

THERMOGRAVIMETRIC INVESTIGATION OF SOME MONONUCLEAR AND BINUCLEAR COMPLEXES OF COPPER(II) ACETATE WITH PYRIDINE DERIVATIVES*

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Binuclear complexes of the type $\text{Cu}_2(\text{CH}_3\text{CO}_2)_4\text{L}_2$ (L = pyridine, 2-chloropyridine, 3-chloropyridine, 2,4-dimethylpyridine, 3,4-dimethylpyridine, isoquinoline) and mononuclear complexes of the type $\text{Cu}(\text{CH}_3\text{CO}_2)_2\text{Py}_3$, $\text{Cu}(\text{CH}_3\text{CO}_2)_2\text{Py}_3\text{H}_2\text{O}$, $\text{Cu}(\text{CH}_3\text{CO}_2)_2(3,4\text{-Lut})_2\text{H}_2\text{O}$ have been investigated by thermogravimetry. A linear correlation is shown to exist between the pK_a of the base ligand and the thermal stability of the corresponding binuclear complexes as determined from the thermal analysis data. The results show that the tendency to eliminate the base ligand from these complexes decreases with decreasing basicity of the substituted pyridine. The strong steric effect associated with α -substituted pyridine ligands on the decomposition temperatures of the corresponding complexes is noted.

Our previous study [1a] of Cu(II) carboxylate complexes with substituted pyridines has shown that an equilibrium is established between mononuclear and binuclear forms of the complexes in nonionizing solvents:



The equilibrium constant, K , which is a measure of the relative stability of the two forms, increases with decreasing basicity of the substituted pyridine. A steric effect has also been observed. This is manifested in an appreciable increase in K for α -substituted pyridine derivatives as compared with those for the base ligands of similar basicity but without an α -substituent [1a].

The K values obtained from solution studies reflect the properties of the system as a whole; they do not, however, supply any information about the stabilities of the two forms taken separately, nor their dependence on the basicity of the ligand L [2].

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Indeed, the solubility isotherms measured for $\text{Cu}(\text{CH}_3\text{CO}_2)_2$ —substituted pyridine—chlorobenzene systems [1b] suggest that the tendency to form complexes of the given type (mononuclear or binuclear) might not obey the rules valid for their relative stabilities in solution. For example, contrary to expectations, the solid complexes of $\text{Cu}(\text{CH}_3\text{CO}_2)_2$ with isoquinoline and 3,4-lutidine, as precipitated from the corresponding pure amine solutions, are binuclear, while the weaker donor pyridine forms mononuclear solid-phase complexes. However, the saturated pure amine solutions in all three systems contain only mononuclear species. These facts indicate that further information is needed on the stabilities of both forms. Hence, we have investigated the effects of the basicity and steric properties of the amine ligand on the strength of the metal—L (L = amine) bond by means of thermogravimetry. No such systematic study has been reported previously, though thermal data exist on several similar complexes [3–5].

In the present work, the TG, DTG and DTA profiles of several binuclear complexes $\text{Cu}_2(\text{CH}_3\text{CO}_2)_4\text{L}_2$: L = 2-chloropyridine (2-Clpy, $\text{pK}_a = 0.72$); 3-chloropyridine (3-Clpy, $\text{pK}_a = 2.74$), pyridine (Py, $\text{pK}_a = 5.2$); 2,4-dimethylpyridine (2,4-Lut, $\text{pK}_a = 6.63$); 3,4-dimethylpyridine (3,4-Lut, $\text{pK}_a = 6.46$); isoquinoline (IQ, $\text{pK}_a = 5.4$) and mononuclear complexes: $\text{Cu}(\text{CH}_3\text{CO}_2)_2\text{Py}_3$, $\text{Cu}(\text{CH}_3\text{CO}_2)_2\text{Py}_3\text{H}_2\text{O}$ and $\text{Cu}(\text{CH}_3\text{CO}_2)_2(3,4\text{-Lut})_2 \cdot \text{H}_2\text{O}$ have been established. The solid mononuclear complexes involving 2-Clpy, 3-Clpy, 2,4-Lut and IQ as ligands could not be obtained, even from the corresponding pure amine solutions.

