CONDENSED HETEROAROMATIC SYSTEMS INCLUDING A THIOPHENE RING. XXXIV.* THERMAL ANALYSIS OF SOME CHELATES BASED ON 2-MERCAPTO-3-FORMYLBENZO[b]THIOPHENE AND ITS SCHIFF BASES

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The thermal stabilities of 2-mercapto-3-formylbenzo[b]thiophene and its chelates with Cu(II) and Co(II), of 2-mercapto-3-iminomethylbenzo[b]thiophene and its chelates with Cu(II), Co(II), Ni(II), and Zn(II), and of N,N'-bis(2-mercaptobenzo[b]-3-thenylidene)ethylenediamine and its chelates with Cu(II), Co(II), and Ni(II) were investigated by differential-thermal and thermogravimetric analysis. The temperature of the onset of decomposition and the character of the decomposition of the ligands and chelates were established. It was found that the investigated chelates can be arranged in the following order with respect to increasing thermal stability: Cu < Co < Zn < Ni. The most thermally stable ligand is N,N'-bis(2-mercaptobenzo[b]-3-thenylidene)ethylenediamine. The effectiveness of the ligands and chelates as stabilizers for polycaproamide fibers were compared. It was found that of the investigated compounds, the copper chelates are effective stabilizers. In a study of the thermal behavior of the copper chelates in an inert gas atmosphere it was established that the character of the thermal decomposition of the most effective of them — {N,N'-bis)2-mercaptobenzo[b]-3-thenylidene)-ethylenediaminato}Cu(II) — is identical both in the presence of air oxygen and in a nitrogen atmosphere, i.e., the chelate does not undergo oxidation at temperatures up to 270°C.

We have previously [2] described a method for the preparation of the ligands 2-mercapto-3-formylbenzo[b]thiophene (LI), its imine (LII), and N,N'-bis(2-mercaptobenzo[b]-3-thenylidene)ethylenediamine (LIII) and have studied their complexing with a number of metals and some of the properties of the chelates obtained thereby. It was also shown that ligands and chelates based on 2-formyl-3-hydroxybenzo[b]thiophene and its Schiff bases inhibit the oxidation of hydrocarbons [3] and are heat and light stabilizers of polycaproamide fibers [4, 5].

In this connection it was of interest to study the effect of replacement of the donor oxygen atom by a sulfur atom and of a different mutual orientation of the functional groups in the ligand on the properties of the chelates, particularly on their ability to inhibit thermal oxidative destruction of polycaproamide.

We investigated the stabilizing capacities of the ligand, its Schiff bases, and their chelates with respect to polycaproamide fibers. It was found (see Table 1) that the copper chelates are effective thermal stabilizers, that the cobalt chelates are considerably less effective stabilizers, and that the nickel and zinc chelates ligands themselves have practically no stabilizing effect on the fiber.

*See [1] for communication XXXIII.

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TABLE 1. Results of Tests of the Stabilizing Capacity of Mercapto Derivatives of Benzo[b]thiophene with Respect to Polycaproamide Fibers

Stabilizer	Amount added to the polymer, %	Relative viscosity of the polymer η	Thermal stability or residual strengths of the fiber (%) after heating at 200° for 2 h	Photostability or residual strength of the fiber (%) after irradiation with an IS apparatus for	
				15 days	30 days
Without a stabilizer	—	2,40	20—24	72	50
LI	—	—	—	—	—
CuLI	0,02	2,35	86—90	81	70
	0,05	2,40	80		
	0,10	2,31	70—73		
CoLI	0,02	2,32	26		
L II	0,02	2,30	26		
CuL II	0,02	2,38	80—83	89	78
	0,05	2,40	85—87		
	0,10	2,32	86—87		
CoL II	0,02	2,35	30		
NiL II	0,02	2,39	23—24		
ZnL II	0,02	2,41	20—23		
L III	0,02	2,45	29		
Cu L III	0,02	2,41	80—85	91	87
	0,05	2,32	85—87		
	0.10	2,34	88		
CoL III	0,02	2,40	34		
NiL III	0,02	2,43	The fiber was destroyed		
Cu LIV*	0,02	2,38	79,0		
	0,05	2,42	80,5		
	0,10	2,40	81,5		

*The CuLIV chelate is {N,N'-bis(3-hydroxybenzo[b]-2-thenylidene)ethylenediaminato}copper (II) [4].

