The Oxysulfide Anion $[NbS_3O]^{3-}$: Synthesis and Crystal Structure of $Ba_6(NbS_4)(NbS_3O)_3$

L. E. RENDON-DIAZMIRON

Instituto de Investigaciones en Materiales, U.N.A.M., Mexico, D.F.

C. F. CAMPANA

Nicolet XRD Corporation, Cupertino, California 95014

AND H. STEINFINK

Department of Chemical Engineering, The University of Texas, Austin, Texas 78712

Introduction

During reactions in which BaS, Nb, and S were sealed in evacuated Vycor tubes to produce intermediate phases in the Ba–Nb–S system, one experiment yielded a significant amount of small yellowish crystals in addition to the usual black crystals. The crystal structure of one such black crystal, with the approximate composition $Ba_4Nb_2S_9$, has been determined and consists of BaS_3 layers with Nb in octahedral interstices formed by 6 S^{2-} (*1*). We investigated the crystal structure of one of the yellow crystals and its composition was eventually shown to be $Ba_6Nb_4S_{13}O_3$. The presence of oxygen was initially unknown. Only after electron density maps consistently showed the presence of an atom with significantly lower X-ray scattering power than S^{2-} was this single crystal subjected to a wavelength dispersive X-ray fluorescence analysis which showed the presence of oxy-gen in addition to Ba, Nb, and S. A subsequent X-ray diffraction powder pattern of the BaS used in the preparation revealed a considerable amount of $BaSO_4$ admixed with BaS; the oxysulfide phase must have been formed because of the presence of this impurity in BaS. The structure shows a novel coordination in which some Nb are tetrahedrally coordinated to 4 S^{2-}, while others are coordinated to 3 S^{2-} and 1 O^{2-}.

Structure Determination

A crystal approximately 0.15 × 0.20 × 0.22 mm was mounted on a Nicolet R3m/E Crystallographic System equipped with a graphite monochromator, a 2.4-kW rated Mo target X-ray tube and an automatic attenuator. Intensities were obtained using a variable ω scan mode with rates varying from 3.91 to 29.30 deg min^{-1}. Stationary background measurements were taken at $\frac{1}{2}$ the scan time 1 deg on either side of peak

TABLE I

ATOMIC PARAMETERS $\times 10^4$ FOR $Ba_6Nb_4S_{13}O_3$ (STANDARD DEVIATIONS IN PARENTHESES)

Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ba 1	2252.6(3)	807.4(6)	9045(1)	107(4)	140(4)	192(5)	−18(3)	−1(3)	−7(4)
Ba 2	458.8(5)	¼	8627(2)	195(7)	139(7)	898(13)	—	242(8)	—
Ba 3	3441.1(5)	¼	2655(2)	330(7)	101(6)	171(7)	—	−11(5)	—
Ba 4	792.9(4)	152.4(7)	2714(1)	195(5)	287(5)	225(5)	42(4)	−41(4)	21(4)
Nb 1	1688.1(7)	¼	4006(2)	112(9)	103(9)	179(9)	—	0(7)	—
Nb 2	3381.0(7)	¼	7776(2)	111(9)	107(9)	154(10)	—	20(7)	—
Nb 3	4181.6(5)	9963.6(8)	2848(2)	91(6)	99(6)	167(7)	−3(5)	6(5)	5(5)
S 1	1686(2)	¼	6942(7)	183(25)	165(26)	209(27)	—	3(22)	—
S 2	3437(1)	408(2)	1156(5)	138(16)	145(18)	222(18)	23(14)	−27(14)	25(15)
S 3	3218(1)	1171(2)	6167(4)	211(18)	133(17)	167(18)	−1(15)	20(15)	−6(15)
S 4	804(2)	¼	3061(9)	164(28)	188(29)	649(43)	—	164(28)	—
S 5	4639(1)	1196(3)	4091(5)	193(18)	159(20)	285(20)	−34(15)	−2(16)	−50(16)
S 6	2120(1)	1200(3)	2983(5)	244(19)	167(19)	271(22)	96(16)	−13(17)	−46(16)
S 7	4735(2)	9145(4)	1259(9)	468(30)	667(39)	1017(49)	−20(29)	−102(32)	241(36)
S 8	4238(2)	¼	8944(8)	151(27)	518(39)	408(35)	—	1(26)	—
O 1	2879(5)	¼	9531(16)	154(66)	185(75)	182(72)	—	0(7)	—
O 2	1078(4)	817(6)	9513(11)	162(47)	189(53)	159(48)	−21(41)	80(40)	−6(43)

