A computational study on structure, stability and bonding in Noble Gas bound metal Nitrates, Sulfates and Carbonates (Metal = Cu, Ag, Au)

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Abstract. A density functional theory based study is performed to investigate the noble gas (Ng = Ar–Rn) binding ability of nitrates, sulfates and carbonates of noble metal (M). Their ability to bind Ng atoms is assessed through bond dissociation energy and thermochemical parameters like dissociation enthalpy and dissociation free energy change corresponding to the dissociation of Ng bound compound producing Ng and the respective salt. The zero-point energy corrected dissociation energy values per Ng atom for the dissociation process producing Ng atom(s) and the corresponding salts range within 6.0–13.1 kcal/mol in NgCuNO₃, 3.1–9.8 kcal/mol in NgAgNO₃, 6.0–13.2 kcal/mol in NgCuSO₄, 3.2–10.1 kcal/mol in NgAgSO₄, 5.1–11.7 kcal/mol in Ng₂Cu₂SO₄, 2.5–8.6 kcal/mol in Ng₂Ag₂SO₄, 8.1–19.9 kcal/mol in Ng₂Au₂SO₄, 5.7–12.4 kcal/mol in NgCuCO₃, 2.3–8.0 kcal/mol in Ng₂Ag₂CO₃ and 7.3–18.2 kcal/mol in Ng₂Au₂CO₃, with a gradual increase in moving from Ar to Rn. For a given type of system, the stability of Ng bound analogues follows the order as Au > Cu > Ag. All dissociation processes are endothermic in nature whereas they become endergonic as well in most of the cases of Kr–Rn bound analogues at 298 K. Natural population analysis along with the computation of Wiberg bond indices, and electron density analyses provide insights into the nature of the Ng–M bonds. The Ng–M bonds can be represented as partial covalent bonds as supported by the different electron density descriptors.

Keywords. Noble metal–noble gas bond; dissociation energy; natural population analysis; electron density analysis.

1. Introduction

The synthesis of Xe⁺[PtF₆][−] by Bartlett¹ in 1962 induced immense interest into the chemistry of noble gas (Ng) compounds and consequently enormous efforts were made by scientists both theoretically as well as experimentally during the last few decades. Ngs are generally known as chemically inactive elements and do not easily participate in chemical bonding. The low chemical tendency of Ngs to bind with other atoms makes it a challenge to discover new compounds involving Ngs. However, Bartlett's synthesis showed that the chemical bonding between Ngs and others atoms is definitely possible to produce new compounds but under certain specific physiochemical conditions and proper choice of reacting agents. To build up this

Ng based field, scientists have been trying to develop a proper theory to get insight into the stability and chemical bonding of the new stable Ng compounds^{2–10} and also to synthesize these compounds using this theoretical understanding or vice versa.^{11–17} These efforts introduced a new dimension in the field of Ng compounds and showed that Ngs are not completely inactive.

Because of less reactivity, combining a coinage metal, also known as noble metal, and Ngs through chemical bond is also turned out to be a tough job. The effort in this regard was first made by Pyykkö^{18a} by exploring the stability of Ng_nAu⁺ (n = 1, 2) through an *in silico* study which were later detected in mass spectrometry.^{18b} Thereafter, Ar and Kr bound AuCl compounds were detected in microwave spectroscopy by Gerry *et al.*,^{16a} and AuXe₄²⁺ was synthesized as a reddish solid compound by Seidel *et al.*,¹⁹ in the same year of 2000. Several NgMX (Ng = Ar, Kr, Xe; M = Cu, Ag, Au; X = F, Cl, Br) compounds¹⁶ were then reported in subsequent years.

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Very recently, NeAuF was also reported by Wang and coworkers.²⁰ Computational studies were devoted in order to analyze the stability of NgMX (X = OH, CN; M = Cu, Ag, Au) compounds.^{21,22} The possibility of Ng insertion within M-X bonds in MX (X = F, OH; M = Cu, Ag, Au) compounds²³ was also tested.

