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Synthesis and Crystal Structure of a Complex [Perrhenate-bis(1,4-dithiane 1,4-dioxide)mono(μ-1,4-dithiane 1,4-dioxide)triaquaholmium(III) polymer] perrhenate-1,4-dithiane 1,4-dioxide

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The title compound $Ho(ReO_4)_3 \cdot 4TDTD \cdot 3H_2O$ (where TDTD = 1,4-dithiane 1,4-dioxide) was synthesized and characterized by infrared and emission spectra, and its three-dimensional crystal structure was determined by X-ray diffraction techniques. The compound crystallizes in the monoclinic system, space group $P2_1/c$, $a = 17.955(3)$, $b = 17.100(6)$, $c = 12.570(3)$ Å, $\beta = 92.48(2)°$, $V = 3855(3)$ Å^3, $M = 1881.3$, $Z = 4$, $D_c = 3.241$ g cm^{-3}, λ(Mo Kα) = 0.71071 Å, $\mu = 11.41$ mm^{-1}, $F(000) = 2939.7$, $R = 0.064$, $R_w = 0.054$, for 3050 reflections with $I > 3\sigma(I)$. The Re atom is coordinated to one oxygen atom of two crystallographically independent TDTD groups (which have their other O-atom uncoordinated) and to two other independent TDTD groups which bridge between neighbouring Ho cations, giving rise to infinite chains along the *a* axis. The remaining coordination polyhedron is formed from one perrhenate and three independent O atoms from water molecules which complete a slightly distorted triangular dodecahedron of point symmetry D_{2d}.

Experimental

The hydrated perrhenate was mixed with *trans*-1,4-dithiane 1,4-dioxide (molar ratio 1:4) and the mixture dissolved in a small amount of warm water. The water was slowly evaporated to crystallize the compound, which was eventually collected and dried *in vacuo* over anhydrous calcium chloride. The isomorphous (as determined by X-ray diffraction) ytterbium complex doped with europium was prepared by the same method but using a 2 mol% of Eu. The compounds are insoluble in most common solvents (except water) and are not hygroscopic.

Lanthanide contents were determined by complexometric titration with EDTA [1], and carbon and hydrogen by usual microanalytical procedures. Infrared spectra were recorded on a Perkin-Elmer model 283 spectrophotometer using Nujol mulls between KRS-5 plates. The emission spectrum of the Eu:Yb compound was measured on a Perkin-Elmer MPF-4 spectrofluorimeter, using 394 nm excitation radiation.

A prismatic crystal of linear dimensions 0.18 × 0.18 × 0.28 mm was mounted on a CAD-4 Enraf-Nonius diffractometer. Cell dimensions and the orientation matrix were calculated by a least-squares method from 25 centered reflections in the range $12.2 < \theta < 18.4°$. Intensities were measured by ω–2θ scans using a variable scan speed between 2.8–10.0° min^{-1}. Of the 5912 reflections collected in the range $-13 < h < 13$, $-2 < k < 18$, $0 < l < 19$ (θ maximum 22°), 4712 were independent ($R_{sym} = 0.032$) and 3035 had $I < 3\sigma(I)$. The intensities of two standard reflections were essentially constant over the duration of the experiment. Data were corrected for Lorentz, polarization and absorption effects.

The structure was solved by direct and difference Fourier methods. Hydrogen atoms were introduced on stereochemical grounds and refined by the riding technique with a common fixed *B*-value of 3.95 Å^2. Least-squares minimizing $\Sigma w(|F_o| - |F_c|)^2$ with $w = 1/[\sigma^2(F_o) + 0.002\ F_o^2]$ was used. Only Ho, Re and S atoms were treated anisotropically. Final *R* factors were $R = 0.064$ and $R_w = 0.054$ for the 3050 reflections with $I > 3\sigma(I)$. A final difference map showed $\Delta\rho$ fluctuations between 0.9 and -0.8 e Å^{-3}. Scattering form factors for non-H atoms were taken from ref. 2; correction for anomalous dispersion from ref. 3; and form factors for H-atoms from ref. 4. Most calculations were performed on a Vax computer; program used: MULTAN [5], SHELX76 [6] and ORTEP [7]. Final positional parameters and isotropic *B* values are available (see 'Supplementary Material'). Interatomic distances and bond angles are given in Tables I and II.

