

Niobium Thiobromide, Nb_3SBr_7 , with Triangle Nb_3 Cluster: Structure and Bonding

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The reaction of Nb, S, and Br_2 in a sealed quartz ampoule at 550°C yielded Nb_3SBr_7 . The structure of Nb_3SBr_7 determined by the single-crystal X-ray diffraction method ($P3m1$, $a = 7.1012(6)$ Å, $c = 6.3040(9)$ Å, $V = 275.30(9)$ Å³, $Z = 1$, $d_{\text{calc}} = 5.248(2)$ g/cm³, $R = 0.0395$, $R_w = 0.0392$) consists of one-layer packing of $\{[\text{Nb}_3\text{SBr}_3]\text{Br}_{6/2}\text{Br}_{3/3}\}_n^2$ layers. The molecular orbitals of the model anions $[\text{Nb}_3\text{Br}_{13}]^{5-}$ and $[\text{Nb}_3\text{SBr}_{12}]^{5-}$, which involve the triangle Nb_3 cluster with the nearest ligand environment in the structures of Nb_3Br_8 and Nb_3SBr_7 , respectively, were calculated by applying the extended Hückel method. The HOMO in $[\text{Nb}_3\text{Br}_{13}]^{5-}$ has slightly metal–metal bonding character which is consistent with an Nb–Nb bond length increase from 2.88 Å in a seven-electron Nb_3Br_8 to 2.896(1) Å in a six-electron Nb_3SBr_7 . The bonding schemes are in accordance with magnetic properties of Nb_3Br_8 , which is paramagnetic, and Nb_3SBr_7 , which is diamagnetic. © 1995 Academic Press, Inc.

INTRODUCTION

Metal atom cluster compounds built from M_3X_{13} groups (molecules) are a well-known type of cluster. They contain a triangular M_3 cluster, coordinated by one μ_3 -X, three μ_2 -X, and nine terminal X ligands. M_3X_{13} groups are known for such metals as Nb, Ta (e.g., $\text{Nb}_3\text{Cl}_7(\text{PMe}_2\text{Ph})_6$ or $[\text{M}_3\text{Cl}_{10}(\text{PET}_3)_3]^-$, $M = \text{Nb, Ta}$) (1), Mo (e.g., $[\text{Mo}_3\text{OCl}_6(\text{OAc})_3]^-$) (2), and W (e.g., $[\text{W}_3\text{Se}_4(\text{NCS})_9]^{5-}$) (3). The number of cluster electrons (4) for these clusters is either six or eight.

The M_3X_{13} group may be also identified in polymer structures, e.g., $[\text{Nb}_3\text{Cl}_4]\text{Cl}_{6/2}\text{Cl}_{3/3}$ in Nb_3Cl_8 (5) or $[\text{Mo}_3\text{O}_4]\text{O}_{6/2}\text{O}_{3/3}$ in $\text{Zn}_2\text{Mo}_3\text{O}_8$ (6). In these cases, terminal X ligands become intercluster bridging ligands to form M_3X_8 layers. The number of cluster electrons observed for

polymer structures is either six ($\text{Zn}_2\text{Mo}_3\text{O}_8$ or $\text{Na}_2\text{Ti}_3\text{Cl}_8$) (7) or seven (Nb_3X_8 , $X = \text{Cl, Br, I}$) (5, 8).

The electronic structure of M_3X_{13} clusters has been investigated repeatedly in the past thirty years. Initially, F. A. Cotton, using simple molecular orbital method for the Mo_3O_{13} cluster, suggested an explanation of the possible number of cluster electrons for the cluster concerned (9). Further calculations (1, 10) by means of the Fenske–Hall molecular orbital method for model clusters such as $[\text{Nb}_3\text{Cl}_{10}(\text{PH}_3)_3]^-$, $[\text{Nb}_3\text{Cl}_7(\text{PH}_3)_6]$, and $[\text{Mo}_3\text{O}_4(\text{OH})_6(\text{H}_2\text{O})_3]^{4+}$ were in a good agreement with an earlier work. Also, the bonding in Nb_3Br_8 was investigated with the help of extended Hückel and molecular orbital calculations (11).

