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Synthesis and Structure of $CsNaLa_6Br_{14}N_2$ and La_3Br_6N: Rare-Earth-Metal Nitride Halides with Isolated Bitetrahedral La_6N_2 Units

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The title compounds were obtained in high yields as pale yellow, transparent crystals after reacting appropriate mixtures of CsBr, NaBr, $LaBr_3$, and LaN in sealed Ta tubing at 850 °C for 20 d. The structures have been established by single-crystal X-ray diffraction techniques and powder diffraction. $CsNaLa_6Br_{14}N_2$ forms a new structure type in the monoclinic space group $P2_1/n$ with the lattice parameters $a = 10.452(1)$ Å, $b = 13.193(2)$ Å, $c = 10.876(2)$ Å, $\beta = 95.07(1)°$, and $Z = 2$. La_3Br_6N is isotypic to Ce_3Br_6N and crystallizes in the orthorhombic space group *Pbca* with $a = 11.212(1)$ Å, $b = 11.828(1)$ Å, $c = 17.176(1)$ Å, and $Z = 4$. The significant structural features of both compounds are pairs of rare-earth-metal tetrahedra that are each centered by N and share a common edge to form La_6N_2 bitetrahedral units. These are surrounded and interbridged by Br atoms to form a three-dimensional network. In the case of $CsNaLa_6Br_{14}N_2$ the Cs and Na atoms are located in bromine-lined cuboctahedral and octahedral cavities, respectively. Although "normal-valent" salts, the structures of the new nitride halides are geometrically closely related to the metal-rich cluster compounds such as $Cs_2La_{10}I_{17}Co_2$ with bioctahedral La_{10} units that are centered by the transition-metal atoms. Calculations of the Madelung part of lattice energy, MAPLE, illustrate the close relationship of the two structures.

Introduction

Oxygen- and nitrogen-centered M_4Z tetrahedra (M = Y, La−Lu; Z = N, O) that are surrounded by halogen atoms are the main structural building units in the chemistry of rare-earth-metal nitride halides and oxide halides. The distinct structure types and, hence, the large variety of compounds originate from different grades of condensation of the tetrahedra over common M−M edges as well as different connectivity patterns through the halide atoms.[1,2] In representatives MOX (X = Cl, Br, I),[3] which all adapt the well-known PbFCl structure type,[4] the M_4O tetrahedra are linked over common M−M edges into layers that are separated from each other by the X atoms. Infinite double chains of condensed tetrahedra are present in β-$M_2Cl_3N_x$ (M = Y, Gd)[5] . The majority of compounds such as α-Gd_2Cl_3N[6] or more recently $Na_2Pr_4Br_9NO$[7] and $AM_9I_{16}N_4$ (A = Na−Cs; M = La, Pr)[8] contain infinite chains of trans-edge-sharing M_4Z units. A novel spherical arrangement of six $(Pr_3Nb)N$ tetrahedra that all share the Nb atom in the center is the significant feature of the unique compound $CsPr_9NbBr_{15}N_6$.[9] Only three representatives, triclinic Gd_3Cl_6N[10] as well as orthorhombic Ce_3Cl_6N[11] and Ce_3Br_6N,[12] are known to have isolated bitetrahedral M_6N_2 units. Finally, there are isolated tetrahedra of divalent rare-earth-metals centered by O in M_4OCl_6 (M^{II} = Yb, Eu, Sm).[13,14]

To learn more about the structural connectivity and features in such rare-earth-metal nitride halides, the introduction of alkali-metal halides into the structural framework has been tried. This increases the halide/rare-earth-metal ratio leaving the nitride/rare-earth-metal ratio unchanged and so forces the formation of a different structural arrangement and connectivity. In addition, the halide framework has to create room to accommodate the alkali-metal cations. The present paper reports on the synthesis of two new compounds containing bitetrahedral units and discusses their structural relationships on the basis of lattice energy calculations.

