found when an M–H moiety and a cis-coordination site available to D_2 and ROH are both present. Two mechanisms are discussed. In mechanism A, M–D_2 exchanges with the cis M–H site, and binding of ROH is followed by exchange with the cis M–D. In this case M–D acts as an intermediate deuterium reservoir in the process.

An alternative pathway (mechanism B) is based on deprotonation of the η^2-D_2 ligand by ROH acting as a base. The data show that mechanism A is certainly important for the coordinating alcohols, but mechanism B cannot be excluded. Conversely, for the noncoordinating alcohol, mechanism B operates.

In the case of hydrogenase, the Ni–C EPR signal has been shown to be associated with a nickel hydride.[18] The H/D exchange activity of the enzyme could therefore result from the presence of a site cis to this hydride at which H_2 and perhaps also H_2O can bind.

Experimental Section

^{2}D NMR spectra were recorded on a Bruker WM 500 spectrometer; chemical shifts were measured by using C_6D_6 as a reference. ^{1}H NMR spectra were recorded on a Bruker WM 250 instrument; chemical shifts were measured with reference to the residual solvent resonances.

Reagents were purchased from Aldrich Chemical Co. CH_2Cl_2, C_6D_6, and $CDCl_3$ were dried over CaH_2 and stored under Ar; the alcohols were distilled before use from CaH_2 (MeOH, CF_3CH_2OH) or Mg (EtOH, *t*-BuOH) under Ar.

The dihydrogen complexes were prepared according to published procedures.[3a,c,4c,7c]

H^+/D_2 Exchange Reactions. $[Ir(bq)(PPh_3)_2H(H_2O)]SbF_6$ (**4**, 6 mg, 5.3×10^{-3} mmol) was dissolved in CH_2Cl_2 (0.5 mL) in an NMR tube. *t*-BuOH (50 μL, 0.53 mmol) was added to the solution and 25 μL of a C_6D_6 solution in CH_2Cl_2, 0.167 M, as a standard. D_2 was bubbled through a solution for 2 min (5 cm^3/min flow), and the sample was immediately placed into the NMR probe. The amount of deuterated alcohol formed was calculated by measuring the integration ratio of the ^{2}D signal at δ 1.2 against the standard C_6D_6 (δ 7.15). Complete relaxation was ensured by using a pulse delay of at least five T_1's.

The H^+/D_2 exchange experiments using MeOH, EtOH, CF_3CH_2OH, and Cy_3COH as protic substrates and the experiments with complexes **1**–**3** as catalysts were carried out in the same way.

Reactions of $[Ir(bq)(PPh_3)_2H(\eta^2\text{-}H_2)]SbF_6$ (5) with Alcohols. Reaction with EtOH. A 0.01 M solution of $[Ir(bq)(PPh_3)_2H(H_2O)]SbF_6$ (42.5 mg, 0.037 mmol) in CD_2Cl_2 (3.5 mL) was prepared in a Schlenk flask. CaH_2 (ca. 20 mg) was added to the solution, and H_2 was introduced in the flask; the mixture was let to stand for 30 min. A 0.5-mL volume of the supernatant solution was transfered to an NMR tube under a H_2 atmosphere. EtOH (6.2 μL, 0.106 mmol) was added to the solution, and a ^{1}H NMR spectrum (250 MHz, 298 K) was recorded. Distinct signals for the new EtOH complex **6** [δ 9.28 (b, 1 H, aromatic), −16.19 (t, $^2J_{H-P}$ = 15.8 Hz, Ir–H)] and for the dihydrogen complex **5** [δ 8.87 (b, 1 H, aromatic), −7.1 (vb, Ir–[H_3])] were observed.

The experiments using MeOH, *t*-BuOH, CF_3CH_2OH, and Cy_3COH as alcohols were carried out in the same way. ^{1}H NMR of the alcohol complexes (250 MHz, 298 K, δ): MeOH, 9.10 (b, 1 H), −16.09 (t, $^2J_{H-P}$ = 15 Hz); *t*-BuOH, −16.08; CF_3CH_2OH, −16.0.

The equilibrium constants were determined by integration of the distinct signals corresponding to **5** (δ 8.87) and the new Ir–ROH complex (aromatic or hydride signal). A pulse delay of at least five T_1's was used to ensure complete relaxation. Alcohol concentrations were determined by NMR integration of the aliphatic ROH signals in each case.

Acknowledgment. We thank the Spanish Ministry of Education and the Fulbright Commission (A.C.A.) and the NSF and NIH for funding.

Registry No. **1**, 135257-57-7; **2**, 135257-58-8; **3**, 97950-57-7; **4**, 98938-36-4; **5**, 102493-45-8; **6**, 135283-76-0; $[Ir(bq)(PPh_3)_2D(D_2O)]SbF_6$, 135310-51-9; $RhCl(PPh_3)_3$, 74735-07-2; *t*-BuOH, 75-65-0; EtOH, 64-17-5; Cy_3COH, 17687-74-0; MeOH, 67-56-1; CF_3CH_2OH, 75-89-8; hydrogenase, 9027-05-8; H_2, 1333-74-0.

---

[18] Moura, J. J. G.; Teixeira, M.; Moura, I.; LeGall, J. In *The Bioinorganic Chemistry of Nickel*; Lancaster, J. R., Ed.; VCH: Weinheim, Germany, 1988; Chapter 9, p 191.

