Pergamon

Polyhedron Vol. 14, No. 20–21, pp. 3171–3173, 1995
Copyright © 1995 Elsevier Science Ltd
Printed in Great Britain. All rights reserved
0277–5387/95 $9.50+0.00

0277–5387(95)00147–6

COMMUNICATION

SYNTHESIS AND CRYSTAL STRUCTURE OF A HEXANUCLEAR RHENIUM CLUSTER COMPLEX $Cs_3K[Re_6(\mu_3\text{-}S)_6(\mu_3\text{-}Te_{0.66}S_{0.34})_2(CN)_6]$. CATIONIC CONTROL OVER ORIENTATION OF THE CLUSTER ANION

YURI V. MIRONOV,* ALEXANDER V. VIROVETS,
VLADIMIR E. FEDOROV and NINA V. PODBEREZSKAYA,

Institute of Inorganic Chemistry, Siberian Branch of RAS, 3 Acad. Lavrentiev pr.,
Novosibirsk 630090, Russian Federation

and

OLEG V. SHISHKIN and YURI T. STRUCHKOV

X-Ray Structural Centre of RAS, 28 Vavilov str., GSP-1 Moscow 117813,
Russian Federation

(*Received* 21 *November* 1994; *accepted* 6 *April* 1995)

Abstract—The hexanuclear complex rhenium salt $Cs_3K[Re_6(\mu_3\text{-}S)_6(\mu_3\text{-}Te_{0.66}S_{0.34})_2(CN)_6]$ (**1**) has been prepared by the reaction of Re_6Te_{15} with molten KSCN and subsequent treatment with an aqueous solution of CsCl. Its crystal structure has been determined by X-ray structural analysis. The anion has the site symmetry $\bar{3}$. The Re_6 octahedron is coordinated to six μ_3-S and two *trans* mixed μ_3-X ligands of the refined composition 66(3)%Te+34(3)%S. In addition there are six almost linear terminal CN ligands in its environment. The Re—Re distances [2.630(2) Å] in the Re_3 faces capped by the μ_3-X ligands are significantly longer than those in the faces capped by the μ_3-S ligands [2.615(2) Å].

The rhenium telluride Re_6Te_{15} has long been known.[1-3] The structure of Re_6Te_{15} is characterized by the presence of the octahedral clusters and the $[Re_6X_8]L_6$ units which are celebrated in the cluster chemistry of rhenium and other early transition metals (Nb, Ta, Mo, W).

The chemical properties of rhenium telluride have remained practically unknown. One of us (V.E.F.) has previously studied the reaction of Re_6Te_{15} with bromine and obtained the cluster tellurobromide $[Re_6Te_4Br_4]Br_6$ in which the octahedral cluster was still retained.[3,4] In this work, we studied the interaction of Re_6Te_{15} with molten KSCN.

EXPERIMENTAL

Synthesis

The cluster hexanuclear rhenium salt $Cs_3K[Re_6(\mu_3\text{-}S)_6(\mu_3\text{-}Te_{0.66}S_{0.34})_2(CN)_6]$ (**1**) has been prepared by the following procedures. First, a related potassium salt was synthesized by heating in an evacuated and sealed silica tube the cluster hexanuclear rhenium telluride Re_6Te_{15} with molten KSCN (the Re_6Te_{15} : KSCN ratio was 1 : 8) at 500°C for 24 h. The resulting mixture was washed

---

* Author to whom correspondence should be addressed.

with hot ethanol for separation of the KSCN and excess KCN. The potassium salt obtained was extracted with water and the dark-red solution was filtered. The red–brown single crystals of **1** were precipitated by adding an aqueous solution of CsCl and then the solvent was slowly evaporated at 30 C.

X-ray diffraction measurements

The structure of **1** was determined by X-ray structural analysis. A red–brown single crystal of a rectangular prismatic form was obtained by precipitation from a saturated aqueous solution. The unit-cell dimensions and the reflection intensities were measured by the standard procedure.* Absorption corrections were applied by using the DIFABS program[5] (transmission = 0.841 – 1.382). The structure was solved by direct methods using the SHELXS-86 program[6] and refined by the full-matrix least-squares method with an anisotropic approximation for Cs, K, Re, Te, S atoms using the SHELXL-93 program.[7] Reflections with $F_{hkl} < 6\sigma(F)$ were omitted and the remaining reflections were used in the refinement with the calculated weighting scheme. The atomic coordinates are deposited. Selected bond lengths and angles are given in Fig. 1.