Note. The temperature factor is $\exp[-(U_{11}h^2 + U_{22}k^2 + U_{33}l^2 + 2(U_{12}hk + U_{13}hl + U_{23}kl))]$.

maxima. Two check reflections were measured every 46 reflections to monitor instrument stability and crystal decay. None was observed. The intensities were corrected for absorption using an empirical psi scan method and the transmission factors ranged from 0.230 to 0.293. Precision lattice constants were obtained from a least squares procedure applied to 25 precise measurements of 2θ in the range 25–35°. The parameters are $a = 23.915(4)$ Å, $b = 14.238(2)$ Å, and $c = 7.778(2)$ Å, space group $Pnma$, with 4 $Ba_6Nb_4S_{13}O_3$ formulas in the unit cell. Data were collected between 3–45° 2θ, and 1599 independent reflections were considered observed on the basis that $I > 3\sigma(I)$, $\sigma(I) = [SC + \tau^2(B_1 + B_2)]^{1/2}$ where SC is the count during the scan and τ is the ratio of the scan time to background time. The data processing has been described in detail previously (2). All calculations were carried out with the program package SHELXTL (Rev 3.0) on the R3m/E system (3). The structure was solved using the direct method which provided Ba

and Nb positions. Three-dimensional electron density maps calculated from amplitudes phased with the heavy atoms revealed the S positions. The conventional R remained around 7%, the temperature factors for two S atoms were anomalously high, and bond lengths to Nb were very short. Replacing these atoms with oxygen permitted refinement of the data to a conventional $R = 4.02\%$ and $\omega R = 4.19\%$ for the observed 1599 independent reflections. A subsequent wavelength dispersive X-ray fluorescence analysis confirmed the presence of oxygen. Values of the neutral scattering factors of the atoms, corrected for the real and imaginary parts of dispersion, were obtained from the "International Tables for X-Ray Crystallography" (4) and used in the calculations. In Table I are shown the final coordinates and Table II contains the list of observed and calculated structure amplitudes.[1]

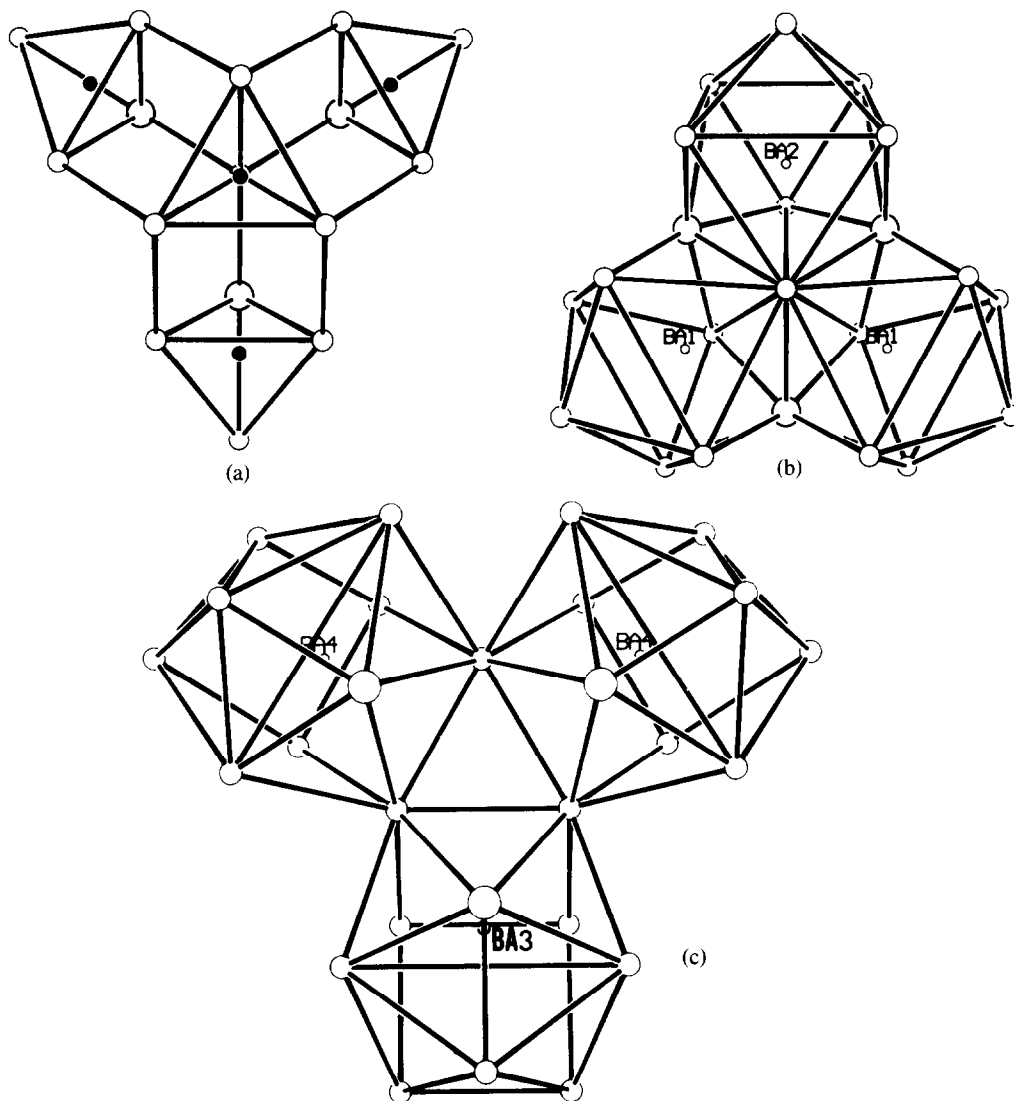[1] See NAPS document No. 04077 for 10 pages of supplementary material. Order from ASIS/NAPS, Mi-

