9708 *J. Am. Chem. Soc.* **1998,** *120,* 9708−9709

Synthesis, Structure and Coordination Chemistry of $MoAs_8^{2-}$

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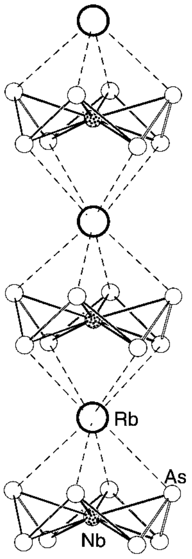
Received June 15, 1998

The coordination chemistry of polyarsenic ring systems is a diverse research area.[1−9] In general, polyarsenic ligands can be divided into two groups, namely the alkyl arsines[1,10,11] $(RAs)_n$ and the bare arsenic ring systems As_n^{x-}.[2,3,12−14] There are a variety of cyclic species in the latter group such as As_3 rings (e.g. η^3-$As_3Mo(CO)_2Cp^*$),[15] As_5^- rings (e.g. η^5-As_5FeCp^*),[16] As_6 rings (e.g. $Cp^xMo(\mu,\eta^6,\eta^6\text{-}As_6)MoCp^x$ where $Cp^x = \eta^5\text{-}C_5Me_4Et$),[17] and an As_8 species (e.g.$(\mu,\eta^4,\eta^4\text{-}As_8)(NbCp'')_2$).[13] All of the bare arsenic ligands are structurally related to cyclic hydrocarbons[3] in that neutral As is electronically equivalent to CH. For example, As_5^- and As_6 are isoelectronic and isostructural to $C_5H_5^-$ and C_6H_6 and their coordination chemistry often mimics those of their hydrocarbon analogues.[3] The $(\mu,\eta^4,\eta^4\text{-}As_8)(NbCp'')_2$ complex contains a cyclooctatetraene-like neutral As_8 unit.[13] The Zintl anion complexes $As_7M(CO)_3^{3-}$ contain norbornadiene-like As_7 ligands and also follow the general electron counting principles. A novel exception to the hydrocarbon coordination chemistry analogy is found in von Schnering's one-dimensional chain complex ${}^{1}_{\infty}[Rb\cdot NbAs_8]^{2-}$ (see **1**).[18] This chain contains a remarkable $NbAs_8^{3-}$ subunit which, for electron counting purposes, can be viewed as an Nb^{5+} ion in the center of an As_8^{8-} ring. The latter is isoelectronic and isostructural to S_8 (or cyclooctane) as expected on the basis of the Zintl formalism (As^- is electronically equivalent to S). We have recently developed a synthesis for the free $NbAs_8^{3-}$ ion (**2**) and are extending the chemistry of the As_8^{8-} ligand and its complexes.[19] Herein we report the synthesis and structure of $MoAs_8^{2-}$ (**3**) and a preliminary study of its gas-phase coordination chemistry through negative ion electrospray mass spectrometry (EMS). To our knowledge, **3** is the first reported free binary transition metal pnictide ion isolated to date. The gas-phase studies of **3** with alkali ions show that the As_8 ring coordinates additional metal ions to form bimetallic coordination complexes. These clusters represent Mo analogues of the $Rb\cdot NbAs_8$ subunits in the polymer species **1**.



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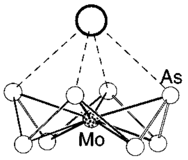

4 ○ = K

5 ○ = Rb

6 ○ = Cs

Ethylenediamine solutions of $Mo(Me\text{-}naphthalene)_2$[20] react with K_3As_7 in the presence of 2,2,2-cryptand to give dark red brown solutions. After filtration and concentration of the solutions, very air sensitive, dark emerald green crystals of $[K(2,2,2\text{-}crypt)]_2[MoAs_8]\cdot NH_2(CH_2)_2NH_2$ can be isolated in 32% crystalline yield.[21] The salt has been characterized by elemental analysis, single-crystal X-ray diffraction,[22] and EMS. The crystals readily dissolve in DMF, giving stable but very air-sensitive dark green solutions. Although the synthesis reaction requires significant fragmentation and disproportionation of the As_7^{3-} ion to give the $MoAs_8^{2-}$ complex, the reactions are reproducible.

