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Structure, bonding, reactivity and aromaticity of some selected Zn-clusters

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ABSTRACT

Geometries of several all-metal clusters with Zn_3^{2-} as the base are optimized within a B3LYP/6-311+G(d) level of theory. It is analyzed that the stability, bonding, reactivity and aromaticity patterns of such clusters often change drastically in the presence of counter cations like Li^+, Na^+ or K^+ and/or through the substitution of Zn_3^{2-} units by Be_5^- or $C_5H_5^-$ rings.

1. Introduction

The discovery of ferrocene [1–4] about six decades ago set a new benchmark for both the experimentalists and the theoreticians to prepare a huge variety of metal sandwiched complexes called metallocenes. Further enrichment of thoughts provoked the genesis of triple and multi-decker forms of these metallocenes which are better known as multi-decker sandwich complexes. Such triple and multi-decker complexes have also been studied experimentally [5–7] and theoretically [8,9]. The breakthrough concept of "all-metal aromaticity" in an Al_4^{2-} system introduced by Boldyrev et al. [10] proved very fruitful to study the structure and bonding patterns of many such all-metal clusters. The Al_4^{2-} species showed π-aromaticity over a σ-framework. The ability of a metal atom to bind with the same atom to form an M–M bond in a compound is a topic of immense interest in metal cluster chemistry. Parkin [11] and Resa et al. [12] in their landmark articles proved the very existence of such a bonding between Zn atoms (Zn–Zn bond) in a complex for the first time. The existence of an all-beryllium chain-cluster (Be_8^{2-}) containing a Be–Be bond has also been recently reported [13]. The trigonal planar Zn_3^{2-} moiety is also well-known [14]. It possesses pure π-type aromaticity without a σ-framework unlike the Al_4^{2-} species which shows both σ- and π-aromaticities [10]. It may, however, be mentioned that many of these molecules are of "fleeting" type and do not correspond to the global minima [15].

In this article, we report the existence of a number of all-zinc chain-like clusters containing the Zn–Zn (2, 3 and 4 Zn atoms) linkage by starting with Zn_3^{2-} as the base. The Zn_3^{2-} moiety is also further complexed with suitable counter cations like Li^+, Na^+, K^+, Be^{2+}, Mg^{2+} and Ca^{2+} to produce mixed-metal clusters. The Zn_3^{2-} ring in some of the all-zinc clusters are also substituted by the cyclopentadienyl anion ($Cp^- \equiv C_5H_5^-$) and Be_5^- ring. We also study a number of possible reactions that may occur upon substitution of the Zn_3^{2-} ring with Cp^- or Be_5^-. The diverse aspects of the all-metal clusters like stability, reactivity trends and aromatic behavior can be well evaluated with the help of conceptual density functional theory [16–19] in conjunction with the various global reactivity descriptors like electronegativity [20–22] (χ), hardness [23–25] (η), electrophilicity [26–28] (ω) and the local descriptors like atomic charges [29] (Q_k) and Fukui functions [30] (f_k). The nucleus independent chemical shift (NICS) values obtained by exploiting the procedure of Schleyer et al. [31] are analyzed to realize the aromaticity patterns of the metal-clustered complexes. The probability of the reactions occurring upon substitution of the Zn_3^{2-} ring by Cp^- or Be_5^- in the all-zinc clusters is explored from their respective changes in enthalpy (ΔH) and electrophilicity ($\Delta\omega$) values.

2. Theoretical background

All spontaneous processes in environment are generally accompanied by a lowering in the energy (E) values of the resultant systems. This situation may further be described by a maximization in the hardness [32–34] (η) and minimization in the polarizability [35,36] (α) and electrophilicity [37,38] (ω) values. The most stable structures are also obtained following these electronic structure principles. In an N-electron system, the electronegativity [20–22] (χ) and hardness [23–25] (η) can be defined as follows:

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Table 1
The total energy (E in au), electronegativity (χ in eV), hardness (η in eV) and electrophilicity (ω in eV) of the different metal clusters.

