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Preparation and Crystal Structure of $Nb_{14}S_5$

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The compound $Nb_{14}S_5$ has been prepared by high-temperature techniques. The crystal structure of $Nb_{14}S_5$ has been determined from a single-crystal X-ray diffraction study using intensities obtained on a single-crystal diffractometer with Mo Kα radiation. The compound crystallizes in the orthorhombic space group *Pnma* with unit cell dimensions $a = 18.480 \pm 7$, $b = 3.374 \pm 2$, and $c = 19.797 \pm 16$ Å. The unit cell contains four formula units. The positional parameters were refined by least-squares treatment using isotropic thermal parameters to a conventional $R = 0.079$. The sulfur atoms have capped trigonal-prismatic coordination. The coordination number of the niobium atoms ranges between 14 and 16.

Introduction

A number of solid metal-rich sulfides of transition elements and compounds with related structures such as selenides and phosphides have been found to be important in systems at temperatures between about 1000 and 1500°. These compounds include $Nb_{21}S_8$,[1] Ti_2S,[2] and Nb_7P_4,[3] for example, all of which are structurally similar. The structural similarities of compounds in this category as well as their similarities in properties such as metallic luster and conductivity, high hardness and brittleness, melting points near those of the free metals, and low volatilities suggest that the compounds in question might fruitfully be examined for similarities and differences to provide insight into the interrelations among the properties and, ultimately, useful bonding models for the solids. This article reports the preparation and the determination of the structure of $Nb_{14}S_5$ and the relationship of this structure to the structures of other metal-rich compounds.

Experimental Section

$Nb_{21}S_8$ was prepared from elemental sulfur and niobium by high-temperature techniques described previously.[4] The niobium metal, obtained from E. I. du Pont de Nemours and Co., was greater than 99.9% pure and the 99.999% pure sulfur was obtained from the American Smelting and Refining Co.

The new phase, $Nb_{14}S_5$, was initially observed as small but well-formed single crystals in a polycrystalline sample consisting mainly of $Nb_{21}S_8$. The thin needlelike crystals of $Nb_{14}S_5$ could easily be distinguished from the larger trapezoidal-shaped $Nb_{21}S_8$ crystals. The sample, which had an initial composition of S:Nb = 0.374 (compared with 0.381 for $Nb_{21}S_8$ and 0.357 for $Nb_{14}S_5$), was partially melted for a few minutes at 1571° in a boron nitride crucible and then cooled at the rate of 2–3°/min. X-Ray powder patterns indicated that the sample consisted of $Nb_{21}S_8$, Nb metal, and a new phase. The composition of the new phase was shown to be $Nb_{14}S_5$ based on results of a complete structure analysis. Attempts to prepare the $Nb_{14}S_5$ phase directly either by arc melting or by high-temperature annealing up to the melting point of the mixture of niobium and $Nb_{21}S_8$ were not successful. High-temperature annealing of the mixture resulted in rapid reaction between Nb and $Nb_{21}S_8$ to form $Nb_{14}S_5$ only when there was initially present some amount of $Nb_{14}S_5$ in the mixture, indicating that the formation of $Nb_{14}S_5$ by reaction of $Nb_{21}S_8$ and Nb is kinetically unfavorable.

A nearly pure $Nb_{14}S_5$ sample was thus prepared in steps as follows. Nb and $Nb_{21}S_8$ were mixed in the proportion to give roughly the stoichiometry of $Nb_{14}S_5$. The sample was then arc melted. After it was completely melted, the power of the arc melter was reduced to keep only the upper one-third of the sample in a molten state. The sample remained partially melted for at least 30 sec before the power was shut off. It was then annealed in a Nb crucible for 30 hr at temperatures above 1350° with a maximum temperature of 1500°. X-Ray analyses indicated that the arc-melted sample consisted of $Nb_{21}S_8$ as the major and $Nb_{14}S_5$ and Nb as the minor components and that the annealed sample consisted essentially of only $Nb_{14}S_5$ with the diffraction pattern of the Nb metal barely detectable. The composition of the annealed sample obtained by combustion analyses was S:Nb = 0.352 (0.357 for $Nb_{14}S_5$). This is consistent with the results of the X-ray analysis which indicated that the sample was contaminated slightly with Nb metal. $Nb_{14}S_5$ does not form readily from the melt; melting of $Nb_{14}S_5$ slightly above 1500° followed by quenching yields Nb and $Nb_{21}S_8$.

