Oxide Addition to a Reactive Polysulfide Flux: Synthesis of $K_4Ba[Ti_6OS_{20}]$ Containing Isolated $[Ti_6OS_8(S_2)_6]^{6-}$ Clusters**

Fu Qiang Huang and James A. Ibers*

Dedicated to Professor Hans-Georg von Schnering on the occasion of his 70th birthday

A plethora of zero-dimensional chalcogenide cluster compounds are known, especially for the early transition metals.[1–3] For Group 4 and 5 metals, the stability of such clusters is often critically dependent on the presence of interstitial atoms.[4] Such interstitial atoms have been introduced adventitiously in syntheses involving solution chemistry,[2] an example being the synthesis of $[PPh_4]_2[Ti_3O(S_2)_3Cl_6]$ from the reaction of $TiCl_4$ with $S(SiMe_3)_2$ in CH_2Cl_2.[5] Introduction of interstitial atoms into solid-state clusters has progressed from the adventitious[6] to the deliberate.[3, 4, 7, 8] Almost all such solid-state syntheses involve the combination of the elements at high temperatures, often achieved by arc melting.

Since the synthesis of $K_4Ti_3S_{14}$ in 1987 by the reaction of Ti metal with a K_2S_n ($n \geq 2$) flux,[9, 10] the so-called "reactive flux method" has been used extensively to synthesize a wide variety of alkali metal (A) or Cu/metal (M)/polychalcogenide (Q_n) compounds, especially for metals from Groups 4 or 5.[9–21] The structures of many of these compounds comprise the hexagonal closest packing of one-dimensional M/Q chains, separated by A atoms.[22] The A/Group 4/Q_n structures are especially interesting, because they all contain linear M/Q chains. Although isolated two-dimensional M/Q layers and one-dimensional M/Q chains are known in solid-state binary[23–26] and ternary Group 4 metal chalcogen compounds,[15, 27] no zero-dimensional M/Q clusters have been found in A/M/Q compounds.[28]

We find that the low-temperature reactive flux method can be modified by the deliberate introduction of diverse potential interstitial species to afford zero-dimensional cluster compounds. We illustrate this with the synthesis of the solid-state cluster compound $K_4Ba[Ti_6OS_{20}]$ from a reactive flux similar to that used in the synthesis of the one-dimensional compound $K_4Ti_3S_{14}$, but augmented by the deliberate introduction of TiO_2. Specifically, this compound results in yields of approximately 70% from the reaction of K_2S_n, BaS, Ti, and TiO_2 at 823 to 873 K.

Two different crystal modifications of $K_4Ba[Ti_6OS_{20}]$ (hexagonal, space group *P6₃22* and orthorhombic, space group *Fddd*) are obtained, depending on the heating regime. Both consist of well-separated $[Ti_6OS_8(S_2)_6]^{6-}$ anionic clusters and K^+ and Ba^{2+} cations. The clusters are essentially identical in the two modifications; one such $[Ti_6OS_8(S_2)_6]^{6-}$ cluster is illustrated in Figure 1. It consists of an O-centered Ti_6 octahedron inscribed in a cube of eight S atoms with an S_2^{2-} group bonded on the outside of the cube to each Ti^{4+} center.

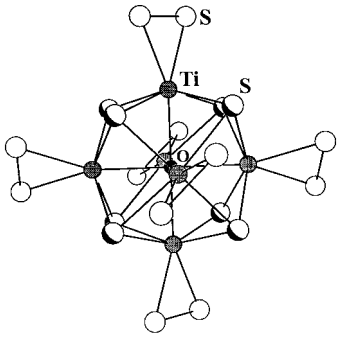

Figure 1. Structure of the $[Ti_6(O)S_8(S_2)_6]^{6-}$ cluster.

Although the idealized symmetry of $[Ti_6(O)S_8(S_2)_6]^{6-}$ could be as high as D_{3d}, it is D_3 in the hexagonal modification and D_{2h} in the orthorhombic modification. A similar core is found in the structures of $[Zr_6SS_8Cp_6]$ ($Cp = C_5H_5$)[29] and $[V_6OSe_8(PMe_3)_6]$.[29] Bond lengths within the anion are given in Table 1. These are normal. In particular, the Ti–O distances of 2.2824(5) to 2.2943(7) Å are expected for a Ti–O single bond, the S–S distances of 2.058(1) to 2.064(1) Å are expected for an S–S single bond, and the Ti···Ti distances are too long to be bonding. The absence of such bonding is consistent with the K/Ba ratio as given and the presence of Ti^{4+}.

