

METAL-ORGANIC COMPOUNDS

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Hydrogen-Bonded Self-Assembly of Tris(2-ammonioethyl)amine Molybdate Hydrate, $4[\text{N}(\text{CH}_2\text{CH}_2\text{NH}_3)_3]^{3+} \cdot 6[\text{MoO}_4]^{2-} \cdot 6\text{H}_2\text{O}$

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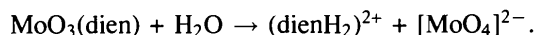
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Abstract

The title compound consists of a three-dimensional network of cations, anions and water molecules linked through hydrogen bonding in which all available hydrogen-bond donors are utilized. In four of the tetrahedral $[\text{MoO}_4]^{2-}$ anions, one O atom is hydrogen bonded with the three protonated groups of a cation. The other O atoms in these four $[\text{MoO}_4]^{2-}$ anions and those of the remaining two $[\text{MoO}_4]^{2-}$ anions are all involved as acceptors in either $\text{O}-\text{H} \cdots \text{O}$ [2.713 (4)–2.865 (4) Å] or $\text{N}-\text{H} \cdots \text{O}$ [2.656 (5)–2.989 (4) Å] hydrogen bonds with water molecules or adjacent cations. The mean Mo—O distance increases with the number of hydrogen bonds for which the O atom acts as an acceptor [1.728 (10), 1.758 (6) and 1.774 (8) Å for one, two and three hydrogen bonds, respectively].

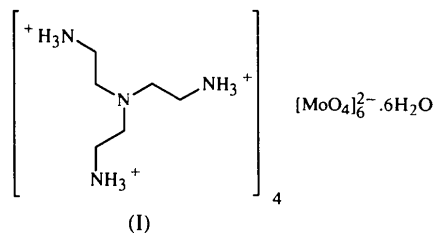
Comment

The transformation of molybdenum trioxide in aqueous solution to the more soluble $[\text{MoO}_4]^{2-}$ anion is of interest because the latter form is that in which the molybdenum is subsequently incorporated into essential molybdo-enzyme systems from its natural aqueous environment (Stiefel, 1977). In an earlier study of the interaction of solid MoO_3 with polydentate amines, the reaction product with diethylenetriamine (dien) was formulated as the neutral adduct $\text{MoO}_3(\text{dien})$ (Marzluff, 1964); the *fac*-octahedral geometry, with $\text{N}-\text{Mo}-\text{N}$ 75° (average) and $\text{O}-\text{Mo}-\text{O}$ 106° (average), was confirmed by X-ray analysis (Cotton & Elder, 1964). Later work (Taylor, Gans, Knowles & Sykes, 1974) indicated that $\text{MoO}_3(\text{dien})$ undergoes extensive protonation in aqueous solution:



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We now report that tris(2-aminoethyl)amine (tren), a potentially tetradentate amine, undergoes hydrogen-bonded self-assembly with solid MoO_3 in aqueous solution to form $(\text{trenH}_3)_4^{3+} \cdot 6[\text{MoO}_4]^{2-} \cdot 6\text{H}_2\text{O}$, (I).



Although formed even when a 1:1 ratio of tren:MoO₃ is employed, the colourless ionic solid is produced in greatest yield (89%) when the tren:MoO₃ ratio is 2:3. Strong hydrogen bonding within the compound is indicated by the presence of an intense broad infrared band due to $\nu(\text{O}-\text{H})$ and $\nu(\text{N}-\text{H})$ (in the range 3400–2100 cm^{-1}) and displacement of the strong $\nu(\text{Mo}=\text{O})$ peak to 810 cm^{-1} (from 940 cm^{-1} in $[\text{MoO}_4]^{2-}$). ¹H NMR spectroscopy in D₂O shows a singlet at δ 4.73 p.p.m., assigned to HDO produced by exchange, and triplets at δ 3.08 and 2.75 p.p.m., assigned to the methylene protons; the ¹H NMR peaks observed for tren itself in D₂O occur at δ 4.78, 2.65 and 2.49 p.p.m. These data did not allow us to distinguish between ionic and neutral formulations of the product.