Results and Discussion

The Ho cation is coordinated to one oxygen atom of each of two crystallographically independent TDTD groups (which have their other O atom uncoordinated) sited on general positions, and to two other independent TDTD groups, sited on centres of symmetry, which bridge between neighbouring Ho cations and give rise to infinite chains along the *a* axis. The rest of the coordination polyhedron is formed from one perrhenate and three independent O atoms from water molecules which complete a slight-

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TABLE I. Interatomic Bond Distances (Å) with Standard Deviations in Parentheses

Ho–O(1)	2.38(2)
Ho–O(2)	2.46(2)
Ho–O(3)	2.30(2)
Ho–O(11)	2.29(2)
Ho–O(21)	2.31(2)
Ho–O(31)	2.26(2)
Ho–O(41)	2.29(2)
Ho–O2(Re3)	2.46(2)
O(1)–O(2)	2.83(3)
O(1)–O(3)	2.80(3)
O(1)–O(21)	2.95(3)
O(1)–O(41)	2.61(2)
O(2)–O(3)	3.03(3)
O(2)–O(21)	2.75(3)
O(2)–O(31)	2.86(3)
O(3)–O(11)	2.76(3)
O(3)–O(31)	3.25(3)
O(3)–O(41)	3.60(3)
O(11)–O(31)	2.85(3)
O(11)–O(41)	2.91(3)
O(11)–O2(Re3)	2.81(2)
O(21)–O(31)	3.49(3)
O(21)–O(41)	3.15(3)
O(21)–O2(Re3)	2.78(3)
O(31)–O2(Re3)	2.88(3)
O(41)–O2(Re3)	2.95(3)

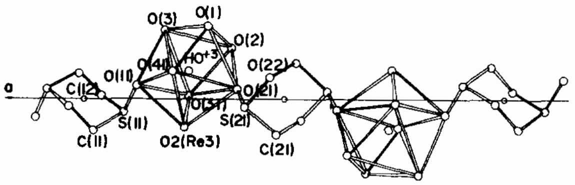

Fig. 1. Projection of the structure showing part of the infinite chain.

ly distorted triangular dodecahedron. Two other independent perrhenate and two other independent TDTD groups which are sited on symmetry centres, none of them coordinated, form the remaining structure.

The mean values for the different triangular dodecahedron edge types are close to theoretical for the 'most favourable polyhedron' of point symmetry D_{2d} ($a = 1.20$, $m = 1.17$, $g = 1.23$, $b = 1.53$) [8]. Figure 1 is a projection of the structure showing part of the infinite chain of coordination polyhedra.

The IR spectrum of the ligand shows a peak at 1015(s) cm^{-1} and a shoulder at 1020 cm^{-1}. The spectrum of the complex presents two peaks and two shoulders in this region: 1020(sh), 1000(s), 990(s) and 980(sh) cm^{-1}. The first one is consistent with the existence of free S–O groups in the structure and the several shifted peaks may be attributed to the different types of ligand coordination.