Experimental

The binuclear complexes were obtained according to procedures reported previously [1, 6]. Mononuclear complexes of the type $\text{Cu}(\text{CH}_3\text{CO}_2)_2\text{L}_x\text{H}_2\text{O}$ were precipitated from a solution of $\text{Cu}(\text{CH}_3\text{CO}_2)_2\text{H}_2\text{O}$ in the appropriate amine, saturated at 60° and cooled to -10° , and were subsequently recrystallized from the pure amine. Anhydrous $\text{Cu}(\text{CH}_3\text{CO}_2)_2\text{Py}_3$ was obtained by dissolution of $\text{Cu}_2(\text{CH}_3\text{CO}_2)_4\text{Py}_2$ in the hot, dry amine (50°), followed by cooling to -10° and recrystallization of the precipitate from the pure amine. All manipulations were performed under moisture-free conditions.

The products were analysed for Cu, H, C, N, amine and H_2O content, according to methods described previously [6]. The data are listed in Table 1.

The TG, DTG and DTA profiles were determined on a Paulik–Paulik–Erdey OD–102 Derivatograph, MOM, Budapest, using 0.1–0.2 g sample masses in corundum crucibles and $\alpha\text{-Al}_2\text{O}_3$ (corundum) as reference. The heating rate was 3 degrees per minute. The thermal decomposition was studied under static air and

Table 1 Micro-analysis data for the solid copper acetate complexes with pyridine ligands

Complex	% Cu		% L		% H ₂ O		% N		% H		% C	
	calc.	exp.	calc.	exp.	calc.	exp.	calc.	exp.	calc.	exp.	calc.	exp.
Cu(CH ₃ CO ₂) ₂ Py ₃ ·H ₂ O mononuclear	14.54	14.6	54.32	56.9	4.12	3.9	9.61	9.5	5.30	5.5	52.22	52.6
Cu(CH ₃ CO ₂) ₂ (3,4-Lut) ₂ H ₂ O mononuclear	15.35	15.2	51.78	57.5	4.35	4.7	6.77	6.5	6.33	5.7	52.22	52.9
Cu(CH ₃ CO ₂) ₂ Py ₃ mononuclear	15.17	15.7	56.64	55.1	0	0	10.03	9.6	5.05	4.9	54.47	54.5
Cu ₂ (CH ₃ CO ₂) ₄ Py ₂ binuclear	24.37	24.2	30.35	32.3	0	0	5.37	4.8	4.25	4.3	41.46	41.7
Cu ₂ (CH ₃ CO ₂) ₄ (IQ) ₂ binuclear	20.45	20.4	—	—	0	0	4.51	4.1	4.22	4.3	50.24	50.5
Cu ₂ (CH ₃ CO ₂) ₄ (2-Clpy) ₂ binuclear	21.53	21.4	—	—	0	0	4.74	4.2	3.41	3.6	36.64	36.9
Cu ₂ (CH ₃ CO ₂) ₄ (3-Clpy) ₂ binuclear	21.53	21.3	—	—	0	0	4.74	4.3	3.41	3.5	36.64	36.8
Cu ₂ (CH ₃ CO ₂) ₄ (2,4-Lut) ₂ binuclear	22.00	22.1	—	—	0	0	4.85	4.3	5.24	5.3	45.75	45.9
Cu ₂ (CH ₃ CO ₂) ₄ (3,4-Lut) ₂ binuclear	22.00	22.0	37.10	38.1	0	0	4.85	4.2	5.24	5.4	45.75	46.0

dynamic argon atmospheres in the temperature range 18–450°. The argon flow rate was 4.8 cm³/min.

The final residues were analysed using a DRON-2 X-ray diffractometer (USSR) and Cu-K_α radiation. The scanning rate of the goniometer was 2 degrees per minute; the time constant was 0.5. The X-ray spectrum was measured within 28–70° of the 2θ angle.

Results and discussion

A. Binuclear complexes

The DTA, TG and DTG curves for the binuclear complexes Cu₂(CH₃CO₂)₄L₂ in a static air atmosphere indicate a double-stage process of decomposition, in the range 18–450° (Fig. 1): endothermic elimination of the pyridine ligand, followed by exothermic decomposition of Cu(II) acetate to CuO:

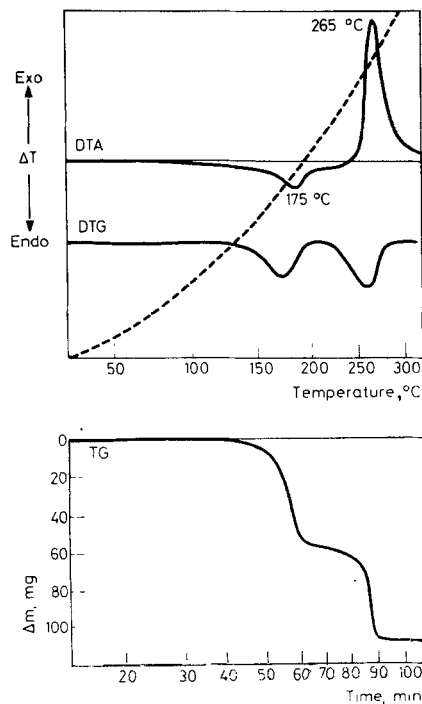
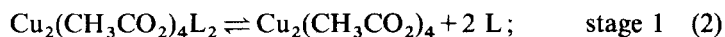


Fig. 1 TG, DTG and DTA curves for Cu₂(CH₃CO₂)₄(2,4-Lut)₂ in static air, sample mass 1400 mg

The X-ray diffraction data confirm CuO as residue for all the complexes investigated in a static air atmosphere (exemplified by $\text{Cu}_2(\text{CH}_3\text{CO}_2)_4\text{Py}_2$ in Table 2). The same compound as residue was also found in a static air atmosphere for $\text{Cu}(\text{CH}_3\text{CO}_2)_2 \cdot \text{H}_2\text{O}$ [7]. When a dynamic argon atmosphere was used, Cu, Cu_2O and CuO were found to comprise the thermal decomposition residue (Table 2). It has been noted that even traces of oxygen in argon result in the oxidation of Cu and Cu_2O to CuO.

Table 2 Identity numbers for powder diffractograms of products of $\text{Cu}_2(\text{CH}_3\text{CO}_2)_4\text{Py}_2$ thermal decomposition

Air		Identified phases [9]	Argon		Identified phases [9]
<i>d/n</i>	<i>I/I</i> ₀		<i>d/n</i>	<i>I/I</i> ₀	
2.74	0.7	CuO	3.00	0.2	Cu_2O
2.53	10.0	CuO	2.74	0.2	CuO
2.32	9.6	CuO	2.53	3.1	CuO
1.86	2.3	CuO	2.45	4.7	Cu_2O
1.71	0.4	CuO	2.32	2.7	CuO
1.58	0.8	CuO	2.12	1.4	Cu_2O
1.50	1.5	CuO	2.08	10.0	Cu
1.41	1.3	CuO	1.86	0.7	CuO
1.37	1.5	CuO	1.81	4.0	Cu
			1.71	0.2	CuO
			1.58	0.3	CuO
			1.51	1.1	CuO, Cu_2O
			1.41	0.4	CuO
			1.37	0.4	CuO
			1.28	1.9	Cu, Cu_2O

The TG and DTG profiles for these complexes in an argon atmosphere are similar to those obtained in air.

$\text{Cu}_2(\text{CH}_3\text{CO}_2)_4(\text{H}_2\text{O})_2$: The water molecules are eliminated in the first decomposition stage. The temperatures corresponding to the maximum of the decomposition rate in both stages are given in Table 3. The initial temperature of the decomposition and the temperature of the DTA minimum correspond closely to those reported previously [8].

$\text{Cu}_2(\text{CH}_3\text{CO}_2)_4(2\text{-Clpy})_2$: The temperature corresponding to the elimination of the 2-chloropyridine ligands is the lowest of those for all the complexes investigated, which corresponds with this ligand having the lowest basicity in the series ($\text{pK}_a = 0.72$). Anhydrous $\text{Cu}_2(\text{CH}_3\text{CO}_2)_4$ is stable in the range 145–195°; decomposition then occurs to give CuO (in a static air atmosphere). A small increase in mass of the sample (1.3%) is noted above 320°.

Table 3 Thermal analysis data for binuclear complexes of the type $[\text{Cu}_2(\text{CH}_2\text{COO})_4]\text{L}_2$