Integrated intensity data were collected with a General Electric XRD-5 diffractometer equipped with a scintillation counter. Zirconium-filtered molybdenum Kα radiation (λ 0.7107 Å) was used with a takeoff angle of 2°. A total of 1214 independent reflections (*hkl*, $k = 0, 1, 2, 3, 4$) were measured in the range $0° < 2\theta < 60°$. Each reflection intensity was obtained by scanning over an angle of 1.5° for 200 sec. The background was counted for 40 sec both before and after the scan.

The method of preparation resulted in single crystals of $Nb_{14}S_5$ with dimensions that seriously limited the number of reflections that could be accurately measured. Of the 1214 reflections measured using the largest single crystal that was obtained, only 502 met the criterion of observable intensity used in this work, namely, $\sigma(I)/I = \sqrt{A + B}/(A - B) < 1.00$, where A and B are the total scan counts and background counts, respectively. This crystal had a needlelike shape with a maximum cross-sectional dimension of 16 μ and a length of 129 μ. The data were collected with the X-ray beam perpendicular to the long dimension of the crystal, which was the direction of the crystal *b* axis. Absorption corrections based on this shape and orientation were made using the computer program ORABS.[5] The total linear absorption coefficient for $Nb_{14}S_5$ is 127.3 cm^{-1} and the transmission factors ranged between 0.874 and 0.859. Lorentz and polarization corrections were applied.

The lattice parameters obtained from the single-crystal diffractometer were improved upon by a least-squares treatment of the 2θ values from a Guinier powder photograph at 25° with KCl, $a = 6.29300 \pm 0.00009$ Å,[6] as an internal standard and nickel-filtered Cu Kα radiation (λ 1.54050 Å): $a = 18.480 \pm 7$, $b = 3.374 \pm 2$, $c = 19.797 \pm 16$ Å; $Z = 4$; $d_{\text{calcd}} = 7.823$ g/cm^3. Table I contains the *d* values observed and calculated with the observed relative intensities.

Structure Determination

From preliminary Weissenberg photographs the conditions limiting the possible reflections were observed to be as follows: *hkl*, no conditions; 0*kl*, $k + l = 2n$; *h*0*l*, no conditions; *hk*0, $h = 2n$. These conditions indicate two possible space groups, $Pna2_1$ ($C_{2v}{}^9$) and *Pnma* ($D_{2h}{}^{16}$), differing by a center of symmetry. It was observed that, aside from angle-dependent factors, the intensities of the *hkl* reflections were equal to the intensities of the $h(k + 2)l$ reflections, indicating that the atoms are in the positions located on the mirror planes of *Pnma*.

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(2) J. P. Owens, B. R. Conard, and H. F. Franzen, *Acta Crystallogr.*, 23, 77 (1967).

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(5) D. J. Wehe, W. R. Busing, and H. A. Levy, "ORABS, a Fortran Program for Calculating Single Crystal Absorption Corrections," U. S. Atomic Energy Commission Report ORNL-TM-229, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1962.

(6) P. G. Hambling, *Acta Crystallogr.*, 6, 98 (1953).

Table I. Guinier X-Ray Data for $Nb_{14}S_5$

hkl	*d*(obsd)	*d*(calcd)	I/I_0
201	8.307	8.354	5
202	6.691	6.742	5
111	3.248	3.266	5
613 }	3.013	3.000	5
405 }		3.003	
504 }	2.964	2.959	10
113 }		2.963	
603	2.788	2.788	8
114	2.754	2.754	5
410	2.727	2.728	30
313 }	2.702	2.703	10
411 }		2.702	
207	2.695	2.701	8
406	2.682	2.682	2
214	2.674	2.671	5
604	2.622	2.613	15
702 }	2.547	2.549	50
115 }		2.545	
413	2.520	2.521	70
506	2.457	2.459	30
512	2.420	2.418	80
414 }	2.389	2.388	8
208 }		2.387	
315	2.364	2.371	12
116	2.343	2.341	90
513 }	2.333	2.333	60
704 }		2.328	
308 }	2.299	2.293	25
801 }		2.293	
216	2.285	2.286	90
610	2.274	2.276	40
802 }	2.244	2.248	5
415 }		2.245	
612	2.219	2.218	60
316	2.206	2.203	45
408	2.184	2.179	35
803		2.179	
416	2.103	2.101	40
804	2.096	2.092	20
902	2.013	2.009	2
509	1.888	1.888	5
3,0,10	1.879	1.882	3
020	1.687	1.691	100

