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$Nb_6Se_{20}Br_6$, a Pseudo One-Dimensional Compound with a Waved Chain Structure

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$Nb_6Se_{20}Br_6$ (single crystal structure, 3053 *h k l*, 289 parameters, $R = 0.039$; space group $P2_1/c$) is built up by four identical chains. Within a chain Nb atoms do not form a straight line but exhibit a waved distribution; short and long Nb–Nb bonds are observed ($\bar{d}$(Nb–Nb) ≃ 3.08 Å, $\bar{d}$(Nb–Nb) ≃ 3.93 Å, respectively). © 1986 Academic Press, Inc.

Introduction

Chemical investigations of chalcogen-rich transition metal chalcogenides MX_n (with M = Nb, Ta; X = S, Se; $n \geq 3$), have led to the characterization of new series of derivatives among which the trichalcogenides MX_3 and the halogenotetrachalcogenides $(MX_4)_nY$ (with Y = halogen) are of great interest for their transport properties. For many years, following its characterization in 1975 (*1*) $NbSe_3$ has been, and still remains, a model compound for the study of charge density wave depinning effects. $(TaSe_4)_2I$ and $(NbSe_4)_{10/3}I$ (*2*) have shown similar properties, i.e., collective dynamics of condensed charge density waves are observed through the appearance of nonlinear dc conductivity at very low applied dc electric field. Studies of such sliding modes of the charge density waves have been recently extended to the blue bronze $K_{0.30}MoO_3$ (*3*).

In this field there is a need for new materials to experimentally support the growing development of theories. Observing that trichalcogenides are built up with various types of MX_3 chains, we tried at first to look for polytypes of these materials which combine similar (or new) chains in different ways. This led to the characterization of monoclinic TaS_3 with a CDW behavior different from that of orthorhombic TaS_3.

On the other hand the selenoiodides $(MSe_4)_nI$ with M = Nb and Ta gave rise to a large family with a nice flexibility in the physical properties in connection with a modulation of the electronic density along the metallic MSe_4 chains (M^{4+} in square antiprismatic coordination made of four Se_2^{2-} pairs) with variable halogen occupancy in sites between these chains (*2*).

But one can also propose changing iodine for another halogen. In that case we will drastically change the interchain couplings and this was the situation in the case of $(MSe_4)_nBr$ compounds. It can be also predicted that the increasing electronegativity from iodine to fluorine may induce structural alterations, with halogen atoms taking

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part directly in the coordination polyhedra of the metal atom. Compounds $NbSe_3Y$ (Y = halogen) reported by Rijnsdorp (*4*), but not structurally characterized, could illustrate the latter proposition. In the course of a study of such compounds, the synthesis of bromine derivatives yielded a new phase which does not belong to the MX_3Y series or to that of $(MX_4)_nY$. This phase, $Nb_6Se_{20}Br_6$, represents a new type of arrangement of niobium chains. Its waved structure allows interesting general comparisons and suggests new possible modes for stabilizing a one-dimensional system.

Experimental

$Nb_6Se_{20}Br_6$ crystals have been isolated from preparations aimed at obtaining $NbSe_3Br$. Mixtures of the elements in stoichiometric proportions were heated under vacuum in sealed silica tubes at 600–700°C for 15 days. Besides the known $NbSe_3Br$ phase (*4*), we observed some black single-crystal plates. A microanalysis of single crystals was made with a scanning electron microscope (microsonde Ouest CNEXO) employing energy selection of the X-ray spectrum emitted by the specimen. Experimental and theoretical values are reported in Table I.