The salt is monoclinic, $C2/c$, containing the $MoAs_8^{2-}$ ion (**3**), two $K(2,2,2\text{-}crypt)^+$ cations, and an ethylenediamine solvate molecule in the crystal lattice. Two views of the $MoAs_8^{2-}$ ion are given in Figure 1. The anion possesses crystallographic 2-fold symmetry; however, the cluster has virtual D_{4d} point symmetry with a molybdenum atom situated in the center of a very regular S_8-like As_8 ring. The As−As bond distances range from 2.423(2) to 2.437(3) Å (2.429 Å, av) and are slightly shorter than those in **1** (2.434 Å, av)[18] and **2** (2.447 Å, av).[19] The As−As−As angles about the ring average 90.6° which are ∼3° more acute than those in **1** (93.7°)[18] and **2** (93.3°).[19] The eight Mo−As contacts average 2.56 Å which are also shorter than the Nb−As bonds in **1** (2.62 Å) and **2** (2.63 Å). In comparison with the niobium complexes **1** and **2**, the structural data indicate that the As_8^{8-} cavity adjusts for the smaller Mo by contracting the As−As bonds and increasing its pucker (more acute As−As−As angles). The

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[21] A melt of nominal composition K_3As_7 (30 mg, 0.078 mmol), 2,2,2-crypt (90 mg, 0.24 mmol), and $Mo(Me\text{-}naphthalene)_2$ (30 mg, 0.079 mmol) was stirred in en at room temperature for 3 h yielding a red-brown solution. The solution was then filtered and, after 24 h, the reaction vessel contained dark green colored crystals which were isolated and dried under vacuum. Yield: 40 mg (32%). Anal. Calcd for $C_{38}H_{80}N_6O_{12}As_8MoK_2$: C, 28.80; H, 5.04; N, 5.29. Found: C, 29.29; H, 5.03; N, 5.03.

[22] X-ray data for $[MoAs_8][K(2,2,2\text{-}crypt)]_2\cdot en$: monoclinic, $C2/c$, a = 23.925(3) Å, b = 11.7373(11) Å, c = 20.703(2) Å, β = 92.288(9)°, V = 5808.9(11) Å^3, Z = 4, D_x = 1.814 g cm^{-3}; T = 153 K, $R(F)$ = 6.92%, $wR(F^2)$ = 16.50% for those 3106 data with $F_o > 4(F_o)$.

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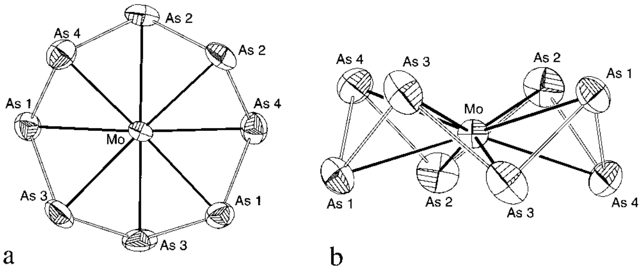

Figure 1. ORTEP drawings showing (a) side and (b) top views of the $MoAs_8^{2-}$ ion.

ethylenediamine solvate and the K(2,2,2-crypt)$^+$ ions are well separated from **3** where the closest contacts involving the ethylenediamine nitrogen are 3.89 and 3.90 Å to As(2) and Mo, respectively.

For electron counting purposes, the complex can be viewed as a composite of an As_8^{8-} ring with a Mo^{6+} ion. Counting each As as a two-electron σ-only donor, Mo attains a 16 electron configuration. Niobium also achieves a 16 electron configuration in **1** and **2**; however, von Schnering et al. showed[18] that there was significant π-donation from the As_8 ring to the Nb center in **1** that allows Nb to achieve its share of 18 electrons. This π-interaction is most likely present in **3** as well and would explain the lack of Lewis acidity of Mo. For example, the complex is prepared in neat ethylenediamine yet it does not coordinate ethylenediamine or naphthalene despite the formal 16 electron (σ-only) configuration. Detailed investigations of the structure and bonding in **2** and **3** as well as investigations of their chemical reactivities will be reported elsewhere.[19]