Experimental Section

Syntheses. Colorless, anhydrous $LaBr_3$ was prepared via the ammonium halide route[15] from La_2O_3 (Aldrich, 99.9%) and NH_4Br (Merck, 99.5%). The raw product was then sublimed under high dynamic vacuum in a 200 mm long and 25 mm wide tantalum crucible which was placed in a fused silica container. The sublimed $LaBr_3$ was characterized by Guinier powder diffraction. LaN was obtained by heating La metal (Chempur, 99.9%) in a Mo crucible under a dried N_2 (Messer Griesheim, 99.999%; possible traces of water were removed by a cold trap cooled by a mixture of dry ice and acetone) flow at 900 °C for 24 h. NaBr (Merck, 99.5%), KBr (Merck, 99.5%) and CsBr (Aldrich, 99.9%) were dried at 250 °C under high vacuum and then also sublimed. Because most of the reagents and products are very sensitive to moisture, all further operations were carried out in

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gloveboxes under a dry argon atmosphere ([H_2O] < 0.2 ppm, [O_2] < 2 ppm). Tantalum was used as material for the reaction containers, which were prepared from metal tubing by welding them in an argon-filled arc-welder. After the reactions were loaded the sealed metal containers were encapsulated in fused silica jackets under dynamic high vacuum. Mixtures of CsBr, NaBr, $LaBr_3$, and LaN with an overall composition $CsNaLa_6Br_{14}N_2$ were heated at 850 °C for 20 days and cooled with 5 °C/h to 500 °C, and then the furnace was turned off. The products were pale yellow crystals of the new phases $CsNaLa_6Br_{14}N_2$ (yield > 80%, estimated from Guinier powder pattern; see below) besides small amounts of CsBr and NaBr. Subsequent reactions loaded with an overall composition of $CsKLa_6Br_{14}N_2$, $KNaLa_6Br_{14}N_2$, $CsLa_6Br_{13}N_2$, and $KLa_6Br_{13}N_2$ as well as $NaLa_6Br_{13}N_2$ all gave large (up to 2 mm in diameter), rectangular, pale yellow crystals of La_3Br_6N besides the respective alkali-metal halides. The high-yield synthesis of this compound was successfully repeated by reacting the exact composition of starting materials without any additional alkali-metal halides.

In addition, some needle-shaped yellow crystals of La_2Br_3N (isotypic to Ce_2Br_3N[12]) and some thin yellow platelets of $La_8Br_{13}N_3O$ (isotypic to $Pr_8Br_{13}N_3O$[7]) could be isolated from the products of the reactions loaded as $NaLa_6Br_{13}N_2$ and $CsLa_6Br_{14}N_2$, respectively. These two new compounds, whose structures contain infinite chains of trans-edge sharing La_4Z tetrahedra, were not detectable in the powder patterns of the products. Accordingly, their lattice parameters were determined with a single-crystal diffractometer.

X-ray Studies. Crystals of $CsNaLa_6Br_{14}N_2$ (size ca. 0.1 × 0.1 × 0.2 mm) were sealed inside thin-walled glass capillaries in the glovebox under an argon atmosphere and found to be suitable for X-ray diffraction experiments with the aid of oscillation and Laue film checks. Through precession photographs of the zeroth to the second layers, the Laue symmetry as well as the systematic reflection absences were found to be characteristic of the space group $P2_1/c$ (No. 14). The nonstandard setting $P2_1/n$ was chosen because here the monoclinic angle $\beta = 92.07°$ is close to 90°. The same crystal was used to determine the cell parameters and the orientation matrices by a least-squares refinement of the setting angles of 18 centered reflections on a Stoe STADI4 diffractometer with graphite-monochromated Mo $K\alpha$ radiation. A total of 3593 data were collected at room temperature ($4° \le 2\theta \le 55°$; $\pm h,+k,+l$). An empirical absorption correction was applied to the full data set with the aid of 23 ψ-scans (Stoe instrument package X-RED). The structure of $CsNaLa_6Br_{14}N_2$ was determined first using direct methods (SHELXS-86[16]) to obtain a structural model, which was then employed in subsequent least-squares refinements and difference Fourier syntheses (programs and scattering factors utilized were those of the program package SHELXL-93[17]). The residuals after an extinction correction and the anisotropic refinement of all atoms were $R(F) = 0.042$ and $R_w(F^2) = 0.114$ for $F_o > 3\,\sigma(F_o)$. The largest residual peak was 1.90 e/Å^3, 1.05 Å apart from La3.

