Computational study of 5d transition metal mononitrides and monoborides using density functional method

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Abstract. 5d-metal mononitrides and monoborides viz. X–N and X–B (X = La, Hf, Ta, W, Re, Os, Ir, Pt, Au, Hg) are studied using density functional method based B3LYP functional with LANL2DZ and SDD basis set. The lowest spin state, electron affinities, ionization potentials and binding energies for mononitrides and monoborides are obtained. The electronic state and electronic configuration of mononitrides and monoborides are discussed. Orbitals involved in bond formation are identified. The properties of mononitrides and monoborides are compared. It is found that 5d-metal atoms form stronger bond with nitrogen atom than the boron atom. The range of binding energy, electron affinity and ionization potential is wider for mononitrides than that for monoborides. The properties of 5d-metal mononitrides and 3d-metal mononitrides are also compared. The binding energies for the former are lower than those for the latter.

Keywords. Density functional method; 5d-metal; mononitrides; monoborides.

1. Introduction

Clusters containing a few to thousands of atoms are of scientific importance. In this regime, their physical and chemical properties change with their size. Therefore, the clusters often demonstrate many unexpected characteristics different from those in the bulk solids. During the past several decades, the cluster science has already obtained huge development. In particular, the transition metal clusters have been intensively investigated both experimentally and theoretically because of their potential applications in nanotechnology and microelectronics industry (Chopra *et al* 1995; Thimoshkin *et al* 2001; Goldberger *et al* 2003; Schmid and Basting 2005; Uneo *et al* 2005). During the last decade nitrides and borides have attracted the material scientists due to their importance in nanotechnology. Due to their important applications in nanotechnology several attempts have been made to synthesize nanotubes composed of nitrides. Clusters containing transition metals are also of significant interest, due to their potential applications in developing new nano-devices (Binns 2001; Wu *et al* 2004; Nikolov 2005; Barnard and Curtiss 2005; Sao-Joao *et al* 2005).

Small clusters composed of transition metal atom are of intensive studies for the past two decades. A large number of studies of transition metal containing clusters, both theoretical as well as experimental, have been reported (Kunze and Harrison 1989; Rao 1989; Wu and

Wang 1997, 1998; Li and Wang 1999; Bridgeman and Rothery 2000; Gutsev *et al* 2000a, b, 2003; Xian *et al* 2000; Broclawik and Borowski 2001; Moravec *et al* 2001; Daoudi *et al* 2003; Chaudhari and Freed 2003; Yamaki *et al* 2003; Dai *et al* 2004; Bertolus *et al* 2004). One of the main motivations behind these studies is to understand the physical properties of the cluster. The study of binary compounds between transition metals and a main group element has received much attention in recent years, mainly because of their relevance as building blocks of new materials. The type of structure formed depends mainly on the nature of the interaction between the transition metal and a main group element. Therefore, theoretical studies of small clusters containing transition metals are very useful to understand the growth mechanisms of the various materials, as well as to obtain insight into their physical and chemical properties.

The investigation of clusters can aid in uncovering the transition from discrete molecular properties to the bulk-like behaviour observed in materials in the condensed phase. Clusters are of particular interest in studying the nature of the chemical bond between a transition metal and a main group element. This is of great interest in many areas of science, e.g. surface chemistry, catalysis, astrophysics, and organometallic chemistry. Recently, the electronic structures of diatomic molecules composed of a 3d metal and a main group of elements H, Li, B, C, N, O, and F, have been reviewed (Harrison 2000). The neutral, cation and anion of 3d-metal oxides and carbides are studied using density functional theory methods (Gutsev *et al* 2003). Neutral 3d-metal phosphides are studied by

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DFT method (Tong *et al* 2003). Neutral, cation and anion species of ScB and ZnB monoborides were examined using density functional methods (Wu 2005). 4*d*-metal monoxides YO and PdO are studied using a modified coupled-pair functional MCPF method (Siegbahn 1993). Mononitrides of 3*d* and 4*d* transition metal are studied using DFT method (Chaudhari and Lee 2007; Kharat *et al* 2009).

