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Research paper Solid-phase synthesis of platinum group metal β -diketonates

Victor Makhaev^{*}, Larisa Petrova

Institute of Problems of Chemical Physics, Russian Academy of Sciences, Chernogolovka 142432, Russian Federation

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ABSTRACT

The mechanical activation (vibration ball milling) of solid starting reactants (mixtures of platinum group metal chlorides with sodium or potassium β -diketonates) followed by heating results in the formation of the corresponding platinum group metal β-diketonates. Simple (PdCl₂, PtCl₂), complex (K₂PtCl₆), and hydrated metal chlorides (RuCl₃·xH₂O, RhCl₃·xH₂O) can be used in the reaction. The considered method is quite general and enables to obtain various platinum group metal β -diketonates with a conversion of up to $\sim 85\%$ directly from their chlorides by using the same process, varying only the duration of milling, milled mixture heating temperature and the product isolation method (sublimation or extraction).

1. Introduction

Platinum group metal β-diketonates are widely used as components of catalytic systems and precursors for the preparation of supported catalysts, as well as thin metal films used in modern electronics, optics, and other industries [1-4]. Known methods for the synthesis of platinum β -diketonates are based on the interaction of β -diketone and a metal salt in aqueous or aqueous-organic solutions. Depending on the nature of the metal and β-diketone, the reagents used, processes, stages and reaction conditions differ significantly [1,5–7]. Therefore, it would be fair to say that a general method for the synthesis of these compounds does not currently exist [8]. Taking this in mind, the possibilities of using alternative methods for their preparation, e.g., microwave [8] or solid-phase synthesis [9], are being studied.

As an alternative technology, mechanical activation is successively used for the acceleration of solid-phase processes [10,11]. A comprehensive review on the use of a number of alternative technologies (including solid-phase one) for the synthesis of various types of organometallic and coordination compounds has recently been published by Beillard et al. [12]. In previous works we showed potential of solidphase mechanochemical methods for the synthesis of various types of transition metal coordination compounds (β-diketonates, ketoiminates, carboxylates, etc.). The mechanical activation (vibration ball milling) of the mixtures of an anhydrous metal chloride and a salt of an organic compound in many cases results in the appearance of a new exothermic effect in the DTA curves that is absent in the mixture of the initial reactants. The effect corresponds to the exothermic interaction of mechanically activated components with the formation of the final products [13–15], and references therein].

Therefore, the aim of this work was to study the possibilities and some patterns of the mechanochemical synthesis of platinum group metal β-diketonates from solid starting reactants (metal chloride and β -diketone salt) in the absence of a solvent. Fort the study, diketones with various electronic and steric properties and volatility of the target products were used, including the simplest one - acetylacetone, fluorinated β-diketones, and 2,2,6,6-tetramethyl heptanedione as a sterically hindered β -diketone (Scheme 1).

2. Experimental

2.1. Materials and methods

Solid sodium trifluoroacetylacetonate – Na(tfac), hexafluoroacetylacetonate - Na(hfac), acetylacetonate - Na(acac), and potassium tetramethyl heptanedionate - K(thd) were prepared as described previously [16]. Freshly prepared β -diketonates were used in the reactions. Anhydrous palladium(II) chloride (technical grade), rhodium(III) chloride hydrate RhCl₃·xH₂O (MRTU 6-09-1833-64; 34% Rh; x ~ 5), ruthenium(III) chloride hydrate RuCl₃·xH₂O (Fluka; 41% Ru; x \sim 2.2), platinum(II) chloride (Aldrich; 98% Pt), potassium(IV) hexachloroplatinate K₂PtCl₆ (Merck, 99%) were used as received. Preparation of precursor mixtures, samples for physicochemical studies, reactor charging and discharging, and other operations with air-sensitive substances were carried out in a dry box under a nitrogen atmosphere.

The milling of the reaction mixtures was carried out in a cylindrical stainless steel reactor $\sim 85 \text{ cm}^3$ using a vibration ball mill as described in

* Corresponding author. E-mail addresses: vim@icp.ac.ru (V. Makhaev), lapetrova@yahoo.com (L. Petrova).