It would be interesting to compare the crystal structures, the number of cluster electrons of the molecular and polymer structures built from M_3X_{13} groups, but the number of compounds with polymer structures was limited to $\text{Zn}_2\text{Mo}_3\text{O}_8$, Nb_3X_8 ($X = \text{Cl, Br, I}$), and $\text{Nb}_2\text{Ti}_3\text{Cl}_8$. Recently, the existence of new ternary Nb_3YX_7 ($Y = \text{chalcogen, } X = \text{halogen}$) compounds was announced (12, 13). We became interested in them because of the assumed structural similarity of Nb_3YX_7 and Nb_3X_8 . We present here the synthesis, crystal structure, measurement of magnetic susceptibility, and molecular orbital treatment for a member of the above family, namely, niobium thiobromide, Nb_3SBr_7 . A description of Nb–Nb bonding in Nb_3Br_8 is also presented in comparison with Nb_3SBr_7 .

EXPERIMENTAL SECTION

Synthesis. Nb_3SBr_7 was obtained by heating a stoichiometric mixture of the elements (input: 776.9 mg Nb, 89.1 mg S, 0.5 ml Br_2) in a quartz ampoule (20 mm in diameter and 180 mm in length) sealed under vacuum. Initially, the ampoule was heated in a horizontal temperature gradient (300–25°C) so that all bromine could react with niobium that was located in a hot zone. The disappearance of Br_2 in the cooler side of the ampoule indicated completeness of this stage. Then, the heating of the ampoule at equal

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² The following supplementary material is available from the corresponding author upon request: Atomic parameters, anisotropic displacement parameters, and full listings of interatomic distances and angles for the crystal structure of Nb_3SBr_7 (4 pages); table of observed and calculated structure factors (4 pages).

temperature (550°C) on both sides for 1 day was followed by the heating in a gradient (800–750°C) for 2 days. Black crystals, having a trigonal prismatic shape, grew in the cooler zone. A preliminary X-ray powder study of them revealed the formation of a hexagonal phase. Its composition, Nb₃SBr₇, was confirmed by further structural analysis.

Crystal structure determination and refinement. A suitable single crystal was selected from the product and mounted on an Enraf-Nonius CAD4F diffractometer. X-ray data were collected at ambient temperature. Unit cell parameters were obtained by indexing 25 randomly found reflections, further refined based on 24 well-centered reflections in the angular range $22^\circ < \theta < 24^\circ$; they coincided with the unit cell parameters calculated from powder data. Lorentz and polarization effects were corrected for. To obtain data for a semiempirical absorption correction, ψ scans of eight reflections were carried out. Important crystallographic data and data collection parameters are listed in Table 1.

After averaging equivalent reflections ($R(I)_{\text{eq}} = 0.075$) and rejecting those for which $F_0 < 6s(F_0)$, 481 independent reflections were kept. Since systematic absences were not observed, we tried to solve the structure in the space group $P3$. Direct methods and subsequent alternation of Fourier syntheses with least-square refinements revealed the coordinates of all atoms. It was noticed that three atoms (Nb and 2Br) each occupied position $(x, -x, z)$. That, taking into account the absence of the center of inversion in the resulting model of the structure, clearly suggested the space group $P3m1$. The final full-matrix least-square refinement with anisotropic thermal parameters in this space group resulted in $R = 0.0395$ and $R_w = 0.0392$. The final Fourier difference map showed random peaks, the highest of which was of $3.2 \text{ e}/\text{\AA}^3$, lying 0.51 \AA from the Nb atom. All calcula-

TABLE 2
Atomic Parameters for Nb₃SBr₇

Atom	Position	x/a	y/b	z/c	$B(\text{is/eq})^a$
Nb	3 <i>d</i>	.19738(8)	− <i>x</i>	.2226(4)	.55(2)
Br1	1 <i>a</i>	0	0	.0000	.75(4)
Br2	3 <i>d</i>	.3361(3)	− <i>x</i>	.4510(4)	.89(3)
Br3	3 <i>d</i>	.5021(1)	− <i>x</i>	.9554(5)	.96(3)
S	1 <i>b</i>	1/3	2/3	.4979(10)	.56(8)

