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THE RELATIONSHIP BETWEEN THE STRUCTURES OF Cu(II) COORDINATION COMPOUNDS AND THEIR THERMAL DECOMPOSITION

XIII. Study of the thermal decomposition of the complexes $Cu_4O(X+Y)_6L_4$

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A study was made of the influence of the composition of the Cu(II) coordination sphere on the course of the thermal decomposition of the complexes $Cu_4O(X+Y)_6L_4$, where X^- and Y were Cl and Br, and L was piperidine or morpholine. The tetrahedral unit Cu_4O with the oxygen atom in its centre was found to be the thermally weakest part of the complex. The decomposition temperatures of the complexes were strongly influenced by the anions X and Y and by the ligand L. The temperature at which decomposition started was found to be the lower, the more chloride anions were substituted by bromide anions. The complexes containing piperidine as ligand L exhibited higher decomposition temperatures than those with morpholine as ligand. The decompositions of all the studied complexes were accompanied by redox reactions. The only compounds identified among the decomposition intermediates by X-ray diffraction were copper(I) halides. Copper(I) bromide underwent oxidation on further heating and a mixture of CuO and CuBr was obtained as the final decomposition product.

Introduction

Coordination compounds of the type $Cu_4O(X+Y)_6L_4$ possess a special type of molecular structure [1], in which the central oxygen atom is tetrahedrally coordinated by four copper(II) atoms bridged by halide atoms. The trigonal-bipyramidal coordination around each copper atom is completed by the ligand L [2]. This type of molecular structure seems to exert a stabilizing effect on the oxidation state II of the copper atom. Compounds containing strongly reductive ligands such as triphenylphosphine [1] or thiourea [2] have been prepared, but their thermal stabilities were relatively

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low, and they decomposed at temperatures of about 45° [1] and 35°C [2]. In contrast, the complexes with pyridine or different picolines as ligands melted without decomposition at 144–275°C [3]. These differences in the thermal stabilities of the compounds, obviously caused by the different bonding properties of the ligands L, together with the fact that the Cu(II) coordination sphere in these compounds is heterogeneous (three different ligands in the equatorial plane), made these compounds of interest for study of the relationship between the structure and composition of the compounds and the course of their chemical reactions. Therefore, we studied the thermal decompositions of the following compounds with piperidine (P) or morpholine (M) as ligands: $Cu_4OCl_6P_4$, $Cu_4OCl_4Br_2P_4$, $Cu_4OCl_3Br_3P_4$, $Cu_4OCl_2Br_4P_4$, $Cu_4OBr_6P_4$, $Cu_4OCl_6M_4$, $Cu_4OCl_4Br_2M_4$, $Cu_4OCl_3Br_3M_4$, $Cu_4OCl_2Br_4M_4$ and $Cu_4OBr_6M_4$.

Experimental

Synthesis of compounds

To methanolic solutions of anhydrous $CuCl_2$ or $CuBr_2$ prepared according to standard methods, freshly prepared copper oxide was added. The reaction mixtures were then heated at 60°C for 4 hours without access of air moisture. After filtration, piperidine or morpholine was added to the solutions under continuous stirring. The dark-brown microcrystalline powders deposited immediately were collected by filtration, washed with diethyl ether and dried in vacuo.

Analytical methods

The copper content was established electrolytically in solutions of samples after their mineralization. The halide content was found argentometrically, with potentiometric indication of the equivalence point. Elemental analysis was performed on a Carlo Erba analyser, and the solvent content was established by means of thermogravimetry. The analytical compositions of the studied compounds are given in Table 1.