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[13–16]. The reactor was charged with weighted amounts of the starting reactants and 20 milling steel balls 12.3 mm in diameter (~150 g), hermetically closed, and subjected to vibration (amplitude 11 mm, frequency 12 Hz, energy intensity of ~ 0.5 W/g) for a predetermined time. Then, the reactor was discharged, the reaction mixture was used for physicochemical studies and isolation of target products. The starting reactants, reaction mixtures and products were studied by powder X-ray diffraction analysis, IR spectroscopy, and thermal analysis. Powder XRD analysis of the samples was carried out on an ADN-2-01 diffractometer (CuK_{α} radiation, Ni filter) using a program for automating the processes of obtaining, processing, and analyzing X-RAY data developed for DRON X-ray diffractometers. IR spectra were recorded on a PerkinElmer Spectrum 100 Fourier-transform IR spectrometer with an ATR accessory in the range of 675–4000 cm^{-1} . Thermal studies were performed on a STA-409 PC LUXX thermal analyzer (Netzsch, Germany) in the temperature range of 20-300 °C, heating rate of 10 °C/min, and sample weight ~ 10 mg. The products were isolated from the reaction mixtures by vacuum sublimation ($\sim 10^{-1}$ mm Hg) or extraction, and identified by chemical analysis and the methods mentioned above. Chemical analysis was performed using the modified Pregl quantitative method of elemental analysis by the staff of the Multi-User Analytical Center of IPCP RAS

2.2. Synthesis

Pd(hfac)₂. A mixture of 0.205 g (1.156 mmol) PdCl₂ and 0.650 g (2.82 mmol) Na(hfac) was ball milled for 2 h. A part of the activated mixture (finely dispersed yellow-orange powder, 0.600 g) was used for isolation of the reaction product by vacuum sublimation (external heating, 140–150 °C). A yellow orange crystalline Pd(hfac)₂ was obtained (0.320 g; conversion rate, 76%). M. p. 93–95 °C (mp 95 °C [17], 99.6 °C [18]). Anal. Calc. for $C_{10}H_2O_4F_{12}Pd$: C, 23.07; H, 0.39; Pd, 20.14. Found: C, 23.02; H, 0.76; Pd, 20.0.

Pd(tfac)₂. The reaction of PdCl₂ (0.190 g, 1.07 mmol) with Na(tfac) (0.450 g, 2.55 mmol), and the product sublimation were carried out as described above. From 0.45 g of the milled mixture, 0.22 g of Pd(tfac)₂ as a pale yellow crystalline solid was obtained (conversion rate, 71%). Melting point 250–252 °C (mp: 230–240 °C) [19]). Anal. Calc. for $C_{10}H_8O_4F_6Pd$: C, 29.11; H, 1.95. Found: C, 29.43; H, 2.18.

Pt(hfac)₂. A mixture of 0.1766 g (0.664 mmol) PtCl₂ and 0.3808 g (1.655 mmol) Na(hfac) was ball milled for 3 h. The activated mixture (free-flowing powder) was preheated in a muffle furnace at ~ 240 °C for 0.5 h and allowed to cool down to room temperature. From 0.2027 g of the preheated mixture, 0.096 g Pt(hfac)₂ (conversion rate, 65%) as an orange crystalline substance was vacuum sublimed at 170–190 °C external heating. Melting point 137–138 °C (mp: 138 °C [20]). Anal. Calc. for C₁₀H₂O₄F₁₂Pt: C, 19.69; H, 0.33; Pt, 32.13. Found: C, 19.60; H, 0.39; Pt, 31.9.

Pt(tfac)₂. The reaction of 0.0994 g (0.374 mmol) of PtCl₂ and 0.1735 g (0.985 mmol) of Na(tfac), and the product sublimation were carried out as described for Pt(hfac)₂. From 0.065 g of the reaction mixture, 0.0255 g of pale yellow Pt(tfac)₂ was obtained (PtCl₂ conversion, 57%). Melting point 172–173 °C (mp: 170 °C [20]). Anal. Calc. for C₁₀H₈O₄F₆Pt: C, 23.96; H, 1.61; Pt, 39.03. Found: C, 23.74; H, 1.66; Pt, 38.8.

