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An Octahedral Rhenium Cluster with (CN) Ligands: the Crystal Structure of $KCs_3Re_6S_8(CN)_6$

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The title compound has been prepared by anionic exchange from Re_6Te_{15}. The structure has been solved from the single crystal X-ray diffraction data. The compound is built of standard $M_6L_8L'_6$ units where L are chalcogens in inner position and L' are apical (CN) groups. The K^+ ion is octahedrally surrounded by apical ligands belonging to six different units, while the Cs^+ ions lie in complex anionic site.

INTRODUCTION

Following the study of the reaction of bromine on Re_2Te_5[1] and the subsequent crystal structure determination of related compounds,[2,3] the crystallochemistry of octahedral Re_6 cluster based materials is now well documented.[4] They appear as $Re_6L_8L'_6$ units in ternary chalcogenides[5] as well as in chalcohalides : in the latter, molecular, 1-D, 2-D and 3-D materials have been obtained, depending on the chalcogen/halogen ratio.[4] Also anionic units have been reported in quaternary chalcohalides,[6–9] where the $[Re_6L_8X_6]^{n-}$ units (n = 1–4) always present only X halogen atoms in »apical«

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positions, *i.e.* on the terminal sites lying on the quaternary axes of the Re_6 octahedron. In this paper we present the crystal structure of a new compound, in which these halogen ligands have been successfully replaced by (CN) groups, opening the way to a new chemistry of these clusters.

EXPERIMENTAL

The cesium/potassium octahedral rhenium cluster salt, ideally formulated $Cs_3K[Re_6(\mu_3\text{-}S_6)(\mu_3\text{-}S_2)(CN)_6]$, has been prepared by a two-stage procedure. First, a related potassium salt was synthesized by heating, in an evacuated and sealed silica tube, the rhenium telluride Re_6Te_{15} with molten KSCN (the Re_6Te_{15} : KSCN ratio was 1:8) at 500 °C for 24 hours. Reaction products were washed with hot ethanol for separation of the KSCN and KCN excess. The potassium salt was extracted with water and the dark-red solution was filtered off. Then, an aqueous solution of CsCl was added to the solution of potassium salt and the red-brown crystals were grown by slow evaporation of the solvent at 30 °C.

The crystallographic system, systematic extinctions (SG $Ia3$-, no. 206) and unit-cell parameters were determined from Weissenberg photographs. The latter was subsequently refined from 25 reflections measured on the CAD4 NONIUS diffractometer (a = 17.780(1) Å). 2322 reflections were collected from a cube shaped single crystal (0.1 mm apex) and 743 independent reflections with $I > 3\sigma(I)$ kept for refinement. The structure was solved from the Patterson function interpretation and Fourier difference maps, and the least square full matrix anisotropically refined down to R = 0.033 (R_w = 0.045, S = 0.87), using the MOLEN program. DIFABS absorption correction was applied.

RESULTS AND DISCUSSION

Taking into account the preparation technique, semiquantitative EDX-EPMA (energy dispersive electron probe microanalysis) was carried out to check the insertion of Cs and the possible presence of Te residues. Indeed, the results have evidenced a K/Cs ratio close to 1/4 and the presence of small amounts of Te with Te/S evaluated at about 0.09. Repeated analyses of up to ten single crystals have shown a very good homogeneity of the sample composition.

Atomic positional parameters are given in Table I and meaningful interatomic distances in Table II. Of course, special attention was paid to the statistical occupancy for various sites (Table III).

The structure is built of isolated anionic $[Re_6L_8(CN)_6]^{4-}$ (L = S, Te) units (Figure 1), very similar, for instance, to the divalent cluster anions $[Re_6(Se_5Cl_3)Cl_6]^{2-}$ present in the $KRe_6Se_5Cl_9$ structure.[6] The Re_6 octahedral cluster is quite regular, with Re-Re = 2.60 – 2.61 Å, in agreement with a two-electron metal-metal bond.[6] The cluster is surrounded, as usual, by 8 inner sulphur atoms forming a pseudo-cube, and then by 6 CN groups in

