

# Self-Assembly of an Alkali Metal Cluster Stabilized by a New Flexidentate Metalloligand: Formation and Structure of Heterobimetallic Na–Mo and Cs–Mo 2D Networks

Snehadrinarayan Khatua,<sup>[a]</sup> Soham Dasgupta,<sup>[a]</sup> Kumar Biradha,<sup>\*[a]</sup> and Manish Bhattacharjee<sup>\*[a]</sup>

**Keywords:** Alkali metals / Heterometallic complexes / Metalloligands / Molybdenum / Self-assembly

A new tridentate ligand, {(3,5-di-*tert*-butyl-2-hydroxybenzyl)amino}acetic acid, has been synthesized. This ligand forms  $[\{\text{Na}_4(\text{H}_2\text{O})_4(\mu\text{-H}_2\text{O})_2\}\text{C}(\text{Mo}_2\text{O}_5\text{L}_2)_2]$  (**1**), which contains an  $\text{Na}_4^{4+}$  cluster cation stabilized by  $[\text{LMoO}_2(\mu\text{-O})\text{MoO}_2\text{L}]^{2-}$ , upon reaction with  $\text{Na}_2\text{MoO}_4$  in aqueous methanol. This compound has been characterized by various spectroscopic techniques and crystallizes in the triclinic space group  $P\bar{1}$ . Furthermore, compound **1** undergoes smooth exchange of  $\text{Na}^+$  for  $\text{Cs}^+$  to give  $[\text{Cs}_2(\text{Mo}_2\text{O}_5\text{L}_2)\cdot\text{H}_2\text{O}]_n$  (**2**) upon treatment

with  $\text{CsCl}$  in aqueous methanol. Similarly, **2** reacts with an excess of  $\text{NaCl}$  to produce **1**. Complex **2** crystallizes in the monoclinic space group  $C2/c$ . The crystal structure of this compound reveals that the geometry of the  $[\text{LMoO}_2(\mu\text{-O})\text{MoO}_2\text{L}]^{2-}$  unit stays almost intact but that it stabilizes a polymeric chain of  $\text{Cs}^+$  cations, unlike in **1**.

(© Wiley-VCH Verlag GmbH & Co. KGaA, 69451 Weinheim, Germany, 2005)

## Introduction

The role of judiciously designed ligands in the synthesis of supramolecular assemblies containing two types of metal ions has been demonstrated.<sup>[1,2]</sup> In recent years, a large number of metalloligands have been synthesized for the assembly of bimetallic complexes.<sup>[3]</sup> The main thrust has been on the aggregation of transition metal ions using main group metals as templates.<sup>[2]</sup> However, alkali metal cluster cations have received scant attention. Molybdates and tungstates have been widely used as ligands for metal ions due to their diverse structural flexibility and their applications in fields such as catalysis, analytical and clinical chemistry, biochemistry, and medicine.<sup>[4]</sup> Although a lot of attention has been paid to the synthesis of transition metal and rare-earth metal derivatives of polyoxometalates, alkali metal complexes of polyoxometalates have received much less attention.<sup>[5–7]</sup> We were interested in the synthesis of a flexible metalloligand that can coordinate alkali metal cations, and the effect of their size on the architecture of the structure. Also, we intended to explore the transmetalation of the alkali metal cations.

Herein we report the synthesis of the ligand {(3,5-di-*tert*-butyl-2-hydroxybenzyl)amino}acetic acid, and the synthesis and structure of an unusual polyoxomolybdate,  $[\{\text{Na}_4(\text{H}_2\text{O})_4$

$(\mu\text{-H}_2\text{O})_2\}\text{C}(\text{Mo}_2\text{O}_5\text{L}_2)_2]$  (**1**), which bears an  $\text{Na}_4^{4+}$  cluster cation stabilized by the metalloligand  $[\text{LMoO}_2(\mu\text{-O})\text{MoO}_2\text{L}]^{2-}$  ( $\text{L}^{\text{Mo}}$ ), and the corresponding cesium compound, a helical 1D infinite chain of  $[\text{Cs}_2(\text{Mo}_2\text{O}_5\text{L}_2)\cdot\text{H}_2\text{O}]_n$  (**2**), obtained by transmetalation of the  $\text{Na}^+$  ions in **1**. The transmetalation behavior of the compounds has also been investigated.

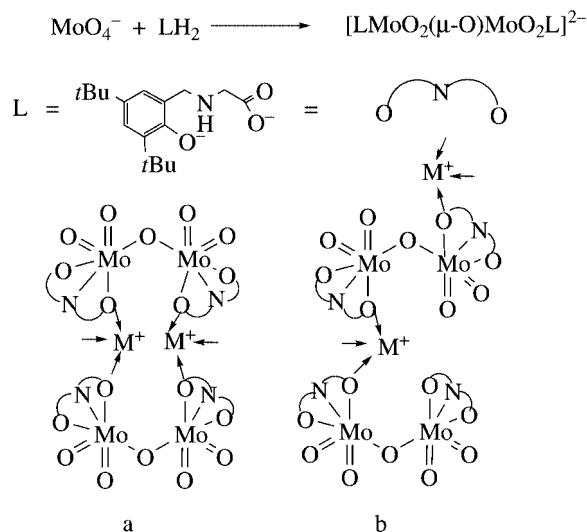
## Results and Discussion

### Synthesis and Characterization of {(3,5-Di-*tert*-butyl-2-hydroxybenzyl)amino}acetic Acid

Our synthetic strategy was to design a tridentate, dibasic ligand (L) containing one carboxylate donor site that is expected to form the metalloligand  $[\text{LMoO}_2(\mu\text{-O})\text{MoO}_2\text{L}]^{2-}$  ( $\text{L}^{\text{Mo}}$ ). This ligand has the potential to coordinate alkali metal cations through bridging carboxylate and self-assemble into various architectures (Scheme 1).

