ISSN 1070-3632, Russian Journal of General Chemistry, 2015, Vol. 85, No. 4, pp. 790–795. © Pleiades Publishing, Ltd., 2015.
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Quantum Chemical Study of Structure of Ionic Complexes of I and II Groups Metals with Xenon or Krypton

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Received January 12, 2015

Abstract—Point symmetry groups and equilibrium structure parameters of the following complexes of gold, silver, copper, mercury, cadmium, zinc, and barium with xenon and krypton have been determined using (U)PBE0/SDD and (U)MP2/SDD quantum chemical methods: $MtNg_2^+$ ($D_{\infty h}$, C_{2v}); $AuNg_3^{2+}$, $AgNg_3^{2+}$, and $CuNg_3^{2+}$ (C_{2v}); $HgNg_3^{2+}$, $CdNg_3^{2+}$, $ZnNg_3^{2+}$, and $BaNg_3^{2+}$ (D_{3h}); $AuNg_4^{2+}$ and $AgNg_4^{2+}$ (D_{4h}); $CuNg_4^{2+}$ (D_{2d}, flattened out tetrahedron); $HgNg_4^{2+}$, $CdNg_4^{2+}$, $ZnNg_4^{2+}$, $BaNg_4^{2+}$, and $MtNg_4^+$ (T_d). The computed free energies of decomposition into the single-charged $MtNg_2^+$ and Ng_2^+ cations show metastability of the twice-charged complexes of Au(II), Ag(II), Cu(II), Hg(II), Cd(II), and Zn(II) with four atoms of xenon or krypton.

Keywords: noble gas, metal complex, Au(II), Ag(II), Cu(II), Hg, Cd, Zn, Ba, Kr, Xe, molecular structure, metastability, quantum chemical simulation, pseudo potential

DOI: 10.1134/S1070363215040039

The interest to incorporation of noble gases (Ng) atoms in the first coordination sphere of metal complexes has emerged after preparation and X-ray diffraction study of $AuXe_4^{2+}(Sb_2F_{11}^-)_2$ salt, a product of gold(III) fluoride interaction with xenon and antimony(V) fluoride in fluoric acid [1]. The salt has been stable up to –40°C and contained a rarely observed Au(II) state with the gold forming coplanar chemical bonds with four square-coordinated xenon atoms [1].

Quantum chemical simulation of the free $AuXe_4^{2+}$ ion using HF, B3LYP, and MP2 methods has confirmed the square-planar coordination unusual for gold compounds, with the D_{4h} point symmetry group [1].

Using the B3LYP/LANL2DZ method, bond lengths in the free xenon-, krypton-, and argon-containing metal complexes and energies of their decomposition into atomic components ($MtNg_k^{\zeta+} \rightarrow Mt^{\zeta+} + k\text{Ng}$) in a vacuum have been determined [2]. The following metal cations Mt have been studied: two-coordinated Hg(II), four-coordinated Au(II), Au(III), Ni(II), Zn(II), and Pt(II), and six-coordinated Cr(III), Co(III), Rh(III), Ir(III), Pt(IV), Mo(VI), and W(VI). The Au–Xe bond length in the $AuXe_4^{2+}$ complex (298 pm) has exceeded that from the X-ray structure analysis by 24 pm. The simulation with a QCISD(T) method using the extended basis set including the polarizing and the diffuse Gauss orbitals and the same effective core potential (LANL2DZ) has given the Au–Xe bond length of 277 pm and the energy of 230 kcal/mol. Similar simulations have been performed for hypothetical $PtXe_4^{2+}$ (265 pm, 234 kcal/mol [2]) and $AuXe_4^{3+}$ (269 pm, 549 kcal/mol [3]) complexes.

In this work we report on simulation of Au(I,II), Ag(I,II), Cu(I,II), Hg(II), Cd(II), Zn(II), and Ba(II) metal complexes with four atoms of Xe or Kr. The simulation was performed using the (U)PBE0/SDD and (U)MP2/SDD quantum chemical methods and GAUSSIAN-09 software [4].

