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STRUCTURE OF NdSBr AND ISOTYPICAL RARE EARTH SULFOBROMIDES*

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Sulfobromides of Pr (β form), Nd, Sm, Gd and Tb are monoclinic. On account of a twinning the structure must be described in a cell whose a parameter is three times smaller than the ones first proposed. Cell dimensions of NdSBr are: a = 6·94; b = 6·91; c = 7·05 Å; γ = 99.28°; space group is $P2_1/b$. There are four formula units in the unit cell. The intensities have been collected with a counter diffractometer using Mo Kα radiation. The structure was solved by the heavy-atom method using Patterson and Fourier calculations and refined by least-squares methods with anisotropic thermal parameters to an R index of 0·062. The neodymium atom is coordinated to seven atoms (4S and 3Br). The structure consists of layers of bromine atoms alternating with layers of Nd_4S tetrahedra.

Neodymium sulfobromide was prepared for the first time in 1967 at the Laboratory of Mineral Chemistry of the Faculte de Pharmacie (Dagron, Etienne and Laruelle, 1967). It belongs to a group of five isotypical monoclinic sulfobromides: PrSBr (β), NdSBr, SmSBr, GdSBr and TBSBr (Dagron and Thevet, 1970).

The preparation and parameters of these sulfobromides have been described elsewhere (Dagron and Thevet, 1971). The principle behind the preparation is to achieve successive combination of the three elements in stoichiometric quantities and at suitable temperatures.

We have attempted to establish the structure of compounds in this group starting with a monocrystal of NdSBr, but all the isolated crystals were actually twins, and this caused us some difficulties.

* This work was carried out in part under the auspices of the U.S. Atomic Energy Commission.

The crystallographic data have been determined from Weissenberg's negatives, which were exposed while rotating the twin (which we still took to be a monocrystal) about the binary Oz axis. A least-squares program resulted in the values: a = 20.823(10); b = 6.906(5); c = 7.046(5)A; γ = 99.28(9)°. The numbers in parentheses are the standard deviations. The systematic absence of k = 2n + 1 reflections for hk0 and ℓ = 2n + 1 for 00ℓ leads to the $P2_1/b$ group. The number of molecules in the mesh is Z = 12. These results are identical with those already published by Dagron and Thevet (1970).

The intensities of the reflections are measured with a General Electric XRD6 diffractometer (Kα radiation from molybdenum). They are corrected by the Lorentz and polarization factors.

A Patterson-function calculation has been performed and permits us to construct a hypothetical structure. We attempted to refine this hypothesis with a least-square method based on the ORFLS program (Busing, Martin and Levy, 1962). This refinement converges poorly and the factor $R = \sum \left| |F_o| - |F_c| \right| / \sum |F_o|$ is never smaller than 21%.

This failure of the refinement procedure together with the pressence of a number of inexplicable systematic extinctions in the negatives (in particular, only the h = 3n reflections are present along the k = 3n lines), as well as the presence of a pseudo-period a/3 in our structure hypothesis, caused us to suspect the existence of a twin.

Close examination of the locations of the reflections within the reciprocal lattice indicated that it is possible to describe the lattice with a mesh whose parameter a* is three times as large. There must obviously be supplementary reflections with such a reciprocal mesh, but everything is explicable if one acknowledges the presence of a second twin along with the first. Fig. 1 represents the projection of the reciprocal lattice on the x*Oy* plane. The reciprocal mesh of the twin 1 (reflections represented by black circles) is referred to the Oh_1k_1 axes; that of twin 2 (reflections represented by crosses) to the Oh_2k_2 axes. The initial reciprocal mesh (corresponding to a = 20.82A) is cross-hatched. This twinning accounts for the anomalies and the pseudo-period of 1/3 along the Ox axis.

