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New cerium nitride chlorides: $Ce_6Cl_{12}N_2$ and CeNCl

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Abstract

The compound CeNCl is shown to be isotypic with tetragonal BiOCl with lattice parameters $a = b = 4.079(2)$ Å, $c = 6.837(2)$ Å. The compound $Ce_6Cl_{12}N_2$ was prepared from $CeCl_3$, Ce and NaN_3 in a sealed Nb tube at 750 °C. The structure of $Ce_6Cl_{12}N_2$ was solved by X-ray single crystal diffraction and shown to contain edge-shared, nitrogen-centered, cerium tetrahedra. The lattice parameters for $Ce_6Cl_{12}N_2$ were determined to be $a = 11.233(4)$ Å, $b = 16.527(8)$ Å, $c = 10.708(3)$ Å, $\beta = 90.15°$ in the spacegroup $P2_1/c$.

1. Introduction

We have synthesized two new cerium nitride chlorides. One, CeNCl, is isostructural with ThNCl [1] but the other, $Ce_6Cl_{12}N_2$, is a Ce(III) compound which assumes an interesting structure of edge-shared tetrahedra of cerium and interstitial nitrogen. This cerium compound is similar to a previously reported compound Gd_3Cl_6N, which also contains pairs of edge-shared gadolinium tetrahedra centered by nitrogen, but the arrangement of the chlorine atoms about the rare earth tetrahedra is different in the cerium and gadolinium compounds. Structurally these cluster compounds can be discussed by using the concept of condensed metal polyhedra in an anionic framework [2]. The Ce–Ce bonds that form the tetrahedra are generally weak, having bond orders less than one half; however, the metal–nitrogen bonds are generally strong with a bond order of about one [3].

2. Experimental details

All manipulations were performed in an Ar-filled drybox unless otherwise stated. In most cases the starting materials were very hygroscopic and oxophilic whereas the products were much more stable towards attack by air. Microprobe analyses were performed on a JEOL 733 Superprobe. Bond orders and Madelung potentials were calculated using the program EUTAX1.3. EUTAX calculates potentials using the method of Tosi [4].

2.1. CeNCl

Ce filings (Cerac) 0.341 g (1.22×10^{-2} mol), $CeCl_3$ (Aesar) 0.30 g (1.22×10^{-3} mol) and NaN_3 (Kodak) 0.79 g (1.22×10^{-2} mol) were reacted at 800 °C for four days, then at 700 °C for four days in a welded niobium tube. The black product was identified using standardless semi-quantitative microprobe analysis and powder X-ray diffraction (XRD); it is isostructural with ThNCl (JCPDS card # 22-933) and therefore BiOCl. Alternatively, CeNCl may be prepared from a non-stoichiometric pressed pellet of CeN and $CeCl_3$ in equimolar amounts in a flow of dry nitrogen gas at 750 °C in two days. An MgO boat was used to contain the pellet. The CeNCl from the latter preparation often contained up to 5% CeN based on the powder diffraction pattern of the product.

2.2. $Ce_6Cl_{12}N_2$

$CeCl_3$ 0.303 g (1.23×10^{-3} mol), Ce 0.172 g (1.23×10^{-3} mol) and NaN_3 0.080 g (1.3×10^{-3} mol) were reacted in a welded niobium tube at 750 °C for five days to yield a mixture of products. Yellow air-stable plate-like crystals were selected from the product mixture.

3. Results

3.1. CeNCl

We have found that CeNCl is isotypic with BiOCl, based on its powder XRD pattern which was only slightly different from that of ThNCl. Observed and calculated peak positions, their intensities and Miller indices are presented in Table 1. Microprobe analysis

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TABLE 1. Powder diffraction data for CeNCl

Reflection	Observed D (Å)	Calculated D (Å)	Observed I/I_0	Calculated I/I_0
001	6.8306	6.8370	22	36
101	3.5005	3.5029	91	68
002	3.4190	3.4185	15	6
110	2.8827	2.8843	66	68
102	2.6186	2.6200	100	100
003	2.2780	2.2790	6	6
112	2.2035	2.2045	25	17
200	2.0387	2.0395	36	34
201	1.9540	1.9544	7	6
113	1.7874	1.7882	15	19
212	1.6095	1.6094	33	45
104	1.5766	1.5764	14	14
203	1.5202	1.5198	8	8
114	1.4710	1.4704	5	10
220	1.4424	1.4421	10	11

