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Thermal stability of zinc formate complex compounds containing urea, thiourea and caffeine[1]

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Abstract

The following complex compounds of zinc formate and urea (u), thiourea (tu) and caffeine (caf) have been prepared: $Zn(HCOO)_2 \cdot u \cdot H_2O$, $Zn(HCOO)_2 \cdot 2u \cdot 0.5H_2O$, $Zn(HCOO)_2 \cdot tu$, $Zn(HCOO)_2 \cdot caf \cdot 0.5H_2O$ and characterized by means of IR spectroscopy, chemical analysis and X-ray patterns. By means of thermal analysis the temperature intervals of the stability of the prepared compounds as well as the mechanisms of their thermal decomposition have been determined. Mass spectrometry has been used to determine the volatiles released during thermal decomposition.

INTRODUCTION

The complex compounds of transition metals containing ligands with N or O atoms have been studied by Allan [1]. We have prepared several new complex compounds of zinc carboxylates (acetates, formates, butyrates and isobutyrates) with N or O donor ligands which have potential antifungal and anticarcinogenic effects.

Thermal stability of zinc acetate based complex compounds is described in ref. 2. In this paper the thermal stabilities of several new zinc formate based complex compounds, prepared at the Department of Inorganic Chemistry of Šafarik University, Košice, are reported.

EXPERIMENTAL

Synthesis of the compounds

In the synthesis of zinc formate-based compounds studied the following chemicals of p.a. grade were used: $ZnSO_4 \cdot 7H_2O$, $(NH_4)_2CO_2$, HCOOH

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[1] Dedicated to Hans Georg Wiedemann.

99% (Lachema, Neratovice); urea, thiourea (Lachema, Brno); caffeine (Farmakon, Hlohovec).

The compounds: $Zn(HCOO)_2 \cdot 3H_2O$, $Zn(HCOO)_2 \cdot u \cdot H_2O$, $Zn(HCOO)_2 \cdot 2u \cdot 0.5H_2O$, $Zn(HCOO)_2 \cdot tu$, $Zn(HCOO)_2 \cdot caf \cdot 0.5H_2O$ were synthesized by the reactions in water solutions at 40–80°C using zinc formate and the respective organic compounds as ligands in stoichiometric ratios.

Zinc formate was prepared from formic acid (diluted in the weight ratio 1:4) and zinc carbonate freshly synthesized for every compound (by mixing solutions of $ZnSO_4$ and $(NH_4)_2CO_3$).

Instrumentation

The elemental analysis of the prepared compounds was carried out by means of a Hewlett Packard Model 185 CHN Analyser. The IR spectra were measured by means of a Specord IR M-80 (Zeiss Jena) using KBr pellets in the region 4000–200 cm^{-1}.

Thermal analysis was carried out using a Derivatograph OD 102 (MOM, Budapest, Hungary) in platinum crucibles, sample mass 0.1 g, gas atmosphere N_2 and heating rate 10 K min^{-1}. DSC measurement was carried out using Perkin Elmer DSC 7 equipment.

The amount of zinc in the synthesized compounds was determined by complexometric titration using EDTA as agent and eriochrome black as indicator.

A MAT 731 mass spectrometer (Finnigan) was used for characterization of volatile thermal decomposition products of the compounds studied.

RESULTS AND DISCUSSION

Characteristics of the synthesized compounds

The compounds are white in colour and stable to light at 20°C in air. The results of the CHN elemental analysis are summarized in Table 1. The results of CHN analysis, as well as zinc content, agree well with the theoretical content corresponding to the chemical compositions of the compounds given above.

The IR spectra of the synthesized compounds are summarized in Table 2, where the characteristic absorption bands are used for compound identification. The absorption bands observed were identified in accordance with the literature data [3, 4].