The selection procedures of the crystals of La_3Br_6N (size ca. 0.1 × 0.2 × 0.2 mm) were the same as described for $CsNaLa_6Br_{14}N_2$. Precession photographs from the zeroth to the third layers indicated the unique orthorhombic space group *Pbca* (No. 61). After the cell parameters and the orientation matrices were determined with the aid of 24 centered reflections, 4622 data were measured ($4° \le 2\theta \le 50°$; $-h,+k,+l$ and the Friedel opposites). An empirical absorption correction using 9 ψ-scans was applied before averaging redundant data ($R_{av} = 0.049$) to give a unique set of 2006 reflections. With the atom positions of Ce_3Br_6N as starting parameters, the structure of La_3Br_6N was then determined as well ($R(F) = 0.052$ and $R_w(F^2) = 0.098$ for $F_o > 3\,\sigma(F_o)$). The largest residual peak was 2.67 e/Å^3, 0.94 Å apart from La1.

Table 1. Crystallographic Data for $CsNaLa_6Br_{14}N_2$ and La_3Br_6N

chem formula	$CsNaLa_6Br_{14}N_2$	La_3Br_6N
fw	2136.00	910.15
space group, Z	$P2_1/n$ (No. 14), 2	*Pbca* (No. 61), 4
lattice consts (Å, deg)		
a	10.452(1)	11.212(1)
b	13.193(2)	11.828(1)
c	10.876(2)	17.176(1)
β	95.07(1)	
V (Å^3)	1493.9(4)	2277.8(3)
T (°C)	23	23
ρ_{calcd} (g/cm^3)	4.73	5.31
λ (Å)	0.7107	0.7107
μ(Mo Kα) (cm^{-1})	282.3	320.4
R, R_w[a] ($F > 3\sigma_F$)	0.044, 0.114	0.052, 0.098

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$, $R_w = [\sum[w(F_o^2 - F_c^2)^2/\sum(F_o^2)^2]^{1/2}$; $w = \sigma_F^{-2}$.

Table 2. Positional x, y, z and Displacement U_{eq}[a] (Å^2) Parameters for $CsNaLa_6Br_{14}N_2$

atom	posn	x	y	z	U_{eq}
La1	4e	0.00119(6)	0.40781(5)	0.87064(6)	0.0180(2)
La2	4e	0.24500(7)	0.36678(5)	0.14273(6)	0.0207(2)
La3	4e	0.70863(6)	0.40886(5)	0.08661(7)	0.0213(2)
Cs	2a	0	0	0	0.0474(4)
Na[b]	4e	0.0453(18)	0.5917(15)	0.5541(15)	0.0628(73)
Br1	4e	0.7846(1)	0.2489(1)	0.8959(1)	0.0306(3)
Br2	4e	0.4960(1)	0.2494(1)	0.1189(1)	0.0272(3)
Br3	4e	0.8272(1)	0.4878(1)	0.6586(1)	0.0307(3)
Br4	4e	0.1824(1)	0.2291(1)	0.9266(1)	0.0330(3)
Br5	4e	0.4602(1)	0.5299(1)	0.1528(1)	0.0266(3)
Br6	4e	0.9644(1)	0.3124(1)	0.1765(2)	0.0365(3)
Br7	4e	0.2152(1)	0.4644(1)	0.6964(1)	0.0292(3)
N	4e	0.8474(9)	0.5109(7)	0.9851(9)	0.0179(19)

[a] $U_{eq} = {}^1/_3\sum_i\sum_j U_{ij}\, a_i{}^*a_j{}^*a_ia_j$. [b] Occupancy = 0.47(3).

Table 3. Positional x, y, z and Displacement U_{eq}[a] (Å^2) Parameters for La_3Br_6N

atom	position	x	y	z	U_{eq}
La1	8c	0.13673(11)	0.02088(9)	0.44054(6)	0.0252(3)
La2	8c	0.34507(11)	−0.03815(9)	0.17382(6)	0.0273(3)
La3	8c	0.01062(11)	0.21832(8)	0.05038(6)	0.0269(3)
Br1	8c	0.2562(2)	−0.2158(2)	0.4541(1)	0.0341(5)
Br2	8c	0.3685(2)	0.0619(2)	0.3386(1)	0.0351(5)
Br3	8c	0.1039(2)	−0.0866(2)	0.2737(1)	0.339(5)
Br4	8c	0.6409(2)	−0.0313(2)	0.4456(1)	0.0289(5)
Br5	8c	0.1658(2)	0.2107(2)	0.1907(1)	0.0349(5)
Br6	8c	0.5343(2)	−0.3121(2)	0.3749(1)	0.0339(5)
N	8c	0.5510(15)	0.0939(11)	−0.0607(8)	0.0260(36)

[a] $U_{eq} = {}^1/_3\sum_i\sum_j U_{ij}\, a_i{}^*a_j{}^*a_ia_j$.