TABLE 2. Crystal data and data collection parameters

Empirical formula	$Ce_6Cl_{12}N_2$
Color; Habit	Yellow plate
Crystal size (mm)	0.26×0.22×0.09
Crystal system	Monoclinic
Space group	$P2_1/c$
Unit cell dimensions	$a = 11.233(4)$ Å
	$b = 16.527(8)$ Å
	$c = 10.708(3)$ Å
	$\beta = 90.15(3)°$
Volume	1987.9(14) Å^3
Z	4
Formula weight	1294.1 amu
Density (calculated)	4.324 Mg m^{-3}
Absorption coefficient	14.29 mm^{-1}
$F(000)$	2264
Radiation	MoKα ($\lambda = 0.710\,73$ Å)
Temperature (K)	298
Monochromator	Highly oriented graphite crystal
2θ range	3.0–55.0°
Scan type	2θ–θ
Scan speed	Variable; 2.00–29.3° min^{-1} in ω
Scan range (ω)	0.60° plus Kα-separation
Background measurement	Stationary crystal and stationary counter at beginning and end of scan, each for 25% of total scan time
Standard reflections	3 measured every 50 reflections
Index ranges	$0 \leq h \leq 14$, $-21 \leq k \leq 0$, $-13 \leq l \leq 13$
Reflections collected	4992
Independent reflections	4590 $R_{int} = 3.86\%$)
Observed reflections	4121 ($F > 3.0\sigma(F)$)
Absorption correction	Semi-empirical
Minimum/Maximum transmission	0.4888/0.9070

of the product showed that the ratio of cerium to chlorine was within 5% of 1:1. We were able to index CeNCl in the tetragonal BiOCl structure to give the following lattice parameters, $a = b = 4.079(2)$ Å, $c = 6.837(2)$ Å, $V = 113.7$ Å^3.

We assume that the differences between the observed and calculated intensities are due to some preferred orientation or polycrystalline grain sizes larger than 50 μm [5].

3.2. $Ce_6Cl_{12}N_2$

The structure of $Ce_6Cl_{12}N_2$ was determined from an air-stable yellow plate-like crystal at room temperature. A suitable crystal was selected and single crystal X-

TABLE 3. Solution and refinement parameters

System used	Siemens SHELXTL PLUS
Solution	Direct methods
Refinement method	Full-matrix least-squares
Quantity minimized	$\Sigma w(F_o - F_c)^2$
Extinction correction	$\chi = 0.000\,539(11)$ where $F^* = F[1 + 0.002\chi F^2/\sin(2\theta)]^{-1/4}$
Weighting scheme	$w^{-1} = \sigma^2(F) + 0.0000F^2$
Number of parameters refined	182
Final R indices (observed data)	$R =$ [illegible] 09%, $wR = 3.42\%$
R indices (all data)	[illegible].59%, $wR = 3.47\%$
Goodness-of-fit	[illegible]
Largest and mean Δ/σ	0.001, 0.00
Data-to-parameter ratio	22.6:1
Largest difference peak	1.90 e Å^{-3}
Largest difference hole	−1.75 e Å^{-3}

TABLE 4. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients (Å$^2 \times 10^3$)

	x	y	z	U_{eq}
Ce(1)	5219(1)	4366(1)	1408(1)	8(1)
Ce(2)	9781(1)	9367(1)	1409(1)	8(1)
Ce(3)	9648(1)	1773(1)	1607(1)	11(1)
Ce(4)	5353(1)	6773(1)	1606(1)	11(1)
Ce(5)	2895(1)	5484(1)	4868(1)	10(1)
Ce(6)	2105(1)	484(1)	4867(1)	10(1)
Cl(1)	10605(2)	3399(1)	1291(2)	20(1)
Cl(2)	5609(2)	1599(1)	−1289(2)	20(1)
Cl(3)	16883(2)	3758(1)	−312(2)	18(1)
Cl(4)	12168(2)	−459(1)	2516(2)	16(1)
Cl(5)	2836(1)	455(1)	−2483(2)	17(1)
Cl(6)	9695(1)	528(1)	3581(2)	13(1)
Cl(7)	8116(2)	−1242(1)	−310(2)	19(1)
Cl(8)	4198(2)	2277(1)	−3967(2)	17(1)
Cl(9)	10807(2)	−2274(1)	−3967(2)	17(1)
Cl(10)	7105(2)	1877(1)	−8308(2)	19(1)
Cl(11)	12106(2)	1876(1)	3309(2)	19(1)
Cl(12)	5310(2)	−529(1)	−1417(2)	14(1)
N(1)	9066(5)	608(3)	515(5)	11(2)
N(2)	14076(5)	4385(3)	−528(5)	10(2)

Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

ray diffraction data were collected on a Syntex $P2_1$ diffractometer using MoKα radiation and a graphite monochromator. The structure was determined and refined by direct methods using the Nicolet SHELXL PLUS software. An empirical absorption correction using the psi scan method was performed. Crystal data are reported in Table 2; solution and refinement parameters are reported in Table 3; atomic coordinates are in Table 4. Bond lengths and angles may be found in Table 5.

TABLE 5. Selected bond lengths and angles

(a) Bond lengths

Bond	Length (Å)
Intracluster distances	
Ce–Ce bonds	
Ce(1)–Ce(1′)	3.704
Ce(1)–Ce(4)	3.986
Ce(1)–Ce(6)	3.786
Ce(1′)–Ce(4)	3.789
Ce(1′)–Ce(6)	3.871
Ce(4)–Ce(6)	3.899
Ce(2)–Ce(2′)	3.706
Ce(2)–Ce(3)	3.795
Ce(2)–Ce(5)	3.879
Ce(2′)–Ce(5)	3.780
Ce(2′)–Ce(3)	3.985
Ce(3)–Ce(5)	3.895
Ce–Cl bonds	
Ce(1)–Cl(2)	2.968
Ce(1)–Cl(4)	3.163
Ce(1)–Cl(5)	2.946
Ce(1)–Cl(8)	2.974
Ce(1)–Cl(12)	3.021
Ce(1′)–Cl(2′)	2.968
Ce(1′)–Cl(3)	2.813
Ce(1′)–Cl(5″)	2.946
Ce(1′)–Cl(8′)	2.974
Ce(2)–Cl(5′)	3.173
Ce(2)–Cl(6)	3.016
Ce(2)–Cl(7)	2.807
Ce(2)–Cl(4′)	2.942
Ce(2)–Cl(9)	2.974
Ce(2′)–Cl(1)	2.969
Ce(2′)–Cl(5‴)	3.173
Ce(2′)–Cl(6)	3.016
Ce(2′)–Cl(7″)	2.807
Ce(3)–Cl(6′)	2.950
Ce(3)–Cl(9′)	3.024
Ce(3)–Cl(9)	2.986
Ce(3)–Cl(10)	2.863
Ce(3′)–Cl(6)	2.950
Ce(3′)–Cl(10‴)	2.863
Ce(3′)–Cl(1″)	2.914
Ce(3′)–Cl(7″)	3.004
Ce(3′)–Cl(11′)	3.308
Ce(4)–Cl(2‴)	2.919
Ce(4)–Cl(3)	2.997
Ce(4)–Cl(8′)	2.990
Ce(4)–Cl(8″)	3.017
Ce(4)–Cl(10′)	3.316
Ce(4)–Cl(11)	2.860
Ce(4)–Cl(12)	2.951
Ce(4′)–Cl(2⁗)	2.918
Ce(4′)–Cl(8‴)	3.017
Ce(4′)–Cl(8)	2.990
Ce(4′)–Cl(10″)	3.316
Ce(4′)–Cl(12⁗)	2.951
Ce(5)–Cl(2″)	2.919

(*continued*)

TABLE 5. (*continued*)

