Synthesis and structure of 1-D Na_6 cluster chain with short Na–Na distance: Organic like aromaticity in inorganic metal cluster†

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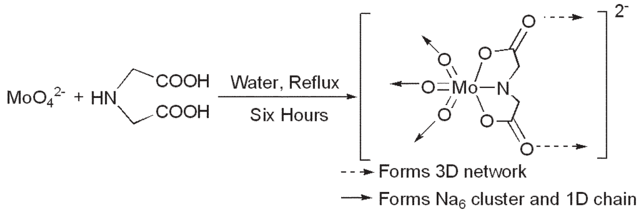
A unique 1-D chain of sodium cluster containing (Na_6) rings stabilized by a molybdenum containing metalloligand has been synthesized and characterized and the DFT calculations show striking resemblance in their aromatic behaviour with the corresponding hydrocarbon analogues

Studies on polymeric metal compounds are receiving more and more attention in recent years due to their properties, which lie between isolated molecules and bulk material.[1] The major developments in this area are synthesis of conducting polymeric materials and metal cluster trapped within the channels of zeolite.[2,3] In recent years bimetallic compounds containing alkali metal clusters have been synthesized.[1a] For example, gallium phosphonates have been shown to form cages containing lithium,[1a] sodium, and potassium[4] ions with short metal–metal contacts. In the lithium compound the lithium ions are arranged in a finite unidimensional wire. These compounds are potential precursors for preparation of ion conductors and molecular sieves.[1a]

We have been interested in alkali metal complexes of molybdenum containing metalloligands and recently reported synthesis and structure of $[\{Na_4(H_2O)_4(\mu\text{-}H_2O)_2\}\subset(Mo_2O_5L_2)_2]$, bearing rectangular Na_4^{4+} cluster cation stabilized by the metalloligand, $[LMoO_2(\mu\text{-}O)MoO_2L]^{2-}$ (LH_2 = {(3,5-di-*tert*-butyl-2-hydroxybenzyl)amino}acetic acid) and the corresponding cesium compound, a helical 1-D infinite chain of $[Cs_2\ (Mo_2O_5L_2).H_2O]_n$.[5] We were interested in exploring methods for assembly of larger cluster. We report here the synthesis and structure of a new metalloligand and its sodium complex $[Na_2MoO_3L(H_2O)_2]_n$ (**1**) {L = iminodiacetate}, which contains infinite one-dimensional chain of hexagonal sodium ions with short Na–Na contacts and theoretical investigation (DFT calculation) of the stability and reactivity of the compound.

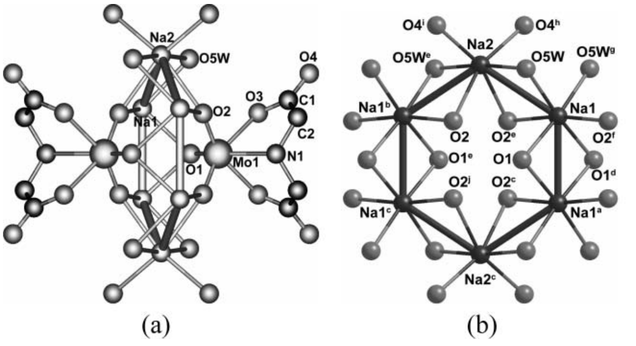
Our synthetic strategy is to use a tridentate, dibasic ligand (L), containing two carboxylate donor sites, that is expected to form the metalloligand, $[LMoO_3]^{2-}$. This polydentate metalloligand has a potential to coordinate alkali-metal cations through Mo=O oxygens and bridging carboxylate and self-assemble into various architectures (Scheme 1).



Scheme 1 Formation and coordination mode of the metalloligand.

Accordingly, a reaction of $Na_2MoO_4{\cdot}2H_2O$ and iminodiacetic acid has been carried out in water and the compound **1** has been isolated in high yield.‡ The compound has been characterized by elemental analyses, thermogravimetric analysis (TGA), and spectroscopic as well as a single crystal X-ray diffraction studies.

