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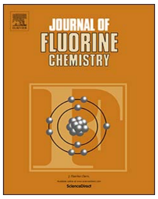

Novel mononuclear mixed ligand complexes of heavy lanthanide trifluoroacetates with diethylenetriamine

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ABSTRACT

Seven mixed ligand complexes of lanthanide trifluoroacetates with diethylenetriamine $[Ln(tfa)_2(deta)_2](tfa)$ (Ln = Y, Dy − Lu; Htfa — trifluoroacetic acid, deta — diethylenetriamine) with mononuclear structure were synthesized and characterized by powder X-ray diffraction, IR and NMR spectroscopy, TGA, conventional elemental analysis; crystal structure of $[Y(tfa)_2(deta)_2](tfa)$ was determined by single crystal X-ray diffraction. The structure of the new type consists of mononuclear complex cations $[Y(tfa)_2(deta)_2]^+$ and outer-sphere tfa^- anions connected into dimeric associates by intra-dimeric H-bonds. The complexes in crystalline state demonstrate high stability to storage in air and also retain tfa^- anions within the coordination sphere in solution according to the results of NMR spectroscopy. Stability of $[Ln(tfa)_2(deta)_2](tfa)$ species was explained by DFT calculations. This allows their application as precursors of rare earth fluorides illustrated by synthesis of $NaYF_4$ powder and thin films.

1. Introduction

At present, many functional materials are produced from metal-organic precursors based on coordination compounds. Rare earth carboxylates are widely used for synthesis of rare earth oxide and fluoride functional materials in form of films and nanoparticles. These materials find application in electronics, optics, nanotechnology, superconductivity, etc. [1–3].

One of the most promising methods of obtaining rare earth oxide and fluoride thin films is Metal Organic Chemical Solution Deposition (MOCSD) [4,5] in which the solutions of rare earth carboxylates are used as precursors. The main advantage of the MOCSD method over physical vapor deposition is easy and cost effective approach to synthesis of desired compounds. The deposited precursors are pyrolyzed at low temperatures (typically 300–600 °C), leading to the removal of the organic parts. This results in formation of amorphous or nanocrystalline films which are of use for different applications, e. g. as a planarizing layer for further deposition of high temperature superconducting thin films. It was recently shown by our research group that the use of monoethanolamine and diethylenetriamine allows to obtain smooth amorphous rare earth oxide [6,7] and alumina thin films [8].

At last decade the upconverting lanthanide-doped materials in form of nanocrystals or thin films are under high interest [3]. Among various matrices for luminescent rare earth ions the cubic (α) and hexagonal (β) $NaYF_4$ phases have been widely studied and hexagonal β-$NaYF_4$ has been found to be the most efficient host [9].

Preparation of $NaYF_4$ films by MOCSD technique requires highly soluble metal-organic compounds stable to storage in solution. This depends on the structure and composition of compounds. The rare earth elements with their high coordination numbers (CN) usually form poorly soluble polymeric compounds. Several classes of fluorinated rare earth compounds, alkoxydes, beta-diketonates and carboxylates, are used as precursors for chemical synthesis of LnF_3 and $NaLnF_4$ nanomaterial [10–13]. Among them the rare-earth trifluoroactetates and their derivatives are most widely studied. It was shown [14] that $Ln(tfa)_3{\cdot}3H_2O$ (Ln = La, Ce; Htfa—trifluoroacetic acid) crystallize as two-dimensional polymers with bridging and chelato-bridging carboxylate ligands. Other $Ln(tfa)_3{\cdot}3H_2O$ are binuclear with only bridging carboxylate ligands. In both structural types, the metal atoms are eight-coordinated.

Rather low solubility of polymeric rare earth carboxylates can be overcome by use of their solutions in highly polar carboxylic acids [15]. Another way is the preparation of precursor solutions in indifferent solvents, most often in alcohols, with addition of ancillary ligands, such as polyglymes and polyamines,—diglyme, monoethanolamine, diethanolamine, etc.—to increase the solubility of the carboxylates by formation of mixed-ligand complexes with lower nuclearity, as the donor ligand saturates the metal ion coordination sphere. Recently, the application of this approach was demonstrated by the example of binuclear $[Ln_2(tfa)_6(diglyme)_2]$ complexes (Ln = Gd, Tm, Yb) and by bi-

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and polynuclear cerium (III) trifluoroacetate complexes with neutral O-donor ligands (THF, Me_2SO, diglyme) which were proven to be precursors for monodisperse LnF_3 nanoparticles [16,17]. Several polymeric single-source precursors for $NaLnF_4$ nanocrystals $[NaLn(TFA)_4(diglyme)]_\infty$ [18,19], $[NaY(TFA)_4(diglyme)]_\infty$, $[[Na(triglyme)_2][Y_2(TFA)_7(THF)_2]]_\infty$ and $[Na_2Y(TFA)_5(tetraglyme)]_\infty$ [20] were also reported.

The reason why composition and structure of trifluoroacetate mixed-ligand complexes are not described systematically is hydrolysis in presence of water traces in precursor solutions, which results in polynuclear hydroxocompounds formation and obstructs isolation of anhydrous complexes in crystalline form [21].