Contribution from the Laboratoire de Chimie des Métaux de Transition, URA-CNRS 419,
Université P. et M. Curie, 4 Place Jussieu, 75252 Paris Cedex 05, France

Synthesis and X-ray Structures of Two Unprecedented Heteropolymetalates $[As_3M_3O_{15}]^{3-}$ (M = Mo, W) and $[As_6CoMo_6O_{30}]^{4-}$. First Examples of Linear Triarsenate(III) and Cyclic Triarsenate(III)

J. Martin-Frère, Y. Jeannin,* F. Robert, and J. Vaissermann

Received March 7, 1991

Two new heteropolymetalates $[As_3M_3O_{15}]^{3-}$ (M = Mo, W) and $[As_6CoMo_6O_{30}]^{4-}$ have been prepared and their structures solved. **1**: $Na_3[As_3Mo_3O_{15}]\cdot 10H_2O$, monoclinic, space group $P2_1/a$, a = 19.160 (1) Å, b = 15.000 (5) Å, c = 8.241 (1) Å, β = 92.26 (1)°, and Z = 4. The structure is made of a Mo_3O_{13} group stabilized by an unprecedented linear $As_3O_7^{5-}$ triarsenate(III). **2**: $Na_3[As_3W_3O_{15}]\cdot 10H_2O$ is isostructural to **1**. **3**: $[Co(H_2O)_6]K_2[As_6CoMo_6O_{30}]$, cubic, space group $Pa3$, a = 14.890 (1) Å, and Z = 4. It was obtained by reaction of Co^{2+} with $[As_3Mo_3O_{15}]^{3-}$. The structure derives from the Anderson type; the central octahedron is filled up by cobalt, and it is capped on both sides by an unprecedented $As_3O_6^{3-}$ *cyclo*-triarsenate(III).

Heteropolymolybdates and heteropolytungstates were isolated for the first time in the second half of the nineteenth century.[1] Several authors became interested in that chemistry and described several species with the only help of chemical analysis. Particularly, several heteropolymolybdates and heteropolytungstates containing low Mo/As(III) and W/As(III) ratios were described by Gibbs[2] and by Ephraim and Feidel.[3] In this series the richest compound in arsenic corresponds to the composition M/As = 1 in atoms. Treated by a solution of a divalent Z cation (Z = Mn^{2+}, Zn^{2+}, Cu^{2+}, Ni^{2+}), arsenomolybdates were found, and Gibbs gave them the formula $6MoO_3, 3As_2O_3, 2ZO, 6H_2O$. The identification of those compounds was only based upon chemical analysis. This family has never been reinvestigated so that their structure remained unknown.

During the course of a general study of arsenic(III)-containing heteropolymetalates, we revisited the work of Gibbs and we have investigated by X-ray diffraction the structures of an arsenatomolybdate and of an arsenatotungstate in which the atom metal/As ratio is equal to 1. Those compounds exhibit an isolated M_3O_{13} group; it is actually stabilized by a linear triarsenate(III), itself observed for the first time. As a matter of fact, a meta-arsenite was crystallographically described by Menary,[4] but it is

---

[1] Marignac, C. *C. R. Acad. Sci.* **1862**, *55*, 888. Marignac, C. *Ann. Chem.* **1862**, *25*, 362.

[2] Gibbs, W. *Am. Chem. J.* **1885**, *7*, 313.

[3] Ephraim, F.; Feidel, H. *Z. Anorg. Chem.* **1910**, *66*, 51.

[4] Menary, J. W. *Acta Crystallogr.* **1958**, *11*, 742.

Table I. Crystal Data for $Na_3[As_3Mo_3O_{15}]\cdot 10H_2O$ (**1**), $Na_3[As_3W_3O_{15}]\cdot 10H_2O$ (**2**), and $[Co(H_2O)_6]K_2[As_6CoMo_6O_{30}]$ (**3**)

	compd		
	1	**2**	**3**
chem formula	$As_3H_{20}Mo_3Na_3O_{25}$	$As_3H_{20}W_3Na_3O_{25}$	$As_6Co_2H_{12}K_2Mo_6O_{36}$
fw	1001.69	1265.43	1809.30
space group	$P2_1/a$ (No. 14)	$P2_1/a$ (No. 14)	$Pa3$ (No. 205)
a, Å	19.160 (1)	19.276 (4)	14.890 (1)
b, Å	15.000 (5)	14.990 (4)	
c, Å	8.241 (1)	8.182 (1)	
β, deg	92.26 (1)	92.36 (2)	
V, Å^3	2366	2362	3301
Z	4	4	4
T, °C	25	25	25
λ, Å	0.71069	0.71069	0.71069
ρ_{calc}, g cm^{-3}	2.81	3.56	3.64
μ(Mo Kα), cm^{-1}	58.36	192.09	94.63
min, max transm coeff	0.926, 1.082	0.762, 1.316	0.935, 1.069
$R(F_o)$	0.027	0.035	0.032
$R_w(F_o^2)$	0.029	0.038	0.032

more correctly described as an infinite chain $(AsO_2)_n$. We then noted the occurrence of a free available lone pair on each arsenic atom. Considering the reaction previously found for the tetraarsenato(III)tetracontatungstate,[5] where free lone pairs occur on arsenic and oxygen atoms, which can then ligate two cobalt atoms, we reacted the triarsenatotrimolybdate with cobalt. The structure of the obtained compound was solved by X-ray diffraction. It is a species derived from the Anderson structure with a $CoMo_6$ core. The triarsenate(III) unit is still present, but it now is a cyclic triarsenate(III), which we describe for the first time.

Synthesis

Compound 1: $Na_3[As_3Mo_3O_{15}]\cdot 10H_2O$, μ_3-[Pentaoxobis(μ-oxo)triarsenato(5–)-O^1,O^2,O^3,O^4,O^5]pentaoxotris(μ-oxo)trimolybdate(3–). The synthesis procedure directly derives from the one described by Ephraim and Feidel.[3] Arsenous anhydride (40 g, 0.2 mol) is dissolved in water (200 mL). The solution is gently heated till full dissolution. Molybdenum oxide MoO_3 (57.6 g, 0.4 mol) is then added slowly under heating. A white residue remains, which is filtrated off. After 1 night, 95 g of large yellow pale parallelepiped crystals grew out of the solution. Yield: 70%.

Compound 2: $Na_3[As_3W_3O_{15}]\cdot 10H_2O$. The synthesis of the arsenatotungstate is identical. Transparent parallelepiped crystals (63 g) were obtained when the starting compound was tungsten oxide $WO_3\cdot H_2O$ (100 g, 0.4 mol). Yield: 37%.

Chemical Analysis. Compound 1. Calcd for $Na_3[As_3Mo_3O_{15}]\cdot 10H_2O$: As, 22.44; Mo, 28.73; Na, 6.89. Found: As, 21.74; Mo, 28.18; Na, 6.80.

