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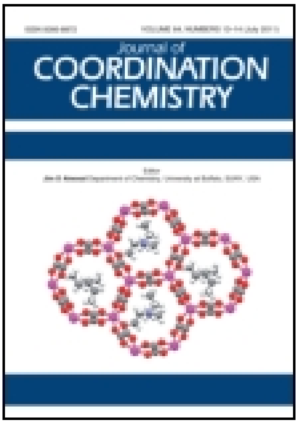

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gcoo20

# Ionic acetamide coordination in its complexes with rare-earth iodides

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Published online: 04 Nov 2011.

To cite this article: Elena V. Savinkina , Denis V. Golubev & Mikhail S. Grigoriev (2011) Ionic acetamide coordination in its complexes with rare-earth iodides, Journal of Coordination Chemistry, 64:21, 3758-3766, DOI: 10.1080/00958972.2011.631214

To link to this article: http://dx.doi.org/10.1080/00958972.2011.631214

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*Journal of Coordination Chemistry*
Vol. 64, No. 21, 10 November 2011, 3758–3766

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# Ionic acetamide coordination in its complexes with rare-earth iodides

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(*Received 28 June 2011; in final form 28 September 2011*)

A series of $[Ln(CH_3CONH_2)_4(H_2O)_4]I_3$ (Ln = rare-earth metal) complexes was completed with seven new compounds (Ln = Ce, Pr, Sm, Tb, Tm, Yb, Lu); two (Ln = Ce, Tm) were studied by X-ray diffraction. The coordination polyhedron of eight oxygen atoms is a distorted square antiprism. No tetrad effect was found for Ln–O bond lengths. The structure is stabilized by a system of intermolecular hydrogen bonds. The most striking feature of the structures is the recently predicted ionic acetamide coordination. The acetamide molecules are non-planar (the Ln–O–C–N torsion angles are 159–170°) and Ln–O–C bond angles vary in the 146.0–156.8° range.

*Keywords*: Acetamide; Rare-earth metals; Complexes; Iodides; Ionic type of coordination

## 1. Introduction

Amides comprise a major functional group in organic chemistry and form key linkages in natural and synthetic macromolecules, so their coordination properties towards metal cations are of interest [1–3]. However, coordination chemistry of one of the simplest amides, acetamide, is poorly studied. A number of acetamide complexes with s-, p-, and d-elements were prepared; structurally characterized complexes usually contain acetamide in a neutral form coordinating through oxygen [1–3]. A few complexes containing acetamido anion coordinating through nitrogen [4–7] and one complex containing protonated acetamide cation in the outer sphere [8] are reported.

The interaction of rare-earth compounds with acetamide has been less studied [3]. $Ce(CH_3COO)_3 \cdot 3CH_3CONH_2 \cdot H_2O$ [9], $LaCl_3 \cdot 5CH_3CONH_2 \cdot 5H_2O$ [10], $YCl_3 \cdot 4CH_3CONH_2 \cdot 5H_2O$ [11] and a similar complex for $ScCl_3$ [12] are reported, but only characterized by chemical analysis and IR spectra. Recently, $[Ln(CH_3CONH_2)_4(H_2O)_4]I_3$ (Ln = La, Gd, Er [13] and Nd, Eu, Dy, Ho, Y [14]) complexes were synthesized and structurally characterized.

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ISSN 0095-8972 print/ISSN 1029-0389 online © 2011 Taylor & Francis
http://dx.doi.org/10.1080/00958972.2011.631214

In this work, we report the synthesis of the complexes of other rare-earth iodides with acetamide and X-ray diffraction analysis of two representative examples, $[Ce(CH_3CONH_2)_4(H_2O)_4]I_3$ (**1**) and $[Tm(CH_3CONH_2)_4(H_2O)_4]I_3$ (**2**), and detailed analysis of the $[Ln(AA)_4(H_2O)_4]I_3$ complexes for all the rare-earth row.

