

Andreas Flemström

Department of Inorganic Chemistry, Arrhenius
Laboratory, Stockholm University, S-106 91
Stockholm, Sweden

Correspondence e-mail: andreasf@inorg.su.se

Key indicators

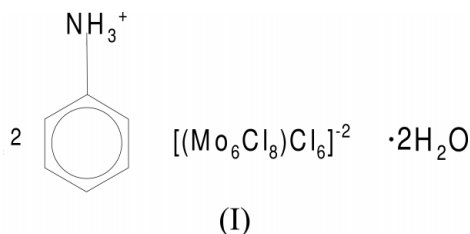
Single-crystal X-ray study
 $T = 293\text{ K}$
Mean $\sigma(\text{C}-\text{C}) = 0.011\text{ \AA}$
 R factor = 0.029
 wR factor = 0.062
Data-to-parameter ratio = 13.9For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.Dianilinium tetradecachlorohexamolybdate
dihydrate, $(\text{PhNH}_3)_2[(\text{Mo}_6\text{Cl}_8)\text{Cl}_6]\cdot 2\text{H}_2\text{O}$ The title compound, $(\text{C}_6\text{H}_8\text{N})_2[(\text{Mo}_6\text{Cl}_8)\text{Cl}_6]\cdot 2\text{H}_2\text{O}$, the anilinium salt of an Mo^{VI} chloride cluster, shows a rigid and stable hydrogen-bonded network. The chloromolybdate cluster dianion occupies a special position on a twofold axis.

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Comment

The title compound, (I), represents the dihydrate of the anilinium salt of the tetradecachloromolybdate dianion, $(\text{PhNH}_3)_2[(\text{Mo}_6\text{Cl}_8)\text{Cl}_6]\cdot 2\text{H}_2\text{O}$ (Figs. 1 and 2). It has been investigated as part of a project aimed at the synthesis of extended molecular assemblies based on the $[(\text{Mo}_6\text{Cl}_8)\text{Cl}_6]^{2-}$ clusters.

On crystallization of the title compound, the pH of the mother liquor was < 0.3 , which implies that equilibrium should be shifted towards protonation of aniline rather than water molecules. In order to confirm this, fluorescence emission spectra were obtained. The neutral aniline species is known to exhibit pronounced emission at 310–400 nm. However, the emission spectrum of the title compound, recorded in the aniline wavelength, shows only the water Raman peak, coinciding with the position of the peak observed in the spectrum of pure $(\text{H}_3\text{O})_2[(\text{Mo}_6\text{Cl}_8)\text{Cl}_6]\cdot 7\text{H}_2\text{O}$. In compounds containing the central $(\text{Mo}_6\text{Cl}_8)^{4+}$ cluster unit, it is the Mo core which is responsible for the emission (Maverick & Gray, 1981) and this does not change when different counter-ions are introduced into the crystal structures. This confirms that aniline exists in this structure as the protonated anilinium cation.

The chloromolybdate cluster dianion occupies a special position on a twofold axis. The negatively charged clusters are linked together along the b direction of the crystal through hydrogen bonds involving the water molecules. Hydrogen bonds involving the anilinium cations link the clusters along the a direction. The $-\text{NH}_3\cdots\text{H}_2\text{O}$ hydrogen bonding completes the three-dimensional hydrogen-bonding framework [Fig. 3(a)–(c)]. Similar hydrogen-bonding systems involving $[(\text{Mo}_6\text{Cl}_8)\text{Cl}_6]^{2-}$ clusters (Fig. 3d) have been observed earlier (Flemström *et al.*, 2002).

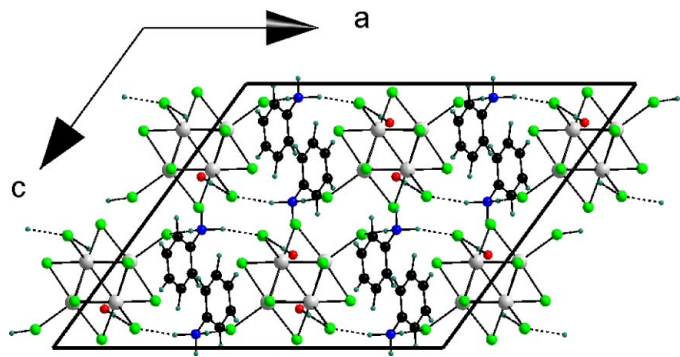


Figure 1
The structure of $(\text{PhNH}_3)_2[(\text{Mo}_6\text{Cl}_8)\text{Cl}_6]\cdot 2\text{H}_2\text{O}$, viewed along the $[010]$ direction. Red atoms: water oxygen, blue: nitrogen, black: carbon and grey: molybdenum.

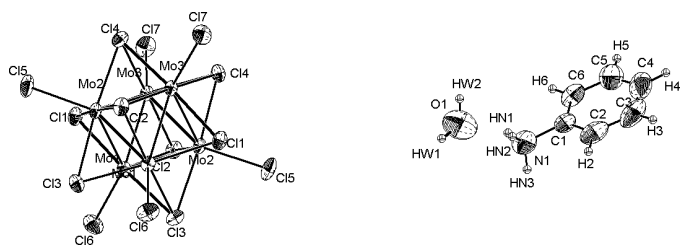


Figure 2
The cation, anion and water molecule in the crystal structure of the title compound. Displacement ellipsoids are drawn at the 50% probability level.