Among the previously described trifluoroacetate mixed ligand complexes with amines are compounds with 2,2′-bipyridine, TMEDA, ethylenediamine as ancillary aminoligands [22,23]. Generally, bi- and polynuclear complexes are most frequently observed. Examples of mononuclear lanthanide (III) carboxylates, which do not contain bridging carboxylate ligands, are extremely rare in occurrence [24–26]. Moreover, such monomers for trifluoroacetate complexes have never been described to the best of our knowledge.

In this paper we report the study of mixed-ligand heavy rare earth trifluoroacetates with diethylenetriamine (deta) of general formula $[Ln(tfa)_2(deta)_2](tfa)$ (Ln = Y, Dy-Lu; **1**–**7** respectively). The complexes were characterized by a variety of methods, including conventional elemental analysis, NMR, FT-IR spectroscopy and TG-DTA analysis. $[Y(tfa)_2(deta)_2](tfa)$ (**1**) was also characterized by single crystal X-ray diffraction. Effectiveness of the new trifluoroacetate complexes as fluoride precursors was demonstrated by the example of $NaYF_4$ powder and thin film syntheses from the solution of **1** and [Na(tfa)(Htfa)] (**8**) as precursors.

2. Experimental

2.1. Synthesis

Rare earth carbonates (Reakhim, Russia), trifluoroacetic acid (Htfa, P & M Invest, Russia) and diethylenetriamine (deta, Aldrich), all analytical grade, were used as received. Acetonitrile (Komponent Reaktiv, Russia) was preliminary dried over P_2O_5, distilled, and stored over 3 Å molecular sieves under argon. Rare earth carboxylates, $Ln(tfa)_3{\cdot}3H_2O$, were obtained by conventional method [27,28] from $Ln_2(CO_3)_3{\cdot}6H_2O$ and stoichiometric quantity of Htfa in deionized water with yield ca. 80%.

Mixed ligand complexes **1**–**7** of general formula $[Ln(tfa)_2(deta)_2](tfa)$ (Ln = Y, Dy − Lu) were synthesized by common route under argon using Schlenk techniques. $Ln(tfa)_3{\cdot}3H_2O$ (Ln = Y, Dy − Lu) (0.69 mmol) were dehydrated within a Schlenk tube under vacuum at 110 °C and dispersed in acetonitrile (1.25 ml). Then deta (1.38 mmol) was added dropwise and the mixture was stirred for 30 min at room temperature. Colorless crystalline precipitate was filtered off and dried in vacuum. Yield 80–90%.

$[Y(tfa)_2(deta)_2](tfa)$ (**1**):

X-ray quality single crystal of **1** was grown by recrystallization from mother liquor. Calc. for $C_{14}H_{26}N_6O_6F_9Y$: C, 26.51%; H, 4.13%; N, 13.25%; Y, 14.02%. Found: C, 26.34%; H, 4.38%; N, 13.11%; Y, 12.9%. FT-IR (ATR, cm^{-1}): 3344m, 3298m, 2948m, 2881m (νNH, νCH); 1685s ($\nu_{as}CO_2$); 1593m ($\nu_{as}CO_2$); 1416 m (ν_sCO_2); 1185s, 1118vs (νCF), 900w, 838m, 793s, 720s. ^{1}H NMR (400 MHz, d_6-Me_2SO/TMS): δ 2.67 (m, 8H, CH_2), 2.55 (m, 8H, CH_2). ^{19}F NMR (376 MHz, d_6-Me_2SO): δ −73.86 (s, 9F, CF_3).

$[Dy(tfa)_2(deta)_2](tfa)$ (**2**):

Calc. for $C_{14}H_{26}N_6O_6F_9Dy$: Dy, 22.96%. Found: 23.2%. FT-IR (ATR, cm^{-1}): 3346m, 3297m, 2940m, 2885m (νNH, νCH); 1682s ($\nu_{as}CO_2$); 1605m ($\nu_{as}CO_2$); 1418m (ν_sCO_2); 1181s, 1115vs (νCF), 980w, 827m, 792s, 718s. ^{19}F NMR (376 MHz, d_6-Me_2SO): δ −86.10 (s, 9F, CF_3).

$[Ho(tfa)_2(deta)_2](tfa)$ (**3**):

Calc. for $C_{14}H_{26}N_6O_6F_9Ho$: Ho, 23.22%. Found: 23.2%. FT-IR (ATR, cm^{-1}): 3342m, 3293m, 2942m, 2886m (νNH, νCH); 1682s ($\nu_{as}CO_2$); 1590m ($\nu_{as}CO_2$); 1416m (ν_sCO_2); 1181s, 1118vs (νCF), 902w, 826m, 793s, 719s. ^{19}F NMR (376 MHz, d_6-Me_2SO): δ −81.37(s, 9F, CF_3).

