

A novel pyramidal multiple alkali metal cluster $[K_3(H_2O)]^{3+}$ stabilized within a capsule containing 16-nitrogen donors

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Received (in Cambridge, UK) 7th May 2003, Accepted 2nd June 2003

First published as an Advance Article on the web 19th June 2003

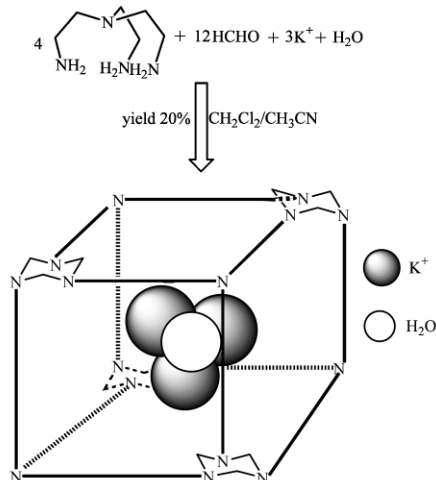
A novel multiple alkali metal cluster $K_3(H_2O)^{3+}$ interior within a high-symmetry cubic capsule containing 16-nitrogen donors is achieved *via* self-assembly from twenty components.

Since the introduction of the cryptands,¹ chemists have striven to design discrete spherical molecular hosts similar to those found in nature, due to the capabilities of entrapping atomic and/or molecular sized guests and the applications in chemistry, biology and materials science.^{2,3} It has been postulated that the interior of cage-like molecules can be considered to provide a new phase of matter in which it becomes possible to stabilize reactive intermediates and to observe new forms of stereoisomer.²⁻⁴ In our previous studies, we found that the large spherical cubic-shaped host ($L = C_{36}H_{72}N_{16}$) could include two water molecules within its $i_{12}O_4$ conformation.⁵ It is expected that the i_{16} conformation of such a host can include larger sized molecules or clusters. Here we report the new multiple alkali metal cluster $[K_3(H_2O)]^{3+}$ interior of the spherical cubic host achieved *via* a one-pot procedure from twenty components (Scheme 1).

On reaction of tris(2-ethylamino)amine with formalin in the presence of $HClO_4$, KI and CdI_2 , pale-yellow crystals of **1**, $[L \subset K_3(H_2O)] [CdI_4][ClO_4]_2 [H_3O]$, were formed.† Crystal structure analysis‡ reveals that the asymmetric unit consists of two slightly different halves $[L \subset K_3(H_2O)]^{3+}$ interior cations, disordered CdI_4^{2-} and ClO_4^- anions as well as disordered hydronium. As shown in Fig. 1, the cage is slightly deformed from the expected T_d symmetry with the four bridge head nitrogen atoms of tris(2-aminoethyl)amine and the four six-member $[N(CH_2)_3]$ rings occupying the vertex positions, and the twelve CH_2CH_2 chains along the edges. The edge of the cubic cage is *ca.* 4.2 Å in length (from the head nitrogen atom to the center of the six-member ring). Unlike the $i_{12}O_4$ conformation⁵ of the host in the compound $[L \subset (H_2O)_2]$, the host in **1** shows i_{16} conformation with all the sixteen nitrogen atoms oriented towards the inside of cavity (*endo*) and the lone

pairs pointed inside the cavity to delineate the intramolecular cavity. The distances from the center (M) of the cavity to the *endo* nitrogen atoms of four six-member $[N(CH_2)_3]$ rings are in the range of 3.09–3.40 Å (on average *ca.* 3.28 Å), which are shorter than the average M–N distance (3.88 Å) of those in the compound $[L \subset (H_2O)_2]$. The separations between the center (M) of the cavity and four bridge head nitrogen atoms of tris(2-aminoethyl)amine are about 4.05 Å, which are slightly longer than those (3.88 Å) in compound $[L \subset (H_2O)_2]$. It seems that both the conformation and the volume of the crypt could be modulated to recognize guests with different sizes and forms.

