11*, 361. For those elements whose van der Waals radii were not included in the original parametrization, the following values (in Å) were used in calculating the ChelpG charges: Cr, 1.7; Co, 1.6; Ni, 1.6; Zn, 1.4; Kr, 2.0; Mo, 1.9; Ag, 1.7; I, 2.0; Xe, 2.2; W, 1.9; Ir, 1.8; Pt, 1.8; Au, 1.7; Hg, 1.6.

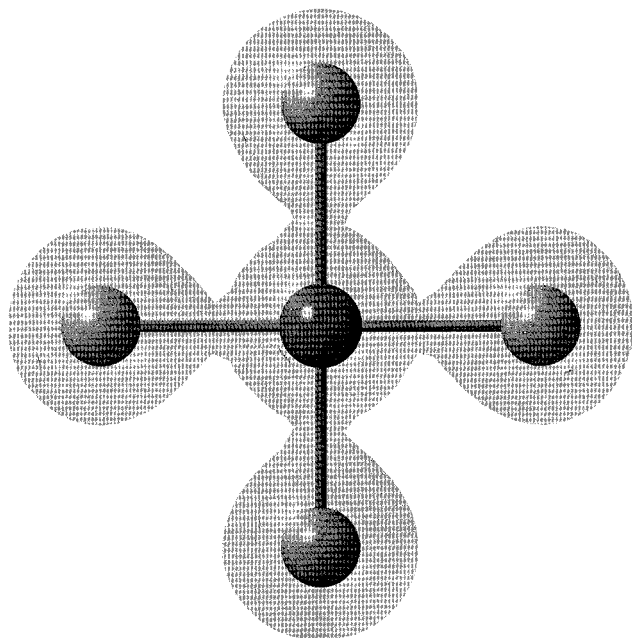


Figure 1. Calculated electron density isosurface (0.06 au) of PtXe_4^{2+} .

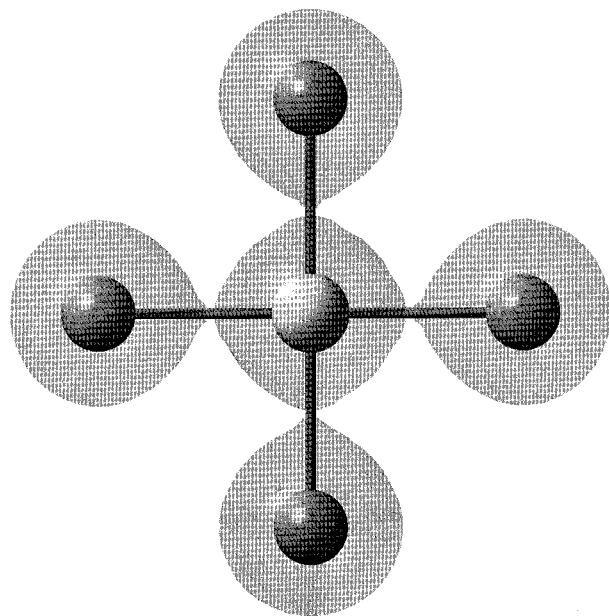


Figure 2. Calculated electron density isosurface (0.06 au) of AuXe_4^{2+} .

charges based on the electrostatic potential (such as ChelpG method) depend on the selection of fitting points, which are somewhat arbitrary. All the calculated charges in Tables 1 and 2 indicate significant charge transfer from the noble gas to the transition metal in the complexes. The charge distribution of the Au complexes is not particularly different from that of other complexes.

