

# Solvothermally derived $\text{Me}_2(\text{H}_2\text{O})_4(5\text{SSA})_3\cdot\text{DMF}$ and $\text{Me}_2(\text{H}_2\text{O})_4(4\text{NSA})_2\cdot\text{DMF}$ : Application as Biginelli reaction catalysts

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The solvothermal synthesis between  $\text{Me}(\text{NO}_3)_x \cdot \gamma\text{H}_2\text{O}$  ( $\text{Me}^{x+} = \text{Fe}^{3+}, \text{Ni}^{2+}, \text{Mn}^{2+}, \text{Co}^{2+}, \text{Cu}^{2+}$ ) and respectively 4-nitrosalicylic (4NSA) and 5-sulfosalicylic (5SSA) acids produced hybrid organic-inorganic compounds composed of  $\text{Me}^{x+}$  ions and organic fragments which include three different functional groups, carboxylic, hydroxyl and sulfonic, each coordinated to the  $\text{Me}^{x+}$  ions. The phase and chemical composition, microstructure and properties of  $\text{Me}_2(\text{H}_2\text{O})_4(5\text{SSA})_3\cdot\text{DMF}$  and  $\text{Me}_2(\text{H}_2\text{O})_4(4\text{NSA})_2\cdot\text{DMF}$  (DMF – dimethylformamide) hybrid compounds were evaluated and discussed. The synthesised materials were characterised by X-ray diffraction (XRD) analysis, scanning electron microscopy (SEM) and nuclear magnetic resonance (NMR) spectroscopy. The catalytic properties of the obtained compounds were also investigated.

**Keywords:** solvothermal synthesis, hybrid organic-inorganic compounds, Biginelli reaction, catalytic activity

## INTRODUCTION

The assembly of multifunctional ligands with metal ions is currently of great interest due to their use in constructing two- and three-dimensional polymers with special properties, such as electrical conductivity, magnetism, host-guest chemistry, catalysis and luminescence [1–4]. Reactions of  $\text{Me}^{x+}\text{NO}_3 \cdot \gamma\text{H}_2\text{O}$  ( $\text{Me}^{x+} = \text{Fe}^{3+}, \text{Ni}^{2+}, \text{Mn}^{2+}, \text{Co}^{2+}$ ) with respectively 4-nitrosalicylic (4NSA) and 5-sulfosalicylic (5SSA)

acids [5] produced hybrid organic-inorganic compounds. One of the most commonly used synthesis methods of hybrid organic-inorganic compounds is the solvothermal synthesis, which is less harmful to the environment. This method is ideal for the synthesis of solid-state compounds such as organic hybrid and inorganic hybrid materials. The solvothermal synthesis method is defined as a heterogeneous reaction in the presence of aqueous or organic solvents under high pressure and temperature to dissolve and crystallise materials which are insoluble under normal conditions [6–9].

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The Biginelli reaction discovered by Pietro Biginelli in 1891 [10–12] is the acid-catalysed reaction between aldehyde,  $\beta$ -ketoester and urea constitutes yielding dihydropyrimidones. Originally, this reaction was conducted by refluxing a mixture of benzaldehyde, ethyl acetoacetate and urea in ethanol in the presence of HCl as a catalyst. These compounds, also called ‘Biginelli compounds’, are interesting materials with a potential for pharmaceutical application. The first step in the reaction mechanism (see Fig. 1) is believed to be the condensation between aldehyde and urea. The iminium intermediate generated acts as an electrophile for the nucleophilic addition of ketoester enol and the ketone carbonyl of the resulting adduct undergoes condensation with the urea  $-NH_2$  to give the cyclised product.

$Me_2(H_2O)_4(5SSA)_3 \cdot DMF$  and  $Me_2(H_2O)_4(4NSA)_2 \cdot DMF$  compounds are possibly acting as Brønsted or Lewis [13] catalysts, donating protons. Proceeding along our research in this area we report here the solvothermal synthesis of hybrid organic-inorganic compounds of  $Fe^{3+}$ ,  $Ni^{2+}$ ,  $Mn^{2+}$ ,  $Co^{2+}$  and  $Cu^{2+}$  ions with 4-nitrosalicylic (4NSA) and 5-sulphosalicylic (5SSA) acids, and the efficient use of

the obtained materials as catalysts in the Biginelli reaction.

## EXPERIMENTAL

Metal nitrate salts, 5-sulphosalicylic acid (5SSA), 4-nitrosalicylic acid (4NSA) *N,N*-dimethylformamide and 2-isopropanol were purchased from Aldrich and Merck and used directly without further purification.

For the synthesis of  $Me_2(H_2O)_4(5SSA)_3 \cdot DMF$ , 0.015 mol of metal ( $Fe^{3+}$ ,  $Ni^{2+}$ ,  $Mn^{2+}$ ,  $Co^{2+}$ ,  $Cu^{2+}$ ) nitrate was added to 60 ml of DMF/ $H_2O$  (1/1 v/v) solution and mixed for 30 min at  $50^\circ C$ . 0.0075 mol of 5SSA added afterwards continues mixing for 15 min at the same temperature. The resulted solution was poured into an autoclave vessel and heated for 24 h at  $120^\circ C$ . The synthesis scheme of  $Me_2(H_2O)_4(5SSA)_3 \cdot DMF$  hybrid organic-inorganic compound is presented in Fig. 2. The reaction solution was filtered and shiny crystals ( $Ni^{2+}$ ,  $Co^{2+}$ ,  $Cu^{2+}$ ) or fine powders ( $Fe^{3+}$ ,  $Mn^{2+}$ ) were obtained. Crystals or powders were immersed in 2-propanol and the residual of DMF/ $H_2O$  solvent was removed.