^a Equivalent isotropic parameters are defined as $4/3 \cdot [a \cdot B_{11}^2 + b \cdot B_{22}^2 + c \cdot B_{33}^2 + a \cdot b \cdot \cos(\gamma) \cdot B_{12} + a \cdot c \cdot \cos(\beta) \cdot B_{13} + b \cdot c \cdot \cos(\alpha) \cdot B_{23}]$.

tions were performed using CSD programs. The positional and thermal parameters are presented in Table 2. Bond distances and angles are given in Table 3.

Magnetic properties. Measurements of the magnetic susceptibility of Nb₃SBr₇ were carried out by using the standard Faraday method. The compound is diamagnetic. The magnetic susceptibility of $\chi = (-1.5 \pm 0.2) \cdot 10^{-6} \text{ emu/g}$ at room temperature was found after applying a diamagnetic correction.

Computational details. Molecular orbitals of model anions [Nb₃Br₁₃]^{5−} and [Nb₃SBr₁₂]^{5−} were calculated applying the extended Hückel method. Molecules possess the C_{3v} point group symmetry. The atomic distances were taken the same as those in the corresponding crystal structures (see Table 3). The coordinate system was chosen so that the origin is at the geometrical center of the Nb₃ triangle, the *z* axis is perpendicular to the triangle, the *y* axis points toward one of the Nb atoms, and the *x* axis is located such as to form a right-handed coordinate system. AOs were approximated by Slater-type orbitals (14). All

TABLE 1
Important Crystallographic Data for Nb₃SBr₇

Space group	$P3m1$ (No 156)
<i>a</i> , Å	7.1012(6)
<i>c</i> , Å	6.3040(9)
<i>V</i> , Å ³	275.30(9)
<i>Z</i>	1
d_{calc} , g/cm ³	5.248(2)
μ , cm ^{−1}	299.81
<i>h</i> , <i>k</i> , <i>l</i> range	± <i>h</i> , ± <i>k</i> , 1
Radiation and λ , Å	MoK α 0.71069
No. of refined parameters	26
$\sin(\theta/\lambda)_{\text{max}}$	0.825
No. of reflections:	
measured ($I > 2 \cdot \sigma(I)$)	2765
used in refinement ($F_0 > 6 \cdot \sigma(F_0)$)	481
$R(F)$, $R_w(F)^a$	0.0395, 0.0392

$$^a W = \frac{1}{\sigma^2(F) + 0.009F_{\text{obs}}^2} \left(1 - \exp(-2.4 \left(\frac{\sin(\theta)}{\lambda} \right)^2) \right).$$

TABLE 3
Bond Distances (Å) for Nb₃SBr₇ in Comparison with Nb₃Br₈ (8) and Angles (deg) for Nb₃SBr₇

		Bonds	
		Nb ₃ SBr ₇	Nb ₃ Br ₈
Nb–2 Nb	2.896(1)	Nb–2 Nb	2.88
Nb–1 S	2.410(5)	Nb–1 Br4	2.60
Nb–2 Br3	2.544(3)	Nb–2 Br1	2.55
Nb–2 Br2	2.687(3)	Nb–2 Br2	2.70
Nb–1 Br1	2.804(2)	Nb–1 Br3	2.80
		Angles for Nb ₃ SBr ₇	
Nb–Nb–Nb	60	Br2–Nb–S	88.5(1)
Br1–Nb–Br2	79.57(7)	Br2–Nb–Br3	90.77(9)
Br1–Nb–Br3	83.36(7)	Br2–Nb–Br2	83.55(9)
Br1–Nb–S	163.9(1)	Br3–Nb–Br3	89.92(8)
Br2–Nb–Br3	162.7(1)	Br3–Nb–S	107.7(1)