Unitary structure factors were obtained from the observed structure factors by a graphical method described by Woolfson.[7] All unitary structure factors with less than 25% uncertainty in the intensity measurement were examined. Application of the direct method resulted in two electron density maps. One map contained peaks at $y = 0$ and $y = 1/2$ violating the special positions 4(c). The other map contained 14 strong peaks per asymmetric unit on the $y = 1/4$ and $y = 3/4$ sections. The electron density map calculated on the basis of this trial structure clearly showed five independent sulfur positions per asymmetric unit. The structure obtained with these niobium and sulfur positions was refined by least-squares computation using a computer program by Busing, Martin, and Levy.[8] Atomic scattering factors given by Hanson, *et al.*,[9] and corrected for anomalous dispersion according to Cromer and Liberman[10] were used. The structure was initially refined with the average value of the isotropic temperature factor coefficients of 0.45 and 0.30 obtained for niobium and sulfur, respectively, in the refinement of the $Nb_{21}S_8$ structure. The unweighted reliability index defined by $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, obtained using all the observable reflections, was 0.102 and the weighted reliability index $R_2 = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$ was 0.162 where the weight w is equal to $1/\sigma^2(F_o)$. Attempts at refinement of the atomic isotropic temperature factor coefficients yielded negative values for some atoms. An examination of F_o *vs.* F_c for intense low-angle reflections indicated that secondary extinction was appreciable.

Table II. Positional[a] and Isotropic Thermal Parameters for $Nb_{14}S_5$

Atom	*x*	*z*	*B*, Å^2
Nb(1)	0.1168 (4)	0.1661 (4)	0.6 (2)
Nb(2)	0.2808 (5)	0.0811 (4)	0.7 (2)
Nb(3)	0.4666 (5)	0.0444 (4)	0.7 (2)
Nb(4)	0.1999 (5)	0.3230 (4)	0.7 (2)
Nb(5)	0.3602 (4)	0.2423 (4)	0.2 (1)
Nb(6)	0.4472 (4)	0.3844 (4)	0.5 (2)
Nb(7)	0.2974 (4)	0.4660 (4)	0.4 (2)
Nb(8)	0.1387 (4)	0.4809 (4)	0.4 (1)
Nb(9)	0.4508 (4)	0.5500 (4)	0.5 (2)
Nb(10)	0.2558 (5)	0.7047 (4)	0.7 (2)
Nb(11)	0.1028 (4)	0.6350 (4)	0.4 (2)
Nb(12)	0.0084 (5)	0.7740 (4)	0.6 (2)
Nb(13)	0.1716 (5)	0.8484 (4)	0.7 (2)
Nb(14)	0.4293 (4)	0.8790 (4)	0.2 (1)
S(1)	0.484 (1)	0.176 (1)	0.2 (4)
S(2)	0.322 (1)	0.589 (1)	0.2 (4)
S(3)	0.380 (1)	0.760 (1)	0.3 (4)
S(4)	0.290 (1)	0.921 (1)	0.8 (4)
S(5)	0.096 (1)	0.968 (1)	0.8 (4)

[a] The *y* positional parameter is 0.25.

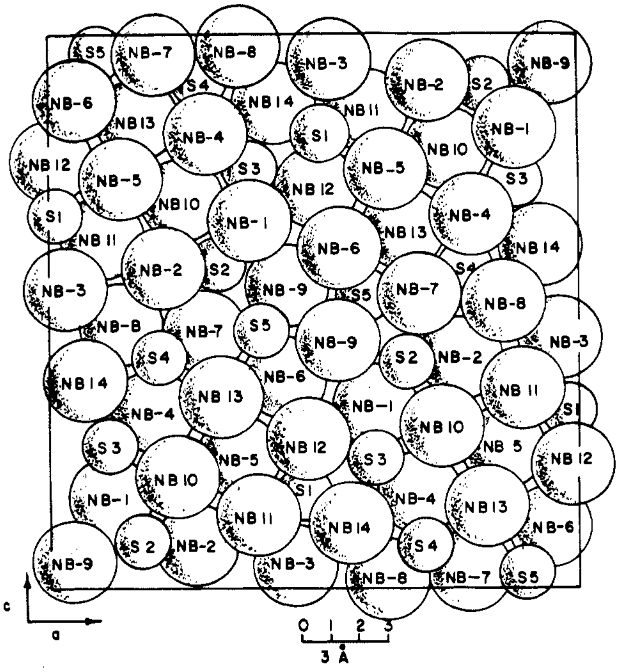

Figure 1. The crystal structure of $Nb_{14}S_5$ viewed along the *b* axis.

