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Key indicators

Single-crystal X-ray study
 $T = 293$ K
Mean $\sigma(\text{C}-\text{C}) = 0.018$ Å
H-atom completeness 94%
 R factor = 0.052
 wR factor = 0.103
Data-to-parameter ratio = 21.0For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

A new chalcocyanide cubane rhenium salt: tetrakis(tetraphenylphosphonium) dodecacyano-hexahedro-telluriumtetrarhenate(IV) trihydrate

The new title cubane cluster salt, $(\text{C}_{24}\text{H}_{20}\text{P})_4[\text{Re}_4\text{Te}_4(\text{CN})_{12}] \cdot 3\text{H}_2\text{O}$, was obtained by the reaction of $\text{Ph}_4\text{P}\text{Cl}$ and $\text{K}_4\text{Re}_4\text{Te}_4(\text{CN})_{12}$ in a water/acetonitrile solution. It is isostructural with the previously described phases $(\text{Ph}_4\text{P})_4[\text{Re}_4\text{Q}_4(\text{CN})_{12}] \cdot 3\text{H}_2\text{O}$ ($\text{Q} = \text{S}, \text{Se}$) and contains Ph_4P^+ cations and $[\text{Re}_4\text{Te}_4(\text{CN})_{12}]^{4-}$ anions. The $[\text{Re}_4\text{Te}_4(\text{CN})_{12}]^{4-}$ anion contains a tetrahedral cluster of Re atoms and a triply bridging Te atom attached to each face of the tetrahedron.

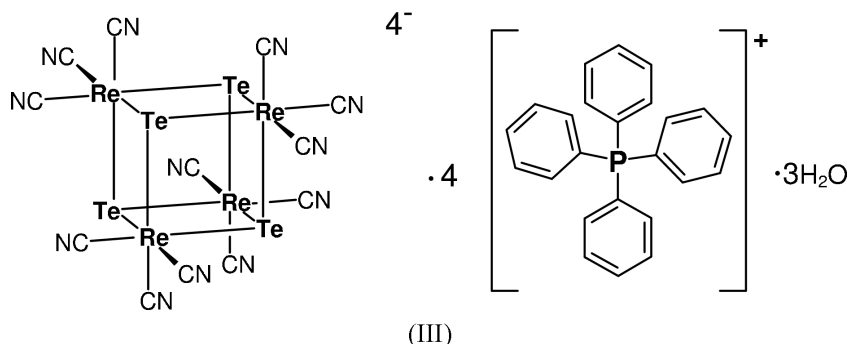
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Comment

The first cubane rhenium clusters were obtained by Griffith and co-workers (Laing *et al.*, 1977). In trying to repeat the preparation of $[\text{Re}(\text{CN})_6]^-$ salts from $\text{K}_2[\text{ReCl}_6]$ in a KSCN melt with excess KCN, they obtained salts of $[\text{Re}(\text{CN})_7]^{4-}$ mixed with those of empirical formula $[\text{ReS}(\text{CN})_3]^-$. Substitution of KSeCN for KSCN gave $[\text{ReSe}(\text{CN})_3]^-$. Crystals obtained by slow evaporation of a water-methanol solution in the presence of $\text{Ph}_4\text{P}\text{Cl}$ were characterized as $(\text{Ph}_4\text{P})_4[\text{Re}_4\text{Q}_4(\text{CN})_{12}] \cdot 3\text{H}_2\text{O}$ [$\text{Q} = \text{S}$ for (I) and Se for (II)]. By using $\text{K}_4\text{Re}_4\text{Te}_4(\text{CN})_{12}$ and $\text{Ph}_4\text{P}\text{Cl}$ in a water/acetonitrile solution, we have crystallized the isostructural tellurium compound $(\text{Ph}_4\text{P})_4[\text{Re}_4\text{Te}_4(\text{CN})_{12}] \cdot 3\text{H}_2\text{O}$, (III) (Fig. 1).