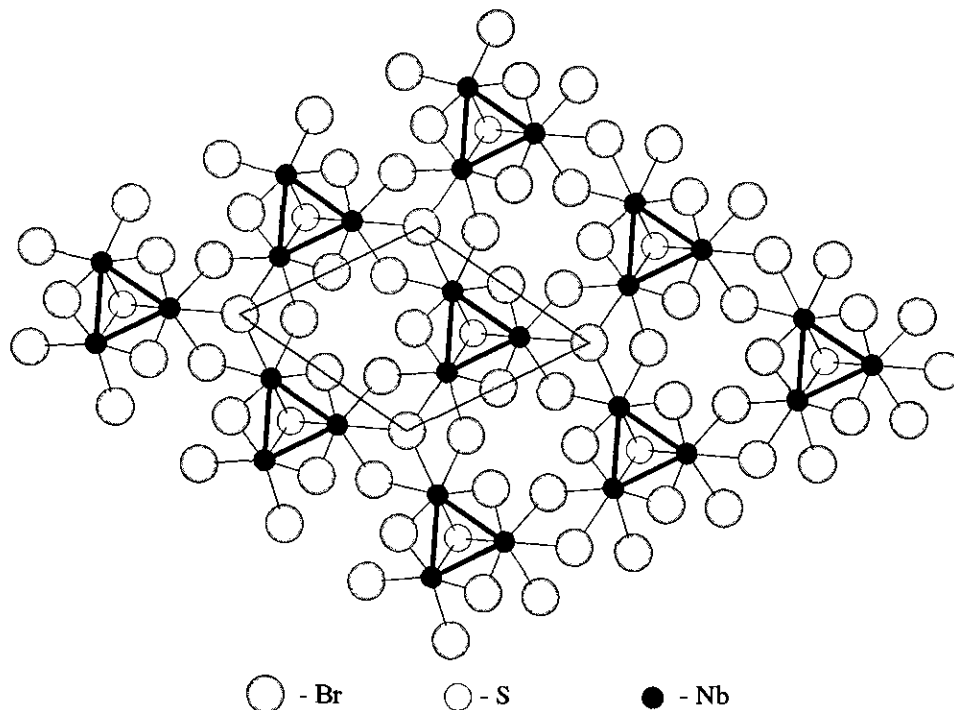


FIG. 1. The projection of the structure Nb_3SBr_7 on the (001) plane.

computational procedures were done using the package of programs "CACAO" (15).

RESULTS AND DISCUSSION

Figure 1 displays the projection of the structure of Nb_3SBr_7 on the (001) plane. This figure shows an infinite layer running perpendicular to the c axis. In such a layer, there are triangular Nb_3 clusters ($d_{\text{Nb-Nb}} = 2.896(1) \text{ \AA}$), each being surrounded by thirteen ligands. As shown in Fig. 2, there is one capping sulfur atom below the Nb_3 plane and three edge-bridging bromine atoms (Br3) above it. Each Nb is further coordinated by three bromine atoms, one of which connects to two other clusters, and two of which connect to one other cluster. Thus, the considered layer is composed of the $\{[\text{Nb}_3\text{SBr}_3]\text{Br}_{6/2}\text{Br}_{3/3}\}_\infty^2$ unit and the composition of the layer is Nb_3SBr_7 . Such layers are placed one on another in such a way as to form one-layer packing (see Fig. 2).

Under the same conditions Nb_3Br_8 could be obtained, which is constructed from the similar M_3X_8 layers (8). As shown in Table 3, the Nb–Nb and Nb–Br bond distances in Nb_3SBr_7 and Nb_3Br_8 are nearly equal, but the compounds are not isostructural. Six-layer packing of M_3X_8 layers is formed in the case of Nb_3Br_8 , while one-layer packing is formed in the case of Nb_3SBr_7 . Thus, substitution of one S atom for the capping Br atom results in a change of layer packing.