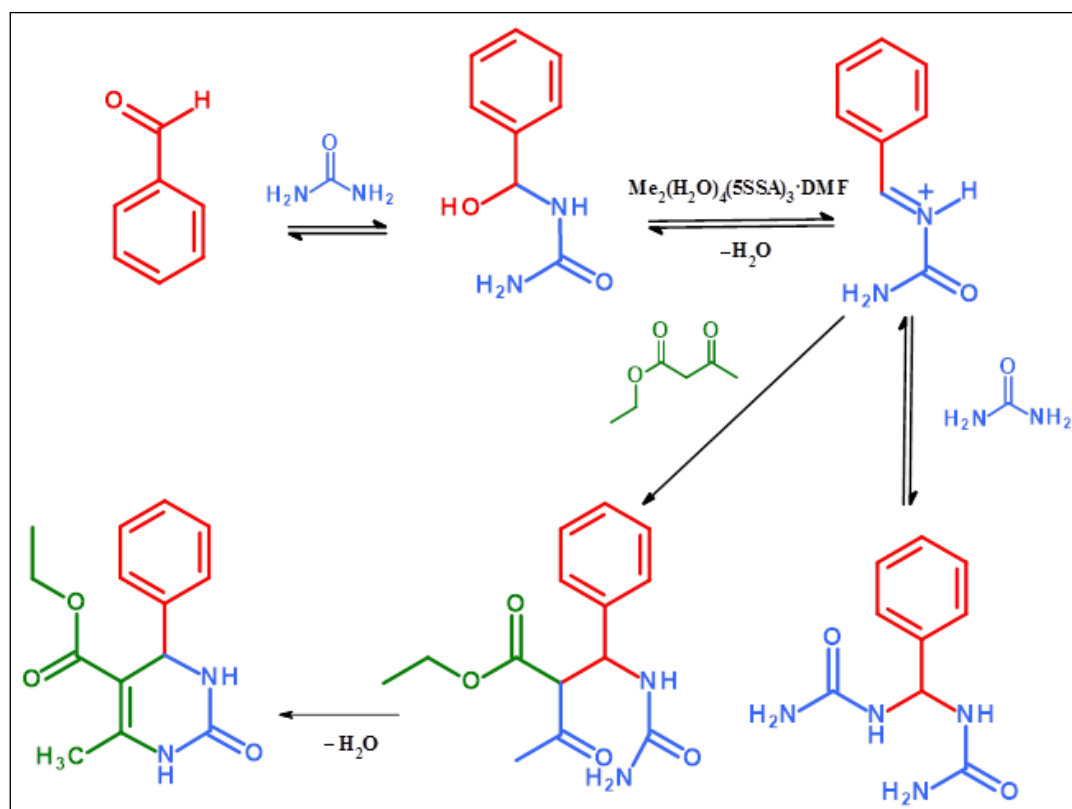
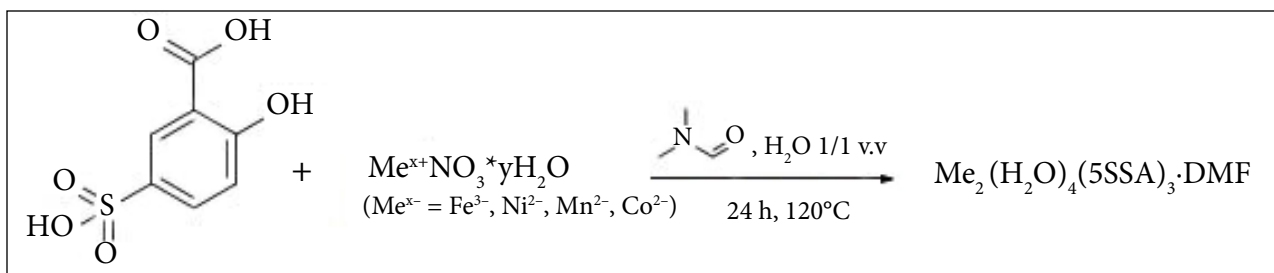


Fig. 1. The proposed Biginelli reaction mechanism [7]