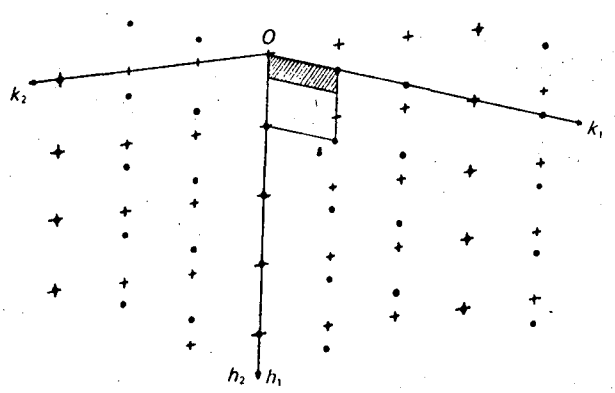

Fig. 1: Projection of the reciprocal lattice on the x*Oy* plane.

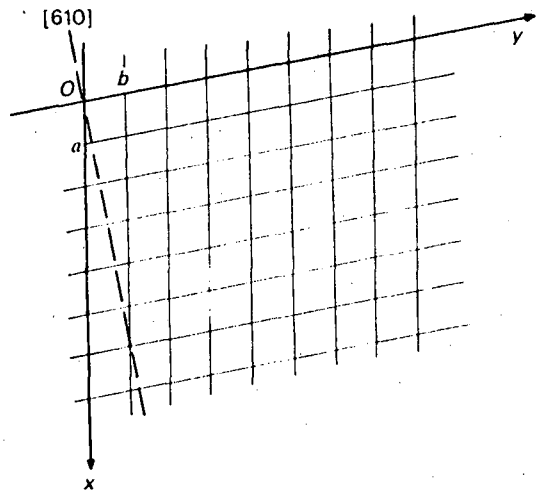

Fig. 2: Section of the direct lattice from the (001) plane.

If we consider the direct lattice with a mesh whose a parameter is 20.82/3 = 6.94A, the cause of the twinning becomes apparent. Fig. 2 represents the section of this lattice through the xOy plane; the [610] line is quasi perpendicular to Oy, trace of the (100) plane. The [610] line and the (100) plane are thus pseudosymmetry elements of the twin. This amounts to twinning by reticular pseudomerism. The obliquity of this twin is very slight (0.25°) which explains why we could not observe splitting, even for high-index reflections.

The structure of NdSBr and the four other isotypical sulfobromides must thus be described by a mesh whose a parameter is three times smaller than that which was originally proposed (Dagron and Thevet, 1971). New parameters for the five compounds are grouped together in Table 1.

Table 1: New parameters for the five isotypical sulfobromides.

	a(Å)	b(Å)	c(Å)	γ
PrSBr (β)	6,98	6,93	7,09	99,30°
NdSBr	6,94	6,91	7,05	99,28°
SmSBr	6,86	6,86	7,01	99,32°
GdSBr	6,80	6,81	6,96	99,23°
TbSBr	6,75	6,77	6,89	99,33°

The space group remains $P2_1/b$ in the new mesh, which is three times smaller. It contains no more than four formula masses.

We then completely repeated the structure determination for the same NdSBr crystal. The intensities of the reflections were measured again, this time with a Picker FACS-1 diffractometer (Kα line of molybdenum). We measured only the reflections due to the diffraction of a single twin, that is to say, those for which the k index is $\neq$ 3n (344 independent reflections). The measurements were

corrected by Lorentz and polarization factors. We added an absorption correction based on a spherical crystal model (the linear absorption coefficient μ for Mo Kα is 286 cm^{-1} and the small μR estimated for our crystal is of the order of 1.70).

The structure formerly envisaged had a pseudo-period t = a/3 parallel to Ox. The hypothesis from which we now depart is that of the reason for the period t. The refinement of this new hypothesis was achieved on CDC 6600 by a least-squares program with complete matrices. The diffusion factors used for neutral atoms are those of Cromer and Waber (1965). The effects of anomalous dispersion are included by utilizing the $\Delta f'$ and $\Delta f''$ furnished by Cromer (1965). This refinement converges very well, and after several cycles we arrived at an R factor of 6.2% with respect to the ensemble of measured reflections.* None of the parameters varied more than 0.0004 times its standard deviation during the course of the final cycle. The atomic positions and anisotropic thermal agitation coefficients for the atoms obtained during the refinement process are grouped in Tables 2 and 3.