$[Er(tfa)_2(deta)_2](tfa)$ (**4**):

Calc. for $C_{14}H_{26}N_6O_6F_9Er$: Er, 23.47%. Found: 24.5%. FT-IR (ATR, cm^{-1}): 3343m, 3292m, 2942m, 2888m (νNH, νCH); 1682s ($\nu_{as}CO_2$); 1589m ($\nu_{as}CO_2$); 1417m (ν_sCO_2); 1181vs, 1115s (νCF), 902w, 838m, 793s, 718s. ^{19}F NMR (376 MHz, d_6-Me_2SO): δ −70.33 (s, 9F, CF_3).

$[Tm(tfa)_2(deta)_2](tfa)$ (**5**):

Calc. for $C_{14}H_{26}N_6O_6F_9Tm$: Tm, 23.65%. Found: 23.6%. FT-IR (ATR, cm^{-1}): 3345m, 3295m, 2948m, 2888m (νNH, νCH); 1684s ($\nu_{as}CO_2$); 1589m ($\nu_{as}CO_2$); 1419m (ν_sCO_2); 1181vs, 1116vs (νCF), 903w, 827m, 792s, 717s. ^{19}F NMR (376 MHz, d_6-Me_2SO): δ −64.87 (s, 9F, CF_3).

$[Yb(tfa)_2(deta)_2](tfa)$ (**6**):

Calc. for $C_{14}H_{26}N_6O_6F_9Yb$: Yb, 24.09%. Found: 24.1%. FT-IR (ATR, cm^{-1}): 3345m, 3293m, 2945m, 2885m (νNH, νCH); 1682s ($\nu_{as}CO_2$); 1588 m ($\nu_{as}CO_2$); 1419m (ν_sCO_2); 1181vs, 1115vs (νCF), 903w, 828m, 793s, 718s. ^{19}F NMR (376 MHz, d_6-Me_2SO): δ −70.31 (m, 9F, CF_3).

$[Lu(tfa)_2(deta)_2](tfa)$ (**7**):

Calc. for $C_{14}H_{26}N_6O_6F_9Lu$: Lu, 24.29%. Found: 24.3%. FT-IR (ATR, cm^{-1}): 3346m, 3293m, 2942m, 2891m (νNH, νCH); 1683 s ($\nu_{as}CO_2$); 1586m ($\nu_{as}CO_2$); 1419m (ν_sCO_2); 1183vs, 1116vs (νCF), 904w, 827m, 793s, 718s. ^{19}F NMR (376 MHz, d_6-Me_2SO): δ −73.91 (m, 9F, CF_3).

[Na(tfa)(Htfa)] (**8**):

The excees of Htfa (2.10 ml, 27.5 mmol) was added dropwise to NaO^tBu (1.182 g, 12.3 mmol) solution in benzene (10 ml) in Schlenk tube under argon. The solvent was then evaporated under reduced pressure to obtain the crystalline precipitate. Yield 95%. Product was stored in desiccator over H_2SO_4. *Anal.* Calc. for $C_4HO_4F_6Na$: Na, 9.20%. Found: Na, 9.3%. **IR** (cm$-{}^{1}$): 2923w, 2854w, 2752w, 2555m, 2481 m (νOH); 1743m, 1651vs ($\nu_{as}CO_2$); 1456s (ν_sCO_2); 1203s, 1154vs (νCF); 857s, 805s, 732s, 705s.

2.2. Physical techniques

C, H, N contents were measured by conventional elemental analysis. Ln content was determined by complexometric titration (acetate buffer, Xylenol orange) and by gravimetric analysis. TG-DTA data were collected in the atmosphere of air using Derivatograph Q-1500 D (heating rate 10 °C/min, mass of sample 50 mg). FT-IR spectra were recorded on a Perkin-Elmer Spectrum One FTIR spectrometer in attenuated total reflectance (ATR) geometry in the range of wave numbers 650–4000 cm^{-1}.

The ^{1}H and ^{19}F NMR spectra were obtained with Agilent 400-MR spectrometer. ^{1}H spectra were used for analysis of mixed ligand complexes composition, namely, deta content, by quantitative NMR (qNMR) technique [29]. The samples for qNMR were prepared as follows: analyte powder (10.0 mg, ca. 0.0146 mmol) and internal standard — hydroquinone (10.0 mg, 0.0908 mmol) were dissolved simultaneously in 0.70 ml of d_6-Me_2SO directly in NMR tube. The composition of the complex was then determined from the ratio of intensities of deta and hydroquinone signals.

Samples for ^{19}F NMR analysis contained 0.040 mmol (ca. 25 mg) of mixed ligand complexes and 0.70 ml of d_6-Me_2SO. No spin-spin coupling constants were measured because of strong paramagnetic shift.

Single crystal X-ray diffraction data were collected on Bruker SMART APEX II DUO diffractometer with CCD area detector using Mo Kα radiation (λ = 0.71073 Å, graphite monochromator). The data were corrected for absorption by SADABS [30]. Crystal structure was solved by direct methods and refined anisotropically for all non-H atoms with full-matrix F^2 least-squares technique (SHELXTL PLUS) [31]. All H atoms were placed in geometrically calculated positions and were refined in a riding mode. Details of the data collection and refinement parameters are summarized in Table 1.