X-ray diffraction analysis§ reveals that the asymmetric unit of **1** contains half of the molybdenum coordinated iminodiacetate, two oxo ligands, two sodium, and one water where two independent Na atoms lies on 2-fold axes and molybdenum (Mo1), N1 and O1 lie on a mirror plane. In **1** the molybdenum center adopts distorted octahedral geometry and is coordinated to three oxo ligands and two oxygens and a nitrogen from iminodiacetate ligand (Fig. 1a). Each of the three Mo=O oxygens bridges two sodium ions in a μ_3 fashion (Fig. 1a). In addition, the two sodium ions (Na1 and Na2) are bridged by one μ_2-oxygen of water. Each of the two carboxylates of the ligand bridge one molybdenum atom and two sodium (Na2). Thus, each of the sodium ions is hexacoordinated in a distorted octahedral geometry. The coordnation environment of the two sodium atoms differs slightly. The Na1 center is coordinated by symmetrically equivalent two Mo=O oxygens (O1), two



(a) (b)

Fig. 1 (a) Molecular structure of **1** (asymmetric unit is labelled). (b) Part of the polymeric structure showing formation of Na_6 ring viewed along *a* axes. Bond lengths (Å): Mo(1)–O(1) 1.755(3), Mo(1)–O(2) 1.741(2), Mo(1)–O(3) 2.228(2), Mo(1)–N(1) 2.306(4), Na(1)–O(1) 2.352(3), Na(1)–O(2)^e 2.378(2), Na(1)–O(5W) 2.393(3), Na(2)–O(2) 2.485(3), Na(2)–O(4)^h 2.360(3), Na(2)–O(5W) 2.354(3), Na(1)–Na(2) 3.2723(17), Na(1)–Na(1)^a 3.076(4) (symmetry code: a: $1 - x, 2 - y, 1 - z$; b: $x, y, -1 + z$; c: $1 - x, 2 - y, -z$; d: x, y, $1 + z$; e: $1 - x, y, -z$; f: $x, y, 1 + z$; g: $1 - x, y, 1 - z$; h: $-1/2 + x, 1.5 - y, z$; i: $1.5 - x, 1.5 - y, -z$; j: $x, 2 - y, z$).

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† Electronic supplementary information (ESI) available: TGA plot, tables for structural data, bond distances and angles, ORTEP, figures and comparison of results between two levels of theory in calculation. See DOI: 10.1039/b611693k

waters (O5W) in *cis* fashion and two Mo=O oxygen (O2) in *trans* fashion, while the Na2 center is coordinated by symmetrically equivalent two Mo=O oxygens (O2), and two waters (O5W) in *trans* fashion (Fig. 1b). In **1**, six Mo=O oxygens from two metalloligands, two Mo=O oxygens (symmetrically equivalent O1) from other two metalloligands and four bridging waters (O5W) bind six sodium ions and form a hexagonal Na_6 ring (Fig. 1b). The observed Na···Na distances {Na1···Na1^a (a = 1 − *x*, 2 − *y*, 1 − *z*) = 3.076 (4) Å and Na1···Na2 = 3.2723 (17) Å} in the ring are distinctly shorter compared to that in elemental sodium (3.82 Å) and other polynuclear oxygen coordinated sodium compounds.[4,6a,6b] The short Na···Na distances clearly show attractive Na–Na interaction in the cluster. In our earlier work on Na_4^{4+} cluster[5] a similar short Na···Na distance was observed. A few years back a tetrasodium dication, Na_4^{2+}, stabilized by two silyl(fluorosilyl)phosphonide with similar short Na–Na distances was reported.[6c] The distinctive feature of **1** is the formation of hexagonal 1-D chain of sodium ions (Fig. 2a). The infinite polymeric chain grows along the crystallograhic *c* axis. Another interesting feature of the 1-D chain is that the hexagonal ring (Na_6) is planer like benzene as three successive torsion angles (*φ*) are zero(0) degree. It is interesting that the carboxylate groups in the metalloligand act as a bridge between Mo and the Na centre of the neighbouring 1-D polymeric units and assist the chain growth along the crystallographic *a* and *b* axes and form a 3-D polymeric network (Fig. 2b).