An extinction correction was made using the effective absorption coefficient $\mu' = \mu + 2gQ(1 + \cos^4 2\theta)/(1 + \cos^2 2\theta)^2$ as given by Zachariasen,[11] where μ is the linear absorption coefficient and $Q = |e^2FK/mc^2V|^2\lambda^3/(\sin 2\theta)$, where K is the polarization factor. A local modification of the least-squares refinement program resulted in values of R_1 and R_2 of 0.079 and 0.057, respectively, and a final value of the extinction parameter g of 2.03 (9) × 10^4. Final positional and isotropic thermal parameters are listed in Table II and the observed and calculated structure factors for all the observed reflections are compared in Table III.[12] The ranges of the occupancy parameters found by refinement were 0.98-1.02 ± 0.02 for niobium and 0.97-1.04 ± 0.05 for sulfur, indicating that the compound is stoichiometric to within the limits of uncertainity.

The thermal ellipsoid plot computer program written by Johnson[13] was used to draw a projection of the structure down

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(7) M. M. Woolfson, "Direct Methods in Crystallography," Oxford University Press, London, 1961, pp 6-13.

(8) W. R. Busing, K. O. Martin, and H. A. Levy, Report ORNL-TM-305, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1962.

(9) H. P. Hanson, F. Herman, J. D. Lea, and S. Skillman, *Acta Crystallogr.*, 17, 1040 (1964).

(10) D. T. Cromer and D. Liberman, *J. Chem. Phys.*, 53, 1891 (1970).

(11) W. H. Zachariasen, *Acta Crystallogr.*, 16, 1139 (1963).

(12) Table III, a listing of structure factors, will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth St., N.W., Washington, D. C. 20036. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche, referring to code number INORG-73-552.

(13) C. K. Johnson, Report ORNL-3794, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1965.