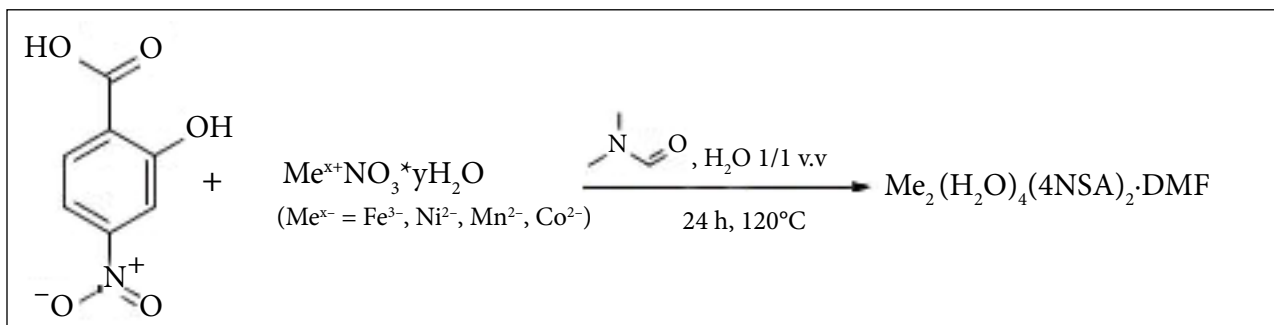
**Fig. 2.** The synthesis scheme of  $\text{Me}_2(\text{H}_2\text{O})_4(5\text{SSA})_3\cdot\text{DMF}$  organic-inorganic hybrid

A similar procedure as for  $\text{Me}_2(\text{H}_2\text{O})_4(5\text{SSA})_3\cdot\text{DMF}$  was used for the synthesis of  $\text{Me}_2(\text{H}_2\text{O})_4(4\text{NSA})_2\cdot\text{DMF}$ . Instead of 5SSA ligand 0.0075 mol of 4NSA was used. The synthesis scheme of  $\text{Me}_2(\text{H}_2\text{O})_4(4\text{NSA})_2\cdot\text{DMF}$  hybrid organic-inorganic compound is presented in Fig. 3.

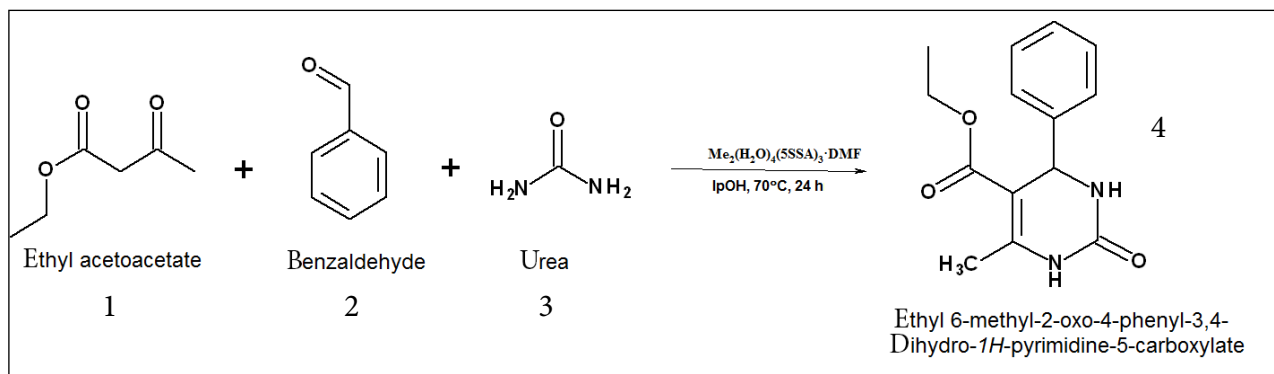
For the synthesis of ethyl 6-methyl-2-oxo-4-phenyl-3,4-dihydro-1H-pyrimidine-5-carboxylate, ethyl acetoacetate (10 mmol) (1), benzaldehyde (10 mmol) (2), urea (10 mmol) (3) and  $\text{Me}_2(\text{H}_2\text{O})_4(5\text{SSA})_3\cdot\text{DMF}$  or  $\text{Me}_2(\text{H}_2\text{O})_4(4\text{NSA})_2\cdot\text{DMF}$  (3 mol%) were mixed by stirring the mixture for 24 h at 80°C. The synthesis scheme of ethyl 6-methyl-2-oxo-4-phenyl-3,4-dihydro-1H-pyrimidine-

5-carboxylate is shown in Fig. 4. The ratio of reagents 1:2:3 was 10:10:10 (mmol). The experiment was performed at reflux conditions in the presence of 2-propanol (12 mL). After the completion of the reaction (monitored by thin layer chromatography), the catalyst was separated from the reaction mixture by filtration and then the liquid part was poured into ice cold water. The obtained solid product was filtered and dried. The crude product was purified by recrystallisation in methanol.

X-ray diffraction (XRD) data were collected in the range of  $20 \leq 2\theta \leq 70$  using Ni-filtered Cu K $\alpha$  radiation on a Rigaku MiniFlex II diffractometer working in Bragg-Brentano ( $\theta/2\theta$ ) geometry.



**Fig. 3.** The synthesis scheme of  $\text{Me}_2(\text{H}_2\text{O})_4(4\text{NSA})_2\cdot\text{DMF}$  organic-inorganic hybrid



