New cluster condensation modes in early transition metal thiophosphates: synthesis, structure and properties of $CsTa_4P_3S_{19}$, a novel layered material

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The new layer compound $CsTa_4S_5(S_2)(PS_4)_3$ was synthesized by the reaction of Ta metal in polythiophosphate melts. Its structure is based on $Ta_4S_5(S_2)$ clusters which are condensed by PS_4^{3-} groups.

In the past 20 years, lamellar transition metal chalcogenophosphates have been studied extensively because of their potential as cathodic materials and their intriguing structural, chemical and physical properties.[1–3] Among the group 5 derivatives, the structural dimensionality can vary from one- to three-dimensional as exemplified by V_2PS_{10},[4] Nb_2PS_{10}[5] and $Ta_4P_4S_{29}$.[6] This can be attributed to the variability in the metal coordination for the group 5 metals as well as the fascinating flexibility in the coordination of the chalcogen ligands.[7] The structures of typical group 5 thiophosphates are based on bicapped M_2S_{12} biprismatic units with a metal–metal bond inside. These biprisms are bonded together to form infinite M_2S_9 chains. In contrast to the 3d transition metal thiophosphates of the MPS_3 series, no intercalation behavior has been reported for group 5 thiophosphates.[8] This is surprising in view of their low-dimensional structures, but may be due to the fact that the complex host structures are not stable during the intercalation process.

In the quest for new intercalated early transition metal thiophosphates we have investigated reactions in $M–P_2Q_5–A_2Q–Q$ melts (M = Nb, Ta; Q = S, Se; A = alkali metal). The most significant results of these studies are that (*i*) a 'quasi-topotactic' cation insertion in porous host structures may be achieved[9] and (*ii*) that low-dimensional compounds with structures that exhibit novel unexpected cluster condensation modes can be obtained from reactions in thiophosphate melts as demonstrated by the first quaternary tantalum thiophosphate $CsTa_4(S_2)S_5(PS_4)_3$ whose synthesis, structure, and properties are reported here.

Single phase samples of the title compound were prepared by reacting the starting materials Ta, P_2S_5, Cs_2S and S in a 8 : 3 : 1 : 11 ratio at 600 °C.‡ The product was isolated in yields $>85\%$ based on Ta. The crystal structure§ of this compound was determined by single-crystal X-ray diffraction. A view of a single anionic layer and the unit cell of $CsTa_4P_3S_{19}$ is given in Fig. 1(*a*). The Cs^+ cations are situated between the layers. The characteristic structural feature is a $(S_4P)_2TaS_2(S_4P)TaS(S_2)Ta(PS_4)_2S_2Ta(PS_4)_2$ fragment with a $Ta_4S_5(S_2)$ core, which is shown in Fig. 1(*b*). The central Ta_2S_{11} unit is located on a crystallographic mirror plane; it is derived from the distorted bicapped biprismatic M_2Q_{12} units encountered in the structures of group 5 thiophosphates by replacing a bridging S_2^{2-} disulfide group by a S^{2-} anion. This leads to a seven-fold coordination for the central Ta atoms. The S–S distance of the S_2^{2-} pair is 2.046(10) Å, whereas the remaining S···S separations span the range from *ca.* 3.2 to 3.8 Å and must be considered non-bonding. Similarly, the Ta···Ta distance of 3.386(1) Å within the Ta_2S_{11} units is outside the metal–metal bonding range. The Ta_2S_{11} groups are not tied to each other through their own edges as is observed for Nb_2PS_{10},[5] but are interconnected by two each of their surrounding sulfur atoms through phosphorus atoms which are located at the center of adjacent tetrahedral PS_4 units and octahedrally coordinated tantalum atoms which share the remaining four S atoms of their coordination sphere with two adjacent PS_4 groups. Thus, each Ta_2S_{11} unit is fused in a *cis*-orientation with two PS_4 and two TaS_6 groups and may be viewed as a four-fold connecting element of the Ta–P–S network. The PS_4 groups act as chelating ligands for two adjacent tantalum atoms and serve as linear spacer units. The TaS_6 groups in turn are linked with two PS_4 groups and one Ta_2S_{11} unit. Thus, they act as centers with threefold connectivity. Combining these three structure elements in a 1 : 3 : 2 ratio {as indicated by the formulation $Cs[Ta_2S_5(S_2)Ta_2(PS_4)_3]$} leads to a network with two different hollows; the larger one (smallest diameter *ca.* 7 Å) takes up the

