## Complex compounds of transition metals with hydroxyaromatic carboxylic acids as precursors for the synthesis of nanosized metal oxides\*

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Eight complex compounds of Mn<sup>II</sup>, Fe<sup>II</sup>, Co<sup>II</sup>, Ni<sup>II</sup> and Cu<sup>II</sup> with 2,4,6-trihydroxybenzoic acid and 3,4,5-trihydroxybenzoic acid were synthesized in a crystalline form. Nanosized metal oxide particles obtained by thermal decomposition of the complexes were studied by X-ray powder diffraction analysis and electron microscopy.

**Key words:** hydroxyaromatic carboxylic acids, complex compounds, thermal decomposition, nanosized metal oxides.

Recent years have seen a rise of research interest in the synthesis of inorganic nanosized oxide materials.<sup>1</sup> Metal oxides nanoparticles are catalytically active in the conversion of various organic compounds. They may be used in information storage devices, as biologically active substances, and in other spheres.<sup>2–7</sup> One of the ways to disperse metal oxides to nanoscale is to use the sol—gel method. This technique involves in the thermal decomposition of precursors, which are usually complex compounds of the corresponding metal with organic ligands.<sup>8</sup> At the same time, a decrease in the onset temperature of decomposition and an increase in the yield of gaseous decomposition products that preserve oxides from the formation of larger particles are important parameters in nanosized particle production.

Earlier, we showed the possibility of using transition metal alkyls and benzyl nitrohydroxylamines,<sup>9</sup> as well as metal complexes of polyhydroxyaromatic compounds<sup>10,11</sup> as precursors for the synthesis of nanosized transition metal oxides of Group IV elements. The disadvantages of these precursors are the high energy intensity of nitrosohydroxylamine derivatives, which often results in explosive decomposition of metal complexes upon heating, as well as the weak complexing ability of polyhydroxyphenols, which complicates the formation of coordination compounds.

In the present work, complex compounds of 2,4,6- and 3,4,5-trihydroxybenzoic acids ( $H_4L^1$  and  $H_4L^2$ , respec-

tively) were used as precursors of nanosized transition metal oxides of Group IV elements. Owing to a low decomposition temperatures of organic ligands (100 °C for  $H_4L^1$  and 240 °C for  $H_4L^2$ )<sup>12,13</sup> and corresponding metal complexes, a low-temperature synthesis of basic products becomes possible.

## **Results and Discussion**

The acid-base properties of  $H_4L^1$  and  $H_4L^2$  are attributed to the presence of four mobile hydrogen atoms in the ligand (one proton is of the carboxyl group and three protons are of the phenol). At complexation, one or more H<sup>+</sup> cations can be replaced by a metal cation. To determine the pH ranges and a charge of the organic anion optimal for the synthesis of coordination compounds, potentiometric titration of  $H_4L^1$  and  $H_4L^2$  ligands, as well as of their mixtures with metal salts, with a solution of sodium hydroxide was carried out. Figure 1 shows the curves of potentiometric titration of  $H_4L^1$  ligand and its equimolar mixture with cobalt(II) chloride as an example. As derived from the present data, the  $H_4L^1$  titration curve has two titration steeply rising portions associated with the successive separation of one (pH 2.0-8.5) and then two hydrogen atoms (pH 9.0–13.5). The dissociation of the fourth proton was not found. A similar curve describes the titration of  $H_4L^2$  ligand.

The titration curves of mixtures of solutions of organic ligands and metal salts are below those of individual ligands at pH > 7.5. According to the existing concepts,<sup>14</sup> such result indicates that the complexation of metal cations

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**Fig. 1.** Potentiometric titration curves of solutions of  $H_4L^1$  (1) ligand and of the equimolar  $H_4L^1$  and CoCl<sub>2</sub> mixture (2).

with  $H_4L^1$  and  $H_4L^2$  starts in weakly alkaline solutions, rather than in neutral or acidic media.

Correspondingly, the ensuing syntheses of complex compounds were carried out in weak alkaline medium, pH ranged from 7.5 to 8.5. Under such conditions, organic molecules are mainly in the form of monoanions which is in agreement with the composition of the isolated metal complexes (M : L = 1 : 2).