(a) Bond lengths

Bond	Length (Å)
Ce(5)–Cl(4′)	2.953
Ce(5)–Cl(5‴)	2.957
Ce(5)–Cl(7″)	3.107
Ce(5)–Cl(10)	2.844
Ce(5)–Cl(12″)	3.098
Ce(5)–Cl(12‴)	3.045
Ce(5′)–Cl(2⁗)	2.919
Ce(5′)–Cl(5⁗)	2.957
Ce(5′)–Cl(7‴)	3.107
Ce(5′)–Cl(10‴)	2.844
Ce(5′)–Cl(12⁗)	3.045
Ce(5′)–Cl(12⁗′)	3.098
Ce(6)–Cl(1′)	2.930
Ce(6)–Cl(5″)	2.952
Ce(6)–Cl(11)	2.841
Ce(6′)–Cl(5)	2.952
Ce(6′)–Cl(3)	3.107
Ce(6′)–Cl(6″)	3.109
N–Ce bonds	
N(1)–Ce(2)	2.436
N(1)–Ce(2′)	2.400
N(1)–Ce(3)	2.344
N(1)–Ce(5)	2.249
N(2)–Ce(1)	2.404
N(2)–Ce(1′)	2.439
N(2)–Ce(4)	2.326
N(2)–Ce(6)	2.265
Intercluster distances	
N(1)–N(1)	7.036
Ce(1)–Ce(4′)	3.789
Ce(1)–Ce(6′)	3.871
Ce(2)–Ce(3′)	3.985
Ce(2)–Ce(5′)	3.780

(b) Selected bond angles

		Angle (°)
Bond angles at cerium		
Bond angles on atom Ce(2)		
Ce(3′)	Ce(5)	60.14
Ce(3′)	Ce(2)	59.00
Ce(3′)	Ce(3)	123.17
Ce(3′)	Ce(5)	89.61
Ce(5′)	Ce(2)	62.41
Ce(5′)	Ce(3)	94.05
Ce(5′)	Ce(5)	122.15
Ce(2′)	Ce(3)	64.17
Ce(2′)	Ce(5)	59.74
Ce(3)	Ce(5)	60.98
Bond angles on atom Ce(2′)		
Ce(2)	Ce(3′)	64.17
Ce(2)	Ce(5′)	59.74
Ce(2)	Ce(3)	59.00

(*continued*)

TABLE 5. (*continued*)

(b) Selected bond angles

		Angle (Å)
Ce(2)	Ce(5)	62.41
Ce(3′)	Ce(5′)	60.98
Ce(3′)	Ce(3)	123.17
Ce(3′)	Ce(5)	94.05
Ce(5′)	Ce(3)	89.61
Ce(5′)	Ce(5)	122.15
Ce(3)	Ce(5)	60.14
Bond angles on atom Ce(3)		
Ce(2)	Ce(2′)	56.83
Ce(2)	Ce(5)	60.58
Ce(2′)	Ce(5)	57.33
Bond angles on atom Ce(5)		
Ce(2)	Ce(2′)	57.85
Ce(2)	Ce(3)	58.44
Ce(2′)	Ce(3)	62.53
Bond angles on atom Ce(1)		
Ce(4′)	Ce(6′)	61.17
Ce(4′)	Ce(1′)	64.27
Ce(4′)	Ce(4)	123.18
Ce(4′)	Ce(6)	93.92
Ce(6′)	Ce(1)	59.92
Ce(6′)	Ce(4)	89.58
Ce(6′)	Ce(6)	122.16
Ce(1′)	Ce(4)	58.91
Ce(1′)	Ce(6)	62.24
Ce(4)	Ce(6)	60.15
Bond angles on atom Ce(1′)		
Ce(1)	Ce(4′)	58.91
Ce(1)	Ce(6′)	62.24
Ce(1)	Ce(4)	64.27
Ce(1)	Ce(6)	59.92
Ce(4′)	Ce(6′)	60.15
Ce(4′)	Ce(4)	123.18
Ce(4′)	Ce(6)	89.58
Ce(6′)	Ce(4)	93.92
Ce(6′)	Ce(6)	122.16
Ce(4)	Ce(6)	61.17
Bond angles on atom Ce(4)		
Ce(1)	Ce(1′)	56.82
Ce(1)	Ce(6)	57.38
Ce(1′)	Ce(6)	60.45
Bond angles on atom Ce(6)		
Ce(1)	Ce(1′)	57.84
Ce(1)	Ce(4)	62.47
Ce(1′)	Ce(4)	58.38
Bond angles on atom Ce(4′)		
Ce(1)	Ce(6′)	60.45
Ce(1)	Ce(1′)	56.82
Ce(6)	Ce(1′)	57.38
Bond angles on atom Ce(6′)		
Ce(1)	Ce(4′)	58.38
Ce(1)	Ce(1′)	57.84
Ce(4′)	Ce(1′)	62.47

(*continued*)

TABLE 5. (*continued*)