Molecular orbitals were represented by linear combinations of Cartesian Gauss-type orbitals: 6*s*5*p*3*d* for the Mt atom and 4*s*4*p*3*d*1*f* for the Ng atom. Apart from the valence orbitals, the basis set included the orbitals of the atoms outer subvalence shells. Other shells were "frozen" and accounted for by exchange of the atom nucleus potentials with the known SDD pseudo potentials.

The equilibrium bond lengths calculated for three xenon-containing cations applying various quantum

Table 1. Equilibrium internuclear distances (pm) calculated by (U)HF/SDD, (U)B3LYP/SDD, (U)PBE0/SDD, and MP2/SDD methods and the results of X-ray structure analysis of three xenon-containing cations

Cation	Bond	HF	B3LYP	PBE0	MP2	X-ray
Xe_2^+	Xe–Xe	316	324	316	310	309 [5]
$AuXe_4^{2+}$	Au–Xe	289 [1]	287 [1]	281	279 [1]	275[a], 273[b]
$F_3AsAuXe^+$	Au–Xe	280	269	264[c]	264[d]	261 [7][e]

[a] The average of the 273–278 pm bond lengths in triclinic $AuXe_4^{2+}(Sb_2F_{11}^-)_2$ modification [1]. [b] The average of the 267–276 pm bond lengths in the tetragonal modification [6]. [c] Bond energy of 32.6 kcal/mol. [d] Bond energy of 29.8 kcal/mol. The MP2/(mixed basis set) method gave the bond length of 261 pm and the bond energy of 32.7 kcal/mol [7]. [e] $F_3AsAuXe^+$ $Sb_2F_{11}^-$ crystal.

Table 2. Average squared spin $<S^2>$, the Mt–Ng internuclear distances, atomic charges, and natural populations of the valence shells of Mt atom in the $MtNg_4^{\zeta+}$ complexes calculated by the (U)PBE0/SDD method

Mt(I, II)	Term[a]	$<S^2>$, a. u.	Mt–Ng, pm	Charge, a. u.		Mt configuration		
				Mt	Ng	*d*	*s*	*p*
Xenon complexes								
Au(II)	$^2B_{1g}//D_{4h}$	0.7544	281	0.102	0.475	9.63	0.72	0.55
Ag(II)	$^2B_{1g}//D_{4h}$	0.7543	284	0.244	0.439	9.73	0.50	0.53
Cu(II)	$^2B_1//D_{2d}$[b]	0.7539	266	0.298	0.426	9.44	0.62	0.63
Hg(II)	$^1A_1//T_d$	0	289	0.465	0.384	10.00	0.91	0.62
Cd(II)	$^1A_1//T_d$	0	287	0.607	0.348	10.00	0.71	0.68
Zn(II)	$^1A_1//T_d$	0	267	0.426	0.393	10.00	0.79	0.78
Ba(II)	$^1A_1//T_d$	0	351	1.390	0.153	0.31	0.12	0.17
Au(I)	$^1A_1//T_d$	0	290	–0.031	0.258	9.97	0.55	0.50
Ag(I)	$^1A_1//T_d$	0	293	0.152	0.212	9.98	0.39	0.47
Cu(I)	$^1A_1//T_d$	0	270	0.049	0.238	9.97	0.47	0.50
Krypton complexes								
Au(II)	$^2B_{1g}//D_{4h}$	0.7537	263	0.524	0.369	9.50	0.57	0.40
Ag(II)	$^2B_{1g}//D_{4h}$	0.7533	264	0.641	0.340	9.59	0.39	0.38
Cu(II)	$^2B_1//D_{2d}$[c]	0.7527	247	0.689	0.328	9.31	0.50	0.50
Hg(II)	$^1A_1//T_d$	0	272	0.859	0.285	9.99	0.70	0.43
Cd(II)	$^1A_1//T_d$	0	269	0.981	0.255	10.00	0.53	0.49
Zn(II)	$^1A_1//T_d$	0	248	0.837	0.291	10.00	0.60	0.55
Ba(II)	$^1A_1//T_d$	0	333	1.643	0.089	0.20	0.06	0.10
Au(I)	$^1A_1//T_d$	0	280	0.348	0.163	9.98	0.36	0.30
Ag(I)	$^1A_1//T_d$	0	282	0.476	0.131	9.99	0.25	0.28
Cu(I)	$^1A_1//T_d$	0	255	0.343	0.164	9.98	0.33	0.35

