Syntheses and Crystal Structures of $(Pr_4N)_2Re_4Q_4(CH_3CONH)_2Cl_8$ (Q = S, Se) – Conversion of Solvent CH_3CN into the Acetamido Ligand

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The first two Re_4 chalcogenide halide clusters $(Pr_4N)_2Re_4Q_4(CH_3CONH)_2Cl_8$ (Q = S, Se) with ionic molecular structures have been synthesized by treatment of neutral molecular clusters $Re_4Q_4Cl_8(TeCl_2)_4$ (Q = S, Se) with Pr_4NCl in refluxing CH_3CN. During the reaction acetonitrile solvent molecules are converted into acetamido ligands, coordinated as dinucleating ligands to Re–Re bonds.

Introduction

Rhenium chalcogenide halide cluster compounds have been studied extensively in recent years, the majority of which contain Re_6 octahedra.[1–4] Recently, the first examples of Re_4 tetrahedra chalcogenide halide clusters of general formula $Re_4Q_4X_8(TeX_2)_4$ with Q = S, Se, Te and X = Cl, Br[5,6] have been prepared. These are neutral molecular compounds that are insoluble in organic solvents and water.

Here we describe two new Re_4 chalcogenide halide clusters with ionic structures $(Pr_4N)_2Re_4Q_4(CH_3CONH)_2Cl_8$ (Q = S, Se). The only known ionic examples of this class of compound are $[Re_4S_4(\mu\text{-}S_3)_6]^{4-}$[7,8] and $[Re_4Q_4(CN)_{12}]^{4-}$[9–11]. We have now successfully extended this work to allow the isolation of the first clusters with terminal chloride ligands. To our surprise the characterised compounds also included bridging acetamido ligands, which are presumably formed by reaction of CH_3CN solvent molecules with H_2O in the metal coordination sphere.

Results

Treatment of molecular clusters $Re_4Q_4Cl_8(TeCl_2)_4$ (Q = S, Se) with Pr_4NCl in refluxing CH_3CN leads to formation of the soluble ionic complexes $(Pr_4N)_2Re_4Q_4(CH_3CONH)_2Cl_8$ (Q = S, Se).

During the reaction acetonitrile solvent molecules are converted into acetamido $(CH_3CONH)^-$ ligands, coordinated as bridging ligands to Re−Re bonds. In total we observe an exchange of four $TeCl_2$ neutral ligands by two acetamido ligands $(CH_3CONH)^-$.

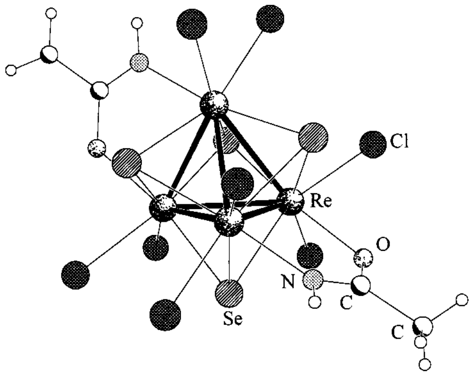

Figure 1. Structure of $[Re_4Q_4(CH_3CONH)_2Cl_8]^{2+}$ [Q = S (**1**), Se (**2**)] cation; selected bond lengths [Å] and angles [°]: **1**: Re1−Re2 2.656(1), Re1−Re1a 2.754(2), Re1−Re2a 2.760(1), Re−S in range 2.301(4)−2.340(5), Re1−O 2.128(12), Re1−N 2.122(15), Re2−Re1−Re1a 61.33(2), Re2−Re1−Re2a 61.10(3), Re1a−Re1−Re2a 57.58(2), Re1−Re2−Re2a 61.32(3), Re1−Re2−Re1a 61.10(3), Re2a−Re2−Re1a 57.57(2), C−O−Re1 122.2(12), C−N−Re2 123.5(13) N−C−O 125(2); **2**: Re1−Re2 2.695(1), Re1−Re1a 2.813(2), Re1−Re2a 2.821(1), Re−Se in range 2.419(2)−2.452(2), Re1−O 2.138(14), Re1−N 2.095(17), Re2−Re1−Re1a 61.57(3), Re2−Re1−Re2a 61.29(4), Re1a−Re1−Re2a 57.16(3), Re1−Re2−Re2a 61.56(3), Re1−Re2−Re1a 61.28(3), Re2a−Re2−Re1a 57.15(3), C−O−Re1 121(2), C−N−Re2 125(2) N−C−O 126(2)