The powder diffraction measurements have been carried out on a "DRON-3M" diffractometer ($\theta/2\theta$ scan with the fixed speed 1° min^{-1}, filtered Cu-K_α radiation).

RESULTS AND DISCUSSION

Compound **1** has an ionic structure. The anion surrounded by the cations is shown in Fig. 1. It has the site symmetry $\bar{3}$ and the structure typical for $Re_6X_8L_6$ clusters.[8] The Re_6 octehedron is coordinated to six μ_3-S and two *trans* μ_3-X ligands of the refined composition 66(3)%Te+34(3)%S. An assumption on the presence of a sulpur in these positions arises from the comparison of the Re—μ_3-X [2.675(6) Å] and Re—(μ_3-Te) in Re_6Te_{15} [2.695(2) Å[2,3]] distances. In addition there are six almost linear terminal CN ligands in its environment. As a whole, compound **1** may be considered as a solid solution of *trans*-$Cs_3K[Re_6S_6Te_2(CN)_6] \cdot 0.51Cs_3K[Re_6S_8(CN)_6]$.

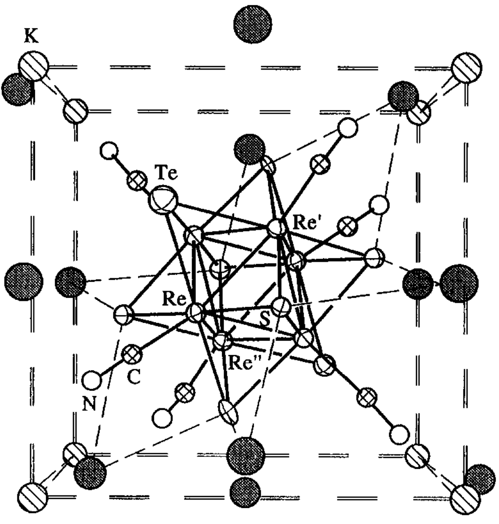

Fig. 1. The anion $[Re_6(\mu_3\text{-S})_6(\mu_3\text{-Te}_{0.66}S_{0.34})_2(CN)_6]^{4-}$ and its nearest cationic environment (1/8 part of the unit cell). The $Cs^+ \cdots (\mu_3\text{-S})$ contacts are shown as broken lines. Selected bond distances: Re—Re′, 2.615(2), Re—Re″, 2.630(2), Re—Te, 2.675(6), Re—S, 2.454(9), 2.423(9), 2.442(9), Re—C, 2.10(4), C—N, 1.19(5) Å.

The Re—Re distances in the Re_3 faces capped by the μ_3-X ligands are significantly longer than those in the faces capped by the μ_3-S ligands [2.630(3) and 2.615(2) Å, respectively]. The latter are close to the value found in Re_6S_8 clusters (av. 2.607 and 2.614 Å for $A[Re_6(\mu_3\text{-S})_8S_{2/2}(S_2)_{4/2}]$ where A = Rb_4 and A = Rb_2K_2, respectively,[9] 2.617 and 2.616 Å for $Li_4[Re_6(\mu_3\text{-S})_8S_{6/2}]$[10] and $Na_4[Re_6(\mu_3\text{-S})_8S_{4/2}(S_2)_{2/2}]$[11]). The Re—($\mu_3$-S) distances (av. 2.440 Å) differ insignificantly from those found in the compounds mentioned above (~2.40–2.44 Å).