[a] Hereinafter the symbols to the left of the "//" sign characterize the symmetry of the electron state (spin multiplicity and irreducible representation of the symmetry group); the symbols to the right of the sign show the symmetry group of the nuclei equilibrium configuration [11]. [b] Flattened tetrahedron with the angles of 96.9° and 139.4°. [c] Flattened tetrahedron with the angles of 93.7° and 150.7°.

Table 3. Average squared spin $<S^2>$, the Mt–Ng internuclear distances, atomic charges, and natural populations of the valence shells of Mt atom in the $MtNg_4^{2+}$ complexes calculated by the (U)MP2/SDD method

Mt(II)	Term	$<S^2>$, a. u.	Mt–Ng, pm	Charges, a. u.		Mt configuration		
				Mt	Ng	*d*	*s*	*p*
Xenon complexes								
Au(II)	$^2B_{1g}//D_{4h}$	0.7694	279	0.40	0.40	9.42	0.59	0.59
Ag(II)	$^2B_{1g}//D_{4h}$	0.7699	281	0.52	0.37	9.48	0.43	0.57
Cu(II)	$^2B_1//D_{2d}$ [a]	0.7523	266	0.67	0.33	9.06	0.58	0.68
Hg(II)	$^1A_1//T_d$	0	287	0.72	0.32	10.00	0.66	0.62
Cd(II)	$^1A_1//T_d$	0	287	0.84	0.29	10.00	0.52	0.63
Zn(II)	$^1A_1//T_d$	0	266	0.62	0.35	10.00	0.63	0.74
Krypton complexes								
Au(II)	$^2B_{1g}//D_{4h}$	0.7618	261	0.86	0.28	9.26	0.45	0.41
Ag(II)	$^2B_{1g}//D_{4h}$	0.7584	261	1.01	0.25	9.25	0.34	0.40
Cu(II)	$^2B_1//D_{2d}$ [b]	0.7519	247	1.01	0.25	9.05	0.42	0.51
Hg(II)	$^1A_1//T_d$	0	271	1.12	0.22	9.99	0.46	0.41
Cd(II)	$^1A_1//T_d$	0	270	1.21	0.20	10.00	0.36	0.43
Zn(II)	$^1A_1//T_d$	0	246	1.02	0.24	10.00	0.45	0.51

[a] Flattened tetrahedron with the angles of 102.1° and 125.5°. [b] Flattened tetrahedron with the angles of 98.6° and 134.5°.

chemical methods using the SDD pseudo potential are compared with X-ray structure analysis data in Table 1. The MP2 and PBE0 methods allowed for fairly good correspondence of the simulation results with the experimental data.

The charges and valence configurations of the atoms in the complexes were obtained by natural population analysis (NPA) [8]. We determined the energy of complete decomposition of the complexes into four noble gas atoms and the metal cation [Eq. (1)], the detachment energy of one of the noble gas atoms [Eq. (2)], and the energy of the twice-charged cation $MtNg_4^{2+}$ decomposition into the single-charged $MtNg_2^+$ and Ng_2^+ cations.

