ISSN 0036-0236, Russian Journal of Inorganic Chemistry, 2006, Vol. 51, No. 4, pp. 541–548. © Pleiades Publishing, Inc., 2006.
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COORDINATION COMPOUNDS

Thulium(III) Trifluoroacetates $Tm(CF_3COO)_3 \cdot 3H_2O$ and $Tm_2(CF_3COO)_6 \cdot 2CF_3COOH \cdot 3H_2O$: Synthesis and Crystal Structure

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Received June 20, 2005

Abstract—Thulium trifluoroacetate compounds have been synthesized, $Tm(CF_3COO)_3 \cdot 3H_2O$ (**I**) and $Tm_2(CF_3COO)_6 \cdot 2CF_3COOH \cdot 3H_2O$ (**II**). The structure of **I** has been refined by the Rietveld method on the basis of the structural data for $Cd(CF_3COO)_3 \cdot 3H_2O$. The structure of **II** has been solved in a single-crystal X-ray diffraction study. Compound **I** has been studied by thermal analysis. Crystals of **I** and **II** are monoclinic: for **I** $a = 9.062(2)$ Å, $b = 18.678(3)$ Å, $c = 9.687(2)$ Å, $\beta = 113.93(1)°$, $Z = 2$, space group $P2_1/c$, $R_1 = 0.062$; for **II** $a = 8.560(4)$ Å, $b = 19.866(5)$ Å, $c = 20.813(7)$ Å, $\beta = 101.69(4)°$, $Z = 8$, space group $C2/c$, $R_1 = 0.0392$. In the molecular structure of **I**, thulium atoms are bonded in pairs through four bridging trifluoroacetate anions to form dimers. The coordination polyhedron of the thulium atom also includes the three O atoms of the water molecules and the O atom of the monodentate trifluoroacetate group; the coordination number of the thulium atom is eight. In the chain structure of **II**, there are two crystallographically independent thulium atoms with coordination numbers 8 and 9. The coordination polyhedra of the Tm(1) and Tm(2) atoms are a distorted monocapped tetragonal antiprism and a distorted tetragonal antiprism, respectively. The Tm–O bond lengths are in the range 2.28(1)–2.85(2) Å. The thulium atoms are bound into chains through carboxylate groups. These chains are linked into layers through hydrogen bonds.

DOI: 10.1134/S0036023606040061

Carboxylates of rare-earth elements form various types of crystal structures owing to their ability to coordinate a great number of atoms [1]. Trifluoroacetates retain this ability of the carboxylates, but at the same time they manifest supplementary properties owing to a higher ionicity of their M–O bonds. A great number of trifluoroacetates are used as precursors for the preparation of oxide and fluoride coatings and materials with various physicochemical properties [2, 3].

Many lanthanide trifluoroacetates have been studied structurally [4–9]. However, the structure of thulium trifluoroacetate is not known. We studied the structures of two thulium trifluoroacetates.

EXPERIMENTAL

Synthesis. Thulium(III) acetate tetrahydrate was dissolved in 99% trifluoroacetic acid taken in 20% excess. The solution was boiled; its volume was kept constant until the precipitate dissolved completely. The solution was cooled; then, an open weighing bottle containing the solution was placed into a desiccator with P_4O_{10} as a desiccant. Within 24 h, colorless crystals of thulium(III) trifluoroacetate trihydrate appeared. The crystals were stable in air.

$$Tm(CH_3COO)_3 \cdot 4H_2O + 3CF_3COOH$$
$$= Tm(CF_3COO)_3 \cdot 3H_2O\ (\mathbf{I}) + 3CH_3COOH + H_2O.$$

The crystals were recrystallized from a mixture of acetonitrile and carbon tetrachloride. X-ray powder diffraction data showed that the compound obtained upon fast crystallization from trifluoroacetic acid and the one recrystallized from acetonitrile and carbon tetrachloride had identical compositions.

Compound **I** was dissolved in trifluoroacetic acid. The solution was allowed to evaporate from a weighing bottle with a small opening placed in a desiccator with P_4O_{10} as a desiccant. Within 1 week, crystals of a new compound appeared.

$$2Tm(CF_3COO)_3 \cdot 3H_2O + 2CF_3COOH$$
$$= Tm_2(CF_3COO)_6 \cdot 2CF_3COOH \cdot 3H_2O\ (\mathbf{II}) + 3H_2O.$$

The sample was characterized using powder X-ray powder diffraction, thermal analysis, and single-crystal X-ray diffraction.