The negative ion electrospray mass spectra[23] of **3**, with and without added alkali halide salts, were recorded from DMF solutions of the crystalline complex (see Figure 2). The calculated and observed spectral envelopes are in excellent agreement and are given in the Supporting Information. The one-electron oxidation product, $MoAs_8^-$, is clearly evident in all the samples (Figure 2a) but the unoxidized molecular anion $MoAs_8^{2-}$ was not detected. Several other Mo−As species are also present in the mass spectra of the crystalline samples. In particular, a prominent mass envelope corresponding to $KMoAs_8^-$ (**4**) is always observed (see Figure 2b). Addition of KBr to the DMF solution results in an increase in the peak intensity of **4** at the expense of $MoAs_8^-$. We postulate that **4** contains an $MoAs_8$ "ligand" bound η^4 to the potassium ion as shown in the drawing. This complex is analogous to a fragment of the linear $^{1}_{\infty}[\mathrm{Rb{\cdot}NbAs_8}]^{2-}$ chain where two $NbAs_8^{3-}$ "ligands" coordinate to the Rb^+ ions in an η^4 fashion.[18] To test this theory, we recorded mass spectra of **3** in the presence of RbCl and CsCl. As expected, the Rb^+ and Cs^+ complexes, $RbMoAs_8^-$ (**5**) and $CsMoAs_8^-$ (**6**), were formed in these reactions as evidenced by their distinctive mass envelopes (see Figure 2c,d). However, EMS analysis of solutions isolated from reactions between Na_3As_7 and $Mo(Me\text{-}naphthalene)_2$ shows the same $MoAs_8^-$ peak but the sodium analogue of **4**, $NaMoAs_8^-$, is not observed even in the presence of excess Na^+. Thus, **3** appears to act as a selective ionophore that binds K^+, Rb^+, and Cs^+ but does not bind Na^+ in the gas phase. The relative alkali ion binding constants and attempts to isolate models of these species, such as (15-crown-5)KAs_8MoK(15-crown-5) type complexes, are under investigation and will be reported elsewhere.

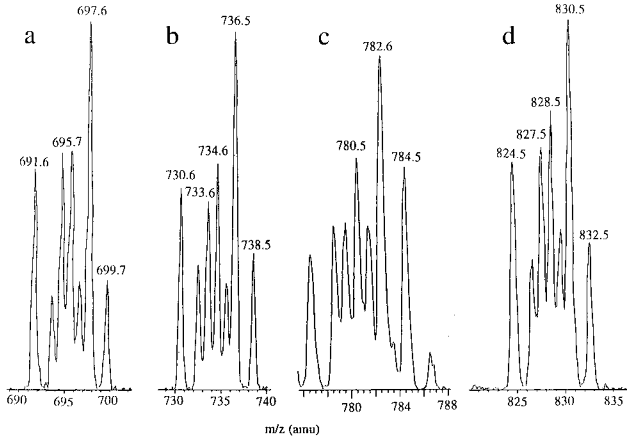

Figure 2. Selected spectral envelopes from the negative ion electrospray mass spectra of **3** recorded from DMF solutions with and without added alkali halide salts (see text): (a) the $MoAs_8^-$ ion, observed primary peak M/Z = 697.6 amu, calcd M/Z = 697.3 amu; (b) the $KMoAs_8^-$ ion **4**, observed primary peak M/Z = 736.5 amu, calcd M/Z = 736.2 amu; (c) the $RbMoAs_8^-$ ion **5**, observed primary peak M/Z = 782.6 amu, calcd M/Z = 782.2 amu; and (d) the $CsMoAs_8^-$ ions **6**, observed primary peak M/Z = 830.5 amu, calcd M/Z = 830.2 amu.

Acknowledgment. We gratefully acknowledge the NSF-CHE for support of this work. We are indebted to Dr. Kangyan Du for the mass spectrometry data. We thank Drs. J. Watkin and S. Grumbine for assistance with the MVS synthesis.

Supporting Information Available: Tables complete crystallographic data, calculated and observed mass spectra (15 pages, print/PDF). See any current masthead page for ordering information and Web access instructions.

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(23) Electrospray mass spectra were recorded from DMF solutions on a Finnigan LCQ mass spectrometer through direct injection. The samples were ionized by using an ESI probe and detected in the negative mode.