In the present work, we have investigated the interaction of Ngs with various nitrates, sulphates and

carbonates of noble metals. Their efficacy to bind Ngs is analyzed through the computations of the dissociation energy and change in free energy (ΔG) and enthalpy (ΔH) at 298 K temperature, for the dissociations of NgMNO₃ (M = Cu, Ag), NgCu(NO₃)₂, NgMSO₄ (M = Cu, Ag), Ng₂M₂SO₄ (M = Cu, Ag, Au), NgCuCO₃ and Ng₂M₂CO₃ (M = Ag, Au) into Ng(s) and the corresponding salts. The nature of bonding for the present cases

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●=C ●=N ●=O ●=S ●=Ar ●=Kr ●=Xe ●=Rn ●=Cu ●=Ag

Figure 1. The optimized geometries of MNO₃ and their Ng bound analogues (M = Cu, Ag; Ng = Ar-Rn) at the MPW1B95/def2-TZVP level. Point groups along with their electronic states are given in the parentheses. The Ng-M and M-O bond distances are given in Å unit.

is investigated through the natural population analysis (NPA), computation of Wiberg bond index (WBI) and a detailed analysis of the electron density.²⁴

2. Computational details

All the studied compounds are fully optimized at the MPW1B95/def2-TZVP level of theory. The MPW1B95 functional is considered for the present study because a recent benchmarking study showed that this functional

could provide the bond dissociation energy and bond distance very close to those obtained at the CCSD(T) level.²⁵ An effective core potential (ECP)²⁶ is employed for the core electrons of Ag, Au, Xe and Rn atoms for the computational efficiency as well as to take care of the relativistic effect. Frequency calculations are also performed at the same level for the characterization of the nature of the stationary points, and to determine zero-point energies (ZPE), enthalpies and free energies. It shows that there is no imaginary frequency for the sta-

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Figure 2. The optimized geometries of MSO_4 and their Ng bound analogues ($\text{M} = \text{Cu}, \text{Ag}$; $\text{Ng} = \text{Ar-Rn}$) at the MPW1B95/def2-TZVP level. Point groups along with their electronic states are given in the parentheses. The Ng-M and M-O bond distances are given in Å unit.

tionary points reported in this study. NPA and WBIs²⁷ are evaluated to get the charge (*q*) at each atomic center and the Ng-M bond order, respectively. All these calculations are carried out with the Gaussian 09 program package.²⁸ The electron density analysis²⁴ is performed using Multiwfn software²⁹ at the MPW1B95/def2-TZVP level in order to understand the nature of interaction.

3. Results and Discussion

The minimum energy structures of NgCuNO₃ correspond to the *C*_{2v} point group symmetry with ¹A₁ electronic state, whereas in cases of NgAgNO₃, Ng atoms bind with Ag in slightly tilted fashion making two ∠Ng-Ag-O bond angles unequal. NgAgNO₃ compounds correspond to *C*_s point group symmetry

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Figure 3. The optimized geometries of M_2SO_4 and their Ng bound analogues ($M = Cu, Ag, Au$; Ng = Ar-Rn) at the MPW1B95/def2-TZVP level. Point groups along with their electronic states are given in the parentheses. The Ng-M and M-O bond distances are given in Å unit.

Color Code:

●=C ●=N ●=O ●=S ●=Ar ●=Kr ●=Xe ●=Rn ●=Cu ●=Ag ●=Au

Figure 4. The optimized geometries of CuCO_3 , M_2CO_3 and their Ng bound analogues ($\text{M} = \text{Ag}, \text{Au}$; $\text{Ng} = \text{Ar-Rn}$) at the MPW1B95/def2-TZVP level. Point groups along with their electronic states are given in the parentheses. The Ng-M and M-O bond distances are given in Å unit.

with $^1\text{A}'$ electronic state (Figure 1). The corresponding C_{2v} symmetric structures possess a small imaginary frequency and the corresponding mode is connected to the bending of Ng-Ag-O moieties. However, the C_s and C_{2v} symmetric structures are almost isoenergetic. We

have also tested the Ng binding ability of $\text{Cu}(\text{NO}_3)_2$ but it is found that it binds Ng atoms very loosely having Ng-Cu bond dissociation energies within the range of 0.7–1.5 kcal/mol. Therefore, related results are provided in the supporting information (see Figure S1