Pt(thd)₂. The reaction of PtCl₂ (0.1651 g, 0.628 mmol) and K(thd) (0.3354 g, 1.508 mmol) and the subsequent preheating of the reaction mixture were carried out as described above. The mixture after preheatig (a viscous mass) was extracted with CH_2Cl_2 , filtered, the solvent was distilled off. The product was dried in vacuum at 100 °C. From 0.401 g of the reaction mixture, 0.110 g of Pt(thd)₂ (38% conversion) was obtained as a beige X-ray amorphous powder. Melting point 252–254 °C (mp: 255 °C [21]). Anal. Calc. for $C_{22}H_{38}O_4Pt$: C, 47.05; H, 6.82; Pt, 34.74. Found: C, 46.95; H, 6.83; Pt, 35.1.

Ru(hfac)₃. The mixture of RuCl₃·xH₂O (0.099 g; 41% Ru, 0.402 mmol) and Na(hfac) (0.4022 g, 1.75 mmol) was milled for 2 h. A part of the milled mixture (finely dispersed black powder, 0.199 g) was preheated to 170 °C in an argon atmosphere and allowed to cool down to room temperature. From the reaction mixture, Ru(hfac)₃ was sublimed as a red–orange crystalline substance (0.096 g; conversion of RuCl₃·xH₂O, 83%). Melting point 100–102 °C (mp: 99–101 °C [22]). Anal. Calc. for $C_{15}H_3O_6F_{18}Ru$: C, 24.95; H, 0.42. Found: C, 25.11; H, 0.52.

Rh(acac)₃. The reaction of RhCl₃·*x*H₂O (0.151 g, 34% Rh, 0.5 mmol) and Na(acac) (0.316 g, 2.59 mmol) and the product isolation were carried out as described above. From 0.186 g of the preheated to 100 °C activated mixture (finely dispersed orange-brown powder), 0.058 g of orange crystalline Rh(acac)₃ (conversion rate, 73%) was obtained by vacuum sublimation (external heating, 180 °C). Melting point 263–265 °C (mp: 267 °C [23]). Anal. Calc. for C₁₅H₂₁O₆Rh: C, 45.01; H, 5.29; Rh, 25.71. Found: C, 44.87; H, 5.54; Rh, 25.44.

Rh(tfac)₃. The reaction of RhCl₃·xH₂O (0.140 g, 34% Rh, 0.462 mmol) with Na(tfac) (0.375 g, 2.13 mmol), and the product sublimation (external heating, 160 °C) were carried out as described above. From 0.27 g of the preheated to 170 °C activated mixture, 0.065 g of an orange crystalline product was obtained (48% conversion of RhCl₃·xH₂O to Rh (tfac)₃). Melting point 148–150 °C (mp: 148–149 °C [24]). Anal. Calc. for $C_{15}H_{12}O_6F_9Rh$: C, 32.05; H, 2,15. Found: C, 31.92; H, 2.29.

Rh(hfac)₃. The synthesis of Rh(hfac)₃ from RhCl₃·xH₂O (0.180 g, 0.595 mmol Rh) and Na(hfac) (0.605 g, 2.63 mmol), and the product sublimation (external heating, 140 °C). were performed as described above. From 0.530 g of the preheated to 170 °C activated mixture, an orange crystalline product (0.245 g; RhCl₃·xH₂O to Rh(hfac)₃ conversion, 84%) was obtained. Melting point 114–115 °C (mp: 114–115 °C [25]). Anal. Calc. for $C_{15}H_3O_6F_{18}Rh$: C, 24.88; H, 0.42. Found: C, 24.76; H, 0.67.



Scheme 1. β-Diketonates used in the study: a, acetylacetone; b, trifluoroacetylacetone; c, hexafluoroacetylacetone; d, tetramethylheptanedione; and e, scheme of keto-enol tautomerism.

Synthesis of Pt(hfac)₂ by the interaction of K_2PtCl_6 with Na (hfac). Milling of a K_2PtCl_6 (0.0916 g, 0.1885 mmol) and Na(hfac) (0.2187 g, 0.9507 mmol) mixture for 4 h resulted in the formation of a fine-dispersed yellow powder. The product was isolated from the reaction mixture by vacuum sublimation (external heating, 250 °C). From 0.250 g of the mixture, 0.0296 g of an orange crystalline product was obtained whose melting point and IR spectroscopy data were identical with those of Pt(hfac)₂ (vide supra) [5,20]. K_2PtCl_6 to Pt(hfac)₂ conversion rate, 32%.

