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$Cs_2Gd_6N_2Te_7$: The first quaternary nitride telluride of the lanthanides

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Abstract

The first quaternary nitride telluride with trivalent gadolinium, $Cs_2Gd_6N_2Te_7$, was obtained by the reaction of metallic gadolinium with cesium azide, elemental tellurium, and gadolinium trichloride as well as cesium chloride as flux at 900 °C for 7 days in evacuated silica tubes. Single crystals occur as long black needles and crystallize in the monoclinic space group *C*2/*m* ($a = 2403.1(2)$ pm, $b = 424.03(3)$ pm, $c = 1142.91(7)$ pm, $\beta = 103.709(4)^\circ$, $Z = 2$). Three crystallographically different Gd^{3+} cations constitute the structure, two are coordinated by one N^{3-} (d(Gd(1/2)–N) = 217 pm) and five Te^{2-} anions (d(Gd(1/2)–Te) = 305–326 pm), and the third Gd^{3+} by two N^{3-} (d(Gd(3)–N) = 244 pm) and four Te^{2-} anions (d(Gd(3)–Te) = 316–317 pm), all forming distorted octahedra about Gd^{3+}. The Cs^+ cation shows a perfect bicapped trigonal prism (C.N. = 8, d(Cs–Te) = 383–431 pm) as coordination sphere. Two of these polyhedra are condensed via a common (non-capped) rectangular face building up double prisms $[Cs_2Te_{12}]^{22-}$. Further linkage via triangular faces (along [0 1 0]) and two of the four caps (along [0 0 1]) results in corrugated layers $[Cs_2Te_7]^{12-}$ running parallel to (1 0 0). However, the main feature of the crystal structure comprises N^{3-}-centered $(Gd^{3+})_4$ tetrahedra (d(N–Gd) = 217 pm (2×) and 244 pm (2×); ∡(Gd–N–Gd) = 107° (2 + 2 + 1×) and 121° (1×)), which are connected via two vertices each to build up one-dimensional infinite chains $^1_\infty\{[N(Gd1)^t_{1/1}(Gd2)^t_{1/1}(Gd3)^v_{2/2}]^{6+}\}$ (t = terminal, v = vertex-shared) along [0 1 0] like in the structure of the M_3NCh_3-type nitride chalcogenides with M = La–Nd, Sm, Gd–Dy, and Ch = S, Se.

Keywords: Lanthanides; Cesium; Gadolinium; Nitrides; Tellurides; Crystal structure

1. Introduction

In the last decade, nitride chalcogenides of the lanthanides (and their halide derivatives) have been demonstrated to possess an extremely rich chemistry of formula and structural types [1]. However, N^{3-}-centered $(M^{3+})_4$ tetrahedra, which can occur isolated or condensed, provide the main feature in the crystal structures for all of them. In ternary compounds such as M_3NCh_3 (M = La–Nd, Sm, Gd–Dy; Ch = S, Se) [2] these $[NM_4]^{9+}$ tetrahedra are connected via two corners forming linear chains $^1_\infty\{[N(M)^t_{2/1}(M')^v_{2/2}]\}$ (t = terminal, v = vertex-shared). The ratio $N^{3-} : M^{3+} = 1 : 2$, realized for the composition $M_4N_2Ch_3$ (M = La–Nd, Sm, Tb; Ch = S, Se, Te) [3], requires a higher degree of linkage of the N^{3-}-centered $(M^{3+})_4$ tetrahedra. The crystal structures of $Sm_4N_2S_3$ [4] and $Tb_4N_2Se_3$ [5,6] show also infinite chains, but now by sharing *cis*-oriented edges according to $^1_\infty\{[N(M)^t_{1/1}(M')^e_{3/3}]^{3+}\}$ (e = edge-connecting) in this case. The nitride chalcogenides $Pr_4N_2S_3$ [7] and $M_4N_2Se_3$ (M = Pr, Nd) [6,7] present a layered arrangement, dominated by N^{3-}-centered $(M^{3+})_4$ tetrahedra again, which share a common edge first. Continuing linkage of the resulting bitetrahedral $[N_2M_6]^{12+}$ units (also a discrete feature in the crystal structure of M_5NSe_6 [8] with M = Pr) via the *non*-connected vertices to layers according to $^2_\infty\{[N(M)^e_{2/2}(M')^v_{2/2}]^{3+}\}$ forms different kinds of tetrahedral nets, which can be described as layers consisting of "four- and eight-rings" for $Pr_4N_2S_3$ and as layers of exclusively "six-rings" for $Pr_4N_2Se_3$. Recently we could prepare and characterize the first nitride tellurides of the lanthanides, $M_4N_2Te_3$ (M = La–Nd) [9], on the basis of single-crystal X-ray diffraction data. The crystal structure is dominated by N^{3-}-centered $(M^{3+})_4$ tetrahedra of course, which build up *non*-linear infinite chains $^1_\infty\{[N(M)^e_{4/2}]^{3+}\}$ by sharing *trans*-oriented edges.