The IR spectra were also used to investigate the character of chemical bonding in the compounds. The influence of the presence of organic ligands on the zinc formate was found for the complex with thiourea. The position of the formate COO^- group asymmetric vibration $\nu_{as}(COO^-)$ was

TABLE 1

Chemical analysis

Compound		C/%		H/%		N/%		Zn/%	
No.	Formula	Exp.	Theor.	Exp.	Theor.	Exp.	Theor.	Exp.	Theor.
1	$Zn(HCOO)_2 \cdot 3H_2O$	11.46	11.46	3.70	3.82			30.74	31.23
2	$Zn(HCOO)_2 \cdot u \cdot H_2O$	15.50	15.43	3.32	3.42	12.05	11.99	27.53	27.94
3	$Zn(HCOO)_2 \cdot 2u \cdot 0.5H_2O$	16.69	16.81	3.65	3.85	19.63	19.60	22.79	22.89
4	$Zn(HCOO)_2 \cdot tu$	15.50	15.55	2.71	2.59	11.90	12.09	27.22	28.24
5	$Zn(HCOO)_2 \cdot caf \cdot 0.5H_2O$	33.50	33.52	3.86	3.63	15.58	15.64	17.21	18.26

shifted 34 cm^{-1} towards higher wavelengths. In the case of urea the shift in this region is not significant, whereas in the case of caffeine a 14 cm^{-1} shift towards lower wavelengths was observed. Consequently interactions of thiourea and caffeine ligands with the COO^- anion of zinc formate can be supposed.

TABLE 2

Characteristic absorption bands (ν/cm^{-1}) in infrared spectra

Assignment	Compound				
	1	2	3	4	5
$\nu_{as}(COO^-)$	1576 vs	1580 vs	1580 vs	1610 vs	1564 s
$\nu_s(COO^-)$	1410–1360 vs	1376 vs	1372 vs	1364 s	1384 s
$\delta(COO^-)$	762 s	750 s	750 s	760 s	760 s
$\nu(O-H)$ (H_2O)	3500 w	3500 w	3500 w		3500 w
$\delta(O-H$ (H_2O)	1600 s	1604 s	1600 s		1600 s
$\nu(N-H)$ $(-NH_2)$		3456 w	3450 w	3390 w	
$\delta(N-H)$ $(-NH_2)$		1628 s	1620 s	1620 s	
$\nu(C=O)$ $(=C=O)$		1680 s	1680 s		
$\nu(C=S)$ $(=C=S)$				1400 m 1330 m 1136 m	
$\nu C-H$ $(-CH_3)$					2900 w
$\delta(C-H)$ $(-CH_3)$					1370 s
$\nu(C=O)$ $(=C=O_{cof})$					1700 s 1680 s
$\nu(C-H)$ $(purin_{cof})$					3070 w
$\delta(C-H)$ $(purin_{cof})$					1024 m
$\gamma(C-H)$ $(purin_{cof})$					750 m

Key: vs, very strong; m, medium; s, strong; w, weak; 1, $Zn(HCOO)_2 \cdot 3H_2O$; 2, $Zn(HCOO)_2 \cdot u \cdot H_2O$; 3, $Zn(HCOO)_2 \cdot 2u \cdot 0.5H_2O$; 4, $Zn(HCOO)_2 \cdot tu$; 5, $Zn(HCOO)_2 \cdot caf \cdot 0.5H_2O$.

In the following the thermal stabilities and behaviour of compounds heated in nitrogen at a rate of 10 K min^{-1} are described on the basis of their thermal analysis and MS results.

Zn(formate)$_2 \cdot 3H_2O$

As is obvious from the TG/DTG and DTA curves in Fig. 1, the compound is stable in nitrogen up to 60°C. When heated above this temperature, release of water takes place starting at 70°C, which is demonstrated by the loss of mass and endothermal DTA effect. The total mass loss which takes place in the temperature range 70–105°C corresponds to three molecules of H_2O. The thermal decomposition of the anhydrous product takes place in one step in the temperature range 200–270°C. As was observed from the mass spectra of the gaseous decomposition products at 250°C, one molecule each of H_2O, CO and CO_2 are released from the sample as the result of thermal decomposition. The final product of the thermal decomposition is metallic zinc.