Table 1. Selected distances for the $[Ti_6OS_8(S_2)_6]^{6-}$ clusters in $K_4Ba[Ti_6OS_{20}]$.

Space group *P6₃22*		Space group *Fddd*	
Ti–S1	2.376(1)	Ti1–S1 (×2)	2.375(1)
Ti–S2	2.370(1)	Ti1–S4 (×2)	2.4273(7)
Ti–S3	2.384(1)	Ti1–S5 (×2)	2.5285(7)
Ti–S3	2.532(1)	Ti2–S2	2.3743(8)
Ti–S3	2.536(1)	Ti2–S3	2.3786(8)
Ti–S4	2.472(1)	Ti2–S4	2.4364(8)
Ti–O	2.2890(7)	Ti2–S4	2.5701(8)
S1–S2	2.058(1)	Ti2–S5	2.3778(8)
Ti···Ti	3.235(2)	Ti2–S5	2.5375(8)
Ti···Ti (×2)	3.237(1)	Ti1–O	2.2943(7)
Ti···Ti	3.240(2)	Ti2–O	2.2824(5)
		S1–S1	2.064(1)
		S2–S3	2.0608(9)
		Ti1···Ti2 × 2	3.2241(7)
		Ti1···Ti2 × 2	3.2483(7)
		Ti2···Ti2	3.224(1)
		Ti2···Ti2	3.2318(1)

Experimental Section

Synthesis: The following reagents were used as obtained: K (Aldrich, 99.5%), BaS (Alfa, 99.7%), Ti (Aldrich, 99.7%), TiO_2 (Aldrich, 98.9+%), and S (Alfa, 99.5%). K_2S was prepared by stoichiometric reaction of the elements in liquid NH_3. Both crystal modifications of $K_4Ba[Ti_6OS_{20}]$ were prepared by the reactions of K_2S, BaS, Ti, TiO_2, and S in the molar ratio of 1:0.25:1:0.25:7. The mixtures were loaded into two carbon-coated fused-

[*] Prof. J. A. Ibers, F. Q. Huang
Department of Chemistry
Northwestern University
2145 Sheridan Road
Evanston, IL 60208-3113 (USA)
Fax: (+1) 847-491-2976
E-mail: ibers@chem.northwestern.edu

[**] This research was supported by the U.S. National Science Foundation (CHE98-19385 and DMR00-96676). This work made use of facilities supported by the MRSEC program of the National Science Foundation (DMR00-76097) at the Materials Research Center of Northwestern University.

  1433-7851/01/4013-2515 $ 17.50+.50/0

silica tubes under an argon atmosphere in a glove box. These tubes were sealed under a 10^{-4} Torr atmosphere and then placed in a computer-controlled furnace. The sample in the first tube was heated to 823 K at 1.5 K min^{-1}, kept at 823 K for three days, very slowly cooled at 4 K h^{-1} to 423 K, then cooled to room temperature to afford black hexagonal plates of the hexagonal modification in about 80% yield. The sample in the second tube was heated to 873 K at 1.5 K min^{-1}, kept at 873 K for two days, when the furnace was turned off. Black needles of the orthorhombic modification were obtained in about 70% yield. The reaction mixtures were washed free of alkali metal chalcogenides with dimethylformamide and then dried with acetone. Analysis of these crystals with an energy-dispersive X-ray (EDX)-equipped Hitachi S-4500 scanning electron microscope showed K/Ba/Ti/S approximately in the ratio 5:1:10:30; the presence of O was observed but could not be quantified.