3. Results and discussion

To achieve the objectives of the study, the effect of mechanical activation (vibration ball milling) and subsequent heat treatment on the physicochemical properties of solid starting reagent (Ru, Rh, Pd, Pt chlorides and sodium or potassium β -diketonates) mixtures was studied.

The visual monitoring of the reaction progress in the PdCl₂–2.4Na (hfac) mixture shows that after the first few minutes of milling, the initial mixture of solid reactants turns into a red-brown free-flowing powder. With further milling, the color of the mixture gradually changes to orange. After milling for 2 h, the XRD pattern of the mixture is composed of reflections of the initial PdCl₂ (intense) and Na(hfac) (weak), and a number of weak unidentified diffraction peaks; the reflections of the target reaction product, Pd(hfac)₂, are absent. In the IR spectra of the milled mixture, a change in the intensity and a shift in the frequency of the initial Na(hfac) absorption bands are observed. The thermal analysis study of the mixture showed the appearance of an exothermic effect in the range of ~ 125–150 °C (broadened peak, ~ 145 °C) followed by an endothermic one with an extremum at 178 °C with a weight loss of ~ 65% in the TG curve corresponding to sublimation of the target product (Fig. 1).

In accordance with the thermal analysis data, after heating the activated mixture to 150 °C, the PdCl₂ and Na(hfac) reflections almost disappear in the XRD pattern, and it mainly correspond to the superposition of the diffraction peaks of the reaction products, namely, NaCl and Pd(hfac)₂ (Fig. 2). The data suggest that the solid-state mechanochemical interaction of PdCl₂ with Na(hfac) in the conditions of the experiment proceeds through the stage of formation of intermediate complexes (probably, Na_x[PdCl₂(hfac)_x]; x = 1, 2) and results in the formation of the target product upon heating the milled mixture:

 $PdCl_2 + 2 Na(hfac) \rightarrow Na_x [PdCl_2(hfac)_x] \rightarrow Pd(hfac)_2$ (1).



fluoroacetylacetonates obtained by us are shown in Table 1, the X-ray powder diffraction data are given in Table 2.

The reaction in the PdCl₂–2.5Na(tfac) mixture proceeds similarly. The DTA curve of the milled mixture shows an exothermic effect with a peak at 195 °C followed by an endothermic one with an extremum at 222 °C. Both effects are accompanied by weight loss in the temperature range ~ 160–230 °C. The X-ray powder diffraction study showed that after heating the activated (milled) mixture at ~ 170 °C, intense diffraction peaks of NaCl and the target product Pd(tfac)₂ appear in the XRD pattern. The absorption bands of Pd(tfac)₂ in the IR spectrum also appear only after heating the milled mixture. The IR spectrum of Pd (tfac)₂ obtained is consistent with published data [27]. The XRD results indicate that the palladium complex is isomorphous with the similar

Fig. 2. XRD monitoring of the PdCl₂ – Na(hfac) reaction: a) PdCl₂; b) Na(hfac);

c) reaction mixture after milling for 2 h; d) the milled mixture after heating; e)

The IR spectrum and diffraction pattern of Pd(hfac)₂ isolated from the reaction mixture by vacuum sublimation are consistent with published data [18,26]. The data of IR spectroscopy for the hexa-

Pd(hfac)₂ sublimed; f) Pd(hfac)₂ [26].

Fig. 1. Thermal analysis data for the $PdCl_2\mbox{-}2.4Na(hfac)$ mixture after milling for 2 h.

3



Table 1

IR spectra of the obtained platinum metal hexafluoroacetylacetonates (ν , cm⁻¹).

