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Effect of Synthesis Conditions on the Molecular and Crystal Structures of Heterometallic 1D-Polymeric Acetate Complexes with the $\{Dy_2Co\}_n$ Motif

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Abstract—New heterometallic 1D-polymeric acetate complexes with the $\{Dy_2Co\}_n$ motif of the metallic framework, $[Dy_2Co(CH_3COOO)_8(H_2O)_4]_n \cdot 6nH_2O$ (**I**) and $[Dy_2Co(CH_3COOO)_8(H_2O)_2]_n \cdot 2nCH_3COOH$ (**II**), are synthesized and studied. The molecular structures of the obtained compounds (CIF files CCDC nos. 1861619 (**I**) and 1861620 (**II**)) differ by the qualitative composition of the coordination environment of Dy as well as by the coordination modes of the acetate anions, which substantially affects the lengths of the corresponding Dy···Dy and Dy···Co distances in the chain. The mentioned distinctions and different solvate compositions of **I** and **II** are determined by the synthesis conditions of the complexes.

Keywords: heterometallic coordination compounds, 1D-polymeric complexes, carboxylate complexes, dysprosium, crystal structure

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INTRODUCTION

Currently, the development of methods for direct synthesis and comprehensive investigation of new representatives of 3*d*-4*f* heterometallic coordination compounds is one of the most important interdisciplinary problems [1–3]. Such interest is due to the possibility of these compounds to manifest unique and practically important properties, for example, magnetic [4–6] and luminescence [7]. Therefore, they can be used as active components of functional materials [8]. In addition, in the case of an appropriate stoichiometric ratio of heterometallic atoms, these complexes can be used as precursors for mixed oxides, which are already being applied as a basis for functional materials [9–12].

It is known that the structure has a decisive effect on the properties of almost all compounds (including coordination compounds). The structure, in turn, is determined, to a high extent, by the synthesis conditions: the nature of the reagents, their stoichiometric ratio, etc. In the case of coordination compounds, their properties can be controlled at the level of individual structural units [13, 14] and crystal structure. The latter is mainly achieved by the variation of solvate molecules [15, 16]. Evidently, both indicated methods can successfully be applied for the controllable modification of coordination compounds and improvement of their valuable characteristics (magnetic, luminescence, etc.). However, these procedures should be preceded by the thorough study of complex formation in each particular system.

Herein, we studied the influence of the synthesis conditions on the molecular and crystal structures of the heterometallic acetate complexes formed in a $Co(Acac)_2 \cdot 2H_2O–Dy(Acac)_3 \cdot 3H_2O–CH_3COOH–C_2H_5OH$ system.

EXPERIMENTAL

The following commercial reagents and solvents were used for the synthesis of new compounds: $CoCl_2 \cdot 6H_2O$ (reagent grade, Labtekh), $DyCl_3 \cdot 6H_2O$ (>99%, LANKHIT), acetylacetone HAcac (99%, Acros Organics), a concentrated aqueous solution of ammonia (reagent grade, Labtekh), glacial acetic acid (reagent grade, Khimmed), and ethanol (96%). All reagents were used as received.

Acetylacetonates $Co(Acac)_2 \cdot 2H_2O$ and $Dy(Acac)_3 \cdot 3H_2O$ were synthesized by the exchange reactions in aqueous solutions of the corresponding chlorides with ammonium acetylacetonate formed in situ [17].

Table 1. Main crystal data and structure refinement for compounds **I** and **II**

Parameter	Value	
Compound	**I**	**II**
T, K	173(2)	120(2)
Crystal system	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$
a, Å	8.1587(2)	9.0696(2)
b, Å	10.2000(2)	9.2538(2)
c, Å	11.2955(2)	10.5208(2)
α, deg	111.4820(10)	79.8531(4)
β, deg	108.3450(10)	75.2262(4)
γ, deg	92.8960(10)	77.4092(4)
V, Å^3	815.49(3)	826.44(3)
Z	1	1
ρ_{calcd}, g/cm^3	2.110	2.034
μ, mm^{-1}	5.134	5.055
F(000)	507	491
Crystal size, mm	0.2 × 0.12 × 0.1	0.2 × 0.16 × 0.12
Range of θ, deg	2.076–31.563	2.274–31.522
Index range	$-12 \le h \le 12$, $-15 \le k \le 15$, $-16 \le l \le 16$	$-12 \le h \le 10$, $-13 \le k \le 12$, $-15 \le l \le 15$
Collected reflections	12194	9703
Independent reflections, R_{int}	5359, 0.0238	5002, 0.0224
Completeness to θ = 25.242°, %	100	100
Max, min transmission	0.7462, 0.4142	0.7462, 0.496
Refined parameters	249	222
GOOF	1.007	1.054
R_1, wR_2 ($I > 2\sigma(I)$)	0.0198, 0.0500	0.0206, 0.0480
R_1, wR_2 (all data)	0.0215, 0.0508	0.0224, 0.0488
$\Delta\rho_{max}/\Delta\rho_{min}$, e Å^{-3}	1.280, –0.898	1.041, –0.855