Table 3 lists the B3LYP/LANL2DZ and B3LYP/B2 results for some well-known transition-metal complexes and AuI_4^{2-} and AuI_4^- , which are isoelectronic to AuXe_4^{2+} and AuXe_4^{3+} , respectively. Compared with the data in Table 1, at the B3LYP/LANL2DZ level the LBEs of the Xe and Kr complexes formed by the trivalent metal ions are higher than those of the neutral carbonyl compounds and are about 60% of the LBE of $\text{Co}(\text{NH}_3)_6^{3+}$. Furthermore, the LBEs of the xenon and krypton complexes formed by the tetravalent and hexavalent metal ions are comparable to those of AuCl_4^- and PtCl_6^{2-} . It is also interesting to note that although AuI_4^{2-} is isoelectronic to

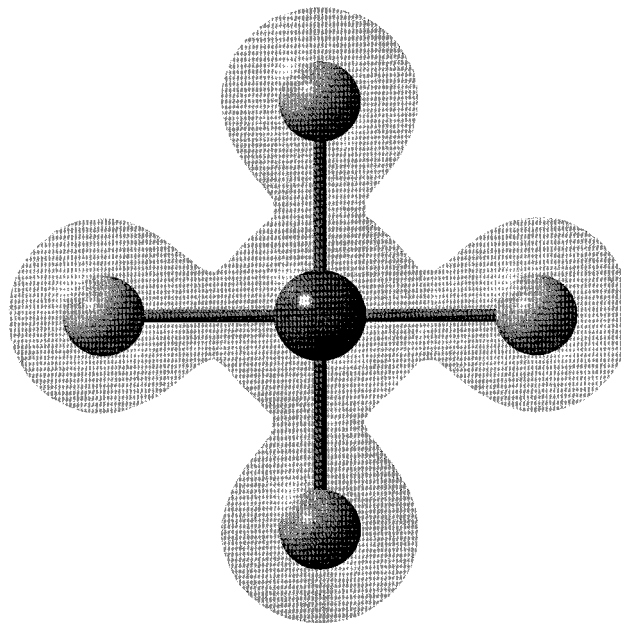


Figure 3. Calculated electron density isosurface (0.06 au) of PtCl_4^{2-} .

Table 3. Calculated Ligand-Binding Energies (LBE, in kcal/mol), Bond Lengths (in Å), and Atomic Charges on the Metal Atoms at the B3LYP/LANL2DZ and B3LYP/B2 Levels

	B3LYP/LANL2DZ			B3LYP/B2		
	LBE	R_{M-X}	charge	LBE	R_{M-X}	charge
HgI_2	62	2.747	0.63 (0.37)			
$\text{Ni}(\text{CO})_4$	145	1.849	-0.83 (-0.12)			
$\text{Mo}(\text{CO})_6$	263	2.060	-1.29 (0.42)			
$\text{Ag}(\text{NH}_3)_4$	101	2.177	0.38 (0.50)			
$\text{Pt}(\text{NH}_3)_4$	433	2.109	0.04 (0.63)			
$\text{Co}(\text{NH}_3)_4$	875	2.041	1.01 (0.39)			
AuCl_4^-	1474	2.440	0.55 (-0.12)	1414	2.334	0.58 (0.35)
AuI_4^-	1411	2.779	0.37 (-0.52)	1392	2.683	0.50 (-0.66)
PtCl_4^{2-}	707	2.474	0.25 (-0.32)	664	2.379	0.48 (0.15)
AuI_4^{2-}	641	2.872	0.36 (-0.22)	630	2.833	0.84 (-0.72)
PtCl_6^{2-}	2432	2.467	1.40 (-0.36)	2329	2.385	1.17 (-0.04)

AuXe_4^{2+} , instead of being D_{4h} in symmetry, its optimized structures are significantly distorted square planar with C_{2v} symmetry at both the B3LYP/LANL2DZ and B3LYP/B2 levels. Increasing the basis set size seemed to decrease the LBE slightly (<10%) and shorten the bond length by 0.04–0.1 Å for those complex anions in Table 3.