To our knowledge no systematic and comparative study of 5*d* transition metal mononitride and 5*d* transition metal monoboride has been done so far. The aim of this work is to perform the systematic study of 5*d* transition metal mononitrides and 5*d* transition metal monoborides and compare their properties using DFT method. We have obtained the ground state multiplicity of each diatomic molecules X–N and X–B (X = La, Hf, Ta, W, Re, Os, Ir, Pt, Au, Hg). We have also studied the cation and anion of these diatomic molecules and obtained the electron affinities and ionization potentials. The binding energies, vibrational frequencies, dipole moments, atomic charges and bond lengths for these diatomic molecules, mononitrides and monoborides are also obtained. The properties of mononitrides and monoborides are compared. This article is organized as follows: Next section gives the computational details. Results are reported, discussed and compared in section 3. Conclusions are inferred in last section.

2. Computational details

All calculations were performed using the Gaussian 03 suite of programs (Frisch *et al* 2004). Geometries of the 5*d* transition metal mononitrides and monoborides were optimized using the Becke three-parameter hybrid functional combined with Lee, Yang, and Parr correlation (B3LYP) (Hay and Wart 1985; Becke 1988, 1993, 1997; Schmider and Becke 1998). Geometry optimizations were performed using two effective core potential (ECP) basis sets viz. LANL2DZ and SDD. Frequency calculations were also performed at the same level of theory.

3. Results and discussion

The geometries of 5*d*-metal mononitrides and monoborides are optimized for various spin multiplicities to find out the lowest spin state for each dimer at B3LYP/LANL2DZ and B3LYP/SDD levels. Relative stability of these dimers is reported in tables 1 and 2. The lowest spin state of 5*d*-metal mononitride and monoboride shows oscillatory nature across the row. The lowest spin state increases from IrN to HgN. In case of monoborides the lowest spin state decreases from OsB to AuB. The quintet state of TaB is just 0.003 kcal/mol higher in energy than the ground state triplet. The lowest spin states of 5*d*-metal mononitrides and monoborides is also obtained at

B3LYP/SDD level. The ground state is triplet, quartet, triplet, quintet and quintet for TaN, WN, LaB, TaB and ReB, respectively at B3LYP/SDD level whereas it is singlet, doublet, quintet, triplet and triplet at B3LYP/LANL2DZ level, respectively.

The bond lengths, dipole moment and vibrational frequency for 5*d*-metal mononitrides and monoborides are presented in table 3. The bond length for mononitride decreases from LaN to IrN and then increases up to HgN whereas in monoborides no systematic trend is observed. The longest bond length of 3.024 Å and 4.381 Å is obtained for HgN and HgB, respectively which clearly indicates the weaker bonding of Hg with both nitrogen and boron. The bond lengths in monoborides are longer than the corresponding bond lengths in mononitrides. The vibrational frequency in mononitride increases from LaN to IrN across the row and then decreases up to HgN. No systematic trend is observed for vibrational frequencies in monoborides. The highest (lowest) vibrational frequency is observed for IrN (HgN) at 1204 (72) cm⁻¹. The vibrational frequencies in XN are higher than that for corresponding XB dimer except for AuN. The largest dipole moment of 7.87 Debye is obtained for LaN and it decreases across the row up to PtN. The dipole moment in monoboride decreases from ReB to HgB across the row.

The electronic state for each mononitride and monoboride at its lowest spin is also defined. The electronic configuration and electronic state of 5*d*-metal mononitrides and monoborides are represented in table 4. The electronic state for 5*d*-metal mononitrides at their lowest spin state is $1\Sigma^+$, $2\Sigma^+$, $1\Sigma^+$, 2Δ , 3Δ , $2\Sigma^+$, $1\Sigma^+$, $2\Sigma^+$, 3Π and $4\Sigma^-$ for LaN, HfN, TaN, WN, ReN, OsN, IrN, PtN and HgN, respectively whereas electronic state for monoborides of 5*d*-metal at their lowest spin state is $5\Sigma^-$, $4\Sigma^-$, $3\Sigma^+$, $6\Sigma^-$, $3\Sigma^-$, 4Δ , 3Δ , $2\Sigma^+$, $1\Sigma^+$, $2\Sigma^+$ for LaB, HfB, TaB, WB, ReB, OsB, IrB, PtB and HgB, respectively. The Σ^- state is generated for HgN, LaB, HfB, ReB and WB due to the presence of two electrons with parallel spin in two different Π or δ orbitals. The electronic states for TaN, WN, OsN, PtN, LaB, TaB and ReB are 3Δ , $4\Sigma^-$, 2Δ , 2Π , 3Π , 5Δ and $4\Sigma^-$, respectively at B3LYP/SDD level and are different from what were obtained at B3LYP/LANL2DZ level.