Accordingly, the ligand was synthesized by a one-pot Mannich reaction of glycine, 2,4-di-*tert*-butylphenol, and formaldehyde in aqueous ethanol. Glycine and formaldehyde (40%) were dissolved in water in a 1:10 ratio and an ethanolic solution of the phenol was added. The reaction solution afforded the ligand on standing for about 10 h. The ligand was characterized by elemental analysis, mass spectrometry, and IR, UV/Vis, and  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopy. The elemental analysis and mass spectral measurements agreed well with the proposed composition. The  $^1\text{H}$  and  $^{13}\text{C}$  NMR data were also in agreement with the proposed structure (see Experimental Section).

[a] Department of Chemistry, Indian Institute of Technology Kharagpur, Kharagpur 721 302, India  
Fax: +91-3222-282252  
E-mail: mxb@iitkgp.ac.in  
kbiradha@chem.iitkgp.ernet.in



Scheme 1.

### Synthesis, Characterization, and Solution Properties of the Molybdenum Complexes **1** and **2**

Compound **1** was synthesized by the reaction of  $\text{LH}_2$  with  $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$  in aqueous methanol and **2** was obtained by the reaction of  $\text{CsCl}$  with **1** in aqueous methanol. Compound **2** can also be prepared from an in situ reaction between an excess of  $\text{CsCl}$  and  $\text{Na}_2\text{MoO}_4$  and the ligand. It should be noted that  $\text{Cs}^+$  ions can be exchanged by  $\text{Na}^+$  ions by treating **2** with an excess of  $\text{NaCl}$ . Thus, it is clear that both compounds show the ability to exchange cations and are interconvertible, which is rare in such molecules.

The elemental analyses agree well with the compositions. The compounds were further characterized by IR, UV/Vis, and  $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{95}\text{Mo}$ , and  $^{23}\text{Na}$  (compound **1**) NMR spectra and solution conductivity measurements. The IR spectrum of the compounds show two sharp bands at about 920 and 880  $\text{cm}^{-1}$  due to symmetric and antisymmetric *cis*- $\text{Mo}=\text{O}$  stretches, respectively, and a band at around 780  $\text{cm}^{-1}$  due to the  $\text{Mo}-\text{O}-\text{Mo}$  stretch; these clearly show the presence of the  $[\text{MoO}_2(\mu\text{-O})\text{MoO}_2]$  moiety. The UV/vis spectra of the compounds show strong bands due to a ligand-to-metal charge-transfer transition at about 350 nm along with internal ligand transitions.

The  $^1\text{H}$  NMR spectra of **1** in  $[\text{D}_6]\text{DMSO}$  show signals at  $\delta = 1.20$  (br. s, 9 H) and 1.30 ppm (br. s, 9 H) due to the methyl protons of the *tert*-butyl groups. The  $\text{CH}_2$  proton signals appear at  $\delta = 3.36$  (br. m, 2 H) and 4.25 ppm (br. m, 2 H). The signal at  $\delta = 4.80$  ppm (br. s, 1 H) can be assigned to the NH proton. We could not observe the signals due to the protons of coordinated water. This may be due to excessive broadening of the signals. The signals for the aromatic protons appear at  $\delta = 6.85$  (br. m, 1 H) and 7.10 ppm (br. m, 1 H). The  $^{13}\text{C}$  NMR spectrum of **1** in  $[\text{D}_6]\text{DMSO}$  shows signals at  $\delta = 29.6$ , 29.9, 30.1, 31.5, 31.7, 33.7, 34.4, and 34.5 ppm due to the  $\text{CH}_3$  and tertiary carbons of the *tert*-butyl group. The  $\text{CH}_2$  signals appear at  $\delta = 51.3$ , 51.6, 52.7, and 53.1 ppm, with the aromatic carbon signals at  $\delta = 121.5$ , 121.9, 122.5, 122.7, 123.0, 124.1, 124.3,

136.7, 136.8, 137.9, 138.3, 159.8, and 159.9 ppm. The carboxylate carbon signals appear at  $\delta = 175.2$  and 175.3 ppm. The appearance of two signals for each carbon indicates that the ligands are bonded in a slightly different fashion. Thus, the  $^1\text{H}$  and  $^{13}\text{C}$  NMR and IR spectral studies clearly indicate the presence of an  $[\text{LMoO}_2(\mu\text{-O})\text{MoO}_2\text{L}]$  moiety in solution and the solid state. The  $^{23}\text{Na}$  NMR spectrum of **1** shows a single broad signal at  $\delta = 2.0$  ppm (relative to  $\text{NaCl}$  as an external reference). This clearly shows that the coordinated nature of the sodium is maintained even in solution and that all the sodium ions are in a similar chemical environment. The observed low-field position of the  $^{23}\text{Na}$  NMR signal, with respect to the  $\text{NaCl}$  reference, indicates the existence of an interaction between the sodium ions and between sodium and molybdenum, even in solution. The  $^{95}\text{Mo}$  NMR spectra of the compounds show a sharp signal at  $\delta = 0.3$  ppm, which indicates that the molybdenum atoms are in a predominantly oxo environment. Similar spectral features were observed in the case of **2**. The observed molar conductance of **1** in methanol ( $95 \Omega^{-1}\text{cm}^2\text{mol}^{-1}$ ) clearly indicates that the aggregate  $[\{\text{Na}_4(\text{H}_2\text{O})_4(\mu\text{-H}_2\text{O})_2\}\text{C}(\text{Mo}_2\text{O}_5\text{L}_2)_2]$  partially disintegrates in solution. The high-resolution ESI mass spectrum (methanol solution) of **1** shows a peak at  $m/z = 936.3138$ , which corresponds to  $\text{C}_{34}\text{H}_{54}\text{Mo}_2\text{N}_2\text{Na}_2\text{O}_{13}$  [or  $[\text{Na}_2(\text{Mo}_2\text{O}_5\text{L}_2)(\text{H}_2\text{O})_2]$ ]. Similarly, the mass spectrum of compound **2** shows a peak at  $m/z = 1138.2913$  corresponding to  $\text{C}_{34}\text{H}_{52}\text{Cs}_2\text{Mo}_2\text{N}_2\text{O}_{12}$ , which can be formulated as  $[\text{Cs}_2(\text{Mo}_2\text{O}_5\text{L}_2)(\text{H}_2\text{O})]$ . The mass spectral studies clearly show that the coordinated nature of the alkali metals is maintained even in solution and that the clusters undergo partial disintegration in solution.