The crystal structure analysis shows that the solid material contains protonated $(\text{trenH}_3)^{3+}$ cations, tetrahedral $[\text{MoO}_4]^{2-}$ anions and water molecules in a 4:6:6 ratio in the asymmetric unit; these moieties are all linked by an extensive three-dimensional hydrogen-bonded network which utilizes all available hydrogen bond donors. All H atoms in the asymmetric unit were clearly visible in difference maps and were allowed for as riding atoms.

There are four distinct cation–anion hydrogen-bonded pairs in the asymmetric unit of (I); one of these is shown in Fig. 1. In each of these, one O atom ($\text{O}i1$, $i = 1-4$) is hydrogen bonded with the three protonated groups of a $(\text{trenH}_3)^{3+}$ cation [$\text{N}(\text{H}) \cdots \text{O}$ 2.739 (4)–2.832 (4) Å]; the mean non-bonding distance between such an O atom and the central N of the cation to which it is triply hydrogen-bonded is 3.27 (4) Å. The other O atoms in these four $[\text{MoO}_4]^{2-}$ anions and those of the remaining two $[\text{MoO}_4]^{2-}$ anions are all involved as acceptors in either $\text{O}-\text{H} \cdots \text{O}$ [2.713 (4)–2.865 (4) Å] or $\text{N}-\text{H} \cdots \text{O}$ [2.656 (5)–2.989 (4) Å] hydrogen bonds with water molecules or adjacent $(\text{trenH}_3)^{3+}$ cations. The hydrogen-bonding pattern is completed by additional $\text{O}-\text{H} \cdots \text{O}$ hydrogen bonds between water molecules [$\text{O} \cdots \text{O}$ 2.834 (4)–2.947 (5) Å].

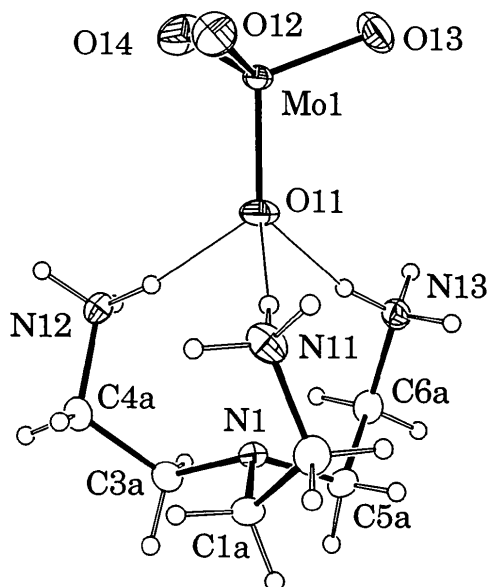


Fig. 1. A view of one of the cation-anion hydrogen-bonded pairs in (I), showing the atom-numbering scheme used. The non-H atoms are shown as displacement ellipsoids drawn at the 30% probability level. For clarity, H atoms are drawn as small spheres of arbitrary size.

The O—Mo—O angles in (I) range from 106.6 (1) to 112.2 (1)°; these distortions from tetrahedral symmetry can be attributed to hydrogen bonding to water molecules and individual protonated amine groups. As might be expected, there is a trend in the Mo—O distances; the more hydrogen bonds formed by the molybdate oxygen as an acceptor, the longer is the Mo—O bond. The mean Mo—O distances are 1.728 (10), 1.758 (6) and 1.774 (8) for formation of one, two and three hydrogen bonds, respectively. In ethylenediammonium molybdate, (H₃N—CH₂—CH₂—NH₃)²⁺·[MoO₄]²⁻ (Bensch, Hug, Emmenegger, Reller & Oswald, 1987), a molybdate anion [with Mo—O distances 1.748 (3), 1.753 (3), 1.763 (3) and 1.768 (3) Å] is hydrogen bonded to ethylenediammonium cations; the O atoms associated with the two shorter bonds each take part in one N—H···O hydrogen bond and those with the two longer ones take part in two.