Pd(hfac) ₂	Pt(hfac) ₂	Ru(hfac) ₃	Rh(hfac) ₃	Assignment
1629 vw			1627 vw	ν(C <u></u> C)
1599 m,	1586 m,	1583 w,	1604 m,	ν(C <u>···</u> O) +
1560vw,	1560vw,	1559vw, 1535	1560vw,	ν(C <u>···</u> C)
1535vw,	1535 vw,	vw, 1463 vw,	1533vw,	
1450 m	1438 m	1421w	1462vw,	
			1423w	
1345 w	1348 w	1348 vw	1348 w	$\nu_{s}(C-CF_{3})$
1262 m,	1259 m,	1255 m, 1208	1257 m,	ν (C–CF ₃),
1230sh,	1206 s	S	1216sh, 1204	ν(C–F),
1204 m,			m, 1164sh,	ν(C <u></u> C)
1180 m				
1151vs	1151vs	1148 vs	1153vs	δ(C—H) in
				plane
1107 m	1105 s	1101 m	1103 m	
958 vw	955 vw	948 vw	955 vw	ν(C <u>···</u> O)
832 vw, 815	835vw, 819	823 w, 814 w	828 vw, 812	$\delta_{as}(C-CF_3)$
m	m		m	
754 w	755 w	749 w	752 w	$\delta_{s}(C-CF_{3})$
719 m	723 m	699 wide, m	706 m	ring def.

Table 2

X-ray diffraction patterns of the obtained platinum metal hexa-fluoroacetylacetonates (d, Å; I_{rel} ,%).

Pd(hfac) ₂	Pt(hfac) ₂	Ru(hfac) ₃	Rh(hfac) ₃
8.845 (100)	10.164 (88)	9.665 (62)	9.118 (100)
6.371 (21)		7.468 (22)	
6.130 (35)		6.026 (13)	
	5.867 (27)	5.829 (15)	5.717 (6)
		5.505 (9)	
	5.096 (53)	4.809 (15)	4.848 (9)
4.575 (4)		4.647 (21)	4.552 (65)
4.439 (6)		4.473 (21)	
		4.133 (75)	4.281 (32)
4.013 (70)		4.049 (59)	4.004 (40)
		3.995 (100)	
3.900 (87)	3.842 (100)	3.926 (29)	
		3.715 (34)	
3.655 (26)			3.562 (5)
	3.408 (27)		3.447 (14)
3.192 (17)		3.164 (9)	3.038 (67)
2.945 (10)	2.931 (7)	2.993 (14)	2.908 (6)
2.840 (16)	2.831 (15)		2.810 (4)
2.759 (11)			
2.553 (4)	2.557 (20)		2.578 (7)
2.501 (12)	2.525 (14)	2.536 (9)	2.532 (8)
2.411 (5)	2.356 (21)	2.430 (25)	2.420 (11)
2.330 (4)	2.330 (29)		2.344 (6)
2.206 (5)	2.233 (25)	2.273 (22)	2.290 (9)
2.166 (15)	2.199 (10)	2.159 (11)	2.159 (7)
2.132 (15)			2.120 (3)
2.047 (15)	2.045 (17)	2.062 (3)	2.087 (3)
			1.996 (5)
1.953 (8)	1.945 (9)	1.933 (9)	1.953 (6)
	1.914 (8)		1.924 (3)
1.886 (4)	1.840 (10)	1.886 (8)	
1.807 (7)	1.814 (6)		1.826 (5)
1.740 (8)	1.704 (7)	1.757 (7)	

platinum complex, which is consistent with published data indicating that the structure of $Pd(tfac)_2$ was not determined because of the poor quality of single crystals [28].

The data indicate that the reaction proceeds upon heating the sample, and the product formed can be isolated by vacuum sublimation. The IR spectroscopy data for the trifluoroacetylacetonates obtained by us are given in Table 3, the XRD data are listed in Table 4.

X-ray diffraction patterns of the mechanically activated $PtCl_2-2.5Na$ (hfac) mixture show only reflections of the starting materials, and in the IR spectra, slightly shifted absorption bands of the starting Na(hfac) are observed. The DTA curve of the mixture milled for 2–3 h exhibits a

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Table 3

IR spectra of the obtained platinum metal trifluoroacetylacetonates (ν , cm⁻¹).

