Complex Compounds of Ti(IV), Ni(II), Cu(II) and Zn(II) with 3-Hydroxypicolinic acid (3-HPA) and 3,5-Dinitrosalicylic acid (3,5-DNSA) as Precursors of Micro- and Nano-sized Oxides

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Abstract

Nine complex compounds of Ti(IV), Ni(II), Cu(II) and Zn(II) with 3-hydroxy picolinic acid (3-HPA) and 3,5dinitrosalicylic acid (3,5-DNSA) of the composition ML₂ (M: Ni²⁺, Cu²⁺ and Zn²⁺; L: 3-HPA and 3,5-DNSA) and TiOL₂ were isolated and studied by spectroscopic methods and X-ray structure analysis. The coordination of 3-HPA with the metals involves the N pyridine atom and an O atom of the neighboring COOH group. For 3,5-DNSA, a chelate cycle is formed with two O atoms of carboxylic and hydroxy-groups. This was proved by X-ray analysis for Cu complexes and UV-VIS and IR spectra of all other complexes in comparison with the exact data for Cu complexes. The introduction of 9,10-phenanthroline prevents the coordination of 3,5-DNSA with Cu, and it acts as a counter-ion. Thermal decomposition of the isolated complexes and their mixtures leads to the formation of micro-sized metal oxides (3-30 μ m) and nano-sized metal(II) titanates (30-100 nm).

Keywords: 3-hydroxypicolinic acid; 3,5-dinitrosalicylic acid; metal complexes; structure; nano-sized oxides

1. INTRODUCTION

Heterogeneous catalysts based on individual and modified transition metal oxides are used in a wide variety of fields of science and technology [1,2] in wastewater and polluted air purification systems from man-made pollutants. Unlike homogeneous systems, they are easily separated from the reaction mixture, do not pollute it, and have a wide pH range for catalytic action. Reducing the size of catalysts to the nanometer scale (from 1 to 100 nm) increases the area of the active surface and thus increases their activity. Such systems also find practical application in various fields of everyday life, such as electronics and materials science [3,4]. The industrial application of nanoparticles is associated with their use as magnetic seals in motors, data carriers, and other fields [5-10].

A promising method for obtaining nanoscale oxide particles is the hydrothermal method, in which inorganic precursors (hydroxides, nitrates, carbonates, oxalates) are precipitated from aqueous solutions followed by calcination [11-15]. The use of organic metal complexes is much more effective since their thermal decomposition releases a large number of gaseous decomposition products (mainly CO₂ and H₂O), which prevent the oxide particles from clumping into large agglomerates and leads to a significant reduction in the grain size of the oxide catalyst and an improvement in their surface properties. From an economic point of view, it is crucial to reduce the temperature and processing time of the precursors while maintaining the physical and chemical characteristics of the resulting catalyst. Therefore, the search for optimal precursors based on cheap raw materials and optimization of ways to obtain nanoscale catalysts are very relevant. Previously, we published synthesis and thermal transformations of complexes of transition metals with several polyhydroxy phenols [16-18]. The present study is devoted to isolation, studies on the structure and properties of complex compounds of 3-hydroxy picolinic acid (**3-HPA**) and 3,5-dinitrosalicylic acid (**3,5-DNSA**) with Ti⁴⁺, Ni²⁺, Cu²⁺ and Zn²⁺, and thermal decomposition of individual complexes and mixtures of Ti-complexes with corresponding complexes of divalent metals and some characteristics of the formed oxide phases and composites.

2. MATERIALS AND METHODS

3-Hydroxypicolinic acid, 3,5-dinitrosalicylic acid (Fig. 1), Ti(OBu)₄ and inorganic salts: NiCl₂· $6H_2O$, CuCl₂· $2H_2O$, and Zn(NO₃)₂· $6H_2O$, were purchased from Merck and Sigma-Aldrich. All reagents of 99% purity are used without further purification.