In the (trenH₃)³⁺ cations the central N atoms, which are not involved in hydrogen bonding, have pyramidal geometry with average C—N—C 110.9 (7)° and average C—N 1.472 (5) Å. Other mean bond distances [C—C 1.515 (6), C—NH₃⁺ 1.482 (7) Å] and angles within the amine moieties are all normal. The N—C—N torsion angles have close to *gauche* values [range 62.8 (4)–68.8 (5), mean 65 (2)°].

Experimental

The compound (I) was synthesized by refluxing a suspension of molybdenum trioxide (6 mmol) in a solution of tren

(4 mmol) in 12 ml of deionized water until a pale yellow solution was obtained. Dropwise addition of the cooled solution to 60 ml of rapidly stirred absolute ethanol gave a white solid (1.47 g; 89% yield). Dissolving the white powder in deionized water, adding ethanol until the solution was turbid and cooling in a refrigerator gave crystals suitable for the X-ray analysis.

Crystal data

4(C₆H₂₁N₄)₆[MoO₄]₆·
6H₂O
M_r = 1664.74
Monoclinic
*P*2₁/*n*
a = 16.374 (2) Å
b = 20.082 (2) Å
c = 19.137 (5) Å
β = 90.610 (10)°
V = 6292 (2) Å³
Z = 4
D_x = 1.757 Mg m⁻³

Mo *Kα* radiation

λ = 0.71069 Å

Cell parameters from 25 reflections

θ = 9.00–20.50°

μ = 1.22 mm⁻¹

T = 293 K

Block

0.27 × 0.25 × 0.24 mm

Colourless

Data collection

Enraf-Nonius CAD-4 diffractometer

θ/*2θ* scans

Absorption correction:

empirical (nine *ψ* scans, 4° steps)

T_{min} = 0.495, *T_{max}* = 0.620

14 084 measured reflections

13 688 independent reflections

11 057 observed reflections

[*I* > 3.0σ(*I*)]

R_{int} = 0.018

θ_{max} = 26.92°

h = -20 → 20

k = 0 → 25

l = 0 → 24

3 standard reflections

frequency: 60 min

intensity decay: 2.5%

Refinement

Refinement on *F*

R = 0.030

wR = 0.045

S = 1.25

11 057 reflections

686 parameters

C—H, N—H and O—H = 0.95 Å

w = 1/[σ²(*F*) + 0.0008*F*²]

(Δ/σ)_{max} = 0.007

Δ*ρ*_{max} = 0.85 e Å⁻³

Δ*ρ*_{min} = -0.73 e Å⁻³

Extinction correction:

Larson (1970)

Extinction coefficient:

2472 (314)

Atomic scattering factors

from *International Tables*

for *X-ray Crystallography*

(1974, Vol. IV, Table

2.2B)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²)

Molybdate O atoms are numbered O*i*1–O*i*4 (*i* = 1–6); O atoms of water molecules are O1–O6. *U*_{eq} = (1/3)Σ_{*i*}Σ_{*j*}*U*_{*ij*}*a*_{*i*}^{*}*a*_{*j*}^{*}.

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq}
Mo1	0.93116 (2)	0.62372 (1)	0.17245 (1)	0.0244 (1)
Mo2	1.12131 (2)	0.82552 (1)	0.32474 (1)	0.0268 (1)
Mo3	0.07086 (2)	0.39263 (1)	0.32872 (1)	0.0270 (1)
Mo4	0.60273 (2)	0.66249 (1)	0.33249 (1)	0.0267 (1)
Mo5	0.29051 (2)	0.60533 (1)	0.26958 (1)	0.0246 (1)
Mo6	0.73040 (2)	0.38788 (1)	0.22626 (2)	0.0248 (1)
O11	0.93392 (16)	0.62361 (13)	0.26564 (12)	0.0396 (14)
O12	0.84946 (16)	0.67307 (15)	0.14424 (15)	0.0520 (15)
O13	1.02158 (16)	0.65678 (15)	0.14075 (15)	0.0523 (15)
O14	0.9180 (2)	0.54328 (14)	0.14220 (15)	0.0619 (19)