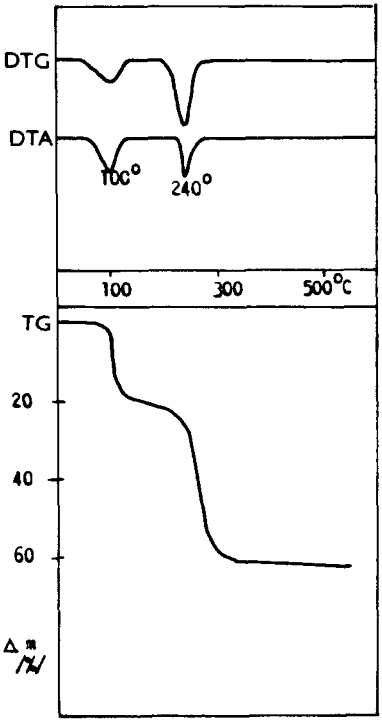

Fig. 1. TG/DTG and dTA curves of Zn(formate)$_2 \cdot 3H_2O$.

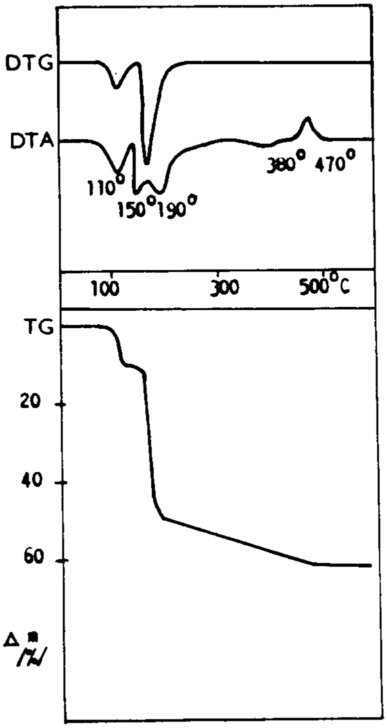

Fig. 2. TG/DTG and DTA curves of Zn(formate)$_2$ · u · H_2O.

Zn(formate)$_2$ · urea · H_2O

As follows from Fig. 2, this compound is stable in nitrogen up to 80°C. Above this temperature the sample loses 1 molecule of H_2O, as demonstrated by the TG curve and the DTA endothermal effect (Fig. 2). At 115–140°C the melting of anhydrous complex compounds is supposed, which is indicated by the DTA endothermic effect which peaks at 150°C. Above 155°C, the thermal decomposition of the sample takes place, lasting to 470°C, as indicated by the mass loss on the TG curve and DTA endothermal effects peaking at 190°C and 380°C respectively. Zinc oxide is the final decomposition product. Its high defect stage is believed to change into a more disperse consolidated structure above 470°C, as indicated by the shift of the DTA baseline. This statement will be confirmed by means of emanation thermal analysis (ETA) [5, 6] which is suitable for studying changes in the defect stage of solids.

It was of interest to investigate the difference between the thermal behaviour of pure urea and urea bonded as ligand in the complex with zinc formate.

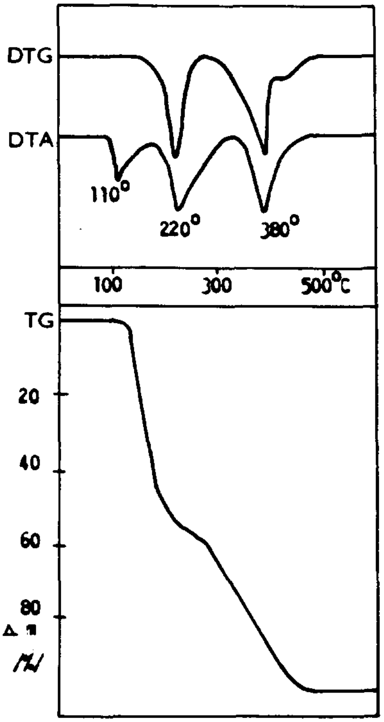

Fig. 3. TG/DTG and DTA curves of urea.

The results of TG/DTG and DTA characterization of the thermal behaviour of urea during heating in nitrogen are demonstrated in Fig. 3. The DTA endothermal effect (maximum at 110°C) corresponds to the melting of urea, followed by the DTA endothermal effects at 220°C and 380°C reflecting the decomposition in two steps. This is in good agreement with the results presented by Czekchovskich et al. [7].

Zn(formate)$_2$ · 2urea · 0.5H$_2$O

As follows from TG/DTG and DTA curves shown in Fig. 4, this compound is stable up to 100°C, above which 0.5 molecule H_2O is released. The anhydrous compound is stable between 120 and 160°C.

