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Mechanochemical synthesis of thenoyltrifluoro-acetone-1,10-phenanthroline europium complex

Research Article

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Abstract: The paper considers the possibilities for mechanochemical synthesis of rare earth complexes. The complex $Eu(TTA)_3$•phen (HTTA – 2-thenoyltrifluoroacetone, phen – 1,10-phenanthroline) is synthesized by mechanical treatment of a mixture of $EuCl_3.6H_2O$, HTTA, phen and NaOH in planetary ball mill Pulverisette 7 for 30 min at 800 min^{-1}. The non reacted starting reagents and reaction side products are separated by treating activated mixture with water-ethanol solution following a procedure proposed in the literature. The elemental composition, X-ray diffraction pattern, IR spectra, optical properties (excitation and emission spectra, luminescence lifetime) and morphology of the mechanochemically synthesized complex are compared with those of the complex prepared from solution by the conventional method. The results confirm close similarity in the molecular structure and identity of the elemental composition, X-ray diffractograms and fluorescence properties of the compounds prepared by both methods.

Keywords: *Rare earth compounds • Mechanochemical processing • Optical properties • SEM • X-ray diffraction*

1. Introduction

Europium (III) complexes attract considerable attention due to their strong luminescence with high quantum yield and relatively long lifetime. Therefore, many rare earth complexes have been synthesized and used as emitters in photoluminescence and electroluminescence devices [1]. They are promising candidates as novel optical oxygen sensing materials [2]. Strategies for the design of luminescent lanthanide complexes and especially such with weak emission intensity are proposed in [3]. Basic facts on lanthanoide luminescence, its sensitization by organic ligands, and application as luminescent probes and in bioanalyses are discussed in detail by Bünzli [4]. The chemistry and application, especially of lanthanide β-diketonates, has been the subject of several reviews [5-7].

The complexes $Eu(TTA)_3$•phen and $Sm(TTA)_3$•phen (HTTA – 2-thenoyltrifluoroacetone, phen - 1,10-phenanthroline) have attracted attention because of their high fluorescence emission efficiency, which is owed to the high absorption coefficient of HTTA and the synergistic effect of 1, l0-phenanthroline. The synthesis of $Eu(TTA)_3$•phen is described in [8] and is based on the reaction between HTTA, phen, 1M NaOH and $EuCl_3$•$6H_2O$ in ethanol-aqueous solution at 60ºC (mole ratio Eu:HTTA:phen:NaOH = 1:3:1:3), washing of the formed precipitate with ethanol and water, recrystallization and drying under vacuum.

The mechanical activation is a well-known method for the preparation of a number of chemical substances. In the last decade, it has played an important role in crystal engineering and supramolecular chemistry. In principal, the main advantages of the mechanoactivation applied as the sole synthetic method or as an auxiliary step in conventional reactions are in avoiding or limiting solvent usage and of time- and labor-consuming "wet" procedures, increasing the reaction rates, enhancing solid state reactions, lowering of reaction temperatures, and the possibility for synthesis of novel molecular and supramolecular solids. However, the investigations on the mechanochemical synthesis of lanthanoid complexes are rather limited [9-13]. The activation had been performed in centrifugal-planetary ball mill AGO-2 for 1-10 min at 1000 min^{-1} at room temperature in air or as a suspension in water or ethanol. The activated products

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had been washed with water-ethanol mixture to dissolve unreacted starting reagents. $Ln(NO_3)_3$•2D (Ln = Eu or Tb, D = 2,2-dipiridyle, phen, diphenylguanidine) and $EuDik_3$•nH_2O (Dik = dibenzoylmethane, benzoylacetone, benzoyltrifluoraceton) have been synthesized. The effect of the mechanical treatment conditions and the nature of the initial products on the synthesis of mixed-ligand Eu complexes of the type $EuDik_3$.D [12] along with the morphology and particle size distribution of the products are studied [13]. 2-Thenoyltrifluoroacetone and 1,10-phenanthroline are mentioned in a few other studied ligands but not any specific data for $Eu(TTA)_3$•phen are reported. In our previous work [14], the mechanochemical behavior of the systems $EuCl_3$•$6H_2O$ – dibenzoylmethane and $EuCl_3$•$6H_2O$ – dibenzoylmethane –phenathroline were studied in more detail. Fully satisfied optical properties of the produced complexes were registered despite the fact that no phase homogeneous product was obtained.

In the present paper, the mechanochemical route for the synthesis of $Eu(TTA)_3$•phen is explored studying the X-ray diffraction, IR spectral patterns, morphology and fluorescence properties of the obtained product.