On comparison of the effectiveness of the stabilizing effect of copper chelates of mercaptohydroxy derivatives [4, 5] of benzo[b]thiophene it can be noted that replacement of the donor oxygen atom in the ligand by a sulfur atom leads to a certain increase in the ability of the chelate to inhibit the thermal oxidative destruction of polycaproamide.

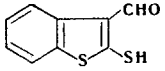
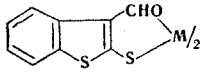
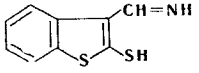
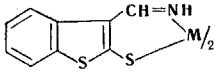
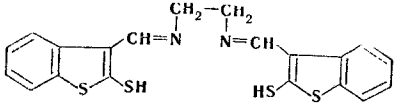
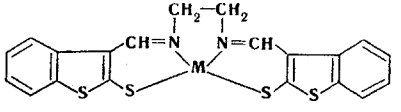
In the modern technological process for the production of polycaproamide and fibers from it, stabilizing additives are introduced into the polymer during its synthesis and are subjected to high temperatures. The probability of oxidation of the stabilizers themselves increases at high temperatures. Thermal analysis of the ligands and chelates makes it possible to ascertain differences in and peculiarities of their behavior over a broad temperature range (up to 600°).

In order to achieve this we made a differential-thermal (DTA) and thermogravometric (TGA) analysis of the mercapto derivatives of the benzo[b]thiophene series and of its chelates with Cu(II), Co(II), Zn(II), and Ni(II). The DTA thermograms obtained are shown in Figs. 1 and 3, the TGA curves corresponding to them are shown in Figs. 2 and 4, and the characteristics of the DTA and TGA curves are presented in Table 2.

It is apparent from the figures that the DTA curves of the chelates recorded in air (Fig. 1) have a number of features in common. Thus, for example, exothermic decomposition, which is manifested on the DTA curves as peaks of different sizes and is accompanied by weight losses (see the TGA curves in Fig. 2), is distinctly seen on all of the thermograms of the chelates.

More or less distinct endothermic peaks are observed only for the ligands: a distinct peak at 183° for ligand LII, and a less distinct peak for ligand LI at 145°. Ligand LIII has a small endothermic peak at 265°, which is preceded by an exothermic peak of partial decomposition. It must be noted that in an inert gas atmosphere ligands LI and LII retain the endothermic character of the decomposition, although the endothermic peaks of their DTA curves are shifted somewhat (see Fig. 3). In the case of ligand LIII in a nitrogen atmosphere the exothermic peak disappears, and more clearly expressed endothermic decomposition is observed.

TABLE 2. Characteristics of the DTA and TGA Curves of the Ligands and Chelates Based on Mercapto Derivatives of Benzo-[b]thiophene

Investigated compound		In air										In a nitrogen atmosphere									
formula	code	onset of decomposition	endothermic peak maximum, °C	exothermic peak maximum, °C	Weight loss, %									onset of decomposition	endothermic peak maximum °C	exothermic peak maximum, °C	Weight loss, %								
					100°	150°	200°	250°	300°	350°	400°	450°	500°				100°	150°	200°	250°	300°	350°	400°	450°	500°
	L I	70	145	—	2,14	—	8,5	—	17,1	—	20,0	—	31,4	95	130	—	—	2,66	5,34	—	14,68	—	24,0	—	42.6
 M = Cu, Co	CuL I	60	—	240	2,14	—	3,14	—	21,4	—	24,3	—	—	90	150	—	1,33	—	4,67	—	13,35	—	18,68	24,0	—
	CoL I	170	—	190	0,71	—	7,8	—	16,4	—	24,2	—	—	—	—	—	—	—	—	—	—	—	—	—	—
	L II	160	183	—	—	—	5,0	—	16,25	—	25,0	—	—	175	190	—	—	—	5,34	—	15,6	—	25,32	—	—
 M=Cu, Co, Zn, Ni	CuL II	150	—	185, 365	—	1,25	5,0	17,5	32,5	40,0	57,5	—	—	150	180, 240	—	—	—	4,0	15,55	26,7	—	—	—	—
	CoL II	200	—	300, 530	—	—	—	2,5	30,0	—	37,5	—	—	—	—	—	—	—	—	—	—	—	—	—	—
	ZnL II	260	—	300, 580	—	—	—	—	11,25	21,25	33,5	—	—	—	—	—	—	—	—	—	—	—	—	—	—
	NiL II	290	—	305, 520	—	—	—	—	8,75	32,5	35,0	40,0	—	—	—	—	—	—	—	—	—	—	—	—	—
	L III	250	265	260	—	—	—	1,25	15,0	—	27,5	—	—	25(	275	—	—	—	—	—	17,32	—	34,0	—	48,7
 M=Cu, Co, Ni	CuL III	270	—	285	—	—	—	—	10,0	15,0	17,5	20,0	—	27(	—	285	—	—	—	—	9,34	18,68	24,0	29,3	—
	CoL III	275	—	390	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
	Ni LIII	360	—	460	—	—	—	—	—	—	4,2	12,8	—	—	—	—	—	—	—	—	—	—	—	—	—