L Base ligand	pK_a	Temp. range of decomp. °C, stage 1 (DTA minimum)		Temp. range of decomp. °C, stage 2 (DTA minimum)		-Δm % stage 1		Temp. range of decomp. °C, stage 2 (DTA minimum)		-Δm % stage 1 + 2			
		(air)	(argon)	(air)	(argon)	theor.	exp.		(air)	(argon)	theor.	exp.	
							(air)	(argon)				(air)	(argon)
2-Clpy	0.72	95-145 (120)	185-180 (125)	38.47	36.8	40.8	195-330 (270, 290, 310)	200-300 (260, 275)	73.1	72.8	74.0		
3-Clpy	2.74	140-210 (195)	130-210 (200)	38.47	38.8	38.0	220-310 (270, 300)	220-290 (270, 280)	73.1	75.4	75.0		
Py	5.20	150-220 (205)	160-220 (210)	30.34	31.2	32.0	215-310 (290)	220-300 (270)	69.5	69.0	69.5		
2,4-Lut	6.63	125-185 (175)	180-210 (185)	37.10	39.2	40.0	185-275 (265)	210-290 (265)	72.5	77.1	75.0		
IQ	5.40	stage 1 + 2 170-260 (210, 230)	stage 1 + 2 170-265 (210, 235)	—	—	—	—	—	74.4	65.0	61.0		
3,4-Lut	5.46	stage 1 + 2 165-360 (215, 320)	stage 1 + 2 165-370 (215, 320)	—	—	—	—	—	72.5	71.9	73.0		
$\text{Cu}_2(\text{CH}_3\text{CO}_2)_4$ $(\text{H}_2\text{O})_2$		90-170 (155)	100-160 (150)	9.02	7.9	9.0	230-300 (270)	230-300 (275)	60.2	66.0	64.0		

$Cu_2(CH_3CO_2)_4(3-Cipy)_2$: The TG, DTG and DTA profiles are similar to those for the binuclear 2-Cipy complex. However, the base ligand is eliminated at higher temperatures, which is consistent with its higher basicity and the lack of steric hindrance at the donor *N* atom. A small increase in the mass of the sample is also observed in the final section of the TG profile, which may result from the presence of chlorine in the gaseous decomposition products over the sample. Only the complexes containing chloropyridine ligands show this effect.

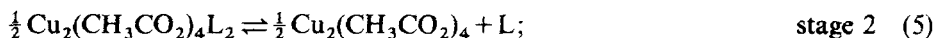
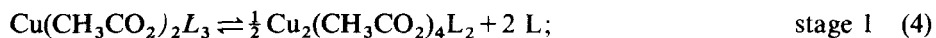
$Cu_2(CH_3CO_2)_4Py_2$: The TG and DTG profiles show two well-resolved stages of decomposition. In accordance with the higher pK_a value of pyridine, the elimination of the base ligand occurs at a higher temperature than that for the binuclear complexes discussed previously (Table 3).

$Cu_2(CH_3CO_2)_4(2,4-Lut)_2$ (Fig. 1): The character of the TG and DTA curves resembles that for the binuclear complexes discussed previously. The two decomposition stages are well resolved, but the pyrolysis of the Cu(II) acetate commences just after stage 1. The two molecules of 2,4-dimethylpyridine are eliminated at a relatively low temperature (Table 3), despite the comparatively high basicity of the ligand ($pK_a = 6.63$). This behaviour may be rationalized in terms of the steric effect of the α -methyl group of the base ligand, which results in a decreased metal-ligand bond strength.

$Cu_2(CH_3CO_2)_4(IQ)_2$ and $Cu_2(CH_3CO_2)_4(3,4-Lut)_2$: The character of the TG, DTG, DTA profiles for both these complexes differs appreciably from that of the curves obtained for the other binuclear complexes. Stages 1 and 2 both commence at $\sim 170^\circ$. Two minima are apparent in the DTA curves (Table 3). In the case of the isoquinoline complex, the process of decomposition still continues above $\sim 400^\circ$ (Table 3, $-\Delta m\%$ value). The decomposition profiles for the isoquinoline complex in a separate measurement in a dynamic oxygen atmosphere indicate complete oxidation below 330° . The temperature of the DTA minimum and the initial temperature of base ligand elimination suggest an increased stability of the binuclear complexes with 3,4-dimethylpyridine and isoquinoline as ligands. This feature may, in turn, be reflected in the unusually high tendency for these complexes to form binuclear structures in the solid state, as found in the solubility experiments discussed previously. Thus, the fact that in solutions of Cu(II) acetate in pure isoquinoline and 3,4-dimethylpyridine the complexes are mononuclear (equilibrium (1) is shifted to the left) may result from strong preferential stabilization of the mononuclear form by a strongly basic amine ligand. The different behaviour of these complexes in solution as compared to the solid state is a reflection of the crystal packing and solute-solvent effects on the stabilities of the two forms. The bulkiness of the amine ligand may also be a contributing factor.

B. Mononuclear complexes

The TG and DTG curves for these complexes indicate that decomposition occurs in three independent stages:



The reversibility of reaction (4) (stage 1) was verified in a separate experiment: the mononuclear complex was sealed in a small glass vessel at ambient temperature and was heated to the final temperature of the first decomposition stage. The binuclear complex resulted. Cooling to 10 degrees below the initial decomposition temperature yielded the corresponding mononuclear complex quantitatively.