General crystallographic details: Bruker Smart 1000 CCD diffractometer,[30] graphite-monochromatized $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å), $T = 153$ K. Data were collected by an ω scan of 0.3° in groups of 606, 606, and 606 frames at ϕ settings of 0°, 120°, and 240° for the hexagonal modification and in groups of 606, 606, 606, and 606 frames at ϕ settings of 0°, 90°, 180°, and 270° for the orthorhombic modification. The exposure times were 15 s frame^{-1}. Intensity data were collected with the program SMART.[30] Cell refinement and data reduction were carried out with the use of the program SAINT,[30] face-indexed absorption corrections were carried out with the program XPREP,[31] and the frame variations were further corrected with the use of the program SADABS.[30] The structures were solved with the direct methods program SHELXS and refined with the least-squares program SHELXL of the SHELXTL-PC suite of programs.[31] The final refinements included anisotropic displacement parameters and a secondary extinction correction. Crystal structure analysis of $K_4Ba[Ti_6OS_{20}]$: black hexagonal plate, $0.040 \times 0.078 \times 0.084$ mm, hexagonal, $P6_322$, $a = 9.3386(4)$, $c = 18.130(1)$ Å, $V = 1369.3(1)$ Å^3, $T = 153$ K, $Z = 2$, $\rho_{calcd} = 3.004$ g cm^{-3}, $\theta_{max.} = 28.88°$, 11 429 reflections measured, 1175 unique, 1064 observed with $I > 2\sigma(I)$, $\mu = 52.12$ cm^{-1}, min/max transmission = 0.685/0.816, $R_1 = 0.0374$, $wR_2 = 0.0895$. Black needle, $0.096 \times 0.112 \times 0.248$ mm, orthorhombic, $Fddd$, $a = 11.106(2)$, $b = 15.338(2)$, $c = 32.265(5)$ Å, $V = 5496.0(13)$ Å^3, $T = 153$ K, $Z = 8$, $\rho_{calcd} = 2.993$ g cm^{-3}, $\theta_{max.} = 28.85°$, 16 008 reflections measured, 1749 unique, 1590 observed with $I > 2\sigma(I)$, $\mu = 51.94$ cm^{-1}, min/max transmission = 0.459/0.713, $R_1 = 0.0336$, $wR_2 = 0.0894$.

Further details on the crystal structure investigations may be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: (+49) 7247-808-666; e-mail: crysdata@fiz-karlsruhe.de), on quoting the depository numbers CSD-411697 for the orthorhombic modification and CSD-411698 for the hexagonal modification.

Received: February 22, 2001 [Z16664]