TABLE I

1. Physical, crystallographic, and analytical data
   Formula: $Nb_6Se_{20}Br_6$, molecular weight: 2616.1
   Theoretical weight fraction concentration:
   %Nb = 21.21; Se = 60.36; Br = 18.33
   Microprobe analysis (average on 20 analysis points):
   %Nb = 20.65; Se = 60.45; Br = 18.90
   Crystal symmetry: monoclinic. space group: $P2_1/c$ (n°14)
   Cell parameters (293 K) (Å)
   $a = 19.370(5)$, $b = 13.026(4)$, $c = 13.598(2)$,
   $\beta = 90.062(2)°$,
   $V = 3431$ Å^3, $Z = 4$
   Density: $\rho_{cal} = 5.06$
   Absorption factor: μ (λ Mo$K\alpha$): 298 cm^{-1}
   Crystal size: 0.024 × 0.14 × 0.30 mm^3
2. Data collection
   Temperature: 293 K, radiation: Mo$K\alpha$
   Monochromator: oriented graphite (002). scan mode: $\omega/2\theta$
   Recording angle range: 2–38°, Scan angle: 1.2 + 0.35 tan θ
   Values determining the scan speed:
   Sigpre: 0.5; Sigma: 0.02; VPRE: 3 min^{-1}; TMAX = 120 sec
   Standard reflection: 510, 335, $\bar{2}\bar{3}6$; Periodicity: 3600 sec
3. Refinement conditions
   Reflections for the refinement of the cell dimensions: 25
   Recorded reflections in the quarter-space:
   Utilized reflections: 3053 with $I > 4\sigma(I)$
   Refined parameters: 289
   Reliability factors: $R = \Sigma[|F_o| - |F_c|]/\Sigma|F_o|$
   $R_w = [\Sigma_w(|F_o| - F_c|)^2/wF_o^2]^{1/2}$
4. Refinement results
   $R = 0.039$, $R_w = 0.046$
   Difference Fourier maximum peak intensity: 1.7 e^-/Å^3

TABLE II

X-RAY POWDER DIFFRACTION DATA: ESTIMATED INTENSITIES

$h\,k\,l$	d_{obs}	d_{calc}	I	$h\,k\,l$	d_{obs}	d_{calc}	I
0 2 0	6.524	6.513	wm[a]	6 2 0	2.8923	2.8924	w
$1\,0\,\bar{2}$	6.421	6.417	wm	$5\,1\,\bar{3}$	2.8755	2.8738	wm
1 0 2		6.413		5 1 3	2.8710	2.8710	wm
0 1 2	6.029	6.027	vs	$6\,1\,\bar{2}$	2.8456	2.8469	wm
$1\,1\,\bar{2}$	5.764	5.757	vs	6 1 2		2.8447	
1 1 2		5.754		$3\,3\,\bar{3}$	2.8237	2.8213	wm
$2\,0\,\bar{2}$	5.566	5.567	vw	0 1 5	2.6634	2.6622	w
2 0 2		5.562		$5\,3\,\bar{2}$		2.6609	
$2\,1\,\bar{2}$	5.118	5.119	w	$1\,1\,\bar{5}$	2.6379	2.6378	s
2 1 2		5.115		6 3 0	2.5902	2.5907	sm
4 0 0	4.844	4.842	vw	$4\,2\,\bar{4}$	2.5580	2.5597	w
4 1 0	4.539	4.539	wm	4 2 4		2.5576	
4 1 1	4.298	4.304	vw	$5\,0\,\bar{4}$	2.5544	2.5565	w
0 1 3	4.283	4.281	vw	5 0 4		2.5539	
4 1 2	3.7745	3.7733	vw	0 2 5	2.5088	2.5096	sm
$4\,2\,\bar{1}$	3.7346	3.7372	vw	1 2 5	2.4869	2.4885	m
0 2 3	3.7200	3.7204	vw	0 5 2	2.4319	2.4327	vvw
0 3 2	3.6597	3.6594	vw	6 3 2	2.4206	2.4202	vvw
$3\,1\,\bar{3}$	3.5763	3.5695	s	$6\,3\,\bar{2}$		2.4215	
$5\,1\,\bar{1}$		3.5829		$5\,2\,\bar{4}$	2.3795	2.3797	s
5 1 1		3.5811		5 2 4		2.3776	
0 0 4	3.4035	3.3995	vvw	4 1 5	2.3311	2.3319	wm
$1\,0\,\bar{4}$	3.3494	3.3489	w	$1\,4\,\bar{4}$		2.3347	
1 0 4		3.3478		0 3 5	2.3052	2.3048	vm
0 4 0	3.2604	3.2565	m	6 4 0	2.2908	2.2926	vw
$5\,1\,\bar{2}$		3.2602		$1\,3\,\bar{5}$	2.2880	2.2889	vvw
5 1 2		3.2575					
1 1 4	3.2430	3.2424	wm	$4\,2\,\bar{5}$	2.2310	2.2290	wm
3 2 3	3.2251	3.2223	wm	0 1 6		2.2328	
6 0 0		3.2282		$2\,0\,\bar{6}$	2.2059	2.2072	m
$4\,1\,\bar{3}$	3.2109	3.2088	wm	2 0 6		2.2062	
0 3 3	3.1356	3.1353	vw	$5\,1\,\bar{5}$	2.1958	2.1951	w
1 3 3	3.0957	3.0949	vvw				
$6\,0\,\bar{2}$	2.9172	2.9174	vw				
6 0 2		2.9151					

[a] vvw = very, very weak, vw = very weak, w = weak, m = medium, s = strong, vs = very strong.