The structure of the $[\text{Re}_4\text{Te}_4(\text{CN})_{12}]^{4-}$ anion in (III) is similar to that of the same species in $\text{K}_4[\text{Re}_4\text{Te}_4(\text{CN})_{12}] \cdot 5\text{H}_2\text{O}$ (Mironov *et al.*, 1997). It contains an Re_4Te_4 cubane-like cluster core formed from a nearly regular Re_4 tetrahedron and one Te atom per face of this tetrahedron, with $\text{Re}-\text{Re}$ and $\text{Re}-(\mu_3\text{-Te})$ distances in the ranges 2.8707 (5)–2.8898 (5) and 2.6171 (7)–2.6426 (7) Å, respectively (Table 1). Comparing structures (I), (II) and (III), one can note an increase in the $\text{Re}-\text{Re}$ and $\text{Re}-(\mu_3\text{-Q})$ ($\text{Q} = \text{S}, \text{Se}, \text{Te}$) distances according to the increasing Q covalent radius. Each Re atom is also coordinated by three CN groups, with an average $\text{Re}-\text{C}$ distance of 2.106 (14) Å and an average $(\text{C}-\text{Re}-\text{C})$ angle of 80 (1)°. Thus, the coordination number of each Re atom is 9 if we assume direct $\text{Re}-\text{Re}$ bonds.

Although the water molecule H atoms were not located, O—H···O and O—H···N hydrogen bonds are probably present in (III), based on the proximity of the species in question (Fig. 1).

Experimental

A mixture of PPh₄Cl (30 mg, 0.08 mmol) and K₄Re₄Te₄(CN)₁₂·5H₂O (25 mg, 0.014 mmol) was dissolved in an H₂O—CH₃OH solution (10 ml, 1:1). The solution was heated until the volume reduced to about 3 ml. Dark red crystals of (III) appeared after 20 min and were filtered off and dried (yield 34 mg, 83%).

Crystal data

(C₂₄H₂₀P)₄[Re₄Te₄(CN)₁₂]·3H₂O
M_r = 2978.97
 Monoclinic, *P*₂₁/*n*
a = 15.4635 (8) Å
b = 24.1703 (11) Å
c = 28.5358 (11) Å
 β = 105.181 (1)°
V = 10293.3 (8) Å³
Z = 4
D_x = 1.922 Mg m⁻³
 Mo Kα radiation
 Cell parameters from 3070 reflections
 θ = 2.2–19.5°
 μ = 5.92 mm⁻¹
T = 293 (2) K
 Needle, dark red
 0.10 × 0.04 × 0.02 mm

Data collection

Bruker–Nonius X8APEX CCD diffractometer
 φ scans
 Absorption correction: multi-scan (SADABS; Bruker, 2004)
T_{min} = 0.753, *T_{max}* = 0.888
 76502 measured reflections
 25536 independent reflections
 11085 reflections with *I* > 2σ(*I*)
R_{int} = 0.062
 θ_{max} = 28.3°
h = -20 → 19
k = -28 → 32
l = -22 → 38

Refinement

Refinement on *F*²
R [*F*² > 2σ(*F*²)] = 0.052
wR (*F*²) = 0.103
S = 0.80
 25536 reflections
 1216 parameters
 H-atom parameters constrained
w = 1/[σ²(*F_o*²) + (0.0331*P*)²]
 where *P* = (*F_o*² + 2*F_c*²)/3
 (Δ/σ)_{max} = 0.002
 Δρ_{max} = 1.57 e Å⁻³
 Δρ_{min} = -1.24 e Å⁻³

Table 1

Selected bond lengths (Å).