### Crystal Structures of $[\{\text{Na}_4(\text{H}_2\text{O})_4(\mu\text{-H}_2\text{O})_2\}\text{C}(\text{Mo}_2\text{O}_5\text{L}_2)_2]$ (**1**) and $[\text{Cs}_2(\text{Mo}_2\text{O}_5\text{L}_2) \cdot \text{H}_2\text{O}]_n$ (**2**)

X-ray diffraction analysis revealed that the asymmetric unit of **1** contains only half of the cluster as it sits on an inversion center, with one  $\text{L}^{\text{Mo}}$  unit, two Na atoms, and three water molecules being present (Figure 1). The coordination environments of the two Mo atoms are almost similar: both have an octahedral geometry and are bonded to five oxygens and one nitrogen. The ligand  $\text{L}^{\text{Mo}}$  binds the two sodium atoms in two different ways and one of the Mo centers has an interaction with sodium [ $\text{Mo1} \cdots \text{Na2} = 3.553(5) \text{ \AA}$ ]. The distinctive feature of the structure is the formation of a rectangular  $(\text{Na}_4)^{4+}$  cluster cation (Figure 2, a). The distinctly shorter  $\text{Na} \cdots \text{Na}$  distances of 3.539(5)  $\text{ \AA}$  ( $\text{Na1}-\text{Na2}$ ) and 3.728(6)  $\text{ \AA}$  ( $\text{Na1}-\text{Na1}'$ ) compared to that in elemental sodium (3.82  $\text{ \AA}$ ) show attractive  $\text{Na}-\text{Na}$  interactions in the cluster. The  $\text{Na1}-\text{Na2}'$  distance [3.898(5)  $\text{ \AA}$ ] is longer than that in elemental sodium. Recently, a tetrasodium dication,  $\text{Na}_4^{2+}$ , stabilized by two silyl(fluorosilyl) phosphonides, with a similar structure but with shorter  $\text{Na}-\text{Na}$  distances has been reported.<sup>[8]</sup> The  $(\text{Na}_4)^{4+}$  unit binds six O atoms to form a  $\text{Na}_4\text{O}_6$  cluster that can be described as a dicubane unit of the type  $\text{M}_6\text{O}_6$  in which the two ex-

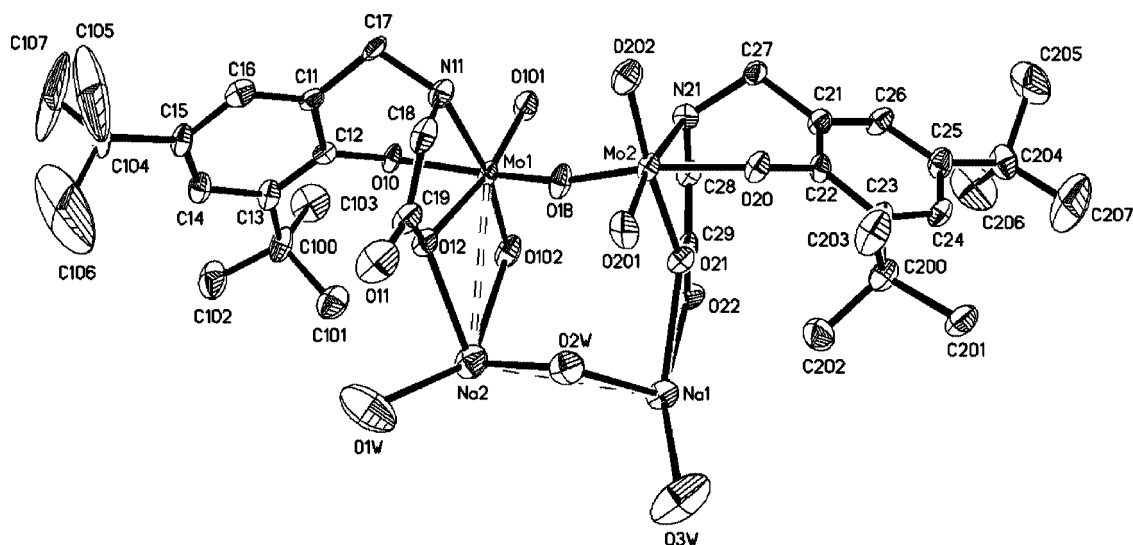


Figure 1. ORTEP drawing of the asymmetric unit of **1** (thermal ellipsoids at 50% probability).

tre and opposite corners have been removed (Figure 2, b). Two of the  $\text{Na}^+$  ions (Na1) in the  $\text{Na}_4\text{O}_6$  cluster are coordinated to five oxygens, and two (Na2) are hexacoordinate. Each of the four  $\text{Na}^+$  ions is coordinated to one terminal water molecule [ $\text{Na1}-\text{O3W} = 2.277(9)$  and  $\text{Na2}-\text{O1W} = 2.301(11)$  Å] and are bridged by one water molecule [ $\text{Na2}-\text{O2W} = 2.366(8)$  and  $\text{Na1}-\text{O2W} = 2.512(7)$  Å;  $\text{Na1}-\text{O2W}-\text{Na2} = 93.0(2)^\circ$ ]. In addition, Na1 and Na2 are also bridged by a  $\text{Mo}-\text{O}_{\mu_3}$  oxygen (O102) [ $\text{Na2}-\text{O102} = 2.727(7)$  Å] and one carboxylate oxygen (O22) bridges three sodiums in a  $\mu_3$ -fashion [ $\text{Na1}-\text{O22} = 2.567(6)$ ,  $\text{Na2}-\text{O22} = 2.318(6)$  Å; Figure 2, b]. The compound forms a one-dimensional chain through  $\text{Mo}-\text{O}\cdots\text{H}-\text{N}$  hydrogen bonding, and the 1D chains are joined by  $-\text{COO}\cdots\text{O}$  and  $\text{Mo}-\text{O}\cdots\text{O}$  hydrogen bonds to form a 2D network (Figure 3).