The structures of both compounds $(Pr_4N)_2Re_4S_4(CH_3CONH)_2Cl_8$ (**1**) and $(Pr_4N)_2Re_4Se_4(CH_3CONH)_2Cl_8$ (**2**) were determined by single-crystal X-ray analysis. The view of the cluster anion **2** is shown in Figure 1. Compounds **1** and **2** are isostructural and possess crystallographic $\bar{3}$ symmetry. Each contains an Re_4Q_4 cubane-like core formed from a nearly regular Re_4 tetrahedron with two slightly shorter Re−Re distances, resulting from the coordination of acetamido ligands to these bonds. Distances are similar [2.656(1) (**1**) and 2.695(1) Å (**2**)] for these acetamido-bridged Re−Re bonds and in the ranges 2.754(2)−2.760(1) (**1**) and 2.813(2)−2.821(1) Å (**2**) for the remaining Re−Re bonds. Each Re atom is further ligated by two terminal chloro ligands [Re−Cl distances are in range 2.395(5)−2.413(5) for **1** and 2.419(6)−2.438(6) Å for **2**] and by an oxygen or nitrogen atom of a bridging acetamido ligand, with Re−O and Re−N distances of 2.13(1) and 2.12(2) Å in **1** and 2.14(1) and 2.10(2) Å in **2**.

An interesting feature of these syntheses is the conversion of the solvent molecules (CH_3CN) into acetamido ligands. Conversion of acetonitrile into acetamide in the metal coordination sphere is well known for Pt complexes and takes

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place in alkaline solution.[12,13] A similar conversion into the one discussed in the present work has recently been described for the reaction of K_2PtCl_6 with *cyclo*-$(CH_3AsO)_n$ in a sealed tube at 100 °C, with further coordination taking place to a Pt−As bond.[14] In the present work, formation of the acetamido ligand has been observed at a lower temperature and normal pressure.

In the title compounds the C−O and C−N distances of 1.27(2) and 1.29(2) Å in the (CH_3CONH) units of **1** and 1.32(3) and 1.26(3) Å (**2**) are close to each other and similar to the values found for Pt complexes.[14] The determination of the positions of O and N atoms was made by comparison of the corresponding isotropic temperature factors and by the localisation of an H atom at the appropriate site for an amide nitrogen atom in a difference Fourier synthesis. The mechanism of formation of the acetamido ligands may be proposed to involve initial N coordination of a solvent CH_3CN molecule to an Re atom to afford the intermediate compound $(Pr_4N)_2Re_4Q_4(CH_3CN)_2Cl_{10}$. Subsequent nucleophilic attack on the C atom of the C≡N bond by an oxygen atom of water followed by deprotonation (giving HCl) and coordination of this O atom to the neighbouring Re atom, generates **1** and **2**. The formation of these clusters is not observed when the reactions are performed in carefully dried CH_3CN under argon.

The presence of the acetamido ligands in **1** and **2** is confirmed by spectroscopic studies. In the IR spectra of these two complexes the N−H stretching vibrations occur at 3384 (**1**) and 3381 cm^{-1} (**2**) as very sharp lines. Two bands at 1542 and 1521 (**1**) and 1540 and 1517 cm^{-1} (**2**) correspond to C=O vibrations of acetamido ligands. In ^{1}H-NMR spectra $\delta(NH) = 7.23$ (**1**) and 7.07 (**2**); $\delta(CH_3) = 2.39$ (**1**) and 2.47 (**2**). The resonances exhibit an integral ratio of 1:3.

Experimental Section

All manipulations were performed in air. $Re_4Q_4Te_4Cl_{16}$ (Q = S, Se) were obtained as described before.[5] − ^{1}H NMR: Bruker AM 400 FT-NMR. − FTIR: Perkin−Elmer 1760X. − Elemental analyses: Elemental Analyser system Vario E1.

$(Pr_4N)_2Re_4S_4(CH_3CONH)_2Cl_8$ (1): $Re_4S_4Te_4Cl_{16}$ (195 mg, 0.1 mmol) was refluxed in 20 mL of CH_3CN with Pr_4NCl (222 mg, 1 mmol) for 1 h. The final solution was filtered and the filtrate concentrated in air at room temperature. The solid product was then redissolved in 5 mL of CH_3CN, and recrystallised from the system CH_3CN/toluene to afford brown-red crystals of **1** which were filtered, washed with methanol and ether, and then dried. Yield 90 mg (55%). − $C_{28}H_{64}Cl_8N_4O_2Re_4S_4$ (1645.47): calcd. C 20.4, H 3.9, N 3.4, S 7.8; found C 20.1, H 3.9, N 3.3, S 7.6. − IR (KBr): $\tilde{\nu}$ = 3390 (m), 2969 (m), 2878 (w), 1541 (m), 1522 (m), 1460 (s), 1195 (m), 1034 (w), 970 (m), 751 (w), 704 (m), 670 (m), 588 (w). − ^{1}H NMR (CD_3CN): δ = 0.921−0.96 (m, CH_3), 1.60−1.70 (m, CH_2), 3.03−3.07 (m, CH_2) (Pr_4N); δ = 2.39 (CH_3), 7.23 (NH) (CH_3CONH).