Compound 2. Calcd for $Na_3[As_3W_3O_{15}]\cdot 10H_2O$: As, 17.78; W, 43.58; Na, 5.45. Found: As, 17.76; W, 44.34; Na, 5.45.

Anions of Compounds 3 and 4: $[As_6CoMo_6O_{30}]^{4-}$, Bis[μ_7-[*cyclo*-trioxotris(μ-oxo)triarsenato(3–)-O^1,O^2,O^3]]dodecaoxohexakis(μ-oxo)(cobalthexamolybd)ate (4–). Cobalt chloride $[Co(H_2O)_6]Cl_2$ (1 g, 4.2 mmol) and compound 1 (2.5 g, 2.5 mmol) were dissolved into water (100 mL) at room temperature. The solution is orange; it is treated with a KCl- or NH_4Cl-saturated solution (1 mL). After 24 h, large orange octahedral crystals of $[Co(H_2O)_6]K_2[As_6CoMo_6O_{30}]$ (compound 3) or $[Co(H_2O)_6](NH_4)_2[As_6CoMo_6O_{30}]$ (compound 4) were formed.

Chemical Analysis. Compound 3. Calcd for $[Co(H_2O)_6]K_2[As_6CoMo_6O_{30}]$: As, 24.80; Mo, 31.80; Co, 6.50; K, 4.31. Found: As, 22.36; Mo, 31.29; Co, 6.08; K, 4.25.

Compound 4. Calcd for $[Co(H_2O)_6](NH_4)_2[As_6CoMo_6O_{30}]$: As, 25.45; Mo, 32.57; Co, 6.60; N, 1.50. Found: As, 25.41; Mo, 34.00; Co, 5.30; N, 2.31.

The X-ray study was carried out on 3 because crystals of 4 could not be used. Although the chemical analysis of 4 is not as good as the one of 3, it is assumed that the structure of 4 is identical with the one of 3.

Attempts to prepare the same compound with tungsten instead of molybdenum led to a violet solution from which powders were crystallized; unfortunately their chemical analyses were not reproducible. A mixture of several species was very likely obtained, but we failed to separate it into pure species.

Crystallographic Study

Data were recorded at room temperature with a Philips PW1100 diffractometer for 1 and 2 (Euler geometry) and with an Enraf-Nonius CAD4F diffractometer for 3 (κ geometry); both diffractometers had a beam monochromator. An absorption correction was applied to collected intensities.[6] The three structures were solved by using CRYSTALS.[7] Heavy-atom positions were determined by direct methods. Oxygen atoms and cations were located from successive Fourier series. Atomic parameters were refined by least squares by inverting the full matrix. Form factors were taken from ref 8. Extinction was corrected. Crystal data are given in Table I. Atomic parameters and standard deviations are given in Tables II–IV.

Table II. Fractional Atomic Coordinates with Esd's in Parentheses and Equivalent Isotropic Thermal Parameter U(eq)'s for **1**[a]

atom	x/a	y/b	z/c	U(eq), Å^2
Mo(1)	0.62465 (3)	0.64654 (3)	0.55949 (6)	0.0151
Mo(2)	0.63084 (3)	0.86757 (3)	0.54573 (6)	0.0138
Mo(3)	0.75447 (2)	0.74664 (4)	0.36445 (6)	0.0147
As(1)	0.80500 (3)	0.91587 (4)	0.62875 (8)	0.0190
As(2)	0.73530 (3)	0.75848 (4)	0.82995 (7)	0.0169
As(3)	0.79559 (3)	0.58502 (4)	0.65254 (8)	0.0182
O(1)	0.7022 (2)	0.7551 (3)	0.6219 (4)	0.0140
O(2)	0.5938 (2)	0.6559 (3)	0.7532 (6)	0.0234
O(3)	0.6029 (2)	0.8702 (3)	0.7409 (5)	0.0205
O(4)	0.7143 (2)	0.9395 (3)	0.5930 (5)	0.0197
O(5)	0.8198 (2)	0.8331 (3)	0.4828 (5)	0.0206
O(6)	0.8153 (2)	0.6571 (3)	0.4922 (5)	0.0201
O(7)	0.7035 (2)	0.5705 (3)	0.6252 (5)	0.0212
O(8)	0.5688 (2)	0.5710 (3)	0.4673 (6)	0.0244
O(9)	0.5830 (2)	0.7578 (3)	0.4760 (5)	0.0163
O(10)	0.5780 (2)	0.9425 (3)	0.4425 (5)	0.0229
O(11)	0.6926 (2)	0.8376 (3)	0.3384 (5)	0.0183
O(12)	0.7949 (2)	0.7399 (3)	0.1843 (5)	0.0255
O(13)	0.6877 (2)	0.6608 (3)	0.3514 (5)	0.0189
O(14)	0.7970 (2)	0.8460 (3)	0.8072 (5)	0.0246
O(15)	0.7932 (2)	0.6658 (3)	0.8187 (5)	0.0219
O(101)	0.5172 (3)	0.4623 (4)	0.1884 (6)	0.0371
O(102)	0.5753 (3)	0.6517 (4)	0.0982 (6)	0.0358
O(103)	0.4284 (3)	0.7434 (4)	0.0017 (6)	0.0386
O(104)	0.4638 (3)	0.9509 (3)	0.8335 (6)	0.0306
O(105)	0.5937 (3)	0.8660 (3)	0.0862 (6)	0.0309
O(106)	0.6986 (3)	0.0362 (4)	0.9081 (7)	0.0402
O(107)	0.5640 (2)	0.1074 (3)	0.6846 (6)	0.0297
O(108)	0.4449 (2)	0.6504 (3)	0.3344 (6)	0.0315
O(109)	0.5512 (3)	0.2206 (4)	0.3293 (6)	0.0359
O(110)	0.3386 (3)	0.5251 (5)	0.0836 (8)	0.0564
Na(1)	0.5101 (1)	0.7728 (2)	0.2209 (3)	0.0310
Na(2)	0.5799 (2)	0.0024 (2)	0.9165 (4)	0.0367
Na(3)	0.4483 (2)	0.5875 (2)	0.0652 (4)	0.0446

[a] $U(eq) = [U(11)U(22)U(33)]^{1/3}$. Oxygen atoms indexed from 101 to 110 belong to water molecules.