Preliminary X-ray study on these crystals by photographic methods indicated a monoclinic symmetry (*2/m* Laüe symmetry). The unit cell parameters $a = 19.370(5)$

Å, b = 13.026(4) Å, c = 13.598(2) Å, and β = 90.06°(2) were refined from Guinier powder data (Guinier Nonius FR552), using strictly monochromatized Cu$K\alpha$ radiation (λ = 1.54056 Å). Silicon was used as internal standard. Indexed powder spectrum of the 67 first reflections of the phase is given in Table II.

A single crystal was mounted on a Nonius CAD4 diffractometer, (λ Mo$K\alpha$ radiation). The experimental conditions used to collect the data are reported in Table I. The observed systematic absences ($h0l$ for $l = 2n + 1$, $0k0$ for $k = 2n + 1$) agree with space group $P2_1/c$. An absorption correction was applied according to the approximate (parallelepipedic idealized shape) size of the crystal, i.e., 0.024 × 0.14 × 0.30 mm^3, (μ = 298 cm^{-1}). Lorentz and polarization effects were corrected as usual.

Solution and Structure Refinement

The structure was solved by means of direct methods using a Multan 11/82 version and subsequent Fourier syntheses. All parameters were refined by full matrix least squares, minimizing $\Sigma w(|F_o| - |F_c|)^2$. Anisotropic refinement converged to give a final R value of 0.039 (R_w = 0.045 with unit weight). The final Fourier difference map showed random peaks, the highest one corresponding to 1.7 e^- Å^{-3}.

The scattering factors for the neutral atoms were taken from the "International Tables for X-Ray Crystallography" (Vol. 4) and corrected for anomalous dispersion. All calculations were performed with SDP Enraf–Nonius programs written by Frenz (*5*). The positional and thermal parameters are listed in Tables IIIa–b. A list of the observed and calculated structure factors can be requested from the authors.

Description and Discussion of the Structure

Figure 1 shows the projection of the structure on the ($xy0$) plane. This figure clearly shows infinite distorted chains running along the a axis. Within these chains, Nb atoms do not form a straight line but exhibit a waved distribution. This waving occurs in the c direction as it is shown in the ($x0z$) plane projection (see Fig. 2). A schematic representation of the arrangement of Nb atoms along a chain is given in Fig. 3. This reveals a broken line due to different z elevations of Nb atoms. Angles and bond lengths between Nb are reported. One can notice three Nb practically aligned, namely Nb2, Nb3, Nb4, with nearly identical intervals (Nb–Nb ~ 3.09 Å), separated by a bridge. That bridge corresponds to a very long Nb–Nb distance (ex: Nb4–Nb5 = 3.944 Å). Three other Nb