Powder X-ray powder diffraction study was performed on a STADI/P (Stoe) instrument (CuK_α radiation) with a plane detector (Ge monochromator). The structure of $Tm(CF_3COO)_3 \cdot 3H_2O$ was refined by the Rietveld method using the RIETAN97 program package [10]. The structural data for $Gd(CF_3COOO)_3 \cdot 3H_2O$ were used as the starting model for the refinement [7]. *f*-Curves for Tm^{3+}, O^{2-}, C^{3+}, and F^- were used

Table 1. Experimental details and refined parameters for the structure of $Tm(CF_3COO)_3 \cdot 3H_2O$ (**I**)

Crystal system	Monoclinic
Space group	*P*21/*c*
2θ range, deg	5–71
θ step, deg	0.03
I_{max} (pulses)	3164
Unit cell parameters	
a, Å	9.062(2)
b, Å	18.678(3)
c, Å	9.687(2)
β, deg	113.93(1)
V, $Å^3$	1498.8(5)
Z	2
ρ_{calc}, g/cm^3	1498.6
Number of collected reflections	713
Number of refined parameters	
structural	79
other	17
Discrepancies	
R_{wp}, %	0.1234
*R*I, %	0.062
S	2.54
D-Wd	0.38

Table 2. Atomic coordinates in the structure of **I**

Atom	*x*	*y*	*z*
Tm(1)	0.213(3)	0.068(7)	0.029(1)
O(1)	0.335(4)	0.112(8)	−0.123(5)
O(2)	0.261(7)	0.223(3)	−0.209(2)
O(3)	0.262(3)	−0.036(1)	−0.065(5)
O(4)	−0.027(9)	0.090(4)	0.059(6)
O(5)	−0.008(2)	0.062(1)	−0.208(1)
O(6)	0.231(5)	−0.011(3)	0.221(7)
O(7)	0.092(2)	0.182(3)	0.151(1)
O(8)	0.335(9)	0.140(6)	0.247(1)
O(9)	0.470(2)	0.024(3)	0.116(2)
C(1)	0.442(1)	0.162(4)	−0.283(8)
C(2)	0.331(1)	0.165(9)	−0.200(7)
C(3)	0.159(5)	−0.166(7)	−0.204(6)
C(4)	0.140(6)	−0.089(4)	−0.102(5)
C(5)	−0.218(3)	0.072(4)	−0.445(6)
C(6)	−0.149(1)	0.044(1)	−0.272(4)
F(1)	0.542(9)	0.131(2)	−0.212(1)
F(2)	0.467(1)	0.215(3)	−0.313(1)
F(3)	0.369(1)	0.109(4)	−0.386(7)
F(4)	0.136(7)	−0.212(2)	−0.105(4)
F(5)	0.297(5)	−0.164(9)	−0.180(4)
F(6)	0.057(5)	−0.170(9)	−0.300(4)
F(7)	−0.138(1)	0.060(8)	−0.522(2)
F(8)	−0.189(6)	0.127(1)	−0.443(6)
F(9)	−0.360(7)	0.065(1)	−0.519(1)

for the refinement. The peak profiles were described using a modified pseudo-Voigt function (Mod-TCH pseudo-Voigt). The background profiles were described by a tenth-order polynomial.

The refinement of the positional parameters of atoms and all other parameters (background, profile, unit-cell parameters, scale parameters, origin shift parameters) showed a good agreement of the calculated and experimental X-ray powder diffraction patterns. Thermal parameters were not refined. Selected experimental details and refined parameters for the structure of **I** are listed in Table 1. Tables 2 and 3 display the refined position parameters and selected interatomic distances for **I**. Figure 1 shows fragments of the experimental, simulated, and difference X-ray powder diffraction patterns.

Thermal analysis was performed on a D-2 derivatograph (heating rate 5 K/min, a 75-mg sample, an alumina crucible). The measurements were carried out in nitrogen or air.

Single-crystal X-ray diffraction study of **II** was performed on a CAD4 Enraf-Nonius diffractometer (MoK_α radiation, graphite monochromator, ω scan mode). The unit cell parameters were determined from the positions of 20 centered reflections in a θ range of 20°–25°. The structure was solved by the direct method (SHELXS97) [11]. The crystal parameters of **II** are listed in Table 4; atomic coordinates and thermal parameters, in Table 5; selected interatomic distances, in Table 6.

RESULTS AND DISCUSSION

Compound **I** is a member of the series of isostructural lanthanide trifluoroacetate trihydrates $Ln(CF_3COO)_3 \cdot 3H_2O$ (Ln = La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, or Y). The existence of this isostructural series was hypothesized in [12]. In [12] the composition of the compounds was determined from the results of elemental analysis. The X-ray diffraction