---

[5] Leyrie, M.; Hervé, G.; Tezé, A.; Robert, F.; Jeannin, Y. *Inorg. Chem.* **1979**, *19*, 1746.

[6] Walker, N.; Stuart, O. *Acta Crystallogr.* **1983**, *A39*, 158.

[7] Watkin, D. J.; Carruthers, J. R. CRYSTALS, An Advanced Crystallographic Computer Program, Chemical Crystallography Laboratory, University of Oxford, 1986.

[8] *International Tables* for *X-ray Crystallography*; Vol. IV, Kynoch Press: Birmingham, England, 1974; Vol. IV.

Table III. Fractional Atomic Coordinates with Esd's in Parentheses and Equivalent Isotropic Thermal Parameters *U*(eq)'s for **2**[a]

atom	*x/a*	*y/b*	*z/c*	*U*(eq), Å^2
W(1)	0.62511 (3)	0.64610 (4)	0.55480 (9)	0.0104
W(2)	0.63109 (3)	0.86765 (4)	0.54279 (8)	0.0095
W(3)	0.75528 (3)	0.74716 (5)	0.36767 (7)	0.0111
As(1)	0.8032 (1)	0.9164 (1)	0.6334 (2)	0.0151
As(2)	0.73364 (8)	0.7581 (1)	0.8333 (2)	0.0136
As(3)	0.7946 (1)	0.5850 (1)	0.6551 (2)	0.0145
O(1)	0.7022 (5)	0.7545 (8)	0.622 (1)	0.0105
O(2)	0.5943 (6)	0.6539 (7)	0.753 (2)	0.0090
O(3)	0.6023 (7)	0.8699 (7)	0.742 (2)	0.0161
O(4)	0.7147 (7)	0.9409 (8)	0.592 (2)	0.0195
O(5)	0.8179 (6)	0.8330 (8)	0.485 (2)	0.0179
O(6)	0.8140 (6)	0.6577 (8)	0.495 (2)	0.0132
O(7)	0.7030 (6)	0.5709 (7)	0.623 (2)	0.0145
O(8)	0.5689 (7)	0.5695 (8)	0.461 (2)	0.0204
O(9)	0.5822 (5)	0.7576 (8)	0.474 (1)	0.0212
O(10)	0.5772 (6)	0.9445 (8)	0.443 (2)	0.0138
O(11)	0.6900 (6)	0.8365 (8)	0.341 (1)	0.0206
O(12)	0.7941 (6)	0.7406 (9)	0.183 (1)	0.0210
O(13)	0.6867 (6)	0.6623 (8)	0.355 (1)	0.0138
O(14)	0.7942 (7)	0.8465 (8)	0.811 (1)	0.0180
O(15)	0.7918 (6)	0.6654 (8)	0.819 (1)	0.0134
O(101)	0.5175 (8)	0.4621 (9)	0.194 (2)	0.0268
O(102)	0.5723 (7)	0.6512 (9)	0.091 (2)	0.0284
O(103)	0.4246 (7)	0.741 (1)	0.007 (2)	0.0328
O(104)	0.4635 (7)	0.9500 (9)	0.833 (2)	0.0251
O(105)	0.5918 (7)	0.8646 (8)	0.085 (2)	0.0245
O(106)	0.6963 (8)	1.037 (1)	0.913 (2)	0.0368
O(107)	0.5630 (7)	0.1074 (8)	0.680 (2)	0.0234
O(108)	0.4462 (7)	0.6499 (9)	0.340 (2)	0.0233
O(109)	0.5496 (7)	0.2215 (9)	0.326 (2)	0.0337
O(110)	0.3393 (9)	0.531 (1)	0.082 (2)	0.0504
Na(1)	0.5096 (4)	0.7723 (5)	0.2200 (9)	0.0293
Na(2)	0.5785 (4)	1.0009 (6)	0.914 (1)	0.0331
Na(3)	0.4495 (4)	0.5869 (5)	0.0644 (9)	0.0301

[a] $U(eq) = [U(11)U(22)U(33)]^{1/3}$. Oxygen atoms indexed from 101 to 110 belong to water molecules.

Table IV. Fractional Atomic Coordinates with Esd's in Parentheses and Equivalent Isotropic Thermal Parameters *U*(eq)'s for **3**[a]

atom	*x/a*	*y/b*	*z/c*	*U*(eq), Å^2
Co(1)	0.00000	0.00000	0.00000	0.0063
Mo(1)	0.00300 (6)	−0.15895 (6)	0.15710 (5)	0.0130
As(1)	−0.15788 (8)	−0.17053 (6)	−0.00862 (7)	0.0205
O(1)	−0.0881 (4)	−0.0930 (4)	0.0519 (4)	0.0100
O(2)	0.0844 (4)	−0.1754 (5)	0.2356 (4)	0.0211
O(3)	−0.0529 (5)	−0.0570 (4)	0.2139 (4)	0.0168
O(4)	−0.0758 (4)	−0.2398 (5)	0.1772 (5)	0.0204
O(5)	−0.2150 (5)	−0.0907 (5)	−0.0797 (5)	0.0243
Co(2)	0.00000	−0.50000	0.00000	0.0234
O(6)	0.0521 (8)	−0.5858 (6)	0.0980 (6)	0.0443
K(1)	0.2527 (2)	−0.2527 (2)	0.2473 (2)	0.0253

[a] $U(eq) = [U(11)U(22)U(33)]^{1/3}$.

Description of Structures

$Na_3[As_3Mo_3O_{15}]\cdot 10H_2O$ (1) and $Na_3[As_3W_3O_{15}]\cdot 10H_2O$ (2). The structures of compounds **1** and **2** were solved, and the two compounds are isostructural (Figure 1). The anion contains three metal atoms. Three MO_6 octahedrons share a vertex and two by two an edge so that this anion is the M_3O_{13} building block of the Keggin structure[9] and of many other polyanions.