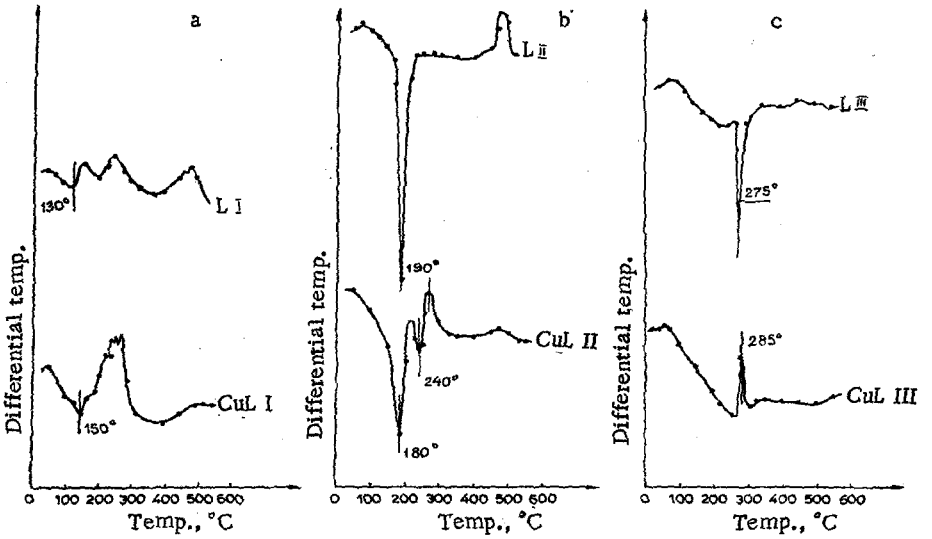


Fig. 1. DTA curves of ligands LI, LII, and LIII in air.

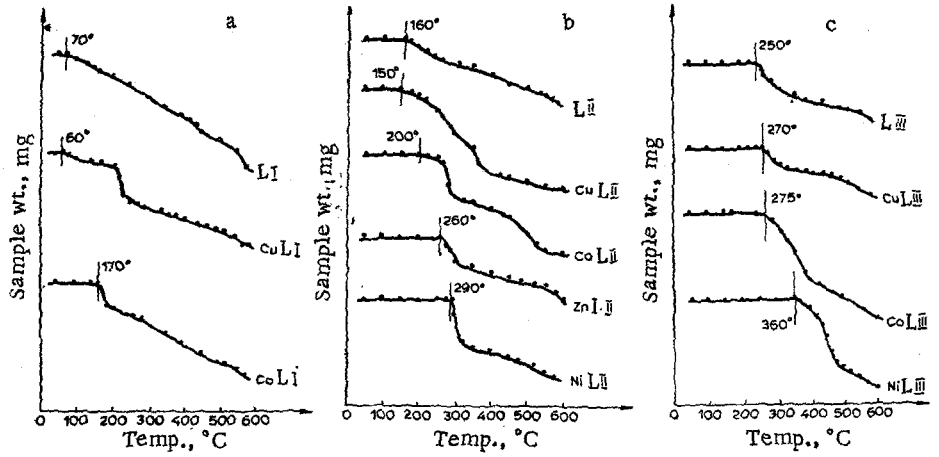


Fig. 2. TGA curves of the ligands and chelates in air. The starting weights of the samples were as follows: 200 mg for LII, CuLII, CoLII, ZnLII, NiLII, LIII, and CuLIII, and 350 mg for LI, CuLI, CoLI, CoLIII, and NiLIII.