Electronic absorption spectra of 50% water-ethanol solutions containing organic ligands at various pH values and their titration spectra with aqueous solutions of metal salts were recorded on a Cary-50 spectrophotometer at $22 \pm 1^{\circ}$ C without background electrolyte to establish accurate ionic strength values in the wavelength range 200-450 nm in 1.0cm wide cuvettes. The concentration of the solutions was selected individually for each titration and were values on the order of 10^{-4} mol/L.

FTIR spectra of the samples were recorded using an AVATAR 370 spectrometer (Thermo Nicolet, USA) at a temperature of 20°C in the range of 4000–400 cm⁻¹ with a resolution of 4 cm⁻¹ in KBr pellets.

The X-ray diffraction data for single crystals of Cu(3-HPA)₂ and [Cu(Phen)₂Cl](3,5-DNSA) were collected on the Xcalibur, Eos automated diffractometer at 100.(2) and 150(2) K (k Mo Ka, graphite monochromator, /–x scanning for both). The data were indexed and integrated using the utility iMOSFLM from the CCP4 program suite [19] and then scaled and corrected for absorption using the Scala program [20]. The structure was determined by a direct method and refined by full-matrix least square technique on F2 in anisotropic approximation for non-hydrogen atoms. Other hydrogen atoms were placed in the calculated positions and refined within the riding model with fixed isotropic displacement parameters [Uiso(H) =1.5Ueq(C) for the methyl groups and 1.2Ueq(C) for other groups]. All calculations were carried out using the SHELXTL program suite [21]. The crystallographic data have been deposited with the Cambridge Crystallographic Data Center. The supplementary crystallographic data can be obtained free of charge from the Cambridge Crystallographic Data Center via https://www.ccdc.cam.ac.uk/data_request/cif. The crystal and refinement data for studied compounds are presented in Table (1).

Compound	Cu(3-HPA) ₂	[Cu(Phen) ₂ Cl](3,5-DNSA)	
Chemical formula	$C_{12}H_8CuN_2O_6$	C ₃₁ H ₁₉ ClCuN ₆ O ₇	
Mr	339.74	686.51	
Crystal system, space group	Monoclinic, P 21/c	Triclinic, P-1	
Temperature (K)	100(2)	150(2)	
<i>a, b, c</i> (Å)	6.31760(18), 11.3753(4), 7.9723(2)	7.5150(3), 11.5529(7), 15.8796(9)	
α, β, γ (°)	90, 92.979(3), 90 90.042(5), 90.869(4), 102.		
$V(Å^3)$	572.15(3)	1346.70(13)	
Z	2	2	
Radiation type	MoK\α	MoK\α	
μ (mm ⁻¹)	0.976	0.976	
Crystal size (mm)	0.5x2x4	2x5x7	
Data collection			
Diffractometer	Xcalibur, Eos Xcalibur, Eos		
Absorption correction			
$\theta_{\min}, \theta_{\max}$	3.5710, 28.9750	3.6020, 29.0050	
No. of measured, independent and	2564, 1322, 1081	6198, 5393, 5183	
$\frac{\text{observed } [1 \ge 2\sigma(1)] \text{ reflections}}{p}$	0.0410.0.0207	0.1248.0.1122	
	0.0419, 0.0307	0.1248, 0.1122	
CCDC No		2422153	

Table 1. Experimental details for single crystal determination of Cu(3-HPA)₂ and [Cu(Phen)₂Cl](3,5-DNSA).

X-ray phase analysis of oxide phases obtained after thermal decomposition of complex precursors and conducted using a Tongda TD-3700 X-ray diffractometer (CuK α radiation, Ni filter) at room temperature in the range 20 20-90 deg. The crystallite size was estimated using the Scherrer formula [22] and the Williamson-Hall method [23,24]. The physical broadening was calculated considering the geometric broadening of the device and the type of profile functions. To determine the geometric broadening of the device, pre-annealed at 300°C Si powder was used.

SEM images of the oxide phases and composites were obtained with a TESCAN BRNO-Mira 3 LMU electron microscope.