## 2. Experimental

### 2.1. *Materials and measurements*

Hydroiodic acid was purified from iodine by distillation with $HPH_2O_2$. Cerium and thulium iodides were synthesized by the treatment of corresponding carbonates with hydroiodic acid (20% excess); the resulting solutions were concentrated at 110°C and cooled. Crystals of hydrated iodides were removed with a glass filter and dried over KOH. All other reagents were purchased from commercial sources and used without additional purification. IR spectra (in Nujol) were recorded with a Fourier IR spectrometer FT-02 (Infralum) from 500 to 4000 $cm^{-1}$. Lanthanide content was determined by titration with EDTA at pH 5.2–5.5 (acetate buffer, xylenol orange). Iodide content was determined by weighing as AgI.

### 2.2. *Synthesis of tetra(aqua)tetra(acetamide)cerium(III) iodide $[Ce(CH_3CONH_2)_4(H_2O)_4]I_3$ (1)*

Cerium iodide nanohydrate (8.33 g, 12.2 mmol) was acidified with several drops of hydroiodic acid and mixed with acetamide (3.60 g, 60.9 mmol) producing a transparent viscous solution, which was stored in air. In 10 days, colorless crystals of **1** (6.57 g, 65%) was formed. m.p. 99–100°C. IR (Nujol): 1046 ($\nu_s$ CN), 1131 ($\rho$ $NH_2$), 1312 ($\nu$ CN), 1560 ($\delta$ $NH_2 + \nu$ CO), 1648 ($\delta$ $NH_2$), 1650 ($\nu$ CO $+ \delta$ $NH_2 + \delta$ HOH), 3185, 3332 ($\nu$ OH $+ \nu$ NH). Anal. Calcd for $C_8H_{28}CeI_3N_4O_8$ (%): I, 45.92. Found (%): I, 45.73.

### 2.3. *Synthesis of tetra(aqua)tetra(acetamide)thulium(III) iodide $[Tm(CH_3CONH_2)_4(H_2O)_4]I_3$ (2)*

Thulium iodide octahydrate (5.23 g, 7.54 mmol) was acidified with several drops of hydroiodic acid and mixed with acetamide (2.17 g, 36.7 mmol) producing a transparent viscous solution, which was stored in air. In 10 days, yellowish-green crystals of **2** (5.56 g, 86%) was formed. m.p. 105–107°C. IR (Nujol): 1019 ($\nu_s$ CN), 1149 ($\rho$ $NH_2$), 1377 ($\nu$ CN), 1594 ($\delta$ $NH_2 + \nu$ CO), 1646 ($\delta$ $NH_2$), 1650 ($\nu$ CO $+ \delta$ $NH_2 + \delta$ HOH), 3173 ($\nu$ OH $+ \nu$ NH). Anal. Calcd for $C_8H_{28}I_3N_4O_8Tm$ (%): Tm, 19.69; I, 44.37. Found (%): Tm, 18.94; I, 43.88.

Other complexes $[Ln(CH_3CONH_2)_4(H_2O)_4]I_3$ (Ln = Pr, Sm, Tb, Yb, Lu) were prepared by similar technique.

**$[Pr(CH_3CONH_2)_4(H_2O)_4]I_3$:** m.p. 114–115°C. IR (Nujol): 1051 ($\nu_s$ CN), 1106 ($\rho$ $NH_2$), 1372 ($\nu$ CN), 1540 ($\delta$ $NH_2 + \nu$ CO), 1645 ($\delta$ $NH_2$), 1660 ($\nu$ CO $+ \delta$ $NH_2 + \delta$ HOH), 3168 ($\nu$ OH $+ \nu$ NH). Anal. Calcd for $C_8H_{28}I_3N_4O_8Pr$ (%): Pr, 16.78; I, 45.98. Found (%): Pr, 16.22; I, 44.71.

**$[Sm(CH_3CONH_2)_4(H_2O)_4]I_3$:** m.p. 106–108°C. IR (Nujol): 1043 ($\nu_s$ CN), 1106 ($\rho$ $NH_2$), 1379 ($\nu$ CN), 1554 ($\delta$ $NH_2 + \nu$ CO), 1642 ($\delta$ $NH_2$), 1659 ($\nu$ CO $+ \delta$ $NH_2 + \delta$ HOH), 3176 ($\nu$ OH $+ \nu$ NH). Anal. Calcd for $C_8H_{28}I_3N_4O_8Sm$ (%): Sm, 17.92; I, 45.36. Found (%): Sm, 17.52; I, 45.08.