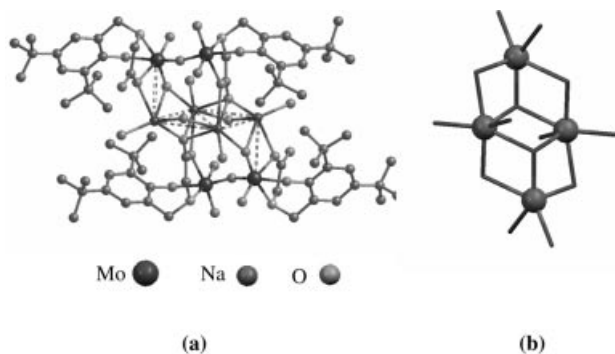


Figure 2. (a) Illustration of the tetramolybdate cluster **1**. The double dashed lines are long-distance interactions; H atoms have been omitted for the sake of clarity. (b) Illustration of the  $\text{Na}_4\text{O}_6$  cluster with its terminal O atoms on Na; some atoms have been omitted for the sake of clarity.

The crystal structure of **2** reveals that the geometry of  $\text{L}^{\text{Mo}}$  (Figure 4) is almost the same as that of compound **1**. However, unlike in structure **1**, the asymmetric unit in **2** contains half of  $\text{L}^{\text{Mo}}$ , one  $\text{Cs}^+$  ion, and one  $\text{H}_2\text{O}$ . The  $\text{Cs}^+$  ions are found to form an infinite 1D-helical chain, which is stabilized by coordination of the  $-\text{COO}^-$  and  $\text{Mo}-\text{O}$

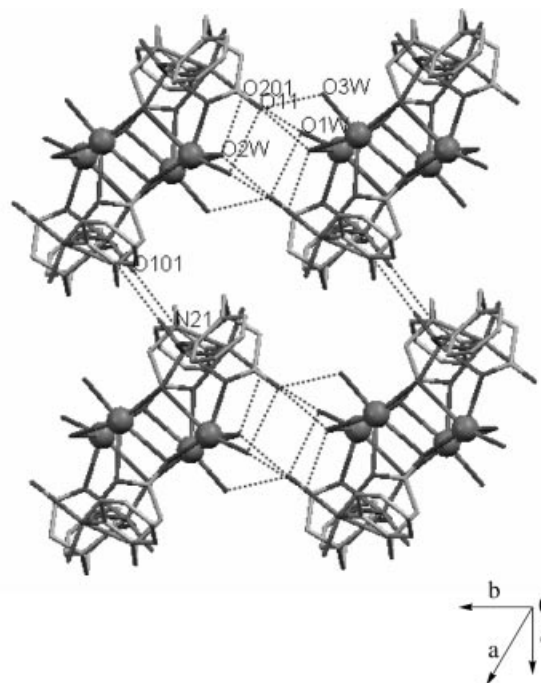


Figure 3. View of the 2D hydrogen-bonding network along the  $c$  axis (H bonds are shown as dotted lines; *tert*-butyl groups have been omitted for clarity).

groups of  $\text{L}^{\text{Mo}}$ , and are coordinated to six oxygens (Figure 5, a). This polymeric chain is generated by two  $\text{Cs}-\text{Cs}$  distances of 4.093(11) and 4.717(12) Å. The shorter  $\text{Cs}-\text{Cs}$  bond is bridged by two O atoms of two  $-\text{COO}^-$  groups [ $\text{Cs}-\text{O11} = 3.099(6)$  and 3.263(7) Å], whereas the longer one is not bridged by O atoms (Figure 5, b). The observed  $\text{Cs}\cdots\text{Cs}$  distance clearly shows that there is substantial interaction between the  $\text{Cs}^+$  ions. Similar to the structure **1**, the Mo atom interacts with  $\text{Cs}^+$  with a distance of 4.172 Å. Interestingly, unlike **1**, the water molecules do not bind to the alkali metal ion ( $\text{Cs}^+$ ) but join the one-dimensional polymeric chains of  $[(\text{Cs})_2\text{LO}_2\text{Mo}-\text{O}-\text{MoO}_2\text{L}]$  via hydrogen

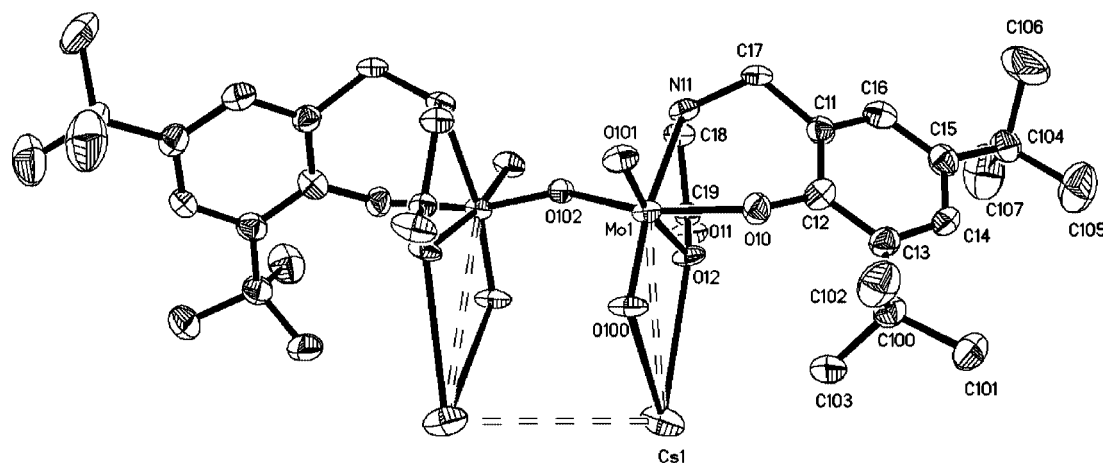


Figure 4. ORTEP drawing of the  $[\text{Cs}_2(\text{LO}_2\text{Mo}-\text{O}-\text{MoO}_2\text{L})]$  unit in the crystal structure of **2** (thermal ellipsoids at 50% probability). The double dashed lines represent long-distance interactions.

