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Tetrakis(tetrabutylammonium) tetrakis[(*p*-cyanophenyl)trioxoarsonato]tetratriacontaoxododecamolybdate(4–)

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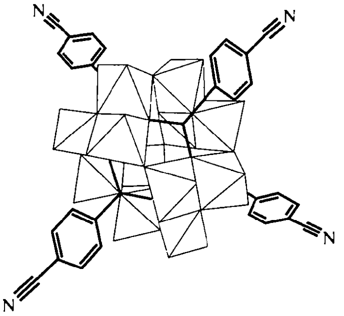
Abstract

Crystals of the title compound, $(C_{16}H_{36}N)_4[(p\text{-NC-}C_6H_4As)_4Mo_{12}O_{46}]$ or $(C_{16}H_{36}N)_4[\{As(C_7H_4N)\}_4Mo_{12}O_{46}]$, were synthesized by the reaction of *p*-cyanophenylarsonic acid and sodium molybdate at low pH. With nitrile groups pointed in tetrahedral directions, these new organically modified polyoxometalate clusters are potential building blocks in coordination networks.

Comment

During the course of our studies into extended network solids, a new type of building block was synthesized as the tetrabutylammonium (TBA) salt. This building block, a hybrid $[(p\text{-NC-}C_6H_4As)_4Mo_{12}O_{46}]^{4-}$ cluster, (I), is related to the organically modified polyoxometalate clusters synthesized by Barkigia *et al.* (1981). It has been shown that these types of polyoxometalate clusters can be synthesized with a variety of organic groups (benzene, aniline, methyl, 2-hydroxyethyl) and differing molybdenum to arsenic ratios (Kwak *et al.*, 1976; Matsumoto, 1979). We have synthesized a new organic derivative with a molybdenum/arsenic ratio of 3:1 and benzonitrile groups. This derivative was developed as a potential tetrahedral linking unit for networks based on the well developed coordination chemistry of aryl nitriles (Hoskins & Robson, 1990; Liu & Tilley, 1997, 1998; Hirsch *et al.*, 1995, 1998). The organic precursors for these functionalized polyoxometalate clusters are arsonic acids. The literature contains a fair number of syntheses, and the synthesis of $p\text{-}H_3O_2AsC_6H_4CN$ by the Bart method is relatively straightforward (Bart, 1922).



$(p\text{-NC-}C_6H_4As)_4Mo_{12}O_{46}$

(I)

The crystal structure of the title compound consists of $[(p\text{-NC-}C_6H_4As)_4Mo_{12}O_{46}]^{4-}$ anions (Fig. 1) that are packed in layers of staggered clusters. The intercluster space is filled by four charge-balancing tetrabutylammonium ions for each discrete cluster. Two of the butyl side chains are disordered over two positions. Some of the C—C bond distances are shorter than expected as a result of coupled translational and librational motions in this non-rigid molecule. Due to the large cation size, the crystal density is significantly lower than that of the related compound $[(p\text{-}H_3NC_6H_4As)_4Mo_{12}O_{46}]\cdot 10CH_3CN\cdot 6H_2O$ (Barkigia *et al.*, 1981) ($1.86\,g\,cm^{-3}$ *versus* $2.27\,g\,cm^{-3}$). No solvent molecules were found within the crystal. The structure of the anion is similar to that of $[(p\text{-}H_3NC_6H_4As)_4Mo_{12}O_{46}]$. It can be described as an 'inverse Keggin' cluster, where four tetrahedral atoms bridge a metal–oxygen core, instead of a tetrahedral interior atom bridging the metal–oxygen exterior. The molybdenum–oxygen skeleton contains four corner-sharing groups of three edge-sharing Mo—O octahedra, which are bridged by tetrahedral As atoms. The Mo—O distances coincide with those found for the cluster substituted with protonated aminophenylarsonic acid groups, namely 1.690–1.705 Å for terminal O atoms, 1.876–1.900 Å for doubly bridging O atoms, 2.037–2.060 Å for triply bridging O atoms bound to three Mo atoms, and 2.282–2.347 Å for triply bridging O atoms