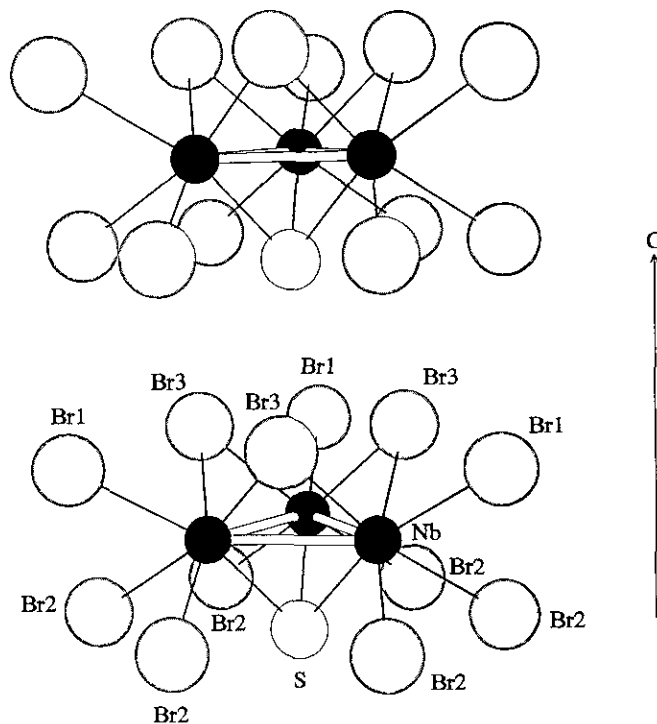


FIG. 2. The fragment of crystal structure of Nb_3SBr_7 .

An alternative description of the structure on the base of the closest packings can be applied. In this term, an ideal structure can be considered as a hexagonal close-packed array (... *h* ...) of sulfur and bromine atoms, with niobium atoms occupying 3/4 of octahedral interstices in every second layer. Niobium atoms are moved from the octahedral centers (see angles in Table 3) to form the Nb₃-cluster. The structure of Nb₃Br₈ can be described as twelve-layer closest packing (*hhcc*)₃.

The replacement of one bromine by sulfur results in a change not only of packing of layers, but also of the number of cluster electrons from seven to six. The question is why the number of cluster electrons can vary. To answer this question we calculated molecular orbitals of model anions [Nb₃Br₁₃]⁵⁻ and [Nb₃SBr₁₂]⁵⁻ applying the extended Hückel method. The basic results of our calculation are given in Fig. 3, which shows a part of bonding diagram with the contour plots of metal–metal bonding MOs. The molecular orbital analysis revealed only four metal–metal bonding MOs (13a₁, 18e, 14a₁) with an essential contribution of metal atom orbitals, d_{x²-y²} (56%), d_{xy} (63%), and d_{z²} (60%), respectively. Hence, the number of cluster elec-

trons that can fill only metal–metal bonding MOs is equal to eight, which is consistent with the existence of molecular eight-electron clusters mentioned previously (1).

The 6a₂ molecular orbital and MOs laying below the 17e have a large contribution of *p* and *s* AOs of ligands, and correspond to metal–ligand bonds or lone electron pairs of ligands. MOs lying above the 14a₁ are mostly metal–metal antibonding orbitals. Both metal–metal bonding and antibonding orbitals are not purely composed of Nb orbitals; they also have nonnegligible contributions from ligand AOs. These are metal–ligand antibonding MOs and the following illustrates this well. We found the predominant ligand contribution in 13a₁ MO to be a *p_z* AO of a capping (*μ₃-X*) ligand, the contribution having increased from 8% to 15% under transition from [Nb₃Br₁₃]⁵⁻ to [Nb₃SBr₁₂]⁵⁻. The increase in contribution appears to be accounted for by the reduction of Nb–(*μ₃-X*) bond length from 2.60 Å (Nb–Br) to 2.410(5) Å (Nb–S). If the orbital has an antibonding character its energy should increase, as it occurs in the case of [Nb₃Br₁₃]⁵⁻ and [Nb₃SBr₁₂]⁵⁻ (Fig. 3).

As is clear from the figure, 14a₁ is the HOMO in a seven-electron cluster, and the LUMO in a six-electron cluster.