Synthesis of complex compounds of Ti^{4+} , Ni^{2+} , Cu^{2+} , and Zn^{2+} with 3-HPA and 3,5-DNSA were isolated according to the following procedure. 10 mL ethanol solution containing 1 mmol of 3-HPA or 3,5-DNSA was slowly added to 5 mL aqueous solutions containing 0.5 mmol of corresponding metal chloride or $Ti(OBu)_4$. The formed solutions were stirred continuously for 1 h and then kept in the air. After partial evaporation, powdered metal complexes were precipitated from the solution, filtered off, washed with a small amount of cooled ethanol, and dried in an oven at 100°C until the constant mass. Yields 60-70%.

2.1. Elemental analysis, found/calculated, %:

Ni(3-HPA)₂, M 334.90; C 43.52/43.04; N 8.43/8.36; H 2.80/2.41; Ni 17.87/17.52; Cu(3-HPA)₂, M 339.75; C 42.10/42.42; N 8.53/8.25; H 2.77/2.37; Cu 18.92/18.70; Zn(3-HPA)₂·2H₂O, M 363.61: Zn 17.98/18.23; C 39.64/40.09; N 3.85/3.46; H 3.33/4.12; TiO(3-HPA)₂, M 340.08; C 42.27/42.38; N 8.35/8.24; H 2.64/2.37; Ti 14.38/14.08; Ni(3,5-DNSA)₂, M 512.91; C 32.45/32.78; N 10.98/10.92; H 1.03/1.18; Ni 11.83/11.44; Cu(3,5-DNSA)₂, M 517.77; C 32.06/32.48; N 10.88/10.82; H 1.05/1.17; Cu 12.99/12.27; Zn(3,5-DNSA)₂·2H₂O, M 555.63; C 30.54/30.26; N 9.87/10.08; H 2.04/1/81; Zn 11.43/11.77; TiO(3,5-DNSA)₂, M 518.10; C 33.46/32.46; N 10.96/10.81; H 1.15/1.17; Ti 9.51/9.24.

Plate-like blue single crystals of $Cu(3-HPA)_2$ were isolated at slow evaporation from 50% ethanol-aqueous solution. Green plates of $[Cu(Phen)_2Cl](3,5-DNSA)$ (Phen – 9,10 phenanthroline) were isolated according to the following procedure. 1,10-phenanthrene chloride monohydrate (0.5 mmol, 0.1173 g) in 5 mL ethanol, after neutralization with NaOH in a 1:1 molar ratio. 3,5-Dinitro salicylic acid (0.5 mmol, 0.1140 g) in 5mL ethanol. A mixture of 1,10-phenanthroline and 3,5-dinitro salicylic acid was slowly added to 5 mL aqueous CuCl₂ solution (0.5 mmol, 0.0855 g CuCl₂·2H₂O), stirred continuously for 1 h, and then filtered. X-ray diffraction quality crystals were obtained by slow evaporation. The other studied compounds were isolated as amorphous powders, which could not be examined by X-ray analysis.

3. RESULTS AND DISCUSSION

Two compounds, i.e., $Cu(3-HPA)_2$ and $[Cu(Phen)_2Cl] \cdot (3,5-DNSA)$, were isolated as single crystals and studied by X-ray analysis. The molecular structures of $Cu(3-HPA)_2$ and $[Cu(Phen)_2Cl] \cdot (3,5-DNSA)$ are presented on Fig. 2.



Figure 2. Molecular structures of Cu(3-HPA)₂ (1) and [Cu(Phen)₂Cl]·(3,5-DNSA) (2).

They indicate that in Cu(3-HPA)₂, the 3-HPA ligand acts as bidentate chelate species to coordinate Cu-cation through an N-pyridine atom and an O-atom of a deprotonated COO⁻ group. The CuN(1)O(1)N(1A)O(1A) fragment is planar, the distances CuO(1) 1.9533(18)Å, CuN(1) 1.9684(19) Å, < O(1)CuN(1) 83.93(8) deg. In the lattice, two additional CuO(3B) and CuO(3C) contacts are formed (2.707(1) Å) (Fig. 3). This leads to the formation of the pseudo-octahedral structure of the central ion with elongation of axial bonds. On the contrary, no intermolecular contacts or H-bonds were found in the lattice of [Cu(Phen)₂Cl]·(3,5-DNSA).