O21	1.11853 (17)	0.83144 (13)	0.23236 (12)	0.0445 (14)	Mo3—O32	1.720 (3)	Mo6—O62	1.766 (2)
O22	1.19033 (16)	0.88370 (12)	0.36049 (14)	0.0451 (14)	Mo3—O33	1.731 (3)	Mo6—O63	1.723 (3)
O23	1.1504 (2)	0.74540 (13)	0.34872 (17)	0.070 (2)	Mo3—O34	1.714 (3)	Mo6—O64	1.755 (2)
O24	1.02439 (18)	0.83987 (17)	0.35495 (17)	0.0691 (19)				
O31	0.07991 (17)	0.38274 (13)	0.23692 (12)	0.0414 (14)	N11...O11	2.781 (4)	N33...O14 ^v	2.757 (4)
O32	-0.00736 (19)	0.44638 (19)	0.34851 (19)	0.081 (2)	N11...O44	2.731 (4)	N33...O31	2.819 (4)
O33	0.16025 (18)	0.4262 (2)	0.36264 (17)	0.088 (3)	N11...O62 ⁱ	2.805 (4)	N33...O64 ^v	2.721 (4)
O34	0.0510 (3)	0.31773 (13)	0.36805 (18)	0.105 (3)	N12...O11	2.817 (4)	N41...O3 ^{iv}	2.803 (5)
O41	0.59605 (16)	0.65477 (17)	0.23964 (12)	0.0399 (14)	N12...O32 ⁱⁱ	2.680 (4)	N41...O41	2.786 (4)
O42	0.53216 (17)	0.72042 (14)	0.36103 (15)	0.0530 (15)	N12...O61	2.849 (3)	N41...O61	2.853 (4)
O43	0.5808 (2)	0.58578 (14)	0.37115 (15)	0.063 (2)	N13...O11	2.792 (4)	N42...O12	2.803 (4)
O44	0.69974 (17)	0.68671 (18)	0.35770 (17)	0.071 (2)	N13...O23	2.749 (4)	N42...O41	2.832 (4)
O51	0.31600 (15)	0.68367 (12)	0.23432 (13)	0.0396 (13)	N13...O53 ⁱⁱⁱ	2.802 (4)	N42...O64 ⁱ	2.847 (4)
O52	0.2945 (2)	0.60795 (16)	0.35910 (15)	0.067 (2)	N21...O5 ⁱ	2.954 (5)	N43...O34 ⁱⁱⁱ	2.656 (5)
O53	0.19136 (14)	0.58371 (13)	0.24095 (14)	0.0421 (13)	N21...O21	2.806 (4)	N43...O41	2.760 (4)
O54	0.35773 (17)	0.54360 (14)	0.23901 (15)	0.0548 (16)	N21...O62 ⁱ	2.719 (4)	N43...O51	2.840 (4)
O61	0.71739 (15)	0.46592 (11)	0.26805 (13)	0.0374 (13)	N22...O13	2.798 (4)	O1...O43	2.713 (4)
O62	0.65988 (14)	0.32783 (12)	0.25576 (13)	0.0377 (12)	N22...O21	2.739 (4)	O1...O61	2.865 (4)
O63	0.7226 (2)	0.39946 (15)	0.13723 (14)	0.0579 (18)	N22...O51 ⁱⁱⁱ	2.936 (4)	O2...O22 ^{iv}	2.766 (4)
O64	0.82801 (14)	0.35754 (13)	0.24772 (14)	0.0445 (14)	N23...O21	2.783 (4)	O2...O54	2.786 (4)
O1	0.63750 (18)	0.46184 (14)	0.40043 (14)	0.0518 (16)	N23...O33 ⁱ	2.658 (4)	O3...O2 ⁱ	2.947 (5)
O2	0.3642 (2)	0.50795 (14)	0.09851 (15)	0.0584 (19)	N23...O54 ⁱ	2.989 (4)	O3...O24	2.778 (5)
O3	0.9664 (2)	0.95917 (18)	0.4086 (2)	0.090 (3)	N31...O31	2.810 (4)	O4...O2 ⁱⁱⁱ	2.920 (4)
O4	0.7191 (2)	0.39589 (16)	-0.00812 (17)	0.069 (2)	N31...O42 ⁱⁱⁱ	2.717 (4)	O4...O63	2.782 (4)
O5	0.5022 (2)	0.48762 (17)	0.2867 (3)	0.105 (3)	N31...O51 ⁱⁱⁱ	2.902 (4)	O5...O43	2.848 (5)
O6	0.2742 (2)	0.61820 (18)	0.50301 (16)	0.074 (2)	N32...O22 ^{iv}	2.842 (4)	O5...O54	2.765 (4)