TABLE IIIa

POSITIONAL PARAMETERS AND THEIR ESTIMATED STANDARD DEVIATIONS

No.	Atom	x	y	z	B (Å^2)
1	Br1	0.0434(1)	0.1577(2)	0.1085(2)	1.75(5)
2	Br2	0.2467(2)	0.1608(2)	0.1018(2)	1.95(5)
3	Br3	0.5431(1)	0.1752(2)	0.6356(2)	1.77(5)
4	Br4	0.7441(1)	0.1748(2)	0.6448(2)	1.88(5)
5	Br5	0.1475(1)	0.0901(2)	0.3070(2)	1.23(4)
6	Br6	0.6436(1)	0.0979(2)	0.4419(2)	1.23(4)
7	Nb1	0.0447(1)	0.2298(2)	0.2940(2)	0.98(4)
8	Nb2	0.2468(1)	0.2363(3)	0.2852(2)	0.97(4)
9	Nb3	0.3956(1)	0.2484(2)	0.3656(2)	0.99(3)
10	Nb4	0.5436(1)	0.2444(2)	0.4496(2)	0.96(3)
11	Nb5	0.7471(1)	0.2385(2)	0.4579(2)	0.96(4)
12	Nb6	0.8961(1)	0.2358(2)	0.3802(2)	0.97(3)
13	Se1	0.1421(1)	0.3533(2)	0.2171(2)	1.47(4)
14	Se2	0.1467(1)	0.3335(2)	0.3872(2)	1.55(4)
15	Se3	0.3066(1)	0.4046(2)	0.3468(2)	1.64(5)
16	Se4	0.3500(1)	0.3368(2)	0.2026(2)	1.65(5)
17	Se5	0.2897(1)	0.1614(2)	0.4539(2)	1.48(4)
18	Se6	0.3251(1)	0.0805(2)	0.3087(2)	1.37(4)
19	Se7	0.4391(1)	0.3475(2)	0.5245(2)	1.63(5)
20	Se8	0.4827(1)	0.4066(2)	0.3763(2)	1.53(5)
21	Se9	0.4667(1)	0.0874(2)	0.4310(2)	1.34(4)
22	Se10	0.5033(1)	0.1603(2)	0.2824(2)	1.32(4)
23	Se11	0.6479(1)	0.3369(2)	0.3519(2)	1.36(4)
24	Se12	0.6456(1)	0.3661(2)	0.5198(2)	1.41(4)
25	Se13	0.8223(1)	0.0765(2)	0.4470(2)	1.45(4)
26	Se14	0.7891(1)	0.1484(2)	0.2957(2)	1.46(4)
27	Se15	0.8108(1)	0.3970(2)	0.3873(2)	1.73(5)
28	Se16	0.8519(1)	0.3384(2)	0.5366(2)	1.68(5)
29	Se17	0.9385(1)	0.3264(2)	0.2165(2)	1.72(5)
30	Se18	0.9836(1)	0.3927(2)	0.3607(2)	1.60(5)
31	Se19	0.9688(1)	0.0709(2)	0.3236(2)	1.33(4)
32	Se20	0.0059(1)	0.1554(2)	0.4667(2)	1.43(4)

TABLE IIIb

GENERAL TEMPERATURE, FACTOR EXPRESSIONS—U VALUES

Name	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Br1	0.023 (1)	0.024 (1)	0.019 (1)	−0.001 (1)	−0.0023(9)	−0.001 (1)
Br2	0.029 (1)	0.028 (1)	0.017 (1)	−0.008 (1)	0.004 (1)	−0.003 (1)
Br3	0.024 (1)	0.027 (1)	0.016 (1)	0.004 (1)	0.0037(9)	0.002 (1)
Br4	0.024 (1)	0.031 (1)	0.017 (1)	−0.007 (1)	−0.0000(9)	−0.002 (1)
Br5	0.0083(9)	0.015 (1)	0.024 (1)	−0.002 (1)	0.0029(8)	0.001 (1)
Br6	0.0064(9)	0.015 (1)	0.026 (1)	0.001 (1)	0.0011(8)	−0.000 (1)
Nb1	0.0060(8)	0.015 (1)	0.0162(8)	−0.0015(8)	0.0013(7)	0.0012(9)
Nb2	0.0077(8)	0.013 (1)	0.0161(8)	−0.0012(9)	0.0007(7)	−0.0007(9)
Nb3	0.0077(7)	0.0140(9)	0.0160(8)	−0.000 (1)	−0.0018(6)	0.003 (1)
Nb4	0.0076(8)	0.014 (1)	0.0155(8)	−0.0004(9)	−0.0000(7)	−0.0012(9)
Nb5	0.0075(8)	0.014 (1)	0.0155(8)	0.0004(9)	0.0018(7)	−0.0002(9)
Nb6	0.0091(8)	0.0117(9)	0.0163(8)	−0.000 (1)	0.0020(7)	0.0004(9)
Se1	0.010 (1)	0.019 (1)	0.027 (1)	0.001 (1)	0.0001(9)	0.008 (1)
Se2	0.010 (1)	0.024 (1)	0.024 (1)	−0.000 (1)	0.0006(9)	−0.008 (1)
Se3	0.010 (1)	0.014 (1)	0.038 (1)	0.002 (1)	−0.004 (1)	−0.003 (1)
Se4	0.018 (1)	0.023 (1)	0.022 (1)	−0.002 (1)	−0.0030(9)	0.009 (1)
Se5	0.015 (1)	0.022 (1)	0.019 (1)	−0.001 (1)	−0.0011(9)	0.003 (1)
Se6	0.011 (1)	0.014 (1)	0.027 (1)	−0.002 (1)	−0.0027(9)	−0.000 (1)
Se7	0.016 (1)	0.025 (1)	0.022 (1)	0.004 (1)	−0.0012(9)	−0.008 (1)
Se8	0.012 (1)	0.014 (1)	0.032 (1)	−0.001 (1)	−0.0046(9)	0.003 (1)
Se9	0.013 (1)	0.016 (1)	0.023 (1)	−0.001 (1)	−0.0019(9)	0.006 (1)
Se10	0.012 (1)	0.021 (1)	0.018 (1)	−0.001 (1)	0.0000(8)	−0.003 (1)
Se11	0.011 (1)	0.020 (1)	0.020 (1)	−0.002 (1)	0.0020(8)	−0.000 (1)
Se12	0.012 (1)	0.018 (1)	0.024 (1)	−0.001 (1)	0.0007(9)	−0.007 (1)
Se13	0.011 (1)	0.019 (1)	0.025 (1)	0.002 (1)	0.0036(9)	0.004 (1)
Se14	0.013 (1)	0.021 (1)	0.022 (1)	−0.002 (1)	0.0021(9)	−0.005 (1)
Se15	0.010 (1)	0.019 (1)	0.036 (1)	0.003 (1)	0.005 (1)	0.005 (1)
Se16	0.016 (1)	0.024 (1)	0.024 (1)	−0.002 (1)	0.0036(9)	−0.007 (1)
Se17	0.017 (1)	0.024 (1)	0.025 (1)	0.005 (1)	0.0042(9)	0.006 (1)
Se18	0.014 (1)	0.012 (1)	0.035 (1)	−0.002 (1)	0.005 (1)	−0.000 (1)
Se19	0.013 (1)	0.012 (1)	0.025 (1)	−0.002 (1)	0.0039(9)	−0.003 (1)
Se20	0.016 (1)	0.021 (1)	0.017 (1)	0.001 (1)	0.0013(9)	0.005 (1)