Figure 3. Formation of intermolecular contacts in Cu(3-HPA)₂.

The 3,5-DNSA monoanion is not involved in coordination with the Cu atom in the case of $[Cu(Phen)_2Cl] \cdot (3,5-DNSA)$ (Fig. 2 &3-), which explains a minimal shift of v (C=O) compared with non-coordinated 3,5-DNSA. The Cu-N(phenanthroline) bond lengths (2.005(7); 2.019(6); 2.079(7) and 2.079(7) Å) are similar to other previously published papers of mononuclear penta-coordinated Cu complexes with $[CuCl(Phen)_2]^+$ fragment [25-29]. The determination of the crystal structure of Cu-complexes helped us to assign changes in spectral characteristics of the ligands at complexation and to predict the coordination modes of the ligands. The electronic absorption spectra obtained from ethanol solutions of non-coordinated ligands are characterized by long-wave absorption bands in the region of 330 (loge 4.03) for 3-HPA and 340 (loge 4.14) for 3,5-DNSA, respectively. The stepwise addition of aqueous solutions of 3d-metal salts to ethanol solutions of the ligands causes different changes in the spectra (Fig. 4).

A significant bathochromic shift of a long-wave adsorption band of 3-HPA at complexation with Cu (Fig. 1a) may be explained by the involvement of an N-heterocyclic atom of the ligand in coordination and a strong metal-to-ligand electron transition. In the case of other studied metals, the shift is not so significant and is almost neglectable in the case of Ti^{4+} because of the lack of 3d-electrons, which could interact with the ligand. In the case of 3,5-DNSA (Fig. 2a,b), a strong intramolecular H-bond between neighboring COOH and OH groups exists. At complexation, the proton involved in H-bonding is replaced by a metal cation, but the total redistribution of the electronic density does not change a lot, and the position of the adsorption band does not change a lot. The distortion of the chelate ring because of the difference in size of M^{2+} and H atoms causes a partial decrease in the intensity of the long-wave absorption band. The volume of inorganic salts added to 20 mL of the solutions of the ligands was less than 0.2 mL. Thus, the changes in the spectra were not because of dilution or changes in the solvent.

The IR spectra of non-coordinated 3-HPA and 3,5-DNSA are characterized by strong absorption bands, which were assigned to the C=O stretching of carboxylic groups (Table 2). At coordination, they shift to lower frequencies, indicating their involvement in coordination. In the case of $[Cu(Phen)_2Cl] \cdot (3,5-DNSA)$ where according to X-Ray analysis, 3,5-DNSA acts as a counter-ion, the shift of v (C=O) absorption band compared to that of uncoordinated 3,5-DNSA is neglectable.



Figure 4. Changes in the electronic adsorption spectra of ethanol solutions of 3-HPA (1) and 3,5-DNSA (2) at stepwise addition of CuCl₂ (a) and NiCl₂ (b) aqueous solutions.

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Table 2. Position of v (C=O)) adsorption bands (cm ⁻¹) in the FTIR spectra	of 3-HPA, 3,5-DNSA	and their metal
complexes.				

Ligand	Compound	v(C=O)	Ligand	Compound	v(C=O)
Î	3-HPA	1695	HO	3,5-DNSA	1620
	Ni(3-HPA) ₂	1653		Ni(3,5-DNSA) ₂	1605
ОН	Cu(3-HPA) ₂	1645	OH	$Cu(3,5-DNSA)_2$	1600
	Zn(3-HPA) ₂ ·2H ₂ O	1653		$TiO(3,5-DNSA)_2$	1587
∽ он	TiO(3-HPA) ₂	1675	O ₂ N NO ₂	[Cu(Phen) ₂ Cl]·(3,5-DNSA)	1618

Taking into consideration the results of the X-ray analysis of Cu-complexes and comparing them with the spectral characteristics of the complexes isolated in the form of powders we can propose the structures of the isolated compounds (Fig. 5).