$(Pr_4N)_2Re_4Se_4(CH_3CONH)_2Cl_8$ (2): 120 mg (66%) of **2** was obtained from $Re_4Se_4Te_4Cl_{16}$ (214 mg, 0.1 mmol) and Pr_4NCl (222 mg, 1 mmol) as described for **1**. − $C_{28}H_{64}Cl_8N_4O_2Re_4Se_4$ (1833.07): calcd. C 18.4, H 3.5, N 3.1; found C 18.3, H 3.6, N 3.1. − FAB MS; *m/z* (%): 1652 (20) $[M - (Pr_4N)]^-$, 1463 (20) $[M - 2\,(Pr_4N)]^-$, 732 (10) $[M - 2\,(Pr_4N)]^{2-}$, 1428 (100) $[M - 2\,(Pr_4N) - Cl]^-$, 1389 (50) $[M - 2\,(Pr_4N) - 2\ Cl]^-$, 1289 (26) $[M - 2\,(Pr_4N) - 5\,Cl]^-$, 1253 (32) $[M - 2\,(Pr_4N) - 6\,Cl]^-$, 1219 (37) $[M - 2\,(Pr_4N) - 7\,Cl]^-$. − IR (KBr): $\tilde{\nu}$ = 3385 (m), 2967 (m), 2876 (w), 1539 (m), 1517 (m), 1456(s), 1186 (m), 1037 (w), 968 (m), 750 (w), 700 (m), 668 (m), 586 (w). − ^{1}H NMR (CD_3CN): δ = 0.91−0.95 (m, CH_3), 1.59−1.69 (m, CH_2), 3.02−3.06 (m, CH_2) (Pr_4N); δ = 2.48 (CH_3), 7.07 (NH) (CH_3CONH).

X-ray Structural Analyses: Siemens P4 difractometer, graphite monochromator, Mo-K_α radiation (λ = 0.71073 Å), SHELXS-86[15] for structure solution by direct methods and SHELXL-93[16] for refinement by full-matrix least squares. Semi-empirical absorption corrections were applied to the intensity data by use of ψ scans. Hydrogen atoms were included at calculated position.[17]

1: $(Pr_4N)_2Re_4S_4(CH_3CONH)_2Cl_8$, $M = 1645.47$, trigonal, space group $P3_221$, $a = b = 12.670(3)$, $c = 26.09(1)$ Å, $V = 3627(2)$ Å^3, $Z = 3$, $D_{calcd.} = 2.260$ g cm^{-3}, $\mu = 10.63$ mm^{-1}. Crystal size 0.43 × 0.38 × 0.25 mm; ω-scan, scan range: $2\theta \le 55.02°$ ($0 \le h \le 16$, $-16 \le k \le 0$, $0 \le l \le 33$), 3313 symmetry-independent reflection from 5515 collected ($R_{int} = 0.0772$), max./min. transmission: 0.627, 0.289; 229 parameters refined; $R = 0.052$ [$I > 2\sigma(I)$], $wR_2 = 0.127$ [all reflections], $S = 0.826$; $\Delta\rho_{max} = 1.79$ eÅ^{-3}, $\Delta\rho_{min} = -2.78$ eÅ^{-3}.

2: $(Pr_4N)_2Re_4Se_4(CH_3CONH)_2Cl_8$, $M = 1833.07$, trigonal, space group $P3_221$, $a = b = 12.726(1)$, $c = 26.534(5)$ Å, $V = 3721.6(\ )$ Å^3, $Z = 3$, $D_{calcd.} = 2.454$ g cm^{-3}, $\mu = 13.12$ mm^{-1}. Crystal size 0.2 × 0.2 × 0.12 mm; ω-scan, scan range: $2\theta \le 55.02°$ ($0 \le h \le 16$, $-14 \le k \le 14$, $0 \le l \le 34$), 3743 symmetry independent reflection from 5721 collected ($R_{int} = 0.0540$), max./min. transmission: 0.570, 0.307; 224 parameters refined; $R = 0.063$ [$I > 2\sigma(I)$], $wR_2 = 0.149$ [all reflections], $S = 1.025$; $\Delta\rho_{max} = 1.56$ eÅ^{-3}, $\Delta\rho_{min} = -1.14$ eÅ^{-3}.

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[17] Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre. Copies of the data (deposition numbers CCDC-112135 and -112136) may be obtained free of charge on application to the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: int. code + 44-1223/336-033, E-mail: deposit@ccdc. cam.ac.uk).

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