TABLE II. Bond Angles (°) with Standard Deviations in Parentheses

O(11)–S(11)–C(11)	107(1)
O(11)–S(11)–C(12)	106(1)
C(11)–S(11)–C(12)	99(1)
S(11)–C(11)–C(12)	113(1)
C(11)–C(12)–S(11)	113(1)
O(21)–S(21)–C(21)	106(1)
O(21)–S(21)–C(22)	103(1)
C(21)–S(21)–C(22)	97(1)
S(21)–C(21)–C(22)	111(1)
C(21)–C(22)–S(21)	116(1)
O(31)–S(31)–C(31)	105(1)
O(31)–S(31)–C(32)	104(1)
C(31)–S(31)–C(32)	99(1)
S(31)–C(31)–C(34)	113(1)
S(31)–C(32)–C(33)	113(1)
O(41)–S(41)–C(41)	104(1)
O(41)–S(41)–C(42)	104(1)
C(41)–S(41)–C(42)	98(1)
S(41)–C(41)–C(43)	112(1)
S(41)–C(42)–C(44)	113(1)
O(51)–S(51)–C(51)	109(1)
O(51)–S(51)–C(52)	107(1)
C(51)–S(51)–C(52)	98(1)
S(51)–C(51)–C(52)	114(1)
C(51)–C(52)–S(51)	110(1)
O(42)–S(42)–C(43)	105(1)
O(42)–S(42)–C(44)	108(1)
C(43)–S(42)–C(44)	98(1)
C(41)–C(43)–S(42)	114(1)
C(42)–C(44)–S(42)	114(1)
O(32)–S(32)–C(33)	105(1)
O(32)–S(32)–C(34)	107(1)
C(33)–S(32)–C(34)	101(1)
C(32)–C(33)–S(32)	116(1)
C(31)–C(34)–S(32)	113(1)
O(61)–S(61)–C(61)	103(1)
O(61)–S(61)–C(62)	105(1)
C(61)–S(61)–C(62)	103(1)
S(61)–C(61)–C(62)	116(1)
S(61)–C(62)–C(61)	113(1)

Bands at 907(s) and at 320(m) cm^{-1} attributed to ionic perrhenate [9] and several others attributed to coordinated perrhenate at 915(sh), 895(w), 872(w), 372(w), 362(m) and 350(w) cm^{-1} are observed. The broad band at 405 cm^{-1} may be attributed to ν-(Ln–O) of the different ligands [10].

Figure 2 shows the fluorescence spectrum of the Yb complex doped with Eu. Weak bands are observed at 77 K. It is possible to distinguish a $^5D_0 \rightarrow {}^7F_0$ band at 575 nm, peaks attributed to the $^5D_0 \rightarrow {}^7F_1$ transition (~590 nm) and a relatively intense band attributed to the $^5D_0 \rightarrow {}^7F_2$ transition (~615 nm). The existence of one band at 575 nm is only possible for C_n, C_{nv} and C_{nh} symmetries. The second band is split into two and the third into three peaks and in this case presents two small shoulders. The shape and

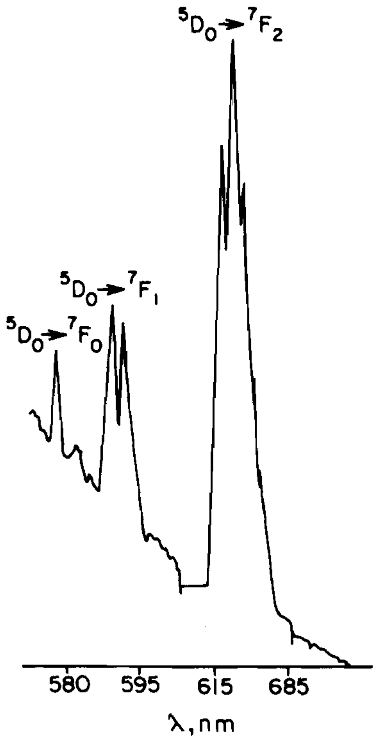

Fig. 2. Fluorescence spectrum of the ytterbium complex doped with europium.

number of bands are interpreted in terms of C_{2v} symmetry for the coordination polyhedron rather than D_{2d} [11], which indicates the sensitivity of forbidden transitions to small geometrical distortions [12].

Supplementary Material

Final positional parameters and isotropic B values are obtainable from author E.E.C. on request.

Acknowledgements

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