The electron affinity, ionization potential and binding energy of 5*d*-metal mononitrides and 5*d*-metal monoborides are presented in table 5. LaB, ReB and IrB are having higher electron affinity values than that for corresponding mononitrides at B3LYP/LANL2DZ level. The ionization potential values for all mononitrides are higher than the corresponding values for monoborides except for AuN dimer. HfB dimer shows negative ionization potential value which indicates that further ionization is not possible in HfB. The binding energy for LaN, HfN, TaN, WN, ReN, OsN, and IrN is higher whereas that for PtN, AuN and HgN is lower than the binding energy of respective XB. Electron affinities and ionization potential values of

Table 1. Relative stability, ΔE (kcal/mol) of 5d transition metal mononitrides at B3LYP/LANL2DZ level for various spin multiplicities, S .

S	ΔE									
	LaN	HfN	TaN	WN	ReN	OsN	IrN	PtN	AuN	HgN
1	0	—	0	—	21.57	—	0	—	42.92	—
2	—	0	—	0	—	0	—	0	—	66.59
3	23.95	—	44.42	—	0	—	68.81	—	0	—
4	—	43.62	—	50.95	—	69.34	—	19.74	—	0
5	51.54	—	95.18	—	84.82	—	78.21	—	77.73	—
6	—	66.01	—	100.62	—	123.73	—	42.08	—	109.3

Table 2. Relative stability, ΔE (kcal/mol) of 5d transition metal monoborides at B3LYP/LANL2DZ level for various spin multiplicities, S .

S	ΔE									
	LaB	HfB	TaB	WB	ReB	OsB	IrB	PtB	AuB	HgB
1	33.37	—	13.14	—	63.19	—	14.31	—	0	—
2	—	11.76	—	14.64	—	13.30	—	0	—	0
3	20.44	—	0	—	0	—	0	—	61.53	—
4	—	0	—	9.69	—	0	—	92.36	—	51.03
5	0	—	0.003	—	14.82	—	89.52	—	165.31	—
6	—	12.34	—	0	—	81.49	—	159.3	—	322.3
7	92.47	—	—	—	—	—	—	—	—	—
8	—	—	—	23.35	—	—	—	—	—	—

Table 3. Bond length, vibrational frequency, binding energy and dipole moment for 5d-metal mononitrides and 5d-metal monoborides at B3LYP/LANL2DZ level of theory. The values in parentheses are at B3LYP/SDD level.

X	Bond length (Å)		Vibrational frequency (cm ⁻¹)		Dipole moment (Debye)	
	X–N	X–B	X–N	X–B	X–N	X–B
La	1.952 (1.785)	2.435 (2.336)	828 (935)	511 (496)	7.87 (7.64)	4.29 (5.02)
Hf	1.866 (1.764)	2.157 (2.195)	857 (939)	613 (580)	3.71 (5.70)	2.44 (2.60)
Ta	1.701 (1.726)	2.001 (2.184)	1119 (1034)	721 (555)	3.50 (5.07)	2.68 (1.44)
W	1.681 (1.699)	2.161 (1.990)	1151 (1067)	526 (725)	2.96 (4.45)	2.61 (2.67)
Re	1.662 (1.673)	1.842 (1.875)	1153 (1129)	867 (853)	2.37 (2.55)	2.99 (2.29)
Os	1.650 (1.637)	1.813 (1.814)	1195 (1204)	955 (919)	2.14 (2.88)	2.17 (2.23)
Ir	1.637 (1.637)	1.806 (1.811)	1204 (1189)	936 (898)	1.86 (1.86)	1.72 (1.68)
Pt	1.751 (1.736)	1.809 (1.815)	929 (921)	906 (863)	0.91 (2.15)	1.18 (1.11)
Au	1.962 (1.963)	1.997 (2.003)	541 (533)	559 (590)	2.23 (2.33)	0.68 (0.73)
Hg	3.024 (3.210)	4.381 (2.535)	72 (40)	19 (177)	0.44 (0.06)	0.27 (1.20)