Table IV. Nearest Neighbors and Their Interatomic Distances in $Nb_{14}S_5$

Central atom	Type of neighbors	No. of neighbors	Distances,[a] Å
Nb(1)	S(3)	2	2.511
	S(2)	2	2.541
	Nb(10)	2	2.996
	Nb(12)	2	3.097
	Nb(9)	2	3.113
	Nb(6)	1	3.290
	Nb(1)	2	3.374
	Nb(2)	1	3.466
	Nb(4)	1	3.467
	S(5)	1	3.949
Nb(2)	S(2)	2	2.538
	Nb(11)	2	2.935
	Nb(8)	2	3.000
	Nb(10)	2	3.048
	Nb(7)	2	3.181
	S(4)	1	3.178
	Nb(2)	2	3.374
	Nb(1)	1	3.466
	Nb(5)	1	3.511
	Nb(3)	1	3.514
	S(5)	1	4.080
Nb(3)	S(1)	1	2.626
	Nb(3)	2	2.733
	Nb(11)	2	2.775
	Nb(8)	2	2.867
	Nb(14)	2	2.975
	Nb(8)	1	3.220
	Nb(14)	1	3.349
	Nb(3)	2	3.374
	Nb(2)	1	3.511
	S(4)	1	4.080
Nb(4)	S(4)	2	2.570
	S(3)	2	2.574
	Nb(13)	2	2.954
	Nb(10)	2	3.001
	Nb(14)	2	3.126
	Nb(8)	1	3.323
	Nb(7)	1	3.354
	Nb(5)	1	3.365
	Nb(14)	2	3.374
	Nb(1)	1	3.467
	S(1)	1	3.990
Nb(5)	S(1)	1	2.639
	Nb(13)	2	2.759
	Nb(11)	2	2.799
	Nb(10)	2	2.828
	Nb(12)	2	3.024
	Nb(6)	1	3.240
	Nb(4)	1	3.365
	Nb(5)	2	3.374
	Nb(2)	1	3.514
	S(1)	2	4.283
Nb(6)	S(5)	2	2.491
	Nb(9)	2	2.844
	Nb(13)	2	2.859
	Nb(12)	2	2.881
	Nb(7)	1	3.205
	Nb(5)	1	3.240
	Nb(1)	1	3.290
	Nb(9)	1	3.278
	Nb(6)	2	3.374
	S(5)	1	4.026
Nb(7)	S(2)	1	2.483
	S(4)	2	2.500
	S(5)	2	2.588
	Nb(13)	2	2.930
	Nb(8)	1	2.945
	Nb(2)	2	3.181
	Nb(6)	1	3.205
	Nb(9)	1	3.288
	Nb(4)	1	3.354
	Nb(7)	2	3.374
	S(2)	2	4.189
Nb(8)	S(4)	2	2.448
	Nb(3)	2	2.867
	Nb(14)	2	2.914
	Nb(7)	1	2.945
	Nb(2)	2	3.000
	Nb(11)	1	3.122
	Nb(3)	1	3.220
	Nb(4)	1	3.323
	Nb(8)	2	3.374
	S(2)	1	4.003
Nb(9)	S(5)	2	2.505
	S(2)	2	2.513
	S(5)	1	2.715
	Nb(6)	2	2.844
	Nb(1)	2	3.113
	Nb(9)	2	3.173
	Nb(6)	1	3.278
	Nb(7)	1	3.288
	Nb(9)	2	3.374
	Nb(12)	1	3.643
	S(2)	2	4.207
Nb(10)	S(3)	1	2.548
	S(2)	1	2.586
	Nb(5)	2	2.828
	Nb(1)	2	2.996
	Nb(4)	2	3.001
	Nb(2)	2	3.048
	Nb(11)	1	3.146
	Nb(13)	1	3.245
	Nb(10)	2	3.374
	S(3)	2	4.228
Nb(11)	S(1)	2	2.467
	Nb(5)	2	2.775
	Nb(3)	2	2.799
	Nb(2)	2	2.935
	Nb(10)	1	3.146
	Nb(8)	1	3.122
	Nb(14)	1	3.219
	Nb(12)	1	3.262
	Nb(11)	2	3.374
	S(2)	1	4.141
Nb(12)	S(3)	1	2.460
	S(1)	2	2.575
	Nb(6)	2	2.881
	Nb(5)	2	3.024
	Nb(1)	2	3.097
	Nb(11)	1	3.262
	Nb(14)	1	3.359
	Nb(13)	1	3.364
	Nb(12)	2	3.374
	Nb(9)	1	3.643
	S(3)	2	4.162
Nb(13)	S(4)	1	2.613
	S(5)	1	2.736
	Nb(5)	2	2.759
	Nb(6)	2	2.859
	Nb(7)	2	2.930
	Nb(4)	2	2.954
	Nb(10)	1	3.245
	Nb(12)	1	3.359
	Nb(13)	2	3.374
	S(4)	2	4.235
Nb(14)	S(3)	1	2.523
	S(1)	2	2.568
	S(4)	1	2.704
	Nb(8)	2	2.914
	Nb(3)	2	2.975
	Nb(4)	2	3.126
	Nb(11)	1	3.219
	Nb(3)	1	3.349
	Nb(12)	1	3.364
	Nb(14)	2	3.374
	S(3)	2	4.213

Table IV (*Continued*)

Central atom	Type of neighbors	No. of neighbors	Distances,[a] Å
S(1)	Nb(11)	2	2.467
	Nb(12)	2	2.576
	Nb(14)	2	2.568
	Nb(3)	1	2.626
	Nb(5)	1	2.639
	S(3)	2	3.276
S(2)	Nb(7)	1	2.483
	Nb(9)	1	2.513
	Nb(2)	2	2.538
	Nb(1)	2	2.541
	Nb(10)	1	2.586
	S(5)	1	3.310
S(3)	Nb(12)	1	2.460
	Nb(14)	1	2.523
	Nb(1)	2	2.511
	Nb(4)	2	2.570
	Nb(10)	1	2.548
	S(1)	2	3.276
S(4)	Nb(8)	2	2.448
	Nb(7)	2	2.500
	Nb(4)	2	2.574
	Nb(13)	1	2.613
	Nb(14)	1	2.704
	Nb(2)	1	3.178
	S(4)	1	3.374
S(5)	Nb(9)	2	2.505
	Nb(6)	2	2.491
	Nb(7)	2	2.588
	Nb(9)	1	2.715
	Nb(13)	1	2.736
	S(2)	2	3.310

[a] The uncertainties in the interatomic distances are ±0.001 Å for Nb–Nb, ±0.0015 Å for Nb–S, and ±0.002 Å for S–S distances.

the *b* axis. This view, which uses Slater's radii,[14] is illustrated in Figure 1. The nearest neighbors and interatomic distances for each independent atom given in Table IV were also calculated using this program. For each independent atom the next nearest neighbors, which are not included in the coordination polyhedra, are listed in the last row for each central atom in Table IV.