2. Experimental procedure

2.1. Materials

2-Thenoyltrifluoroacetone (HTTA, puriss, supplied by Fluka), 1, 10-phenanthroline (phen, 99%, Alfa Aesar), $EuCl_3$•$6H_2O$, (99%, Fluka) and NaOH (p.a.) were used as starting materials for complex production.

2.2. Complex synthesis

Five grams of a mixture of $EuCl_3$•$6H_2O$ – HTTA – phen in mole ratio 1:3:1 with 0.02 g NaOH were exposed to mechanoactivation for 30 min at 800 min^{-1} in planetary ball mill Pulverisette 7. The 45 mL-zirconia vessels were filled to 2/3 of the volume with balls of 5 (mainly) and 10 mm in diameter of the same material. The milled material was treated while stirring in a great excess of a mixture of ethanol and water (volume ratio 1) [11] for 6 h. The complex was further purified by recrystallization from 200 mL ethanol/acetone solution (1:3 volume ratio). After evaporation of 3/4 of the volume at ~50°C and cooling to room temperature, the residue was filtered and dried at 40°C at ambient or reduced pressure (≤133 Pa).

The obtained products were compared with $Eu(TTA)_3$•phen, prepared by the "wet" chemical method described in [8]. The yield of the product prepared by mechanical activation is ~76%, rather close to the yield of "wet" produced complex obtained by our group (~78%) or reported in the literature (80% [15]).

Table 1. Elemental composition (%) of $Eu(TTA)_3$•phen.

Sample	H	C	N	S
Theoretically expected	2.02	43.42	2.81	9.64
Prepared from solution	2.16	43.38	2.82	9.52
Mechanochemically synthesized	2.22	43.46	2.79	9.56

2.3. Analysis and characterization

The content of H, C, N and S was determined by means of the elemental analyzer Vario EL III V5.018. The IR spectra were recorded by a Bruker spectrometer in KBr pellets. The X-ray diffractograms were taken by a powder diffractometer Siemens D500 at CuK_α, 40 kV, 2θ step 0.02°/2 s. The morphology was studied by scanning electron microscopy (JEOL JS M 5510). The absorption and emission photoluminescence spectra and the lifetime of the excitation states were recorded by Cary Eclipse fluorescence spectrometer (Varian) in solid state.

3. Results and discussion

3.1. Elemental composition

The experimentally found elemental composition (after drying of products under reduced pressure) is in agreement with the theoretically expected composition for the $Eu(TTA)_3$•phen complex (Table 1). The mechanochemically produced complex stoichiometry is confirmed by the mass-loss found by the thermogravimetric analysis - 81.7% at theoretically expected 82.1% accepting Eu_2O_3 as final product. The drying at ambient pressure leads to some excess of hydrogen in the elemental analysis results.

3.2. X-ray diffraction data

X-ray diffractograms of the "wet" produced $Eu(TTA)_3$•phen and of product resulting from the initial material mechanoactivation are shown on Fig. 1. The data for interplanar distances and relative intensities are summarized in Table 2. The results confirm the phase homogeneity of the mechanochemically obtained compound. Its diffractogram is practically identical to the one of the "wet" produced sample. Distinctions in the interplanar distances exist only for part of the reflexes, mainly with decreased values in the mechanochemically produced complex (Table 2). It must be mentioned that analogous mechanochemical procedure for synthesis

and following purification of the obtained product from unreacted initial reagents does not ensure production of single phase Eu - dibenzoylmethane and Eu - mixed ligand dibenzoylmethane – 1,10-phenanthroline complexes [14].

The crystallites' size calculated from the broadening of the most intensive reflexes of the starting products and of the complexes prepared by the two methods are (nm): $EuCl_3$•$6H_2O$ – 290, phen - 318, HTTA – 725, $Eu(TTA)_3$•phen – 304 (prepared from solution) and 353 (mechanochemically produced).

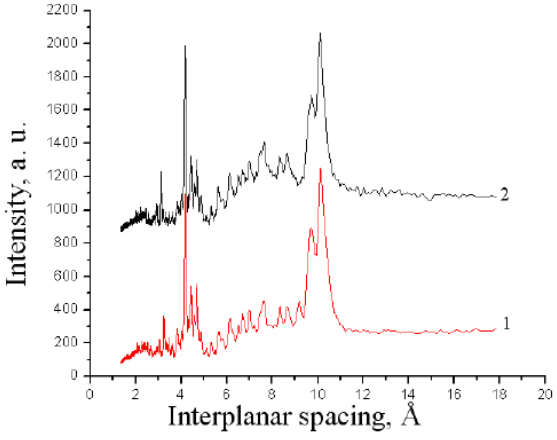

Figure 1. X-ray diffractograms of "wet" produced $Eu(TTA)_3$•phen (1) and mechanoactivated $EuCl_3.H_2O$–HTTA-phen mixture (2).