In our opinion, the most interesting feature of **1** is the absence of full orientation disorder of the cluster anion (with S and Te uniformly distributed over all μ_3 positions), as in some other mixed-type $[Re_6X_{8-n}Y_n]$ clusters (e.g. $[Re_6(\mu_3\text{-Se})_{8-n}(\mu_3\text{-Cl})_n]$[12] or $[Re_6(\mu_3\text{-S})_{8-n}(\mu_3\text{-Cl})_n]$[13]), despite the relatively high crystallographic symmetry. We suppose that the reason for this phenomenon is the presence of the relatively short $Cs^+ \cdots (\mu_3\text{-S})$ contacts of 3.564 and 3.811 Å (Fig. 1). These contacts are permissible for sulphur (e.g. in $Cs_4[Re_6(\mu_3\text{-S})_8S_{1.45}Se_{1.35}]$, there are $Cs \cdots (\mu_3\text{-S})$ contacts of 3.31(1), 3.34(1) Å[9]) but evidently too short for Te (which has a van der Waals radius ~0.3 Å longer than S[14]). At the same time, the μ_3-X ligands have no cations closer than 4.4 Å. Therefore, it is reasonable to suggest that the

---

* $C_6Cs_3KN_6Re_6S_{6.68}Te_{1.32}$, FW = 2092.79, cubic, $a = 17.757(2)$ Å, $V = 5599(1)$ Å^3, space group *Ia*3 (No. 206), $Z = 8$, $D_x = 4.965$ g cm^{-3}, crystal size 0.15 × 0.10 × 0.09 mm, "Siemens P3/PC", λ(Mo-K_α), $\mu = 316.79$ cm^{-1}, $\theta/2\theta$ scans with $V_{min} = 2.02°$ min^{-1} up to $2\theta = 50°$ at room temperature, 4854 total and 834 independent reflections ($R_{av} = 0.0508$), $R_F = 0.0782$ for 508 $F_o > 6\sigma(F_o)$, $R(wF^2) = 0.1275$, GOF = 1.517, $w = 1/[\sigma^2(F_o^2) + 896 \times 2819 \times P]$, where $P = (F_o^2 + 2F_c^2)/3$.

orientation of the cluster anion is controlled by the cationic environment.

The powder diffraction data (deposited) show good agreement with single crystal results. This means that the crystal used for the X-ray structural analysis is representative.

Acknowledgements—The research described in this publication was made possible in part by Grant No. RBS000 from the International Science Foundation.

REFERENCES

1. A. A. Opalovski, V. E. Fedorov, B. G. Erenburg, E. U. Lobkov, Ya. V. Vasiliev, L. N. Senchenko and B. I. Tzikanovski, *Zh. Phys. Khim.* 1971, **45**, 2110 (in Russian).
2. F. Klaiber, W. Petter and F. Hulliger, *J. Solid State Chem.* 1983, **46**, 112.
3. V. E. Fedorov, N. V. Podberezskaya, A. V. Mischenko, G. F. Khudorozko and I. P. Asanov, *Mat. Res. Bull.* 1986, **21**, 1335.
4. A. A. Opalovski, V. E. Fedorov, E. U. Lobkov and B. G. Erenburg, *Zh. Neorgan. Khim.* 1971, **16**, 3175 (in Russian).
5. N. Walker and D. Stuart, *Acta Cryst.* 1983, **A39**, 158.
6. G. M. Sheldrick, *Acta Cryst.* 1990, **A46**, 467.
7. G. M. Sheldrick, *J. Appl. Cryst.* in preparation.
8. A. Perrin and M. Sergent, *New. J. Chem.* 1988, **12**, 337.
9. W. Bronger, H. J. Miessen, R. Neugroschel, O. Schmitz and M. Spangenberg, *Z. Anorg. Allg. Chem.* 1985, **525**, 41.
10. W. Bronger, H. J. Miessen, P. Muller and R. Neugroschel, *J. Less-Common Met.* 1985, **105**, 303.
11. S. Chen and W. R. Robinson, *J. Chem. Soc., Chem. Commun.* 1978, 879.
12. O. M. Yaghi, M. J. Scott and R. H. Holm, *Inorg. Chem.* 1992, **31**, 4778.
13. J.-C. Gabriel, K. Boubekeur and P. Batail, *Inorg. Chem.* 1993, **32**, 2894.
14. S. S. Batsanov, *Zh. Neorganich. Khimii* 1991, **36**, 3015 (in Russian).