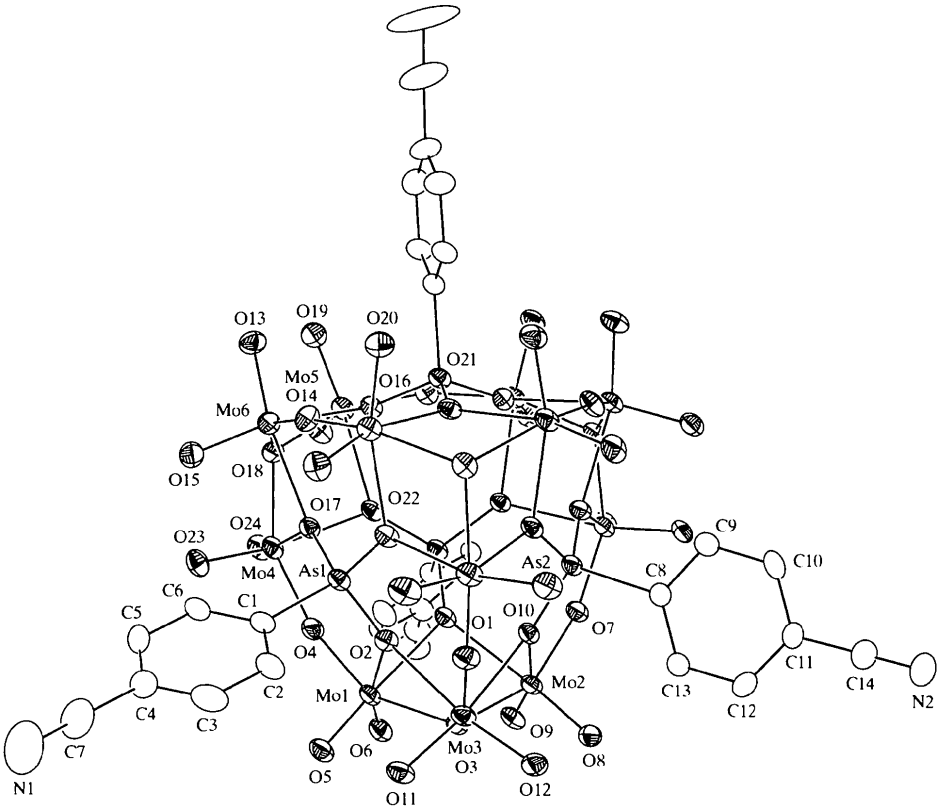


Fig. 1. The structure of the title anion. Displacement ellipsoids are drawn at the 30% probability level.

shared between two Mo and one As atom. While the As—O distances (1.692–1.697 Å) also agree with those found in the aminophenyl-substituted cluster, the As—C distances are longer (1.919–1.924 Å, compared with 1.85–1.89 Å). The increase in As—C bond length may be due to an electron-withdrawing effect of the benzonitrile group. The arrangement of nitrile groups into tetrahedral directions is a desirable feature for the construction of three-dimensional cluster networks by ligand coordination.

Experimental

p-$H_2O_3AsC_6H_4CN$ was prepared by the Bart method (Bart, 1922). p-Aminobenzonitrile (4.0 g) was treated with concentrated HCl (8.8 ml) and a solution of $NaNO_2$ (2.57 g) in H_2O (100 ml) at 273 K to form the diazonium salt in solution. (Caution: dry diazonium salts can be explosive; they should be kept in solution.) A second solution was prepared with As_2O_3 (5.02 g) and NaOH (6.09 g) in H_2O (50 ml) at room temperature. The cold diazonium solution was then added slowly to the sodium arsenite solution over a period of approximately 30 min. During the addition step, the solution turned red, then brown with the release of N_2 gas. After all of the diazonium solution had been added, the solution was stirred for 15 min and then treated with concentrated HCl until the pH reached a value of approximately 1. As the pH was lowered, the solution turned yellow, and a brown precipitate separated from the solution. The precipitate was removed by filtration. The clear yellow solution was reduced in volume to 50 ml and then cooled to room temperature, which produced an off-white powder of p-$H_2O_3AsC_6H_4CN$. FT-IR (KBr): 2231 (C≡N), 1090 (As—C), 907 cm^{-1} (As=O); ^1H NMR (d_6-DMSO): 8.07 p.p.m. (dd); ^{13}C NMR (d_6-DMSO): 115.7, 118.3 (C≡N), 131.4, 133.6, 139.5 p.p.m.