3.3. IR spectral data

The presence of traces of water in the "wet" produced complex is proved by the broad band centered on 3432 cm^{-1} accompanied with one at 1627 cm^{-1}. In the mechanically obtained complex, the latter band is only exhibited as a shoulder. It can be assumed that traces of ethanol left after the purification procedure are bonded as an adduct, which is not removed during drying at 40ºC that may contribute to the OH-band around 3430 cm^{-1} and to the slightly increased content of H and C found in the elemental analysis. The bands described in [8] as specific for the $Eu(TTA)_3$•phen (at 1601, 1413, 1309, 787 cm^{-1}) are present in both types of complexes prepared in this work. The differences between the spectra of two complexes are mainly in the relative intensity of the bands but deviations in some of their positions are also at hand (Table 3) suggesting some differences in the molecular structure of the compounds.

3.4. Fluorescence properties

The excitation spectra of the complexes prepared by both routes are similar, spread between 315-440 and 320-410 nm intervals for "wet" and mechano - produced samples, respectively, without clearly expressed maxima. Emission spectra of the two complexes in solid state are practically identical (Fig. 2). The spectra exhibit typical ligand-sensitized emission of Eu^{3+} ions. Along with the main maximum at 612 nm, the typical,

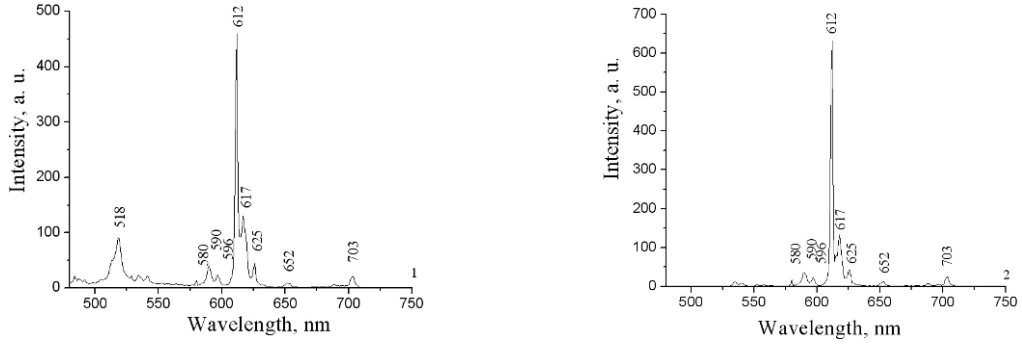

Figure 2. Emission spectra of "wet" (1) and mechanochemically (2) produced $Eu(TTA)_3$•phen in solid state.

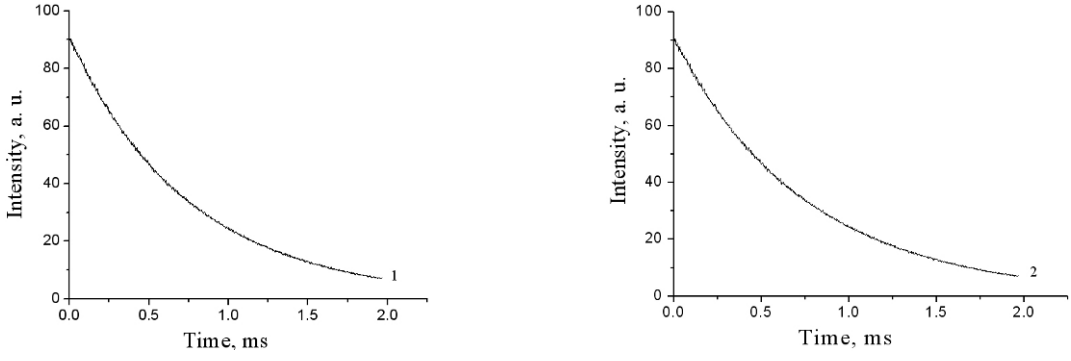

Figure 3. Luminescence lifetime of $Eu(TTA)_3$•phen prepared from solution (1) and mechanochemically synthesized (2).

