metal-organic compounds

Tetraaquatetraureaneodymium(III) triiodide

Ludmila Yu. Alikberova,[a] Dmitry V. Albov,[b]* Denis V. Golubev,[a] Valery V. Kravchenko[a] and Nataliya S. Rukk[a]

[a]Lomonosov State Academy of Fine Chemical Technology, Prosp. Vernadskogo 86, 117571, Moscow, Russian Federation, and [b]Department of Chemistry, Moscow State University, 119991, Moscow, Russian Federation
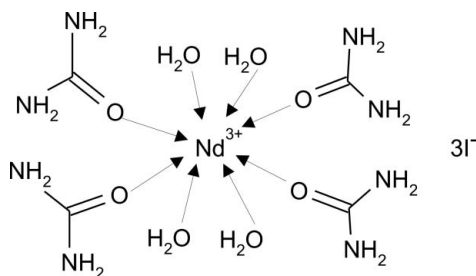
Correspondence e-mail: albov@struct.chem.msu.ru

In the ionic title complex, $[Nd\{CO(NH_2)_2\}_4(H_2O)_4]I_3$, the neodymium is located on a twofold rotation axis and is coordinated by four urea and four water molecules in a distorted square-antiprismatic geometry.

Related literature

For lanthanide complexes with urea, see: Dilebaeva & Sulajmankulov (1973); Dilebaeva *et al.* (1975); Aitimbetov *et al.* (1977); Rukk *et al.* (1984); Alikberova *et al.* (1990); Savinkina *et al.* (2005). For related literature, see: Huber *et al.* (1985); Sulejmanov *et al.* (1971).

Experimental

Crystal data

$[Nd(CH_4N_2O)_4(H_2O)_4]I_3$	a = 7.7633 (19) Å
M_r = 837.25	b = 10.597 (4) Å
Monoclinic, $P2/c$	c = 15.140 (4) Å
β = 108.136 (19)°	μ = 6.15 mm^{-1}
V = 1183.7 (6) Å^3	T = 293 (2) K
Z = 2	$0.20 \times 0.20 \times 0.20$ mm
Mo $K\alpha$ radiation	

Data collection

Enraf–Nonius CAD-4 diffractometer	3446 independent reflections
Absorption correction: ψ scan (North *et al.*, 1968)	2589 reflections with $I > 2\sigma(I)$
T_{min} = 0.293, T_{max} = 0.304	1 standard reflection frequency: 120 min intensity decay: 2%
3446 measured reflections	

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.035	126 parameters
$wR(F^2)$ = 0.070	H-atom parameters constrained
S = 1.00	$\Delta\rho_{max}$ = 0.73 e Å^{-3}
3446 reflections	$\Delta\rho_{min}$ = −0.55 e Å^{-3}

Data collection: *CAD-4 EXPRESS* (Enraf–Nonius, 1994); cell refinement: *CAD-4 EXPRESS*; data reduction: *XCAD4* (Harms & Wocadlo, 1995); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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supplementary materials

Tetraaquatetraureaneodymium(III) triiodide

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Comment

An increased attention to investigation of different salts interaction with carbamide $CO(NH_2)_2$ (*Ur*) is determined by the special features of the structure and properties of this ambidentate ligand which could be coordinated by the metal cation *via* both nitrogen atom of amino–group and oxygen atom of the carbonyl group. It should be noted that O–coordinated carbamide has a possibility to participate in the formation of the hydrogen bonding developed system as well as layered and channel structures of the clathrate–coordination nature, these systems being related to supramolecular ones (Sulejmanov *et al.*, 1971). The neodymium–containing complexes are of great importance for preparation of laser, fiber optic and luminescent and other materials with interesting properties.

It has been found out that interaction of the lanthanide salts with carbamide leads to a number of different complexes whose composition is to a great extent temperature dependent. For example, at 288 and 303 K lanthanide chlorides yield the anhydrous complexes of different composition such as $LnCl_3 \cdot 4Ur$, $LnCl_3 \cdot 6Ur$ (*Ln* = La, Ce, Pr, Nd, Sm, Gd, Dy, Ho, Er, *etc.*) as well as $ErCl_3 \cdot 2Ur \cdot 6H_2O$ and $TmCl_3 \cdot 2Ur \cdot 4H_2O$ (Dilebaeva & Sulajmankulov, 1973; Dilebaeva *et al.*, 1975). At the same temperature conditions lanthanide bromides give analogous compounds $LnBr_3 \cdot 4Ur$, $LnBr_3 \cdot 6Ur$ (*Ln* = La, Ce, Er, *etc.*), as well as $ErBr_3 \cdot Ur \cdot 6H_2O$ (Aitimbetov *et al.*, 1977).