N1	0.93192 (15)	0.62174 (13)	0.43420 (13)	0.0251 (12)	N32...O31	2.773 (4)	O6...O1 ^{viii}	2.834 (4)
N11	0.85871 (17)	0.72417 (15)	0.34134 (16)	0.0377 (15)	N32...O53	2.777 (3)	O6...O52	2.785 (4)
N12	0.85642 (16)	0.51995 (13)	0.33863 (14)	0.0320 (13)				
N13	1.07924 (16)	0.62150 (14)	0.34323 (15)	0.0327 (13)				
N2	1.10646 (16)	0.83586 (13)	0.06286 (14)	0.0283 (13)				
N21	0.97021 (17)	0.85117 (15)	0.16055 (15)	0.0366 (15)				
N22	1.16994 (18)	0.72482 (15)	0.15513 (16)	0.0392 (15)				
N23	1.17979 (18)	0.93798 (15)	0.15607 (17)	0.0424 (16)				
N3	0.07533 (15)	0.38332 (12)	0.06285 (13)	0.0239 (12)				
N31	0.12073 (18)	0.27060 (14)	0.15673 (15)	0.0363 (15)				
N32	0.17427 (17)	0.46990 (13)	0.15964 (15)	0.0325 (13)				
N33	-0.06181 (16)	0.40760 (14)	0.15611 (15)	0.0349 (14)				
N4	0.61183 (15)	0.66288 (13)	0.06893 (13)	0.0251 (13)				
N41	0.6426 (2)	0.54463 (14)	0.16104 (16)	0.0424 (17)				
N42	0.70428 (19)	0.74222 (14)	0.17056 (15)	0.0390 (15)				
N43	0.46302 (17)	0.68812 (16)	0.15706 (16)	0.0419 (16)				
C1A	0.8811 (2)	0.67731 (17)	0.45856 (16)	0.0296 (16)				
C2A	0.8895 (2)	0.73815 (17)	0.41314 (19)	0.0371 (18)				
C3A	0.8984 (2)	0.55729 (16)	0.45689 (17)	0.0312 (16)				
C4A	0.8280 (2)	0.53449 (18)	0.41017 (19)	0.0360 (17)				
C5A	1.0167 (2)	0.62958 (18)	0.45960 (17)	0.0326 (16)				
C6A	1.07722 (19)	0.59232 (17)	0.41437 (19)	0.0339 (17)				
C1B	1.0217 (2)	0.84730 (18)	0.03996 (17)	0.0354 (17)				
C2B	0.9620 (2)	0.81775 (17)	0.0918 (2)	0.0362 (18)				
C3B	1.1352 (2)	0.76992 (18)	0.03892 (17)	0.0356 (18)				
C4B	1.2022 (2)	0.74146 (18)	0.08526 (19)	0.0400 (18)				
C5B	1.1614 (2)	0.88917 (18)	0.03918 (19)	0.0399 (18)				
C6B	1.1522 (3)	0.95090 (19)	0.0844 (2)	0.049 (2)				
C1C	0.0941 (2)	0.31569 (16)	0.03872 (16)	0.0289 (15)				
C2C	0.1547 (2)	0.28050 (17)	0.08519 (19)	0.0354 (17)				
C3C	0.13805 (19)	0.43121 (16)	0.04044 (16)	0.0291 (15)				
C4C	0.1437 (2)	0.49022 (17)	0.08990 (19)	0.0356 (17)				
C5C	-0.00619 (19)	0.40475 (16)	0.03832 (16)	0.0298 (16)				
C6C	-0.07244 (19)	0.37885 (17)	0.08551 (19)	0.0334 (18)				
C1D	0.6343 (2)	0.59641 (17)	0.04487 (18)	0.0347 (17)				
C2D	0.6889 (2)	0.56124 (17)	0.0973 (2)	0.0407 (19)				
C3D	0.6739 (2)	0.71237 (17)	0.04885 (17)	0.0338 (17)				
C4D	0.6783 (2)	0.76880 (18)	0.1014 (2)	0.0412 (19)				
C5D	0.5306 (2)	0.68356 (18)	0.04265 (17)	0.0350 (17)				
C6D	0.4622 (2)	0.65639 (18)	0.0874 (2)	0.041 (2)				