Table 2. Interplanar distances (d, n.10^{10} m) and relative intensity (I,%) of the initial $EuCl_3 \cdot 6H_2O$, phen, HTTA,"wet" produced $Eu(TTA)_3 \cdot$phen and mechanoactivated $EuCl_3 \cdot 6H_2O$–HTTA-phen mixture.

Initial products								"Wet" produced $Eu(TTA)_3 \cdot$ phen		Mechanoactivated mixture $EuCl_3 \cdot 6H_2O$-HTTA-phen		
$EuCl_3 \cdot 6H_2O$			Phen			HTTA						
d	I	hkl[1]	d	I	hkl[2]	d	I	d	I	d	I	Δ,%[3]
								10.11	83	10.11	55	-
								9.72	42	9.72	13	-
								9.17	15			
			8.98	25	110							
								8.67	12	8.67	11	-
								8.35	12	8.31	10	-0.5
								7.63	20	7.63	10	-
								7.00	13	7.00	<5	-
								6.71	12	6.71	<5	-
6.54	100	010						6.51	7	6.51	<5	-
6.33	37	$\bar{1}01$										
			6.26	30	111							
								6.15	16	6.13	5	-0.3.
6.01	8	101										
			5.89	11	210			5.81	< 5	5.83	<5	0.3
						5.75	82	5.70	13	5.63	5	-1.2
						5.56	12					
5.39	20	110				5.37	8	5.32	9	5.31	<5	-0.2
			5.19	55	300			4.87	8	4.89	5	0.4
5.05	46	011				5.08	20					
						4.63	6	4.68	33	4.70	12	0.4
4.81	31	200	4.86	56	211							
4.58	9	$\bar{1}11$						4.57	< 5	4.58	8	0.2
			4.47	79	220	4.47	6	4.44	33	4.43	25	-0.2
4.38	9	111	4.31	14	301	4.30	25					
						4.18	22	4.17	100	4.17	100	-
3.98	8	002	3.96	100	221	3.94	5					
3.87	6	210	3.86	22	112			3.83	13	3.83	5	-
						3.72	5					
3.56	11	$\bar{2}11$				3.58	100					
						3.52	11					
3.42	10	012	3.40	8	410	3.42	20					
3.28	13	112	3.30	8	321			3.23	26	3.21	5	-0.6

[1] *JCPDS 73-0549*
[2] *JCPDS 29-1839*
[3] *Δ –difference between interplanar distances of the "wet" and mechanoactivated complexes related to the value of the first one.*

much weaker bands at 573 ($^5D_0 \rightarrow {}^7F_0$), 592 ($^5D_0 \rightarrow {}^7F_1$), 650 ($^5D_0 \rightarrow {}^7F_2$) and 701 ($^5D_0 \rightarrow {}^7F_4$) nm are observed. The band appearing at $^5D_0 \rightarrow {}^7F_1$ along with the bands at 617 and 625 nm is due to induced electric dipole transition $^5D_0 \rightarrow {}^7F_2$ suggesting presence of Eu^{3+} in site without an inverse center [16]. The data for the observed luminescence lifetime are perfectly fitted with a single exponent indicating a single average site distribution (a uniform surrounding environment) and existence of only one emission center in both studied specimens, *i.e.*, an ordered Eu^{3+} environment. The lifetime of the excited states (Fig. 3) are 0.760 and 0.733 ms for the complex prepared from solution and by the mechanochemical process, respectively.

3.5. Morphology

Fig. 4 represents SEM images of the initial non activated $EuCl_3 \cdot 6H_2O$, HTTA and phen as well as of $Eu(TTA)_3 \cdot$phen, prepared by both methods. The complexes have a similar morphology, which is rather different from that of the initial materials. The complexes prismatic form is confirmed by the fluorescence microscopy.