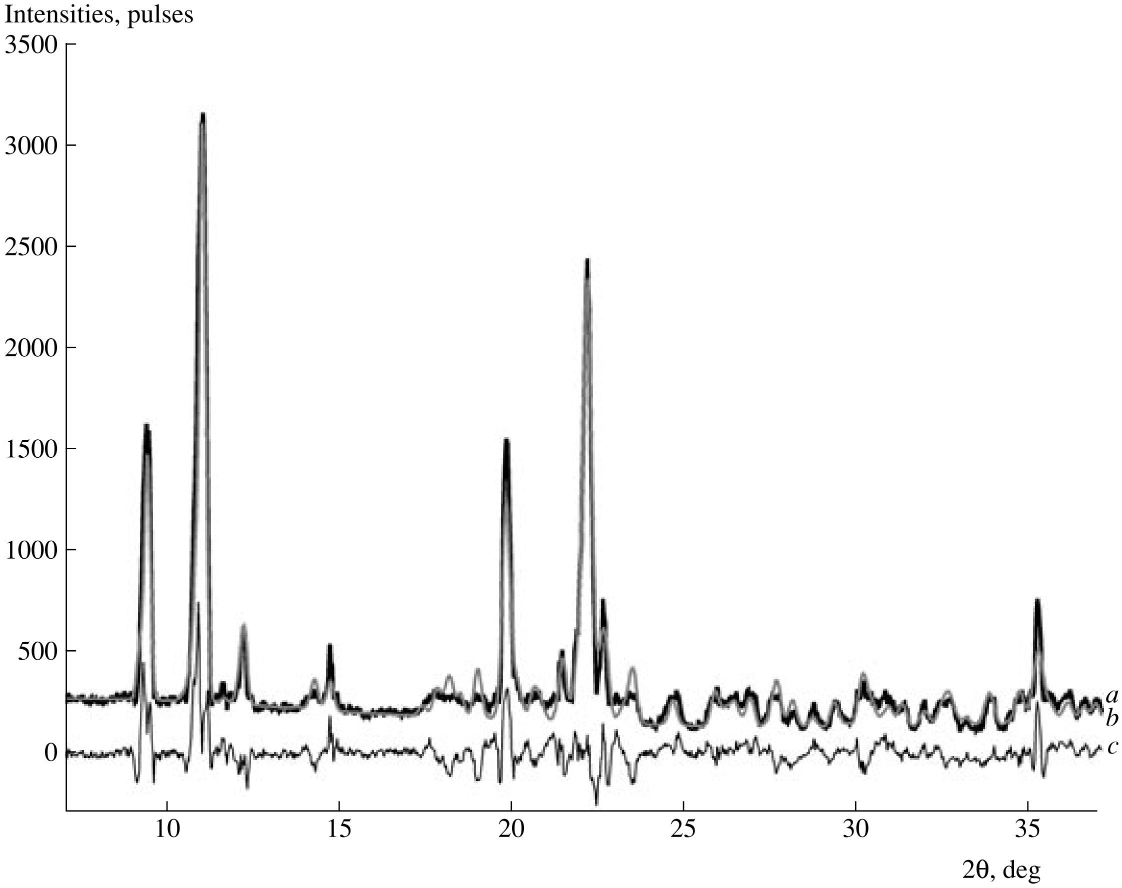

Fig. 1. Fragments of (*a*) experimental, (*b*) simulated, and (*c*) difference X-ray powder diffraction patterns for $Tm(CF_3COO)_3 \cdot 3H_2O$ (**I**).

study of single-crystal was carried out only for Pr [6], Eu [4], Gd [7], Tb [9], and Dy [5] compounds.

The molecular structure of **I** consists of dimeric structural units (symmetry C_2). The metal atoms are bound together by four bidentate bridging carboxylate groups (Fig. 2). The coordination polyhedron of the thulium atom also includes the three oxygen atoms of water molecules and an oxygen atom of the monodentate trifluoroacetate group. The coordination number of thulium atom is eight. The Tm–O distances vary in the range 2.28(1)–2.85(2) Å. The shortest distance corresponds to the Tm–O(1) bond with the monodentate trifluoroacetate group. The $Tm–O(7)_{H_2O}$ distance (2.85(2) Å) is significantly longer than the distances to the O atoms of the other two water molecules, which are comparable to the Tm–O distances (bidentate trifluoroacetate groups) and are in the range 2.28(1)–2.36(4) Å. For the single-crystal X-ray structures of lanthanide trifluoroacetates, the spread of bond length values is not so significant; in the structure of dysprosium trifluoroacetate, the Dy–O distances vary within 2.33(3)–2.42(3) Å. This fact may be due to a greater error of structure determination by the X-ray powder diffraction method. In **I**, dimeric molecules are linked into chains through hydrogen bonds.