Table 4 shows the results for a series of calculation using B3LYP, QCISD(T), and CCSD(T) methods with B1, B2, and B3 basis sets on AuXe_4^{2+} , AuXe_4^{3+} , and PtXe_4^{2+} . The vibrational frequencies and the corresponding IR and Raman intensities of these three ions were calculated at the B3LYP/B2 level, and they are included in the Supporting Information. It is clearly seen in Table 4 that with the same basis set, higher levels of correlation calculation tend to shorten the bond lengths, especially for AuXe_4^{2+} . From B3LYP to QCISD(T) or CCSD(T), the predicted Au–Xe bond lengths in AuXe_4^{2+} decrease by 0.06–0.07 Å. At the QCISD(T)/B2 level the Au–Xe bond length is 2.774 Å, which is close to the high end of the experimental values. (In the crystal structure, three fluorine atoms are close to the AuXe_4^{2+} plane, and this might have some effects on the geometry.) With the B1 basis set, higher-level correlation calculation decreases the LBE slightly, but there are almost no changes in the LBE when the B2 basis set is used. The QCISD(T) and CCSD(T) methods essentially give the same results when the B1 set is used. When CCSD(T)/B2 energy

Table 4. Calculated Ligand-Binding Energies (LBE, in kcal/mol) and Bond Lengths (in Å) at Various Levels

	B3LYP/B1		QCISD(T)/B1		CCSD(T)/B1		B3LYP/B2		QCISD(T)/B2		B3LYP/B3	
	LBE	R_{M-X}	LBE	R_{M-X}	LBE	R_{M-X}	LBE	R_{M-X}	LBE	R_{M-X}	LBE	R_{M-X}
AuXe ₄ ²⁺	227	2.867	223	2.808	223	2.807	232	2.842	230 (229) ^a	2.774 ^b	233	2.842
AuXe ₄ ³⁺	556	2.774	540	2.726	539	2.726	565	2.746	566 (565)	2.747	565	2.746
PtXe ₄ ²⁺	225	2.721	222	2.692	221	2.691	233	2.691	234 (234)	2.650	234	2.692

^a Numbers in parentheses are LBEs calculated at the CCSD(T)/B2 // QCISD(T)/B2 level. ^b Experimental⁶ value: 2.728–2.750 Å.

calculation is performed on the QCISD(T)/B2 geometry, the LBEs are almost identical to the QCISD(T)/B2 values. The B3LYP/B3 and B3LYP/B2 results are also essentially the same. Table 4 thus suggests that converged higher-level correlation calculation is required to obtain accurate geometry parameters for noble-gas-coordinated complexes. The LBEs, however, can be modeled as accurately as by higher-level correlation methods using the B3LYP density functional theory, provided a good valence basis set is used. It is noted that the incomplete treatment of the relativistic effects,¹⁶ which are very important in heavy metals, might contribute some errors to the calculation.

Summary

Various noble-gas (Xe, Kr, and Ar)-coordinated transition-metal complex ions have been studied by density functional theory, quadratic configuration interaction, and coupled-cluster methods with a series of basis sets. The combination of quality basis sets and high-level correlation method seemed to be required to obtain accurate geometry parameters, while the ligand-binding energies can be estimated satisfactorily by the

B3LYP method with a good basis set. Our calculation also showed that if [AuXe₄]²⁺ is stable, several other trivalent transition-metal complexes of xenon or krypton might also be stable. In addition, the tetravalent or hexavalent metal ions (Pt⁴⁺, Mo⁶⁺, W⁶⁺) are predicted to form octahedral Xe and Kr complexes with LBEs as high as those of some stable ammonia and chloride complexes. Of course, it is understood that a high LBE does not necessarily mean easy synthesis or air and thermal stability. However, we hope that the calculated results in this study would encourage the search for suitable procedures to synthesize other stable noble-gas-coordinated complexes.

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Supporting Information Available: Tables of Gaussian basis sets used in the current study, electron density isosurface plots, calculated vibrational frequencies, and IR and Raman intensities (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

(16) Pyykkö, P. *J. Am. Chem. Soc.* **1995**, *117*, 2067.