X-ray powder patterns of samples mounted in an airtight assembly between pieces of cellophane were collected with the aid of an Enraf-Nonius Guinier camera with Cu Kα radiation ($\lambda = 1.5406$ Å) and with Si introduced as an internal standard. The final lattice constants of the two compounds were obtained by least-squares refinements of the lines (73 for $CsNaLa_6Br_{14}N_2$ and 84 for La_3Br_6N) which were indexed on the bases of the model patterns calculated from single-crystal structural data. All yields were estimated according to the relative intensities of the powder pattern lines for each known phase present. Some data collection and refinement parameters are given in Table 1. The final atomic coordinates as well as the isotropic-equivalent ellipsoid values and their standard deviations are listed in Tables 2 and 3.

Results and Discussion

Structural Description. The compound $CsNaLa_6Br_{14}N_2$ represents a novel structure type that contains pairs of edge-sharing La_4 tetrahedra that are centered by N. This characteristic La_6N_2 unit is also present in La_3Br_6N for which the formula may be written as $La_6Br_{12}N_2$ to rationalize better the structural features and to illustrate the relationship to the alkali-metal representative. In both compounds the bitetrahedral unit is defined by three crystallographically distinct La atoms. The

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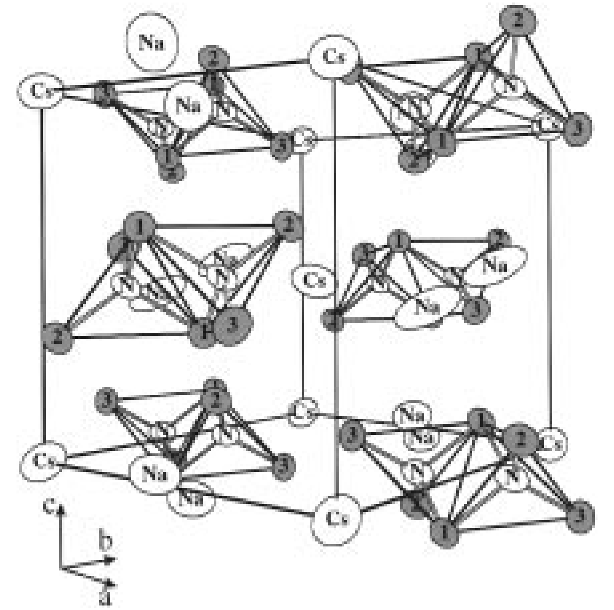

Figure 1. $CsNaLa_6Br_{14}N_2$: Perspective view of the unit cell to show the arrangement of the La_6N_2 units and the alkali-metal atoms (dark gray, La; empty spheres, Cs, Na, N; atoms numbered crystallographically according to Table 2; 98% probability thermal ellipsoids; thin lines between La atoms represent only geometric relationships).

Table 4. Important Interatomic Distances (in Å) for $CsNaLa_6Br_{14}N_2$ (**1**) and La_3Br_6N (**2**)

	1	**2**		**1**	**2**
La1−La1	3.720(1)	3.717(2)	La3−Br1	3.083	3.093(3)
La1−La2	3.873(1)	3.878(2)	La3−Br1		3.093(3)
La1−La2	3.932(1)	4.017(1)	La3−Br2	3.089(1)	3.098(2)
La1−La3	3.894(1)	3.882(1)	La3−Br4		3.295(2)
La1−La3	3.922(1)	3.945(2)	La3−Br4		3.319(2)
La2−La3	3.912(1)	3.926(2)	La3−Br5	3.154(2)	
			La3−Br5	3.197(2)	
La1−Br1	3.105(2)	3.112(2)	La3−Br6	3.087(2)	3.251(2)
La1−Br1		3.346(2)	La3−Br7	2.977(2)	
La1−Br2	3.434(2)	3.080(2)	La3−N	2.29(1)	2.27(1)
La1−Br3	3.072(2)	3.092(2)			
La1−Br4	3.071(2)	3.075(2)	Cs^a−Br1	4.117(2)	
La1−Br7	3.075(2)		Cs^a−Br3	3.777(2)	
La1−N	2.44(1)	2.44(1)	Cs^a−Br4	3.676(2)	
La1−N	2.48(1)	2.51(2)	Cs^a−Br5	3.804(2)	
La2−Br1	3.162(2)		Cs^a−Br6	4.568(2)	
La2−Br2	3.066(2)	3.080(2)	Cs^a−Br7	3.756(2)	
La2−Br3	3.006(2)	3.092(2)	Na−Br2	2.83(2)	
La2−Br3		3.254(2)	Na−Br3	2.91(2)	
La2−Br4	3.024(2)	3.075(2)	Na−Br3	2.92(2)	
La2−Br5	3.113(2)	2.987(2)	Na−Br4	3.37(2)	
La2−Br6	3.054(2)	3.111(2)	Na−Br6	3.20(2)	
La2−N	2.318(9)	2.36(1)	Na−Br7	2.86(2)	

[a] All Cs−Br distances occur twice.