Table 2: Coordinates (x 10^4) of the atoms.
The standard deviations (x 10^4) are given in parentheses.

	x	y	z
Nd	3177 (1)	2106 (1)	4647 (1)
S	5543 (7)	83 (7)	2396 (6)
Br	847 (3)	2872 (3)	1160 (3)

Table 3: Anisotropic thermal agitation parameters of the atoms.
The standard deviations (x 10^2) are given in parentheses. The β_{ij} coefficients (expressed in A^2) are defined by the expression:

$$T = \exp\left[-\tfrac{1}{4}(\beta_{11}h^2a^{*2} + \beta_{22}k^2b^{*2} + \beta_{33}l^2c^{*2} + 2\beta_{12}hka^*b^* + 2\beta_{13}hla^*c^* + 2\beta_{23}klb^*c^*)\right].$$

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Nd	2,17 (7)	1,80 (7)	1,44 (7)	0,61 (4)	−0,03 (3)	−0,03 (3)
S	2,25 (20)	1,83 (27)	0,92 (17)	0,55 (15)	−0,13 (14)	−0,11 (13)
Br	2,28 (10)	2,59 (10)	2,05 (10)	0,40 (7)	−0,41 (7)	0,59 (6)

Description of the Structure

All interatomic distances less than 4 A calculated following the refinement process are listed in Table 4.

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* The list of observed and calculated structure factors can be obtained from the National Lending Library, England (supplementary publication No. SUP 30101). Copies can be obtained by writing to: The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH 1 1 NZ, England.

Table 4: Interatomic distances (less than 4 A).
The standard deviations (x 10^3) are given in parentheses.

Nd-S	Nd-Br	S-Br	S-S	Br-Br
2,811 (6)	3,034 (3)	3,966 (8)	3,457 (9)	2 × 3,722 (3)
2,783 (5)	2,992 (4)	3,763 (6)	3,743 (9)	3,714 (5)
2,800 (5)	3,155 (4)	3,519 (7)	2 × 3,454 (3)	2 × 3,933 (3)
2,811 (5)				

The neodymium atom has a coordination number of 7 (Fig. 3). It is surrounded on one side by four atoms of sulfur and on the other by three bromine atoms. The average Nd-S distance is 2.80 A. The average Nd-Br distance is 3.06 A.

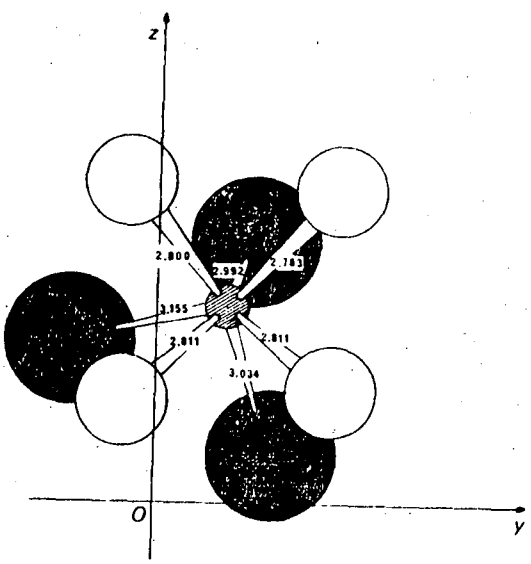

Fig. 3: Environment of the neodymium atom as seen from a direction perpendicular to the (100) plane.