Re1—Re2	2.8820 (5)	Re4—Te1	2.6235 (7)
Re1—Re3	2.8707 (5)	Re4—Te2	2.6280 (7)
Re1—Re4	2.8898 (5)	Re4—Te3	2.6251 (7)
Re2—Re3	2.8818 (6)	Re1—C11	2.122 (10)
Re2—Re4	2.8873 (6)	Re1—C12	2.105 (11)
Re3—Re4	2.8743 (6)	Re1—C13	2.093 (10)
Re1—Te2	2.6324 (7)	Re2—C21	2.078 (10)
Re1—Te3	2.6317 (7)	Re2—C22	2.121 (11)
Re1—Te4	2.6300 (8)	Re2—C23	2.113 (12)
Re2—Te1	2.6426 (7)	Re3—C31	2.109 (12)
Re2—Te3	2.6334 (8)	Re3—C32	2.092 (10)
Re2—Te4	2.6269 (7)	Re3—C33	2.095 (10)
Re3—Te1	2.6171 (7)	Re4—C41	2.110 (11)
Re3—Te2	2.6345 (8)	Re4—C42	2.114 (10)
Re3—Te4	2.6312 (7)	Re4—C43	2.116 (10)

The structure of (III) in space group *P*₂₁/*n* can be transformed to those of (I) and (II) (space group *P*₂₁/*c*) by the transformation matrix (101, 010, $\bar{1}$ 00). H atoms of the tetraphenylphosphonium cations were placed in idealized locations and refined as riding and H atoms of the water molecules were not located. H atoms bound to carbon were

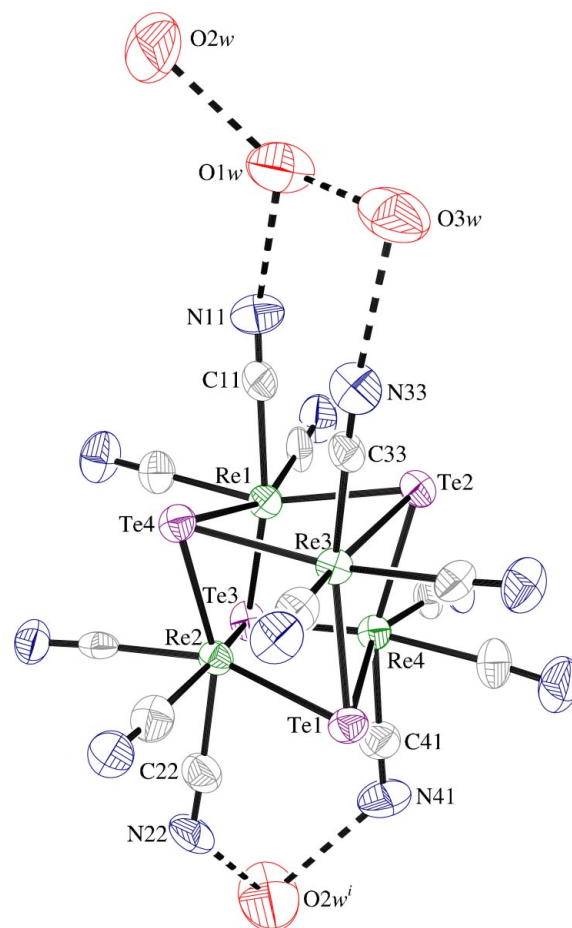


Figure 1

Detail of (III), showing the [Re₄(μ₃-Te)₄(CN)₁₂]⁴⁻ anion and nearby water O atoms (50% displacement ellipsoids). The dashed lines represent possible O—H···O and O—H···N hydrogen bonds [symmetry code: (i) $\frac{1}{2} + x, \frac{3}{2} - y, \frac{1}{2} + z$].

placed in calculated positions and allowed to ride during subsequent refinement, with *U*_{iso}(H) = 1.2*U*_{eq}(C). The maximum and minimum electron-density peaks in the final difference map were located 1.41 Å from Re4 and 0.89 Å from Re2, respectively.

Data collection: APEX2 (Bruker, 2004); cell refinement: SAINT (Bruker, 2004); data reduction: SAINT; program(s) used to solve structure: SHELXTL (Bruker, 2004); program(s) used to refine structure: SHELXTL; molecular graphics: SHELXTL; software used to prepare material for publication: SHELXTL.

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