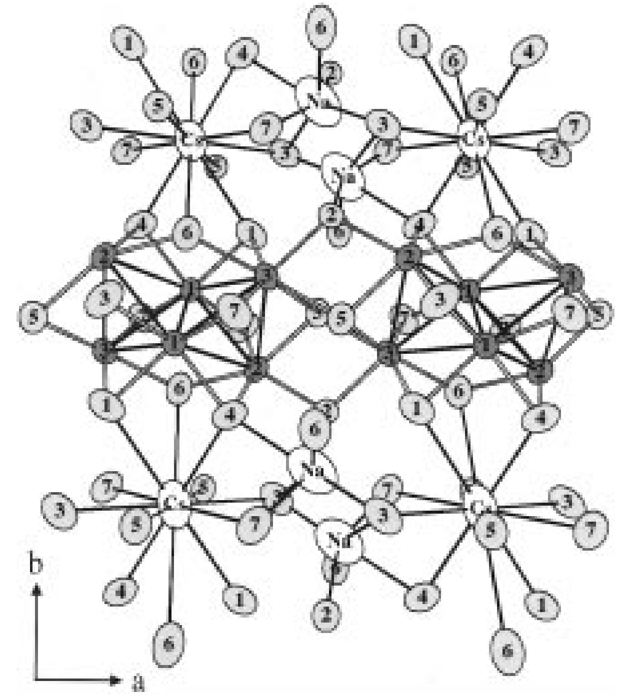

Figure 2. $CsNaLa_6Br_{14}N_2$: Part of the structure to illustrate how the rare-earth metal units and the alkali-metal atoms are interconnected by the Br atoms (dark gray, La; light gray, Br; N atoms omitted for clarity; 98%).

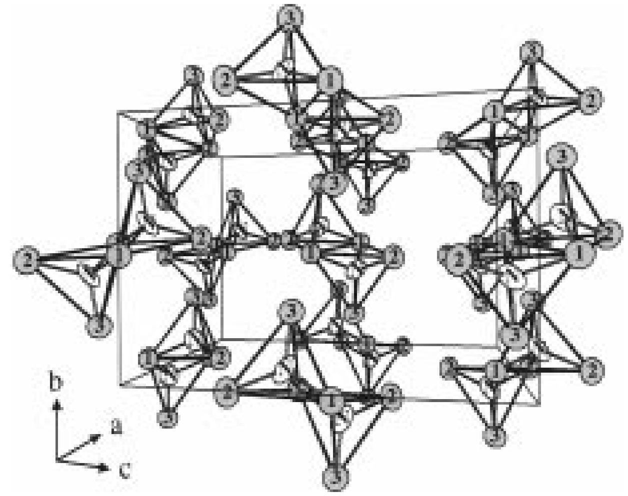

Figure 3. La_3Br_6N: Perspective view of the unit cell to show the arrangement of the La_6N_2 units (dark gray, La; empty spheres, N; atoms numbered crystallographically according to Table 3; 98%; thin lines between La atoms represent only geometric relationships).

two La1 atoms form the shared edge with an inversion center (C_i) on its midpoint at [$^1/_2$, 0, $^1/_2$] for $CsNaLa_6Br_{14}N_2$ and at [0, 0, $^1/_2$] for La_3Br_6N in the unit cell, while the La2 and La3 atoms constitute the equatorial, nearly rectangular plane. The distances La1−La1 are significantly shorter ($\Delta d \approx 0.2$ Å) than the other La−La separations within the tetrahedra. This stands in good agreement with the observations for other compounds containing condensed polyhedra and is largely due to an ionic matrix effect of the non-metal atoms.[8] Figures 1 and 3 illustrate the arrangement of the La_6N_2 units in the unit cell of the respective compound. Table 4 gives interatomic distances. Despite the similarities of the tetrahedral units, the structural differences between $CsNaLa_6Br_{14}N_2$ and La_3Br_6N become most obvious in the surrounding and connectivity patterns displayed by the Br atoms which connect the La_6N_2 units into a three-dimensional network (see below). After the structure refinement, these Br atoms were crystallographically numbered in a way such that atoms with corresponding numbers cover equivalent La−La edges of the La_6N_2 units in the structure of both compounds.