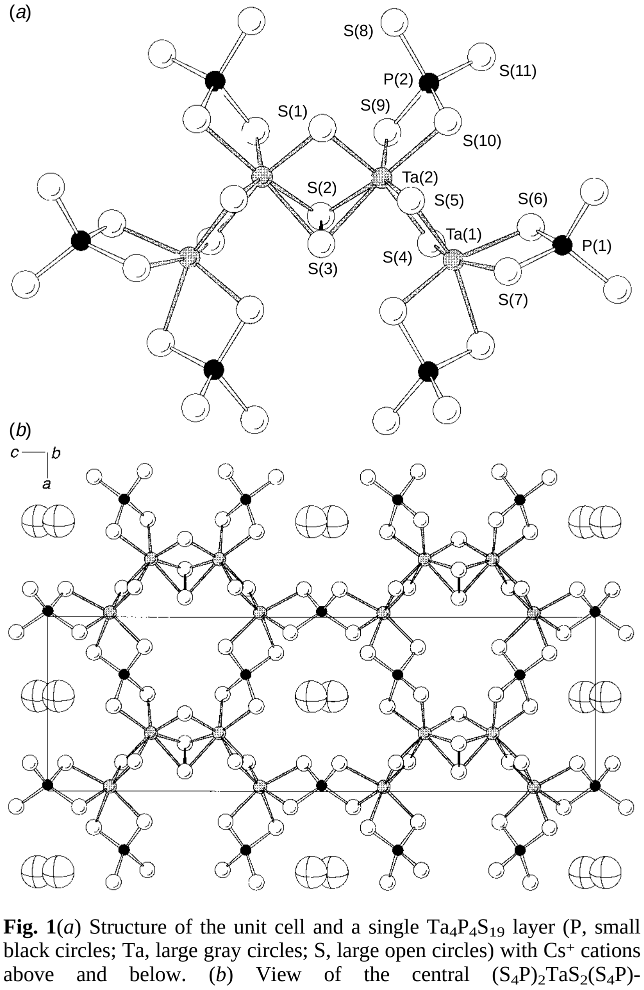

Fig. 1(*a*) Structure of the unit cell and a single $Ta_4P_4S_{19}$ layer (P, small black circles; Ta, large gray circles; S, large open circles) with Cs^+ cations above and below. (*b*) View of the central $(S_4P)_2TaS_2(S_4P)TaS(S_2)Ta(PS_4)_2S_2Ta(PS_4)_2$ unit with atomic labeling scheme. Selected distances (Å): Ta(1)–Ta(2) 3.371(1), Ta(2)–Ta(2) 3.386(1), S(2)–S(3) 2.045(10), Ta(1)–S(4) 2.317(5), Ta(1)–S(5) 2.274(5), Ta(1)–S(6) 2.497(4), Ta(1)–S(7) 2.548(5), Ta(1)–S(8) 2.460(4), Ta(1)–S(11) 2.626(5), Ta(2)–S(1) 2.373(5), Ta(2)–S(3) 2.556(5), Ta(2)–S(4) 2.459(4), Ta(2)–S(5) 2.534(5), Ta(2)–S(9) 2.474(5), Ta(2)–S(10) 2.495(4), P(1)–S(7) 2.020(6), P(1)–S(6) 2.034(6), P(2)–S(11) 2.014(6), P(2)–S(10) 2.053(7), P(2)–S(8) 2.044(7), P(2)–S(9) 2.023(7).