FIG. 1. Sections of clusters in the $Ba_6Nb_4S_{13}O_3$ structure. Views are along [001]; a is vertical and b horizontal. Small open circles are S, large open circles are O and solid circles are Nb. (a) The Nb tetrahedra; (b) The Ba1 and Ba2 capped trigonal prismatic arrangement; (c) The Ba3 and Ba4 polyhedra.

Discussion

The pseudohexagonal character of the structure implied by the lattice constant relationship $b \approx \sqrt{3}\ a$, and by the distribution of intense reflections in reciprocal space, is quite evident from the arrangement of the Nb and Ba coordination polyhedra shown in Figs. 1a–c. Of the three

crystallographically independent Nb, Nb1 is tetrahedrally coordinated to 4 S, while Nb2 and Nb3 are tetrahedrally coordinated to 3 S and 1 O. The Nb1 and S1 atoms lie on a pseudo threefold axis and 1 Nb2 and 2 Nb3 tetrahedra are trigonally arranged around it. In Fig. 1b the trigonal prisms formed by 6 S around Ba1 and Ba2 have the rectangular faces capped by 1 S and 2 O so that the cations are in ninefold coordination.

The Ba3 and Ba4 ions in the section shown in Fig. 1c are in tenfold coordination. The polyhedron can be described as a distorted cube with an oxygen atom near one edge of the cube, which becomes elongated to accommodate this atom. A sulfur atom caps the distorted cube face. This section of the "cube," the 4 S and 1 S atoms form nearly a regular pentagon which is then capped by oxygen. This pentagonal pyramid has a square of 4 S atoms opposite its vertex.

When all Ba polyhedra are articulated with the polyhedra shown in Fig. 1a, it is found that Ba3 and Ba4 are opposite the top rectangular faces of the empty trigonal prisms, i.e., these rectangular faces are part of the distorted cube around the cations. The Ba1 trigonal prism shares corners with Ba4 and Ba3 cubes and the Ba2 trigonal prism articulates with two Ba4 cubes by

corner sharing. The three sections of the clusters shown in 1a–c are drawn to the same scale and can be superimposed to see the articulations. A stereoscopic view of the complete cluster is shown in Fig. 2. The space group symmetry causes this cluster to be repeated four times in the unit cell.

Bond distances are shown in Table III. The Ba–S and Ba–O distances are essentially sums of the ionic radii. The tetrahedral Nb–O distance of 1.84 Å is considerably longer than the average tetrahedral Nb–O = 1.67 Å in Nb_2O_5 (5). Niobium, when bonded to oxygen, is usually encountered in octahedral or pentagonal bipyramidal coordination; the latter is prevalent in organometallic complexes. The Nb–O distances in these structures vary from about 1.7 to 2.4 Å and apparently depend primarily on the chemical environment of oxygen, i.e., whether it is bridging or terminal (6–10). In niobium oxides where the cation is primarily in octahedral coordination, the average Nb–O bond is 2.0 Å. The tetrahedral NbO_4^{3-} ion is encountered in rare earth compounds $RENbO_4$ which have structures based on either the wolframite or scheelite arrangements (11). However, no detailed structure determinations have been carried out and reliable values of Nb–O are unavailable.
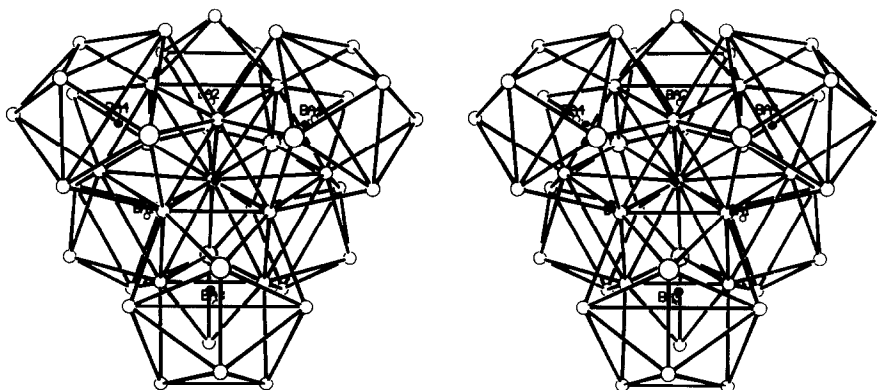
The tetrahedral Nb–S distance of 2.27 Å

