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The Ternary System $\text{Cu}_2\text{HIO}_6 \cdot 2\text{H}_2\text{O}-\text{H}_5\text{IO}_6-\text{H}_2\text{O}$ at 303 K

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Copper hexaoxiodates $4\text{CuO} \cdot \text{I}_2\text{O}_7 \cdot 5\text{H}_2\text{O}$, $3\text{CuO} \cdot \text{I}_2\text{O}_7 \cdot 3\text{H}_2\text{O}$ and $3\text{CuO} \cdot 2\text{I}_2\text{O}_7 \cdot 7\text{H}_2\text{O}$ have been isolated from the ternary system $\text{Cu}_2\text{HIO}_6 \cdot 2\text{H}_2\text{O}-\text{H}_5\text{IO}_6-\text{H}_2\text{O}$ at 303 K and studied by chemical, thermal X-ray diffraction and infrared spectroscopic methods. Some of the intermediates obtained on isothermal heating of the parent compounds have been characterised.

INTRODUCTION

A number of copper hexaoxiodates (VII) have been prepared by many workers but the reports on their composition are contradictory.¹⁻¹³ As a part of the general programme of the study of hexaoxiodates formed in the three component system $\text{M}_2\text{HIO}_6-\text{H}_5\text{IO}_6-\text{H}_2\text{O}$ (where M = divalent metal), the possibility of the existence of different copper hexaoxiodates has been explored in the system $\text{Cu}_2\text{HIO}_6 \cdot 2\text{H}_2\text{O}-\text{H}_5\text{IO}_6-\text{H}_2\text{O}$ at 303 K.

The present work is devoted to the systematic investigation of new solid phases obtained from the phase study and their characterisation by X-ray diffractometric, infrared spectrometric and thermoanalytical techniques.

EXPERIMENTAL

The parent compound $4\text{CuO} \cdot \text{I}_2\text{O}_7 \cdot 5\text{H}_2\text{O}$ ($\equiv \text{Cu}_2\text{HIO}_6 \cdot 2\text{H}_2\text{O}$) was prepared and analysed by the method described previously.¹⁴ The experiments which form the immediate subject of this paper were planned as follows: Finely powdered copper periodate was added in excess to a series of 250 ml capacity airtight polythene bottles containing a fixed volume of different concentrations of the periodic acid. The securely stoppered bottles were clamped on to a shaker in a thermostatically controlled water bath at 303 ± 0.1 K. In order to check the attainment of the equilibrium condition, the specimens of the supernatant liquids from the bottles were withdrawn intermittently with pipettes fitted with a very small cut off sintered glass filtering crucible to prevent the uptake of crystalline material. The equilibrium was ordinarily reached after two weeks. The solution was analysed by the usual chemical analysis technique,¹⁴ whereas the compositions of the 'solid residues' were determined by the well known 'Schreinmaker's wet residue' method.¹⁵

As a general practice followed in the phase studies of periodates¹⁶⁻²⁰ and in order to overcome the difficulties of expressing the formulations of the new solid phases with unusual molar ratios of metal to iodine, it was preferred to express the analytical results (Table I) uniformly, in terms of their respective oxide forms. Water was calculated by difference and confirmed thermogravimetrically.

The thermal curves of the parent compounds were obtained on 'Stanton Mass Flow Thermobalance' as described previously.¹⁴ The thermoanalytical curves of solid phases obtained from the phase study were scanned on a locally fabricated