Cs^+ cations whereas the smaller one (smallest diameter *ca.* 3 Å) remains empty.

The most significant structural feature of $CsTa_4P_3S_{19}$ that makes it unique compared to the known ternary group 5 thiophosphates is that the familiar bonding mode of a M_2Q_{11} or M_2Q_{12} cluster which is linked through its four outer coordination sites to four neighboring PS_4 groups is not observed and an additional structural motif, the TaS_6 group, is found instead. This may be caused by the size requirements of the counter cations which are located between layers or in channels of the anion framework. Since the TaS_6 fragment has a connectivity of three in these network structures, a more versatile structural chemistry may be envisaged.

The electronic structure of $CsTa_4P_3S_{19}$ may be approached in a zeroth order approximation by assigning formal charges according to $[Cs^+][(Ta^{5+})_4(S^{2-})_5(S_2^{2-})(PS_4^{3-})_3]$; the oxidation state of 5+ has been observed in other thiophosphates such as $Ta_4P_4S_{29}$;[6] this is in harmony with the observed non-bonding Ta$\cdots$Ta distances; thus diamagnetic and semiconducting behavior are expected. Consequently, the optical spectrum of $CsTa_4P_3S_{19}$ (diffuse reflectance measurement) exhibits a sharp optical gap which is consistent with semiconducting behavior. The experimentally determined value is $E_g = 1.65$ eV.

From a synthetic point of view, $CsTa_4P_3S_{19}$ is the first group 5 compound that has been synthesized from a reactive chalcogenophosphate flux system.[11] Finally, the alkali ion-filled tunnels in the two-dimensional structure of $CsTa_4P_3S_{19}$, the three-dimensional structure of $CsNb_2P_2S_{12}$,[9] in which Cs^+ cations replace an isolated S_{10} ring from the $Ta_4P_4S_{29}$ structure,[6] as well as the observed ion conductivity in $LiTi_2(PS_4)_3$[12] suggest the possibility of ion exchange reactions.

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Notes and References

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‡ Ta metal (Starck, 99.999%, 0.724 g, 4 mmol), P_2S_5 (Merck, 99.5%, 0.111 g, 1.5 mmol), Cs_2S (0.149 g, 0.125 mmol) and S (Aldrich, 99.99%, 0.176 g, 5.5 mmol) were sealed under vacuum (10^{-4} Torr) in a quartz tube, heated slowly to 200 °C and prereacted overnight. Subsequently the samples were heated to 600 °C at a rate of 1 °C min^{-1} and kept at this temperature for 7 days. Afterwards the samples were cooled to room temperature at a rate of 1 °C min^{-1}. The product can be separated from admixed polychalcogenides by washing with ethanol in *ca.* 85% yield. Sample homogeneity was checked by X-ray powder diffraction and electron microprobe analysis.

§ *Crystal data* for $CsTa_4P_3S_{19}$ at 25 °C: orthorhombic, space group *Pbcm* (no. 57), $a = 8.637(2)$, $b = 11.940(2)$, $c = 27.202(5)$ Å, $U = 2805.2(10)$ Å^3, $Z = 4$, $\lambda = 0.710\,73$ Å, $D_c = 3.691$ g cm^{-3}, μ(Mo-Kα) = 18.411 mm^{-1}, crystal platelike, dimensions $0.1 \times 0.15 \times 0.15$ mm, $\theta_{max} = 54°$, data collected at 25° on a Nicolet $P2_1$ four circle diffractometer, 5794; unique data, 3081; data with $F_o^2 > 4\sigma(F_o^2)$, 2340; number of variables, 134. Structure solved and refined using SHELXS86 and SHELXL93, An empirical absorption correction based on ψ scans was applied to the data. Final R, R_w = 0.062, 0.134 (0.093, 0.147 for all data). CCDC 182/786.

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