Single-crystal X-ray diffraction. Experimental data for compounds $[Dy_2Co(CH_3COOO)_8(H_2O)_4]_n \cdot 6nH_2O$ (**I**) and $[Dy_2Co(CH_3COOO)_8(H_2O)_2]_n \cdot 2nCH_3COOH$ (**II**) were collected on a Bruker SMART APEX2 diffractometer (λ(MoK_α), graphite monochromator) [18] (Table 1). An absorption correction was applied semiempirically by equivalents (SADABS) [19]. The structures were determined by a combination of a direct method and using Fourier techniques and were refined by full-matrix anisotropic–isotropic least squares. The hydrogen atoms of the methyl fragments were calculated from the geometric concepts and refined in the riding model. The hydrogen atoms bound to the oxygen atoms were localized from the difference Fourier synthesis and refined in the isotropic approximation. All calculations were performed using the SHELXS and SHELXL programs [20].

The experimental data for the structures of compounds **I** and **II** were deposited with the Cambridge Crystallographic Data Centre (CIF files CCDC nos. 1861619 and 1861620 for **I** and **II**, respectively); deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

Powder X-ray diffraction analysis was conducted on a Bruker D8 Advance diffractometer (CuK_α, Ni filter, LYNXEYE detector, reflection geometry).

Elemental analyses were carried out on a EURO EA 3000 automated C,H,N analyzer (Carlo Erba).

Synthesis of compound I. A solution of Dy(Acac)$_3$ · 3H$_2$O (0.3 g, 0.58 mmol) in EtOH (10 mL) was added with stirring to a solution of Co(Acac)$_2$ · 2H$_2$O (0.171 g, 0.58 mmol) in EtOH (10 mL). Then a mixture of glacial acetic acid (10 mL) and ethanol (30 mL) was poured to the reaction mixture. The obtained crimson-red solution was evaporated in a water bath under reduced pressure (water-jet pump) at 76°C and cooled to room temperature. Crimson-red crystals of compound **I** formed in several hours were separated from the mother liquor and washed with cold ethanol. The yield was 0.21 g (70%).

For $C_{16}H_{44}O_{26}CoDy_2$

Anal. calcd., %	C, 18.54	H, 4.28
Found, %	C, 18.35	H, 4.05

According to the X-ray diffraction data, the compound is single-phase (Fig. 1a).

Synthesis of compound II. Glacial acetic acid (20 mL) was poured to a mixture of Co(Acac)$_2$ · 2H$_2$O (0.15 g, 0.51 mmol) and Dy(Acac)$_3$ · 3H$_2$O (0.526 g, 1.02 mmol), and the resulting mixture was stirred to complete dissolution. Ethanol (15 mL) was added to the obtained crimson-red solution, and the obtained mixture was evaporated in a water bath under reduced pressure (water-jet pump) at 90°C. Crimson-red crystals of compound **II** were formed within several hours on cooling to room temperature, separated from the mother liquor, and washed with cold ethanol. The yield was 0.33 g (68%).

For $C_{20}H_{36}O_{22}CoDy_2$

Anal. calcd., %	C, 23.20	H, 3.49
Found, %	C, 23.73	H, 3.58

According to the powder X-ray diffraction data, the product contains trace amounts of compound **I** (peak 1, Fig. 1b).