There are novel pyramidal multiple alkali metallic $[K_3(H_2O)]^{3+}$ clusters within the cages. Fig. 2 shows one of the two slightly different cations in the crystal structure, the cluster has C_2 symmetry with a water molecule and three K^+ ions occupying the four vertex positions in which only two positions are independent. The water molecule and one of the K^+ ions, K(2), occupy the same positions with the site occupancy factors each fixed at 0.5. Statistically the pyramidal cluster has the formula $[K_3(H_2O)]^{3+}$. Each metal (or water) center is surrounded by four closed nitrogen atoms with the K–N distances in the range of 2.31–2.56 Å. Such distances are shorter than those of K–N bonds 2.76–2.98 Å in $K(CH_3CN)_n$,^{6a} 3.15–3.18 Å in bireceptor of pyridine containing cage,^{6b} 2.82–3.23 Å in potassium triazene complex,^{6c} and 2.48–2.55 Å of Au_2K unit in macrocycle.^{6d} The basic properties of small metallic clusters are believed to be an important link in the understanding of the fundamental mechanisms of catalyses and numerous chemical transformations.⁷ Despite considerable recent efforts, the structures of small atomic metal clusters remain largely unknown. Alkali metal ionic clusters are only found in zeolites⁸ and significant advances relating to the structural electronic, magnetic, and optical properties of excess electron states have been made. There are also alkali metal clusters of which the metal atoms were bridged by donors, such as oxygen, nitrogen atoms in other systems with long-distance metal–metal separa-



Scheme 1

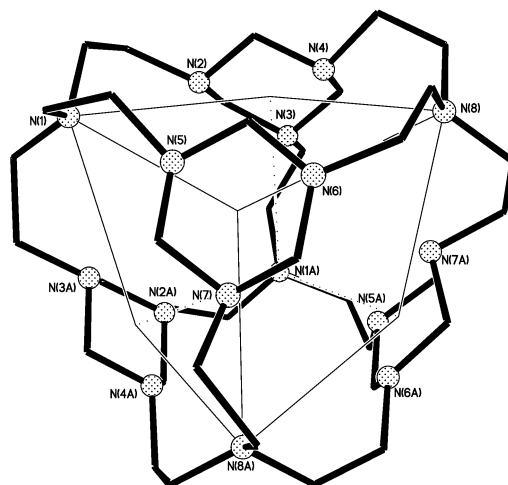


Fig. 1 Perspective view of one of the hosts showing the potential T_d symmetry of the cube.

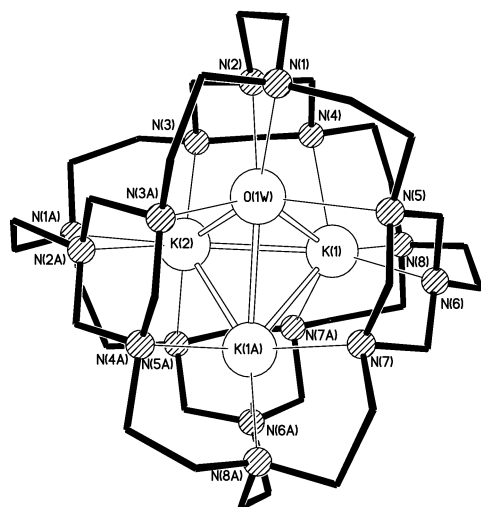


Fig. 2 Perspective view of one of the host-cluster cations, $[L C K_3(H_2O)]^{3+}$. Selected interatomic contacts (Å): K(1)–N(4) 2.478(6), K(1)–N(6) 2.311(7), K(1)–N(8) 2.395(6), K(1)–N(7A) 2.581(7), K(2)–N(1A) 2.474(6), K(2)–N(2A) 2.471(7), K(2)–N(3) 2.444(7), K(2)–N(5A) 2.473(7), K(1)–O(1W) 2.614(4), K(1)–K(2) 2.837(4), K(2)–O(1W) 2.448(6), K(1)–K(1A) 2.818(4). Symmetry code A: $x, -y + 1/2, -z$.