FIG. 2. Stereoscopic view of a cluster. View along [001]; a is vertical and b horizontal.

TABLE III

Bond Distances and Angles in $Ba_6Nb_4S_{13}O_3$

Distances (Å)

Ba1–S1	3.214(1)	Nb1–S1	2.284(5)	S4–2S5	3.745(4)
S2	3.323(3)	S4	2.238(5)	2S6	3.651(3)
S2	3.282(4)	2S6	2.264(4)	2S7	3.652(6)
S3	3.257(3)			2O2	3.713(9)
S3	3.454(4)	Nb2–2S3	2.302(3)		
S6	3.333(4)	S8	2.243(6)	S5–S5	3.714(5)
S6	3.130(4)	O1	1.819(13)	S7	3.666(7)
O1	2.863(1)			S7	3.945(8)
O2	2.833(9)	Nb3–S2	2.304(4)	O2	3.356(10)
		S5	2.283(4)	O2	3.650(10)
Ba2– S1	3.214(5)	S7	2.154(6)		
S4	3.546(7)	O2	1.817(9)	S6–S6	3.702(5)
2S5	3.232(4)			O1	3.732(4)
2S7	3.016(7)	S1– S4	3.682(8)	O2	3.714(9)
S8	3.539(5)	2S6	3.740(4)		
2O2	2.900(9)	O1	3.493(13)	S7–S7	3.374(9)
		O2	3.443(9)	S8	3.397(6)
Ba3–2S2	3.199(3)			O2	3.193(11)
2S3	3.366(3)	S2–S5	3.838(5)		
2S5	3.592(3)	S6	3.621(5)	S8–O1	3.284(13)
2S6	3.671(3)	S6	3.635(5)		
S8	3.459(6)	S7	3.589(7)		
O1	2.778(13)	S8	3.938(3)		
		O1	3.501(3)		
Ba4–S2	3.346(4)	O2	3.348(9)		
S3	3.256(4)				
S4	3.354(1)	S3–S3	3.785(5)		
S5	3.436(4)	S5	3.763(5)		
S5	3.563(4)	S6	3.609(5)		
S6	3.514(4)	S6	3.748(5)		
S7	3.194(7)	S8	3.769(3)		
S7	3.017(6)	O1	3.330(3)		
S8	3.897(1)				
O2	2.750(9)				

Angles (°)

S6–Nb1–S4	108.39(9)	O1–Nb2–S8	107.44(25)	O2–Nb3–S7	106.7(3)
S6–Nb1–S1	110.65(9)	O1–Nb2–S3	107.21(8)	O2–Nb3–S5	109.4(3)
S6–Nb1–S6	109.67(14)	S8–Nb2–S3	112.06(8)	O2–Nb3–S2	108.1(3)
S4–Nb1–S1	109.04(18)	S3–Nb2–S3	110.58(14)	S7–Nb3–S5	111.4(2)
				S7–Nb3–S2	107.2(2)
				S5–Nb3–S2	113.7(1)

is shorter than the Nb–S bonds seen for this cation in octahedral, trigonal prismatic, or pentagonal bipyramidal coordination. In these polyhedra, the Nb–S distances are 2.4–2.7 Å and the distance depends on the chemical environment of the sulfur ion (6, 9, 12, 13–16). A Nb–S = 2.28 Å was encountered in the structure of $Ba_{16.5}Nb_9S_{42}$. In that case three NbS_6 octahedra share faces. One Nb is in the center of the middle

octahedron, while the other two Nb are displaced 0.39 Å from their respective octahedral centers away from the edge shared faces. In these octahedra two Nb–S distances of 2.683 and 2.279 Å, respectively, are observed (1).