Three AsO_3 pyramids build an As_3O_7 chain, which lies on the trimetallic group. The chain shares five oxygen atoms with the M_3O_{13} group. The central arsenic is bound to the oxygen atom common to the three MO_6 octahedrons. Each external arsenic atom is bound to two oxygen atoms belonging to two different MO_6 octahedrons. The polyanion has a plane of symmetry that contains atoms M(3), As(2), O(1), O(9), and O(12); this plane is not a crystallographic symmetry plane. Main distances and angles are given only for compound **1** in Table V.

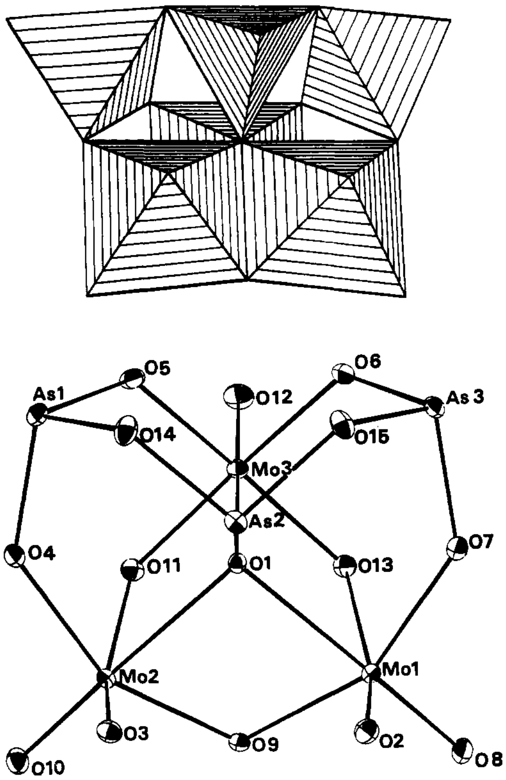

Figure 1. ORTEP view of the $[As_3Mo_3O_{15}]^{3-}$ anion and a polyhedral sketch. Details dealing with the As_3O_7 fragment are given in Figure 2.

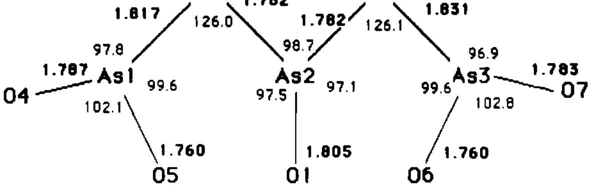

Figure 2. Schematic drawing with distances and angles of the As_3O_7 fragment.

The MoO_6 and WO_6 octahedrons are distorted as usually observed in heteropolyanions but with a particular influence of triarsenate(III), which induces the internal symmetry. For instance, in the metal–oxygen chain involving oxygen atoms binding octahedrons, the following distances are observed:

O(9) --- M(1) --- O(13) --- M(3) --- O(11) --- M(2) --- O(9)

M=Mo 1.962 2.147 1.816 1.814 2.164 1.960 Å

M=W 1.97 2.07 1.83 1.84 2.09 1.97 Å

Distances and angles in the As_3O_7 chain demonstrate the symmetry of the polyanion (Figure 2 refers to the molybdenum compound). Each arsenic atom exhibits one As–O distance longer than the two others. The average shorter length is 1.78 Å (1.776 (4) and 1.78 (1) Å for Mo and W compounds, respectively), and the longer is 1.82 Å (1.818 (4) and 1.81 (1) Å for Mo and W compounds, respectively). As–O–As angles are rather open with an average value of 126 and 126.1°. In the metaarsenite described by Menary,[4] this angle only is 118.5°.

Na cations are octahedrally surrounded by oxygen atoms belonging either to polyanions or to water molecules. Thus, chains of octahedrons are built that share either vertices, or edges, or faces. Those chains form the link between polyanions.

$[Co(H_2O)_6]K_2[As_6CoMo_6O_{30}]$ (3). This anion has a unique structure derived from the Anderson structure.[10] It is centrosymmetrical, and cobalt is located on the inversion center. The polyanion also has a ternary axis, which is a crystallographic axis

---

[9] Keggin, J. F. *Proc. R. Soc. A* **1934**, *144*, 75.

[10] Anderson, J. S. *Nature* **1937**, *140*, 850.

Table V. Main Distances (Å) and Angles (deg) for Compound **1**[a]

Mo(1)–O(1)	2.250 (4)	Mo(1)–O(2)	1.730 (4)
Mo(1)–O(7)	1.952 (4)	Mo(1)–O(8)	1.716 (4)
Mo(1)–O(9)	1.962 (4)	Mo(1)–O(13)	2.147 (4)
Mo(2)–O(1)	2.246 (4)	Mo(2)–O(3)	1.716 (4)
Mo(2)–O(4)	1.955 (4)	Mo(2)–O(9)	1.960 (4)
Mo(2)–O(10)	1.715 (4)	Mo(2)–O(11)	2.164 (4)
Mo(3)–O(1)	2.384 (4)	Mo(3)–O(11)	1.814 (4)
Mo(3)–O(5)	2.026 (4)	Mo(3)–O(12)	1.705 (4)
Mo(3)–O(6)	2.043 (4)	Mo(3)–O(13)	1.816 (4)
As(1)–O(4)	1.787 (4)	As(1)–O(5)	1.760 (4)
As(1)–O(14)	1.817 (5)	As(2)–O(1)	1.805 (4)
As(2)–O(14)	1.782 (4)	As(2)–O(15)	1.782 (4)
As(3)–O(6)	1.760 (4)	As(3)–O(7)	1.783 (4)
As(3)–O(15)	1.831 (4)	Na(1)–O(9)	2.488 (5)
Na(1)–O(102)	2.446 (6)	Na(1)–O(103)	2.384 (6)
Na(1)–O(105)	2.427 (6)	Na(1)–O(107)*	2.437 (5)
Na(1)–O(108)	2.429 (5)	Na(2)–O(3)	2.504 (5)
Na(2)–O(104)	2.427 (7)	Na(2)–O(104)*	2.361 (6)
Na(2)–O(105)	2.486 (6)	Na(2)–O(106)	2.334 (7)
Na(2)–O(107)	2.486 (6)	Na(3)–O(101)	2.489 (7)
Na(3)–O(101)*	2.339 (6)	Na(3)–O(102)	2.621 (7)
Na(3)–O(103)	2.423 (7)	Na(3)–O(108)	2.414 (6)
Na(3)–O(110)	2.311 (7)		