The nature of the metal—ligand interaction is confirmed by spectrophotometric titration of  $H_4L^1$  and  $H_4L^2$ with NaOH and inorganic metal salts solutions (Fig. 2).

The electronic absorption spectrum of  $H_4L^1$  in neutral medium is characterized by three main absorption bands,



**Fig. 2.** Changes in electronic absorption spectra during spectrophotometric titration of  $H_4L^1(a, b)$  and  $H_4L^2(c, d)$  ligands with NaOH (a, c) and  $CuCl_2(b, d)$  solutions.

Note. Fig. 2 is available in full color on the web page of the journal (https://link.springer.com/journal/volumesAndIssues/11172).

 $\lambda_{\text{max}}$ /nm (log $\epsilon$ ): 289 (3.21), 257 (3.93), and 219 (4.38). When a NaOH solution is added within the pH range 3.5–8.0, a bathochromic shift of the absorption bands occurs at 350 (2.17), 276 (4.11), and 220 nm (4.51) (see Fig. 2, *a*). The appearance of isosbestic points attests to the equilibrium nature of ionization. Additionally, during ionization, a bathochromic shift of the long-wavelength band (see Fig. 2, *c*) from 261 (log $\epsilon$  3.92) to 267 nm (log $\epsilon$ 3.94) is observed in the H<sub>4</sub>L<sup>2</sup> spectrum.

Characteristic changes in the electronic absorption spectra of ethanol solutions of the  $H_4L^1$  and  $H_4L^2$  ligands upon the gradual addition of metal salts (see Fig. 2, b, d) corresponds to the changes in their spectra upon ionization. This fact is consistent with the complexation entailed by ligand ionization. The position and intensities of the absorption bands in the electronic spectra of the complex compounds are given in Experimental and correspond to the changes observed in the course of spectrophotometric titration.

The nature of the coordination of organic molecules by metal cations can be derived from the change in the characteristic vibrations of the carboxyl group in the IR spectra when the transition from uncoordinated  $H_4L^1$  and  $H_4L^2$  ligands to metal complexes occurs.

In the IR spectrum of  $H_4L^1$ , a strong broad absorption band in the region of  $3400-3250 \text{ cm}^{-1}$  with a maximum at 3340 cm<sup>-1</sup> (v(OH)) and an absorption band at 1654 cm<sup>-1</sup> (v(C=O)) of the carboxyl group) are readily found. The shift of the latter band to the low-frequency region is associated with the participation of the carboxyl group of  $H_4L^1$  in the formation of a strong intramolecular hydrogen bond with the neighboring hydroxy group. The bathochromic shift of the (C=O) band by  $15-25 \text{ cm}^{-1}$  observed in the spectra of complexes is due to the formation of metalligand coordination bonds with a significant degree of covalency. The persistence of the v(C=O) band in the spectra of the  $H_4L^1$  metal complexes seems to indicate that complexation involves ionization of the neighboring hydroxy group with the formation of metal chelate rings of type A.



In the case of the  $H_4L^2$  ligand, the intramolecular hydrogen bond between the hydroxy and carboxyl groups is hardly possible and the stretching vibration band v(C=O) in the uncoordinated ligand appears at 1706 cm<sup>-1</sup>. As complexation proceeds, the carboxyl group of  $H_4L^2$  is ionized and the band at 1706 cm<sup>-1</sup> disappears. At the same time, in the spectra of both metal complexes, two bands

related to antisymmetric and symmetric vibrations of the carboxylate anion are found at the frequencies below  $1600 \text{ cm}^{-1}$ . The value  $\Delta v(\text{COO}^-) = v^{as}(\text{COO}^-) - v^s(\text{COO}^-)$  in the spectra of complex compounds is in the range of  $124-144 \text{ cm}^{-1}$ , which corresponds to the bidentate coordination of the carboxyl group (**B**).<sup>15</sup>



The thermal stability data for the  $H_4L^1$  and  $H_4L^2$  complex compounds are summarized in Table 1. The thermogravigram of Ni $(H_3L^1)_2 \cdot 2H_2O$  complex is shown as an example in Fig. 3.