Table 4. Electronic state and electronic configuration of 5d-metal mononitrides and 5d-metal monoborides at B3LYP/LANL2DZ level. The electronic states given in parenthesis are at B3LYP/SDD level.

Mononitride			Monoboride		
Dimer	Electronic configuration	Electronic state	Dimer	Electronic configuration	Electronic state
LaN	$4\sigma^2 2\Pi^4 5\sigma^2$	$1\Sigma^+ (^1\Sigma^+)$	LaB	$2\Pi^2 5\sigma^1 6\sigma^1$	$5\Sigma^- (^3\Pi)$
HfN	$2\Pi^4 5\sigma^2 6\sigma^1$	$2\Sigma^+ (^2\Sigma^+)$	HfB	$2\Pi^2 5\sigma^2 6\sigma^1$	$4\Sigma^- (^4\Sigma^-)$
TaN	$2\Pi^4 5\sigma^2 6\sigma^2$	$1\Sigma^+ (^3\Delta)$	TaB	$2\Pi^4 5\sigma^1 6\sigma^1$	$3\Sigma^+ (^5\Delta)$
WN	$5\sigma^2 \delta^2 6\sigma^1$	$2\Delta (^4\Sigma^-)$	WB	$2\Pi^3 5\sigma^1 \delta^2 6\sigma^1$	$6\Sigma^- (^6\Sigma^-)$
ReN	$5\sigma^2 \delta^3 6\sigma^1$	$3\Delta (^3\Delta)$	ReB	$2\Pi^4 \delta^2 5\sigma^1$	$3\Sigma^- (^5\Sigma^-)$
OsN	$2\Pi^4 \delta^4 6\sigma^1$	$2\Sigma^+ (^2\Delta)$	OsB	$2\Pi^4 \delta^3 5\sigma^1 6\sigma^1$	$4\Delta (^4\Delta)$
IrN	$2\Pi^4 \delta^4 6\sigma^2$	$1\Sigma^+ (^1\Sigma^+)$	IrB	$2\Pi^4 \delta^3 5\sigma^2 6\sigma^1$	$3\Delta (^3\Delta)$
PtN	$2\Pi^4 \delta^4 6\sigma^2 7\sigma^1$	$2\Sigma^+ (^2\Pi)$	PtB	$2\Pi^4 5\sigma^2 \delta^4 6\sigma^1$	$2\Sigma^+ (^2\Sigma^+)$
AuN	$\delta^4 3\Pi^3 6\sigma^1$	$3\Pi (^3\Pi)$	AuB	$\delta^4 5\sigma^2 6\sigma^2$	$1\Sigma^+ (^1\Sigma^+)$
HgN	$\delta^4 4\sigma^2 2\Pi^2 5\sigma^1$	$4\Sigma^- (^4\Sigma^-)$	HgB	$3\sigma^2 4\sigma^2 5\sigma^1$	$2\Sigma^+ (^2\Sigma^+)$

Table 5. Electron affinities (eV), ionization potentials (eV) and binding energy (eV) of 5*d*-metal mononitrides and 5*d*-metal monoborides at B3LYP/LANL2DZ level. The values in parenthesis are at B3LYP/SDD level.