The thermal decomposition of the anhydrous compound takes place in the temperature range 160–570°C. In the temperature range 160–280°C the release of NH_3 and CO was confirmed by mass spectrometry. The onsets of the thermal decomposition of urea ligand in the complex compound and pure urea do not differ significantly.

It was of interest to use DSC for determination of the enthalpy of the effects corresponding to the processes taking place during heating of

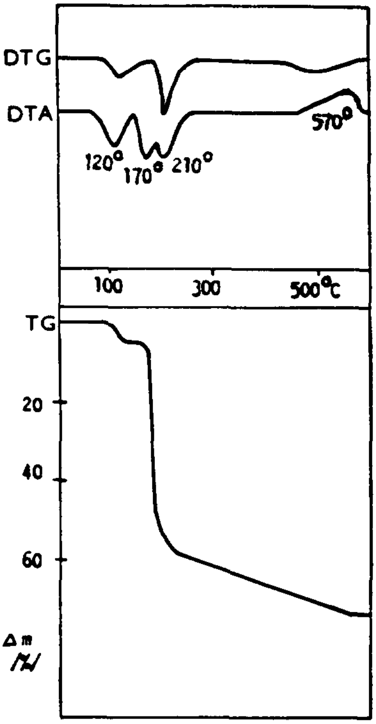

Fig. 4. TG/DTG and DTA curves of Zn)formate$)_2$ · 2urea · $0.5H_2O$.

Zn(formate$)_2$ · 2urea. The endothermal effect in Fig. 5 which peaked at 164°C and reflects the melting of urea, was evaluated as an enthalpy effect of 264.5 J g^{-1}. The thermal decomposition processes taking place during subsequent heating are represented by endothermal effects of 203.18 J g^{-1} (peak temperature 203.2°C) and 139.3 J g^{-1} (peak temperature 223.8°C).

The highly dispersed stage of ZnO was formed above 600°C. This statement is confirmed by independent ETA measurements [6] and X-ray powder diffraction.

Zn(formate$)_2$ · thiourea

The TG/DTG and DTA curves are shown in Fig. 6. It is obvious that the compound is stable up to 70°C. Upon heating above this temperature thermal decomposition takes place in three steps as indicated by the DTA and DTG curves. The decomposition process is finished at 650°C.

It was of interest to compare the thermal analysis results for this complex compound containing thiourea as ligand (see Fig. 6) with those of thiourea alone which are shown in Fig. 7. It follows from Fig. 7 that the decomposition of thiourea begins at 180°C and lasts until 600°C. Two endothermal effects at 180 and 250°C reflect two stages of the process which

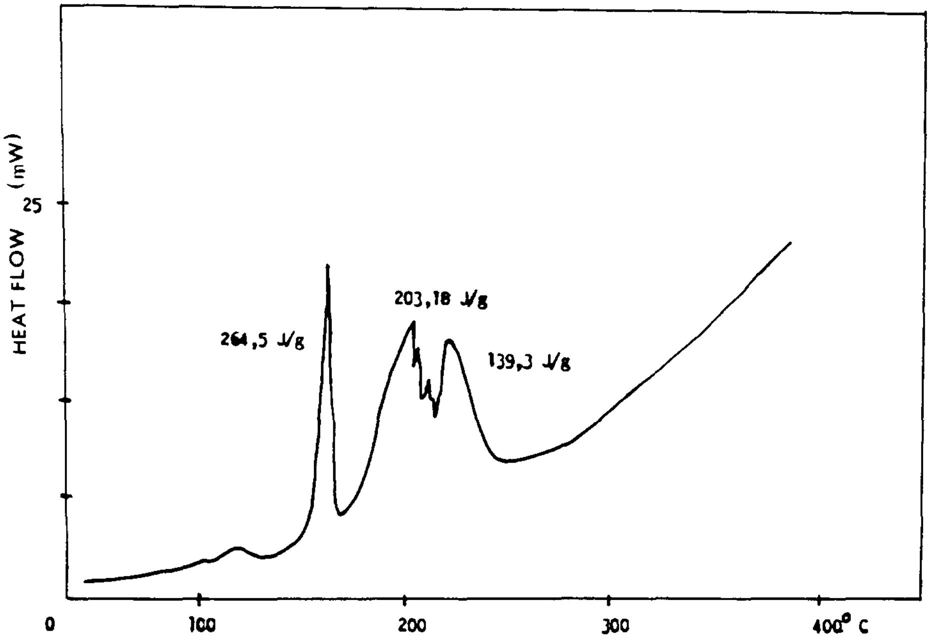

Fig. 5. DSC curve of Zn(formate)$_2$ · 2urea · 0.5H$_2$O.