Table 1. ZPE corrected dissociation energy (D_0 , kcal/mol) of Ng-M bonds, enthalpy change (ΔH , kcal/mol) at 298 K and free energy change (ΔG , kcal/mol) at 298 K for the dissociation process: $\text{NgMY} \rightarrow \text{Ng} + \text{MY}$ ($\text{M} = \text{Cu, Ag; Y} = \text{NO}_3, \text{SO}_4, \text{CO}_3$), NPA charge at M and Ng centers (q , au), Wiberg bond indices of Ng-M bonds (WBI), HOMO–LUMO energy gaps (Gap, eV), and Ng-M bond distances ($r_{\text{Ng-M}}$, Å) at the MPW1B95/def2-TZVP level.

Compounds	D_0	ΔH	ΔG	$q(\text{M})$	$q(\text{Ng})$	WBI	Gap	$r_{\text{Ng-M}}$
CuNO_3				0.81			4.574	
ArCuNO_3	6.0	6.0	0.1	0.68	0.09	0.19	5.837	2.356
KrCuNO_3	8.7	8.6	3.2	0.64	0.12	0.25	5.974	2.427
XeCuNO_3	12.2	12.2	6.4	0.59	0.17	0.34	6.078	2.534
RnCuNO_3	13.1	13.0	7.6	0.58	0.17	0.35	5.877	2.608
AgNO_3				0.83			4.198	
ArAgNO_3	3.1	3.0	−1.8	0.75	0.05	0.10	4.911	2.725
KrAgNO_3	5.2	5.1	−0.5	0.71	0.08	0.16	5.108	2.734
XeAgNO_3	8.5	8.4	3.1	0.65	0.13	0.26	5.312	2.776
RnAgNO_3	9.8	9.7	4.4	0.64	0.14	0.28	5.201	2.830
CuSO_4				0.86			4.100	
ArCuSO_4	6.0	6.0	−0.3	0.73	0.09	0.19	4.717	2.364
KrCuSO_4	8.7	8.7	2.3	0.69	0.12	0.25	4.796	2.432
XeCuSO_4	12.3	12.3	5.8	0.63	0.17	0.34	4.856	2.538
RnCuSO_4	13.2	13.2	6.7	0.63	0.18	0.35	4.747	2.612
AgSO_4				0.88			4.327	
ArAgSO_4	3.2	3.1	−2.6	0.81	0.05	0.11	4.656	2.729
KrAgSO_4	5.3	5.2	−0.3	0.77	0.08	0.17	4.757	2.736
XeAgSO_4	8.7	8.6	3.0	0.71	0.13	0.26	4.853	2.782
RnAgSO_4	10.1	9.9	4.9	0.69	0.15	0.29	4.801	2.835
CuCO_3				1.02			4.296	
ArCuCO_3	5.7	5.7	0.2	0.89	0.09	0.18	4.898	2.430
KrCuCO_3	8.1	8.0	2.3	0.84	0.13	0.24	4.970	2.506
XeCuCO_3	11.3	11.2	5.3	0.79	0.17	0.33	5.010	2.611
RnCuCO_3	12.4	12.3	6.4	0.78	0.19	0.34	4.921	2.684

Table 2. ZPE corrected dissociation energy (D_0 , kcal/mol) of per Ng-M bonds, enthalpy change (ΔH , kcal/mol) at 298 K and free energy change (ΔG , kcal/mol) at 298 K for the dissociation process: $\text{Ng}_2\text{M}_2\text{Y} \rightarrow 2\text{Ng} + \text{M}_2\text{Y}$ ($\text{M} = \text{Cu, Ag, Au; Y} = \text{SO}_4, \text{CO}_3$), NPA charge at M and Ng centers (q , au), Wiberg bond indices of Ng-M bonds (WBI), HOMO–LUMO energy gaps (Gap, eV), and Ng-M bond distances ($r_{\text{Ng-M}}$, Å) at the MPW1B95/def2-TZVP level.