X	X–N			X–B		
	EA	IP	BE	EA	IP	BE
La	0.74 (0.42)	6.75 (6.29)	4.35 (5.85)	1.01 (0.41)	5.61 (5.42)	2.49 (2.10)
Hf	2.82 (1.95)	9.32 (7.70)	4.27 (5.00)	1.02 (1.05)	−0.69 (7.01)	2.70 (2.64)
Ta	1.57 (1.84)	10.24 (8.28)	5.70 (5.46)	1.36 (1.43)	7.07 (7.35)	2.49 (2.48)
W	1.95 (1.69)	10.44 (8.88)	5.41 (2.40)	1.44 (1.39)	8.39 (7.27)	2.74 (2.88)
Re	1.19 (1.40)	11.03 (8.34)	4.57 (4.95)	1.37 (1.39)	9.01 (8.24)	2.77 (4.18)
Os	1.38 (2.16)	9.92 (8.38)	4.65 (4.83)	1.01 (1.75)	8.15 (8.01)	3.99 (4.77)
Ir	0.44 (1.69)	10.29 (9.30)	4.40 (4.20)	5.06 (1.50)	4.66 (8.43)	4.86 (4.35)
Pt	3.35 (2.50)	7.58 (9.71)	0.84 (2.81)	2.00 (2.01)	8.77 (8.67)	5.43 (4.86)
Au	1.46 (1.50)	11.07 (9.98)	1.41 (1.51)	0.08 (0.92)	8.79 (8.72)	2.96 (3.04)
Hg	0.26 (0.70)	9.46 (9.48)	0.04 (0.02)	0.63 (0.90)	7.10 (7.40)	0.002 (0.17)

5*d*-metal atoms have been studied earlier (Wu and Kawazoe 2006). They concluded that the electron affinity and ionization potential values at B3LYP/SDD level are more accurate than those at B3LYP/LANL2DZ level. So we have incorporated the electron affinity and ionization potential values of 5*d*-metal mononitrides and 5*d*-metal monoborides at B3LYP/SDD level in table 5.

The atomic charges from Mulliken and natural orbital population analysis for mononitrides and monoborides are collected in table 6 along with natural orbital electronic configuration. The Mulliken charge in mononitride and monoboride is positive on metal atom and negative on nitrogen/boron atom except for HgB dimer for which the opposite is true. Similar is the case for natural charge in mononitrides. The natural charge on metal atom is negative and it is positive on boron atom in ReB, OsB, IrB, PtB and AuB dimers. The oxidation state of all 5*d*-metal is greater than one except for La and Au. Boron also has +1 oxidation state. Due to this the bonding characteristic in 5*d*-metal monoborides is of covalent ionic character with dominant covalent characteristic. In case of WB, W can accept one electron from boron atom to half fill the 5*d* orbital. From LaB to IrB the 2*p* orbital of boron and 5*d* orbital of transition metal are involved in the bonding. In case of PtB and AuB, 2*p* orbital of boron and 6*s* orbital of metal atom are involved in bonding. The bonding of Hg and B is very weak since Hg has all its orbitals filled which is also confirmed from its longer bond length. Bonding in 5*d*-metal mononitrides has covalent ionic characteristics for all XN. For HfN and IrN, three unpaired electrons in nitrogen can go to 5*d* orbital of Hf and Ir. It makes 5*d* orbital of Hf and Ir completely half filled and fulfilled in HfN and IrN, respectively.

The bonding in mononitrides and monoborides can be explained from natural orbital electronic configuration. Mainly the 5*d*, 6*s* orbital of metal atom and 2*s* and 2*p* orbital of N and B are involved in the complex bonding

of monoborides and mononitrides. In case of XN (X = Hf, Ta, W, Re, Au), the 5*d* orbital of metal atom loses its electron whereas for rest of the XN (X=Os, Ir, Pt) 5*d* orbital gains electrons from 2*s* orbital of nitrogen atom. In case of HgN the 5*d* orbital is completely out of the bonding and very small transfer of electrons from 6*s* of metal atom to 2*p* orbital of nitrogen takes place. The 6*s* orbital of metal atom loses electrons in all XN except for AuN where it gains few electrons. In most of the mononitrides few electrons are also transferred to the 6*p* orbital of metal atom. In case of monoborides, mostly 5*d* orbital of metal atom and 2*p* orbital of boron gains electrons from 6*s* orbital of metal atom and 2*s* orbital of boron. 5*d* orbital of metal atom loses electron only in case of HfB and AuB. 6*s* orbital of metal atom loses electrons in all XB except HgB and AuB. Unlike in mononitride, few electrons are also transferred to 6*p* orbital of metal atom.