The observed geometry of the (Na_6) units in the 1-D chain prompted us to investigate the characteristics of this cluster theoretically and look for a possible aromatic behavior. In recent years, all metal aromaticity has attracted a great deal of attention.[7] A few organometallic all metal aromatic compounds have been reported.[7e] Apart form these reports, the major focus has been on the gas phase synthesis and theoretical studies on aluminium cluster.[7] Starting from the experimental geometry of (Na_{4n+2}), $n = 1$–5, clusters single point calculations have been performed at the B3LYP/6-311+G* (for $n = 1$–4) and B3LYP/6-31G* (for $n = 5$) levels of theory. In the case of $n = 5$, the B3LYP/6-311+G* level of theory did not show any convergence. Thus in this case, the B3LYP/6-31G* level of theory has been used. For all $C_{4n+2}H_{2n+4}$, $n = 1$–5, B3LYP/6-311+G* basis set is used. The electronic properties were also calculated at the B3LYP/LanL2DZ level of theory. It has been found that, except for absolute values, the trends of various electronic properties remain the same as those calculated using B3LYP/LanL2DZ level of theory (ESI†). Various electronic properties like energy (*E*), hardness (*η*),[8] polarizability (*α*),[9] eletrophilicity (*ω*),[10] and nucleus independent chemical shift at the ring center {NICS(0)}[11] have been calculated using standard techniques.[12] Fig. 3 presents the plots of *E*, *η*, *α*, and *ω* per (Na_6) unit in (Na_{4n+2}), $n = 1$ to 5 clusters, which provides a transparent view of the stability and reactivity. As the chain length increases, its energy per (Na_6) unit increases and the hardness decreases as expected from the maximum hardness principle.[13] This implies that the average reactivity increases with the increase in chain length. Except for one or two smallest clusters, the observed trend of variation in *α* and *ω* are as expected from the principles of the minimum polarizability[14] and electrophilicity.[15] Corresponding linear arenes (Fig. 3) exhibit identical reactivity and stability patterns. These electronic structure principles have been shown to be adequate in explaining the aromatic and antiaromatic behaviour of all metal compounds[16] like Al_4^{2-} and Al_4^{4-} or the prototypical organic analogues like benzene and cyclobutadiene.[17] In order to check the possible aromatic character of the Na_{4n+2} clusters, their NICS(0) values have been calculated and compared with those values (B3LYP/6-311+G*) of the corresponding linear arenes.[18] The comparison is shown in Fig. 4. It is interesting to note that these (Na_{4n+2}), clusters exhibit striking resemblance, in their aromatic behaviour, with that of linear polyacenes. Not only their NICS (0) values are comparable, "the more reactive inner rings actually are more aromatic than the less reactive outer rings and even more aromatic than benzene itself"[19] for the linear arenes as well as (Na_{4n+2}) clusters.

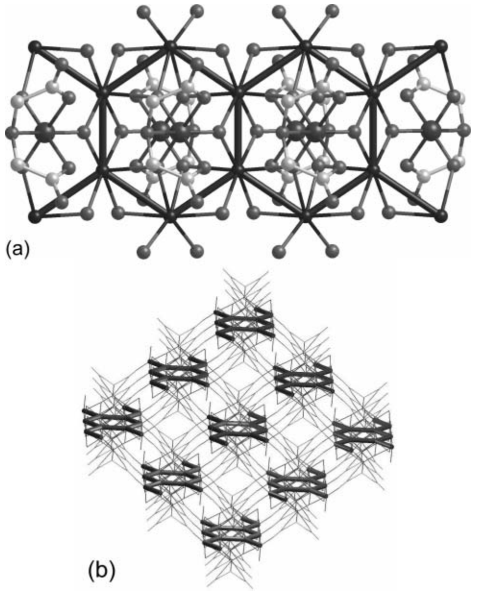

Fig. 2 (a) View of the formation of 1-D chain of the Na_6 cluster along the *a* axis. (b) The 3-D polymeric network in **1** along the *c* axis depicted by OLEX.[20] 1-D chain of Na_6 unit shown as a dark thick line in both figures.

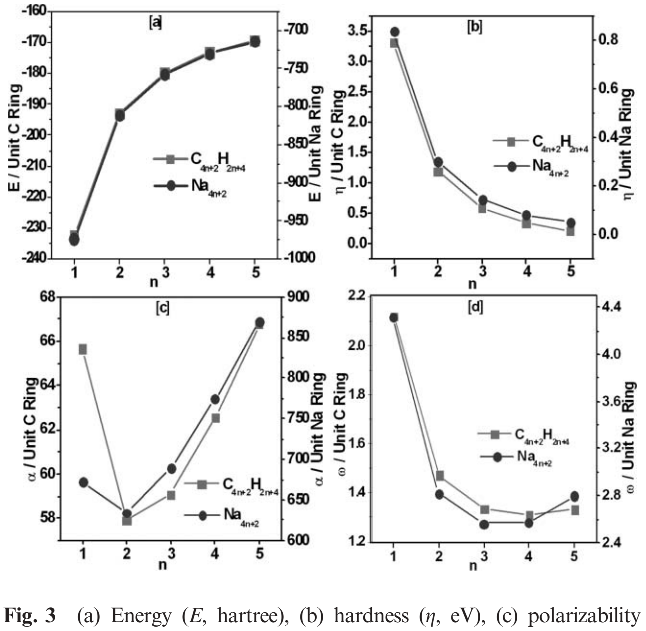

Fig. 3 (a) Energy (*E*, hartree), (b) hardness (*η*, eV), (c) polarizability (*α*, a.u.) and (d) electrophilicity (*ω*, eV) profiles per unit C_6 ring/Na_6 ring.