Table 3. Selected bond lengths (*d*) in the structure of **I**

Bond	*d*, Å	Bond	*d*, Å
Tm(1)–O(1)	2.33(1)	O(6)–C(6)	1.21(2)
Tm(1)–O(3)	2.28(1)	O(6)–C(5)	1.62(3)
Tm(1)–O(4)	2.35(5)	O(5)–C(6)	1.21(9)
Tm(1)–O(5)	2.36(4)	O(4)–C(4)	1.24(9)
Tm(1)–O(6)	2.34(1)	C(1)–F(1)	1.06(9)
Tm(1)–O(7)	2.85(2)	C(1)–F(2)	1.07(7)
Tm(1)–O(8)	2.36(2)	C(1)–F(3)	1.37(1)
Tm(1)–O(9)	2.28(6)	C(3)–F(6)	1.01(3)
O(1)–C(2)	1.23(3)	C(3)–F(5)	1.17(6)
C(1)–C(2)	1.52(3)	C(3)–F(4)	1.35(9)
O(2)–C(2)	1.22(8)	C(5)–F(8)	1.05(1)
O(3)–C(4)	1.42(1)	C(5)–F(9)	1.20(2)
C(3)–C(4)	1.79(8)	C(5)–F(7)	1.25(1)

Table 4. Crystallographic parameters and experimental details for the structure of $Tm_2(CF_3COO)_6 \cdot 2CF_3COOH \cdot 3H_2O$ (**II**)

Formula unit	$Tm_2(CF_3COO)_6 \cdot 2CF_3COOH \cdot 3H_2O$
FW	822
Crystal system	Monoclinic
Space group	$C2/c$
a, Å	8.560(4)
b, Å	19.866(5)
c, Å	20.813(7)
β, deg	101.69(4)
V, $Å^3$	3466(2)
Z	8
ρ_{calc}, g/cm^3	2.522
$\mu(MoK_\alpha)$, cm^{-1}	5.295
θ_{max}, deg	25.97
Number of collected reflections	3400
Number of reflections with $F^2 > 2\sigma(F^2)$	2825
Number of refined parameters	282
R_1/WR_2	0.0392/0.0994
Temperature, K	293
GOOF	1.084

Table 5. Atomic coordinates, isotropic equivalent thermal parameters of non-hydrogen atoms, and isotropic thermal parameter of the hydrogen atoms (U_H) in the structure of **II**

Atom	x	y	z	U_{eq}, $Å^2$
Tm(1)	0.5	0.16305(2)	0.75	0.0283(2)
Tm(2)	1	0.07052(2)	0.75	0.0278(2)
O(1)	0.7395(5)	0.1093(3)	0.6952(2)	0.037(1)
O(2)	0.5743(6)	0.1869(3)	0.6478(3)	0.038(1)
O(3)	0.2703(6)	0.2042(3)	0.6877(3)	0.055(2)
O(4)	1.0312(7)	0.1612(3)	0.6882(3)	0.054(2)
O(5)	1.1687(6)	0.0278(3)	0.6877(3)	0.046(1)
O(6)	0.4069(6)	0.0727(3)	0.6874(3)	0.043(1)
O(7)	0.9421(9)	−0.1449(3)	0.6331(3)	0.055(2)
O(8)	0.449(1)	0.2782(4)	0.5545(4)	0.076(2)
H(1)	0.49(1)	0.258(4)	0.581(4)	0.05(2)
O(9)	0.8695(7)	−0.0216(3)	0.6899(3)	0.058(2)
O(10)	0.5	0.2804(4)	0.75	0.087(4)
C(1)	0.6759(8)	0.1421(4)	0.6470(4)	0.035(2)
C(2)	0.706(1)	0.1230(5)	0.5785(5)	0.058(2)
C(3)	1.1233(8)	0.2047(4)	0.6769(4)	0.041(2)
C(4)	0.046(1)	0.2698(6)	0.6470(7)	0.075(3)
C(5)	0.3022(8)	0.0291(4)	0.6744(4)	0.035(2)
C(6)	0.346(1)	−0.0322(5)	0.6374(6)	0.065(3)
C(7)	0.419(1)	0.3365(4)	0.5768(5)	0.049(2)
C(8)	1.155(1)	0.1158(5)	0.4777(5)	0.065(3)
F(1)	0.8373(9)	0.0874(4)	0.5825(4)	0.103(3)
F(2)	0.596(1)	0.0846(7)	0.5499(4)	0.174(6)
F(3)	0.718(1)	0.1736(5)	0.5433(4)	0.164(5)
F(4)	−0.1010(8)	0.2746(4)	0.6480(6)	0.153(5)
F(5)	0.119(1)	0.3228(3)	0.6770(6)	0.137(4)
F(6)	0.073(1)	0.2790(5)	0.5885(5)	0.153(4)
F(7)	0.4935(9)	−0.0420(5)	0.6455(6)	0.158(5)
F(8)	0.281(1)	−0.0848(4)	0.6490(8)	0.176(6)
F(9)	0.295(2)	−0.0257(7)	0.5772(5)	0.240(9)
F(10)	0.745(1)	−0.0763(5)	0.5405(4)	0.151(5)
F(11)	0.219(2)	0.1422(5)	0.5295(5)	0.209(8)
F(12)	1.059(1)	0.0763(7)	0.4910(8)	0.227(8)

The results of the thermal analysis for **I** are given in Table 7. The composition of the compound calculated from the thermoanalytical data coincides with $Tm(CH_3COO)_3 \cdot 3H_2O$. The decomposition of this complex proceeds in two stages. At the first stage, crystal water molecules are eliminated. At the second stage, anhydrous thulium trifluoroacetate decomposes to thulium fluoride, which is confirmed by the X-ray powder diffraction study of the product of thermal decomposition. The temperature range and the final decomposition product of **I** coincide with the results for $Nd(CF_3COO)_3 \cdot 3H_2O$ [13].