Note. The form of the anisotropic thermal parameter is: $\exp[-2\pi^2(h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + l^2c^{*2}U_{33} + 2hka^*b^*U_{12} + 2hla^*c^*U_{13} + 2klb^*c^*U_{23})]$ where a^*, b^*, and c^* are reciprocal lattice constants.

atoms (e.g., Nb5, Nb6, Nb1) are also quasi-aligned; slightly different Nb–Nb bonds are observed: Nb5–Nb6 = 3.076 Å, Nb6–Nb1 = 3.109 Å. Finally, another bridge between Nb1 and Nb2 is present along the chain (Nb1–Nb2 = 3.919 Å). Roughly speaking it can be said that the bond sequence is the repetition of one long and two short bonds.

The unit cell contains four identical chains. Looking at the niobium surroundings, various coordination polyhedra of selenium and bromine atoms are observed. First, rectangular planes of Se are perpendicular to the Nb2–Nb3 and Nb3–Nb4 axes (portion of three aligned Nb). The same feature is observed for the Nb5–Nb6–Nb1 alignment. This provides a slightly distorted rectangular antiprismatic arrangement (see Table IVa) of Se atoms around Nb3 and Nb6. Such a situation is found in other series such as $(MSe_4)_nI$ (*2*). Second, between Nb1–Nb2 and Nb4–Nb5 a single Se_2 pair is