TABLE I
Analytical Results

Compound	% CuO		% I ₂ O ₇		% H ₂ O	
	Calcd.	Obsd.	Calcd.	Obsd.	Calcd.	Obsd.
4CuO · I ₂ O ₇ · 5H ₂ O	41.10	40.95	47.28	46.96	11.63	11.50
3CuO · I ₂ O ₇ · 3H ₂ O	36.23	36.12	55.57	55.46	8.19	8.25
3CuO · 2I ₂ O ₇ · 7H ₂ O	21.76	21.72	66.75	66.58	11.49	11.23

high precision instrument in the temperature range 303—1073 K. Some of the intermediates were obtained by isothermally heating the compounds at suitably selected temperatures and were analysed chemically. The compounds were further examined with the help of Beckman IR-4250 dual beam spectrophotometer, in the range 4000—200 cm⁻¹, using KBr pellet techniques. The X-ray diffractograms were obtained on a Philips diffractometer model No. PW 1009/30 NRD 1023, using nickel filtered CuK α radiation (mean λ = 154.18 pm). The powder patterns were indexed by using a computer program known as 'powder diagram indexing routine'.²¹

RESULTS AND DISCUSSION

The isothermal solubility results of the ternary system Cu₂HIO₆ · 2H₂O—H₅IO₆—H₂O are presented in Table II, where the compositions of the liquid phase and wet residue are given as mass fractions. The results are expressed graphically in the triangular diagram in Figure 1. For the sake of better clarity the same results are also expressed on rectangular coordinates in Figure 2 using the modified method proposed by Drátovský²² (The significance of the points S₁, S₂, S₃ and S₄ and of their compositions is the same in both figures).

In the present work, the acidic region was studied comparatively very extensively. However, it was not possible to study the basic region in detail, since even after a period of six months, the equilibrium was not reached and the concentrations of the metal ions and iodine in the liquid phase were too low for analysis. Further, the analysis of the residues showed that they are mixtures of Cu₂HIO₆ · 2H₂O and Cu(OH)₂. Obviously, because of the inherent uncertainties of the results in the basic region, the position of the invariant point E₁ has to be assumed in Figure 2. The other necessary details in this region of the phase diagram are represented by dotted lines. At E₁ two solid phases S₁ and S₅ coexist with their saturated solutions. Point S₅ on the Y-axis represents the percentage of the oxide, CuO in solid hydroxide Cu(OH)₂. For the reasons mentioned above and the nonavailability of accurate data on the solubility of Cu(OH)₂, point R₂ representing extremely low solubility of M(OH)₂ is plotted extremely close to the intersection points of CuO and I₂O₇ axes.

The phase diagram, as given in Figure 2, is divided into ten regions. Solutions represented by points on the curved line AE₂ are in equilibrium with the solid phase represented by S₁ which has the composition of the starting material, 4CuO · I₂O₇ · 5H₂O (\equiv Cu₂HIO₆ · 2H₂O).

The solid phase S₂ in equilibrium with the solution represented by the ternary saturation curve E₂E₃ is a new periodate isolated within the limits of I₂O₇ mass fraction from 12.86% to 37.70%. The ratio of the metal oxide to I₂O₇ in this compound is 3 : 1, leading to an empirical formula which can be represented as 3CuO · I₂O₇ · 3H₂O (\equiv Cu₃(H₂IO₆)₂ · H₂O).

TABLE II
 Solubility in the Three Component System $4\text{CuO} \cdot \text{I}_2\text{O}_7 \cdot 5\text{H}_2\text{O} - \text{H}_5\text{IO}_6 - \text{H}_2\text{O}$ at 303 K

Expt. No.	Liquid phase analysis by weight		Wet residue analysis by weight		Compound
	% CuO	% I_2O_7	% CuO	% I_2O_7	
1.	0.062	2.61	40.80	47.00	4.02
2.	0.012	4.78	40.95	46.96	4.00
3.	0.210	5.47	40.98	47.10	4.00
4.	0.35	8.72	41.04	47.25	4.00
5.	0.39	10.50	40.98	47.00	4.01
6.	0.44	12.86	36.15	55.50	2.99
7.	0.50	16.59	36.25	55.55	2.98
8.	0.47	23.69	36.10	55.10	2.99
9.	0.51	27.70	36.12	55.46	2.99
10.	0.59	34.73	36.08	55.48	2.99
11.	0.62	37.70	36.21	55.45	2.98
12.	0.63	38.85	22.30	55.15	1.86
13.	0.65	40.31	21.70	66.70	1.50
14.	0.67	42.40	21.65	66.72	1.50
15.	0.69	45.12	21.65	66.68	1.50
16.	0.75	47.11	21.72	66.58	1.50
17.	0.79	53.88	21.60	66.55	1.49
18.	0.74	55.72	21.75	66.70	1.50
19.	0.87	57.65	21.58	66.65	1.49
20.	0.55	59.13	0.56	79.90	0.03
21.	0.00	60.35	0.00	80.32	0.00