$$MtNg_4^{\zeta+} \rightarrow Mt^{\zeta+} + 4Ng, \quad (1)$$

$$MtNg_4^{\zeta+} \rightarrow MtNg_3^{\zeta+} + Ng, \quad (2)$$

$$MtNg_4^{2+} \rightarrow MtNg_2^+ + Ng_2^+. \quad (3)$$

The optimal configurations of the complexes formed by spherically symmetrical Au(I), Ag(I), Cu(I), Hg(II), Cd(II), Zn(II), and Ba(II) cations revealed the highest T_d symmetry. The Jahn–Teller theorem states that the complexes of Au(II), Ag(II), and Cu(II) containing 9 electrons in the $(n-1)d$ shell cannot be tetrahedral. The nonlinear nuclei configuration with the symmetry-degenerate electron state is unstable [9, 10]. The equilibrium configuration corresponding to the energy minimum of the Au(II) and Ag(II) complexes was square-planar (D_{4h}). The D_{4h} configuration was a transition state in the case of the Cu(II) complexes; the relatively low symmetry of the Cu(II) complexes with krypton and xenon was due to the less favorable ratio of the metal cation radius to the radii of the four ligands. The energy of inversion of the D_{2d} configuration accounting for ZPE correction was 1.9 kcal/mol ($CuXe_4^{2+}$) and 0.5 kcal/mol ($CuKr_4^{2+}$).

The calculated bond lengths (Tables 2 and 3) were increasing in the Cu(II) < Zn(II) < Cu(I) < Au(II) < Ag(II) < Cd(II) < Hg(II) < Au(I) < Ag(I) < Ba(II) series. The Mt–Kr bonds were shorter than the Mt–Xe ones. From the atomic charges, the electronegativity of the Mt^{2+} dication increased along the Ba(II) < Cd(II) < Hg(II) < Zn(II) < Cu(II) < Ag(II) < Au(II) series.

Positive charge of the noble gas atom was due to the decreased population of the *np* orbital oriented

Table 4. Estimated free energy required for decomposition of the $MtNg_4^{2+}$ complex via routes (1), (2), and (3) (kcal/mol); see text for the routes description

Mt(I, II)	(1)	(2)	(3)	Mt(I, II)	(1)	(2)	(3)
Xenon complexes				Krypton complexes			
Au(II)	–	15	–63	Au(II)	–	15	–55
Ag(II)	–	14	–73	Ag(II)	–	14	–73
Cu(II)	–	13	–62	Cu(II)	–	13	–52
Hg(II)	167	11	–29	Hg(II)	126	10	–27
Cd(II)	139	12	–9	Cd(II)	106	11	–2
Zn(II)	178	13	–5	Zn(II)	144	14	2
Ba(II)	37	6	63	Ba(II)	24	5	88
Au(I)	45	–1	–	Au(I)	25	–1	–
Ag(I)	25	–1	–	Ag(I)	14	–1	–
Cu(I)	39	–2	–	Cu(I)	26	–2	–

towards the metal cation and bound to the $Mt^{\zeta+}$ valence orbital. The population of the valence shells of the metal evidenced its orbitals hybridization. A small admixture of *ns*, np_x, and np_y orbitals into the $(n-1)d_{xx-yy}$ orbital of Au(II) and Ag(II) favored the slight localization of each of the hybrid orbitals at the corresponding Mt–Ng bond, yet is insufficient for the orthogonality of the metal equivalent hybrid orbitals. Due to the strong intraatomic overlap of the four hybrid metal orbitals, the covalent bond in the gold(II) and silver(II) complexes with D_{4h} symmetry was delocalized.[1] The same held for the copper(II) complexes of D_{2d} symmetry, with the hybrid orbitals containing a small admixture of the np_z copper orbital.

The attraction of the polarized noble gas atoms to the $Mt^{\zeta+}$ cation resulted in the lowered energy of the $MtNg_k^{\zeta+}$ system. At the sufficiently short interaction distance the probability of the electron exchange (covalent bonding) between the metal cation and the noble gas atoms appeared, turning stronger with the higher Ng atom charge and the smaller metal cation charge. The highest noble gas charge and the highest covalent contribution to the Mt–Ng bonding was found for the gold(II) complexes, in particular, the $AuXe_4^{2+}$ one. The larger bond energy in the case of Xe as compared to the corresponding Kr complexes was due to the lower electronegativity and the higher polarizability of xenon.