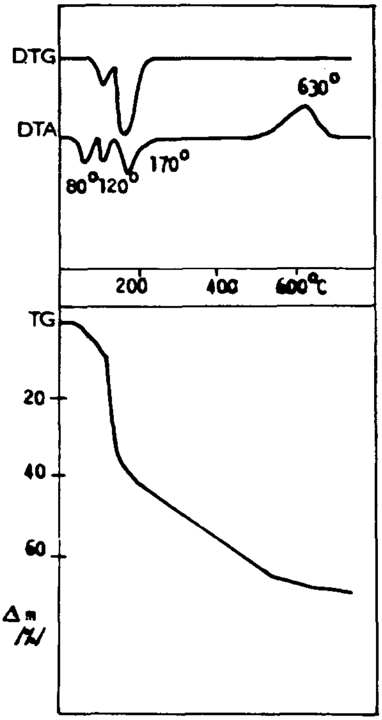

Fig. 6. TG/DTG and DTA curves of Zn(formate)$_2$ · thiourea.

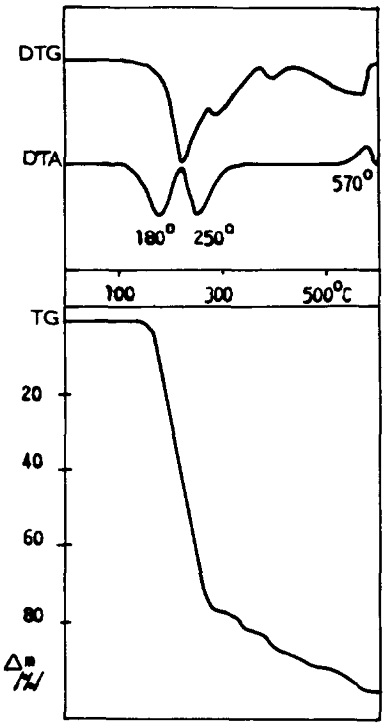

Fig. 7. TG/DTG and DTA curves of thiourea.

take place before 350°C. The final stage, which corresponds to the loss of one molecule of NH_3, is not accompanied by an effect on the DTA curve.

The total mass loss (Fig. 6) after heating to 650°C corresponds to the release of H_2O, 2CO and the decomposition products of thiourea. Zinc oxide is the final decomposition product. It is believed that the initial, highly disordered, state of the decomposition product changes upon heating above 600°C into a sintered product; this is indicated by shift of the DTA baseline. An additional investigation by means of ETA will be carried out with the aim of confirming this statement.

Zn(formate)$_2$ · caffeine · 0.5H_2O

As follows from Fig. 8, the sample is thermally stable up to 100°C, no phase change connected with enthalpy changes being indicated up to this temperature.

The dehydration of the compound starts at 105°C and is finished at 160°C, 0.5 molecule H_2O being released in one step. The thermal decomposition of the anhydrous product starts at 220°C and lasts up to 360°C, as indicated by the TG/DTG curves. As observed on the DTA curve

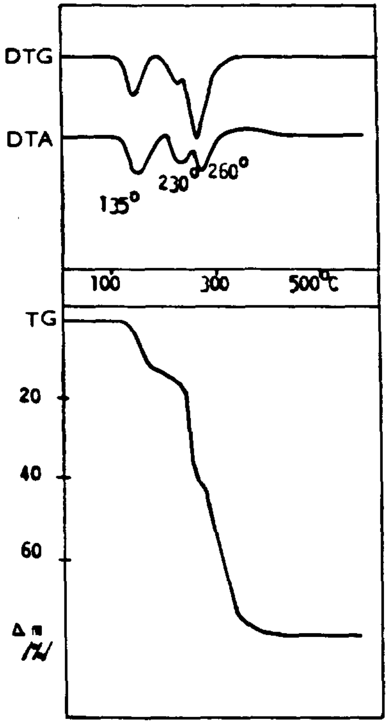

Fig. 8. TG/DTG and DTA curves of Zn(formate)$_2$ · caf · 0.5H$_2$O.

in Fig. 8, this process is accompanied by a double endothermal effect with peaks at 230 and 260°C.