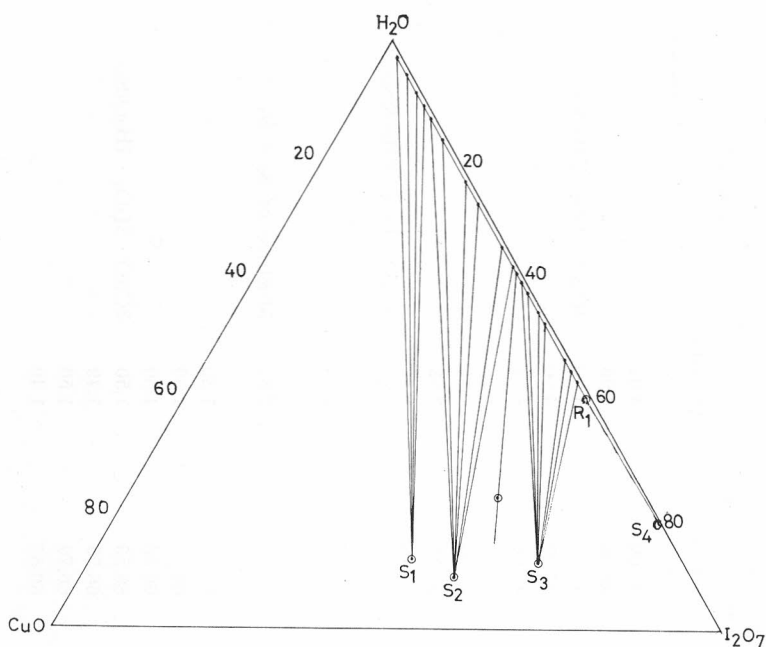


Figure 1. The ternary system $\text{Cu}_2\text{HIO}_6 \cdot 2\text{H}_2\text{O} - \text{H}_5\text{IO}_6 - \text{H}_2\text{O}$ at 303 ± 0.1 K.

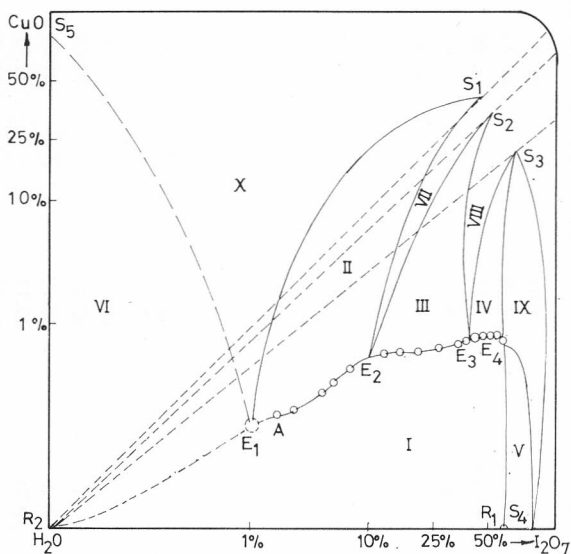


Figure 2. The ternary system $\text{Cu}_2\text{HIO}_6 \cdot 2\text{H}_2\text{O} - \text{H}_5\text{IO}_6 - \text{H}_2\text{O}$ at 303 ± 0.1 K plotted with fifth root component concentration along with coordinate axes.

The region $S_1E_2S_2$ is a three phase region, consisting of an equilibrium of two solid phases, S_1 and S_2 , and their saturated solutions and obviously the system is invariant at point E_2 .