Pd(tfac) ₂	Pt(tfac) ₂	Rh(tfac)3	Assignment
2928 w, 2854 w	2924 m, 2852 m	2928 w, 2854w	vCH ₃)
1598 s, 1584 s	1586 s	1598 s	$\nu_{as}(C_O)$
1521 m	1523 m	1527 m	ν(C C)
1453 m	1464 m, 1453 m	1448 w, 1419w	$\delta_{as}(CH_3) + \nu_s(C - O)$
1367 w	1369 m	1366 w	$\delta_s(CH_3)$
1299 s	1306 s	1290 vs	$\nu(C_C) + \nu(C-CH_3)$
1230 m, 1186 s,	1234 vs, 1188 s,	1233w, 1197	ν (C–F) + ν (C–CF ₃)
1157 s, 1139vs	1158 s, 1142vs	m, 1140vs	δ(C—H) in plane
1027 w	1028 w	1024vw,	ρr(CH ₃)
		1012vw	
949 w	948 w	947 w	ν (C–CH ₃) + ν (C $\underline{-}$ O)
878 m	883 m	876 w	
798 m	803 m	800 w	δ as(C-FC3), δ(C-H)
			out-of-plane
743 m	745 m	741 w	δ s(C-CF3)
690 w	697 m	682 w	ring def.

Table 4

X-ray diffraction patterns of the obtained platinum metal trifluoroacetylacetonates (d, \hat{A} ; I_{rel},%).

Pd(tfac) ₂	Pt(tfac) ₂	Rh(tfac)3
		9.880 (82)
		9.213 (27)
8.758 (59)	8.889 (54)	
7.830 (100)	7.728 (100)	
	7.196 (14)	7.167 (15)
		6.511 (76)
6.215 (40)	6.172 (82)	
5.505 (26)	5.522 (23)	5.539 (20)
		4.942 (36)
		4.758 (31)
4.364 (11)	4.396 (42)	4.220 (21)
		4.040 (100)
3.633 (43)	3.670 (63)	3.562 (20)
3.433 (18)	3.395 (22)	3.296 (53)
3.121 (9)	3.074 (7)	3.121 (15)
	2.931 (9)	3.033 (12)
2.818 (8	2.844 (14)	
2.625 (5)	2.640 (7)	
	2.571 (12)	2.546 (14)
	2.478 (10)	2.475 (18)
	2.217 (10)	2.262 (16)
		2.204 (11)
		2.154 (20)
	1.834 (13)	

strong exothermic effect in a wide temperature range of ~ 150–250 °C with a peak at 237 °C, an endothermic one at ~ 225 °C (Pt(hfac)₂ sublimation) being superimposed on it (Fig. 3). Both effects are accompanied by weight loss in the temperature range ~ 150–250 °C in the TG curve. The target product, Pt(hfac)₂, was isolated by vacuum sublimation from the preheated at ~ 240 °C milled mixture. The IR spectrum of the product corresponds to published data [5]. The data indicate that Pt(hfac)₂ is formed upon heating the milled reaction mixture.

The interaction in the PtCl₂–Na(tfac) system proceeds similarly to the reaction with Na(hfac). The target product, Pt(tfac)₂, was formed upon heating the milled mixture at ~ 240 °C and isolated by vacuum sublimation from the preheated milled mixture. The IR spectroscopy and XRD data correspond to the presence of Pt(tfac)₂ cis and (mainly) trans isomers in the sublimate [5,20].

The presence in the DTA curves of the activated mixtures of the exothermic peak corresponding to the interaction of the components with the formation of products at temperatures below the melting points of the reactants indicates that the reactions discussed above proceed directly in the solid phase, and not in the melt.

In the IR spectrum of the PtCl₂-2.4 K(thd) mixture after milling for 3



Fig. 3. Thermal analysis data for the $\mbox{PtCl}_2\mbox{-}2.5\mbox{Na}(\mbox{hfac})$ mixture after milling for 2 h.

h, a shift and a change in the intensity of the initial K(thd) absorption bands are observed. Weak KCl reflections appear on the XRD pattern. The DTA curve of the milled mixture exhibits an exothermic effect of a complex shape in the 120–250 °C range with maxima at 171 and 234 °C, accompanied by the weight loss on the TG curve. The complex shape of the DTA curve can be explained by the overlapping of the exothermic effect of the interaction of the activated starting reactants with the endothermic effects of the Pt(thd)₂ sublimation and its melting at 255 °C [21].

After heating the activated mixture to ~ 230 °C, a viscous substance was formed, the IR spectrum of which is similar to that of Pd(thd)₂ [29]. The XRD pattern of the preheated mixture contain intense KCl and NaCl reflections and new ones corresponding probably to Pt(thd)₂. The product, Pt(thd)₂, was isolated from the preheated mixture by extraction with methylene chloride. The IR spectroscopy data for Pt(thd)₂ are listed in Table 5.