TABLE I

Positional parameters and root mean square displacements

Atom	x	y	z	B/Å^2	RMSD/Å		
					min.	med.	max.
Re	0.57279(3)	0.03462(3)	0.06497(3)	1.531(9)	0.123	0.144	0.149
K	0.250	0.250	0.250	3.06(3)	0.150	0.150	0.267
Cs	0.250	0.3027(1)	0.000	4.80(4)	0.183	0.190	0.335
S1	0.4608(2)	0.3407(2)	0.0236(2)	1.97(7)	0.139	0.155	0.178
S2	0.1028(2)	0.103	0.103	3.02(2)	0.173	0.173	0.234
C	0.359(1)	0.1520(9)	0.0821(9)	2.2(3)	0.143	0.167	0.190
N	0.1143(9)	0.3194(9)	0.189(1)	3.5(3)	0.138	0.227	0.249

terminal positions (Re-C-N angle = 172(1)° may be deviated from 180° due to constraints). The structure cohesion is obtained by coulombian interactions: K^+ ion is octahedrally surrounded by six N atoms from CN groups belonging to six adjacent cluster units. This site is similar to the one observed in the prototype of ionic octahedral Re_6 cluster-based materials, $KRe_6Se_5Cl_9$,[6] but strongly contrasts with the prismatic potassium site evidenced in the structure

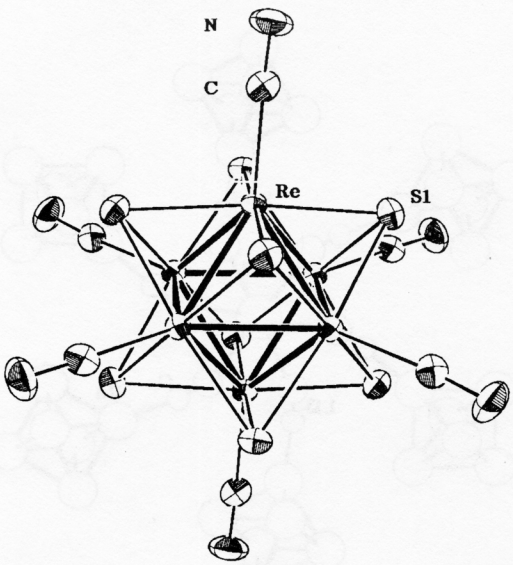

Figure 1. The cluster unit in the structure of $KCs_3Re_6S_8(CN)_6$. For the sake of clarity, S2 atoms are not labelled: one is the apex of the cube facing the reader, the other is deduced from the inversion centre lying in the centre of the cluster.

TABLE II

Principal interatomic distances/Å

Re-Re	2.601(1)	Re-Re	2.611(1)	Re-S1	2.402(4)	Re-S1	2.413(4)
Re-S1	2.418(4)	Re-S2	2.593(3)	Re-C	2.125(2)	C-N	1.13(2)
K-N	2.92(2)	Cs-S1	3.557(4)	Cs-S1	3.836(4)	Cs-C	3.62(2)
Cs-C	3.67(2)	Cs-N	3.12(2)	Cs-N	3.70(2)		

of the brominated analogue.[7] On the other hand, the Cs ions are (8 + 4)-coordinated in a complex polyhedron built of 4 S1 + 4 CN and 2 S2 + 2 CN at a larger distance.

As to site occupancy, it is clear that the Cs position is fully occupied by cesium ions. In contrast, the potassium position exhibits an excess of electron density, corresponding to the presence of some cesium on this site, and calculated to be $K_{0,78}Cs_{0.22}$. The S1 sites are pure sulphur, while the S2 ones, lying on the ternary axes, contain a small amount of tellurium, calculated from electron density to be 0.3 Te for 0.7 S. The final formula, derived from single crystal refinement, is then:

$$K_{0.78}Cs_{3.22}Re_6(S_{7.40}Te_{0.60})(CN)_6$$

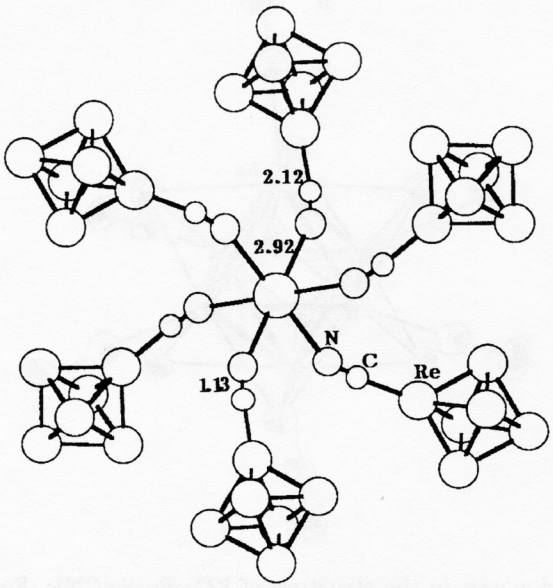

Figure 2. The octahedral environment of the K^+ ion.