The relatively weak bonding of the noble gases with barium cation was electrostatic. The $BaNg_4^{2+}$ complex did not possess any rigid structure. The simulation of the equilibrium Ba–Xe bond length using a PBE0/SDD method with the T_d symmetry gave an energy minimum and the real vibration frequencies close to zero. The (U)MP2/SDD method gave the lower symmetry of the $BaNg_4^{2+}$ cation (C_s).

The calculation predicted metastability of the $AuNg_4^{2+}$, $AgNg_4^{2+}$, $CuNg_4^{2+}$, and $HgNg_4^{2+}$ complexes in a vacuum. The complexes free energies were higher than the sum of energies of the single-charged Ng_2^+ and $MtNg_2^+$ ($D_{\infty h}$) cations. The change in the "symmetry entropy" favored the decomposition of highly symmetrical $MtNg_4^{2+}$ cations into the single-charged cations Ng_2^+ and $MtNg_2^+$. The T_d, D_{4h}, and D_{2d} groups corresponded to the symmetry numbers of σ = 12, 8, and 4; the C_{2v} and $D_{\infty h}$ groups corresponded to the lower σ = 2 [14, 15]. Hence, the decomposition of square $AuNg_4^{2+}$ and $AgNg_4^{2+}$ dications was accompanied with the increase in the "symmetry entropy" by a value of $R\ln 2$, the corresponding value in the cases of tetrahedral dications $HgNg_4^{2+}$, $CdNg_4^{2+}$, $ZnNg_4^{2+}$, and $BaNg_4^{2+}$ being of $R\ln 3$.

[1] The concept of intraatomic overlap of the hybrid atomic orbitals has been earlier applied for description of conjugation in polyphthalocyaninates with siloxane rod [12] and in heterocyclic derivatives of 9,10-dihydroanthracene (see [13] and references therein).

Table 5. Bond angles (θ) and bond lengths Mt–Ng in the $MtNg_2^+$ complexes calculated using the (U)PBE0/SDD method

Metal Mt(I)	Term	θ, deg	Mt–Ng, pm	Term	θ, deg	Mt–Ng, pm
	Xenon complexes			Krypton complexes		
Au(I)	$^1\Sigma_g^+//D_{\infty h}$	180.0	264	$^1\Sigma_g^+//D_{\infty h}$	180.0	252
Ag(I)	$^1\Sigma_g^+//D_{\infty h}$	180.0	275	$^1\Sigma_g^+//D_{\infty h}$	180.0	265
Cu(I)	$^1\Sigma_g^+//D_{\infty h}$	180.0	250	$^1\Sigma_g^+//D_{\infty h}$	180.0	236
Hg(I)	$^2\Sigma_g^+//D_{\infty h}$	180.0	310	$^2\Sigma_g^+//D_{\infty h}$	180.0	300
Cd(I)	$^2A_1//C_{2v}$	110.9	315	$^2A_1//C_{2v}$	98.2	304
Zn(I)	$^2A_1//C_{2v}$	112.6	293	$^2A_1//C_{2v}$	104.6	279
Ba(I)	$^2\Sigma_g^+//D_{\infty h}$	180.0	365	$^2A_1//C_{2v}$	174.9	347

Table 6. Angles θ between the equivalent Mt–Ng bonds and the Mt–Ng and Mt–Ng' bond lengths in the $MtNg_3^{2+}$ complexes calculated using the (U)PBE0/SDD method