O(1)–Mo(1)–O(2)	88.7 (2)	O(1)–Mo(1)–O(7)	82.1 (2)
O(1)–Mo(1)–O(8)	166.9 (2)	O(1)–Mo(1)–O(9)	73.8 (1)
O(1)–Mo(1)–O(13)	73.9 (1)	O(2)–Mo(1)–O(8)	103.5 (2)
O(7)–Mo(1)–O(8)	101.5 (2)	O(9)–Mo(1)–O(8)	99.7 (2)
O(13)–Mo(1)–O(8)	94.2 (2)	O(1)–Mo(2)–O(3)	88.0 (2)
O(1)–Mo(2)–O(4)	82.8 (2)	O(1)–Mo(2)–O(9)	73.9 (1)
O(1)–Mo(2)–O(10)	166.3 (2)	O(1)–Mo(2)–O(11)	73.6 (1)
O(3)–Mo(2)–O(10)	104.5 (2)	O(4)–Mo(2)–O(10)	101.5 (2)
O(9)–Mo(2)–O(10)	98.4 (2)	O(11)–Mo(2)–O(10)	94.3 (2)
O(1)–Mo(3)–O(5)	79.1 (2)	O(1)–Mo(3)–O(6)	80.1 (1)
O(1)–Mo(3)–O(11)	76.7 (2)	O(1)–Mo(3)–O(12)	177.7 (2)
O(1)–Mo(3)–O(13)	76.7 (2)	O(5)–Mo(3)–O(12)	99.4 (2)
O(6)–Mo(3)–O(12)	98.0 (2)	O(11)–Mo(3)–O(12)	105.0 (2)
O(13)–Mo(3)–O(12)	104.5 (2)	O(5)–As(1)–O(4)	102.1 (2)
O(14)–As(1)–O(4)	97.8 (2)	O(14)–As(1)–O(5)	99.6 (2)
O(1)–As(2)–O(14)	97.5 (2)	O(15)–As(2)–O(14)	98.7 (2)
O(1)–As(2)–O(15)	97.1 (2)	O(6)–As(3)–O(7)	102.8 (2)
O(15)–As(3)–O(7)	96.9 (2)	O(15)–As(3)–O(6)	99.6 (2)
As(1)–O(14)–As(2)	126.0 (3)	As(2)–O(15)–As(3)	126.1 (3)

[a] Atoms indexed with asterisks are in the $-x$, $-y$, $-z$ coordinate system.

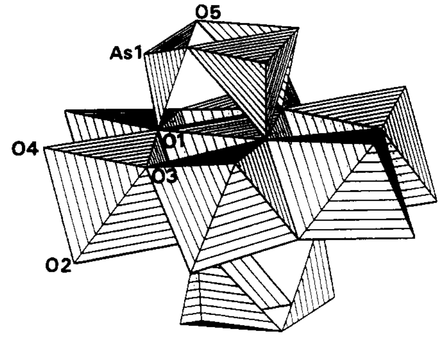

Figure 3. Polyhedral sketch of compound 3. Six edge-sharing MoO_6 octahedrons are around a CoO_6 octahedron. Pyramids consist of AsO_3 groups with arsenic on the free vertex. The O(3) atom shown actually is in the $-y$, $-z$, $-x$ position.

of symmetry. Six MoO_6 octahedrons bound two by two make a crown, the internal octahedral cavity of which is filled up by cobalt(II) (Figure 3). This particular situation exists for compounds such as $[Mo_6TeO_{24}]^{6-}$, $[IMo_6O_{24}]^{5-}$, and $[W_6PtO_{24}]^{8-}$.[11,12] On each side of this fragment two rings of *cyclo*-triarsenate(III) are fixed. Each AsO_3 pyramid is bound to an oxygen atom belonging to the cobalt octahedron CoO_6; this oxygen atom is also shared by two MoO_6 octahedrons. Each AsO_3 pyramid is also bound to two other arsenic atoms, thus closing the As_3O_6 ring. Distances and angles are given in Table VI.

Table VI. Main Distances (Å) and Angles (deg) for Compound **3**[a]

Co(1)–O(1)	2.058 (6)	Co(2)–O(6)	2.089 (8)
Mo(1)–O(1)	2.293 (6)	Mo(1)–O(1)	2.321 (6)
Mo(1)–O(2)	1.702 (6)	Mo(1)–O(3)	1.927 (6)
Mo(1)–O(3)	1.930 (7)	Mo(1)–O(4)	1.708 (6)
As(1)–O(1)	1.796 (5)	As(1)–O(5)	1.804 (7)
As(1)–O(5)	1.813 (7)	K(1)–O(2)	2.763 (7)
K(1)–O(4)*	2.797 (6)		

O(1)–Co(1)–O(1)	93.6 (2)	O(1)–Co(1)–O(1)	86.4 (2)
O(1)–Mo(1)–O(1)*	75.2 (3)	O(2)–Mo(1)–O(1)*	89.5 (3)
O(3)–Mo(1)–O(1)	73.0 (2)	O(3)–Mo(1)–O(1)*	84.4 (2)
O(3)–Mo(1)–O(2)	96.9 (3)	O(3)*–Mo(1)–O(1)	83.1 (3)
O(3)*–Mo(1)–O(1)*	72.2 (2)	O(3)*–Mo(1)–O(2)	101.2 (3)
O(4)–Mo(1)–O(1)	90.9 (3)	O(4)–Mo(1)–O(2)	105.5 (3)
O(4)–Mo(1)–O(3)	100.5 (3)	O(4)–Mo(1)–O(3)*	97.4 (3)
O(5)–As(1)–O(1)	98.2 (3)	O(5)**–As(1)–O(1)	101.6 (3)
O(5)–As(1)–O(5)**	98.5 (5)	As(1)–O(5)–As(1)**	130.4 (4)

[a] Atoms indexed with one asterisk are in the $-y$, $-z$, $-x$ coordinate system, and atoms indexed with two asterisks are in the z, x, y coordinate system.