Compounds	D_0	ΔH	ΔG	$q(\text{M})$	$q(\text{Ng})$	WBI	Gap	$r_{\text{Ng-M}}$
Cu_2SO_4				0.84			4.574	
$\text{Ar}_2\text{Cu}_2\text{SO}_4$	5.1	10.2	−2.0	0.71	0.09	0.18	5.714	2.377
$\text{Kr}_2\text{Cu}_2\text{SO}_4$	7.6	15.1	2.7	0.67	0.12	0.25	5.862	2.439
$\text{Xe}_2\text{Cu}_2\text{SO}_4$	11.0	21.9	8.9	0.61	0.16	0.33	5.975	2.542
$\text{Rn}_2\text{Cu}_2\text{SO}_4$	11.7	23.2	10.2	0.61	0.17	0.33	5.778	2.618
Ag_2SO_4				0.85			4.234	
$\text{Ar}_2\text{Ag}_2\text{SO}_4$	2.5	4.9	−6.8	0.78	0.05	0.10	4.866	2.754
$\text{Kr}_2\text{Ag}_2\text{SO}_4$	4.4	8.6	−3.2	0.74	0.08	0.16	5.058	2.751
$\text{Xe}_2\text{Ag}_2\text{SO}_4$	7.5	14.7	2.6	0.68	0.12	0.25	5.245	2.788
$\text{Rn}_2\text{Ag}_2\text{SO}_4$	8.6	16.9	4.8	0.67	0.14	0.27	5.118	2.842
Au_2SO_4				0.66			3.884	
$\text{Ar}_2\text{Au}_2\text{SO}_4$	8.1	16.5	1.8	0.57	0.11	0.21	5.294	2.457
$\text{Kr}_2\text{Au}_2\text{SO}_4$	12.5	25.2	10.0	0.53	0.16	0.30	5.439	2.513
$\text{Xe}_2\text{Au}_2\text{SO}_4$	18.3	36.7	21.4	0.48	0.22	0.41	5.477	2.603
$\text{Rn}_2\text{Au}_2\text{SO}_4$	19.9	39.9	24.7	0.46	0.24	0.43	5.302	2.669
Ag_2CO_3				0.81			3.355	
$\text{Ar}_2\text{Ag}_2\text{CO}_3$	2.3	4.4	−7.1	0.74	0.05	0.09	3.941	2.765
$\text{Kr}_2\text{Ag}_2\text{CO}_3$	4.1	8.0	−4.1	0.70	0.07	0.15	4.127	2.756
$\text{Xe}_2\text{Ag}_2\text{CO}_3$	7.0	13.8	1.4	0.65	0.12	0.25	4.307	2.791
$\text{Rn}_2\text{Ag}_2\text{CO}_3$	8.0	15.9	3.4	0.63	0.13	0.26	4.177	2.846

Table 2. *Continued.*

Compounds	D_0	ΔH	ΔG	$q(M)$	$q(Ng)$	WBI	Gap	r_{Ng-M}
Au ₂ CO ₃				0.62			3.185	
Ar ₂ Au ₂ CO ₃	7.3	15.0	0.1	0.52	0.11	0.20	4.595	2.476
Kr ₂ Au ₂ CO ₃	11.4	22.9	7.9	0.49	0.15	0.27	4.760	2.528
Xe ₂ Au ₂ CO ₃	16.7	33.5	18.6	0.44	0.21	0.38	4.786	2.615
Rn ₂ Au ₂ CO ₃	18.2	36.5	21.6	0.43	0.22	0.40	4.604	2.681

Table 3. Different topological descriptors (au) at the bond critical points (BCP) in between Ng and M atoms in NgMY (M = Cu, Ag; Y = NO₃, SO₄, CO₃) at the MPW1B95/def2-TZVP level.