3.1 Comparison with 3*d* metal mononitrides

The binding energy, electron affinity and ionization potential of 5*d* transition metal mononitrides are compared with those for 3*d* transition metal mononitrides (Chaudhari and Lee 2007) in table 7. These properties are compared for the dimers from the same group numbers in a periodic table. As can be seen from table 7, the binding energies for the 3*d*-metal mononitrides are higher than those for 5*d*-metal mononitrides. This is due to the fact that the bond lengths of 5*d*-metal mononitrides are longer than those for the 3*d*-metal mononitrides. Due to the weaker bonds in 5*d*-metal mononitrides than the 3*d*-metal mononitrides, the vibrational frequencies for the former are lower than those for the latter. The electron affinities and ionization potential of 5*d*-metal mononitrides are higher than those for 3*d*-metal mononitride except for IrN, HgN and LaN, PtN, respectively.

Table 6. Atomic charges from Mulliken and natural orbital population analysis along with natural orbital electronic configuration of third-row transition metal mononitrides and monoborides.

Dimer	Atom	Mulliken	Natural	Natural orbital electronic configuration
Mononitrides				
LaN	La	0.422	—	—
	N	−0.422	—	—
HfN	Hf	0.354	0.770	[core]6s ^{1.75} 5d ^{1.39} 6p ^{0.10} 6d ^{0.01}
	N	−0.354	−0.770	[core]2s ^{1.92} 2p ^{3.85}
TaN	Ta	0.300	0.741	[core]6s ^{1.73} 5d ^{2.44} 6p ^{0.11} 6d ^{0.01}
	N	−0.300	−0.741	[core]2s ^{1.87} 2p ^{3.87}
WN	W	0.268	0.515	[core]6s ^{1.69} 5d ^{3.72} 6p ^{0.09} 7s ^{0.01} 6d ^{0.01}
	N	−0.268	−0.515	[core]2s ^{1.86} 2p ^{3.65}
ReN	Re	0.266	0.315	[core]6s ^{1.63} 5d ^{4.99} 6p ^{0.08} 7s ^{0.01} 6d ^{0.01}
	N	−0.266	−0.315	[core]2s ^{1.85} 2p ^{3.46}
OsN	Os	0.244	0.171	[core]6s ^{1.56} 5d ^{6.21} 6p ^{0.07} 7s ^{0.01} 6d ^{0.01}
	N	−0.244	−0.171	[core]2s ^{1.85} 2p ^{3.31} 3p ^{0.01}
IrN	Ir	0.201	0.029	[core]6s ^{1.44} 5d ^{7.49} 6p ^{0.05} 7s ^{0.01} 6d ^{0.01}
	N	−0.201	−0.029	[core]2s ^{1.86} 2p ^{3.17} 3p ^{0.01}
PtN	Pt	0.224	0.101	[core]6s ^{1.41} 5d ^{8.27} 6p ^{0.20} 7s ^{0.01} 6d ^{0.01}
	N	−0.224	−0.101	[core]2s ^{1.91} 2p ^{3.18} 3p ^{0.01}
AuN	Au	0.264	0.252	[core]6s ^{1.07} 5d ^{9.64} 6p ^{0.03}
	N	−0.264	−0.252	[core]2s ^{1.95} 2p ^{3.29} 3p ^{0.01}
HgN	Hg	0.039	0.061	[core]6s ^{1.93} 5d ^{10.00} 6p ^{0.01}
	N	−0.039	−0.061	[core]2s ^{2.00} 2p ^{3.06}
Monoborides				
LaB	La	0.334	—	—
	B	−0.334	—	—
HfB	Hf	0.381	0.326	[core]6s ^{1.75} 5d ^{1.83} 6p ^{0.10} 7s ^{0.01}
	B	−0.381	−0.326	[core]2s ^{1.70} 2p ^{1.62} 3p ^{0.01}
TaB	Ta	0.308	0.140	[core]6s ^{1.44} 5d ^{3.36} 6p ^{0.08} 7s ^{0.01}
	B	−0.308	−0.140	[core]2s ^{1.57} 2p ^{1.56} 3p ^{0.01}
WB	W	0.179	0.109	[core]6s ^{1.18} 5d ^{4.63} 6p ^{0.09}
	B	−0.179	−0.109	[core]2s ^{1.90} 2p ^{1.20} 3p ^{0.01}
ReB	Re	0.279	−0.058	[core]6s ^{0.82} 5d ^{6.22} 6p ^{0.04} 7s ^{0.01}
	B	−0.279	0.058	[core]2s ^{1.43} 2p ^{1.51}
OsB	Os	0.158	−0.181	[core]6s ^{1.18} 5d ^{6.97} 6p ^{0.04} 7s ^{0.01}
	B	−0.158	0.181	[core]2s ^{1.57} 2p ^{1.24}
IrB	Ir	0.104	−0.233	[core]6s ^{1.05} 5d ^{8.16} 6p ^{0.04}
	B	−0.104	0.233	[core]2s ^{1.65} 2p ^{1.11} 3p ^{0.01}
PtB	Pt	0.077	−0.284	[core]6s ^{0.96} 5d ^{9.31} 6p ^{0.03}
	B	−0.077	0.284	[core]2s ^{1.69} 2p ^{1.01} 3p ^{0.01}
AuB	Au	0.021	−0.171	[core]6s ^{1.41} 5d ^{9.72} 6p ^{0.04}
	B	−0.021	0.171	[core]2s ^{1.91} 2p ^{0.91} 3p ^{0.01}
HgB	Hg	−0.007	−0.003	[core]6s ^{2.00} 5d ^{10.0} 6p ^{0.01}
	B	0.007	0.003	[core]2s ^{2.00} 2p ^{1.00}