Experimental

The title compound was synthesized by dripping 2 ml of commercial aniline into 20 ml of a hot (360 K) saturated solution of $(\text{H}_3\text{O})_2[(\text{Mo}_6\text{Cl}_8)\text{Cl}_6]\cdot 7\text{H}_2\text{O}$ (Flemström *et al.*, 2002) in 1 M HCl. After 24 h at 280 K, cognac-colored, parallelepiped-shaped crystals precipitated. A well-shaped crystal was chosen and glued on a glass fibre.

Crystal data

$(\text{C}_6\text{H}_8\text{N})_2[(\text{Mo}_6\text{Cl}_8)\text{Cl}_6]\cdot 2\text{H}_2\text{O}$
 $M_r = 1296.24$
 Monoclinic, $C2/c$
 $a = 20.665$ (8) Å
 $b = 11.335$ (3) Å
 $c = 17.347$ (6) Å
 $\beta = 126.21$ (5)°
 $V = 3278.5$ (28) Å³
 $Z = 4$

$D_x = 2.626$ Mg m⁻³
 Mo $K\alpha$ radiation
 Cell parameters from 5000 reflections
 $\theta = 4.1\text{--}28.3^\circ$
 $\mu = 3.38$ mm⁻¹
 $T = 293$ K
 Parallelepiped, cognac brown
 $0.3 \times 0.2 \times 0.1$ mm

Data collection

Stoe IPDS diffractometer
 φ scans
 Absorption correction: numerical (*X-SHAPE*; Stoe & Cie, 1996)
 $T_{\min} = 0.463$, $T_{\max} = 0.634$
 8558 measured reflections
 2368 independent reflections

1908 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.049$
 $\theta_{\text{max}} = 23.9^\circ$
 $h = -23 \rightarrow 23$
 $k = -12 \rightarrow 12$
 $l = -18 \rightarrow 18$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.029$
 $wR(F^2) = 0.062$
 $S = 1.37$
 2368 reflections
 170 parameters

H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.02P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 0.58$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.57$ e Å⁻³

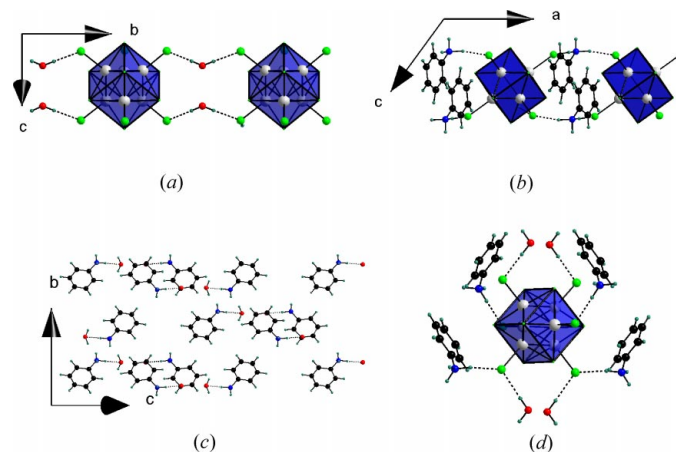


Figure 3
 (a) Infinite chains along the b direction involving hydrogen-bonded water molecules and anionic clusters. (b) Infinite chains along the a direction involving hydrogen-bonded anilinium cations and anionic clusters. (c) $\text{NH}_3\cdots\text{H}_2\text{O}$ hydrogen bonding viewed down the a direction, with the anionic clusters omitted. (d) The hydrogen-bond arrangement around the anionic clusters.

Table 1
Hydrogen-bonding geometry (Å, °).

$D\text{--}H\cdots A$	$D\text{--}H$	$H\cdots A$	$D\cdots A$	$D\text{--}H\cdots A$
$\text{N1--HN1}\cdots\text{O1}$	0.89	1.96	2.810 (13)	160
$\text{N1--HN2}\cdots\text{Cl6}^i$	0.89	2.34	3.229 (6)	174
$\text{N1--HN3}\cdots\text{Cl5}^{ii}$	0.89	2.32	3.174 (6)	161
$\text{O1--HW1}\cdots\text{Cl6}^{iii}$	0.90	2.56	3.321 (8)	143
$\text{O1--HW2}\cdots\text{Cl7}^{iv}$	0.90	2.32	3.165 (8)	155

Symmetry codes: (i) $\frac{1}{2} - x, y - \frac{1}{2}, -\frac{1}{2} - z$; (ii) $x, y, z - 1$; (iii) $x, 1 - y, z - \frac{1}{2}$; (iv) $x, -y, z - \frac{1}{2}$.

The H atoms were placed geometrically. All phenyl H atoms were included in the refinement in the riding-motion approximation. Preliminary positions for the H atoms of the water molecule were generated on the $\text{O}\cdots\text{Cl}$ vector, while for the corresponding positions of the amine H atoms, the $\text{N}\cdots\text{Cl}$ and $\text{N}\cdots\text{O}$ vectors were used. Atoms HW1 and HW2 were restrained in the refinement so that O1--HW1 was 0.90 (2) Å and $\text{HW1}\cdots\text{HW2}$ was 1.43 (2) Å. NH_3 was refined as a rigid group.

Data collection: *IPDS Software* (Stoe & Cie, 1997); cell refinement: *IPDS Software*; data reduction: *IPDS Software*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997) and *JANA2000* (Petricek & Dusek, 2000); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997) and *JANA2000*; molecular graphics: *DIAMOND* (Bergerhoff, 1999); software used to prepare material for publication: *SHELXL97* and *JANA2000*.

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