The solid phase S_3 obtained presently on shaking vigorously copper acetate with periodic acid having the I_2O_7 mass fraction between 40.31% and 57.65% is a hitherto unreported compound having an unusual composition $1.5CuO \cdot I_2O_7 \cdot 3.5H_2O$.

The composition of the solid phase obtained from experiment number 12 (Table II) corresponds to a mixture of solid phases S_2 and S_3 as exhibited in Figure 1 by an isolated line.

The compound S_4 obtained during the phase study had a concentration which is in excellent agreement with the composition (80.21% I_2O_7) corresponding to H_5IO_6 .

The region $S_3E_4S_4$ is a three phase region, consisting of an equilibrium mixture of two solid phases, S_3 and S_4 and their saturated solutions and obviously the system is invariant at point E_4 .

The region $AE_2E_3E_4R_1$ is a one phase region containing the unsaturated solution of periodic acid. Points E_1 , E_2 , E_3 and E_4 are called peritonic points and S_1 , S_2 , and S_4 as the figurative points of compounds.

The straight lines joining the points representing compounds S_1 , S_2 and S_3 , to the water vertex do not intersect the saturation curve for these compounds, rendering their recrystallisation from water impossible.

The chemical individuality of the solid phases S_1 , S_2 and S_3 has been confirmed by the X-ray diffraction technique. The interplanar spacings of compounds S_1 and S_3 calculated from the powder diagrams are given in Table III.

TABLE III
X-ray Diffraction Powder Data

$4CuO \cdot I_2O_7 \cdot 5H_2O(S_1)$		$3CuO \cdot 2I_2O_7 \cdot 7H_2O(S_3)$	
d/pm	I/I ₀	d/pm	I/I ₀
519	VS	574	MW
482	VW	570	VS
413	W	434	W
363	VVW	395	MW
360	W	388	MW
335	VVW	329	VW
274	MW	312	VW
265	W	309	W
262	VW	263	VW
257	VVW	259	VVW
254	VVW	252	VVW
245	VVW	246	VVW
232	VVW	243	VVW
229	VW	240	VVW
217	VVW	238	VVW
215	VVW	220	VVW
212	VVW	199	VVW
208	VVW	197	VVW
191	VVW	192	VVW
189	VW	183	VVW

V = Very, S = Strong, M = Medium (Moderate), W = Weak

The compound S_2 can be indexed on a monoclinic cell, the lattice parameters being $a/\text{pm} = 1077$, $b/\text{pm} = 2126$, $c/\text{pm} = 528$, $\beta/\text{deg} = 100.39$ and $V/\text{pm}^3 \times 10^6 = 1190$. The calculated (3.68 g cm^{-3}) and observed (3.63 g cm^{-3}) densities indicate the presence of four molecules per unit cell. The systematic absence of reflexes ($0k0$, $k = 2n + 1$) suggests the most probable space group to be $P2_1/m$.

The infrared spectral data with the assignments for solid phases S_1 , S_2 , S_3 and some of their respective thermal decomposition products are given in Table V. The occurrence of comparatively strong absorption bands in the region 1300 to 1000 cm^{-1} assignable to the deformation vibrations of the I—OH groups and their weak overtone bands in the region 2400 — 2200 cm^{-1} leads to unambiguous and conclusive support to the presence of I—OH groups in the compounds S_1 leading to its formulation as $\text{Cu}_2\text{HIO}_6 \cdot 2\text{H}_2\text{O}$ instead of $\text{Cu}_4\text{I}_2\text{O}_{11} \cdot 5\text{H}_2\text{O}$ reported earlier.^{23,24}

The bands due to the librational modes of coordinated water which can be distinguished as 'rocking', 'wagging', and Cu—O_{st} are generally located as weak absorptions in the frequency regions 900 — 800 , 600 — 550 and 450 — 400 cm^{-1} respectively.

However, no attempt has been made to assign any bands due to these modes of vibration (in the absence of deuteration study), since they are probably overshadowed by medium to strong intensity bands due to ν (IO) and δ (OIO) occurring in the same regions.