**$[Tb(CH_3CONH_2)_4(H_2O)_4]I_3$:** m.p. 110–111°C. IR (Nujol): 1036 ($\nu_s$ CN), 1106 ($\rho$ $NH_2$), 1372 ($\nu$ CN), 1578 ($\delta$ $NH_2 + \nu$ CO), 1636 ($\delta$ $NH_2$), 1653 ($\nu$ CO $+ \delta$ $NH_2 + \delta$ HOH), 3162, 3323 ($\nu$ OH $+ \nu$ NH). Anal. Calcd for $C_8H_{28}I_3N_4O_8Tb$ (%): Tb, 18.74; I, 44.90. Found (%): Tb, 17.97; I, 44.23.

**$[Yb(CH_3CONH_2)_4(H_2O)_4]I_3$:** m.p. 106–107°C. IR (Nujol): 1015 ($\nu_s$ CN), 1148 ($\rho$ $NH_2$), 1372 ($\nu$ CN), 1554 ($\delta$ $NH_2 + \nu$ CO), 1645 ($\delta$ $NH_2$), 1651 ($\nu$ CO $+ \delta$ $NH_2 + \delta$ HOH), 3317 ($\nu$ OH $+ \nu$ NH). Anal. Calcd for $C_8H_{28}I_3N_4O_8Yb$ (%): Yb, 20.07; I, 44.16. Found (%): Yb, 18.77; I, 41.88.

**$[Lu(CH_3CONH_2)_4(H_2O)_4]I_3$:** m.p. 84–85°C. IR (Nujol): 1078 ($\nu_s$ CN), 1148 ($\rho$ $NH_2$), 1373 ($\nu$ CN), 1554 ($\delta$ $NH_2 + \nu$ CO), 1646 ($\delta$ $NH_2$), 1649 ($\nu$ CO $+ \delta$ $NH_2 + \delta$ HOH), 3175, 3320 ($\nu$ OH $+ \nu$ NH). Anal. Calcd for $C_8H_{28}I_3N_4O_8Lu$ (%): Lu, 20.25; I, 44.06. Found (%): Lu, 20.23; I, 43.27.

In all $[Ln(CH_3CONH_2)_4(H_2O)_4]I_3$ complexes, the Ln : I ratio is 1 : 2.94–3.05. The complexes are hydroscopic and decompose upon dissolution. Therefore, the results of analysis in some cases are understated and the complexes can be studied only in solid state.

### 2.4. *X-ray data collection and structure determination*

X-ray diffraction experiments were carried out on a Bruker KAPPA APEX II autodiffractometer (Mo-Kα radiation, graphite monochromator) at 100 K [15]. Data reduction was made using SAINT-Plus [16]. Absorption correction was made using SADABS [17]. The structures were solved by direct methods (SHELXS-97) and refined on $F^2$ with full-matrix least-squares (SHELXL-97) [18] using all reflections. All non-hydrogen atoms, except a disordered nitrogen with lower occupation factor in the structure of Ce compound, were refined with anisotropic displacement factors.

Hydrogen atoms of the coordinated water molecule were located from difference Fourier maps and refined with O–H distances restrained to 0.85(2) Å and H $\cdots$ H distances to 1.35(2) Å. Their isotropic displacement factors were 1.5 times $U_{eq}$ of adjacent oxygen atoms. Hydrogen atoms of $NH_2$ and $CH_3$ (except disordered acetamide molecules, L1) were placed in geometrically calculated positions with isotropic displacement factors 1.2 and 1.5 times $U_{eq}$ of adjacent N and O, respectively. The crystallographic data and structure refinement parameters for **1** and **2** are given in table 1.

Other complexes were characterized by X-ray diffraction (XRD) patterns, which were collected on a DRON-3 (diffracted-beam flat graphite monochromator) powder diffractometer (Cu-Kα). The patterns were indexed using the FullProf Suite ToolBar software package. Calculated unit cell parameters are listed in table 2.

In complex **2** the *a* and *c* parameters interchange. In the earlier reported $[Ln(CH_3CONH_2)_4(H_2O)_4]I_3$ structures [13, 14], unit cell parameters changed non-monotonically, however interatomic distances varied gradually.