tions,^{9,10} however, no alkali metal ionic clusters have been found in normal conditions, even in the cage-like macrocyclic compounds. This paper gives the first example of the alkali metal ionic cluster interior compound. The separations of $K \cdots K(O)$ are in the range 2.62–2.84 Å. Such distances are much shorter than those in the atomic small potassium clusters K_2 , K_3 and K_4 ,^{8a} (3.87–4.37 Å), and in the potassium-loaded zeolite K_3/K_9-L and L_5/K_9-L ^{8b} (4.07–5.03 Å); 4.5 Å in the K_4N_4 unit of $[(Me_2PhSi)_3CuCNK]_4$ ^{11a} and 3.22 for the $\{K(CyNC(N(SiMe_3)_2)MCy)\}_2$.^{11b} It seems that such short metal–metal separation would reach to the lowest limit of $K^+ \cdots K^+$ separation determined from Shannon's classic table of ionic sizes (1.37 and 1.51 Å for the effective ionic radius and the crystal radius of 4-coordinated K^+ , respectively),¹² notwithstanding the K/O disorder. It is suggested that shortening of the $K^+ \cdots K^+$ and the $K^+ \cdots N$ separations resulted from the special environment of the host.

A new metallic cluster $[K_3(H_2O)]^{3+}$ interior within a high-symmetry cubic capsule with 16-nitrogen donors was achieved via a one-pot procedure from twenty components. It seems that the host provides a special environment within which the $[K_3(H_2O)]^{3+}$ trication was stabilized.

This work was supported by the National Natural Science Foundation of China (No. 20131020). We thank the referees for their detailed suggestion in the revision of the manuscript. We also thank Mr Liu Yong-jiang for collecting the crystal data.

Notes and references

† Into a stirred 100 mL acetonitrile solution containing $HClO_4$ (0.5 mL) and $NaOAc$ (1.2 g, 15 mmol), 200 mL of a dichloromethane solution of tris(2-aminoethyl)amine (1.46 g, 10 mmol) and 200 mL of an acetonitrile solution containing 36% formalin (2.5 g, 30 mmol) were added dropwise,

respectively. The solution was left for one week at room temperature; a white solid that formed was removed by filtration. An acetonitrile–water solution containing CdI_2 (0.9 g, 2.5 mmol) and KI (1.6 g, 10 mmol) was added to the resulting filtrate. The solution was left to stand in the air for a further week; the pale-yellow crystals that formed were used directly for crystal structure analysis. Yield 20%. Anal. Calcd. For $C_{36}H_{76}N_{16}O_{10}K_3CdI_4Cl_2$: C, 25.4; H, 4.6; N, 13.2, Cd, 6.6; K, 6.9%. Found: C, 25.8; H, 4.5; N, 13.5; Cd, 6.2; K, 7.5%.

‡ Crystal data of complex **1**: $[(C_{36}H_{72}N_{16})K_3(H_2O)][CdI_4][ClO_4]_2(H_3O)$, $M_r = 1702.34$, orthorhombic, space group $Pbcm$, $a = 13.512(3)$, $b = 27.115(5)$, $c = 31.756(6)$ Å, $V = 11635(4)$ Å³, $Z = 8$, $\mu = 2.868$ mm⁻¹. Intensity data were collected on a Bruker CCD system. The structure was solved by direct methods. 51644 reflections measured of which 10351 ($R_{int} = 0.086$) were independent reflections and all were included in the refinement. 987 parameters based on 4202 observed reflections gave the final refined circle $R_1 = 0.076$ and $wR_2 = 0.186$, respectively. The carbon atoms and nitrogen atoms in one of the crypts (atoms numbered as C(21) to C(56), N(21) to N(36), respectively) were refined disordered. The atoms in the perchlorate anions were also refined disordered. To assist the refinement, several restraints were applied: (1) Cl–O bonds, C–C bonds, C–N bonds were restrained to be similar, respectively; (2) thermal parameters on adjacent atoms in disordered moieties were restrained to be similar. CCDC 196621. See <http://www.rsc.org/suppdata/cc/b3/b305001g/> for crystallographic data in CIF or other electronic format.

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