As evident from Table 1, the thermal decomposition of complex compounds starts with their dehydration at temperatures from 70 to 168 °C (endothermic peaks) and from 150 to 200 °C (exothermic peaks). This indicates that one part of the water molecules is in an adsorbed form, and the other part is involved in the formation of a coordination bond. The decomposition of the organic fragment of the H<sub>4</sub>L<sup>1</sup> complexes starts with endothermic decarboxylation in the temperature range of 150–250 °C, and a complete burnout of organics includes several exothermic reactions and ends at temperatures of 450–600 °C. The decomposition of the H<sub>4</sub>L<sup>2</sup> metal complexes starts at higher temperatures (280–295 °C), the carboxyl groups are removed simultaneously with the burnout of organics and these reactions are characterized by *exo*-effects.

Figure 3 illustrates the release of the adsorption and crystallization water from Ni $(H_3L^1)_2 \cdot 2H_2O$  characterized by an *endo*-effect in the temperature range of 65–100 °C with a maximum at 75 °C. Water molecule removal corresponds to two weight loss steps on the TG curve: A (weight loss of 6.83%) and B (weight loss of 4.08%). The total weight loss in this temperature range is 10.91%, which is in good agreement with the calculated data (10.75%). In the temperature range of 180–250 °C, referred to as region C (maximum at 186 °C, endo-effect), decarboxylation of organic ligands occurs together with the release of two CO<sub>2</sub> molecules (experimental weight loss of 21.82%, calculated weight loss of 17.78%). The decarboxylation reaction partially overlaps with the initial decomposition of the organic fragment of the complex (region D, overlap of several exo-effects in the region of 250-450 °C with a maximum at 313 °C). Burnout of organics almost ends at 450 °C. The total weight loss is 82.16%. The solid residue after calcination (17.40%) corresponds to NiO (cal-

Compound	Temperature range/°C, thermal effect	The process stages, solid residue	Weight loss (%)	
			Experiment	Calculation
$\overline{Mn(H_3L^1)_2 \cdot 2H_2O(1)}$	$70-110 (T_{max} = 105), endo$	-2 H <sub>2</sub> O	8.21	8.39
	$150-230 \ (T_{\text{max}} = 192), endo$	$-2 \tilde{CO}_2$	18.89	20.51
	$230-450 \ (T_{\text{max}} = 320), exo$	Removal of organics		
		Solid residue — $Mn_3O_4$	19.23	17.79
$Fe(H_3L^1)_2 \cdot 2H_2O(2)$	125, endo	$-2 H_2 O$	7.87	8.37
	185, endo	$-CO_2$	12.30	10.23
	$200-600 (T_{max} = 334), exo$	Removal of organics		
		Solid residue — $Fe_3O_4$	18.76	17.88
$Co(H_3L^1)_2 \cdot 2H_2O(3)$	$81 - 168 (T_{max} = 160), endo$	$-2 H_2O$	10.75	8.35
	205, endo	-CO	10.05	10.20
	$250-570 (T_{max} = 303), exo$	Removal of organics		
		Solid residue $-Co_3O_4$	17.88	18.63
$Ni(H_3L^1)_2 \cdot 2H_2O$ (4)	75, endo	$-2 H_2O$	10.75	10.91
	$180-250 (T_{max} = 186), endo$	$-2 \tilde{O}_2$	17.78	21.82
	$250-450 (T_{max} = 313), exo$	Removal of organics		
		Solid residue – NiO	17.84	17.40
$Cu(H_3L^1)_2 \cdot 2H_2O$ (5)	120, endo	$-2 H_2O$	7.96	8.22
	205, endo	$-CO_{2}$	11.98	10.04
	$245-420 (T_{max} = 325), exo$	Removal of organics		
		Solid residue — $Cu_2O$	16.57	16.32
$Cu(H_3L^2)_2 \cdot 4H_2O(6)$	$90-125 (T_{max} = 113), endo$	$-2 H_2 O^{2}$	8.15	7.59
	$195-200 (T_{max} = 196), exo$	$-2 H_{2}^{2}O$	6.57	7.59
	$295-500 (T_{max} = 371), exo$	Removal of organics		
		Solid residue — $Cu_2O$	14.78	15.08
$Co(H_3L^2)_2 \cdot 6H_2O(7)$	$80-155 (T_{max} = 132), endo$	-4 H <sub>2</sub> O	14.68	14.26
	$185-200 (T_{max} = 198), exo$	$-2 H_2O$	6.96	7.13
	$280-550 (T_{max} = 365), exo$	Removal of organics		
		Solid residue $-Co_3O_4$	16.78	15.89
$Ni(H_3L^2)_2 \cdot 6H_2O(8)$	$80-120 (T_{max} = 112), endo$	-4 H <sub>2</sub> O	13.28	14.26
	$150-195 (T_{max} = 189), exo$	$-2 H_2 O$	8.74	7.13
	$280-480 (T_{max} = 374), exo$	Removal of organics		
		Solid residue — NiO	14.82	14.79