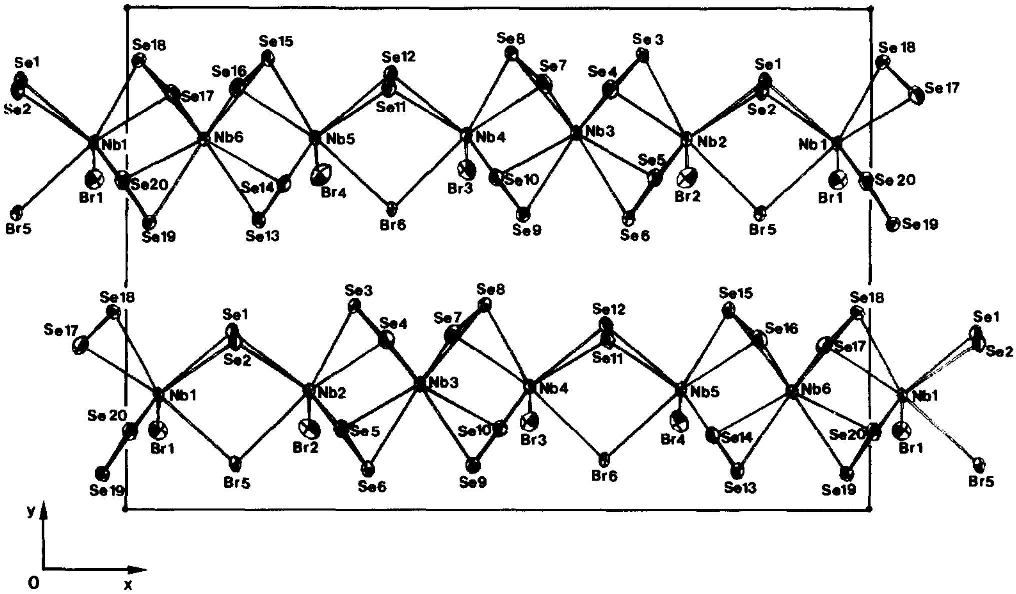
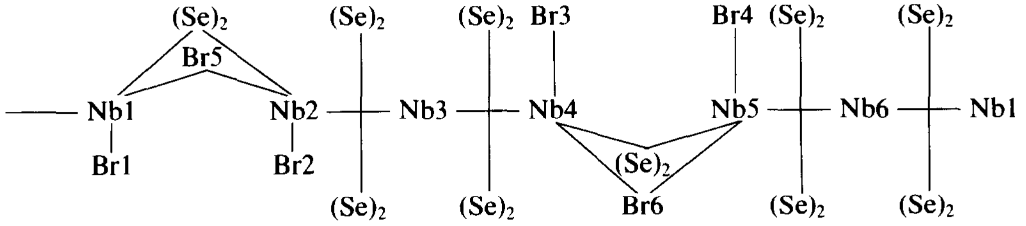


FIG. 1. (001) projection of the crystal structure of $Nb_6Se_{20}Br_6$.

shared by the two niobium of the bridge, i.e., the Se1–Se2 pair (2.329 Å) is located in the middle part of the Nb1–Nb2 bridge, and Se11–Se12 (2.314 Å) is adjacent to the Nb4–Nb5 bridge. But both Nb atoms involved in the bridges are also strongly bound to two Br atoms in the following way: Br1 is closely bonded to Nb1 (Nb1–Br1: 2.622 Å) and Br2 to Nb2 (Nb2–Br2: 2.680 Å). Moreover, two additional bromine atoms Br5 and Br6 are shared by Nb1–Nb2 (Nb1–Br5: 2.703 Å, Nb2–Br5: 2.724 Å) and Nb4–Nb5 (Nb4–Br6: 2.721 Å, Nb5–Br6: 2.724 Å), respectively. All the interatomic distances within each polyhedron of niobium are gathered in Table IVa.

A schematic arrangement along the chain is represented by



Bromine atoms are responsible for the breaking of the Nb alignment within the chain because an undistorted linear Nb chain would lead to too short van der Waals contacts between bromine atoms and the adjacent Se_2 pairs, see, e.g., Franzen *et al.* (*6*). The distortion stabilizes the structure as is demonstrated through extended Hückel band structure calculations which will be reported by Whangbo *et al.* (*7*). Onto the (*x*0*z*) projection plane, Br3 is attached to Nb4 (Nb4–Br3 = 2.685 Å) but it is not far enough from Se10 (belonging to the adjacent chain) to exclude any slight bond-