(b) Selected bond angles

Bond angles on atom Ce(5')		
Ce(2)	Ce(3)	62.53
Ce(2)	Ce(2)	57.85
Ce(3)	Ce(2)	58.44
Bond angles on atom Ce(3')		
Ce(2)	Ce(5')	57.33
Ce(2)	Ce(2')	56.83
Ce(5')	Ce(2')	60.58
Bond angles on chlorine over edges of tetrahedra		
Ce–Cl–Ce angles, Cl over edges		
Ce(2)–Cl(9)–Ce(3)		79.08
Ce(2)–Cl(6)–Ce(3)		83.79
Ce(2)–Cl(7)–Ce(3)		81.45
Ce–Cl–Ce, Cl bridging		
Ce(4)–Cl(11)–Ce(3)		147.85
Ce(3)–Cl(10)–Ce(4)		147.85

4. Description of the structure

4.1. CeNCl

CeNCl crystallizes with the well known BiOCl structure, and due to the similarity in size between cerium and thorium, there is only a slight structural difference between these two compounds. For ThNCl the lattice parameters ($a = 4.097$ Å, $c = 6.895$ Å) are reported with bond lengths for Th–Cl 3.21 Å and Th–N 2.34 Å [1]. Scaling the bond lengths with the lattice parameters for CeNCl ($a = 4.079(2)$ Å, $c = 6.837(2)$ Å) one would expect Ce–Cl 3.20 Å and Ce–N 2.33 Å. In $CeCl_3$, the Ce–Cl bond length is 2.96 Å and in CeN, which assumes the NaCl structure, Ce–N is 2.5 Å. When one compares this ternary with the binaries $CeCl_3$ and CeN, the facts that the ternary Ce–Cl distance is longer than the Ce–Cl distance in $CeCl_3$ and that the ternary Ce–N distance is shorter than that found in CeN show the importance of Ce–N bonding in the ternary material.

4.2. $Ce_6Cl_{12}N_2$

The most prominent feature of the $Ce_6Cl_{12}N_2$ structure are the pairs of edge-shared cerium tetrahedra centered by nitrogen atoms, shown in Fig. 1, a view down the [0 0 1] axis and Fig. 2, a view down the [1 0 0] axis. The chlorine atoms have not been shown in these figures for clarity and the box denotes the unit cell. In Fig. 3 the chlorine atoms are included in a view tilted slightly from the *a* axis. The cerium clusters are spaced 7.0 Å apart based on the minimum intercluster distance between interstitial nitrogen. Due to the Ce–N bonding, the structure may be most clearly described as edge-shared cerium tetrahedra but the minimum intercluster Ce–Ce distance (3.789 Å) shows that the clusters are not spatially isolated. The cerium tetrahedra are distorted in that the shared edge (3.7 Å) is shorter than the other edges (3.8–3.9 Å) of the tetrahedra. Ignoring the distortion of the tetrahedra present in the gadolinium compound, Gd_3Cl_6N (spacegroup $P\bar{1}$), these two compounds share the structural motif of edge-shared nitrogen-centered tetrahedra. Unique to both the cerium and gadolinium compounds are the array of chlorine anions in which the edge-shared tetrahedra are arranged.