$CsNaLa_6Br_{14}N_2$. In the structure of $CsNaLa_6Br_{14}N_2$ (Figure 2) the Br1 and Br7 atoms bridge the four La1−La3 edges. While Br1 is bonded as Br^{i-a}[18] to a La2 atom of an adjacent La_4

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(18) Schäfer, H.; von Schnering, H. G. *Angew. Chem.* **1964**, *76*, 833. Examples for the notation: The ligand X^a is connected only to one vertex of a metal array, X^i bridges one M−M edge, X^{i-a} bridges one edge and is coordinated to the vertex of another cluster, and X^{a-a-a} links three different clusters via their vertices.

tetrahedron as well as to Cs, the Br7 atoms have no additional La as next neighbor (Br^{i}) but are also coordinated to both alkali-metal atoms. Br2 exhibits the uncommon Br^{a-a-a} functionality by connecting three La_6N_2 units at the same time via their corners formed by the La1, La2, and La3 atoms, respectively. The La1−La2 edges are bridged by Br3 and Br4 atoms. Both display Br^{i} functionality and are also linked to Cs and Na. Br5 atoms act as Br^{i-a} linkages and interconnect the La2−La3 edges of one unit with a La3 corner atom of another. They are also connected to Cs. Each Br atom with the functionality Br^{i-a} has a crystallographically equivalent counterpart at the same tetrahedral unit that displays Br^{a-i} connectivity. Finally, Br6 atoms are located over the saddles of the bitetrahedral unit and are coordinated to La2 (3.05 Å) and La3 (3.08 Å) and, at a greater distance, also to the two La1 atoms of the shared edge. The separations from the latter are quite different (3.59 and 3.74 Å); hence, the Br6 atoms are shifted out of the plane comprised by the La2 and La3 atoms of the La_6N_2 unit. This observation is even more obvious in the structure of La_3Br_6N as discussed below. To illustrate the bridging modes of the halide atoms, the formula may be written as $CsNa(La_6N_2)Br^{i}_{8}Br^{i-a}_{4/2}Br^{a-i}_{4/2}Br^{a-a-a}_{6/3}$. The Cs atoms are located in distorted cuboctahedral Br_{12} polyhedra within the framework of interbonded, nitrogen-centered rare-earth-metal units. The Cs−Br separations range from 3.68 Å for Cs−Br4 to 4.57 Å for Cs−Br6 and average 3.95 Å. For comparison, the distance calculated from Shannon radii[19] for CN 12 amounts to 3.84 Å. As shown in Figure 2, the Na atoms are surrounded by a deformed Br_6 octahedron with Na−Br distances from 2.83 Å for Na−Br2 to 3.37 Å for Na−Br4 with an average of 3.02 Å (2.98 Å from Shannon radii for CN 6). Two of these octahedra share a common Br3−Br3 edge with an inversion center on its midpoint at [$^1/_2$, 0, 0] in the unit cell. The C_i symmetry operation would also result in very short Na−Na distances of 2.84 Å by a full occupancy of the Na position. However, the refinement indicates that the particular position is only half-occupied by Na with a refined value of 47(3)%. Furthermore, these results make an ionic formulation as $Cs^{+}Na^{+}La^{3+}{}_{6}Br^{-}{}_{14}N^{3-}{}_{2}$ possible without any electrons left for metal−metal bonding between the La atoms. This concurs with the transparent appearance of the crystals. The relatively large ellipsoids observed for the Cs and Na atoms as well as the statistical occupancy of the Na positions parallels the experiences with similar compounds such as $ALa_9I_{16}N_4$ (A = Na−Cs)[8] or $Na_2Pr_4Br_9NO$,[7] with the alkali-metal atoms in poorly proportioned, low-symmetry sites. Obviously, the nitrogen and rare-earth-metal atoms as well as the bridging halides often build strong, dominant frameworks while the alkali-metal cations largely fulfill only charge requirements for the particular compound.