Table 1. General temperature intervals of thermal decomposition of  $H_4L^1$  and  $H_4L^2$  complexes

culated amount 17.84%). When the sample is heated to a temperature above 800 °C, another weight loss is observed (region *E*), which may be caused by partial dissociation of nickel oxide at high temperatures.

Nanosized metal oxide particles were prepared by calcining the weighed samples of  $H_4L^1$  complex compounds in a muffle furnace at 600 °C for 30 min. Figure 4 shows the X-ray diffraction patterns of the obtained compounds.

The assignment of peaks was performed by using the literature data.<sup>9,16–19</sup> As follows from the analysis of the diffraction patterns, the final products of the thermal decomposition of the  $H_4L^1$  metal complexes are nanosized metal oxides:  $Mn_3O_4$ ,  $Fe_3O_4$  (magnetite), NiO,  $Co_3O_4$ ,  $Cu_2O$ . The average granule size is 35.40, 24.93, 35.00, 11.96, and 19.60 nm, respectively.

The broad diffuse bands at low  $2\theta$  values in the diffraction patterns of iron, manganese, and cobalt oxides is indicative of the presence of an amorphous phase in the samples, apparently related to the decomposition products of the organic part of the precursors.

The morphology of the obtained nanosized oxides (Fig. 5) reveals the formation of a well-developed pore structure with a large surface area.

Thus, eight complex compounds of  $Mn^{II}$ ,  $Fe^{II}$ ,  $Co^{II}$ ,  $Ni^{II}$ , and  $Cu^{II}$  with 2,4,6- and 3,4,5-trihydroxybenzoic acids ( $H_4L^1$  and  $H_4L^2$ , respectively) were isolated and characterized by spectral analysis methods. It was found that the coordination of the  $H_4L^1$  ligand with metal cations is bidentate chelating with the involvement of the oxygen atom of the non-deprotonated carboxyl group and the oxygen atom of the neighboring deprotonated hydroxy group. The  $H_4L^2$  ligand is coordinated by metal cations in a bidentate mode with the participation of a deprotonated carboxyl group. Organic molecules are involved in the structure of metal complexes in the form of monoanions.

A low thermal stability of the  $H_4L^1$  complex compounds, the decomposition of which starts with dehydr-



**Fig. 3.** Thermogravimetric and DSC curves for  $Ni(H_3L^1)_2 \cdot 2H_2O$  complex.



**Fig. 4.** XRD patterns of the products of thermal decomposition of  $Fe(H_3L^1)_2 \cdot 2H_2O(a)$ ,  $Ni(H_3L^1)_2 \cdot 2H_2O(b)$ ,  $Mn(H_3L^1)_2 \cdot 2H_2O(c)$ ,  $Co(H_3L^1)_2 \cdot 2H_2O(d)$ , and  $Cu(H_3L^1)_2 \cdot 2H_2O(e)$  complexes.



Fig. 5. SEM images of NiO powder synthesized by thermal decomposition of Ni $(H_3L^1)_2 \cdot 2H_2O$  complex.

ation and decarboxylation reactions in the temperature range of 70-230 °C, was shown in this work. These compounds were used as precursors for the preparation of metal oxides with particle sizes of 11.96-35.40 nm. The porous structure and a well-developed surface of the formed metal oxide particles makes their efficient application as nanosized oxide catalysts possible.