Based on the knowledge of the formulation of hexaoxiodates the compound S_2 ($3\text{CuO} \cdot \text{I}_2\text{O}_7 \cdot 3\text{H}_2\text{O}$) could either be formulated as $\text{Cu}_3\text{I}_2\text{O}_{10} \cdot 3\text{H}_2\text{O}$ or $\text{Cu}_3(\text{H}_2\text{IO}_6)_2 \cdot \text{H}_2\text{O}$. The first formulation containing bicentric ion $\text{I}_2\text{O}_{10}^{6-}$ can be ruled out since the expected IO valence vibrations exclusively in the range 800 to 750 cm^{-1} for such compounds, as suggested by Siebert,^{25,27} are absent in this case (Table VI).

The positions of the infrared spectral bands are known to be indicative of the number of oxygen atoms bonded to iodine atom²⁸ and are used as accepted guidelines for establishing the structure in periodates. The positions of the I—O stretching and the O—I—O deformation vibrations reported in Table V suggest²⁵ that the compound be best formulated as containing $\text{H}_2\text{IO}_6^{3-}$. The relatively strong bands at 3400 — 3200 cm^{-1} and 1640 cm^{-1} , attributable to stretching and bending modes respectively, are indicative of the presence of crystal water. These spectral results support the formulation of the compounds as $\text{Cu}_3(\text{H}_2\text{IO}_6)_2 \cdot \text{H}_2\text{O}$ in line with the thermoanalytical results.

In the case of compound S_3 , a strong intensity band centered around 850 cm^{-1} characteristic of IO_4^{1-} anion and a group of bands assignable to I—O stretching vibrations, observed down to the frequency 700 cm^{-1} , unfortunately do not lead to any definite type of periodate formulation and also the metal oxide contents for these compounds are in a sense unusual and not a whole number. This is even more so because weaker intensity bands in the region 1300 — 1000 cm^{-1} characteristic of I—OH deformation vibrations and their very weak overtones around 2280 cm^{-1} also appear in the spectrum. Under these circumstances and in the absence of single crystal data, as suggested by Hájek *et al.*,²⁹ no definite molecular formulation other than indicating the mole ratios such as $3\text{CuO} \cdot 2\text{I}_2\text{O}_7 \cdot 7\text{H}_2\text{O}$ could be given.

TABLE IV

Indexed X-ray Powder Diffraction Data for 3CuO · I₂O₇ · 3H₂O

h	k	l	$d_{(obs)}/\text{pm}$	$d_{(cal)}/\text{pm}$	I/I_0
0	0	1	528	528	100
1	0	1	474	473	56
1	1	1	454	453	39
1	2	1	445	444	38
2	4	2	411	411	39
1	4	1	366	365	54
0	6	0	349	348	33
1	4	1	337	338	36
2	6	1	273	273	41
2	6	0	270	270	20
4	0	0	265	265	37
1	6	0		265	
3	3	1	258	257	43
3	5	0	249	249	18
1	2	2	246	246	10
4	2	0		247	
3	4	1	241	241	15
2	1	2	237	237	17
1	3	2		237	
1	8	1		237	
4	1	1	231	231	27
5	3	0	214	214	14
0	6	2	210	211	19
3	7	0		210	
4	5	0	208	208	17
2	1	0		208	
4	1	2	188	188	26
4	2	2		188	

The thermal curves of the solid phases S_1 , S_2 and S_3 are given in Figures 3—5 and the thermoanalytical results of all the compounds are presented in Table VI.

The weight losses on the TG curve of compound S_1 (Figure 3) in the temperature ranges 353—533 K, 543—623 K and 653—773 K correspond respectively to the formation of $4\text{CuO} \cdot \text{I}_2\text{O}_7 \cdot 1.5\text{H}_2\text{O}$ (S_1 —I), an intermediate compound $\text{Cu}_4\text{I}_2\text{O}_{11}$ and its final decomposition to CuO . These weight changes on the TG curve are associated with three endothermic peaks at 508, 583 and 753 K on the DTA diagram (Figure 3). The synthesis of the compound $\text{Cu}_4\text{I}_2\text{O}_{11}$ presented difficulties due to its transient existence. The sharp, exothermic peak at 663 K on the DTA curve, without any accompanying weight loss on the TG curve is probably due to a change in the crystallinity of $\text{Cu}_4\text{I}_2\text{O}_{11}$.