**Fig. 4.** The synthesis scheme of ethyl 6-methyl-2-oxo-4-phenyl-3,4-dihydro-1H-pyrimidine-5-carboxylate

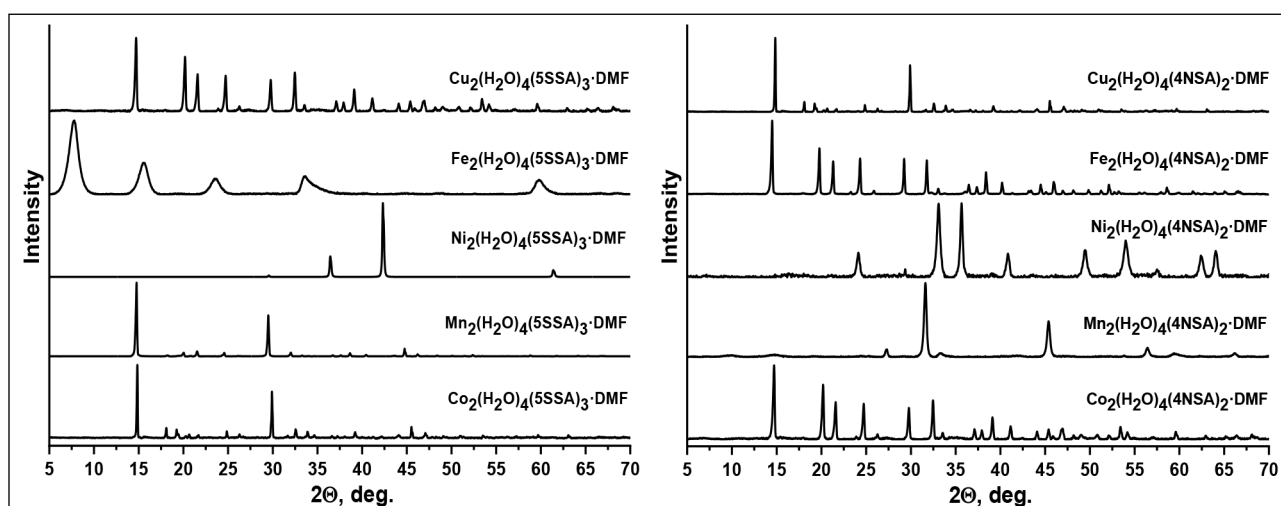
The step width and integration time were 0.02 and 1 s, respectively. The morphology of the final powders was characterised by scanning electron microscopy performed with Hitachi Tabletop Microscope TM3000 scanning electronic microscopes (SEM).  $^1\text{H}$  NMR and  $^{13}\text{C}$  spectra were recorded on a Bruker Ascend 400 spectrometer operating at 9.4 Tesla, corresponding to the resonance frequency of 400 MHz for the  $^1\text{H}$  nucleus, equipped with a direct detection four nuclei probe head and field gradients on the z axis. The samples were analysed in 5 mm NMR tubes.

## RESULTS AND DISCUSSION

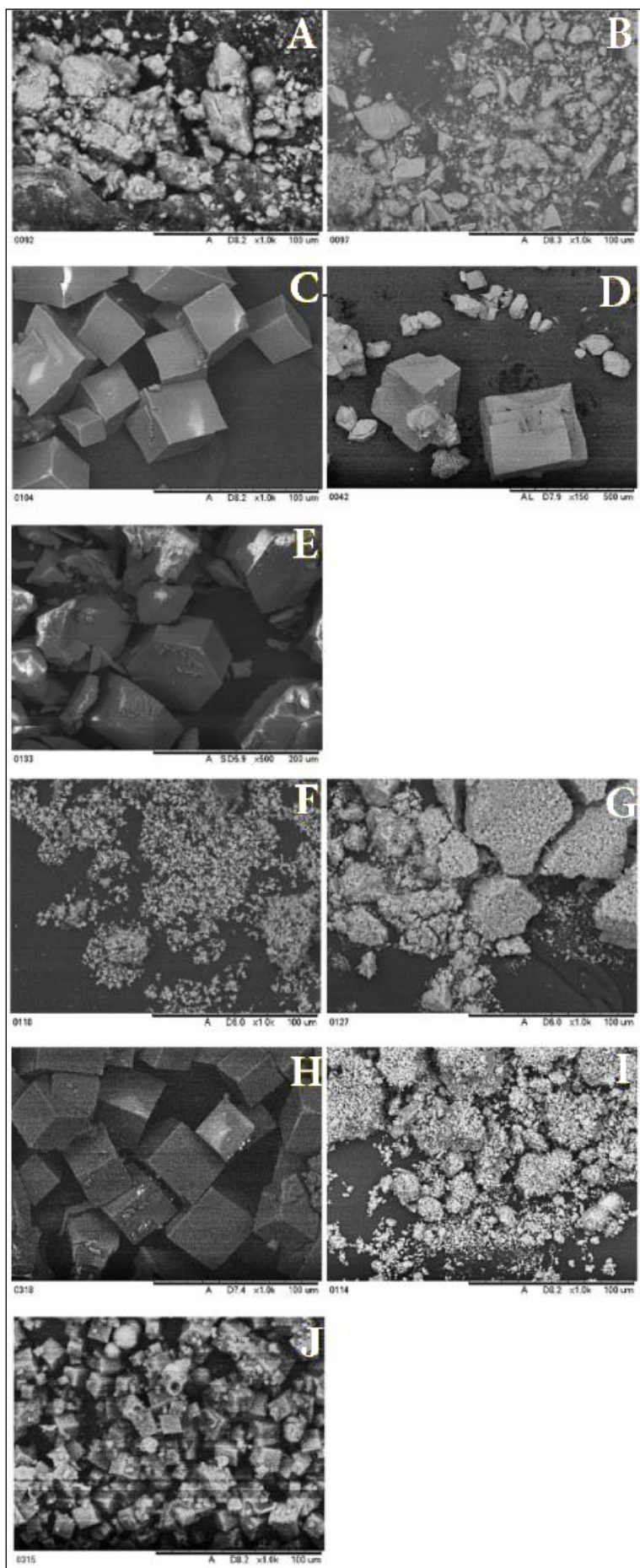
The solvothermal synthesis of hybrid organic-inorganic compounds yielded small crystals or fine powders insoluble in non-polar solvents [14, 15]. Slightly acidic or basic solutions tend to destroy hybrid structure yielding metal salts. As was expected, methanol and ethanol tend to dissolve hybrid organic-inorganic compounds without destruction of the crystalline structure [16]. The powder X-ray diffraction analysis (see Fig. 5) of the synthesised samples indicates the formation of single phase materials and a good crystallinity with the exception of formation of partially amorphous  $\text{Fe}_2(\text{H}_2\text{O})_4(5\text{SSA})_3\cdot\text{DMF}$ . As one can see, the hybrid organic-inorganic compounds obtained with 4NSA are high crystalline materials. The hybrid organic-inorganic compounds with 5SSA also display a moderate crystallinity with the exception of partially amorphous