Compounds	BCP	$\rho(r_c)$	$\nabla^2 \rho(r_c)$	$G(r_c)$	$V(r_c)$	$H(r_c)$
ArCuNO ₃	Ar-Cu	0.046	0.231	0.062	−0.067	−0.004
KrCuNO ₃	Kr-Cu	0.050	0.209	0.059	−0.066	−0.007
XeCuNO ₃	Xe-Cu	0.052	0.173	0.053	−0.062	−0.009
RnCuNO ₃	Rn-Cu	0.050	0.150	0.046	−0.055	−0.009
ArAgNO ₃	Ar-Ag	0.028	0.122	0.031	−0.031	0.000
KrAgNO ₃	Kr-Ag	0.036	0.129	0.035	−0.038	−0.003
XeAgNO ₃	Xe-Ag	0.043	0.128	0.038	−0.043	−0.006
RnAgNO ₃	Rn-Ag	0.043	0.115	0.035	−0.042	−0.006
ArCuSO ₄	Ar-Cu	0.045	0.227	0.061	−0.065	−0.004
KrCuSO ₄	Kr-Cu	0.050	0.206	0.059	−0.066	−0.007
XeCuSO ₄	Xe-Cu	0.053	0.171	0.052	−0.062	−0.009
RnCuSO ₄	Rn-Cu	0.050	0.149	0.046	−0.055	−0.009
ArAgSO ₄	Ar-Ag	0.028	0.121	0.030	−0.031	0.000
KrAgSO ₄	Kr-Ag	0.036	0.129	0.035	−0.038	−0.003
XeAgSO ₄	Xe-Ag	0.043	0.126	0.037	−0.043	−0.006
RnAgSO ₄	Rn-Ag	0.043	0.113	0.035	−0.041	−0.007
ArCuCO ₃	Ar-Cu	0.039	0.188	0.049	−0.051	−0.002
KrCuCO ₃	Kr-Cu	0.043	0.170	0.047	−0.051	−0.005
XeCuCO ₃	Xe-Cu	0.046	0.144	0.043	−0.049	−0.007
RnCuCO ₃	Rn-Cu	0.044	0.125	0.038	−0.044	−0.007

and Table S1 in Supplementary Information). In cases of sulphates, while all the Ng bound CuSO₄ and AgSO₄ geometries correspond to a C_{2v} point group and 2B_2 electronic state, the structures of Ng₂Cu₂SO₄ and Ng₂Ag₂SO₄ belong to a D_{2d} symmetry with 1A_1 electronic state (see Figures 2 and 3). In contrast, the optimized structures of Ng₂Au₂SO₄ correspond to C_2 symmetry and 1A electronic state. It may be noted that the geometry of Au₂SO₄ is slightly different from those of its lighter homologues. While in Cu₂SO₄ and Ag₂SO₄, M centers occupy a position in between two O centers of SO₄ unit providing the structure a D_{2d} symmetry, in Au₂SO₄ the Au atoms bind with only one O center of SO₄ yielding a C_2 symmetric structure. Again the geometry of NgCuCO₃ has a C_{2v} symmetry with 2B_2 electronic state except for ArCuCO₃ which belongs to a C_s symmetry and $^2A'$ electronic state. The C_{2v} symmetric ArCuCO₃ contains an imaginary frequency

which leads to the two unequal $\angle$ Ar-Cu-O bond angles (Figure 4). Moreover, the minimum energy structures of all Ng₂Ag₂CO₃ and Ng₂Au₂CO₃ correspond to a C_{2v} symmetry and 1A_1 electronic states (Figure 4).