It is evident from Table V that the IR spectrum of the first thermal decomposition intermediate of compound (S_1 —I) exhibits similar bands to those obtained in the original case, except for a shift in the frequency region of the bands which is presumably due to the removal of water of hydration. This fact also indicates the retention of the I—O stretching of the parent compound even at this temperature. As expected from TG and DTA results,

TABLE V
Infrared Spectral Data (in cm^{-1}) and Band Assignments

S ₁	S _{1-I}	S _{1-II}	S ₂	S _{2-I}	S ₃	S _{3-I}	S _{3-II}	Assignments
3400— 3200 m, b	3400— 3200 m, b		3400— 3200 m, b		3400 m	3400 w		} ν (OH)
2340 w	2280 vw		2280 vw		2280 w	2280 w		
1620 m	1610 m		1640 m		1640 m	1640 m		2 δ (IOH)
1160 w	1360 vw		1160 s		1250 w	1190 m		} δ (IOH)
1110 m	1270 w		1020 w		1185 w	1155 sh		
1020 vw	1020 w		955 s		1020 vw	1070 s		
720 sh		675 m	850 m,sh	740 sh	840 s	860 sh	800 sh	} ν (IO)
680 m		650 w,sh	720 s	720 sh	790 m,b	850 s	770 sh	
640 w,sh			690 s	665 w,sh	740 s	740 sh	740 vs	
535 sh			550 sh	655 w,sh	680 w	710 s	710 sh	
					620 m,b	670 sh	670 vw,sh	
						660 w,sh	650 vw,sh	
						550 s	530 s	
480 s	470 m,vb	420 w,vb	490 m	470 m,b	470 sh	480 sh	435 m	} δ (OIO)
400 sh	385 sh	380 w,sh	470 sh	340 m,b	450 m,b	450 m		
340 m			420 sh					
			350 s					

v = very, s = strong, m = medium, w = weak, b = broad and sh = shoulder

TABLE VI
Thermoanalytical Results

DTA Temp. K	TG Temp. range K	% loss		Interpretation	% CuO		% I ₂ O ₇		% H ₂ O	
		calcd.	obsd.		calcd.	obsd.	calcd.	obsd.	calcd.	obsd.
508	353—533	8.14	8.15	1) 4CuO · I ₂ O ₇ · 5H ₂ O 4CuO · I ₂ O ₇ · 5H ₂ O → 4CuO · I ₂ O ₇ · 1.5H ₂ O	44.74	44.68	51.47	51.18	3.80	3.65
583	543—623	11.68	11.58	4CuO · I ₂ O ₇ · 1.5H ₂ O →	46.50	46.25	53.50	53.08	—	—
613 sh 663				Cu ₄ I ₂ O ₁₁						
753	653—773	58.90	59.00	Cu ₄ I ₂ O ₁₁ → 4CuO	100.00	99.10	—	—	—	—
618	373—653	8.19	8.25	2) 3CuO · I ₂ O ₇ · 3H ₂ O 3CuO · I ₂ O ₇ · 3H ₂ O → 3CuO · I ₂ O ₇	39.47	39.14	60.53	60.16	—	—
798	723—823	63.77	64.00	3CuO · I ₂ O ₇ → 3CuO	100.00	98.59	—	—	—	—
408	353—443	8.19	8.27	3) 3CuO · 2I ₂ O ₇ · 7H ₂ O 3CuO · 2I ₂ O ₇ · 7H ₂ O → 3CuO · 2I ₂ O ₇ · 2H ₂ O	23.71	23.57	72.72	73.04	3.58	3.52
523—693	493—703	17.33	17.25	3CuO · 2I ₂ O ₇ · 2H ₂ O → 3CuO · 2I ₂ O ₇	24.58	24.12	75.42	74.87	—	—
783	753—853	78.28	78.75	3CuO · 2I ₂ O ₇ → 3CuO	100.00	98.97	—	—	—	—