4. Conclusions

Density functional method has been used for studying and comparing the properties of 5d-metal mononitrides and monoborides. For both, mononitrides and monobo-

rides, the electron affinity values are much lower than the ionization potential values. The range of binding energy is wider for mononitrides than that for monoborides. The bond between 5d-metal atom and nitrogen atom is stronger whereas that between the same metal atom and boron

Table 7. Binding energy, electron affinity and ionization potential (all in eV) of 5d-metal mononitride compared with 3d-metal mononitrides. The values are calculated using B3LYP method.

	Binding energy	Electron affinity	Ionization potential
ScN (LaN)	6.88 (4.35)	0.63 (0.74)	6.93 (6.75)
TiN (HfN)	8.89 (4.27)	1.84 (2.82)	6.43 (9.32)
VN (TaN)	9.60 (5.70)	0.18 (1.57)	7.27 (10.24)
CrN (WN)	10.74 (5.41)	0.82 (1.95)	7.66 (10.44)
MnN (ReN)	7.83 (4.57)	1.11 (1.19)	7.97 (11.03)
FeN (OsN)	8.71 (4.65)	0.54 (1.38)	8.12 (9.92)
CoN (IrN)	5.49 (4.40)	1.52 (0.44)	9.07 (10.29)
NiN (PtN)	6.86 (0.84)	1.52 (3.35)	9.13 (7.58)
CuN (AuN)	4.58 (1.41)	0.72 (1.46)	10.0 (11.07)
ZnN (HgN)	3.05 (0.04)	1.25 (0.26)	8.57 (9.46)

atom is weaker as compared to mononitrides. This results in low vibrational frequencies for the former than the latter. We hope that our computational results will stimulate further experimental studies on these 5d transition metal monoborides and mononitrides.