Compound $Tm_2(CF_3COO)_6 \cdot 2CF_3COOH \cdot 3H_2O$ (**II**) belongs to the family of chain structures with triple carboxylate bridges (the scandium acetate family), according to the classification in [1]. The structure includes two crystallographically independent thulium atoms linked into a chain through the tridentate chelate bridging (3_2) trifluoroacetate group (O(1)O(2)C(1)C(2)) and two bidentate trifluoroacetate groups (O(3)O(4)C(3)C(4) and O(5)O(6)C(5)C(6)). The coordination polyhedron of each thulium atom consists of four oxygen atoms of bridging bidentate tri-

Table 6. Selected bond lengths (*d*) in the structure of **II**

Bond	*d*, Å	Bond	*d*, Å
Tm(1)–O(6)	2.266(5)	C(1)–C(2)	1.54(1)
Tm(1)–O(3)	2.276(5)	C(2)–F(3)	1.26(1)
Tm(1)–O(10)	2.331(9)	C(2)–F(2)	1.26(1)
Tm(1)–O(2)	2.388(5)	C(2)–F(1)	1.31(1)
Tm(1)–O(1)	2.756(5)	C(3)–C(4)	1.52(1)
Tm(2)–O(4)	2.260(5)	C(4)–F(4)	1.26(1)
Tm(2)–O(5)	2.290(5)	C(4)–F(6)	1.29(1)
Tm(2)–O(9)	2.364(5)	C(4)–F(5)	1.31(1)
Tm(2)–O(1)	2.416(5)	C(5)–C(6)	1.527(1)
O(1)–C(1)	1.227(9)	C(6)–F(8)	1.23(1)
O(2)–C(1)	1.246(8)	C(6)–F(9)	1.24(1)
O(3)–C(3)	1.233(9)	C(6)–F(7)	1.25(1)
O(4)–C(3)	1.224(9)	C(7)–O(7)	1.20(1)
O(5)–C(5)	1.230(8)	C(7)–C(8)	1.51(3)
O(6)–C(5)	1.237(8)	C(8)–F(12)	1.21(1)
O(7)–C(7)	1.20(1)	C(8)–F(11)	1.22(1)
O(8)–C(7)	1.29(1)	C(8)–F(10)	1.26(1)

fluoroacetate groups. In addition, each Tm(1) coordinates two oxygen atoms from two tridentate chelate bridging (3_2) trifluoroacetate groups. The oxygen atoms of water molecules complete the coordination number of atoms Tm(1) and Tm(2) to nine and eight, respectively (Fig. 3).

The coordination polyhedra of atoms Tm(1) and Tm(2) are a distorted monocapped tetragonal antiprism and a distorted tetragonal antiprism, respectively. The Tm–O distances are within 2.26(5)–2.76(5) Å. This wide range of bond lengths can be explained by the variety of structural functions of oxygen atoms in the coordination polyhedron of thulium atoms.

The Tm–O distances for the oxygen atoms of the bidentate bridging trifluoroacetate groups (O(3)–O(6)) are similar (2.26(5)–2.29(1) Å). The increased Tm–O distances for water molecules (2.33(9) and 2.36(5) Å) are due to the participation of the water molecules in hydrogen bonds. The atoms O(1) and O(2), belonging to the tridentate chelate bridging trifluoroacetate group, are the most remote from the thulium atoms (2.38(5), 2.41(5), and 2.75(6) Å).

The acid molecules in **II** are hydrogen-bonded (Table 8). An acid molecule acts as the donor of the hydrogen bond O(8)–H(1)···O(2); in the other two hydrogen bonds, the acid molecule acts as the acceptor (O(7)···O(10) and O(7)···O(9)). The atoms O(2) and O(10) belong to the coordination polyhedron of the Tm(1) atom; atom O(9), to the coordination polyhedron of the Tm(2) atom of the neighboring chain (Fig. 4). Thus, the chains of Tm atoms bound by carboxylate groups are linked into layers through hydrogen bonds (Fig. 5).