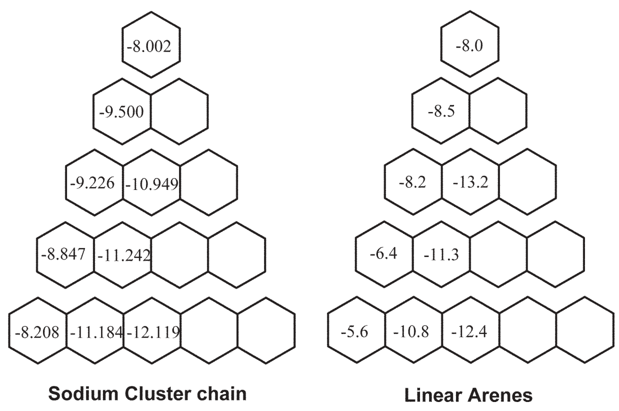

Fig. 4 NICS (0) values (ppm) of each (Na_6) ring in the cluster chain [general formula (Na_{4n+2})] and linear arenes at the 6-311+G* level except for Na_{22} which is calculated at the 6-31G* level.

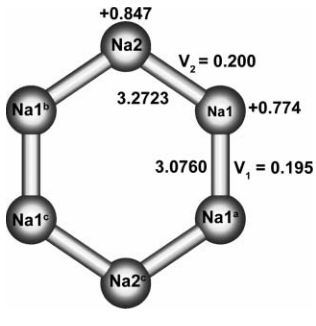

Fig. 5 Calculated charge on the Na atoms and inter Na potential energies in $Na_6[MoO_3L]_3{\cdot}4H_2O$. The metalloligand part is not shown for clarity.

In order to have a more transparent idea about the nature of the bonding in the presence of the metalloligands, we have also computed fractional charges in the (Na_6) ring (Fig. S8 in ESI†) including the metalloligands (B3LYP/LanL2DZ). Fractional charges on Na atoms have been calculated using the Mulliken population analysis scheme. The charges (+0.774 and +0.847) provide the inter sodium potential energies in units of $(4\pi\varepsilon_0)^{-1}$ as 0.195 and 0.200 (Fig. 5).

In conclusion, a unique 1-D chain of hexagonal sodium cluster has been synthesized and structurally characterized. The DFT calculations show that the (Na_6) rings in the chain are highly aromatic in character and the NICS(0) values of the Na_6 rings are almost same as their polyacene analogues. The stability and reactivity pattern of the Na_6 rings also follow the same pattern as their organic analogues. Thus, the inorganic Na_6 chain shows organic like aromaticity.

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Notes and references

‡ An aqueous solution of $Na_2MoO_4{\cdot}2H_2O$ (0.241 g, 1 mmol) was added to an aqueous solution of iminodiacetic acid (0.133 g, 1 mmol). The mixture was refluxed for about 6 h, the resulting mixture was filtered and the filtrate was allowed to stand in air at room temperature. After six weeks colourless block-shaped crystals, suitable for X-ray diffraction, of **1** were obtained. Yield 80%. Elemental analysis calc (%) for $C_4H_9MoNNa_2O_9$(M_w = 357.04): C 13.46, H 2.54, N 3.92, Mo 26.87, Na 12.88; found: C 13.44, H 2.49, N 3.89, Mo 26.39(gravimetric analyses), Na 13.16 (flame photometry). IR (KBr) (ν_{max}/cm^{-1}) 1660, 1400, 890, 840, 760. TGA: Total weight loss: 42.262% from 170 to 470 °C (H_2O and L) The residual weight 57.738% (calc: 57.685%) corresponds to Na_2MoO_4. (ESI†).

§ Crystal data for **1**: $C_4H_9MoNNa_2O_9$, M_w = 357.04, 298(2) K, colourless block (0.2 × 0.2 × 0.1 mm^3), monoclinic, $C2/m$, Z = 4, a = 13.538(5) Å, b = 14.980(3) Å, c = 5.438(2) Å β = 99.622(12)°, V = 1087.4(6) Å^3, ρ_{calcd} = 2.181 Mg m^{-3}, $2\theta_{max}$ = 49.88, λ(Mo Kα = 0.71073 Å, ω-scan, 1039 measured, 997 unique (R_{int} = 0.0266, R_σ = 0.0065). $R1$ = 0.0302, $wR2$ = 0.0822 for 991 reflections with $I > 2\sigma(I)$ and $R1$ = 0.0304, $wR2$ = 0.0823 for all data, max/min residual electron density =1.134/−1.572. CCDC 608214. The details of crystal data collection and refinements and selected bond lengths and angles of **1** are summarized in Table S1 and S2 (ESI).† For crystallographic data in CIF or other electronic format see DOI: 10.1039/b611693k

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