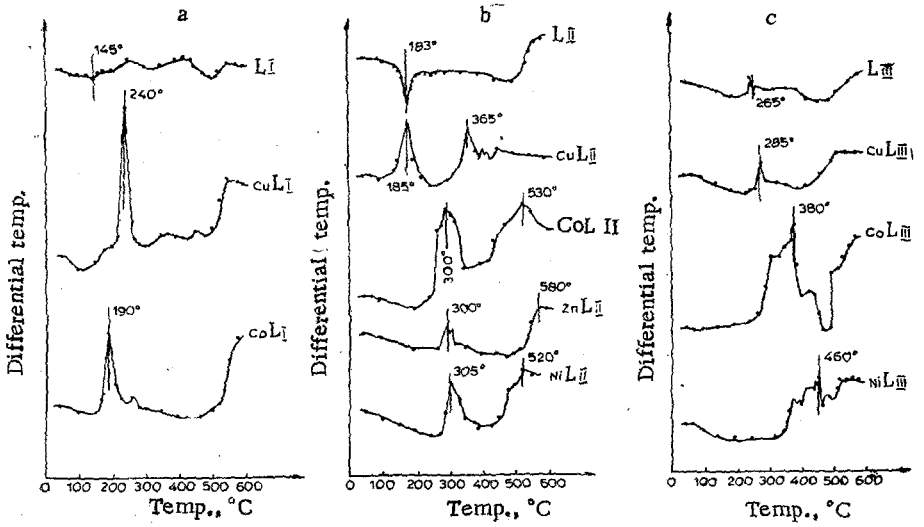


Fig. 3. DTA curves of the ligands and chelates in a nitrogen atmosphere.

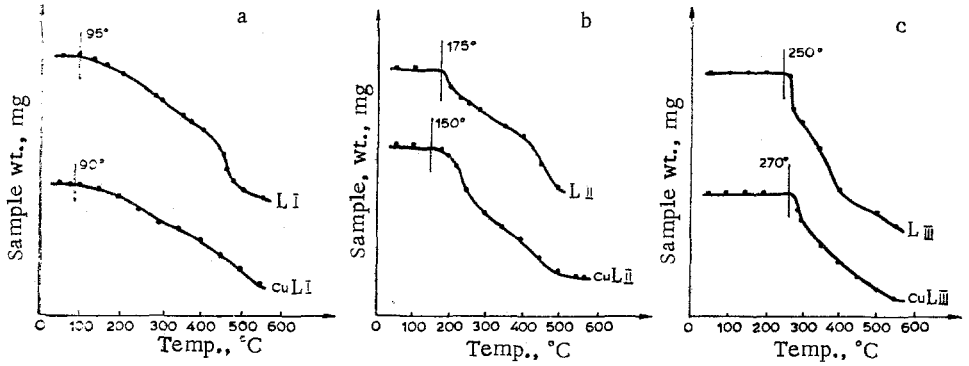


Fig. 4. DTA curves of the ligands and chelates in a nitrogen atmosphere. The starting weight of the samples was 150 mg.

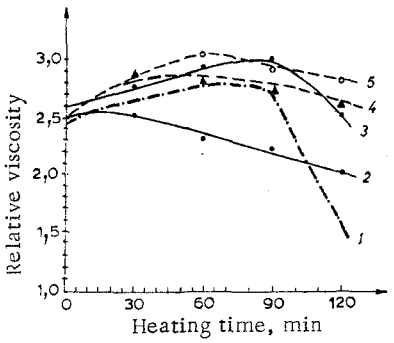


Fig. 5. Change in the relative viscosities of 1% solutions of polycaproamide fibers in 96% H_2SO_4 as a function of the heating time in air at 200°C: 1) without a stabilizer; 2) with 0.02% chelate CuLI; 3) with 0.05% chelate CuLI; 4) with 0.02% chelate CuLIII; 5) with 0.05% chelate CuLIII.