2. Experimental data

$Cs_2Gd_6N_2Te_7$, the first quaternary nitride telluride with cesium and gadolinium, was obtained by the reaction of elemental gadolinium (Gd: ChemPur;

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Table 1
$Cs_2Gd_6N_2Te_7$: crystallographic data and their determination

Formula	$Cs_2Gd_6N_2Te_7$
Crystal system	Monoclinic
Space group	$C2/m$ (no. 12)
Formula units (Z)	2
Lattice constants[a]	$a = 2403.12(15)$ pm, $b = 424.03(3)$ pm, $c = 1142.91(7)$ pm, $\beta = 103.709(4)^\circ$
Molar volume, V_m (cm^3 mol^{-1})	340.68(4)
Calculated density, D_x (g cm^{-3})	6.254
$F(0\,0\,0)$	1744
Diffractometer/wavelength	Kappa-CCD (Nonius)/$\lambda = 71.07$ pm (Mo-Kα)
Index range	$\pm h_{max} = 32$, $\pm k_{max} = 5$, $\pm l_{max} = 15$
Θ_{max} (°)	28.3
Absorption coefficient, μ (mm^{-1})	29.33
Data corrections	Background, polarization and Lorentz factors; numerical absorption correction: program *X-SHAPE* [11]
Collected reflections/unique ones	13978/1590
R_{int}/R_σ	0.092/0.053
Structure solution and refinement	Program package *SHELX-93* and *-97* [12]
Scattering factors	International Tables, vol. C [13]
R_1 (with 4σ barrier)	0.037 (for 1386 reflections)
R_1/wR_2/Goodness of Fit (GooF) (for all reflections)	0.050/0.061/1.122
Extinction (g)	0.00022(3)
Residual electron density, ρ ($e^- \times 10^6$ pm^3)	1.91 (max.), −1.72 (min.)

[a] Single crystal data, further details of the crystal structure investigation can be obtained from the Fachinformationszentrum (FIZ) Karlsruhe, D-76344 Eggenstein-Leopoldshafen, Germany (fax: +49 7247 808 666; e-mail: crysdata@fiz-karlsruhe.de), on quoting the depository number CSD-391315 for $Cs_2Gd_6N_2Te_7$.

Table 2
$Cs_2Gd_6N_2Te_7$: atomic coordinates and anisotropic thermal displacement parameters, U_{ij} (pm^2)[a]

Atom	Wyckoff position	x/a	y/b	z/c
Cs	4*i*	0.06636(4)	0	0.69714(9)
Gd1	4*i*	0.16467(2)	0	0.39163(5)
Gd2	4*i*	0.21612(2)	0	0.13008(5)
Gd3	4*i*	0.41009(2)	0	0.86393(5)
N	4*i*	0.1386(4)	0	0.1964(9)
Te1	2*a*	0	0	0
Te2	4*i*	0.24075(3)	0	0.66158(8)
Te3	4*i*	0.33622(3)	0	0.05830(8)
Te4	4*i*	0.42506(3)	0	0.59543(8)