Regarding lanthanide iodides, anhydrous complexes $LnI_3 \cdot 5Ur$ (*Ln* = La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu) have been prepared at 273 K (Rukk *et al.*, 1984; Alikberova *et al.*, 1990). The compound $SmI_3 \cdot 8Ur$ has been synthesized at room temperature (Savinkina *et al.*, 2005). The single-crystal *X*–ray diffraction studies confirmed the IR spectra investigation results with respect to coordination of the carbamide ligands *via* the O–atom of the carbonyl group.

The aim of the present work is to synthesize and to investigate the new neodymium iodide complex with carbamide at room temperature.

The $[Nd(Ur)_4(H_2O)_4]^{3+}$ complex cation is located on a twofold rotation axis and its geometry represents the distorted square antiprism with eight oxygen atoms (four from water molecules and four from the carbamide ones) located in the mentioned antiprism vertices. The complex cations form double layers, the NH_2 groups of coordinated carbamide molecules of neighboring layers being symmetrically disposed. Almost flat ordered layers built from the iodide–ions are located between the double layers of complex cations. The results of our investigation confirm the early proposed assumption about the layered structure of lanthanide iodide complexes with carbamide, but we were unable to investigate hydrogen bonding geometry because of poor refinement of H atoms in this structure containing such heavy atoms as Nd and I.

supplementary materials

Experimental

Nonahydrate of neodymium(III) iodide NdI$_3$·9H$_2$O was prepared by the reaction of neodymium(III) carbonate with hydroiodic acid preliminary freed from iodine excess (Huber *et al.*, 1985). The complex compound NdI$_3$·4*Ur*·4H$_2$O was synthesized by mixing NdI$_3$·9H$_2$O with CO(NH$_2$)$_2$ in molar ratio 1:5 without water addition. Interaction of crystalline reagents in the course of mixture grinding leads to the crystallization water liberation and formation of viscous transparent solution. Pale violet crystals are obtained after allowing the solution to stay for 2 weeks. The results of chemical analysis (titration with Na$_2$*edta* solution for neodymium content determination and gravimetric analysis *via* AgI formation for iodide–ion content determination) are as follows: Nd (wt.%) 17.23 (calcd.), 16.15 (found); I(wt.%) 45.48 (calcd.), 42.63 (found). The reduced content of Nd and I is possibly related with the compound hygroscopicity. *M*.p. 371 K.

Refinement

Amide H atoms were positioned geometrically and refined using a riding model with N—H = 0.86 Å, O—H = 0.85 Å and U_{iso}(H) = 1.2 times U_{eq} of the parent atom. The largest difference peak is located at 0.6172, 0.1779, 0.2360 with the distance 1.03 Å from Nd1.
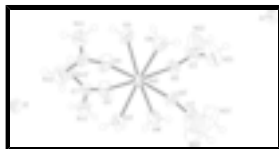
Figures

Fig. 1. *ORTEP*–3 (Farrugia, 1997) view of the title complex, with atom labels. Displacement ellipsoids are drawn at 50% probability. H atoms are presented as a spheres of arbitrary radius. Symmetry code: (i) $1 - x, y, -z + 1/2$.

Tetraaquatetraureaneodymium(III) triiodide

Crystal data

[Nd(C$_1$H$_4$N$_2$O$_1$)$_4$(H$_2$O$_1$)$_4$]I$_3$	F_{000} = 774
M_r = 837.25	D_x = 2.349 Mg m^{-3}
Monoclinic, *P2/c*	Melting point: 371 K
Hall symbol: -P 2yc	Mo *K*α radiation λ = 0.71073 Å
a = 7.7633 (19) Å	Cell parameters from 25 reflections
b = 10.597 (4) Å	θ = 14–15º
c = 15.140 (4) Å	μ = 6.15 mm^{-1}
β = 108.136 (19)º	*T* = 293 (2) K
V = 1183.7 (6) Å^3	Prism, violet
Z = 2	0.20 × 0.20 × 0.20 mm