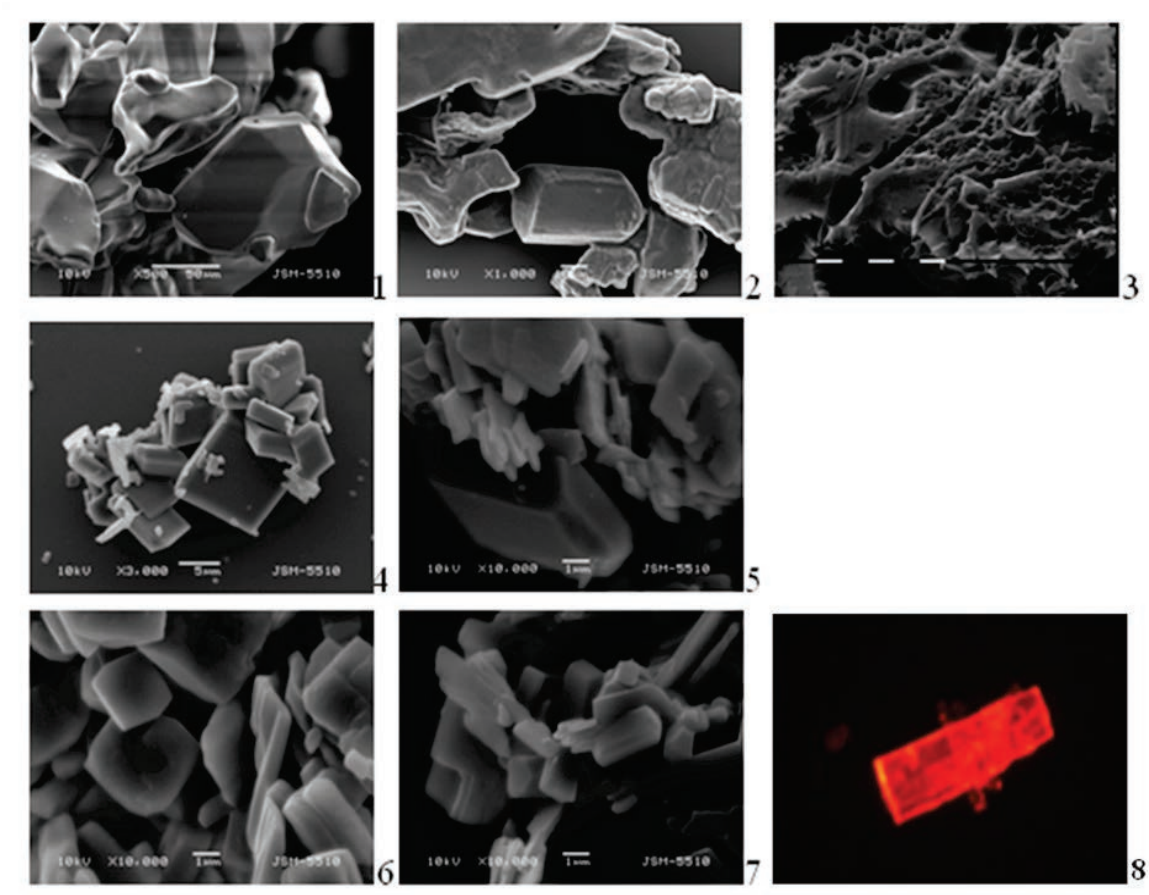

Figure 4. SEM images of unactivated $EuCl_3 \cdot 6H_2O$ (1), phen (2) and HTTA (3); "wet" (4, 5) and mechanochemically (6, 7) produced $Eu(TTA)_3 \cdot phen$ complex; fluorescence microscopy image of the mechanochemically obtained product, x160 (8).

Table 3. Characteristic bands (cm^{-1}) in the IR spectra of the studied products.

"Wet" produced $Eu(TTA)_3 \cdot phen$	Mechanoactivated mixture $EuCl_3 \cdot 6H_2O$-HTTA-phen
3432	3426
1627	1623sh
1601	1595
1413	1412
1310	1310
789	784

4. Conclusions

The main aim of the present paper is to explore the potentiality of mechanochemistry as a synthetic route for complex synthesis. The results reported in the present paper, combined with the limited literature data, ensure that the mechanochemical process is a possible and effective, but not a universal, route for production of complexes. It can be expected that the mechanosynthesis will be of limited application for production of highly thermal-sensitive complexes (like ones with dibenzoylmethane as ligand [14]) due to local temperature increase during the activation. However, the mechanochemical approach is an applicable and effective method (an alternative to the common "wet" methods) for synthesis of complexes with normal stability like the one studied in this work ($Eu(TTA)_3 \cdot phen$). In this particular case, the mechanochemical route does not have spectacular advantages over the conventional method. Both methods lead to the production of practically identical compounds with respect to reaction yield, stoichiometry, phase homogeneity, crystallization degree, ordered Eu^{3+} environment, and fluorescence properties (excitation and emission spectra, lifetime of the excited states). At the same time, the mechanochemical method requires shorter production time and ensures significantly lower content of water in the final product (which is a rather important factor for the increase in fluorescence intensity). The method requires a reduced amount of solvent but it is not solvent-free because of the unavoidable purification step, which both methods employ.

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