Table 1. Crystal data and structure refinement for $[Ce(CH_3CONH_2)_4(H_2O)_4]I_3$ (**1**) and $[Tm(CH_3CONH_2)_4(H_2O)_4]I_3$ (**2**).

| Compound | **1** | **2** |
|---|---|---|
| Empirical formula | $C_8H_{28}CeI_3N_4O_8$ | $C_8H_{28}I_3N_4O_8Tm$ |
| Formula weight | 829.16 | 871.98 |
| Crystal system | Monoclinic | Monoclinic |
| Space group | *P2/c* | *P2/c* |
| Unit cell dimensions (Å, °) | | |
| *a* | 16.2317(4) | 15.4734(5) |
| *b* | 10.7711(3) | 10.4810(3) |
| *c* | 15.5950(4) | 16.0604(5) |
| $\beta$ | 113.754(1) | 113.486(1) |
| Volume (Å$^3$), *Z* | 2495.54(11), 4 | 2388.85(13), 4 |
| Calculated density (Mg m$^{-3}$) | 2.207 | 2.425 |
| Absorption coefficient (mm$^{-1}$) | 5.568 | 7.628 |
| *F*(000) | 1540 | 1612 |
| Crystal size (mm$^3$) | 0.30 × 0.28 × 0.20 | 0.24 × 0.20 × 0.20 |
| $\Theta_{max}$ (°) | 39.99 | 39.99 |
| Reflections collected | 105,016 | 90,472 |
| Independent reflections | 15,415 | 14,420 |
| Reflections with $I \geq 2\sigma(I)$ | 13,986 | 12,454 |
| Number of parameters | 251 | 261 |
| Goodness-of-fit | 1.113 | 1.055 |
| Final *R* indices $[I > 2\sigma(I)]$ | $R_1 = 0.0189$, $wR_2 = 0.0420$ | $R_1 = 0.0207$, $wR_2 = 0.0439$ |
| Largest difference peak and hole (e Å$^{-3}$) | 1.729 and −1.858 | 1.467 and −1.204 |

Table 2. Unit cell parameters for $[Ln(AA)_4(H_2O)_4]I_3$, Ln – Pr, Sm, Tb, Yb, Lu.

| Ln | *a* (Å) | *b* (Å) | *c* (Å) | $\beta$ (°) |
|---|---|---|---|---|
| Pr | 16.1871(0074) | 10.0092(0085) | 15.4622(0076) | 113.197(007) |
| Sm | 16.7747(0075) | 9.2771(0087) | 15.4734(0074) | 112,003(007) |
| Tb | 16.3164(0095) | 9.2506(0064) | 15.4636(0075) | 112.090(013) |
| Yb | 16.0963(0079) | 9.7904(0072) | 15.3091(0057) | 115.555(008) |
| Lu | 15.3763(0087) | 10.3670(0067) | 14.9474(0076) | 114.967(005) |

## 3. Results and discussion

The remaining complexes, $[Ln(CH_3CONH_2)_4(H_2O)_4]I_3$ (Ln – rare-earth metal excluding Pm), were synthesized for Ln = Ce, Pr, Sm, Tb, Tm, Yb, Lu. All the complexes are similar to those synthesized earlier [13, 14]. Structures **1** and **2** are studied by X-ray diffraction. Structural data for $[Ln(CH_3CONH_2)_4(H_2O)_4]I_3$ complexes allow their detailed discussion using structures **1** and **2** as examples.

In structures **1** and **2** (figure 1), as well as in other $[Ln(CH_3CONH_2)_4(H_2O)_4]I_3$, metal is coordinated by four acetamide and four water molecules; iodide ions form the outer sphere. In both structures, one acetamide is disordered with 0.736(4) : 0.264(4) and 0.540(5) : 0.460(5) ratios of the $CNH_2$ disordered components, respectively.

Acetamide coordination through oxygen is supported by IR spectra; bands containing C=O stretching vibration are shifted from ~1605 (amide I) and ~1675 (amide II) cm$^{-1}$ in the spectrum of free acetamide to lower frequencies in spectra of the complexes.