Oxysulfide anions $[MoO_{4-x}S_x]^{2-}$ and $[WO_{4-x}S_x]^{2-}$ and $[ReO_{4-x}S_x]^{2-}$ have been studied in great detail. They are usually prepared as the alkali metal compounds and are precipitated from aqueous solutions (17–19). Recently a series of compounds have been reported with composition $[M'(MO_2S_2)]^{2-}$ where M = Mo and W and M' is Co and Ni (20). This is the first reported synthesis of the tetrahedral anion $[NbS_{4-x}O_x]^{3-}$. On the basis of this crystal structure analysis it can be predicted that the compound $Ba_6Nb_4S_{16}$ should exist and is probably trigonal. Other phases which should occur in this system are those in which only O2 or O1 is present in the structure to yield $Ba_6(NbS_4)_2(NbS_3O)_2$ or $Ba_6(NbS_4)_3NbS_3O$. Indeed, it was noted in the multicomponent product of the synthesis that crystals varying in color from yellow to orange were present. These differently colored crystals may have been due to such compositional variations. It will be interesting to see whether the anions NbS_2O_2 and $NbSO_3$ can be prepared analogously to the Mo and W oxysulfide anions. The previously reported compound $Cd_2Nb_2O_6S$ which has the pyrochlore structure is not an oxysulfide because Nb is octahedrally surrounded by oxygen. That structure can be considered as two interpenetrating sublattices of Cd_2S and Nb_2O_6 (21).

Acknowledgments

References

1. J. S. SWINNEA, H. STEINFINK, L. E. RENDON-DIAZMIRON, AND M. GOMEZ DAZA, J. Solid State Chem., to be published.
2. C. F. CAMPANA, D. F. SHEPARD, AND W. M. LITCHMAN, Inorg. Chem. 20, 4039 (1981).
3. SHELXTL, "User manual," (G. M. Sheldrick, Ed., Nicolet XRD Corp., Cupertino, Calif., July 1981.
4. "International Tables For X-Ray Crystallography," Vol. IV, Kynoch Press, Birmingham, England, 1974.
5. B. M. GATEHOUSE AND A. D. WADSLEY, Acta Crystallogr. 17, 1545 (1964).
6. J. W. MONCRIEF, D. C. PANTALEO, AND N. E. SMITH, Inorg. Nucl. Chem. Lett. 7, 255 (1971).
7. C. M. FLYNN AND G. D. STUCKY, Inorg. Chem. 8, 335 (1969).
8. S. ANDERSSON, Z. Anorg. Allg. Chem. 351, 106 (1967).
9. J. C. DEWAN, D. L. KEPERT, C. L. RASTON, D. TAYLOR, A. H. WHITE, AND E. N. MASLEN, J. Chem. Soc. Dalton Trans. 2082 (1973).
10. J. C. DEWAN, A. J. EDWARDS, AND G. R. JONES, J. Chem. Soc. Dalton Trans. 968 (1978).
11. H. P. ROOKSBY AND E. A. D. WHITE, Acta Crystallogr. 16, 888 (1963).
12. M. G. B. DREW AND J. D. WILKINS, J. Chem. Soc. Dalton Trans. 198 (1974).
13. F. KADIJK AND F. JELLINEK, J. Less Common Met. 19, 421 (1969).
14. A. F. J. RUYSINK, F. KADIJK, A. J. WAGNER, AND F. JELLINEK, Acta Crystallogr. B24, 1614 (1968).
15. J. RIJNSDORP AND F. JELLINEK, J. Solid State Chem. 25, 235 (1978).
16. J. L. TEMPLETON, W. C. DORMAN, J. C. CLARDY, AND R. E. MCCARLEY, Inorg. Chem. 17, 1263 (1978).
17. A. MÜLLER, E. DIEMANN, AND U. HEIDBORN, Z. Anorg. Allg. Chem. 376, 125 (1970).
18. A. MÜLLER, H. SCHULZE, W. SIEVERT, AND N. WEINSTOCK, Z. Anorg. Allg. Chem. 403, 310 (1974).
19. B. KREBS AND E. KINDLER, Z. Anorg. Allg. Chem. 368, 293 (1969).
20. A. MÜLLER, E. KÖNIGER-AHLBORN, E. KRICKEMEYER, AND R. JOSTES, Z. Anorg. Allg. Chem. 483, 69 (1981).
21. J. PANNETIER AND J. LUCAS, Mater. Res. Bull. 5, 797 (1970).