$\text{Fe}_2(\text{H}_2\text{O})_4(5\text{SSA})_3\cdot\text{DMF}$ . The formation of amorphous intermediates or the end products is rather unusual in the common synthesis of such type compounds [17–19].

The morphological data of  $\text{Me}_2(\text{H}_2\text{O})_4(5\text{SSA})_3\cdot\text{DMF}$  and  $\text{Me}_2(\text{H}_2\text{O})_4(4\text{NSA})_2\cdot\text{DMF}$  samples gathered from SEM micrographs reveal differences in particle size and shape (see Fig. 6 and Table 1). The microstructure of  $\text{Ni}_2(\text{H}_2\text{O})_4(4\text{NSA})_2\cdot\text{DMF}$  and  $\text{Fe}_2(\text{H}_2\text{O})_4(4\text{NSA})_2\cdot\text{DMF}$  samples is very similar. The solids are composed of different size (from 5 to 40  $\mu\text{m}$ ) plate-like crystals. However, almost regular cubes were formed in the case of Mn and Co analogues [20]. In the case of  $\text{Cu}_2(\text{H}_2\text{O})_4(4\text{NSA})_2\cdot\text{DMF}$ , the hexagonally shaped solids in size similar to  $\text{Mn}_2(\text{H}_2\text{O})_4(4\text{NSA})_2\cdot\text{DMF}$  and  $\text{Co}_2(\text{H}_2\text{O})_4(4\text{NSA})_2\cdot\text{DMF}$  cubes were formed [21]. When 5-sulfosalicylic (5SSA) acid was used as a ligand, similar regular cubes were formed in the case of  $\text{Mn}_2(\text{H}_2\text{O})_4(5\text{SSA})_3\cdot\text{DMF}$ .  $\text{Cu}_2(\text{H}_2\text{O})_4(5\text{SSA})_3\cdot\text{DMF}$  was also composed of cubic crystallites, however, much smaller in size (5–10  $\mu\text{m}$ ). The plate-like crystals, however, were not formed when 5SSA was used. The  $\text{Fe}_2(\text{H}_2\text{O})_4(5\text{SSA})_3\cdot\text{DMF}$  solids are composed of homogeneously-distributed nanosized (less than 10 nm) spherically-shaped crystallites. A similar microstructure was observed also for the  $\text{Co}_2(\text{H}_2\text{O})_4(5\text{SSA})_3\cdot\text{DMF}$  sample. In this case, however, these nanoparticles show a tendency to form agglomerates. Even larger agglomerates were formed during the synthesis of  $\text{Ni}_2(\text{H}_2\text{O})_4(5\text{SSA})_3\cdot\text{DMF}$  specimens. Interestingly,



**Fig. 5.** The XRD patterns of  $\text{Me}_2(\text{H}_2\text{O})_4(5\text{SSA})_3\cdot\text{DMF}$  (left) and  $\text{Me}_2(\text{H}_2\text{O})_4(4\text{NSA})_2\cdot\text{DMF}$  (right) samples



**Fig. 6.** SEM micrographs of  $\text{Me}_2(\text{H}_2\text{O})_4(4\text{NSA})_2\text{-DMF}$ ;  $\text{Me}^{3+} = \text{Fe}^{3+}$  (A),  $\text{Ni}^{2+}$  (B),  $\text{Mn}^{2+}$  (C),  $\text{Co}^{2+}$  (D),  $\text{Cu}^{2+}$  (E); and  $\text{Me}_2(\text{H}_2\text{O})_4(5\text{SSA})_3\text{-DMF}$ ;  $\text{Me}^{3+} = \text{Fe}^{3+}$  (F),  $\text{Ni}^{2+}$  (G),  $\text{Mn}^{2+}$  (H),  $\text{Co}^{2+}$  (I),  $\text{Cu}^{2+}$  (J)

Table 1. The morphological features of synthesised  $\text{Me}_2(\text{H}_2\text{O})_4(\text{4NSA})_2\cdot\text{DMF}$  and  $\text{Me}_2(\text{H}_2\text{O})_4(\text{5SSA})_3\cdot\text{DMF}$  hybrid materials