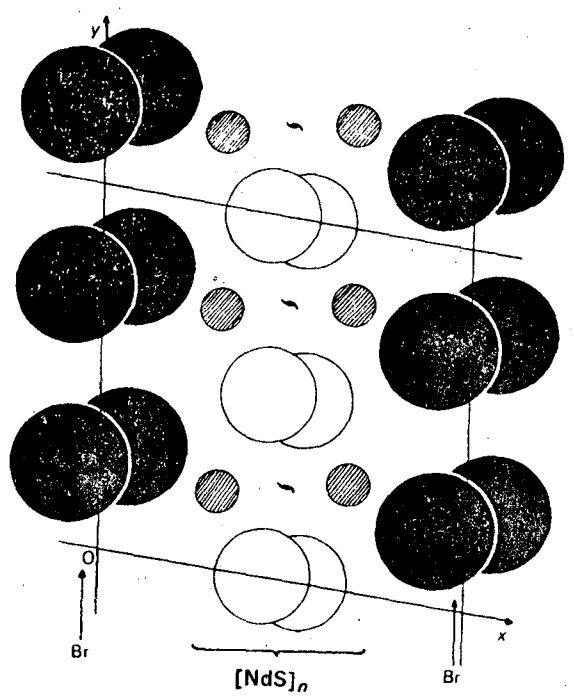

Fig. 4: Projection of the structure on the (001) plane.

A projection of the structure on the xOy plane is illustrated in Fig. 4. We again find the shell structure of the rare earth derivatives with two anions. In effect, we have an alternation between two types of layers parallel to the yOz plane: layers consisting of a double shell of bromine atoms, and shells containing the sulfur and neodymium atoms.

In the bromine double shell, each anion is surrounded by six near neighbor bromine atoms at an average distance of 3.91 A.

The sulfur and neodymium layers are formed of nearly regular Nd_4S tetrahedrons, centered at S (Fig. 5). Two neighboring tetrahedrons share the same edge. Each neodymium atom thus belongs simultaneously to four adjacent tetrahedrons, such that the average composition of the layer is $[NdS]_n$.

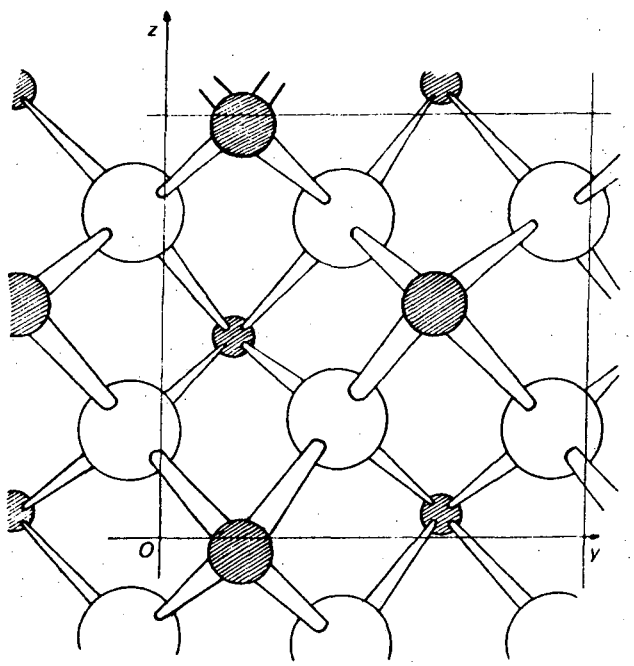

Fig. 5: Layers of Nd_4S tetrahedrons viewed from a direction perpendicular to the (100) plane.

The NdSBr structure is very close to the monoclinic form of EuI_2 (Bärnighausen and Schultz, 1969). In that case, the same polyhedra with seven peaks surrounding the rare earth and the same types of layers were found. If these five isotypical compounds are placed in the framework of the rare earth sulfobromides, a great similarity is observed between their structure and those of the orthorhombic type CeSI (Etienne, 1969) of the lighter rare earth sulfobromides. The two structures result from the superposition of analogous groupings: distorted layers of tetrahedrons $[LS]_n$ alternating with double halogen shells. However, even though only a single layer of each type exists in the NdSBr mesh, this arrangement is twice repeated in the CeSI mesh, for which the height is in the neighborhood of 14 A.

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