The MoO_6 octahedron is distorted as expected for a metal atom bound to three different oxygen atoms: two doubly bonded, two bridging two metal atoms, and two tetraligated to two molybdenum atoms, one cobalt atom, and one arsenic atom. Distances are typical of those observed for instance in $[Mo_6TeO_{24}]^{6-}$ [11] or other Anderson type polyanions.

Concerning the As_3O_6 cyclic moiety, the three As–O distances in each AsO_3 pyramid are identical within experimental errors, and this is different from the case of the preceding polyanion containing the linear triarsenate(III). The As–O–As angle is widely open with a value of 130.4° as in the As_3O_7 chain.

There are two kinds of countercations, two potassium cations and one hexaaquacobalt cation. One cobalt with a centrosymmetrical octahedral surrounding of six water molecules is located at the center of the unit cell and at the middle of each edge. Potassium cations are located on ternary axes and are surrounded by six oxygen atoms belonging to polyanions, and they form links between them.

Discussion and Conclusion

M_3O_{13} is the basic building block of many polyoxometalates, particularly all those deriving from the Keggin structure. It is also found in trimolybdates in which M_3O_{13} units are linked together in infinite chains.[13] However, the M_3O_{13} group as a discrete entity has seldom been isolated although its occurence has been postulated to explain the construction of polyanions in solution. Only recently two examples have been published by Zubieta and al. In the first one of formula $[Mo_3O_7\{CH_3C(CH_2O)_3\}_2]^{2-}$,[14] two triolates maintain the three octahedrons altogether. In the second one of formula $[Mo_3O_7(OCH_3)(C_4O_4)_2]^{3-}$,[15] the methoxo ligand is at the common vertex of the three octahedrons, and the two squarates join two molybdenum atoms as do the two external AsO_2 groups of the linear $As_3O_7{}^{5-}$ trisarsenite. In the title compound as well as for Zubieta's compounds, the stability of M_3O_{13} is due to polydentate ligands bridging metal atoms. In the title compound the role played by the As_3O_7 chain clearly is decisive. This chain prevents oxygen atoms O(4), O(5), O(6), and O(7) from making bonds with other Mo_3O_{13} blocks.

One may note that the O(2) and O(3) oxygen atoms are not bound to arsenic so that they have an available lone pair. The three atoms As(2), O(2), and O(3) are at the corners of a triangle, which suggests the face of octahedron inside which could be placed a cobalt atom. Indeed As–O distances are 3.104 (4) and 3.160

---

(11) Pope, M. T. *Hetero and Isopolyoxometalates*; Springer-Verlag: New York, 1988.

(12) Lee, U.; Ichida, H.; Kobayashi, A.; Sazaki, Y. *Acta Crystallogr.* **1984**, *C40*, 5.

(13) Evans, H. T. *J. Am. Chem. Soc.* **1948**, *70*, 1291.

(14) Ma, L.; Liu, S.; Zubieta, J. *Inorg. Chem.* **1989**, *28*, 175.

(15) Chen, Q.; Ma, L.; Liu, S.; Zubieta, J. *J. Am. Chem. Soc.* **1989**, *111*, 5944.

(4) Å for the molybdenum compound, values close to those observed for the cobalt environment in the polyanion $[As_4Co_2W_{40}O_{140}(H_2O)_2]^{24-}$,[5] in which As–O distances are equal to 3.43 and 3.06 Å. However, the reaction of cobalt with compound **1** did not lead to the expected result but yielded a compound based on an Anderson structure. The reaction is quite clean:

$$Co^{2+} + 2[As_3Mo_3O_{15}]^{3-} \rightarrow [As_6CoMo_6O_{30}]^{4-}$$

Let us point out that the Anderson type tellurium-containing structure shows that an excess of tellurium occurred, since $Te(OH)_6$ neutral groups are present in the crystal. Similarly, an excess of cobalt was needed to crystallize our compound **3** and $[Co(H_2O)_6]^{2+}$ is associated in the crystal structure as a cation.

Some Anderson type compounds have a crown of six MO_6 groups in which the internal octahedral site is void. All sides of the crown tetrahedrons then are fixed. One can attach two AsO_4 groups, two MoO_4 groups, or two AsO_3CH_3 groups.[11] In compound **3**, a rather unique situation is observed. The internal octahedral site is filled up with cobalt, and also two tripod *cyclo*-triarsenate(III) groups, one on each side, are fixed.

As a conclusion, we have prepared and crystallized M_3O_{13}, the building block of many polyanions. It is actually stabilized by a chain triarsenate(III), making $[As_3Mo_3O_{15}]^{3-}$. When reacted with cobalt(II), it yields a unique Anderson structure with a cobalt-filled internal octahedral site and two caps made of two *cyclo*-triarsenate(III), $[As_6CoMo_6O_{30}]^{4-}$.

Supplementary Material Available: Full listings of crystal data for the three compounds **1–3** and tables of the main distances and angles for compound **2** and anisotropic thermal parameters for the three compounds (5 pages); tables of observed and calculated structure factors for the three compounds (20 pages). Ordering information is given on any current masthead page.

Contribution from the Department of Chemistry, University of Ottawa, Ottawa, Ontario K1N 6N5, Canada,
Laboratorium voor Anorganische Chemie, Rijksuniversiteit Groningen, Nijenborgh 16, 9747 AG Groningen, The Netherlands,
Department of Chemistry and Biochemistry, University of California, Los Angeles, California 90024, and Vakgroep Algmene Chemie,
Afdeling Kristal- en Structuurchemie, Rijksuniversiteit Utrecht, Padualaan 8, 3584 CH Utrecht, The Netherlands

Ligand and Alkali Metal Cation Control on the Molecular Complexity of Anionic Chromium(II) Aryloxides. Preparation and Crystal Structure of Dimeric $(PhO)_{10}Cr_2Li_6(THF)_6$ and $(2,6\text{-}Me_2C_6H_3O)_6Cr_2Li_2(THF)_4$ and Trimeric $(GuO)_{14}Cr_3Na_9Cl$ [GuO = $(o\text{-}CH_3O)C_6H_4O$] with an Encapsulated Chloride Ion