Table 2. Selected bond and contact distances (Å)

Mo1—O11	1.784 (2)	Mo4—O41	1.786 (2)
Mo1—O12	1.746 (3)	Mo4—O42	1.732 (3)
Mo1—O13	1.738 (3)	Mo4—O43	1.748 (3)
Mo1—O14	1.729 (3)	Mo4—O44	1.725 (3)
Mo2—O21	1.772 (2)	Mo5—O51	1.764 (2)
Mo2—O22	1.759 (2)	Mo5—O52	1.714 (3)
Mo2—O23	1.738 (3)	Mo5—O53	1.762 (2)
Mo2—O24	1.719 (3)	Mo5—O54	1.762 (3)
Mo3—O31	1.776 (2)	Mo6—O61	1.773 (2)

Symmetry codes: (i) $\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$; (ii) $1 + x, y, z$; (iii) $\frac{1}{2} - x, y - \frac{1}{2}, \frac{1}{2} - z$; (iv) $\frac{3}{2} - x, y - \frac{1}{2}, \frac{1}{2} - z$; (v) $x - 1, y, z$; (vi) $\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$; (vii) $1 - x, 1 - y, -z$; (viii) $1 - x, 1 - y, 1 - z$.

Compound (I) crystallized in the monoclinic system and the $P2_1/n$ space group was determined uniquely by the systematic absences. All H atoms were clearly visible in difference synthesis maps; they were positioned geometrically and included as riding atoms in the structure-factor calculations. Fig. 1 was prepared using ORTEPII (Johnson, 1976). Examination of the structure with PLATON94 (Spek, 1994) showed that there were no solvent accessible voids in the crystal lattice. Data collection and cell refinement were performed using CAD-4-PC Software (Enraf-Nonius, 1992). The NRCVAX (Gabe, Le Page, Charland, Lee & White, 1989) program package was used for data reduction, structure solution and refinement, and to prepare material for publication.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: AB1214). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Cs₆Cl₃[Fe(CN)₆].H₂O: a Mixed-Anion Salt

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Abstract

Hexacaesium trichloride hexacyanoferrate(III) monohydrate, Cs₆Cl₃[Fe(CN)₆].H₂O, is a novel type of compound which contains two different anions. The crystal structure consists of alternating layers, *A* {Cs⁺, Cl⁻, [Fe(CN)₆]³⁻, H₂O} and *B* (Cs⁺, Cl⁻), stacked perpendicularly to the *b* axis. The octahedral complex ion has *m* point symmetry. The water molecules of solvation are disordered and form hydrogen bonds (O—H...Cl and O—H...N) within layer *A*. The Cs⁺ ions have coordination numbers six to eight.