The results of ZPE corrected bond dissociation energy (D_0), thermochemical parameters like ΔH and ΔG as well as the NPA charge on metal (M) and Ng centers and WBI values for Ng-M bonds in NgMY (Y = NO₃, SO₄) and NgCuCO₃ are provided in Table 1. All the thermochemical parameters are computed at one atmospheric pressure and 298 K. Since He and Ne bind with M center very loosely, those results are not included here. The D_0 values for the Ng-M bonds range within 6.0–13.1 kcal/mol in NgCuNO₃, 3.1–9.8 kcal/mol in NgAgNO₃, 6.0–13.2 kcal/mol in NgCuSO₄, 3.2–10.1 kcal/mol in NgAgSO₄ and 5.7–12.4 kcal/mol in NgCuCO₃ with gradual increase along Ar to Rn. This

Table 4. Different topological descriptors (au) at the bond critical points (BCP) in between Ng and M atoms in Ng₂M₂Y (M = Cu, Ag, Au; Y = SO₄, CO₃) at the MPW1B95/def2-TZVP level.

Compounds	BCP	$\rho(\mathbf{r}_c)$	$\nabla^2\rho(\mathbf{r}_c)$	G($\mathbf{r}_c$)	V($\mathbf{r}_c$)	H($\mathbf{r}_c$)
Ar ₂ Cu ₂ SO ₄	Ar-Cu	0.044	0.221	0.059	−0.062	−0.004
Kr ₂ Cu ₂ SO ₄	Kr-Cu	0.049	0.205	0.058	−0.064	−0.007
Xe ₂ Cu ₂ SO ₄	Xe-Cu	0.052	0.172	0.052	−0.061	−0.009
Rn ₂ Cu ₂ SO ₄	Rn-Cu	0.049	0.149	0.046	−0.054	−0.008
Ar ₂ Ag ₂ SO ₄	Ar-Ag	0.026	0.114	0.028	−0.028	0.000
Kr ₂ Ag ₂ SO ₄	Kr-Ag	0.034	0.125	0.034	−0.037	−0.003
Xe ₂ Ag ₂ SO ₄	Xe-Ag	0.042	0.126	0.037	−0.042	−0.005
Rn ₂ Ag ₂ SO ₄	Rn-Ag	0.042	0.113	0.034	−0.041	−0.006
Ar ₂ Au ₂ SO ₄	Ar-Au	0.058	0.242	0.069	−0.078	−0.009
Kr ₂ Au ₂ SO ₄	Kr-Au	0.066	0.216	0.067	−0.080	−0.013
Xe ₂ Au ₂ SO ₄	Xe-Au	0.071	0.166	0.060	−0.078	−0.018
Rn ₂ Au ₂ SO ₄	Rn-Au	0.068	0.143	0.054	−0.072	−0.018
Ar ₂ Ag ₂ CO ₃	Ar-Ag	0.026	0.111	0.028	−0.027	0.000
Kr ₂ Ag ₂ CO ₃	Kr-Ag	0.034	0.124	0.033	−0.036	−0.003
Xe ₂ Ag ₂ CO ₃	Xe-Ag	0.042	0.125	0.037	−0.042	−0.005
Rn ₂ Ag ₂ CO ₃	Rn-Ag	0.041	0.112	0.034	−0.040	−0.006
Ar ₂ Au ₂ CO ₃	Ar-Au	0.055	0.234	0.066	−0.073	−0.007
Kr ₂ Au ₂ CO ₃	Kr-Au	0.063	0.212	0.065	−0.077	−0.012
Xe ₂ Au ₂ CO ₃	Xe-Au	0.069	0.166	0.058	−0.075	−0.017
Rn ₂ Au ₂ CO ₃	Rn-Au	0.066	0.143	0.053	−0.070	−0.017

implies that the Ng atoms with larger atomic masses are bound more strongly with a given system. This is due to the increase in polarizability along the group. It is also found that the Ng binding ability of CuY is higher than that of AgY. This is due to the larger polarizing power of Cu than Ag as Cu has smaller size than Ag. The D_0 values also reveal that these MY and CuCO₃ have very much comparable Ng binding ability. All the dissociation processes are endothermic in nature. However, except for ArCuSO₄, ArAgY and KrAgY (Y = SO₄, NO₃) the dissociations of all other NgMY (Y = SO₄, NO₃, CO₃) compounds under consideration are endergonic in nature at room temperature. The ΔG values for the dissociations of KrAgNO₃ and KrAgSO₄ are only slightly negative (−0.5 and −0.3 kcal/mol, respectively) and therefore, they can be made viable at slightly lower temperature.