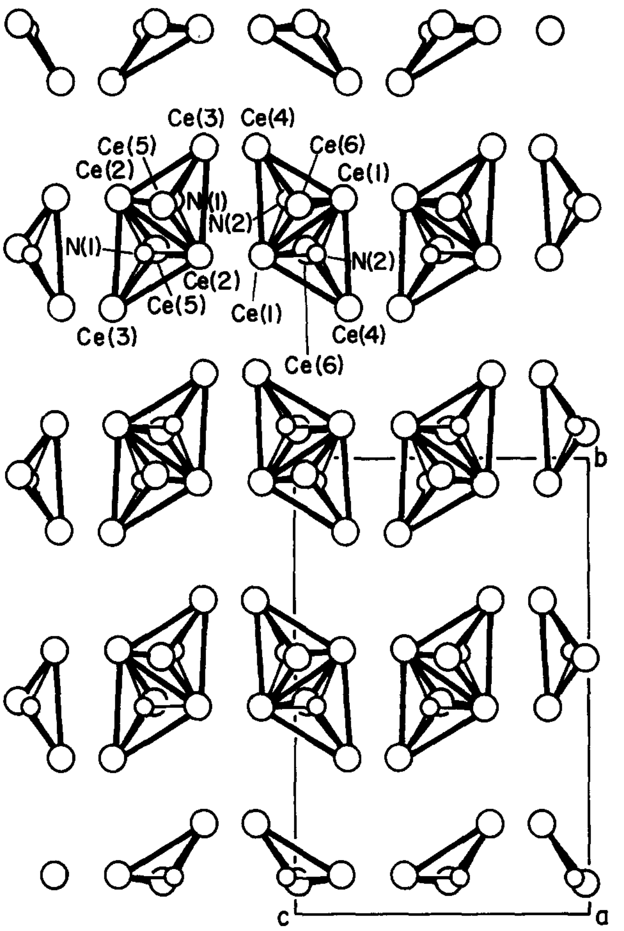

Fig. 1. $Ce_6Cl_{12}N_2$ viewed down the *a* axis, Cl atoms not shown for clarity.

Although the coordination of the clusters by chlorine is different in both compounds, both structures have some non-bonding regions bordered only by chlorine anions as shown in Fig. 3. Some chlorine atoms link the clusters together while others are terminal and form the non-bonding region. Three coordinate chlorine atoms are found in this structure; they bridge an edge of a tetrahedron of cerium and bond to a cerium atom in a neighboring cluster. The Ce–Cl bond lengths to one cluster are usually very similar in length (2.98 Å) and only slightly different from the bond lengths to the cerium in a neighboring cluster (3.02 Å). Other

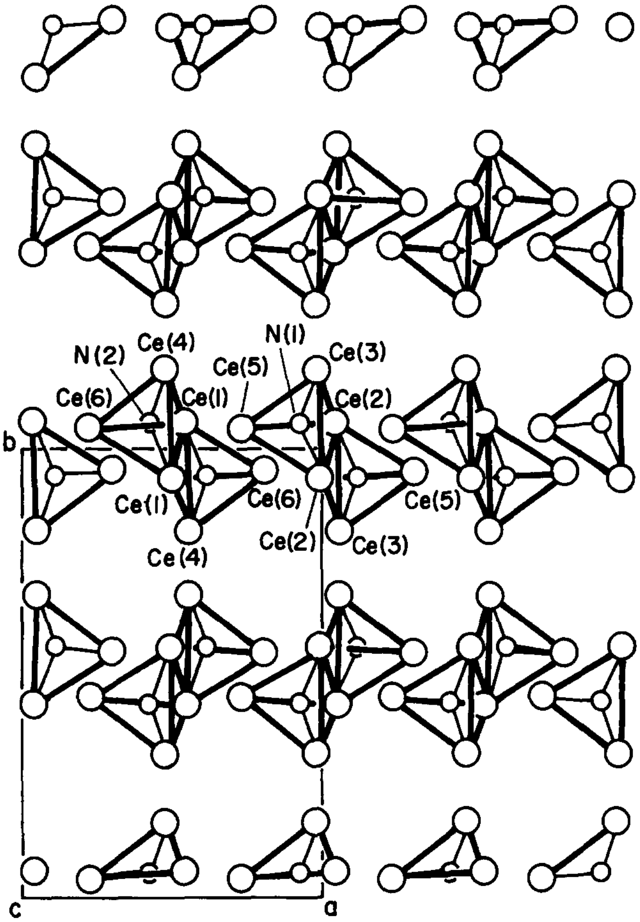

Fig. 2. $Ce_6Cl_{12}N_2$ viewed down the *c* axis, Cl atoms not shown for clarity.