bonds  $[\text{N}-\text{H}\cdots\text{O} = 3.006(8) \text{ \AA} (178^\circ); \text{O}\cdots\text{O} = 2.764(8)]$ ; Figure 5, c]. In **1**, water is able to bridge two  $\text{Na}^+$  ions, whereas, due to the larger size of the cation, water cannot bind the  $\text{Cs}^+$  ions in a similar fashion in **2**. Similarly, in **1**, one of the O atoms of  $-\text{COO}^-$  binds three  $\text{Na}^+$  ions, whereas in **2**, due to the larger size of the  $\text{Cs}^+$  ion, only two cations are

bonded by the  $-\text{COO}^-$  oxygen to form a 1D chain. Thus, both **1** and **2** form 2D networks but in **1** the network is built by hydrogen bonding only, whereas in **2** a 1D network is generated by  $\text{Cs}-\text{Cs}$  polymeric cluster chains that are joined by hydrogen bonding to form a 2D network.

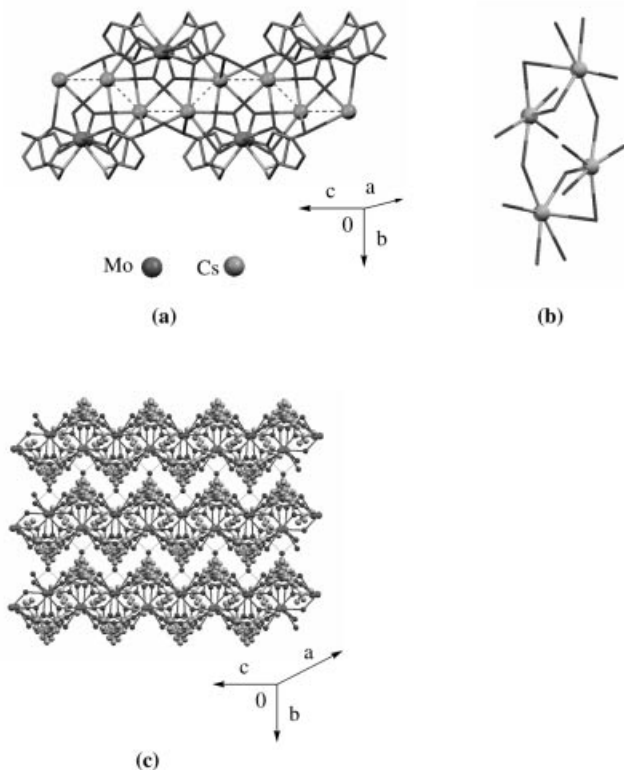


Figure 5. (a) Binding of  $\text{Cs}^+$  ions by  $[\text{LO}_2\text{Mo}-\text{O}-\text{MoO}_2\text{L}]$  units in the crystal structure of **2**. The *tert*-butyl groups have been omitted for the sake of clarity. The 1D chain is parallel to the crystallographic *c* axis. (b) Illustration of the  $\text{Cs}_4\text{O}_6$  unit with its terminal O atoms on Cs; some atoms have been omitted for the sake of clarity. (c) 2D arrays of infinite 1D chains of **2** formed by hydrogen bonds.

## Conclusions

A tridentate dibasic ligand has been designed which forms a new metalloligand,  $[\text{LMO}_2(\mu-\text{O})\text{MoO}_2\text{L}]^{2-}$  ( $\text{L}^{\text{Mo}}$ ) upon reaction with  $\text{MoO}_4^{2-}$ . This metalloligand binds  $\text{Na}^+$  ions to form a heterobimetallic octanuclear compound. It has been shown that the alkali metal cations in **1** and **2** can easily undergo exchange with each other and the resulting compounds are structurally different. It should be noted that such interconvertibility in this type of molecules is rare. The structural differences between **1** and **2** can be attributed to the difference in size of the cations. Thus,  $\text{L}^{\text{Mo}}$  may be treated as a new polydentate flexible metalloligand for assembly of heterobimetallic complexes. These complexes are expected to afford mixed oxides of molybdenum on heating to high temperature, and work in this direction is already in progress. It should be mentioned that such mixed oxides have been shown to be effective catalysts for various coupling and oxidation reactions.<sup>[9]</sup> It would be interesting to explore the reactions of  $\text{L}^{\text{Mo}}$  with various transition metal ions and study their structural, magnetic, and catalytic properties.

## Experimental Section

**General Remarks:** 2,4-Di-*tert*-butylphenol was purchased from Fluka. Glycine, formaldehyde,  $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ , and all solvents used were reagent-grade products. Elemental analyses were performed with a Perkin–Elmer C,H,N analyzer model 2400. Sodium was estimated by a flame photometric method. Molybdenum was estimated by gravimetric analysis [dioxobis(oxinate)molybdenum];



$\text{MoO}_2(\text{C}_9\text{H}_9\text{ON})_2$ .  $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{23}\text{Na}$ , and  $^{95}\text{Mo}$  NMR spectra were recorded in  $\text{CDCl}_3$ ,  $\text{CD}_3\text{OD}$ , or  $[\text{D}_6]\text{DMSO}$  on a Bruker AC-200 instrument. The IR spectra were recorded on a Perkin–Elmer model 883 spectrometer. UV/vis spectra were recorded in solution with a Shimadzu model UV-1601 spectrophotometer. For the mass spectral measurements a methanolic solution of the compounds was prepared and the spectra recorded on a Waters LCT mass spectrometer using the electrospray ionization ( $\text{ES}^+$  mode) technique.