La_3Br_6N. Figure 4 shows the connectivity pattern of Br atoms in the structure of La_3Br_6N. Here Br1 atoms connect two La_6N_2 units via their La1−La3 edges as Br^{i-i} with each other. As observed in the structure of the alkali-metal representative, Br2 displays the unusual functionality Br^{a-a-a} and interconnects three units via their La1, La2, and La3 corner atoms. Br3 and Br4 atoms span the four La1−La2 edges. While Br3 is bonded as Br^{i-a} to a La2 atom of an adjacent La_4 tetrahedron, the Br4 atoms link to additional rare-earth-metal units as Br^{i-a-a} via their La3 atoms. Br5 bridges the two La2−La3 and should be labeled as Br^{i} since its next ligand (La2) is already 0.6 Å further away and should not be considered as a part of the coordination sphere any more. Like in $CsNaLa_6Br_{14}N_2$ the Br6 atoms are located over the saddles of the bitetrahedral unit. They are, however, much more shifted out of the equatorial plane and are now also coordinated with La1 (2.98 Å), La2 (3.05 Å), and La3 (3.08 Å) while the distance to the other La1 atom of the shared edge amounts to 4.58 Å. For La_3Br_6N ($=La_6Br_{12}N_2$) the bromine connectivity may be summarized as $(La_6N_2)Br^{i}_{4}Br^{i-i}_{4/2}Br^{i-a-a}_{2/3}\,Br^{a-a-i}_{4/3}Br^{i-a}_{2/2}Br^{a-i}_{2/2}Br^{a-a-a}_{6/3}$.

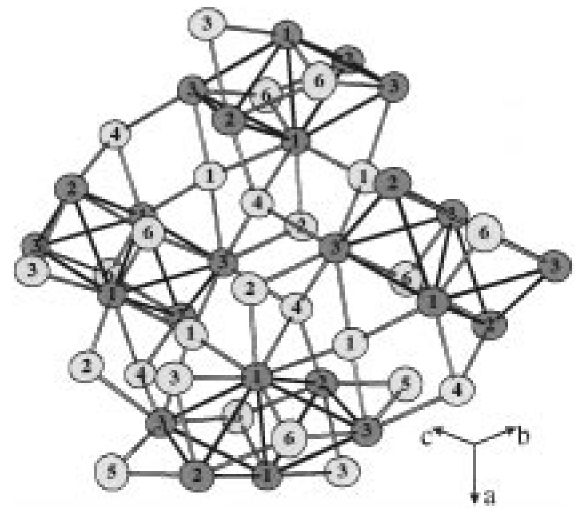

Figure 4. La_3Br_6N: Part of the structure to illustrate the connectivity pattern of the Br atoms (dark gray, La; light gray, Br; N atoms omitted for clarity; 98%).

Structural Interrelationships. Comparing the interconnection pattern of the Br atoms of the two new compounds, one may be tempted to conclude that the bitetrahedral units in La_3Br_6N are packed much more densely through Br^{i-i} and Br^{i-a-a} interactions as they are in $CsNaLa_6Br_{14}N_2$. In addition, the latter has the alkali-metal atoms as spacers which should widen the structure. However, distance calculations utilizing the inversion center at the midpoint of the La1−La1 axis as a reference point reveal that the La_6N_2 units in the structure of $CsNaLa_6Br_{14}N_2$ are on average only little more distant from each other than in La_3Br_6N. They range 9.91−10.87 Å with $\bar{d}$ = 10.23 Å and 8.15−10.43 Å with $\bar{d}$ = 9.61 Å, respectively. Moreover, in both compounds each La_6N_2 unit is surrounded cuboctahedrally by 12 others, and so they create the motif of a cubic-closest packing.

The significant difference is the conformation of the La_6N_2 units in the two structures. Figures 1 and 2 show how the long cross axes (comparable with the N−N axis) of the bitetrahedra in $CsNaLa_6Br_{14}N_2$ are all approximately parallel [100], thus creating space for the alkali-metal atoms. In the structure of La_3Br_6N the cross axes extend in four different directions. The bitetrahedra are tilted here toward each other (Figure 3 and 4) leaving no room for other cations.

The close structural relationship is also impressively documented by calculations of the *Ma*delung *P*art of *L*attice *E*nergy, MAPLE,[20] via the reaction

	2 La_3Br_6N	+	CsBr	+	NaBr	→	$CsNaLa_6Br_{14}N_2$
MAPLE (kJ/mol):	2 × 17094	+	659	+	813	≈	35681

although such a reaction would probably not be feasible topotactically. Calculations were performed for each compound on bases of their refined crystal structures. The combined lattice

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[19] Shannon, R. D. *Acta Crystallogr.* **1976**, *A32*, 751.