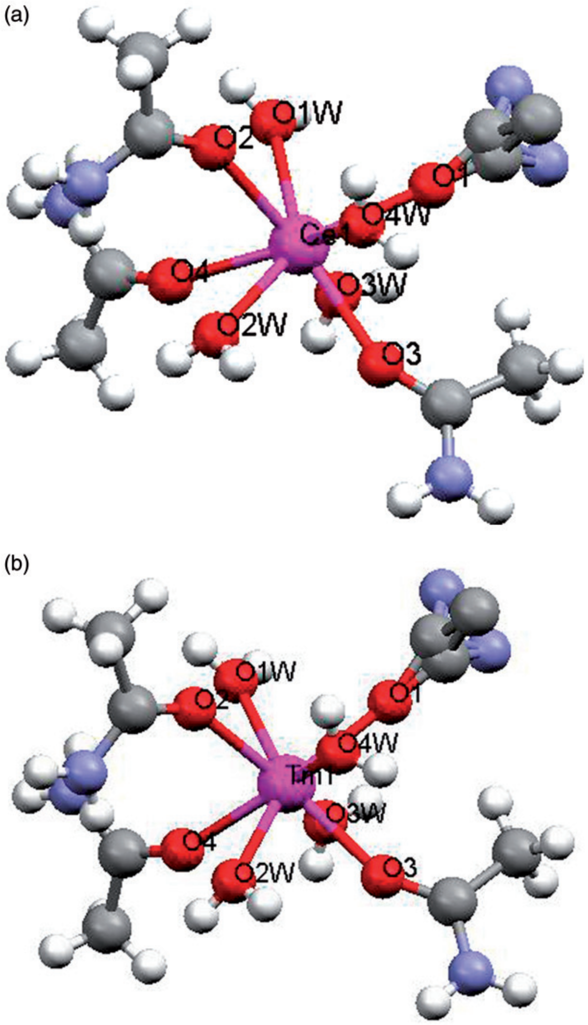

Figure 1. Cationic parts of **1** (a) and **2** (b).

The Ln–O bonds differ slightly for the two types of ligands; Ln–O(w) are ~2.520 Å and ~2.329 Å, Ln–O(L) are ~2.418 Å and ~2.302 Å for Ln = Ce, Tm, respectively (w = $H_2O$, L = $CH_3CONH_2$). Therefore, water is more weakly bonded than acetamide. Structural data for **1** and **2** along with earlier reported $[Ln(CH_3CONH_2)_4(H_2O)_4]I_3$ [13, 14] allow discussion of the dependence of the Ln–O bond lengths on lanthanide atomic number. It is almost linear (figure 2), excluding Gd (Z = 64). For gadolinium, deviations from uniform changes of some properties are often reported; however, we can see no pronounced tetrad effect [19–21], similarly for unit cell parameters (figure 3).

To determine the shape of the coordination polyhedron, we used published criterion [22], based on measuring a set of dihedral angles $\delta$ between pairs of faces intersecting with edges of the b type. Vertexes of A and B types must share four and five edges, respectively; therefore, the b edges combine the B vertexes. The $\delta$ criterion allows

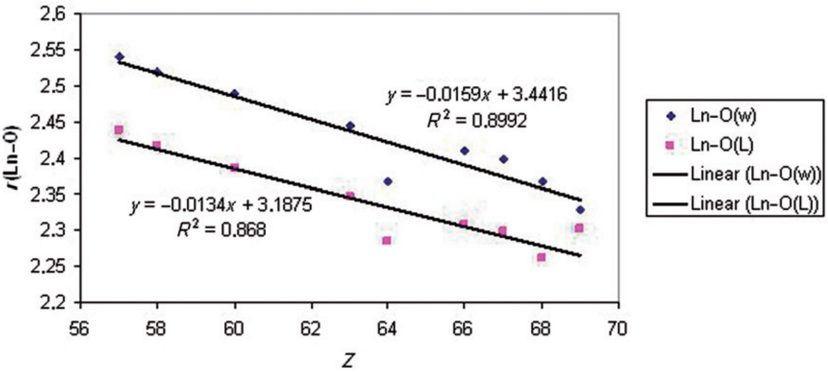

Figure 2. The Ln–O bond lengths (Å) *vs.* atomic numbers for $H_2O$ (w) and acetamide (L) in $[Ln(CH_3CONH_2)_4(H_2O)_4]I_3$.