**Synthesis of  $\{[3,5\text{-Di-}i\text{-tert-butyl-2-hydroxybenzyl}]\text{amino}\}\text{acetic Acid (L)}$ :** Glycine (3.00 g, 40 mmol) was dissolved in water (20 mL), a 40% aqueous formaldehyde (30 mL, 400 mmol) solution was added, and the mixture was stirred for 20 min. An ethanolic solution (30 mL) of 2,4-di-*tert*-butylphenol (2.06 g, 10 mmol) was then added dropwise and the reaction mixture was stirred for 30 min and allowed to stand overnight. The precipitated ligand was filtered, washed with water, dried, and finally recrystallized from a mixture of methanol and dichloromethane. Yield: 2.53 g (86.5%).  $\text{C}_{17}\text{H}_{27}\text{NO}_3$  (293.4): calcd. C 69.59, H 9.28, N 4.77; found C 69.25, H 9.10, N 4.46. IR (KBr pellet):  $\tilde{\nu} = 2960\text{ cm}^{-1}$ , 1710, 1630, 1230, 1122. UV/Vis:  $\lambda_{\text{max}}(\epsilon) = 280\text{ nm}$  (2290), 220 (7470).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta = 1.28$  (s, 9 H), 1.37 (s, 9 H), 3.62 (s, 2 H), 4.10 (s, 2 H), 4.86 (s, 1 H), 6.79 (d,  $J = 2.3\text{ Hz}$ , 1 H), 7.19 (d,  $J = 2.4\text{ Hz}$ , 1 H) ppm.  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta = 29.6$ , 31.4, 34.2, 34.8, 52.0, 53.3, 116.8, 121.9, 122.8, 137.3, 143.5, 149.4, 172.6 ppm. MS:  $m/z = 293$  [ $\text{M}^+$ ] ( $\text{C}_{17}\text{H}_{27}\text{NO}_3$ ).

**Synthesis of  $[\{\text{Na}_4(\text{H}_2\text{O})_4(\mu\text{-H}_2\text{O})_2\}\text{C}(\text{Mo}_2\text{O}_5\text{L}_2)_2\}$  (1):** An aqueous solution (5 mL) of  $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$  (0.121 g, 0.5 mmol) was added to a methanolic solution (25 mL) of the ligand (0.147 g, 0.5 mmol). The solution immediately turned orange. The solution was stirred for 3 h and was then allowed to stand overnight. The precipitated crystalline compound was filtered, washed 3–4 times with water, dried in vacuo, and finally recrystallized from a mixture of methanol and acetonitrile. Yield: 0.13 g (54%).  $\text{C}_{68}\text{H}_{112}\text{Mo}_4\text{N}_4\text{Na}_4\text{O}_{28}$  (1909.3): calcd. C 42.78, H 5.91, Mo 20.10, N 2.93, Na 4.82; found C 43.25, H 6.10, Mo 19.45, N 2.40, Na 4.20 (by flame photometry). IR (KBr pellet):  $\tilde{\nu} = 3433\text{ cm}^{-1}$ , 2960, 1600, 1470, 1250, 1170, 920, 880, 780. UV/Vis:  $\lambda_{\text{max}}(\epsilon) = 355\text{ nm}$  (11830), 270 (22950), 230 (24440).  $^{95}\text{Mo}$  NMR ( $[\text{D}_6]\text{DMSO}$ ) [reference  $\text{Na}_2\text{MoO}_4$  ( $\delta = 0\text{ ppm}$ )]:  $\delta = 0.3\text{ ppm}$ .  $^{23}\text{Na}$  NMR ( $[\text{D}_6]\text{DMSO}$ ) [reference  $\text{NaCl}$  ( $\delta = 0\text{ ppm}$ )]:  $\delta = 2.0\text{ ppm}$ .  $^1\text{H}$  NMR ( $[\text{D}_6]\text{DMSO}$ ):  $\delta = 1.20$  (br. s, 9 H), 1.34 (br. s, 9 H), 3.36 (br. m, 2 H), 4.25 (br. m, 2 H), 4.78 (br.

s, 1 H), 6.85 (br. m, 1 H), 7.10 (br. m, 1 H) ppm.  $^{13}\text{C}$  NMR ( $[\text{D}_6]\text{DMSO}$ ):  $\delta = 29.6$ , 29.9, 30.1, 31.5, 31.7, 33.7, 34.4, 34.5, 51.3, 51.6, 52.7, 53.1, 121.5, 121.9, 122.5, 122.7, 123.0, 124.1, 124.3, 136.7, 136.8, 137.9, 138.3, 159.8, 159.9, 175.2, 175.3 ppm. ESI HRMS:  $m/z = 936.3138$  [ $\text{Na}_2(\text{Mo}_2\text{O}_5\text{L}_2)(\text{H}_2\text{O})_2$ ].