Tris-glycyl neodymium chloride (**III**) [14] and cerium acetate monohydrate (**IV**) [15] are structures with triple carboxylate bridges. In contrast to **II**, these structures include only one type of metal atom linked through three carboxylate groups into chains, but, as in **II**, they contain tridentate carboxylate groups. The structure of **III** includes one tridentate carboxylate group, whereas there are two tridentate carboxylate groups in the structure of cerium acetate monohydrate. Water molecules complete the coordination number of the metal atoms in the structures of **III** and **IV** to nine; the coordination polyhedra are close to monocapped antiprisms.

Among the lanthanide trifluoroacetates that do not belong to the series of isostructural trifluoroacetate tri-

Table 7. Thermoanalytical data for $Tm_2(CF_3COO)_6 \cdot 3H_2O$

Compound	Δ*T*	T_{max}	Weight loss, %		Decomposition product
	°C		exp.	theor.	
$Tm_2(CF_3COO)_3 \cdot 3H_2O$	50–100	75	10.8	9.6	$Tm_2(CF_3COO)_3$
$Tm_2(CF_3COO)_3$	170–200	190	55.5	56	TmF_3

Table 8. Parameters of hydrogen bonds in the structure of **II**

D–H···A, Å	D–H, Å	H···A, Å	D···A, Å	Angle D–H···A, deg
O(2)–H(1)···O(8)	0.721	2.007	2.714	167.25
O(7)···O(9)			2.845	
O(7)···O(10)			2.807	

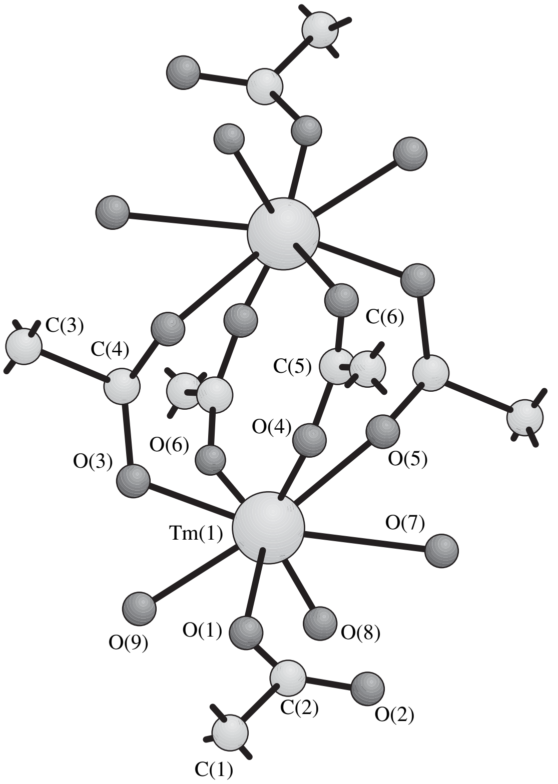

Fig. 2. Fragments of the structure of $Tm(CF_3COO)_3 \cdot 3H_2O$ (**I**).

hydrates, lanthanum and cerium trifluoroacetates [16] are noticeable. These compounds are isostructural. Their structures are layered: three crystallographically independent metal atoms are linked by two carboxylate groups; two of the six carboxylate groups are tridentate. The oxygen atoms of water molecules complete the coordination number of the metal atoms to nine. The increased coordination number of the metal and the elongated M–O bonds in lanthanum and cerium trifluoroacetates compared to the thulium complex can be explained by lanthanide contraction. For example, the La–O distances in lanthanum trifluoroacetate are slightly longer than the Tm–O distances in the structure of **I** and are within 2.42(2)–3.04(4) Å for carboxylate groups and 2.49(1)–2.56(7) Å for water molecules. In the structure of cerium trifluoroacetate the spread of M–O bond lengths is more significant (2.39(2)–2.54(4) Å for carboxylate groups and 2.46(2)–2.53(4) Å for water molecules).

In summary, we have shown that compounds with different structures can form in the lanthanide–trifluoroacetic acid systems. This is made possible by the variety of coordination modes of carboxylate groups, as well as the high coordination number of metal atoms. Further studies of the structure as dependent on the synthesis conditions will allow one to synthesize compounds with designed properties, which will extend their use in practice.