As has been proved by mass spectrometry, the release of caffeine ligands takes place at the beginning of thermal decomposition, followed by the release of water, CO and CO$_2$, resulting from the decomposition of formate anion. The final product of the thermal decomposition is metallic zinc.

The results of thermal analysis of caffeine are shown in Fig. 9. It is obvious from the TG curve in Fig. 9 that thermal decomposition starts at 210°C, and two endothermal effects at 220 and 330°C on the DTA curve indicate two steps of the process. The TA results for Zn-formate · caffeine and those for caffeine alone are in good agreement.

CONCLUSIONS

The thermal decomposition of the hydrated compounds studied begins with the release of water of crystallization. The thermal stability of the anhydrous complex compounds decreases as follows:

$$\underset{240^\circ\mathrm{C}}{\mathrm{Zn(HCOO)_2}} > \underset{220^\circ\mathrm{C}}{\mathrm{Zn(HCOO)_2\cdot caf}} > \underset{170^\circ\mathrm{C}}{\mathrm{Zn(HCOO)_2\cdot 2u}} > \underset{150^\circ\mathrm{C}}{\mathrm{Zn(HCOO)_2\cdot u}} > \underset{80,\,120^\circ\mathrm{C}}{\mathrm{Zn(HCOO)_2\cdot tu}}$$

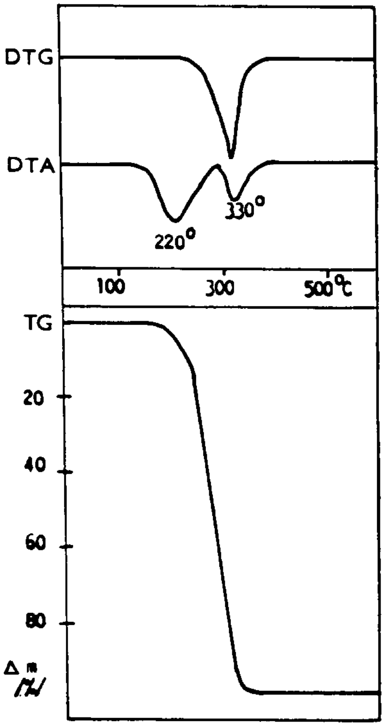

Fig. 9. TG/DTG and DTA curves of caffeine.

During the thermal decomposition of the anhydrous compounds containing different ligands the release of the organic ligands takes place as the first step of the decomposition, followed by the thermal decomposition of the formate anion. By comparison of the thermal stability of zinc formate-based compounds containing various organic ligands and the thermal stability of the respective organic compounds used as ligands the following information was obtained.

In the case of caffeine the temperatures of the release of organic ligands from the complex compounds (220°C) are higher than the decomposition temperatures of the organic ligands themselves (210°C).

The complex compound containing thiourea (Zn-formate$_2$ · tu) decomposes at 80°C, which is 100°C lower than thiourea itself (180°C).

The compounds Zn-formate$_2$ · 2u and Zn-formate$_2$ · u are decomposed at higher temperatures than the respective organic compounds which they contain.

It was found that the presence of ligands in the complex compounds influences the mechanism of thermal decomposition of the formate anion. Organic ligands were released in the temperature range 80–250°C in endothermic processes. During the thermal decomposition of the zinc formate-based compounds containing urea and thiourea, CO and H_2O are released. In the case of caffeine, CO_2, CO and H_2O are released during the decomposition of the zinc-formate based complex compound containing caffeine.

Metallic zinc and zinc oxide are the final decomposition products of all the zinc formate-based complex compounds studied. Carbon monoxide and water were detected in the gaseous products of the decomposition of the compounds if ZnO is formed. Carbon monoxide, carbon dioxide and water were detected in the gaseous products of the decomposition, if metallic zinc is formed. It is supposed that the final decomposition products ZnO and zinc possess different degrees of structural disorder and that they are annealed by heating above 600°C.

ACKNOWLEDGEMENT

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