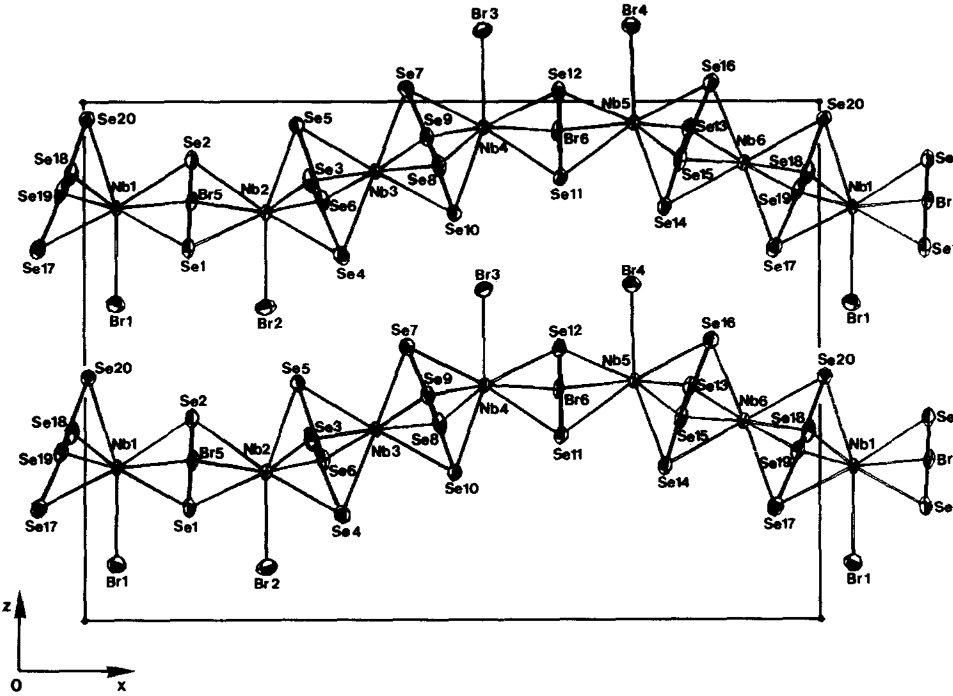


FIG. 2. (010) projection of the crystal structure of $Nb_6Se_{20}Br_6$.

ing; Br3–Se10: 3.029 Å. Other linkings between both chains are observed as there exist short Br–Se bondings in that (*x*0*z*) plane projection (see Table IVb).

The interchain connection is a stronger effect in the (*x*0*z*) plane than for the perpendicular one (i.e., (*xy*0) plane). Indeed, the shortest bonds between chains in the latter case are represented by the Br1–Se18 (3.517 Å) and Br2–Se15 (3.616 Å) bond lengths, whereas shorter Br–Se bonds are noticed in the (*x*0*z*) plane direction, e.g., Br–Se ≤ 3.20 Å (see Table IVb). Thus, $Nb_6Se_{20}Br_6$ appears to be a 2D compound built up from the stacking of slabs parallel to the *a–c* plane. $Nb_6Se_{20}Br_6$ can be regarded as $Nb_4^{4+}Nb_2^{5+}(Se_2^{2-})_{10}Br_6^-$. Of course, this formulation does not imply a fully ionic character. We were hesitant to label positions 5 and 6 as bromine rather than selenium. Choosing selenium would have led to $Nb_6Se_{22}Br_4$ which would have meant four bromine positions (Br1, Br2, Br3, and Br4) well distinguishable from the others. Selenium atoms would then occur in (Se_2^{2-}) pairs (10 times) and Se^{2-} anions (2 times). Our final choice ($Nb_6Se_{20}Br_6$) was determined from chemical analysis results (theoretical values for $Nb_6Se_{22}Br_4$ are Nb: 21.32%, Se: 66.45%, Br: 12.23% to compare with experimental results listed in Table I). No change in the reliability factors *R*

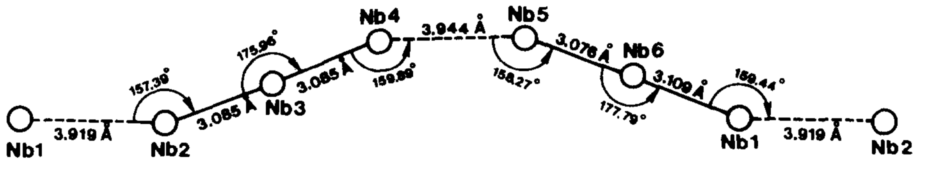


FIG. 3. A schematic representation of the chain along the *a* axis.

TABLE IVa

INTERATOMIC DISTANCES (Å)