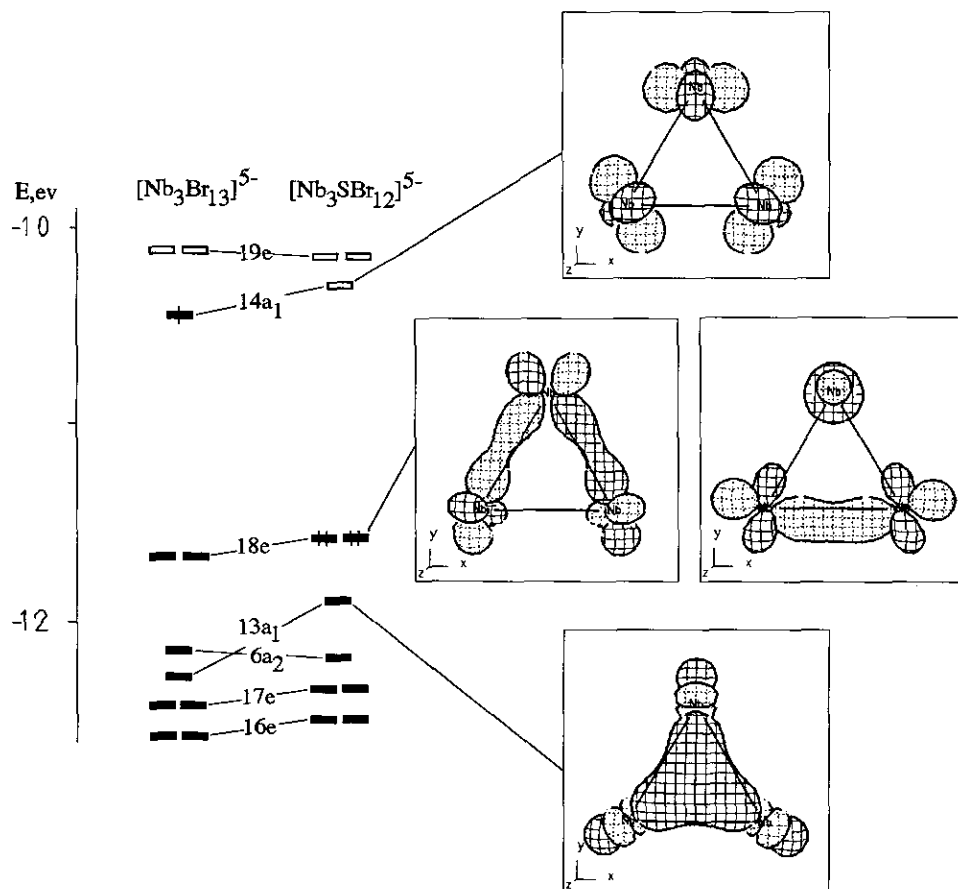


FIG. 3. A part of molecular orbital level diagrams of [Nb₃Br₁₃]⁵⁻ and [Nb₃SBr₁₂]⁵⁻ with contour plots of Nb–Nb bonding MOs.

As Nb–Nb distances are large for efficient overlap of d_{z^2} AOs, the $14a_1$ orbital is slightly metal–metal bonding. The transition from a seven- to a six-electron cluster, by removing one electron from the $14a_1$ MO, should not lead to dramatic changes in the electronic and geometrical structures and must be accompanied by the changing of magnetic properties and the increasing of Nb–Nb bond length. Our data show that $d_{\text{Nb–Nb}}$ in the six-electron Nb₃Sb₇ is ca. 0.016 Å greater than that in the seven-electron Nb₃Br₈, and that Nb₃Sb₇ is diamagnetic, while Nb₃Br₈ is paramagnetic (8).

To produce a cluster with the number of cluster electrons less than six, at least one electron must be removed from the $18e$ MO; taking into account its strongly metal–metal bonding character, this should rather lead to the cluster destruction.

The fact that seven-electron clusters are known for polymer structures only seems to be explained by the possibility of delocalization of unpaired electrons via bridging atoms of halogens. Such delocalization could stabilize the structure additionally. Diamagnetism of Nb₃I₈ is a good example of the existence of extended interactions in the considered structures.

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