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Preliminary Communication

Extrusion of molecular clusters from solid-state materials: synthesis by application of γ-irradiation. Molecular and crystal structure of $(H_9O_4)(Et_4N)[Mo_3S_7Br_6]$

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Abstract

The cluster $[Mo_3S_7Br_6]^{2-}$ has been obtained by a γ-irradiation of the polymeric compound $Mo_3S_7Br_4$ in concentrated hydrobromic acid. The X-ray structure of $(H_9O_4)(Et_4N)[Mo_3S_7Br_6]$ (**1**) was determined, whereby an unexpected aggregation of the $[Mo_3S_7Br_6]^{2-}$ anions with short S...Br contacts was observed. Crystal data for **1**: orthorhombic space group *Pbca* with $a=15.192(2)$, $b=13.771(2)$, $c=29.525(6)$ Å, $Z=8$, $D_{calc}=2.570$ g/cm^3, $R=0.063$, $R_w=0.056$.

Keywords: Crystal structures; Molybdenum complexes; Chalcogenide complexes; Clusters; Gamma-irradiation

Extrusion of molecular clusters from crystalline or amorphous solid-state materials is a method used in modern inorganic chemistry for different purposes [1,2]. The method is not only applied for the synthesis of new molecular complexes but also for structural characterization of amorphous materials (e.g. MoS_3 [3]).

X-ray diffraction studies of $Mo_3S_7X_4$ (X = Cl Br) indicated that these materials have a polymeric structure with bridging halogen atoms (i.e. $[Mo_3S_7X_2X_{4/2}]$ [4]). The polymeric structure influences the low reactivity of the compounds. Depolymerization of these compounds usually only takes place under rather severe conditions. Thus, $Mo_3S_7X_4$ interacts for instance with molten PPh_4X to produce the $(PPh_4)_2[Mo_3S_7X_6]$ salts (in high yields) [5]. The reactivity of $Mo_3S_7X_4$ considerably increases under the conditions of mechanochemical activation (in the vibrational mill) [6]. On the other hand, interaction of the same compounds with Et_4NX under refluxing conditions in concentrated hydrochloric or hydrobromic acid produces Et_4N salts only in very low (and poorly reproducible) yields [7].

In the present work we have used a simple method for the extrusion of the $Mo_3S_7^{4+}$ cluster. Steady-state radiolysis of 1.5 g of $Mo_3S_7Br_4$ in 2 ml of concentrated hydrobromic acid was performed in a ^{60}Co γ-ray source, calibrated with a Fricke dosimeter, using $G(Fe^{3+})=15.5$ [8]. After γ-irradiation for 72 h with 50 Mrad the sample was heated for 30 min in 20 ml of concentrated hydrobromic acid. The $(Et_4N)_2[Mo_3S_7Br_6]$ (**2**) salt could be isolated (yield 1.06 g, 56%) by addition of 1.5 g of Et_4NBr to the solution. Recrystallization of 1.0 g of **2** from 100 ml of concentrated HBr yielded single crystals of $(H_9O_4)(Et_4N)[Mo_3S_7Br_6]$ (**1**)[1] (yield 0.81 g, 85%). Sat-

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[1] Crystal data for **1**: $C_8H_{29}NO_4Mo_3S_7Br_6$ space group *Pbca*, crystal system orthorhombic, $a=15.192(2)$, $b=13.771(2)$, $c=29.525(6)$ Å, $Z=8$, $D_c=2.570$ g/cm^3, Mo Kα radiation ($\lambda=0.71073$ Å)/ω scan mode with variable speed (3.97–29.30°/min.), $T=294$ K, 2θ range 4.0–54.0°, reflections collected 6998, observed reflections 3689, $F_o>4.0\sigma(F_o)$, $R=0.063$, $R_w=0.056$. Data were collected on a Siemens R3m/V diffractometer. The structure was solved using direct methods and refined by full matrix least-squares techniques. All atoms were refined anisotropically except hydrogen atoms of the Et_4N cation in calculated positions which were refined as riding on the corresponding C atoms (fixed U values, C–H = 0.96 Å).

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isfactory analytical data (C, H, N, Mo and S) were obtained for both salts.

Polymers, when irradiated, often undergo degradation processes [9,10]. The degradation (here the chain fission) is most likely due to ionization and excitation of the irradiated polymeric material. In such a manner the reactivity of $Mo_3S_7Br_4$ considerably increases under the influence of γ-radiation, and the products easily react with hydrobromic acid to form the discrete cluster $[Mo_3S_7Br_6]^{2-}$.

Thus, γ-irradiation seems to be usefully applicable for the extrusion of discrete clusters from solid-state materials. At present we are investigating the extrusion of cubane-type molecular thio and seleno clusters from $M_4Y_4X_4$ (M = Nb, Mo; Y = S, Se; X = Cl, Br, I) and other compounds with solid-state structures.