Data collection

Enraf–Nonius CAD-4	R_{int} = 0.000

diffractometer

Radiation source: fine–focus sealed tube	$\theta_{max} = 30.0°$
Monochromator: graphite	$\theta_{min} = 1.9°$
$T = 293(2)$ K	$h = -10 \rightarrow 10$
non–profiled ω–scans	$k = -14 \rightarrow 0$
Absorption correction: ψ scan (North *et al.*, 1968)	$l = -21 \rightarrow 9$
$T_{min} = 0.293$, $T_{max} = 0.304$	1 standard reflections
3446 measured reflections	every 120 min
3446 independent reflections	intensity decay: 2%
2589 reflections with $I > 2\sigma(I)$	

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.035$	H-atom parameters constrained
$wR(F^2) = 0.070$	$w = 1/[\sigma^2(F_o{}^2) + (0.0298P)^2]$ where $P = (F_o{}^2 + 2F_c{}^2)/3$
$S = 1.00$	$(\Delta/\sigma)_{max} = 0.001$
3446 reflections	$\Delta\rho_{max} = 0.73$ e Å^{-3}
126 parameters	$\Delta\rho_{min} = -0.55$ e Å^{-3}
Primary atom site location: structure-invariant direct methods	Extinction correction: none

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of F$^2 > 2\sigma$(F^2) is used only for calculating R–factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. R–factors based on F^2 are statistically about twice as large as those based on F, and R–factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	y	z	$U_{iso}*/U_{eq}$
Nd1	0.5000	0.15416 (3)	0.2500	0.03067 (8)
I1	0.0000	0.53143 (5)	0.2500	0.05980 (15)
I2	0.82533 (5)	0.78527 (3)	0.49371 (3)	0.05522 (11)
O1	0.3857 (6)	0.3168 (4)	0.1427 (3)	0.0869 (14)
C1	0.3636 (7)	0.4170 (5)	0.0989 (4)	0.0535 (13)
N11	0.2203 (6)	0.4292 (5)	0.0241 (4)	0.0677 (13)
H11A	0.1446	0.3680	0.0067	0.081*

H11B	0.2030	0.4984	−0.0072	0.081*
N12	0.4807 (7)	0.5126 (5)	0.1217 (4)	0.0891 (19)
H12A	0.5769	0.5061	0.1688	0.107*
H12B	0.4600	0.5807	0.0892	0.107*
O2	0.4141 (5)	−0.0102 (3)	0.3359 (3)	0.0595 (10)
C2	0.3219 (7)	−0.1020 (6)	0.3391 (5)	0.0649 (16)
N21	0.2945 (10)	−0.1930 (6)	0.2739 (5)	0.121 (3)
H21A	0.3421	−0.1863	0.2299	0.145*
H21B	0.2293	−0.2578	0.2764	0.145*
N22	0.2716 (12)	−0.1279 (7)	0.4085 (6)	0.165 (4)
H22A	0.3023	−0.0796	0.4565	0.198*
H22B	0.2065	−0.1938	0.4078	0.198*
O3	0.2249 (5)	0.2324 (4)	0.2831 (3)	0.0635 (10)
H3A	0.179	0.303	0.262	0.076*
H3B	0.207	0.225	0.3356	0.076*
O4	0.2283 (5)	0.0663 (4)	0.1314 (3)	0.0709 (12)
H4A	0.131	0.107	0.105	0.085*
H4B	0.209	−0.008	0.109	0.085*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Nd1	0.03188 (14)	0.02026 (13)	0.03909 (17)	0.000	0.00991 (12)	0.000
I1	0.0509 (3)	0.0385 (2)	0.0817 (4)	0.000	0.0085 (2)	0.000
I2	0.0559 (2)	0.03773 (17)	0.0624 (2)	0.00232 (14)	0.00431 (16)	0.00285 (15)
O1	0.083 (3)	0.062 (3)	0.113 (4)	0.021 (2)	0.027 (3)	0.057 (3)
C1	0.052 (3)	0.042 (3)	0.068 (3)	0.010 (2)	0.020 (3)	0.023 (3)
N11	0.059 (3)	0.055 (3)	0.081 (3)	−0.005 (2)	0.009 (3)	0.020 (3)
N12	0.064 (3)	0.064 (3)	0.108 (4)	−0.012 (3)	−0.018 (3)	0.030 (3)
O2	0.0502 (19)	0.048 (2)	0.077 (3)	−0.0097 (16)	0.0149 (18)	0.0219 (19)
C2	0.056 (3)	0.049 (3)	0.087 (4)	−0.006 (3)	0.020 (3)	0.025 (3)
N21	0.152 (7)	0.087 (5)	0.120 (6)	−0.049 (5)	0.039 (5)	−0.008 (4)
N22	0.234 (10)	0.125 (7)	0.209 (10)	−0.068 (6)	0.175 (9)	−0.025 (6)
O3	0.063 (2)	0.053 (2)	0.086 (3)	0.0198 (19)	0.039 (2)	0.016 (2)
O4	0.056 (2)	0.053 (2)	0.079 (3)	0.0128 (18)	−0.0164 (19)	−0.027 (2)