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Cs	307(5)	300(5)	313(5)	0	28(4)	0
Gd1	144(3)	150(3)	140(3)	0	19(2)	0
Gd2	112(3)	136(3)	170(3)	0	44(2)	0
Gd3	104(3)	141(3)	162(3)	0	23(2)	0
N	81(41)	163(51)	115(50)	0	−3(37)	0
Te1	167(6)	148(6)	374(8)	0	−104(6)	0
Te2	160(4)	153(4)	163(4)	0	13(3)	0
Te3	134(4)	154(4)	171(4)	0	38(3)	0
Te4	163(4)	164(4)	227(5)	0	81(3)	0

[a] Defined as temperature factor according to: $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{23}klb^*c^* + 2U_{13}hla^*c^* + 2U_{12}hka^*b^*)]$.

Table 3
$Cs_2Gd_6N_2Te_7$: selected internuclear distances, d (pm), and angles, ∡ (°)

Cs		Gd1		Gd2	
–Te3 (2×)	383.2	–N (1×)	217.0	–N (1×)	217.1
–Te4 (2×)	393.8	–Te4 (2×)	305.3	–Te3 (2×)	307.1
–Te4′ (2×)	400.6	–Te2 (1×)	319.2	–Te2 (2×)	317.3
–Te1 (1×)	414.0	–Te2′ (2×)	326.9	–Te3′ (1×)	318.2
–Te2 (1×)	430.5				
Gd3		**N**			
–N (2×)	244.1	–Gd1 (1×)	217.0	Gd1–N–Gd3 (2×)	107.0
–Te3 (1×)	315.5	–Gd2 (1×)	217.1	Gd2–N–Gd3 (2×)	107.2
–Te1 (2×)	316.1	–Gd3 (2×)	244.1	Gd1–N–Gd2 (1×)	107.3
–Te4 (1×)	317.3			Gd3–N–Gd3′ (2×)	120.6

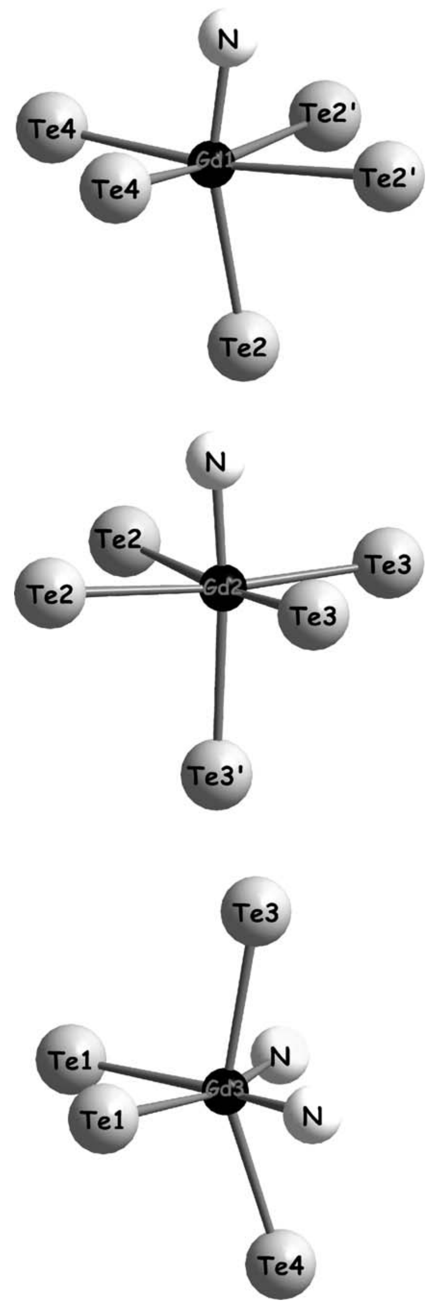

Fig. 1. Coordination polyhedra [(Gd1)NTe_5], [(Gd2)NTe_5], and [(Gd3)N_2Te_4] (top to bottom) in the crystal structure of $Cs_2Gd_6N_2Te_7$.