Mt(II)	Term	θ, deg	Mt–Ng, pm	Mt–Ng', pm	Term	θ, deg	Mt–Ng, pm	Mt–Ng', pm
	Xenon complexes				Krypton complexes			
Au(II)	$^2A_1//C_{2v}$	161.7	269	279	$^2A_1//C_{2v}$	167.0	253	263
Ag(II)	$^2A_1//C_{2v}$	163.9	274	282	$^2A_1//C_{2v}$	169.4	257	264
Cu(II)	$^2A_1//C_{2v}$	147.7	256	260	$^2A_1//C_{2v}$	153.0	238	242
Hg(II)	$^1A_1//D_{3h}$	120.0	281	281	$^1A_1//D_{3h}$	120.0	265	265
Cd(II)	$^1A_1//D_{3h}$	120.0	280	280	$^1A_1//D_{3h}$	120.0	263	263
Zn(II)	$^1A_1//D_{3h}$	120.0	259	259	$^1A_1//D_{3h}$	120.0	241	241
Ba(II)	$^1A_1//D_{3h}$	120.0	349	349	$^1A_1//D_{3h}$	120.0	331	331

The binding energy of the noble gas atoms with the single-charged cations Au(I), Ag(I), and Cu(I) was much lower than that in the case of doubly-charged cations of transition metals (Table 4), the "symmetry entropy" favoring the cleavage of noble gas atoms from all $MtNg_4^{\zeta+}$ tetrahedral complexes. Mt(I) cations could not bind more than two atoms of Xe or Kr at room temperature.

PBE0/SDD simulation predicted triangular structure with C_{2v} symmetry for the free $CdNg_2^+$, $ZnNg_2^+$, and $BaKr_2^+$ cations and linear structure with $D_{\infty h}$ symmetry for the $AuNg_2^+$, $AgNg_2^+$, $CuNg_2^+$, $HgNg_2^+$, and $BaXe_2^+$ cations (Table 5). The planar T-shaped structures of the $AuNg_3^{2+}$, $AgNg_3^{2+}$, and $CuNg_3^{2+}$ cations contained two equivalent Mt–Ng bond and the longer Mt–Ng' bond, whereas the three Mt–Ng bonds were equivalent in the highly symmetrical (D_{3h}) $HgNg_3^{2+}$, $CdNg_3^{2+}$, $ZnNg_3^{2+}$, and $BaNg_3^{2+}$ cations (Table 6).

When in the condensed phase, the above-listed cations can decompose or change the symmetry due to addition of the solvent molecules or the interaction with the anion in crystal. In particular, the X-ray analysis data showed that the angle θ between the Au–Xe bonds in the *cis*-$AuXe_2^{2+}(Sb_2F_{11}^-)_2$ crystal was significantly smaller than the simulated equilibrium bond angle of 118º in the free $AuXe_2^{2+}$ cation; vice versa, the corresponding angle in the less stable *trans*-$AuXe_2^{2+}(SbF_6^-)_2$ crystal was much larger than the simulated one [6]. At the same time, the simulated length of the Au–Xe bond of 267 pm (PBE0/SDD) was close to the X-ray diffraction analysis data: 266 and 267 pm (*cis* Au–Xe bonds) or 259 and 262 pm (*trans* Au–Xe bonds).

$MtNg_4^{2+}$ cations were stabilized via the Coulombic attraction to the counterions in the $AuXe_4^{2+}(Sb_2F_{11}^-)_2$ crystal. Moreover, the large $Sb_2F_{11}^-$ anions and the

crystal lattice in general prevented the spreading of the charged fragments to the distance corresponding to the Coulombic repulsion. However, at $T > -40°C$ the crystal liquefies, xenon stands out, and the substance color changes from dark-red into pale-orange [1]. When in solution, the noble gas atoms can be displaced from the complex by solvent molecules, counterions, and F^- ions cleaved from the fluorine-containing counterions.

To conclude, quantum chemical simulation demonstrated the metastability of the Au(II), Ag(II), Cu(II), and Hg(II) complexes with four noble gas atoms in the first coordination sphere and the possibility of their decomposition into a pair of single-charged cations ($MtNg_2^+ + Ng_2^+$). The symmetry of such complexes, the internuclear distances, and the charge distribution between the metal and the ligand pointed to a significant covalent contribution in the formed chemical bonds.

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