The results show that in the case of PtCl₂ compared to PdCl₂ a higher heating temperature is necessary for the formation of the target products from the milled mixtures. The substantially lower PtCl₂ reactivity can be explained by a higher Pt–Cl bond energy compared to Pd–Cl [30].

The interaction of sodium β -diketonates with hydrated chlorides MCl₃·xH₂O (M = Ru, Rh) differs from reactions with anhydrous PdCl₂ and PtCl₂, in particular, by the presence of the stage of partial dehydration of the initial MCl₃·xH₂O upon heating the activated mixtures, and caused by this fact the need to use a larger excess of sodium β -diketonate. The XRD patterns of the RhCl₃·xH₂O-4.4Na(hfac) mixture milled for 2–4 h show mainly reflections of the initial Na(hfac); the IR

Table	5
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IR s	spectra o	of the	obtained	Rh(acac)3	and	$Pt(thd)_2$	(ν,	cm	۱)
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Rh(acac) ₃	Pt(thd) ₂	Assignment
2924 m	2957 m, 2928 s	$\nu_{as}(CH_3)$
2853 w	2854 m	$\nu_{\rm s}({\rm CH}_3)$
1575 vs, 1520 s	1595 w, 1531 vs	$\nu(C_O) + \nu(C_C)$
1411 vs, wide	1499 s, 1462 w	δ _{as} (C—H)
1366 s	1382 s, 1359 m	δ _s (C—H)
1275 w	1251 w	ν (C···C) + ν (C–CH ₃)
1201 w	1229 w, 1188 w	δ(C—H) in plane
	1147 m	
1019 w	1027 vw, 1012 vw	$\rho_r(CH_3)$
938 w	937 vw	$\nu(C_{-}CH_3) + \nu(C_{-}CH_3)$
855 vw	884 m	_
771 w	797 m, 768 w	δ(C—H) out-of-plane
699 w		ring def

spectrum contains slightly shifted Na(hfac) absorption bands.

The thermal analysis data for the mixture milled for 2 h (Fig. 4) show endothermic effects with minor weight loss in the range of 50–100 °C, corresponding to the partial dehydration of RhCl₃·*x*H₂O, hydrolysis of Na(hfac) and evaporation of the formed hexafluoroacetylacetone (bp 70–71 °C) and water. In the range of 125–200 °C, a strong exothermic effect with superimposed on it endothermic one (extremum, ~ 170 °C) corresponding to the progress of the target reaction and major weight loss (sublimation of the target product, Rh(hfac)₃), are observed.

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After heating the milled mixture to 150 °C, its XRD pattern and the IR spectrum are radically changed. In the XRD pattern, Na(hfac) reflections almost disappeared, and NaCl and Rh(hfac)₃ [31] reflections appeared. The IR spectrum of the mixture after heating is similar to that of Rh (hfac)₃ [25,32]. The product, Rh(hfac)₃, was isolated by vacuum sublimation from the milled mixture preheated to 150 °C and then cooled down in an argon atmosphere. In this and subsequent experiments, the preliminary heating to a temperature close to that of the exothermic effect peak is necessary to avoid thermal explosion and sudden outburst of the reaction mixture into the condensation zone caused by the occurrence of exothermic reaction of the target product formation. According to the XRD data [31], the Rh(hfac)₃ sublimed consists of a mixture of hexagonal (mainly) and monoclinic modifications (Table 2).

The interaction proceeds similarly in the RhCl₃·xH₂O–4.6Na(tfac) mixture. The X-ray diffraction pattern of the milled for 2 h mixture shows the presence of an amorphous phase, after heating of which to 150 °C intense NaCl diffraction peaks appear. The thermal analysis data for the mixture show an endothermic effect with extremum at 78 °C and an exothermic one in the range of ~ 120–190 °C, both accompanied by the sample weight loss. The product was isolated from the preheated mixture by vacuum sublimation. X-ray powder diffraction data correspond to the presence of trans and cis isomers of Rh(tfac)₃ in the sublimed crystals [24] (Table 4).

An analogous reaction pattern is observed for the RuCl₃·xH₂O–4.4Na (hfac) system. After heating the milled for 2 h mixture to 170 $^\circ$ C, the Na



Fig. 4. Thermal analysis data for the RhCl₃ $xH_2O-4.4Na(hfac)$ mixture after milling for 2 h.