**Reaction of 1 with CsCl. Synthesis of  $[\text{Cs}_2(\text{Mo}_2\text{O}_5\text{L}_2) \cdot \text{H}_2\text{O}]_n$  (2):** Compound 1 (0.048 g, 0.025 mmol) was dissolved in methanol (20 mL), an aqueous solution (5 mL) of CsCl (0.037 g, 0.2 mmol) was added, and the reaction solution was stirred for 5 h. On standing for about 20 days orange crystals of 2 were obtained in 50% yield.  $\text{C}_{34}\text{H}_{52}\text{Cs}_2\text{Mo}_2\text{N}_2\text{O}_{12}$  (1138.5): calcd. C 35.87, H 4.60, Mo 16.85, N 2.46; found C 36.05, H 4.34, Mo 17.15, N 2.54. IR (KBr pellet):  $\tilde{\nu} = 2960\text{ cm}^{-1}$ , 1580, 1475, 1260, 906, 870, 790. UV/Vis:  $\lambda_{\text{max}}(\epsilon) = 356\text{ nm}$  (6460), 213 (27590). ESI HRMS:  $m/z = 1138.2913$  [ $\text{Cs}_2(\text{Mo}_2\text{O}_5\text{L}_2)(\text{H}_2\text{O})$ ].  $^1\text{H}$  NMR ( $[\text{D}_6]\text{DMSO}$ ):  $\delta = 1.27$  (br. s, 9 H), 1.39 (br. s, 9 H), 3.28 (br. m, 2 H), 4.64 (br. s, 1 H), 6.95 (br. m, 1 H), 7.20 (br. m, 1 H) ppm.

**Independent Synthesis of  $[\text{Cs}_2(\text{Mo}_2\text{O}_5\text{L}_2) \cdot \text{H}_2\text{O}]_n$  (2):** An aqueous solution (5 mL) of  $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$  (0.061 g, 0.25 mmol) was added to a methanolic solution (25 mL) of the ligand (0.073 g, 0.25 mmol). The solution immediately turned orange. The reaction solution was stirred for 6 h and then CsCl (0.2524 g; 1.5 mmol) was added and solution was stirred for a further hour. On standing for 10 days crystals of compound 2 were obtained in 60% yield.

**X-ray Crystallographic Study:** Suitable crystals of 1 and 2 were grown from dilute acetonitrile/MeOH and MeOH/water solutions, respectively, at room temperature over a period of 5 to 20 days. The single crystal data were collected on Bruker–Nonius Mach3 CAD4 X-ray diffractometer that uses graphite monochromated  $\text{Mo-K}_\alpha$  radiation ( $\lambda = 0.71073\text{ \AA}$ ) by the  $\omega$ -scan method. No absorption correction was used. The structure was solved by direct methods and refined by least-squares methods on  $F^2$  using SHELX-97.<sup>[10]</sup> Non-hydrogen atoms were refined anisotropically and hydrogen atoms on C atoms were fixed at calculated positions and refined using a riding model. The H atoms of the water molecules in 1 and 2 and N atoms in 1 and 2 could not be located. The details of crystal data are given in Table 1; selected bond lengths are summarized in Table 2.

CCDC-269980 (for 1) and -269981 (for 2) contain the supplementary crystallographic data for this paper. These data can be ob-

Table 1. Crystal data for  $[\{\text{Na}_4(\text{H}_2\text{O})_4(\mu\text{-H}_2\text{O})_2\}\text{C}(\text{Mo}_2\text{O}_5\text{L}_2)_2\}$  (1) and  $[\text{Cs}_2(\text{Mo}_2\text{O}_5\text{L}_2) \cdot \text{H}_2\text{O}]_n$  (2).

|                                             | 1                                                                          | 2                                                                         |
|---------------------------------------------|----------------------------------------------------------------------------|---------------------------------------------------------------------------|
| Empirical formula                           | $\text{C}_{68}\text{H}_{112}\text{Mo}_4\text{N}_4\text{Na}_4\text{O}_{28}$ | $\text{C}_{34}\text{H}_{52}\text{Cs}_2\text{Mo}_2\text{N}_2\text{O}_{12}$ |
| Formula mass                                | 1909.34                                                                    | 1138.47                                                                   |
| Temperature [K]                             | 293(2)                                                                     | 293(2)                                                                    |
| Wavelength [ $\text{\AA}$ ]                 | 0.71073                                                                    | 0.71073                                                                   |
| Crystal system                              | triclinic                                                                  | monoclinic                                                                |
| Space group                                 | $P\bar{1}$                                                                 | $C2/c$                                                                    |
| $a$ [ $\text{\AA}$ ]                        | 10.746(2)                                                                  | 38.280(8)                                                                 |
| $b$ [ $\text{\AA}$ ]                        | 11.517(2)                                                                  | 10.961(2)                                                                 |
| $c$ [ $\text{\AA}$ ]                        | 18.427(4)                                                                  | 10.391(2)                                                                 |
| $\alpha$ [ $^\circ$ ]                       | 104.26(3)                                                                  |                                                                           |
| $\beta$                                     | 94.19(3)                                                                   | 103.41(3)                                                                 |
| $\gamma$                                    | 90.62(3)                                                                   |                                                                           |
| Volume [ $\text{\AA}^3$ ]                   | 2203.4(8)                                                                  | 4241.1(15)                                                                |
| $Z$                                         | 1                                                                          | 4                                                                         |
| $D_{\text{calcd.}}$ [ $\text{Mg/m}^3$ ]     | 1.439                                                                      | 1.783                                                                     |
| Absorption coefficient [ $\text{mm}^{-1}$ ] | 0.649                                                                      | 2.340                                                                     |
| $F(000)$                                    | 984                                                                        | 2240                                                                      |
| Final $R$ indices [ $I > 2\sigma(I)$ ]      | $R_1 = 0.0751$ , $wR_2 = 0.1834$                                           | $R_1 = 0.0550$ ; $wR_2 = 0.1343$                                          |