Molecules	E (au)	χ (eV)	η (eV)	ω (eV)
$[Zn_3]^{2-}$	−5337.96696	−4.139	1.230	6.963
Zn_3–Zn	−7117.42290	4.276	3.558	2.570
$[Zn_3$–Zn–$Zn_3]^{2-}$	−12455.47682	−3.042	1.248	3.705
$[Zn_3$–Zn–Zn–$Zn_3]^{2-}$	−14234.85248	−2.715	1.266	2.911
$[Zn_3$–Zn–Zn–Zn–$Zn_3]^{2-}$	−16014.21790	−2.432	1.212	2.439
$[Zn_3$–Zn–Zn–Zn–Zn–$Zn_3]^{2-}$	−17793.58082	−2.203	1.182	2.052
$[Zn_3$–Li$]^{-}$	−5345.61752	−0.443	1.595	0.062
$[Zn_3$–Na$]^{-}$	−5500.40622	−0.347	1.542	0.039
$[Zn_3$–K$]^{-}$	−5938.03877	−0.308	1.274	0.037
Zn_3–Be	−5352.76070	4.043	2.999	2.725
Zn_3–Mg	−5538.16729	3.852	3.073	2.413
Zn_3–Ca	−6015.65893	3.307	2.477	2.207
Li–Zn_3–Li	−5353.12638	3.119	2.432	2.001
Na–Zn_3–Na	−5662.69519	2.984	2.300	1.936
K–Zn_3–K	−6537.96708	2.494	1.844	1.687
[Be–Zn_3–Be$]^{2+}$	−5366.84043	13.772	3.316	28.595
[Mg–Zn_3–Mg$]^{2+}$	−5737.69138	12.742	3.197	25.389
[Ca–Zn_3–Ca$]^{2+}$	−6692.76523	11.108	2.708	22.785
$[C_5H_5]^{-}$	−193.56993	−1.512	3.423	0.334
C_5H_5–Zn–C_5H_5	−2166.45825	3.698	3.894	1.756
C_5H_5–Zn–Zn–C_5H_5	−3945.84289	3.718	4.160	1.661
C_5H_5–Zn–Zn–Zn–C_5H_5	−5725.19950	3.845	3.714	1.991
$[Be_5]^{-}$	−73.56509	−0.521	2.024	0.067
Be_5–Zn–Zn–Be_5	−3705.81149	4.257	1.796	5.045
Be_5–Zn–Zn–Zn–Be_5	−5485.16880	4.196	1.695	5.194
Be_5–Zn–Zn–Zn–Zn–Be_5	−7264.52353	4.113	1.610	5.255

Table 2
The point groups (PG) and NICS(0) values of different metal clusters.

Molecules	Point group (PG)	NICS(0) in ppm
$[Zn_3]^{2-}$	D_{3h}	−7.591(Zn_3)
Zn_3–Zn	T_d	−16.8454(Zn_3)
$[Zn_3$–Zn–$Zn_3]^{2-}$	D_{3d}	−24.396(Zn_3), −24.396(Zn_3)
$[Zn_3$–Zn–Zn–$Zn_3]^{2-}$	D_{3h}	−24.228(Zn_3), −24.228(Zn_3)
$[Zn_3$–Zn–Zn–Zn–$Zn_3]^{2-}$	D_{3h}	−26.080(Zn_3), −26.080(Zn_3)
$[Zn_3$–Zn–Zn–Zn–Zn–$Zn_3]^{2-}$	D_{3h}	−25.702(Zn_3), −25.702(Zn_3)
$[Zn_3$–Li$]^{-}$	C_{3v}	−27.750(Zn_3)
$[Zn_3$–Na$]^{-}$	C_{3v}	−24.619(Zn_3)
$[Zn_3$–K$]^{-}$	C_{3v}	−23.013(Zn_3)
Zn_3–Be	C_{3v}	−28.650(Zn_3)
Zn_3–Mg	C_{3v}	−20.300(Zn_3)
Zn_3–Ca	C_{3v}	−24.637(Zn_3)
Li–Zn_3–Li	D_{3h}	−33.291(Zn_3)
Na–Zn_3–Na	D_{3h}	−31.435(Zn_3)
K–Zn_3–K	D_{3h}	−29.919(Zn_3)
[Be–Zn_3–Be$]^{2+}$	D_{3h}	−28.579(Zn_3)
[Mg–Zn_3–Mg$]^{2+}$	D_{3h}	−22.486(Zn_3)
[Ca–Zn_3–Ca$]^{2+}$	D_{3h}	−30.811(Zn_3)
$[C_5H_5]^{-}$	D_{5h}	−12.531(C_5H_5)
C_5H_5–Zn– C_5H_5	C_1	−7.407(C_5H_5), −11.564(C_5H_5)
C_5H_5–Zn–Zn–C_5H_5	D_5	−14.880(C_5H_5), −14.810(C_5H_5)
C_5H_5–Zn–Zn–Zn–C_5H_5	D_5	−14.937(C_5H_5), −14.974(C_5H_5)
$[Be_5]^{-}$	D_{5h}	−4.776(Be_5)
Be_5–Zn–Zn–Be_5	D_5	6.770(Be_5), 6.770(Be_5)
Be_5–Zn–Zn–Zn–Be_5	D_{5d}	6.833(Be_5), 6.833(Be_5)
Be_5–Zn–Zn–Zn–Zn–Be_5	D_{5d}	6.867(Be_5), 6.867(Be_5)