[20] Hoppe, R. *Angew. Chem.* **1966**, *78*, 52; **1970**, *82*, 7; *Angew. Chem., Int. Ed. Engl.* **1966**, *5*, 95; **1970**, *9*, 20.

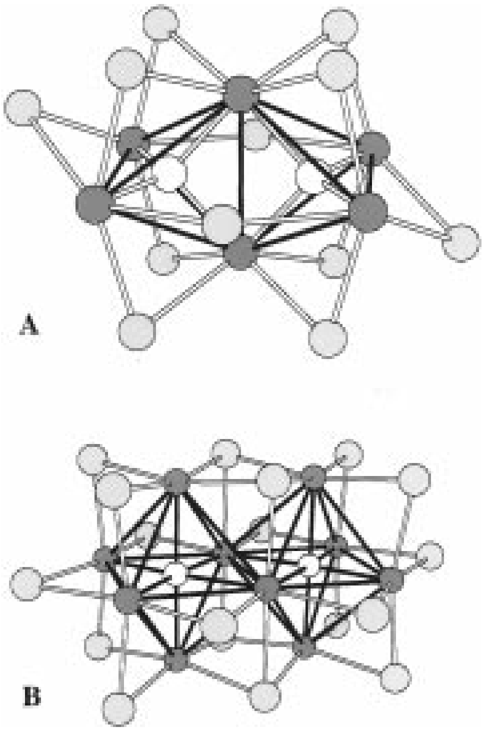

Figure 5. Comparison of the La_6N_2 unit (A) in $CsNaLa_6Br_{14}N_2$ with the $La_{10}Co_2$ cluster (B) in $Cs_2La_{10}I_{17}Co_2$, both with their halide environment (dark gray, La; light gray, halogen; empty spheres, N and Co, respectively).

energy calculated for the binary and ternary compounds on the left side of the equation is almost identical to the result for the quinquinary compound on the right ($\Delta = 21$ kJ/mol $\equiv 0.06\%$). This result may also serve as additional evidence of the half-occupancy of the Na position and demonstrates that the compound contains only one Na per formula unit.

Although the nitride bromides described here have no excess electrons for metal−metal bonding and should be classified as salts, their structures show many similarities to representatives of the metal-rich cluster chemistry. For example, Figure 5 compares the bitetrahedral La_6N_2 unit of $CsNaLa_6Br_{14}N_2$ with the recently discovered bioctahedral $La_{10}Co_2$ cluster in the structure of $Cs_2La_{10}I_{17}Co_2$.[21,22] Both tetrahedra and octahedra are centered by interstitial atoms, the distances between the rare-earth-metal atoms are almost the same including the shorter separations of the atoms forming the shared edges, and all outer edges are bridged characteristically by halide atoms that interconnect the metal units into a three-dimensional network.

Phase Relationships. Another important and interesting aspect of this research is the failure to synthesize compounds with similar compositions such as $CsKLa_6Br_{14}N_2$, $KNaLa_6Br_{14}N_2$, $CsLa_6Br_{13}N_2$, and $KLa_6Br_{13}N_2$ as well as $NaLa_6Br_{13}N_2$. Under the experimental conditions used here solely the ternary phase La_3Br_6N was obtained together with the (unreacted) binary alkali-metal bromides. Only the combination Cs and Na as "large" and "small" cations seems to favor the formation of the quinquinary phase. Quaternary phases have not been observed so far. In one reaction, loaded as $NaLa_6Br_{13}N_2$, some crystals of another ternary phase, La_2Br_3N, were isolated. Traces of oxygen in the starting materials, most probably from contamination of the highly moisture-sensitive $LaBr_3$ during their storage in the glovebox, resulted in small amounts of $La_8Br_{13}N_3O$.

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Supporting Information Available: Tables providing more details regarding the data collection and refinement for $CsNaLa_6Br_{14}N_2$ and $La_3Br_6N_2$ and anisotropic displacement parameters (3 pages). Ordering information is given on any current masthead page.

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(21) Lulei, M.; Maggard, P. A.; Corbett, J. D. *Angew. Chem.* **1996**, *108*, 1798; *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1704.
(22) Lulei, M.; Martin, J. D.; Hoistad, L. M.; Corbett, J. D. *J. Am. Chem. Soc.* **1997**, *119*, 513.