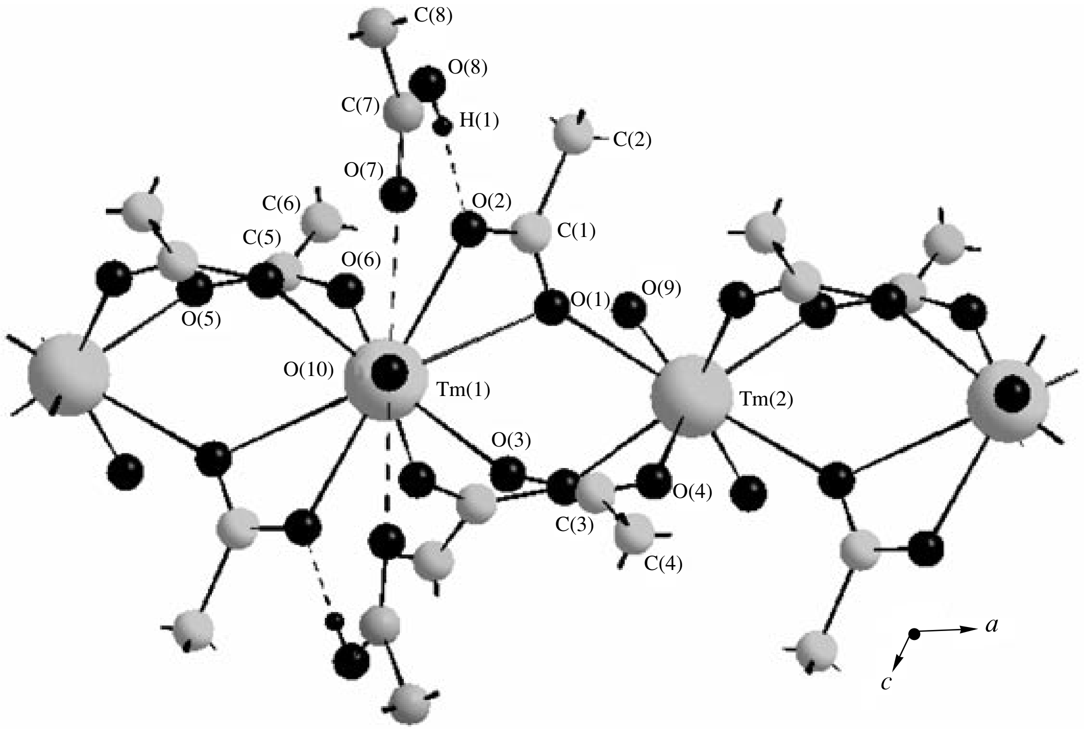

Fig. 3. Fragments of the structure of $Tm_2(CF_3COO)_6 \cdot 2CF_3COOH \cdot 3H_2O$ (**II**).

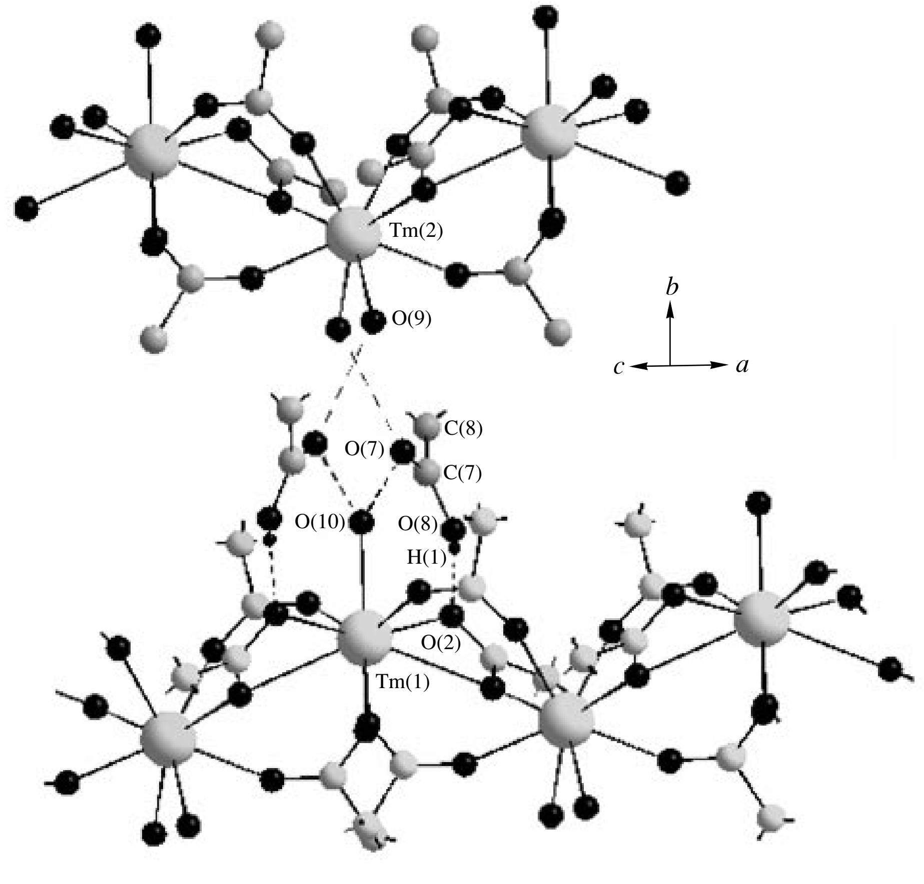

Fig. 4. Packing of structural units in the crystal of **II**.