Table 3
The atomic charges (Q_k) and fukui functions (f_k^+, f_k^-, MPA) of the different metal clusters.

Molecules	Unit	Atomic charge(Q_k)	f_k^+ (MPA)	f_k^- (MPA)
$[Zn_3]^{2-}$	Zn_3	−0.668, −0.665, −0.666	0.348, 0.327, 0.325	0.335, 0.332, 0.333
Zn_3–Zn	Zn_3	0.000, 0.000, 0.000	0.250, 0.250, 0.250	0.289, 0.270, 0.228
	Zn	0.000	0.250	0.212
$[Zn_3$–Zn–$Zn_3]^{2-}$	Zn_3	−0.320, −0.320, −0.320	0.483, 0.483, 0.483	0.163, 0.163, 0.163
	Zn_3	−0.320, −0.320, −0.320	0.483, 0.483, 0.483	0.163, 0.163, 0.163
	Zn	−0.078	−1.898	0.020
$[Zn_3$–Zn–Zn–$Zn_3]^{2-}$	Zn_3	−0.451, −0.451, −0.451	0.514, 0.514, 0.514	0.224, 0.224, 0.224
	Zn_3	−0.451, −0.451, −0.451	0.514, 0.514, 0.514	0.224, 0.224, 0.224
	Zn	0.354	−1.043	−0.171
	Zn	0.354	−1.043	−0.171
$[Zn_3$–Zn–Zn–Zn–$Zn_3]^{2-}$	Zn_3	−0.435, −0.435, −0.435	0.473, 0.473, 0.473	0.204, 0.204, 0.204
	Zn_3	−0.435, −0.435, −0.435	0.473, 0.473, 0.473	0.204, 0.204, 0.204
	Zn	0.254	−1.317	−0.164
	Zn	0.254	−1.317	−0.164
	Zn	0.101	0.793	0.106
$[Zn_3$–Zn–Zn–Zn–Zn–$Zn_3]^{2-}$	Zn_3	−0.421, −0.421, −0.421	0.436, 0.436, 0.436	0.190, 0.190, 0.190
	Zn_3	−0.421, −0.421, −0.421	0.436, 0.436, 0.436	0.190, 0.190, 0.190
	Zn	−0.051	0.275	0.109
	Zn	−0.051	0.275	0.109
	Zn	0.313	−1.084	−0.179
	Zn	0.313	−1.084	−0.179
$[Zn_3$–Li$]^{-}$	Zn_3	−0.209, −0.209, −0.209	−0.288, −0.298, −0.263	0.159, 0.159, 0.159
	Li	−0.373	1.849	0.524
$[Zn_3$–Na$]^{-}$	Zn_3	−0.202, −0.202, −0.202	−0.100, −0.058, −0.008	0.133, 0.133, 0.133
	Na	−0.395	1.166	0.602
$[Zn_3$–K$]^{-}$	Zn_3	−0.227, −0.227, −0.227	0.003, −0.069, −0.022	0.093, 0.093, 0.092
	K	−0.317	1.089	0.722
Zn_3–Be	Zn_3	−0.004, −0.004, −0.004	0.316, 0.316, 0.316	0.223, 0.222, 0.222
	Be	0.011	0.052	0.333
Zn_3–Mg	Zn_3	−0.018, −0.018, −0.018	0.323, 0.323, 0.323	0.158, 0.158, 0.158
	Mg	0.053	0.032	0.526
Zn_3–Ca	Zn_3	−0.119, −0.119, −0.119	0.158, 0.158, 0.158	0.147, 0.147, 0.147
	Ca	0.356	0.525	0.560
Li–Zn_3–Li	Zn_3	−0.148, −0.148, −0.148	0.119, 0.119, 0.119	0.156, 0.156, 0.156
	Li	0.221	0.322	0.266
	Li	0.221	0.322	0.266

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