Now, we have checked the stability of Ng₂M₂SO₄ (M = Cu, Ag, Au) and Ng₂M₂CO₃ (M = Ag, Au) and the related results are provided in Table 2. The D_0 values per Ng-M bond lie within the range of 5.1–11.7 kcal/mol in Ng₂Cu₂SO₄, 2.5–8.6 kcal/mol in Ng₂Ag₂SO₄, 8.1–19.9 kcal/mol in Ng₂Au₂SO₄, 2.3–8.0 kcal/mol in Ng₂Ag₂CO₃ and 7.3–18.2 in Ng₂Au₂CO₃ with a gradual increase in moving from Ar to Rn. The corresponding dissociation processes producing Ngs and M₂Y are found to be spontaneous only in cases of Ar₂Cu₂SO₄,

Ar₂Ag₂Y and Kr₂Ag₂Y (Y = SO₄ and CO₃). The rest of the systems are viable even at room temperature.

According to maximum hardness principle,³⁰ a molecule with higher HOMO-LUMO energy gap is associated with greater stability and hence less reactivity. The related energy gap is found to increase considerably in all Ng bound cases, implying additional stability in Ng bound MY and M₂Y systems compared to the corresponding bare structures (Tables 1 and 2).

NPA reveals that transfer of electronic charge takes place from Ng to the M center in NgMY and Ng₂M₂Y. The degree of electron transfer is low for lighter Ng cases in comparison to heavier Ng atoms. Also, the trend in electron transfer from Ng centers follows the order of Rn > Xe > Kr > Ar as the ionization energy increases in reverse order. Furthermore, the extent of electron transfer from a given Ng atom is the largest when Au is the binding center and it follows the order as Au > Cu > Ag. The extent of covalent character in the Ng-M bonds can be predicted from the WBI values. The WBI values corresponding to Ng-M bonds also exhibit the similar trend having a lower value for lighter Ng atoms and a higher value for heavier analogues. The low value of WBI indicates the interaction as of noncovalent type which occurs in case of lighter Ng atoms and a large value of WBI indicates the significant covalent character in the Ng-M bond as in the cases of heavier

analogues. In addition, for a given Ng and Y the Au analogues are most covalent followed by Cu and Ag analogues.

Electron density analysis provides further insight into the nature of bonding. Tables 3 and 4 represent different topological descriptors evaluated at the bond critical points (BCPs) of Ng-M bonds present in these compounds. Local electron energy density ($H(\mathbf{r}_c)$) is computed as the sum of local kinetic energy density ($G(\mathbf{r}_c)$) and local potential energy density ($V(\mathbf{r}_c)$). In general, the accumulation and depletion of electron density ($\rho(\mathbf{r}_c)$) reflecting from the corresponding negative and positive values of Laplacian of $\rho(\mathbf{r}_c)$ ($\nabla^2\rho(\mathbf{r}_c)$), respectively, at the BCPs indicate the covalent and non-covalent types of bonding, respectively. However, there are several systems involving 3d transition metals and other heavier atoms, where a covalent bond cannot be explained using this descriptor.^{24,31}

The $H(\mathbf{r}_c)$ is also used along with $\nabla^2\rho(\mathbf{r}_c)$ to characterize a chemical bond. For example, if $\nabla^2\rho(\mathbf{r}_c) > 0$ and $H(\mathbf{r}_c) < 0$ then the bond may be treated as partial