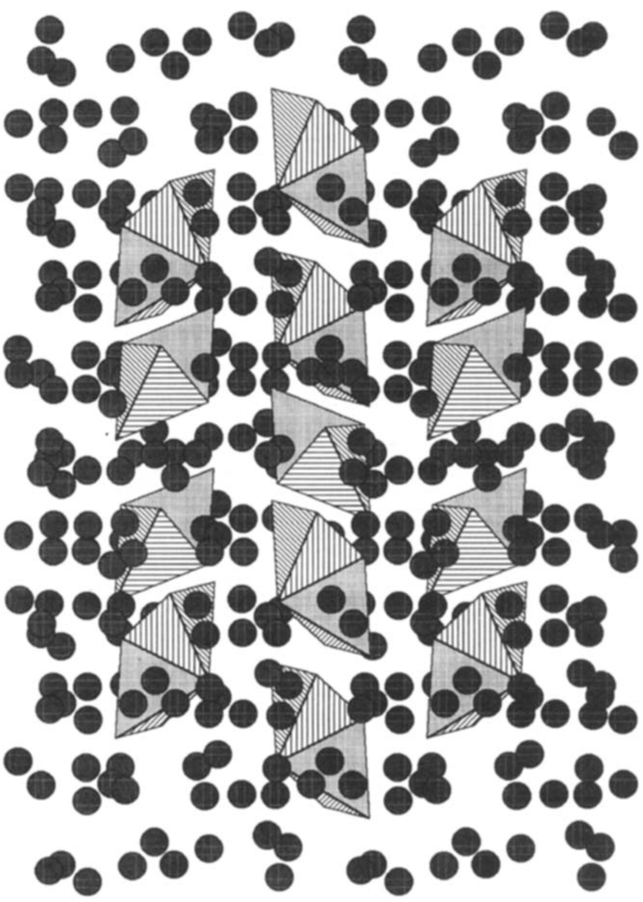

Fig. 3. $Ce_6Cl_{12}N_2$ tilted slightly from the *a* axis.

chlorine atoms link the clusters together in a two-coordinate fashion. These atoms, Cl(8) and Cl(9), form an angle between two Ce(4) and Ce(3) of 155.30° and 155.04° respectively. Because the Ce–Cl bond lengths are about the same in all cases (2.986–3.024 Å), these two coordinate chlorine atoms have a smaller calculated bond valence than the others (Cl(8) = 0.834, Cl(9) = 0.774). It is not surprising that these Ce-Cl bond lengths are similar to those found in $CeCl_3$ (2.96 Å) and that the average calculated valence for chlorine is 0.962.

Because this is formally a Ce^{3+} compound, one would not expect significant Ce–Ce bonding. This is evident when the Ce–Ce bond distances in this compound (3.7–3.9 Å) are compared with those of cerium metal (3.65 Å). In addition, the Ce–N distance in this compound is slightly shorter than the Ce–N distance in CeN (2.25–2.35 Å *vs.* 2.5 Å), most likely because here the nitrogen is four-coordinate whereas in CeN the nitrogen is six-coordinate. The bond order calculated for these Ce–N bonds varied from 0.77 to 1.28 and averaged 0.97, suggesting that the Ce–N bond is, in fact, a full single bond. The calculated bond valences to chlorine were consistent with their respective coordination numbers, two and three. As a further check on the reliability of the $Ce_6Cl_{12}N_2$ structure determination, we calculated Madelung potentials, experience showing that nitrogen atoms in inorganic nitrides usually have site potentials of 30–32 V [6]. The potentials of the nitrogen atoms found in the $Ce_6Cl_{12}N_2$ structure were 31.66 V and 30.99 V, indicating that these nitrogen atoms are in essentially equivalent environments in the crystal. We were unable to isolate enough crystals for magnetic susceptibility measurements in order to examine more fully the cerium electronic state.

5. Conclusion

The reaction of Ce, $CeCl_3$ and a source of nitrogen such as CeN or NaN_3 yields at least two nitride chlorides with the stoichiometries CeNCl and $Ce_6Cl_{12}N_2$. The first compound assumes the tetragonal BiOCl structure, whereas the second assumes a unique structure with edge-shared nitrogen-centered cerium tetrahedra. Calculated bond valences and Madelung potentials indicate that this structure determination is reliable.

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References

1 R. Juza and R. Sievers, *Z. Anorg. Allg. Chem., 363* (1968) 258.
2 A. Simon and T. Köhler, *J. Less-Common Met., 116* (1986) 279.
3 N.E. Brese and M. O'Keeffe, *Acta Crystallogr. B, 47* (1991) 192.
4 M.P. Tosi, *Solid State Phys., 16* (1964) 1.
5 D.L. Bish and R.C.J. Reynolds, in D.L. Bish and J.E. Dost (eds.), *Mod. Powder Diffract.*, The Mineralogical Society of America, Washington, *20* (1989) 78.
6 N.E. Brese and M. O'Keeffe, *Struct. Bond., 79* (1992) 307.