Geometric parameters (Å, °)

Nd1—O1[i]	2.345 (4)	N12—H12A	0.8600
Nd1—O1	2.345 (4)	N12—H12B	0.8600
Nd1—O2	2.389 (3)	O2—C2	1.218 (6)
Nd1—O2[i]	2.389 (3)	C2—N22	1.259 (9)
Nd1—O3[i]	2.484 (3)	C2—N21	1.348 (9)
Nd1—O3	2.484 (3)	N21—H21A	0.8600
Nd1—O4	2.487 (3)	N21—H21B	0.8600
Nd1—O4[i]	2.487 (3)	N22—H22A	0.8600
O1—C1	1.235 (6)	N22—H22B	0.8600
C1—N11	1.324 (7)	O3—H3A	0.8500

C1—N12	1.333 (7)	O3—H3B	0.8500
N11—H11A	0.8600	O4—H4A	0.8500
N11—H11B	0.8600	O4—H4B	0.8500
O1^i—Nd1—O1	85.4 (3)	N11—C1—N12	118.1 (5)
O1^i—Nd1—O2	105.55 (16)	C1—N11—H11A	120.0
O1—Nd1—O2	143.45 (14)	C1—N11—H11B	120.0
O1—Nd1—O2^i	105.55 (16)	H11A—N11—H11B	120.0
O2—Nd1—O2^i	86.4 (2)	C1—N12—H12A	120.0
O1—Nd1—O3^i	77.19 (16)	C1—N12—H12B	120.0
O2—Nd1—O3^i	139.17 (13)	H12A—N12—H12B	120.0
O1—Nd1—O3	74.39 (15)	C2—O2—Nd1	150.6 (4)
O2—Nd1—O3	74.34 (13)	O2—C2—N22	123.1 (8)
O2^i—Nd1—O3	139.17 (13)	O2—C2—N21	120.2 (6)
O3^i—Nd1—O3	140.99 (19)	N22—C2—N21	115.8 (7)
O1^i—Nd1—O4	145.93 (14)	C2—N21—H21A	120.0
O1—Nd1—O4	73.87 (16)	C2—N21—H21B	120.0
O2—Nd1—O4	78.60 (15)	H21A—N21—H21B	120.0
O2^i—Nd1—O4	69.62 (12)	C2—N22—H22A	120.0
O3^i—Nd1—O4	124.67 (16)	C2—N22—H22B	120.0
O3—Nd1—O4	71.41 (15)	H22A—N22—H22B	120.0
O1—Nd1—O4^i	145.93 (14)	Nd1—O3—H3A	121
O2—Nd1—O4^i	69.62 (12)	Nd1—O3—H3B	124
O3—Nd1—O4^i	124.67 (16)	H3A—O3—H3B	105.1
O4—Nd1—O4^i	136.01 (18)	Nd1—O4—H4A	125
C1—O1—Nd1	164.4 (4)	Nd1—O4—H4B	130
O1—C1—N11	118.9 (5)	H4A—O4—H4B	105.2
O1—C1—N12	123.0 (5)		

Symmetry codes: (i) $-x+1$, y, $-z+1/2$.

Fig. 1