Nb1 -Se1	= 2.693(1)	Nb1 -Se17	= 2.631(1)
Se2	= 2.708(1)	Se18	= 2.594(1)
Br5	= 2.703(1)	Se19	= 2.570(1)
Br1	= 2.692(1)	Se20	= 2.649(1)
Se1 -Se2	= 2.329(1)	Se17-Se18	= 2.313(1)
		Se19-Se20	= 2.347(1)
Nb2 -Se1	= 2.700(1)	Nb2 -Se3	= 2.616(1)
Se2	= 2.702(1)	Se4	= 2.641(1)
Br5	= 2.724(1)	Se5	= 2.627(1)
Br2	= 2.680(1)	Se6	= 2.552(1)
Se1 -Se2	= 2.329(1)	Se3 -Se4	= 2.310(1)
		Se5 -Se6	= 2.341(1)
Nb3 -Se3	= 2.679(1)	Nb3 -Se7	= 2.653(1)
Se4	= 2.648(1)	Se8	= 2.668(1)
Se5	= 2.634(1)	Se9	= 2.661(1)
Se6	= 2.692(1)	Se10	= 2.637(1)
Se3 -Se4	= 2.310(1)	Se7 -Se8	= 2.318(1)
Se5 -Se6	= 2.341(1)	Se9 -Se10	= 2.343(1)
Nb4 -Se7	= 2.634(1)	Nb4 -Se11	= 2.702(1)
Se8	= 2.616(1)	Se12	= 2.707(1)
Se9	= 2.542(1)	Br6	= 2.721(1)
Se10	= 2.641(1)	Br3	= 2.685(1)
Se7 -Se8	= 2.318(1)	Se11-Se12	= 2.314(1)
Se9 -Se10	= 2.343(1)		
Nb5 -Se11	= 2.721(1)	Nb5 -Se13	= 2.570(1)
Se12	= 2.708(1)	Se14	= 2.629(1)
Br6	= 2.724(1)	Se15	= 2.590(1)
Br4	= 2.674(1)	Se16	= 2.638(1)
Se11-Se12	= 2.314(1)	Se13-Se14	= 2.350(1)
		Se15-Se16	= 2.309(1)
Nb6 -Se13	= 2.680(1)	Nb6 -Se17	= 2.650(1)
Se14	= 2.628(1)	Se18	= 2.668(1)
Se15	= 2.674(1)	Se19	= 2.682(1)
Se16	= 2.654(1)	Se20	= 2.645(1)
Se13-Se14	= 2.350(1)	Se17-Se18	= 2.313(1)
Se15-Se16	= 2.309(1)	Se19-Se20	= 2.347(1)

TABLE IVb

INTERATOMIC DISTANCE (Å)

Within the chain	
Br1-Nb1	= 2.692(1)
Br2-Nb2	= 2.680(1)
Br3-Nb4	= 2.685(1)
Br4-Nb5	= 2.674(1)
Between chains (*x*0*z* projection, Fig. 2)	
Br1-Se20	= 3.190(1)
Br2-Se5	= 3.179(1)
Br3-Se10	= 3.029(1)
Br4-Se14	= 3.205(1)
Between chains (*x*0*y* projection, Fig. 1)	
Br1-Se18	= 3.517(1)
Br2-Se15	= 3.616(1)

were found when considering both formulations.

This structural arrangement leads to two different comments about the relation existing between $Nb_6Se_{20}Br_6$ and the other pseudo 1D derivatives of niobium and the mechanism of stabilization of such broken chains.

Indeed, concerning the first point, some structural analogies appear which clearly show the constant presence of building groups similar to the chains, and a regular change in their gathering from one compound to another. $Nb_6Se_{20}Br_6$ is to be compared to niobium phases with an antiprismatic coordination. The basic arrangement in these networks is the double pyramid Nb_2Se_4 or Nb_2S_4. This arrangement exists as an isolated group in NbS_2Cl_2 (*8*), in which the Nb_2S_4 pyramids are separated by chlorines. It is found again in Nb_2Se_9 (*9*) in which Se_5 polyanions are found between the Nb_2Se_4 group, and in such compounds as PV_2S_{10}, PNb_2S_{10}, and P_2NbS_8 reported by Brec *et al.* (*10–12*). Infinite condensation of M_2X_4 bipyramids leads to MX_4 chains that are found alone in VS_4 (*13*) or separated by halogen columns in the $(NbSe_4)_nI$ series.

Nb_2Se_4 groups are associated to form Nb_3Se_8 units in $Nb_6Se_{20}Br_6$. In these units, terminal niobium atoms are bonded to bromine atoms. We find there a situation intermediary between the case of isolated bipyramids and that of infinite condensation, which are the only situations known previously. A new compound studied presently in our group seems to correspond to the next step of condensation with four metal atoms associated in a Nb_4Se_{12} group. It is known that in the case of tetrachalcogenides, the presence of the iodine counterion modulates the Nb–Nb distance succession. Along the chain there exists a stabilization corresponding to the pinned form of a charge density wave. $Nb_6Se_{20}Br_6$ does not show anything like that. However the wave distortion along the chains constitutes another form of stabilization.

The Nb1–Nb2 or Nb4–Nb5 distances are by far too long to allow any electronic delocalization along the chains. Indeed resistivity measurements indicate $Nb_6Se_{20}Br_6$ to be an insulator.

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