Sample	Crystallite/particle shape	Average size, $\mu\text{m}$
$\text{Fe}_2(\text{H}_2\text{O})_4(\text{5SSA})_3\cdot\text{DMF}$	Spherical particles	<0.01
$\text{Ni}_2(\text{H}_2\text{O})_4(\text{5SSA})_3\cdot\text{DMF}$	Spherical nanoparticles forming aggregates	8–10
$\text{Mn}_2(\text{H}_2\text{O})_4(\text{5SSA})_3\cdot\text{DMF}$	Cubic crystallites	41–44
$\text{Co}_2(\text{H}_2\text{O})_4(\text{5SSA})_3\cdot\text{DMF}$	Spherical particles forming aggregates	0.8–1.1
$\text{Cu}_2(\text{H}_2\text{O})_4(\text{5SSA})_3\cdot\text{DMF}$	Cubic crystallites	5–10
$\text{Fe}_2(\text{H}_2\text{O})_4(\text{4NSA})_2\cdot\text{DMF}$	Plate-like crystallites	5–41
$\text{Ni}_2(\text{H}_2\text{O})_4(\text{4NSA})_2\cdot\text{DMF}$	Plate-like crystallites	18–32
$\text{Mn}_2(\text{H}_2\text{O})_4(\text{4NSA})_2\cdot\text{DMF}$	Cubic crystallites	35–38
$\text{Co}_2(\text{H}_2\text{O})_4(\text{4NSA})_2\cdot\text{DMF}$	Cubic crystallites	261–268
$\text{Cu}_2(\text{H}_2\text{O})_4(\text{4NSA})_2\cdot\text{DMF}$	Hexagonal crystallites	45–60

the morphology of these  $\text{Ni}_2(\text{H}_2\text{O})_4(\text{5SSA})_3\cdot\text{DMF}$  agglomerates could be on the transformation to a hexagonal microstructure stage [22]. The morphological features of the synthesised hybrid materials are summarised in Table 1. Interestingly, only the manganese containing hybrids synthesised with different ligands (5SSA and 4NSA) show almost identical morphology and are composed of cubic crystallites in both of the cases.

The  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of the synthesised Biginelli compounds are presented in Fig. 7. The NMR analysis data clearly revealed that the pure product (ethyl 6-methyl-2-oxo-4-phenyl-3,4-dihydro-1*H*-pyrimidine-5-carboxylate) could be synthesised from benzaldehyde, ethyl acetoacetate and urea using the coordination polymers as reaction catalysts. The spectral data of the obtained Biginelli product (ethyl 6-methyl-2-oxo-4-phenyl-3,4-dihydro-1*H*-pyrimidine-5-carboxylate) are the following:  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) = 8.26 (s, 1H), 7.37–7.28 (m, 5H), 5.83 (s, 1H), 5.44–5.39 (m, 1H), 4.09 (qd,  $J = 7.1, 2.1$  Hz, 2H), 2.36 (d,  $J = 0.9$  Hz, 3H), 1.18 (t,  $J = 7.1$  Hz, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) = 165.65, 146.35, 143.74, 128.71, 127.95, 126.61, 101.34, 77.36, 77.04, 76.72, 60.02, 55.74, 30.95, 18.67, 14.15. FTIR:  $\text{cm}^{-1}$  3241, 3113, 1727, 1711, 1656.