Jilles J. H. Edema,[†] Auke Meetsma,[†] Sandro Gambarotta,[*,‡] Saeed I. Khan,[§] Wilberth J. J. Smeets,[‖] and Anthony L. Spek[‖]

Received October 24, 1990

Two new anionic, dimeric chromium(II) alkoxides, $(PhO)_{10}Cr_2Li_6(THF)_6$ (**3**) and $(2,6\text{-}Me_2C_6H_3O)_6Cr_2Li_2(THF)_4$ (**4**), have been prepared and characterized by X-ray structure determination. The two complexes possess similar $Cr_2(OR)_2$ cores with a fairly long Cr–Cr distance [$Cr\cdots Cr'$ = 3.149 (2) and 3.091 (1) Å for **3** and **4**, respectively]. In complex **3**, the unit $Cr_2(OPh)_2$ is incorporated into two separated $(PhO)_4Li_3(THF)_3$ polyhedra, while in complex **4** the same core is attached to two $(RO)Li(THF)_2$ units with an overall linear arrangement of the Li–Cr–Cr–Li backbone. Replacement with TMEDA of the four THF molecules attached to lithium cleaved the dimeric structure of **3** and **4**, forming the monomeric $(RO)_4CrLi_2(TMEDA)_2$ [R = Ph (**5a**), $2,6\text{-}Me_2C_6H_3O$ (**5b**)]. Reaction of $CrCl_2(THF)_2$ with 2 equiv of GuONa [GuO = $(o\text{-}CH_3O)C_6H_4O$] led to the formation of the polymeric $[(GuO)_2Cr]_n$ as an insoluble, pyrophoric solid. Further reaction with an excess of (GuO)Na formed the trinuclear $(GuO)_{14}Cr_3Na_9Cl$ (**6**). Treatment of **6** with 18-crown-6 led to the disruption of the trinuclear arrangement and formation of the polymeric $[(GuO)_2Cr]_n$ species. Crystal data for **3**, **4**, and **6** are as follows. **3** is triclinic, space group $P\bar{1}$, with a = 12.511 (1) Å, b = 13.145 (1) Å, c = 15.260 (2) Å, α = 98.77 (1)°, β = 106.27 (1)°, γ = 117.18 (1)°, V = 2024.2 (3) Å^3, and Z = 1; **4** is monoclinic, space group $C2/c$, with a = 15.318 (4) Å, b = 18.245 (4) Å, c = 22.113 (6) Å, β = 100.90 (2)°, V = 6069 (3) Å^3, and Z = 4; **6** is orthorhombic, space group $Pba2$, with a = 26.720 (1) Å, b = 26.916 (2) Å, c = 15.670 (2) Å, V = 11269.8 (17) Å^3, and Z = 4.

Introduction

A recent revival of interest in the literature of group 1 metals has shown that, among the properties of these metals, the Lewis acidity is responsible for several important features including the (i) high degree of nuclearity observed in the solid-state structures of these compounds,[1] (ii) strong interactions with unsaturated organic systems,[2,3] and (iii) σ-acceptor interactions with transition metals.[3]

A very important ancillary role of the alkali-metal cation has been recognized in the stabilization and reactivity of anionic transition metalates.[5,6] However, the molecular geometry of these species seems to be determined mainly by the electronic configuration of the transition metal and by the nature of the ligand. By contrast, recent results in the chemistry of tetravalent zirconium[7] and divalent chromium[8,9] have shown that alkali-metal cations are capable of playing a preeminent role in determining the molecular complexity (monomeric versus di-, oligo-, and

---

[†] Rjiksuniversiteit Groningen.

[‡] University of Ottawa.

[§] University of California.

[‖] Rjiksuniversiteit Utrecht.

(1) (a) McGarrity, J. F.; Ogle, C. A. *J. Am. Chem. Soc.* **1984**, *107*, 1805. (b) Seebach, D.; Hässig, R.; Gabriel, J. *Helv. Chim. Acta* **1983**, *66*, 308. (c) Tecle, B.; Rahman, A. F. M.; Oliver, J. P. *J. Organomet. Chem.* **1986**, *317*, 267. (d) Armstrong, D. R.; Barr, D.; Clegg, W.; Mulvey, R. E.; Reed, D.; Snaith, R.; Wade, K. *J. Chem. Soc., Chem. Commun.* **1986**, 869. (e) Barr, D.; Clegg, W.; Mulvey, R. E.; Smith, R.; Wade, K. *J. Chem. Soc., Chem. Commun.* **1986**, 295. (f) Anderson, D. M.; Hitchcock, P. B.; Lappert, M. F.; Leung, W. P.; Zora, J. A. *J. Organomet. Chem.* **1987**, *333*, C13. (g) Bauer, W.; Feigel, M.; Müller, G.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1988**, *110*, 6033.

(2) (a) Beno, M. A.; Hope, H.; Olmstead, M.; Power, P. P. *Organometallics* **1985**, *4*, 2117. (b) Dietrich, H.; Mahdi, W.; Knorr, R. *J. Am. Chem. Soc.* **1986**, *108*, 2462. (c) Wilhelm, D.; Courtneidge, J. L.; Clark, T.; Davies, A. G. *J. Chem. Soc., Chem. Commun.* **1984**, 810. (d) Stezowski, J.; Hoier, H.; Wilhelm, D.; Clark, T.; Schleyer, P. v. R. *J. Chem. Soc., Chem. Commun.* **1985**, 1263. (e) Wilhelm, D.; Clark, T.; Schleyer, P. v. R.; Dietrich, H.; Mahdi, W. *J. Organomet. Chem.* **1985**, *280*, C6. (f) Stucky, G. D.; Brooks, J. J. *J. Am. Chem. Soc.* **1972**, *94*, 7333. (g) Patterman, S. P.; Karle, I. L.; Stucky, G. D. *J. Am. Chem. Soc.* **1970**, *92*, 1150. (h) Bartlett, R. A.; Dias, H. V. R.; Power, P. P. *J. Organomet. Chem.* **1988**, *341*, 1.

0020-1669/91/1330-3639$02.50/0