[1] T. Saito, *Adv. Inorg. Chem.* **1997**, *44*, 45 – 91.
[2] T. Saito in *Early Transition Metal Clusters with π-Donor Ligands* (Ed.: M. H. Chisholm), VCH, New York, **1995**, pp. 63 – 164.
[3] J. D. Corbett, *Inorg. Chem.* **2000**, *39*, 5178 – 5191.
[4] J. D. Corbett, E. Garcia, Y.-U. K. Kwon, A. Guloy, *Pure Appl. Chem.* **1990**, *62*, 103 – 112.
[5] U. Müller, V. Krug, *Angew. Chem.* **1988**, *100*, 277; *Angew. Chem. Int. Ed. Engl.* **1988**, *27*, 293 – 294.
[6] A. Simon, *J. Solid State Chem.* **1985**, *57*, 2 – 16.
[7] J. D. Corbett, *J. Alloys Compd.* **1995**, *229*, 10 – 23.
[8] F. Rogel, J. Zhang, M. W. Payne, J. D. Corbett in *Electron Transfer in Biology and the Solid State. Inorganic Compounds with Unusual Properties*, *Vol. 226* (Eds.: M. K. Johnson, R. B. King, D. M. Kurtz, Jr., C. Kutal, M. L. Norton, R. A. Scott), American Chemical Society, Washington, DC, **1990**, pp. 369 – 402.
[9] S. A. Sunshine, D. Kang, J. A. Ibers, *J. Am. Chem. Soc.* **1987**, *109*, 6202 – 6204.
[10] S. A. Sunshine, D. Kang, J. A. Ibers, *Mater. Res. Soc. Symp. Proc.* **1987**, *97*, 391 – 396.
[11] D. Kang, J. A. Ibers, *Inorg. Chem.* **1988**, *27*, 549 – 551.
[12] P. M. Keane, J. A. Ibers, *Inorg. Chem.* **1991**, *30*, 1327 – 1329.
[13] J. A. Cody, J. A. Ibers, *Inorg. Chem.* **1994**, *33*, 2713 – 2715.
[14] M. A. Pell, J. A. Ibers, *Chem. Mater.* **1996**, *8*, 1386 – 1390.
[15] M. A. Pell, J. A. Ibers, *Chem. Ber.* **1997**, *130*, 1 – 8.
[16] D. Röhnert, C. Näther, W. Bensch, *Acta Crystallogr. Sect. C* **1997**, *53*, 165 – 167.
[17] S. Herzog, C. Näther, P. Dürichen, W. Bensch, *Z. Anorg. Allg. Chem.* **1998**, *624*, 2021 – 2024.
[18] W. Bensch, C. Näther, P. Dürichen, *Angew. Chem.* **1998**, *110*, 140 – 142; *Angew. Chem. Int. Ed.* **1998**, *37*, 133 – 135.
[19] O. Krause, C. Näther, W. Bensch, *Acta Crystallogr. Sect. C* **1999**, *55*, 1197 – 1199.
[20] S. Herzog, C. Näther, W. Bensch, *Z. Anorg. Allg. Chem.* **1999**, *625*, 969 – 974.
[21] W. Bensch, P. Dürichen, C. Näther, *Solid State Sci.* **1999**, *1*, 85 – 108.
[22] F. Q. Huang, J. A. Ibers, *Inorg. Chem.* **2001**, *40*, 865 – 869.
[23] P. Monceau, *Electronic Properties of Inorganic Quasi-One-Dimensional Compounds*, D. Reidel, Dordrecht, Netherlands, **1985**.
[24] H. Fjellvåg, A. Kjekshus, *Solid State Commun.* **1986**, *60*, 91 – 93.
[25] S. Furuseth, H. Fjellvåg, *Acta Chem. Scand.* **1991**, *45*, 694 – 697.
[26] S. Furuseth, L. Brattås, A. Kjekshus, *Acta Chem. Scand.* **1973**, *27*, 2367 – 2374.
[27] J. A. Cody, M. F. Mansuetto, M. A. Pell, S. Chien, J. A. Ibers, *J. Alloys Compd.* **1995**, *219*, 59 – 62.
[28] Note added in proof: Prof. W. Bensch has called our attention to an abstract describing the related compound $K_6TiS_{18}O$ (R. Tillinski, C. Näther, W. Bensch, *Z. Kristallogr. Suppl.* **1999**, *16*, 66).
[29] D. Fenske, A. Grissinger, M. Loos, J. Magull, *Z. Anorg. Allg. Chem.* **1991**, *598/599*, 121 – 128.
[30] SMART Version 5.054 Data Collection and SAINT-Plus Version 6.02A Data Processing Software for the SMART System, Bruker Analytical X-Ray Instruments, Inc., Madison, WI, USA, **2000**.
[31] G. M. Sheldrick, SHELXTL DOS/Windows/NT Version 5.10, Bruker Analytical X-Ray Instruments, Inc., Madison, WI, USA, **1997**.

Switching a Catalyst System from Ethene Polymerization to Ethene Trimerization with a Hemilabile Ancillary Ligand**

Patrick J. W. Deckers, Bart Hessen,* and Jan H. Teuben

The chemistry of transition metal complexes with hemilabile ancillary ligands (i.e., with multidentate ligands that have a mixture of tightly bound and substitutionally labile functionalities) is enjoying an increasing popularity.[1] These hemilabile ligands can stabilize reactive metal centers by the chelate effect, but keep the metal accessible for substrate molecules by virtue of the substitutionally labile character of one of the functionalities. Examples of such hemilabile ligands include phosphine – ether, cyclopentadienyl – alkene, and phosphine – arene ligands. In some cases, hemilabile ligands were found to influence the selectivity and stability of transition metal catalysts.[2] Here we report that the catalyst system $[(\eta^5\text{-}C_5H_4CMe_2R)TiCl_3]$/MAO (MAO = methylalumoxane) is transformed from an ethene polymerization catalyst into an ethene trimerization catalyst, producing 1-hexene, by simply changing the ligand substituent R from a methyl to a

[*] Dr. B. Hessen, P. J. W. Deckers, Prof. Dr. J. H. Teuben
Dutch Polymer Institute/Center for Catalytic Olefin Polymerization
Stratingh Institute for Chemistry and Chemical Engineering
University of Groningen
Nijenborgh 4, 9747 AG Groningen (The Netherlands)
Fax: (+31) 50-3634315
E-mail: hessen@chem.rug.nl

[**] Netherlands Institute for Catalysis Research (NIOK) publication RUG 01-04-02.

  1433-7851/01/4013-2516 $ 17.50+.50/0