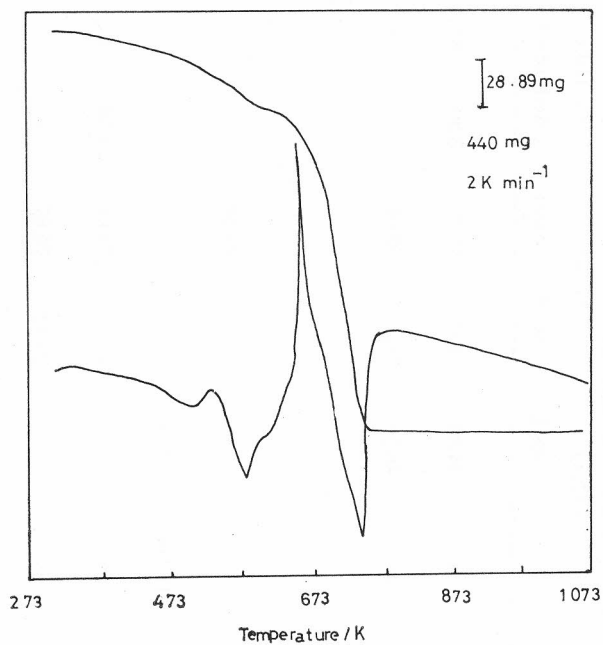


Figure 3. Thermoanalytical curves of the solid phase $4\text{CuO} \cdot \text{I}_2\text{O}_7 \cdot 5\text{H}_2\text{O}$ (S_1).

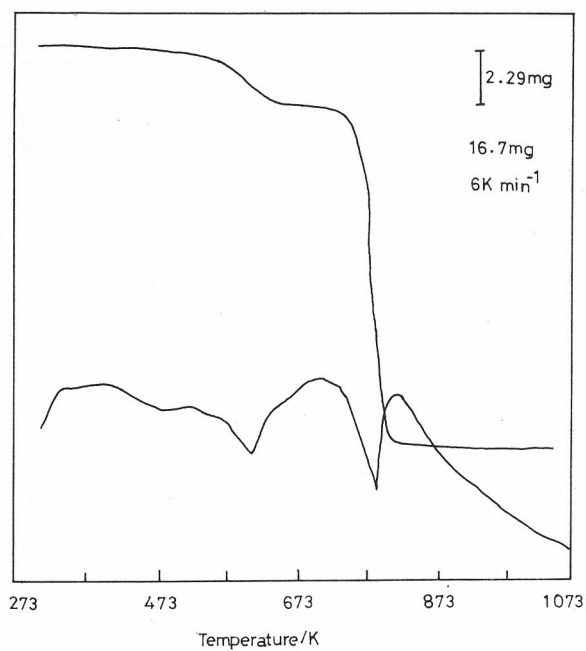


Figure 4. Thermoanalytical curves of the solid phase $3\text{CuO} \cdot \text{I}_2\text{O}_7 \cdot 3\text{H}_2\text{O}$ (S_2).