$[TBA]_4[(p\text{-}NC\text{-}C_6H_4As)_4Mo_{12}O_{46}]$, (I), was obtained by adding $Na_2MoO_4{\cdot}2H_2O$ (3.18 g) to a solution of p-H_2O_3-AsC_6H_4CN (1.0 g) in H_2O (100 ml). The solution was acidified with concentrated nitric acid to a pH value less than 1. The acidic solution was stirred for 15 min, after which time 1.50 g of tetrabutylammonium bromide was added. An off-white powder precipitated immediately from solution and was collected by filtration. Crystals of this material suitable for X-ray crystallography were grown from a 2:1 (v:v) CH_3CN/H_2O solution of (I) in an open vial which was placed in a sealed jar containing diethyl ether. After diethyl ether vapor was allowed to diffuse into the solution of (I) for several days, colorless crystals with a nearly orthorhombic habit appeared. FT-IR (KBr): 2230 (C≡N), 1087 (As—C), 950 (Mo—O), 924 (Mo—O), 874 cm^{-1} (Mo—O).

Crystal data

$(C_{16}H_{36}N)_4[\{As(C_7H_4N)\}_4$-$Mo_{12}O_{46}]$
M_r = 3565.24
Monoclinic
$C2/c$

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 8192 reflections
θ = 1.43–25.00°

$a = 26.9834\,(6)$ Å
$b = 16.8216\,(4)$ Å
$c = 28.1000\,(4)$ Å
$\beta = 90.164\,(1)^\circ$
$V = 12754.6\,(5)$ Å^3
$Z = 4$
$D_x = 1.857$ Mg m^{-3}
D_m not measured

$\mu = 2.248$ mm^{-1}
$T = 173\,(2)$ K
Block
0.28 × 0.20 × 0.12 mm
Colorless

Data collection

Siemens SMART Platform CCD diffractometer
Multi-scans
Absorption correction: empirical (*SADABS*; Sheldrick, 1996)
$T_{\min} = 0.445$, $T_{\max} = 0.763$
31 322 measured reflections
11 061 independent reflections

7586 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.042$
$\theta_{\max} = 25^\circ$
$h = -32 \rightarrow 32$
$k = 0 \rightarrow 19$
$l = 0 \rightarrow 33$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.046$
$wR(F^2) = 0.102$
$S = 1.076$
11 061 reflections
729 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0588P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 1.947$ e Å^{-3}
$\Delta\rho_{\min} = -1.051$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Data collection: *SMART* (Siemens, 1994*b*). Cell refinement: *SAINT* (Siemens, 1994*b*). Data reduction: *SHELXTL-Plus* (Siemens, 1994*a*). Program(s) used to solve structure: *SHELXTL-Plus*. Program(s) used to refine structure: *SHELXTL-Plus*. Molecular graphics: *SHELXTL-Plus*. Software used to prepare material for publication: *SHELXTL-Plus*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: DA1056). Services for accessing these data are described at the back of the journal.

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Aquadiisothiocyanato(*N*,*N*,*N*′,*N*′-tetramethylethylenediamine-*N*,*N*′)copper(II)

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Abstract

The crystal structure of [Cu(NCS)$_2$(*N*,*N*,*N*′,*N*′-tmen)(H$_2$O)] (*N*,*N*,*N*′,*N*′-tmen is *N*,*N*,*N*′,*N*′-tetramethylethylenediamine, $C_6H_{16}N_2$) consists of discrete non-centrosymmetric molecules connected by a network of O—H···S hydrogen bonds. The coordination polyhedron around the Cu$^{\rm II}$ atom is square pyramidal, with the Cu atom about 0.22 Å above the plane of the four N atoms. The Cu—N basal-plane bond length has a mean value of 1.9999 Å. The fifth (apical) position is occupied by the O atom of the water molecule [Cu—O 2.342 (3) Å]. The *N*,*N*,*N*′,*N*′-tetramethylethylenediamine chelate ring displays an unsymmetrical '*gauche*' configuration.

Comment

Replacement of the ethylenediamine (en) in [Cu(en)$_2$(SCN)$_2$] (Brown & Lingafelter, 1964) by *N*-methylethylenediamine (*N*-meen) to give [Cu(*N*-meen)$_2$(SCN)$_2$] (Pajunen & Hämäläinen, 1972) and by *N*,*N*′-dimethylethylenediamine (*N*,*N*′-deen) to give [Cu(*N*,*N*′-deen)$_2$(NCS)$_2$] (Korvenranta & Pajunen, 1970), leads to a different orientation of the thiocyanate groups in the coordination polyhedron of the Cu$^{\rm II}$ atom. The different orientation of the thiocyanate groups in these three structures is not due to electronic effects, but instead to reticular or environmental requirements.

We have determined the crystal structure of [Cu(*N*,*N*,*N*′,*N*′-tmen)(NCS)$_2$(H$_2$O)], (I), where *N*,*N*,*N*′,*N*′-tmen is *N*,*N*,*N*′,*N*′-tetramethylethylenediamine, which