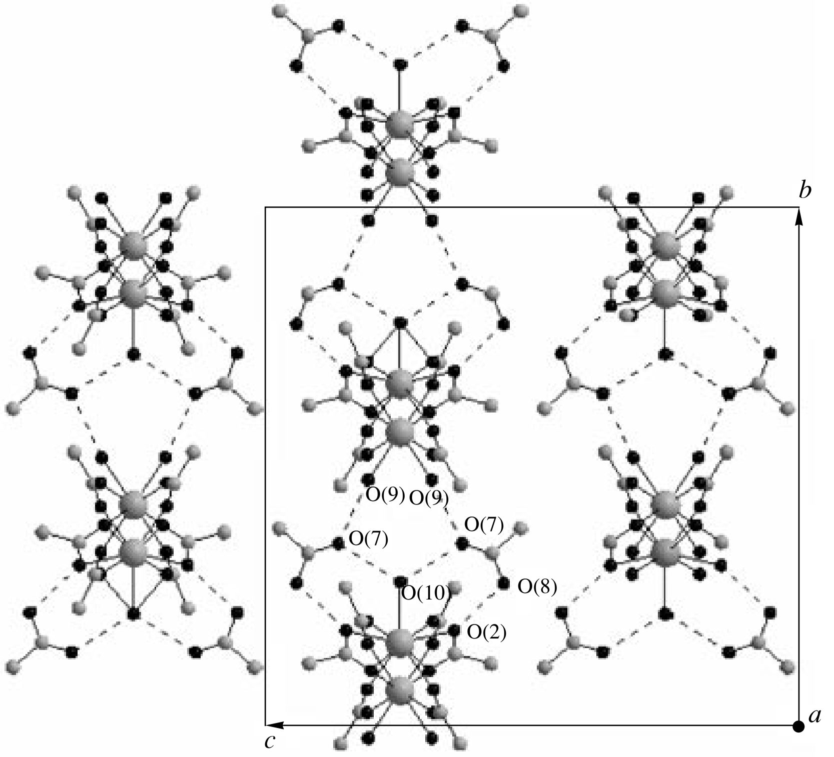

Fig. 5. Hydrogen bonds in the structure of $Tm_2(CF_3COO)_6 \cdot 2CF_3COOH \cdot 3H_2O$ (**II**).

ACKNOWLEDGMENTS

This study was supported by the Russian Foundation for Basic Research (project no. 05-03-33038).

REFERENCES

1. M. A. Porai-Koshits, Itogi Nauki Tekh., Ser. Kristallokhim. **15**, 3 (1981).
2. S. Fujihara, M. Tada, and T. Kimura, J. Sol-Gel Sci. Technol. **19**, 311 (2000).
3. B. Barja, R. Baggio, M. T. Garland, P. F. Aramendia, O. Penà, and M. Perec, Inorg. Chim. Acta, No. 346, 187 (2003).
4. V. Ya. Kavun, T. A. Kaidalova, V. I. Kostin, E. S. Panin, and B. N. Chernyshov, Coord. Chem. **10**, 1502 (1984).
5. G. V. Romanenko, N. P. Sokolova, and S. V. Larionov, J. Struct. Chem. **40**, 387 (1999).
6. P. C. Junk, C. J. Kepert, L. Wei-Min, B. W. Skelton, and A. H. White, Aust. J. Chem. **52**, 459 (1999).
7. J. Zhang, S. Zhang, X. Miao, G. Wei, N. Hu, and Z. Jin, Chin. J. Chem. **5**, 30 (1988).
8. S. R. Drake, A. Lyons, D. J. Otway, and D. J. Williams, Inorg. Chem. **33**, 1230 (1994).
9. A. A. Rastorguev, A. A. Remova, G. V. Romanenko, N. P. Sokolova, V. I. Belyi, and S. V. Larionov, J. Struct. Chem. **42**, 907 (2001).
10. F. Izumi, *The Rietveld Method*, Ed. by R. A. Young (Oxford Univ. Press, New York, 1993), Chapter 13.
11. G. M. Sheldrick, *SHELXS97 and SHELXL97* (Univ. of Göttingen, Göttingen, 1997).
12. M. Singh, S. N. Misra, and R. D. Verma, J. Am. Chem. Soc. **40**, 1939 (1978).
13. J. E. Roberts, J. Am. Chem. Soc. **83**, 1087 (1961).
14. K. F. Belyaeva, M. A. Porai-Koshits, T. I. Malinovskii, L. A. Aslanov, L. S. Sukhanova, and L. I. Martynenko, Zh. Strukt. Khim., No. 10, 557 (1969).
15. G. G. Sadikov, G. A. Kukina, and M. A. Porai-Koshits, Zh. Strukt. Khim., No. 8, 551 (1967).
16. P. C. Junk and J. C. Kepert, Aust. J. Chem. **52**, 459 (1999).