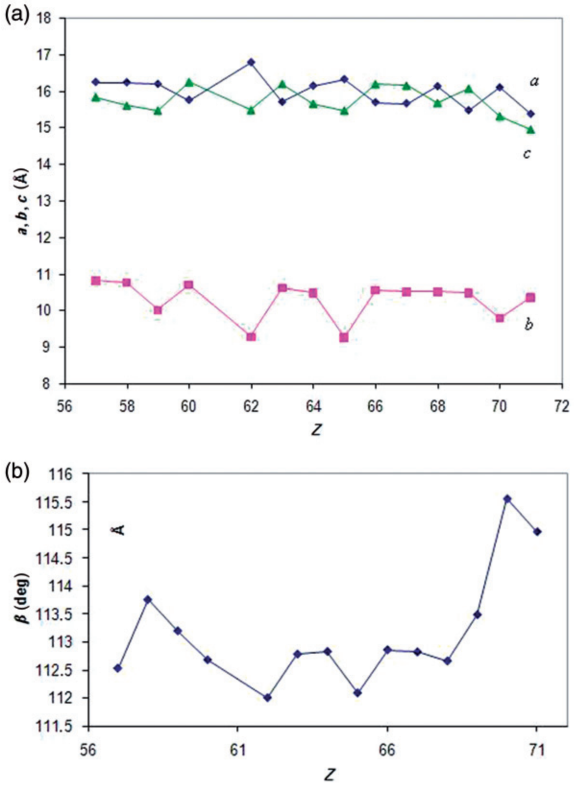

Figure 3. The unit cell parameters *a*, *b*, *c* (a) and $\beta$ (b) *vs.* atomic numbers in $[Ln(CH_3CONH_2)_4(H_2O)_4]I_3$.

distinguishing dodecahedron, square antiprism and two-capped trigonal prism; for an ideal square antiprism, $\delta_1 = \delta_2 = 0$, $\delta_3 = \delta_4 = 52.5°$. In structures **1** and **2**, $\delta_1 = 3.81°$ and $7.15°$, $\delta_2 = 3.67°$ and $7.40°$, $\delta_3 = 46.48°$ and $48.65°$, $\delta_4 = 40.18°$ and $38.20°$, respectively. Therefore, the coordination polyhedra in **1** and **2** are a distorted square antiprism;

the distortion is less for the thulium complex. Distortions are caused by variations in bond lengths. As a result, the symmetries of polyhedra are $C_2$ in structures **1** and **2**, whereas it should be $D_{4d}$ for an ideal square antiprism or $D_{2d}$ for a distorted square antiprism [19, 22, 23].

Two water molecules and two acetamides occupy opposite vertices of the square bases. The ratio of bond lengths for two different types of ligands in a square antiprism is 1.0 (1.2 in a dodecahedron) [9]. The Ln–O(w) : Ln–O(L) ratios are 1.04 and 1.01 for **1** and **2**, respectively, supporting distorted square antiprism as the coordination polyhedra in **1** and **2**.

The coordination polyhedron possesses two symmetry operations, *E* (identical transformation) and $C_2$. The point group for complex cation and formula moiety differs from that for the coordination polyhedron. It has no symmetry elements besides identity (point group $C_1$). Low symmetry is caused by the presence of acetamide (and iodide ions). Increase in the number of formula moieties leads to higher symmetry. The point group for the unit cell (containing 4 complex cations and 12 iodides) is $C_i$.

The most interesting feature in the $[Ln(CH_3CONH_2)_4(H_2O)_4]I_3$ structures is the coordination mode of acetamide. Despite the limited amount of structural information that exists for metal acetamide compounds [2, 24–28], some general observations can be made from its analysis and compared to those for **1** and **2**.