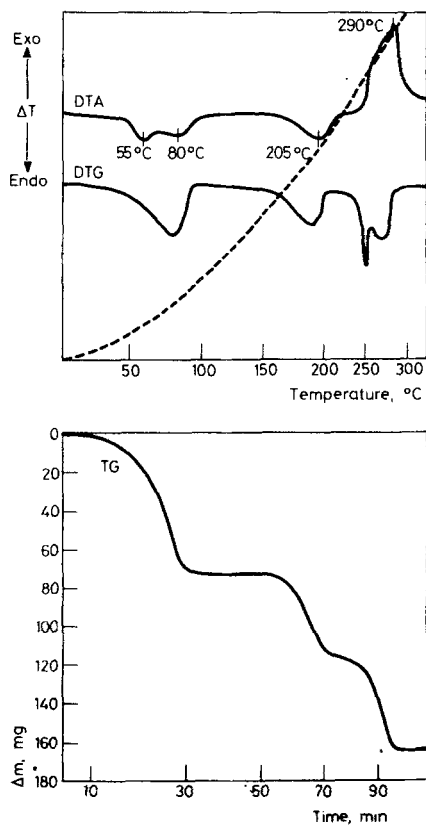


Fig. 2 TG, DTG and DTA curves for $\text{Cu}(\text{CH}_3\text{COO})_2)_2\text{Py}_3$ in static air; sample mass 200 mg

Table 4 Thermal analysis data for mononuclear complexes

Complex	Temp. range of decomp. °C, stage 1 (DTA min)		theor.	-Δm, % stage 1	
	(air)	(argon)		exp.	
				(air)	(argon)
Cu(CH ₃ CO ₂) ₂ Py ₃	30-90 (55, 80)	30-95 (55, 85)	37.76	37.0	37.2
Cu(CH ₃ CO ₂) ₂ Py ₃ · H ₂ O	40-100 (70, 85)	45-100 (70, 85)	40.32	40.5	40.0
Cu(CH ₃ CO ₂) ₂ (3,4-Lut) ₂ · H ₂ O	60-130 (95)	65-130 (100)	30.23	30.0	30.3

Complex	Temp. range of decomp. °C, stage 2 (DTA min)		theor.	-Δm, % stage 1 + 2	
	(air)	(argon)		exp.	
				(air)	(argon)
Cu(CH ₃ CO ₂) ₂ Py ₃	150-210 (205)	160-215 (210)	56.64	57.5	57.0
Cu(CH ₃ CO ₂) ₂ Py ₃ · H ₂ O	160-215 (205)	160-215 (210)	59.2	60.0	59.9
Cu(CH ₃ CO ₂) ₂ (3,4-Lut) ₂ · H ₂ O	160-340 (210, 320)	170-350 (215, 320)	—	—	—

Complex	Temp. range of decomp. °C, stage 3 (DTA min)		theor.	-Δm, % stage 1 + 2 + 3	
	(air)	(argon)		exp.	
				(air)	(argon)
Cu(CH ₃ CO ₂) ₂ Py ₃	216-310 (290)	220-300 (270)	81.0	83.5	82.0
Cu(CH ₃ CO ₂) ₂ Py ₃ · H ₂ O	220-310 (290)	220-300 (270)	81.8	83.3	82.2
Cu(CH ₃ CO ₂) ₂ (3,4-Lut) ₂ · H ₂ O	—	—	80.8	82.7	81.5

$Cu(CH_3CO_2)_2Py_3$: The elimination of the base ligand from the mononuclear complex occurs in two stages (Table 4). The binuclear bis-pyridine complex is stable between 90 and 150°, but it then decomposes as described in A. The thermal decomposition of $Cu(CH_3CO_2)_2Py_3 \cdot H_2O$ is analogous to that of the anhydrous homologue. The water molecule is eliminated in the first stage, together with two pyridine molecules.

$Cu(CH_3CO_2)_2(3,4-Lut)_2H_2O$: One of the 3,4-dimethylpyridine ligands and the water molecule are split off in stage 1. The temperature corresponding to the DTA minimum is slightly higher than that for the analogous pyridine complex, which suggests that the 3,4-dimethylpyridine molecule is more tightly bound than the pyridine ligand; this is consistent with a higher basicity. The binuclear bis(3,4-dimethylpyridine) complex is stable between 130 and 160°.