Comment

Potassium hexacyanoferrate(III), K₃[Fe(CN)₆], has been studied extensively by different techniques because of its interesting properties, such as the existence of polytypes (Vannerberg, 1972; Figgis, Skelton & White, 1978; Murgich & Oja, 1987; Murgich, 1994), one-dimensional disorder (Murgich & Oja, 1987), the possible existence of incommensuration in the low-temperature phase (Murgich & Oja, 1987), *etc.* In addition, the crystal and magnetic structures, phase transitions and spectroscopic data of several mixed-cation salts, such as Cs₂M[Fe(CN)₆] (*M* = Li, Na, K) have been determined (Jones, Swanson & Kubas, 1974; Fletcher & Gibb, 1977; Swanson, Lucas & Ryan, 1977; Daul *et al.*, 1988).

As a part of a study on the effects of different cations on the structure and properties of hexacyanoferrate(III), the preparation of the Cs₃[Fe(CN)₆] salt was attempted, following the synthesis of Garg & Goel (1970). Microscopic examination of the resultant product showed

two different types of crystals, orange–yellow prisms and yellow needles, neither of which turned out to be the target compound. A crystal structure determination of the orange–yellow prisms revealed that they were Cs₂K[Fe(CN)₆], already studied by several authors (Fletcher & Gibb, 1977; Herren & Ludi, 1979; Figgis, Kucharski, Raynes & Reynolds, 1990). This paper reports the structure of the mixed salt Cs₆Cl₃[Fe(CN)₆].H₂O that forms the yellow needles.

The crystal structure of the title compound contains Cs⁺, Cl⁻ and [Fe(CN)₆]³⁻ ions and disordered water molecules of solvation. Some of the Cs⁺ and Cl⁻ ions lie on the mirror plane (*y* = $\frac{1}{4}$, Wyckoff *c* sites). Since the N(1)C(1)FeC(2)N(2) axis of [Fe(CN)₆]³⁻ also lies on the mirror plane, the octahedral complex has *m* crystallographic point symmetry.

The average values of the Fe—C (1.941 Å) and C—N (1.15 Å) bond lengths are in good agreement with the mean values of 1.937 and 1.146 Å compiled by Orpen *et al.* (1989). All four independent Fe—C distances are equal within three e.s.d.'s. The differences between the C—N bond lengths are somewhat larger (up to five e.s.d.'s), but probably not significant. The octahedral geometry of the [Fe(CN)₆]³⁻ ion is moderately distorted. All of the C—Fe—C and Fe—C—N angles are within 5° of 90 or 180°, but their values depart significantly from the nominal values.

The O(1*w*) atom of the water molecule is close (0.68 Å) to the mirror plane and was given an occupancy of 0.5, because both of the mirror-related positions are mutually exclusive. The largest residual electron density peak (1.4 e Å⁻³) is located on the mirror plane between the symmetry-related O(1*w*) atoms (the next largest peak is of a magnitude similar to that of the most negative peak).

The Cs⁺ and Cl⁻ ions are spherical and of similar sizes, but the [Fe(CN)₆]³⁻ ion has a more complex shape, with six protruding arms, which may produce voids in the crystal structure. The water molecule fills one of these voids, which is somewhat larger than the volume of the water molecule and allows disorder. The actual disorder of the solvent molecules is caused by their hydrogen bonding. One of the hydrogen bonds is to Cl(1), which lies on the mirror plane and is unique, but the other one is directed to N(4), which has two equally accessible mirror-related positions. The location of the water molecule on either side of the mirror plane is determined by this second hydrogen bond and therefore a 50–50% distribution is expected.

Each of the four Cs⁺ ions is surrounded by six to eight negatively charged atoms (O, N and Cl⁻). The neighbouring atoms form irregular polyhedra, with distances in the ranges 2.99–3.35 for Cs⁺...O, 3.17–3.61 for Cs⁺...N and 3.41–3.75 Å for Cs⁺...Cl⁻. These values are within –6.3 to 10.7% of the sums of the respective radii [Cl⁻ and Cs⁺ (CN = 6, 8) from