## **Experimental**

**Electronic absorption spectra** of organic molecules and their complexes in ethanol solution with various pH were measured on a Cary-50 instrument at wevelenths from 200 to 700 nm.

**IR-spectra** were recorded using KBr pallets on a FT-801 spectrometer within the 4000-400 cm<sup>-1</sup> range.

**Thermogravimetric analysis** was carried out on a Netzsch STA 449-F3 instrument in the temperature range of 35-900 °C in air. The samples were heated in Al<sub>2</sub>O<sub>3</sub> crucibles at a rate of 5 °C min<sup>-1</sup>.

The synthesis of the complexes of 2,4,6- and 3,4,5-trihydroxybenzoic acids ( $H_4L^1$  and  $H_4L^2$ , respectively) with iron(II), manganese, cobalt, nickel, and copper cations were carried out in weak alkaline aqueous solutions. The  $H_4L^1$  and  $H_4L^2$  ligands (0.85 g,  $5 \cdot 10^{-3}$  mol) were dissolved in 20 mL of distilled water and the pH of the solutions was adjusted to 8 with a 0.1 M NaOH solution. Then, the obtained solutions were gradually added to vigorously stirred 10 mL aqueous solutions of MnCl<sub>2</sub>, FeSO<sub>4</sub>, CoCl<sub>2</sub>, NiCl<sub>2</sub>, and CuCl<sub>2</sub> (with an amount of the salt of  $5 \cdot 10^{-3}$  mol each). The starting inorganic salts (reagent grade) were used in the form of corresponding crystalline hydrates. The resulting mixtures were heated in a water bath to 60 °C, kept for 20 min at stirring, slowly cooled to ~20 °C, and then stored for 2-3 days before crystallization began. The formed precipitates were isolated from the mother liquor by centrifugation and, if needed, washed with a small amount of distilled water until the filtrate gives a negative reaction for the inorganic cation. The yield of the products was 60-65%. The elemental composition and spectral characteristics of the obtained complexes 1-8 are given below.

Mn(H<sub>3</sub>L<sup>1</sup>)<sub>2</sub>•2H<sub>2</sub>O complex (1). Found (%): C, 39.34; H, 3.07; Mn, 12.74. C<sub>14</sub>H<sub>14</sub>MnO<sub>12</sub>. Calculated (%): C, 39.18; H, 3.29; Mn, 12.80. UV–Vis,  $\lambda_{max}$ /nm (logε): 287 (3.51), 257 (3.84), 217 (4.20). IR, v/cm<sup>-1</sup>: 3185 OH); 1631 (C=O).

**Fe(H<sub>3</sub>L<sup>1</sup>)<sub>2</sub> • 2H<sub>2</sub>O complex(2).** Found (%): C, 39.17; H, 3.67; Fe, 13.08. C<sub>14</sub>H<sub>14</sub>FeO<sub>12</sub>. Calculated (%): C, 39.10; H, 3.28; Fe, 12.98. UV–Vis,  $\lambda_{max}$ /nm (logɛ): 295 (3.48), 257 (4.04), 223 (4.38). IR, ν/cm<sup>-1</sup>: 3230 (OH); 1629 (C=O).

**Co**(H<sub>3</sub>L<sup>1</sup>)<sub>2</sub> • 2H<sub>2</sub>O complex (3). Found (%): C, 39.03; H, 3.64; Co, 13.08. C<sub>14</sub>H<sub>14</sub>CoO<sub>12</sub>. Calculated (%): C, 38.82; H, 3.26; Co, 13.60. UV–Vis,  $\lambda_{max}$ /nm (logε): 340 (3.81), 296 (3.63). IR, v/cm<sup>-1</sup>: 3360 (OH); 1635 (C=O).