The ranges of observed M–O–C angles for divalent transition metals (14 compounds), such as Co(II), Ni(II), Zn(II), Cd(II), Re(II), and uranyl compounds (4 instances) are 125–140° and 139–151°, respectively [2, 24–28]. The same angles in $[Ln(CH_3CONH_2)_4(H_2O)_4]I_3$ structures are noticeably larger. The smallest Ln–O–C angles in structures **1** and **2** are 149.3° and 146.0°, respectively, for one of the acetamides, L2. For two more acetamide ligands, L3 and L4, they are 153.4° and 156.8° in **1** and 153.9° and 152.6° in **2**. Since the fourth acetamide, L1, is disordered in both structures, it is impossible to estimate the corresponding Ln–O–C angle. However, no disorder was found for this molecule in some other $[Ln(CH_3CONH_2)_4(H_2O)_4]I_3$ structures [13, 14]; therefore, we can analyze all the Ln–O–C angles in these complexes. In one complex, $[Gd(CH_3CONH_2)_4(H_2O)_4]I_3$, all the Ln–O–C angles involving acetamide ligands are close to 158°. In other complexes, three Ln–O–C angles vary in the 151–157° range and one angle is 162–169°.

The co-planarity of the metal with respect to the amide depends markedly on the metal type; while all examples involving divalent transition metal are planar, none of the uranyl examples are [2, 24–27]. In **1** and **2**, the M–O–C–N fragment for only one acetamide ligand, L3, is planar. For two other ligands, L2 and L3, the metal is out of the amide plane by ~0.35 and ~0.62 Å, respectively; the fourth acetamide, L1, is disordered. Other $[Ln(CH_3CONH_2)_4(H_2O)_4]I_3$ structures [13, 14] also contain non-planar M–O–C–N fragments.

The geometric features of the coordinated amide oxygen are shown in figure 4 [29]. In the idealized covalent case, optimal overlap between a metal centered orbital with a $sp^2$ oxygen orbital occurs at an M–O–C angle near 120°, the metal ion lying in the plane of the amide. A set of empirical relationships was derived to assign MM3 force field parameters as a function of the metal ion size, charge, and electronegativity; the ideal M–O–C angles for Ni(II) and U(IV) are 126° and 146°, respectively [29, 30]. In the idealized ionic case, the optimal interaction occurs when the metal aligns with the dipole moment of the ligand, an angle of 154° at an M–O distance of 2.5 Å. The values

Figure 4. The optimal orientation for the amide oxygen donor. Predicted M–O–C angles based on ideal geometries for a pure covalent interaction (left) and a pure ionic interaction (right). Arrow depicts the orientation of the acetamide dipole moment [29].

of M–O=C angles were calculated on the basis of the ionic character of the M–O bond derived from differences in electronegativity of oxygen and the metal [30].

The parameters of the $[Ln(CH_3CONH_2)_4(H_2O)_4]I_3$ structures are close to ionic acetamide coordination. This can be explained by appropriate difference in electronegativity of oxygen and lanthanides, good fit of the Ln–O distance to the required value of 2.5 Å for ionic coordination and the large number of acetamide ligands per central atom preventing rigid geometry of covalently bonded acetamide molecules. We conclude that the pure ionic interaction for acetamide is first found in the $[Ln(CH_3CONH_2)_4(H_2O)_4]I_3$ structures.

Both water and acetamide in **1** and **2** are involved in hydrogen bonds O–H $\cdots$ I and N–H $\cdots$ I, respectively; the O $\cdots$ I and N $\cdots$ I distances vary in the 3.40–3.67 and 3.67–3.91 Å ranges. Intramolecular hydrogen bonds are absent.

The unit cells in **1** and **2** contain four independent (two are in special positions) iodides differing by involvement in H-bonding. Every iodide unites four adjacent cations forming hydrogen bonds through water and/or acetamide ligands, excluding I2 in complex **2** combining only three cations.

## 4. Conclusion

We were able to synthesize the remaining complexes of the $[Ln(CH_3CONH_2)_4(H_2O)_4]I_3$ row (Ln – rare-earth metal excluding Pm) and two (Ln = Ce, Tm) were characterized by X-ray diffraction. The pure ionic interaction for acetamide is first found in the $[Ln(CH_3CONH_2)_4(H_2O)_4]I_3$ structures.

## Supplementary material

CCDC-823163 and 823164 contain the supplementary crystallographic data for this article. These data can be obtained free of charge at www.ccdc. cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre (CCDC), 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44(0)1223-336033; E-mail: deposit@ccdc.cam.ac.uk].

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