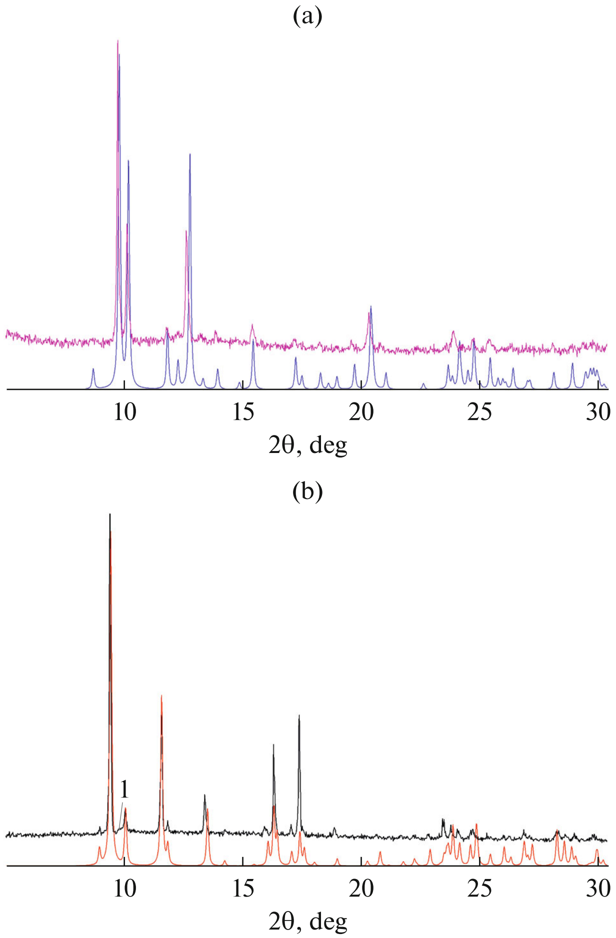

Fig. 1. X-ray diffraction patterns of synthesis products (a) **I** and (b) **II**. The upper curve is experimental, and the bottom curve is theoretical.

RESULTS AND DISCUSSION

The method for the synthesis of 3*d*-4*f* heterometallic complexes used in this work and based on the reaction of metal *tris*-acetylacetonates with carboxylic acids has been applied previously for the synthesis of the homometallic carboxylate complexes of lanthanides [12, 13, 21, 22]. Obviously, the driving force of the corresponding reactions is a substantial distinction between the acidic properties of acetylacetone and carboxylic acids. In the case of formation of complexes **I** and **II**, $K_a(CH_3COOH) \approx 2 \times 10^{-5}$ [23], which exceeds the corresponding value for acetylacetone by four orders of magnitude ($K_a \approx 1.5 \times 10^{-9}$ [24]). Thus, it can be asserted that the formation of compounds **I** and **II** is thermodynamically favorable. A more complete running of similar reactions is also facilitated by the partial removal of the reaction by-product, molecular acetylacetone, from the reaction medium due to

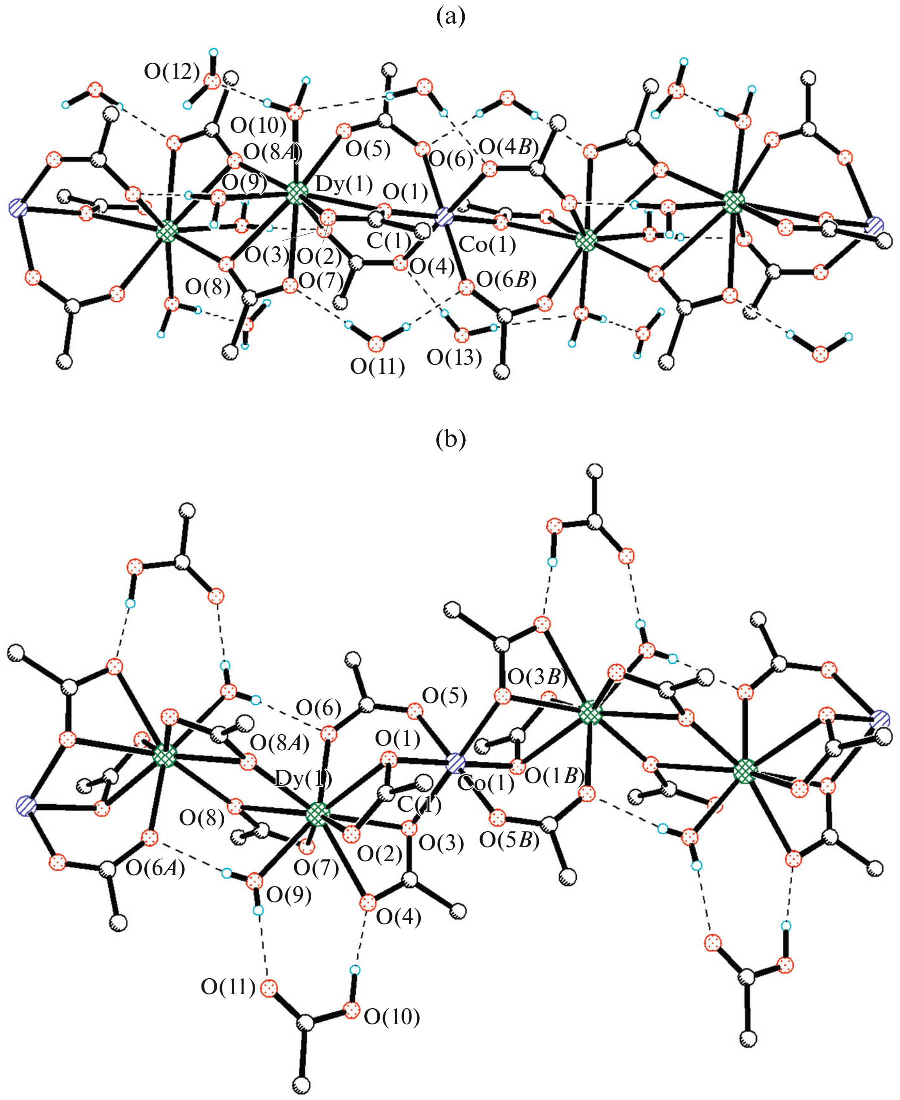

Fig. 2. Structures of the polymeric chains in compounds (a) **I** and (b) **II**.

the gradual evaporation of the mother liquor on heating.