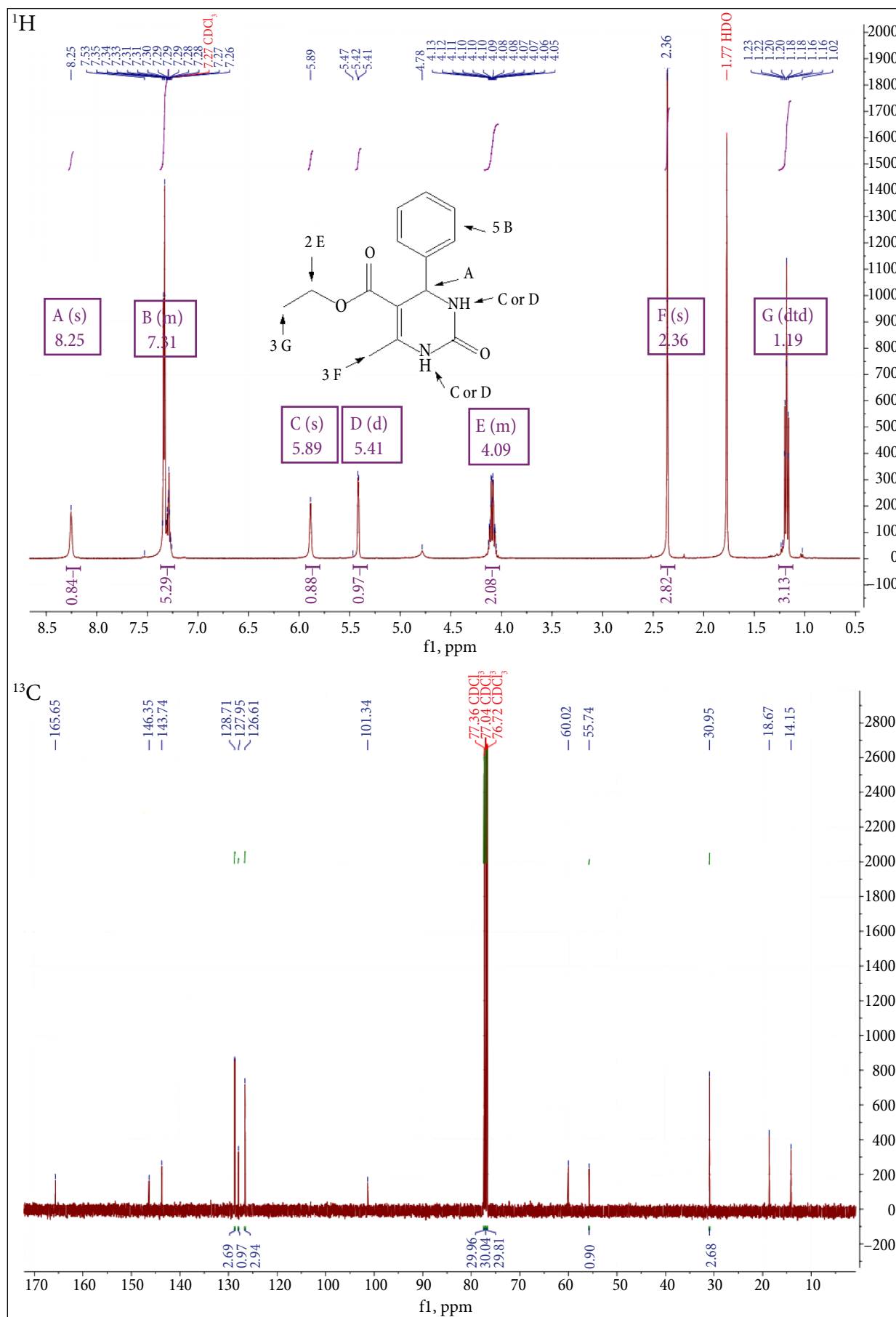
The yields of the products of heterogeneous catalysis using the synthesised hybrid organic-inorganic compounds are displayed in Table 2. As seen, the  $\text{Ni}_2(\text{H}_2\text{O})_4(\text{5SSA})_3\cdot\text{DMF}$  and  $\text{Cu}_2(\text{H}_2\text{O})_4(\text{4NSA})_2\cdot\text{DMF}$  catalysts yielded

a higher conversion ratio than Mn, Fe and Co analogues. Surprisingly, the most effective catalysts  $\text{Cu}_2(\text{H}_2\text{O})_4(\text{4NSA})_2\cdot\text{DMF}$  and  $\text{Ni}_2(\text{H}_2\text{O})_4(\text{5SSA})_3\cdot\text{DMF}$  for the Biginelli reaction have showed a slightly different surface microstructure from other studied hybrid materials.  $\text{Cu}_2(\text{H}_2\text{O})_4(\text{4NSA})_2\cdot\text{DMF}$  was composed of hexagonal crystallites and  $\text{Ni}_2(\text{H}_2\text{O})_4(\text{5SSA})_3\cdot\text{DMF}$  agglomerates showed an evident tendency of transformation to hexagonal crystallites. Therefore, we can conclude that the catalytic activity of the synthesised hybrid organic-inorganic compounds was very dependent on the surface microstructure of these hybrid materials. The possible defects in the structure also could create open sites and increase catalytic activity [23]. Since the catalysts are heterogeneous, they could be recycled for at least several times [24].

Table 2. The results obtained for the Biginelli reactions of benzaldehyde with ethyl acetoacetate and urea

Catalyst	Yield, %
$\text{Mn}_2(\text{H}_2\text{O})_4(\text{4NSA})_2\cdot\text{DMF}$	1.5%
$\text{Mn}_2(\text{H}_2\text{O})_4(\text{5SSA})_3\cdot\text{DMF}$	4%
$\text{Fe}_2(\text{H}_2\text{O})_4(\text{4NSA})_2\cdot\text{DMF}$	13%
$\text{Fe}_2(\text{H}_2\text{O})_4(\text{5SSA})_3\cdot\text{DMF}$	20%
$\text{Co}_2(\text{H}_2\text{O})_4(\text{5SSA})_3\cdot\text{DMF}$	21%
$\text{Co}_2(\text{H}_2\text{O})_4(\text{4NSA})_2\cdot\text{DMF}$	24%
$\text{Cu}_2(\text{H}_2\text{O})_4(\text{5SSA})_3\cdot\text{DMF}$	28%
$\text{Ni}_2(\text{H}_2\text{O})_4(\text{4NSA})_2\cdot\text{DMF}$	40%
$\text{Cu}_2(\text{H}_2\text{O})_4(\text{4NSA})_2\cdot\text{DMF}$	74%
$\text{Ni}_2(\text{H}_2\text{O})_4(\text{5SSA})_3\cdot\text{DMF}$	76%