Figure 5. The proposed structures of the isolated complexes.

To isolate nano-sized metal oxide particles the samples of complex precursors were heated in air at 700°C for 5 hours to obtain. These optimal conditions were elaborated in our early studies [16]. The formed samples were tested by X-ray powder analysis (Fig. 6) and SEM microscopy (Fig. 7). The Zn complexes are presented here as an example. The results obtained for other divalent metals are similar to those of Zn.



Figure 6. XRD pattern of the samples isolated at the thermal decomposition of Zn(3-HPA)₂·2H₂O (1) and Zn(3,5-DNSA)₂·2H₂O (2).

As it is evident from Fig. (6), the phase composition of the product does not depend on the nature of the complex precursor and is related to zinc oxide ZnO. The particle sizes $3-13 \ \mu m$. In the case of Ti(IV) complexes, the thermal decomposition of all the precursors leads to the formation of the TiO₂ phase (mixture of anatase and rutile modifications) of almost the same sizes.

To decrease the particle size, we calcinated an equimolar mixture of complex compounds of Ni(II) and Zn(II) complexes with the complex of Ti(IV) with the corresponding ligand (3-HPA or 2,3-DNSA). The resulting mixtures presented a composite mixture of the corresponding metal titanate with the additions of anatase and rutile (Fig. 8).



TiO2ZnOZnTiO3 $(l = 30 \ \mu m; d = 0.3 \ \mu m)$ $(l = 50 \ \mu m; d = 0.35 \ \mu m)$ $(l = 200 \ nm; d = 20 \ nm)$ Figure 7. SEM images of TiO2, ZnO and ZnTiO3 samples isolated at thermal decomposition of Zn(3-HPA)2·2H2O, TiO(3-HPA)2 and their 1:1 molar mixture.



Figure 8. XRD pattern of products of thermal decompositions of equimolal ratios of Ni(3-HPA)₂ and TiO(3-HPA)₂ (1); Ni(3,5-DNSA)₂ and TiO(3,5-DNSA)₂ (2); Cu(3-HPA)₂ and TiO(3-HPA)₂ (3).

In the case of Cu-complex, the CuO phase was detected instead of copper titanate. The particle size was detected as 30-100 nm. The almost amorphous X-ray diffraction pattern with diffuse broad peaks of sample 2, obtained by thermal decomposition of a mixture containing complex precursors of nickel(II) and titanium(IV) with 3,5-DNSA which is prone to detonation, indicates high dispersion compared to samples 1 and 3 based on complex precursors with 3-HPA. **CONCLUSION**

Nine complex compounds of Ti(IV), Ni(II), Cu(II), and Zn(II) with 3-hydroxy picolinic acid (3-HPA) and 3,5-dinitro salicylic acid (3,5-DNSA) were isolated, and studied by UV-VIS, FTIR spectroscopy, and X-ray structure analysis. The similarity of the character of changes in IR and UV-VIS spectra of the complexes isolated in the form of powders with those of single crystalline samples helped to predict the coordination modes of the ligands. It was established that coordination of 3-HPA with the metals involves the N pyridine atom and an O atom of the neighboring COOH group. For 3,5-DNSA, a chelate cycle is formed with two O atoms of carboxylic and hydroxy-groups. The introduction of 9,10-phenanthroline prevents the coordination of 3,5-DNSA with Cu, and it acts as a counter-ion. Thermal decomposition of the isolated complexes and their mixtures leads to the formation of micro-sized metal oxides (3-30 µm) and nano-sized needle-like metal(II) titanates (20-200 nm).

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References

- 1. J. D. Aiken, R. G. Finke, J. Mol. Cat. A. 145, 1-44, (1999).
- 2. X. Q. Li, L. P. Zhou, J. Gao, H. Miao, H. Zhang, J. Xu, Power Technol. 190, 324-326, (2009).
- 3. Z. B. Huang, Y. Zhu, S. T. Wang, G. F. Yin, Cryst. Growth Des. 6, 1931-1935, (2006).