It is noteworthy that the DTA curves in most cases do not have distinct endothermic melting peaks, inasmuch as melting of the ligands and chelates is accompanied by partial decomposition both in the presence of air oxygen and in an inert atmosphere. This is also seen during the determination of their melting points in capillaries.

A definite temperature of onset of decomposition is characteristic for each ligand and chelate (see Figs. 2 and 4). Mercapto aldehyde LI, which decomposes appreciably even at 70°, is the least resistant to the simultaneous action of temperature and air oxygen. Mercaptoaldimine LII begins to decompose at 150°, while Schiff base LIII begins to decompose above 250°. The temperature of the onset of decomposition of ligands LI and LII is raised by 15-25° in a nitrogen atmosphere (Fig. 4). Ligand LIII is the most resistant to the action of oxygen and had the lowest temperature of onset of decomposition, both in the presence of air oxygen and in nitrogen.

It is interesting to note that the thermal stabilities of the chelates of ligand LIII are also higher than the stabilities of the corresponding chelates of ligands LI and LII.

An analysis of the thermal stabilities of the chelates obtained from the same ligand makes it possible to expose a definite principle. Thus, in conformity with the established temperatures of the onset of decomposition, the chelates of ligand LII can be arranged in the following order of increasing thermal stability: Cu < Co < Zn < Ni (Fig. 2, curve b). The chelates of ligand LIII repeat this series (Fig. 2, curve c). We note that in the case of chelates of ligand LI, the cobalt complex is more stable than the copper complex (Fig. 2, curve a). On the basis of the results obtained it can be assumed that chelates of other ligands based on benzo[b]thiophene will also repeat, in the same sequence, the order of relative thermal stabilities.

The observed regularities in the thermal stabilities of the investigated chelates coincide with data on the stabilities of chelates of N-benzoyl-N-phenylhydroxylamine [6]. The exothermic character of decomposition in the latter case was explained by the exothermic formation of nitrogen during decomposition of the ligand.

On comparing the copper chelates of various ligands it can be seen that the copper chelates of the more thermally stable ligands LII and LIII retain their high stabilization effect over a broader range of concentrations (from 0.02 to 0.1%) than in the case of the copper chelate of the less thermally stable ligand LI. It is possible, as noted in [5], that this is associated primarily with the fact that, as a result of their stability, the liberation of a copper sol in a concentration sufficient for the initiation of the thermal oxidative destruction of polycaproamide does not occur. The destruction process does not proceed identically in fibers stabilized by copper chelates of ligands LI and LII, which

differ with respect to their thermal stabilities. This is attested to by data on the change in the relative viscosities of solutions of fibers subjected to heating at 200° [5] for times of varying duration. The relative viscosity of fibers with added CuLIII (temperature of onset of decomposition 270°) does not fall as sharply as, for example, the relative viscosity of fibers with added bis(2-mercapto-3-formylbenzo[b]thiophene)Cu(II) (CuLI) (temperature of onset of decomposition in air 70°).

The thermograms of decomposition of the copper chelates in an inert gas (nitrogen) supplement the pattern of thermal behavior of the stabilizers (Figs. 3 and 4). Endothermic peaks at 150° in the case of chelate CuLI and at 180° in the case of chelate CuLII appear on the DTA curves (Fig. 3). The DTA curve of chelate CuLIII does not change in character: the exothermic decomposition peak is retained at 285°. The temperature of the onset of decomposition changes only in the case of chelate CuLI (it is raised 30°).

Thus the CuLIII chelate — {N,N'-bis(2-mercaptobenzo[b]-3-thenylidene)ethylenediamina-to}Cu(II) — which displays a higher stabilizing effect with respect to polycaproamide as compared with the other investigated chelates, is the most resistant to oxidation at high temperatures.

EXPERIMENTAL METHOD

The methods for the preparation of the investigated compounds and their physical constants were presented in [2].

The thermograms were recorded with a Paulik—Paulik—Erdey 676 derivatograph. The investigated samples were heated at 6°/min to 600°. The sample weight was 220-350 mg.

The effect of thermal stabilization and photostabilization of polycaproamide fibers by means of the additive was estimated by the method in [4].

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