**Fig. 7.** The NMR spectra of synthesised Biginelli compounds: <sup>1</sup>H NMR (top) and <sup>13</sup>C (bottom)

## CONCLUSIONS

Hybrid organic-inorganic compounds  $\text{Me}_2(\text{H}_2\text{O})_4(5\text{SSA})_3\cdot\text{DMF}$  and  $\text{Me}_2(\text{H}_2\text{O})_4(4\text{NSA})_2\cdot\text{DMF}$  were prepared by solvothermal synthesis using reactions between metal ( $\text{Fe}^{3+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Co}^{2+}$  and  $\text{Cu}^{2+}$ ) nitrates and 4-nitrosalicylic (4NSA) and 5-sulfosalicylic (5SSA) ligands. The XRD analysis revealed that all samples displayed a good crystallinity with the exception of  $\text{Fe}_2(\text{H}_2\text{O})_4(5\text{SSA})_3\cdot\text{DMF}$  which was partially amorphous. The SEM micrographs revealed differences in the particle size and crystallite shape of the obtained hybrid materials. The  $\text{Ni}_2(\text{H}_2\text{O})_4(4\text{NSA})_2\cdot\text{DMF}$  and  $\text{Fe}_2(\text{H}_2\text{O})_4(4\text{NSA})_2\cdot\text{DMF}$  samples were composed of different size (from 5 to 40  $\mu\text{m}$ ) plate-like crystals. However, almost regular cubes were formed in the case of the  $\text{Mn}_2(\text{H}_2\text{O})_4(4\text{NSA})_2\cdot\text{DMF}$  and  $\text{Co}_2(\text{H}_2\text{O})_4(4\text{NSA})_2\cdot\text{DMF}$  samples analogues. The hexagonally shaped solids of  $\text{Cu}_2(\text{H}_2\text{O})_4(4\text{NSA})_2\cdot\text{DMF}$ , however, were formed. In the case of manganese, similar regular cubes were formed when 5-sulfosalicylic (5SSA) acid was used as a ligand.  $\text{Cu}_2(\text{H}_2\text{O})_4(5\text{SSA})_3\cdot\text{DMF}$  MOFs were also composed of cubic crystallites, however, much smaller in size (5–10  $\mu\text{m}$ ). The  $\text{Fe}_2(\text{H}_2\text{O})_4(5\text{SSA})_3\cdot\text{DMF}$ ,  $\text{Co}_2(\text{H}_2\text{O})_4(5\text{SSA})_3\cdot\text{DMF}$  and  $\text{Ni}_2(\text{H}_2\text{O})_4(5\text{SSA})_3\cdot\text{DMF}$  solids were composed of homogeneously-distributed nanosized (less than 10 nm) spherically-shaped crystallites with a different tendency to form agglomerates. The  $\text{Ni}_2(\text{H}_2\text{O})_4(5\text{SSA})_3\cdot\text{DMF}$  agglomerates showed an evident tendency of transformation to hexagonal crystallites. The solvothermally derived  $\text{Me}_2(\text{H}_2\text{O})_4(5\text{SSA})_3\cdot\text{DMF}$  and  $\text{Me}_2(\text{H}_2\text{O})_4(4\text{NSA})_2\cdot\text{DMF}$  hybrid organic-inorganic compounds were investigated as catalysts in the Biginelli reaction. It was demonstrated that  $\text{Ni}_2(\text{H}_2\text{O})_4(5\text{SSA})_3\cdot\text{DMF}$  and  $\text{Cu}_2(\text{H}_2\text{O})_4(4\text{NSA})_2\cdot\text{DMF}$  catalysts yielded a higher conversion ration than Mn, Fe and Co analogues. In conclusion, the catalytic activity of the synthesised hybrid organic-inorganic compounds was influenced by the surface microstructure of these hybrid materials.

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**SOLVOTERMIŠKAI SUSINTETINTI  
 $\text{Me}_2(\text{H}_2\text{O})_4(5\text{SSA})_3 \cdot \text{DMF}$  IR  
 $\text{Me}_2(\text{H}_2\text{O})_4(4\text{NSA})_2 \cdot \text{DMF}$ : PANAUDOJIMAS  
BIGINELLI REAKCIJOS KATALIZATORIAIS**

*Santrauka*

Solvoterminiu sintezės metu tarp  $\text{Me}(\text{NO}_3)_x \cdot y\text{H}_2\text{O}$  ( $\text{Me}^{x+} = \text{Fe}^{3+}, \text{Ni}^{2+}, \text{Mn}^{2+}, \text{Co}^{2+}, \text{Cu}^{2+}$ ) ir atitinkamai 4-nitrosalicilo (4NSA) ir 5-sulfosalicilo (5SSA) rūgščių susintetinti hibridiniai organiniai–neorganiniai junginiai, sudaryti iš  $\text{Me}^{x+}$  jonų ir organinių fragmentų, turinčių tris skirtingas funkcines grupes: karboksilo, hidroksilo ir sulfono. Ištirta susintetintų  $\text{Me}_2(\text{H}_2\text{O})_4(5\text{SSA})_3 \cdot \text{DMF}$  ir  $\text{Me}_2(\text{H}_2\text{O})_4(4\text{NSA})_2 \cdot \text{DMF}$  (DMF-dimetilformamidas) hibridinių junginių fazinis grynumas ir mikrostruktūra. Sintetintos medžiagos buvo apibūdintos rentgeno spindulių difrakcijos (XRD) analize, skenuojančia elektrone mikroskopija (SEM) ir branduolinio magnetinio rezonanso (NMR) spektroskopija. Taip pat buvo tiriamos gautų junginių katalitinės savybės.