covalent in nature.³² Specifically when the bond has either zero or a very small bonding electron density ($\rho(\mathbf{r}_c)$) then it should be investigated with the aid of the $H(\mathbf{r}_c)$. In our cases, although the $\nabla^2\rho(\mathbf{r}_c)$ is found to be positive at the BCPs of all Ng-Cu, Ng-Ag and Ng-Au bonds in all the systems under consideration, the bonding electron densities ($\rho(\mathbf{r}_c)$) are so small that we have to consider $H(\mathbf{r}_c)$. Almost all the Ng bound compounds contain negative $H(\mathbf{r}_c)$ value at the BCPs of Ng-M bonds except for ArAgNO_3 , ArAgSO_4 , $\text{Ar}_2\text{Ag}_2\text{SO}_4$ and $\text{Ar}_2\text{Ag}_2\text{CO}_3$. It signifies that all these bonds are partially covalent in nature. It has to be mentioned here that $H(\mathbf{r}_c)$ becomes more negative in moving from Ar to heavier Ngs suggesting an increase in covalent character along the same. The contour plots of $\nabla^2\rho(\mathbf{r})$ are displayed in Figures 5 and 6 for NgMNO_3 ($M = \text{Cu, Ag}$) and NgMSO_4 ($M = \text{Cu, Ag}$), respectively (for the other compounds see Figures S2 in Supporting Information). In these plots, while the red-colored region displays the area having $\nabla^2\rho(\mathbf{r}) > 0$, the green-colored region shows the area of $\nabla^2\rho(\mathbf{r}) < 0$. It is obvious from

Figure 5. Contour plots of the Laplacian of the electron density of NgMNO_3 ($\text{Ng} = \text{Ar, Kr, Xe, Rn}$) at a particular plane computed at the MPW1B95/def2-TZVP level; the red-colored region shows the area of $\nabla^2\rho(\mathbf{r}) > 0$, whereas the green-colored region shows the area of $\nabla^2\rho(\mathbf{r}) < 0$.

Figure 6. Contour plots of the Laplacian of the electron density of NgMSO_4 ($\text{Ng} = \text{Ar}, \text{Kr}, \text{Xe}, \text{Rn}$) compounds at a particular plane computed at the MPW1B95/def2-TZVP level; the red-colored region shows the area of $\nabla^2\rho(\mathbf{r}) > 0$, whereas the green-colored region shows the area of $\nabla^2\rho(\mathbf{r}) < 0$.

the plots that there is no development of green region ($\nabla^2\rho(\mathbf{r}) < 0$) in between Ng and M. The shape of the valence orbitals of Ng atoms only gets deformed and the deformation continuously increases along Ar to Rn.

4. Conclusions

The Ng binding ability of MY and M_2Y ($\text{M} = \text{Cu}, \text{Ag}, \text{Au}$ and $\text{Y} = \text{NO}_3, \text{SO}_4, \text{CO}_3$) compounds is assessed in the present study. The Ng-M bond dissociation energy (D_0) values for these metal nitrates, sulphates and carbonates vary within 5.1–13.2 kcal/mol, 2.3–10.1 kcal/mol and 7.3–19.9 kcal/mol for Cu, Ag and Au as binding sites, respectively. For a given Ng and Y, Au analogue shows the highest Ng binding ability followed by Cu and Ag. The D_0 value also increases gradually from Ar to Rn. Most of the dissociation processes are found to be endergonic in nature at room temperature, except for those involving ArCuSO_4 , ArAgY , KrAgY ($\text{Y} = \text{NO}_3, \text{SO}_4$), $\text{Ar}_2\text{Ag}_2\text{Y}$, $\text{Kr}_2\text{Ag}_2\text{Y}$ ($\text{Y} = \text{CO}_3, \text{SO}_4$), and $\text{Ar}_2\text{Cu}_2\text{SO}_4$. There is some degree of electron transfer from Ng to M center as highlighted by natural population analysis and it gradually increases in moving

from Ar to its heavier congeners. The Wiberg bond indices indicate that there is partly covalent character in Ng-M bonds, especially for Xe and Rn bound analogues. Increase in the HOMO–LUMO energy gap in the Ng bound analogues compared to that of the bare compounds reflects larger electronic stability of the former. The negative value of local electron energy density, $H(\mathbf{r}_c)$, at the bond critical points of Ng-M bonds indicates the partial covalent character as provided by the electron density analysis.

Supplementary Information (SI)

Figures S1 and S2, and Table S1 are available as Supplementary Information at www.ias.ac.in/chemsci.

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