The combined action of the above indicated factors leads to a substantial increase in the yields of compounds **I** and **II** compared to the yields of the earlier studied isomorphous complexes of other Ln obtained by the exchange reactions [25].

The structures of compounds **I** and **II** are formed by polymeric chains (Fig. 2) and solvate molecules of H_2O (**I**) or CH_3COOH (**II**). The coordination environment of the Co and Dy atoms in compounds **I** and **II** is the same: the Co atoms are localized in the inversion center, and the coordination polyhedron is an octahedron. The coordination number of Dy atoms is 9, and the polyhedron is a one-capped square antiprism.

In the structure of compound **I**, two μ_2-η^2:η^1-CH_3COO ligands link two Dy atoms into a centrosymmetric dimer, and two μ_2-CH_3COO ligands and one μ_2-η^2:η^1-CH_3COO ligand bind the Dy and Co atoms. Two $O(H_2O)$ atoms complete the coordination environment of Dy.

In the structure of compound **II**, two μ_2-η^2:η^1-CH_3COO ligands link two Dy atoms into a centrosymmetric dimer, and one μ_2-CH_3COO ligand and two μ_2-η^2:η^1-CH_3COO ligands bind the Dy and Co atoms. One $O(H_2O)$ atom completes the coordination environment of Dy.

This distinction in the chain structures results in a substantial difference in the lengths of the Dy···Dy and Dy···Co distances in the chain: 3.974 and 4.309 Å in **I** vs. 3.578 and 4.050 Å in **II**. Owing to such significant differences in the distances, it seems interesting to compare the most important physicochemical properties of compounds **I** and **II**, for example, magnetic properties, thermal behavior, and others. The studies in these directions will be continued.

The crystals of compound **I** are isostructural with the crystals of CoNd [26], CoGd [25], CoTb [27], MnNd [27], and MnGd [25, 28]. The crystals of compound **II** are isostructural with the corresponding CoEu, CoGd, CoTb, CoHo, CoEr, CoTm, CoYb, CoLu, MnEu, MnGd, MnTb, MnHo, MnEr, MnTm, MnYb, and MnLu analogs [27].

The data on the synthesis of $Na_2[Nd_2Mn(CH_3COOO)_8(H_2O)_4]_n(OH)_{2n} \cdot 2nH_2O$ ($a = 8.255$, $b = 10.394$, $c = 11.550$ Å, $\alpha = 111.48°$, $\beta = 107.86°$, $\gamma = 93.51°$, space group $P\bar{1}$) were reported earlier [29]. The value of U_{equiv} of the Na atom in this structure is 0.094 Å^2, whereas ones of the O atoms (H_2O, OH) range from 0.037 to 0.062 Å^2. The coordination number of the Na atom is 4, and the Na···O distances are in a range of 2.74–2.99 Å. The calculation of the balance of valence forces according to [30] gives an unreal value of 0.25 for Na. All these data unambiguously indicate that the crystals of the compound synthesized previously [29] are isostructural to the crystals of compound **I** and have been described earlier [27].

It can be asserted that different molecular structures (the number of water molecules coordinated by the Dy atoms) and solvate compositions of complexes **I** and **II** are determined by the synthesis conditions for these compounds. Indeed, complex **I** bearing more H_2O molecules was obtained from the system containing a water excess due to the use of nondehydrated ethanol containing up to 4 vol % water. On the contrary, compound **II** was synthesized in the presence of a high excess of glacial acetic acid and a substantially lower water excess than that used for the formation of compound **I** (owing to the use of a smaller amount of ethanol). In this case, an excess of CH_3COOH provides the “displacement” of the solvate water molecules and also the retention of water molecules in the solution (due to the formation of a strong system of hydrogen bonds) and their subsequent removal by evaporation.

Thus, the results of this study revealed the decisive influence of the synthesis conditions (composition of the solvate system, temperature) on the molecular and crystal structures of the heterometallic 1D polymeric acetate complexes formed in the $Co(Acac)_2 \cdot 2H_2O$–$Dy(Acac)_3 \cdot 3H_2O$–CH_3COOH–C_2H_5OH system. Although the studied complexes are characterized by the same motif of the metal framework, $\{Dy_2Co\}_n$, they differ by the qualitative composition of the coordination environment of the Dy atoms due to the number of coordinated H_2O molecules. In turn, this distinction leads to a substantial change in the Dy···Dy and Dy···Co distances in the chains of the studied complexes, which evokes interest in the further comparative study of the obtained compounds (in particular, their magnetic properties).

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