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References

- Barnard A S and Curtiss L A 2005 *Rev. Adv. Mater. Sci.* **10** 105
 Becke A D 1988 *Phys. Rev.* **A38** 3098
 Becke A D 1993 *J. Chem. Phys.* **98** 5648
 Becke A D 1997 *J. Chem. Phys.* **107** 8554
 Bertolus M, Finocchi F and Millie P 2004 *J. Chem. Phys.* **120** 4333
 Binns C 2001 *Surf. Sci. Rep.* **44** 1
 Bridgeman A J and Rothery J 2000 *J. Chem. Soc. Dalton Trans.* 211
 Broclawik E and Borowski T 2001 *Chem. Phys. Lett.* **339** 433
 Chaudhari A and Lee S -L 2007 *Int. J. Quant. Chem.* **107** 212
 Chaudhuri R K and Freed K F 2003 *J. Chem. Phys.* **119** 5995
 Chopra G, Luyken R J, Cherrey K, Crespi V H, Cohen M L, Louie S G and Zettl A 1995 *Science* **269** 966
 Dai B, Yang L and Tian J 2004 *J. Chem. Phys.* **120** 2746
 Daoudi A, Filalibaba M, Elkhatabi S, Rogemond F and Chermette H 2003 *Mol. Phys.* **101** 2929
 Frisch M J *et al* 2004 *Gaussian 03* (Wallingford, CT: Gaussian Inc.)
 Goldberger J, He R, Zhang Y, Lee S, Yan H, Choi H J and Yang P D 2003 *Nature* **422** 599
 Gutsev G L, Rao B K and Jena P 2000a *J. Phys. Chem.* **A104** 5374
 Gutsev G L, Rao B K, Jena P, Li X and Wang L S 2000b *J. Chem. Phys.* **113** 1473
 Gutsev G L, Jena P, Zhai H J and Wang L S 2001 *J. Chem. Phys.* **115** 7935
 Gutsev G L, Andrews L and Bauschlicher Jr C W 2003 *Theor. Chem. Acc.* **109** 298
 Harrison J F 2000 *Chem. Rev.* **100** 679
 Hay P J and Wart W R 1985 *J. Chem. Phys.* **82** 299
 Kharat B, Deshmukh S B and Chaudhari A 2009 *Int. J. Quant. Chem.* **109** 1103
 Kunze K L and Harrison J F 1989 *J. Phys. Chem.* **93** 2983
 Li X and Wang L S 1999 *J. Chem. Phys.* **111** 8389
 Moravec V D, Klopčič S A, Chatterjee B and Jarrold C C 2001 *Chem. Phys. Lett.* **341** 313
 Nikolov I D 2005 *Curr. Nanosci.* **1** 211
 Rao C N R 1989 *Ann. Rev. Phys. Chem.* **40** 291
 Sao-Joao S, Giorgio S, Penisson J M, Chapon C, Bourgeois S and Henry C 2005 *J. Phys. Chem.* **B109** 342
 Schmid R and Basting D 2005 *J. Phys. Chem.* **A109** 2623
 Schmider H L and Becke A D 1998 *J. Chem. Phys.* **108** 9624
 Siegbahn P E M 1993 *Chem. Phys. Lett.* **201** 15
 Thimoshkin A I, Bettinger H F and Schaefer H F III 2001 *J. Phys. Chem.* **A105** 3249
 Tong G S M, Jeung G H and Cheung A S C 2003 *J. Chem. Phys.* **118** 9224
 Uneo L T, Roberto-Neto O, Canuto S and Machado F B C 2005 *Chem. Phys. Lett.* **413** 65
 Wu H and Wang L S 1997 *J. Chem. Phys.* **107** 8221
 Wu H and Wang L S 1998 *J. Phys. Chem.* **A102** 9129
 Wu Y, Cui Y, Huynh L, Barrelet C J, Bell D C and Lieber C M 2004 *Nano. Lett.* **4** 433
 Wu Z J 2005 *J. Mol. Struct.: Theor. Chem.* **728** 167
 Wu Z J and Kawazoe Y 2006 *Chem. Phys. Lett.* **423** 81
 Xian H, Cao Z X, Xu X, Lu X and Zhang Q E 2000 *Chem. Phys. Lett.* **326** 485
 Yamaki T, Sekiya M and Tanaka K 2003 *Chem. Phys. Lett.* **376** 487