The cluster anion $[Mo_3S_7Br_6]^{2-}$ in **1** contains the $Mo_3S_7{}^{4+}$ fragment which has been widely investigated over the last few years [11]. The variation of the total charge of the $[Mo_3S_7L_6]$ cluster from -2 to $+1$ results, as expected, in a shortening of the metal–metal bond from 2.757(1) Å in $[Mo_3S_7Cl_6]^{2-}$ to 2.719(4) Å in $[Mo_3S_7(dtc)_3]^{+}$ (see Ref. [11]). The average Mo–Mo distance in **1** (2.747 Å) is in good agreement with this rule. The mean value of the Mo–Br bond lengths (2.612 for three Br atoms in a *cis*-position with respect to the apical-S atom and 2.659 for the others) is in accordance with $(Et_4N)\{[Mo_3S_7(NH_2Ph)_3Br_3]Br\}Br$ (**3**) (2.638 Å) [11]. Mo–S bond lengths have values as expected.

The most striking feature of **1** is its crystal packing (for the crystal data see footnote on p. 5). Practically all $[M_3Y_7X_6]$ type crystal structures (M = Mo, W; Y = S, Se) include a donor atom Z (one of the X atoms), which has short contacts to the Y atoms of another anion (see Fig. 1). It has been previously shown [12,13] that Y...Z distances are essentially shorter than the normal Y...Z non-bonding contacts. We suggest calling them '$3Y_{ax}$...Z' or 'axial contacts'. These rather strong interactions play an outstanding role in the crystal packing.

In the crystal structure of **1** three unusual S_{ax}...Br contacts are present between a terminal Br atom of the cluster anion and axial sulfur atoms of the anion connected with it by the crystallographic plane *b* of the *Pbca* space group, resulting in the formation of the infinite chain anions running along the *y* direction (see Fig. 1). It is worth noting that these contacts are realized despite the electrostatic repulsion between the anions. The S...Br distances (3.125, 3.388, 3.640 Å) are essentially shorter than the sum of the van der Waals radii of S and Br (3.80 Å [14]) but longer than in **3** (2.927–3.311 Å) [11], where electrostatic attraction between the cluster cation and Br^- is favourable for the formation of axial contacts.

Structure **1** gives the first example of the formation of anion chains in $[M_3Y_7X_6]$ type structures. So far, only the formation of centrosymmetric dimers (as in $(PPh_4)_2[Mo_3S_7Cl_6]$ [5]) or Cl...$[Mo_3S_7Cl_6]^{2-}$ associates (as in $(Et_4N)_3[Mo_3S_7Cl_6]Cl \cdot CH_2Cl_2$ [15]) has been found [12].

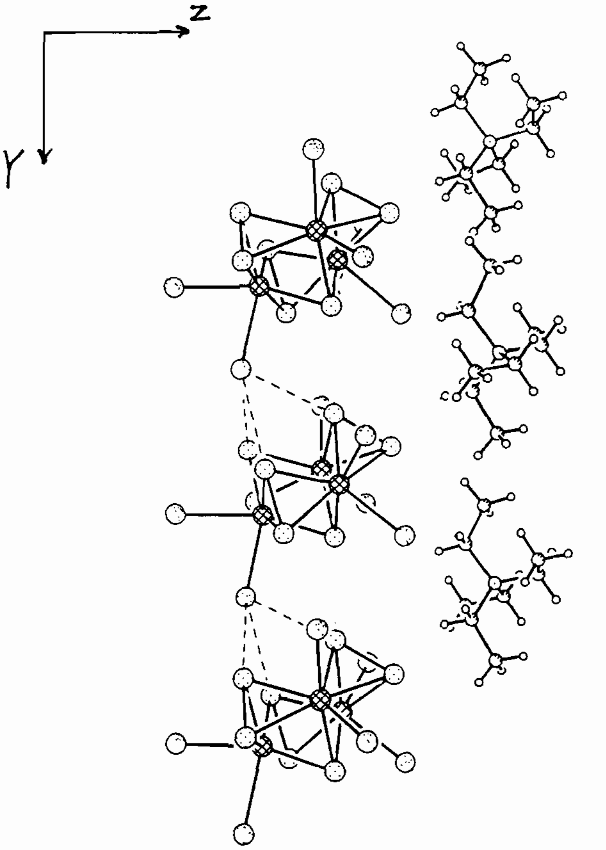

Fig. 1. Crystal packing of $(H_9O_4)(Et_4N)[Mo_3S_7Br_6]$ (view along *x* axis). S...Br contacts are shown as broken lines.

Supplementary material

Tables of crystal data, atomic parameters, anisotropic thermal parameters, bond angles and hydrogen atoms of the Et_4N cation (in calculated positions refined as riding on the corresponding C atoms) as well as thermal ellipsoids of the anisotropic atoms are available from the authors on request.

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