(hfac) reflections almost disappear, while the NaCl reflections increase significantly. The IR spectrum of the mixture after preheating is similar to that of Ru(hfac)₃ [33]. The product was isolated from the preheated mixture by vacuum sublimation in a high yield (RuCl₃·*x*H₂O conversion to Ru(hfac)₃ ~ 85%). According to XRD data, the obtained Ru(hfac)₃ is isomorphous to Rh(hfac)₃ [31] and consists of a mixture of hexagonal and monoclinic modifications (Table 2).

The results indicate that the formation of platinum metal β -diketonates in the reactions discussed above proceeds mainly upon heating the milled mixtures.

The reaction proceeds differently in the RhCl₃·xH₂O-5.2Na(acac) mixture. The color of the reaction mixture milled for 1–2 h changed from dark gray to orange brown. Reflections of the starting reactants disappeared, and NaCl diffraction peaks appeared in the XRD patterns of the mixture. After milling for 1 h, only a few shifted absorption bands of the initial Na(acac) were observed in the IR spectrum of the mixture, and after 2 h, the IR spectrum mainly comprised the absorption bands of the target product. Rh(acac)₃ (Table 5). A change in the color of the reaction mixture upon milling and the presence of Rh(acac)₃ absorption bands in its IR spectrum indicate that the formation of the product occurs directly during the milling. The thermal analysis data for the mixture milled for 1–2 h show an exothermic effect with a peak at \sim 70 °C followed by an endothermic one (extremum, \sim 120 °C) with a weight loss of \sim 8% (evaporation of water and acetylacetone formed during hydrolysis of Na (acac) excess). In our opinion, the presence of the exothermic effect at \sim 70 °C shows that under the experimental conditions the reaction of Rh (acac)₃ formation is not completed, and its completion requires heating the activated mixture or further milling. The formation of the final reaction products in the process of milling correlates with a low temperature of the exothermic effect, which is likely to be achieved upon the collisions of the milling balls [13,34].

Preliminary experiments have shown that platinum group metal β -diketonates can also be obtained from tetravalent metal complexes, e. g., K₂PtCl₆. The IR and XRD patterns of the milled for 4 h K₂PtCl₆–5Na (hfac) mixture show the presence of the starting materials only. But the thermal analysis data for the milled mixture show the appearance of a strong exothermic effect at ~ 185–250 °C with a peak at 233 °C corresponding to a weight loss in the TG curve (Fig. 5). The target product, Pt (hfac)₂, was vacuum sublimed from the milled mixture under heating.

The obtained data suggest that the processes under study consist of several major stages: (1) grinding and mixing of the starting reagents; (2) activation of the reaction mixture, and (3) chemical interaction of the components to form a target product. The third stage can take place both simultaneously or stepwise, upon milling in the reactor and/or subsequent heating, depending on the reactants' nature.

4. Conclusions

The data obtained show that the vibration ball milling of solid mixtures of alkali metal β -diketonates with platinum metal chlorides followed by heating the milled mixtures results in the formation of the corresponding platinum group metal β-diketonates. Simple (PdCl₂, PtCl₂) and complex (K₂PtCl₆) metal chlorides, as well as RuCl₃·xH₂O and RhCl₃·xH₂O hydrates can be used in the reaction. The considered method is quite general and enables to obtain various platinum group metal β -diketonates with a rather high conversion rate directly from their chlorides by using the same process, varying only the duration of milling, the temperature of the milled mixture heating and the product isolation technique (sublimation or extraction). The possibilities and conditions of using this approach depend on the nature of β -diketonate ligands. In our belief, further studies will make it possible to substantially increase the yield of the target products and to use the approach to obtain other types of platinum group metal complexes, e.g., β-ketoiminates and β-diiminates, the synthesis of which in solutions is complicated by the hydrolytic instability of the corresponding ligands.



Fig. 5. Thermal analysis data for the $K_2 PtCl_6\mathchar`-5Na(hfac)$ mixture after milling for 4 h.

CRediT authorship contribution statement

Victor Makhaev: Conceptualization, Supervision, Writing - review & editing. Larisa Petrova: Investigation, Writing - original draft.

Declaration of Competing Interest

The authors declare that they have not known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.ica.2020.120231.

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