- 4. S. Manna, A. K. Deb, J. Jagannath, S. K. De, J. Phys. Chem. 112, 10659-10662, (2008).
- 5. X. W. Lou, D. Deng, J. Y. Lee, J. Feng, L. A. Archer, Adv. Mater. 20, 258-262, (2008).
- 6. R. Siriwardane, H. J. Tian, G. Richards, T. Simonyi, J. Poston, Energy Fuels. 23, 3885-3892, (2009).
- 7. S. Rackauskas, A. G. Nasibulin, H. Jiang, Y. Tian, V. I. Kleshch, J. Sainio, E. D. Obraztsova, S. N. Bokova, A. N. Obraztsov, E. I. Kauppinen, *Nanotechnol.* 20, 165603, (2009).
- 8. Q. J. Yu, X. H. Ma, Z. Lan, M. Z. Wang, C. J. Yu, J. Phys. Chem. 113, 6969-6975, (2009).
- 9. H. Kung, T. Foeke, MRS Bull. 24, 14-19, (1999).
- 10. H. Hahn, J. Logas, R. S. Averback, J. Mater. Res. 5, 609-614, (1990).
- 11. Y. C. Zhou, M. N. Rahaman, J. Mater. Res. 8, 1680-1686, (1993).
- 12. J. Tartaj, J. Zarate, P. Tartaj, E. E. Lachowski, Adv. Eng. Mater. 4, 17-21, (2002).
- 13. G. Oskam, J. Sol-Gel Sci. Techn. 37, 161-164, (2006).
- 14. Husen, M. Iqbal, Nanomaterials and Plant Potential. 3-29, (2019).
- 15. M. Negrescu, M. S. Killian, S. N. V. Raghu, P. Schmuki, A. Mazare, A. Cimpean, J. Funct. Biomater. 13, 274, (2022).
- 16. Y. Absalan, M. A. Ryabov, O. V. Kovalchukova, Mater. Sci. Eng. C97, 813-826, (2019).
- 17. Y. Absalan, I. G. Bratchikova, O. V. Kovalchukova, J. Molec. Liq. 268, 882-894, (2018).
- 18. Y. Absalan, R. Alabada, M. Ryabov, V. Tolstoy, L. Butusov, V. Nikolskiy, V. Kopylov, M. Gholizadeh, O. Kovalchukova, *Envir. Nanotechnol. Monitoring & Management.* 14, 100304, (2020).
- 19. T. G. G. Battye, L. Kontogiannis, O. Johnson, H. R. Powell, A. G. Leslie, *Acta Crystallogr. D Biol. Crystallogr.* 67, 271-281, (2011).
- 20. P. Evans, Acta Crystallogr. D Biol. Crystallogr. 62, 72-82, (2006).
- 21. G. M. Sheldrick, Acta Crystallogr. C, Struct. Chem. 71, 3-8, (2015).
- 22. K. Singh (ed.). Advanced X-ray Techniques in Research and Industries. Ios Pr Inc. (2005).
- 23. S. Devesa, A. P. Rooney, M.P. Graça, D. Coope, L. C. Costa, Mater. Sci. Eng. B. 263,114830, (2021).
- 24. Y.T. Prabhu, K.V. Rao, V. S. S. Kumar, B. S. Kumari, J. Nano Sci. Eng. 4, 43743, (2014).
- 25. J. A. Rusanova, O. V. Kozachuk, V. V. Dyakonenko, Acta Cryst. E 69, 4976-4978, (2013).
- 26. H. I. Buvailo, J. A. Rusanova, V. G. Makhankova, V. N. Kokozay, R. I. Zubatyuk, Acta Cryst. E 70, 147-148, (2014).
- 27. K. Petrovič, I. Potočňák, K. Ráczová, E. Čižmár, M. Petrovič, Trans. Met. Chem. 40, 541-553, (2015).
- 28. T. Q. Shi, D. S. Liu, G. P. Zhou, S. F. Liu, Acta Cryst. E 63, 950-952, (2007).
- 29. X. Q. Du, M. L. Zhu, F. Gao, Acta Cryst. E 62, 363-365, (2006).

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