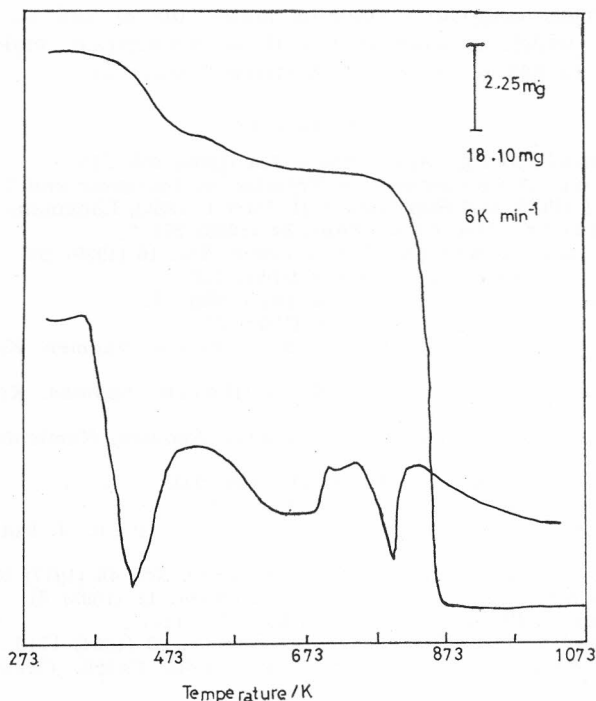


Figure 5. Thermoanalytical curves of the solid phase $3\text{CuO} \cdot 2\text{I}_2\text{O}_7 \cdot 7\text{H}_2\text{O}$ (S_3).

the second intermediate (S_1 —II) shows considerably different frequencies in the lower region of the spectrum, probably indicating a change in the structure of the original compound.

The thermal decomposition of the compound S_3 proceeds in two stages, as evident from the TG curve (Figure 4). The weight losses in temperature ranges 373—653 K and 723—823 K correspond to the formation of the anhydrous compound $3\text{CuO} \cdot \text{I}_2\text{O}_7$ (S_2 —I) and copper(II) oxide respectively. The corresponding endothermic effects are clearly seen at 618 K and 798 K on the DTA diagram (Figure 4). An additional small endothermic effect at 470 K is probably due to the intermediate formation of the compound $\text{Cu}_3(\text{H}_2\text{IO}_6)_2$. As expected, in the spectrum of the dehydrated compound (Table V) the bands due to stretching and bending modes of water are absent.

It is seen from the TG curve (Figure 5) that the compound S_3 begins to lose water steadily at 353 K and the process is complete at 703 K in two steps, leading to the formation of dihydrate $3\text{CuO} \cdot 2\text{I}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$ (S_3 —I) and anhydrous compound $3\text{CuO} \cdot 2\text{I}_2\text{O}_7$ (S_3 —II) respectively. There are two endothermic peaks, one sharp and the other broad, appearing in the temperature range 353—473 K and 523—693 K, on the DTA curve, in conformity with the TG results. The infrared spectral data (Table V) of the dihydrate contains all the characteristics bands of the original compound, whereas the spectrum of the anhydrous compound shows the absence of the bands due to $\delta(\text{I—OH})$, $\delta(\text{H}_2\text{O})$ and $\nu(\text{OH})$, as expected.

The anhydrous compound remains stable up to 753 K, finally giving CuO at 853 K which is associated with a symmetrical endothermic peak between 753 K to 823 K on the DTA curve (Figure 5).

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SAŽETAK

Ternarni sustav $\text{Cu}_2\text{HfO}_6 \cdot 2\text{H}_2\text{O} - \text{H}_5\text{IO}_6 - \text{H}_2\text{O}$ pri 303 K

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Iz ternarnoga sustava $\text{Cu}_2\text{HfO}_6 \cdot 2\text{H}_2\text{O} - \text{H}_5\text{IO}_6 - \text{H}_2\text{O}$ izolirani su bakrovi heksa-oksojodati $4\text{CuO} \cdot \text{I}_2\text{O}_7 \cdot 5\text{H}_2\text{O}$, $3\text{CuO} \cdot \text{I}_2\text{O}_7 \cdot 3\text{H}_2\text{O}$ i $3\text{CuO} \cdot 2\text{I}_2\text{O}_7 \cdot 7\text{H}_2\text{O}$. Ti su spojevi proučavani različitim metodama: kemijskom i termalnom analizom, difrakcijom X-zrakâ i infracrvenom spektroskopijom. Dobiveni su te opisani i neki intermedijarni produkti izoternnog zagrijavanja opisanih triju spojeva.