Ni(H<sub>3</sub>L<sup>1</sup>)<sub>2</sub> • 2H<sub>2</sub>O complex (4). Found (%): C, 39.11; H, 3.45; Ni, 13.87. C<sub>14</sub>H<sub>14</sub>NiO<sub>12</sub>. Calculated (%): C, 38.84; H, 3.26; Ni, 13.56. UV–Vis,  $\lambda_{max}$ /nm (logε): 395 (3.84), 298 (2.98), 281 (3.00), 257 (3.74). IR, ν/cm<sup>-1</sup>: 3380 (OH); 1638 (C=O).

**Cu**(H<sub>3</sub>L<sup>1</sup>)<sub>2</sub> • 2H<sub>2</sub>O complex (5). Found (%): C, 38.62; H, 3.50; Cu, 14.31. C<sub>14</sub>H<sub>14</sub>CuO<sub>12</sub>. Calculated (%): C, 38.41; H, 3.22; Cu, 14.51. UV–Vis,  $\lambda_{max}$ /nm (logε): 306 (3.17), 262 (3.80), 218 (4.33). IR, ν/cm<sup>-1</sup>: 3330 (OH); 1639 (C=O).

**Cu**(H<sub>3</sub>L<sup>2</sup>)<sub>2</sub> • **4H**<sub>2</sub>O complex (6). Found (%): C, 35.64; H, 3.91; Cu, 13.24. C<sub>14</sub>H<sub>18</sub>CuO<sub>14</sub>. Calculated (%): C, 35.49; H, 3.83; Cu, 13.41. UV–Vis,  $\lambda_{max}$ /nm (loge): 325 (3.65), 261 (3.73), 217 (4.44). IR, v/cm<sup>-1</sup>: 3325 (OH); 1549 (v<sup>as</sup>(COO<sup>-</sup>)), 1425 (v<sup>s</sup>(COO<sup>-</sup>)).

**Co(H<sub>3</sub>L<sup>2</sup>)<sub>2</sub> · 6H<sub>2</sub>O complex (7).** Found (%): C, 33.65; H, 4.95; Co, 11.54. C<sub>14</sub>H<sub>22</sub>CoO<sub>16</sub>. Calculated (%): C, 33.28; H, 4.39; Co, 11.66. UV–Vis,  $\lambda_{max}$ /HM (logε): 348 (3.72), 267 (3.92), 215 (4.36). IR, v/cm<sup>-1</sup>: 3315 (OH); 1548 (v<sup>as</sup>(COO<sup>-</sup>)), 1412 (v<sup>s</sup>(COO<sup>-</sup>)).

**Ni(H<sub>3</sub>L<sup>2</sup>)<sub>2</sub> · 6H<sub>2</sub>O complex (8).** Found (%): C, 33.15; H, 4.97; Ni, 11.45.  $C_{14}H_{22}NiO_{16}$ . Calculated (%): C, 33.30; H, 4.39; Ni, 11.62. UV–Vis,  $\lambda_{max}/nm$  (logɛ): 393 (3.76), 260 (3.72), 216 (4.19). IR, v/cm<sup>-1</sup>: 3370 (OH); 1587 (v<sup>as</sup>(COO<sup>-</sup>)), 1443 (v<sup>s</sup>(COO<sup>-</sup>)). X-ray diffraction patterns of the products of thermal decomposition of complexes 1–8 were collected on a DRON-7 automatic X-ray powder diffractometer for polycrystalline materials in a step scan mode (scan range  $2\theta = 5-60^\circ$ , scan step  $2\theta = 0.02^\circ$ , counting time per data point 3 s). Ni-filtrated Cu-K $\alpha$  radiation ( $\lambda = 1.5418$  Å) was used, the peaks were decomposed into its K $_{\alpha l}$ - and K $_{\alpha 2}$ -components. The patterns were approximated using the pseudo-Voigt function. The refinement was carried out stepwise and monitored using statistical criteria. The diffraction data processing and ensuing calculations were performed using the PDWin software.<sup>20</sup> The average particle sizes (coherent scattering regions (CSRs)) were estimated based on the half-width of diffraction reflexes.<sup>21</sup>

**Micrographs** of the oxide nanoparticles were taken on a VEGA3 TESCAM scanning electron microscope.

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