Table 2. The bond lengths [ $\text{\AA}$ ] around the Mo and alkali metal atoms in compounds **1** and **2**.<sup>[a]</sup>

| <b>1</b>                  |           | <b>2</b>                  |          |
|---------------------------|-----------|---------------------------|----------|
| Mo(1)–O(1B)               | 1.887(5)  | Mo(1)–O(101)              | 1.702(5) |
| Mo(1)–O(10)               | 1.947(5)  | Mo(1)–O(100)              | 1.729(5) |
| Mo(1)–O(12)               | 2.235(5)  | Mo(1)–O(102)              | 1.887(2) |
| Mo(1)–O(101)              | 1.707(6)  | Mo(1)–O(10)               | 1.944(5) |
| Mo(1)–O(102)              | 1.750(7)  | Mo(1)–O(12)               | 2.248(5) |
| Mo(1)–N(11)               | 2.360(7)  | Mo(1)–N(11)               | 2.355(6) |
| Mo(2)–O(1B)               | 1.904(5)  | Cs(1)–O(12) <sup>a</sup>  | 3.048(6) |
| Mo(2)–O(20)               | 1.931(5)  | Cs(1)–O(100)              | 3.066(5) |
| Mo(2)–O(21)               | 2.211(5)  | Cs(1)–O(11) <sup>b</sup>  | 3.263(7) |
| Mo(2)–O(201)              | 1.725(6)  | Cs(1)–O(100) <sup>c</sup> | 2.986(5) |
| Mo(2)–O(202)              | 1.706(7)  | Cs(1)–O(101) <sup>c</sup> | 3.287(5) |
| Mo(2)–N(21)               | 2.343(6)  | Cs(1)–O(11) <sup>d</sup>  | 3.099(6) |
| Na(1)–O(2W)               | 2.511(7)  |                           |          |
| Na(1)–O(3W)               | 2.277(13) |                           |          |
| Na(1)–O(21)               | 2.511(7)  |                           |          |
| Na(1)–O(22)               | 2.567(7)  |                           |          |
| Na(1)–O(22) <sup>e</sup>  | 2.476(6)  |                           |          |
| Na(1)–O(102) <sup>e</sup> | 3.409(7)  |                           |          |
| Na(2)–O(1W)               | 2.300(12) |                           |          |
| Na(2)–O(2W)               | 2.367(8)  |                           |          |
| Na(2)–O(12)               | 2.395(7)  |                           |          |
| Na(2)–O(102)              | 2.726(8)  |                           |          |
| Na(2)–O(22) <sup>e</sup>  | 2.319(7)  |                           |          |

[a] Symmetry transformations used to generate equivalent atoms: a:  $1 - x, y, 1/2 - z$ ; b:  $1 - x, -y, -z$ ; c:  $x, -y, -1/2 + z$ ; d:  $x, -y, 1/2 + z$ ; e:  $2 - x, 1 - y, -z$ .

tained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

## Acknowledgments

This work was funded by DST, Government of India, New Delhi. The single crystal XRD facility was provided by DST under the FIST Program.

- [1] a) X. Sun, D. W. Johnson, D. L. Caulder, R. E. Powers, K. N. Raymond, E. H. Wong, *Angew. Chem. Int. Ed.* **1999**, *38*, 1303–1307; b) X. Sun, D. W. Johnson, D. L. Caulder, K. N. Raymond, E. H. Wong, *J. Am. Chem. Soc.* **2001**, *123*, 2752–2763; c) X. Sun, D. W. Johnson, K. N. Raymond, E. H. Wong, *Inorg. Chem.* **2001**, *40*, 4504–4506.
- [2] K. Fukaya, T. Yamase, *Angew. Chem. Int. Ed.* **2003**, *42*, 654–658.
- [3] a) X. Lin, D. M. J. Doble, A. J. Blake, A. Harrison, C. Wilson, M. Schroder, *J. Am. Chem. Soc.* **2003**, *125*, 9476–9483; b) S. M. Contakes, T. B. Rauchfuss, *Chem. Commun.* **2001**, 553–554; c) S. Noro, H. Miyasaka, S. Kitagawa, T. Wada, T. Okubo, M. Yamashita, T. Mitani, *Inorg. Chem.* **2005**, *44*, 133–146; d) K. Yaum, S. Huh, Y. J. Park, S. Park, M. Choi, M. Jun, *Chem. Commun.* **2004**, 2384–2385.
- [4] a) *Polyoxometalates: From Platonic Solids to Anti-Retroviral Activity* (Eds.: M. T. Pope, A. Müller), Kluwer Academic Publishers, Dordrecht, The Netherlands, **1994**; b) A. Müller, E. Krickmeyer, H. Bogge, M. Schmidtman, B. Botar, M. O. Talismanova, *Angew. Chem. Int. Ed.* **2003**, *42*, 2085–2090; c) Y. Wong, Y. Yan, E. H. Chan, Q. Yang, T. W. Mak, D. P. Ng, *J. Chem. Soc. Dalton Trans.* **1998**, 3057–3064.
- [5] a) D. Hergman, P. Hergman, J. Zubieta, *Angew. Chem. Int. Ed.* **1999**, *38*, 3165–3168; b) P. Hargman, D. Hargman, J. Zubieta, *Angew. Chem. Int. Ed.* **1999**, *38*, 2638–2684; c) B. J. S. Johnson, S. A. Geers, W. W. Brennessel, V. G. Young Jr., A. Stein, *Dalton Trans.* **2003**, 4678–4681; d) R. S. Rarig Jr., J. Zubieta, *J. Chem. Soc. Dalton Trans.* **2001**, 3446–3452.
- [6] Q. Chen, J. Zubieta, *Coord. Chem. Rev.* **1992**, *114*, 107–167.
- [7] a) W. Yang, C. Lu, X. Lin, H. Zhung, *Inorg. Chem.* **2002**, *41*, 452–454; b) V. Shivaiah, M. Nagaraju, S. K. Das, *Inorg. Chem.* **2003**, *42*, 6604–6606.
- [8] M. Driess, H. Pritzkow, M. Skipinski, U. Winkler, *J. Am. Chem. Soc.* **1998**, *120*, 10774–10775.
- [9] a) S. A. Driscoll, U. S. Ozkan, *J. Phys. Chem.* **1993**, *97*, 11524–11529; b) A. Erdoheily, K. Fodor, R. Nemeth, A. Hancz, A. Oszko, *J. Catal.* **2001**, *199*, 328–337.
- [10] G. M. Sheldrick, *Program for solution and refinement of crystal structures*, University of Göttingen, Germany, **1997**.

Received: July 6, 2005

Published Online: November 2, 2005