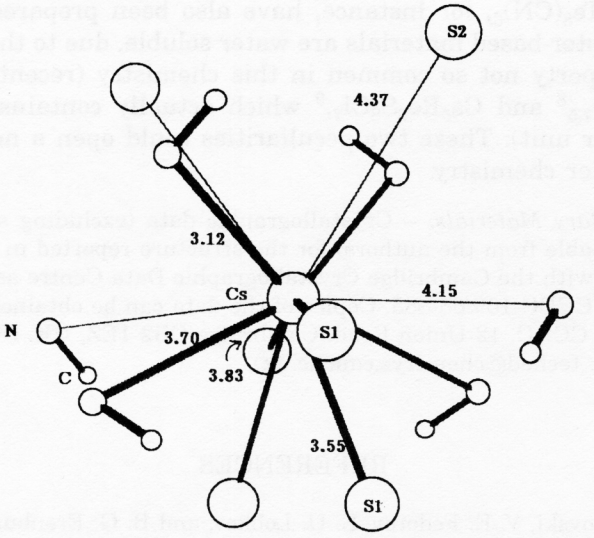

Figure 3. The environment of the Cs^+ ion.

in good agreement with the EPMA results. Of course, it is expected that the K/Cs and the Te/S distributions are likely to vary with some changes in the synthesis conditions.

The electronic count on the cluster leads to 24 VEC meaning insulating properties (as inferred from the transparency of the red crystals which charge up under electron beam): thus, a regular Re_6 octahedron was expected.[10] The very slight deviation observed is interpreted as the effect of a steric constraint due to the presence of a certain amount of Te on the "S2" *xxx* site. Indeed, the latter feature is also reflected in the Re-"S2" distance, significantly longer than the Re-S1 ones.

In conclusion, the first example of an octahedral Re_6 cluster with (CN) groups as apical ligands is reported. Related compounds, like $K_4Re_6Se_8(CN)_6$

TABLE III

Site multiplicities (MU) and the atomic occupancies derived

Atom	Site	MU site	MU refined	Atomic occupancy
Cs	24d	0.5	0.499(2)	1
K	8b	0.167	0.236(4)	0.78 K + 0.22 Cs
S1	48c	1	1.04(1)	1
S2	16c	0.333	0.557(5)	0.70 S + 0.30 Te

and $KCs_3Re_6Te_8(CN)_6$, for instance, have also been prepared. In addition, these new cluster-based materials are water soluble, due to the large anionic charge, a property not so common in this chemistry (recent examples are $Rb_{2.5}Re_6S_{6.5}Cl_{7.5}$[8] and $Cs_5Re_6S_8Cl_7$,[9] which actually contains a tetravalent anionic cluster unit). These two peculiarities could open a new field in the rhenium cluster chemistry.

Supplementary Materials. – Crystallographic data (excluding structure factors which are available from the authors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-109/68-885. Copies of the data can be obtained on application to the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK. (Fax: 44 (0) 1223-336033; E-mail: teched@chemcrys.cam.ac.uk).

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SAŽETAK

Oktaedarski renijev kluster s ligandima CN: Kristalna struktura spoja $KCs_3Re_6S_8(CN)_6$

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Spoj $KCs_3Re_6S_8(CN)_6$ priređen je anionskom zamjenom iz Re_6Te_{13}. Struktura je riješena metodom difrakcije rentgenskih zraka na monokristalu. Spoj se sastoji iz jedinica $M_6L_8L'_6$ u kojima su L atomi halkogena u unutarnjem položaju, a L' su apikalne skupine CN. Ion K^+ oktaedarski je okružen apikalnim ligandima iz 6 različitih jedinica, dok ioni Cs^+ leže na položaju aniona u kompleksu.