Description and Discussion

The coordination of the sulfur and niobium atoms in $Nb_{14}S_5$ is similar to that found in a broad class of transition metal compounds in which atoms are located in mirror planes perpendicular to short (about 3.5 Å) axes. Some examples of compounds belonging to this class are $Nb_{21}S_8$,[1] Ti_2S,[2] Nb_7P_4,[3] Nb_5P_3,[15] Fe_2P,[16] and Co_2P.[17]

Each sulfur atom in $Nb_{14}S_5$ is partially coordinated by a trigonal prism of niobium atoms with additional atoms off the quadrilateral faces. S(2) and S(3) have trigonal-prismatic coordination polyhedra with idealized threefold axes in the mirror plane and have only a single capping atom (Nb(10) in both cases). S(1), S(4), and S(5) are coordinated by niobium atoms in trigonal prisms with idealized threefold axes perpendicular to the mirror planes. The S(1) and S(5) coordination prisms are bicapped and that for S(4) is tricapped. These coordinations are common for nonmetals in many of the structures in the class.

The coordination numbers of the niobium atoms in $Nb_{14}S_5$ range between 14 and 16. The niobium atoms in this compound exhibit two rather regular partial coordination prisms and a number of markedly unsymmetrical and irregular partial coordination prisms. Both the symmetrical and unsymmetrical polyhedra occur frequently in the subchalcogenides and subpnictides in the class mentioned above. One prominent symmetrical partial coordination configuration is a cubic prism such as is found in body-centered cubic metals. Nb(3), Nb(5), Nb(10), and Nb(13) are found with this partial coordination. In each of these cases the total coordination number is 14 with eight niobium atoms forming the cube and six additional capping atoms, consisting either of two sulfur and four niobium atoms or of one sulfur and five niobium atoms. This arrangement of capped cubic coordination similar to that found in body-centered cubic metals is commonly found in the metal-rich chalcogenides and pnictides of the metals which form body-centered cubic structures in the elemental form, as has been previously discussed.[18]

The second rather symmetrical partial coordination arrangement is the pentagonal-prismatic arrangement found for Nb(1) and Nb(4) with four sulfur atoms in the prisms and for Nb(2) with two sulfur atoms in the pentagonal prisms. In all three cases there are additional atoms in the mirror plane at rather large interatomic distances (3.3–3.5 Å) and two more atoms off the pentagonal faces.

The remaining Nb atoms (Nb(6), Nb(7), Nb(8), Nb(9), Nb(11), Nb(12), and Nb(14)) have rather unsymmetrical coordination polyhedra, which occur with sufficient frequency in the metal-rich compounds to warrant some consideration. The partial coordination polyhedra of Nb(6), Nb(8), and Nb(11) appear to be related to the symmetrical cubic arrangements discussed above with two metal atoms in the cubes replaced by two sulfur atoms, resulting in a further distortion of the ideal fourfold axis. All three of the niobium atoms Nb(6), Nb(8), and Nb(11) also have four capping niobium atoms in the mirror plane and two additional niobium atoms in the directions perpendicular to the mirror plane to complete the coordination number of 14.

The coordination polyhedra of Nb(9), Nb(12), and Nb(14) appear to be further distortions of the substituted cubic coordinations discussed immediately above. There remain four atoms in a plane above the coordinated atom and four related to these atoms by the mirror through the coordinated atom. The four atoms form trapezoids which can be viewed as arising from an increase in the in-plane Nb–Nb–Nb angle. The coordination prism of Nb(7), on the other hand, appears to arise from a two-sulfur pentagonal prism by the removal of two of the Nb atoms.

The structures of all of the compounds in the class under discussion can be viewed as arising from the five partial coordination prisms of the metal atoms and the trigonal partial coordination prism of the nonmetal. This suggests that the recognition of the importance of these prisms will be important in the future solution of structures of metal-rich chalcogenides and pnictides and that the occurrence of the prisms has an underlying chemical basis which it would be profitable to explore theoretically.

Registry No. $Nb_{14}S_5$, 37215-26-2.

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