Conclusion

1. The tendency to eliminate the base ligand from binuclear and mononuclear Cu(II) acetate pyridine complexes in which the donor *N* atom of the pyridine ligand is not sterically hindered decreases with increasing amine basicity. From Fig. 3 it is apparent that a linear correlation exists between the temperature of the DTA minimum and the initial temperature of thermal decomposition or the pK_a of the amine ligand. The increased thermal stabilities of complexes with stronger pyridine ligands appear to support a simple electrostatic theory [2], which predicts increased stabilization of the binuclear Cu(II) carboxylates by more basic pyridine ligands. Thus, the different behaviour of the complexes in solution (the relative stability of the binuclear complexes decreases with the decreasing pK_a of the amine ligand) may be ascribed to a stronger basicity effect on the mononuclear complexes.

2. A steric effect is evident for the α -substituted pyridine complexes. Figure 3

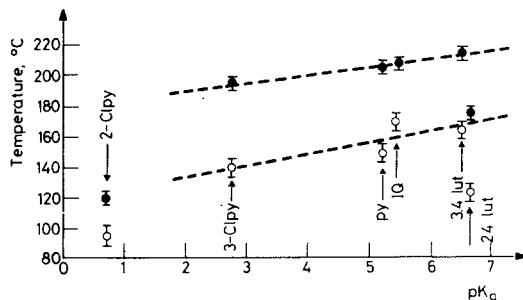


Fig. 3 Plot of ● - DTA minimum temperatures and ○ - initial temperatures of decomposition for stage 1 vs. pK_a of the base ligand

shows that the DTA minima and initial temperatures of amine liberation for the 2,4-dimethylpyridine and 2-chloropyridine complexes are lower than expected from the overall correlation with the corresponding pK_a values.

3. The relatively high thermal stabilities of the binuclear complexes with isoquinoline and 3,4-dimethylpyridine in the solid state explain, at least partly, why the solid-phase binuclear complexes are in equilibrium with the solutions containing only the corresponding mononuclear species.

4. The thermogravimetric profiles determined for $Cu(CH_3CO_2)_2Py_3 \cdot H_2O$ suggest that dehydration of the corresponding monohydrate complex is not possible at elevated temperatures.

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Zusammenfassung — Binukleare Komplexe des Typs $Cu_2(CH_3CO_2)_4L_2$ (L = Pyridin, 2-Chlorpyridin, 3-Chlorpyridin, 2,4-Dimethylpyridin, 3,4-Dimethylpyridin, Isoquinolin) und mononukleare Komplexe des Typs $Cu(CH_3CO_2)_2Py_3$, $Cu(CH_3CO_2)_2Py_3 \cdot H_2O$ und $Cu(CH_3CO_2)_2(3,4-Lut)_2 \cdot H_2O$ werden thermogravimetrisch untersucht. Aus den thermoanalytischen Daten ergibt sich eine lineare Korrelation zwischen den pK_a Wert der basischen Liganden und der thermischen Stabilität der entsprechenden binuklearen Komplexen. Die Tendenz zur Eliminierung der basischen Liganden dieser Komplexe nimmt mit abnehmender Basizität der substituierten Pyridine ab. Auf den beträchtlichen, mit dem α -substituierten Pyridinliganden zusammenhängenden sterischen Effekt auf die Zersetzungstemperatur der entsprechenden Komplexes wird hingewiesen.

Резюме — Термогравиметрическим методом исследованы двухядерные комплексы типа $\text{Cu}_2(\text{CH}_3\text{CO}_2)_4\text{L}_2$ (L = пиридин, 2- и 3-хлорпиридин, 2,4- и 3,4-диметилпиридин и изохинолин), а также мооядерные комплексы типа $\text{Cu}(\text{CH}_3\text{COO})_2\text{Pu}_3$, $\text{Cu}(\text{CH}_3\text{COO})_2\text{Pu}_3 \cdot \text{H}_2\text{O}$ и $\text{Cu}(\text{CH}_3\text{COO})_2(3,4\text{-лутидин})_2 \cdot \text{H}_2\text{O}$. Найдена линейная корреляция между pK_a лиганда-основания и термоустойчивостью соответствующих двухядерных комплексов. Результаты термического исследования показали, что тенденция к выделению лиганда уменьшается с уменьшением основности замещенного пиридина. Установлен значительный стерический эффект для α -замещенных пиридиновых лигандов на температуры разложения соответствующих комплексов.