The thermal decompositions of all the studied compounds were carried out on an OD 102 derivatograph (MOM, Hungary). The sample mass used was 100 mg, with a heating rate of 10 deg·min^{-1}. The temperature was measured with Pt/Pt-Rh thermocouples, and α-Al_2O_3 was used as inert

Table 1 Analytical composition of the studied compounds

Compound		%Cu	%Cl	%Br	%C	%H	%N
Cu_4OClP_4,	calc.	30.87	25.83		29.17	5.39	6.80
	found	30.41	25.51		29.63	4.20	7.12
$Cu_4OCl_4Br_2P_4$,	calc.	27.86	15.54	17.52	26.33	4.86	6.14
	found	26.58	15.64	16.60	25.29	4.94	7.25
$Cu_4OCl_3Br_3P_4$,	calc.	26.56	11.12	25.05	25.11	4.64	5.86
	found	25.62	11.53	24.41	23.60	4.62	6.20
$Cu_4OCl_2Br_4P_4$,	calc.	25.39	7.08	31.92	23.99	4.43	5.68
	found	24.46	7.02	30.88	22.10	4.56	6.11
$Cu_4OBr_6P_4$,	calc.	23.32		43.97	22.03	4.07	5.14
	found	23.39		43.81	20.00	3.95	5.19
$Cu_4OCl_6M_4$,	calc.	30.57	25.59		23.12	4.37	6.74
	found	29.38	25.79		22.16	4.62	6.67
$Cu_4OCl_4Br_2M_4$,	calc.	27.62	15.41	17.37	20.88	3.94	6.09
	found	26.75	15.06	17.07	20.64	4.00	7.04
$Cu_4OCl_3Br_3M_4$,	calc.	26.35	11.05	24.85	19.92	3.76	5.81
	found	25.27	11.13	23.75	18.84	3.75	6.01
$Cu_4OCl_2Br_4M_4$,	calc.	25.19	7.03	31.67	19.04	3.59	5.55
	found	24.30	6.70	31.53	18.29	3.33	5.91
$Cu_4OBr_6M_4$,	calc.	23.15		43.66	17.50	3.31	5.10
	found	22.74		43.47	17.14	3.39	5.21

material. The intermediates were prepared by isothermal decomposition of the compounds at the temperatures indicated on the derivatograms.

The infrared spectra of the starting compounds and the decomposition intermediates were taken in Nujol suspension in the region 400–3800 cm^{-1}, on a Specord IR-75 spectrophotometer (Carl Zeiss, Jena).

The X-ray powder patterns of the starting compounds, the intermediates and the products of the decomposition reactions were taken on a Dron goniometer (USSR) with CuK_α radiation and a Ni filter.

Results and discussion

The thermal decompositions of the compounds studied in this work had not been reported previously. To our knowledge, the crystal structure is known only for the compounds $Cu_4OCl_6P_4$ [5]. A detailed description of the syntheses and spectral and magnetic properties is given elsewhere [6]. In the present paper, we deal with the structures of the complexes under study only to the extent necessary for our purposes. The powder diffractograms indicate that the crystal structures of the complexes in both studied series are quite similar. This mutual similarity is more marked in the piperidine series (Table 2), in which the interplanar distances vary with changing ratio of $[Cl^-]:[Br^-]$ in the compounds: the interplanar distances are the greater, the higher the bromine content in the compound. The relationship between the crystal structures of complexes containing morpholine as ligand L and different ratios of $[Cl^-]:[Br^-]$ is more complicated (Table 3). The molecule of morpholine (C_4H_9ON) may be coordinated to the central atom through its nitrogen or oxygen atoms. However, the electronic spectra of the studied compounds [6] demonstrate that the structures of the Cu(II) coordination polyhedra are affected by the substitution of Br^- for Cl^-, or of piperidine for morpholine, to only a very small extent. We concluded, therefore, that the coordination of the morpholine in these compounds takes place through the nitrogen atom. This conclusion is supported by the IR spectra of the respective compounds [6]. In the IR spectra of all the studied compounds, absorption bands indicative of the presence of the unit Cu_4O [1] were found (Table 4). The wavenumbers of these bands were found to be dependent on the ratio $Cl^-:Br^-$ in the complex. The shift in $\nu(Cu_4O)$ to lower wavenumbers with increasing content of bromine indicates a decrease in bond energy in the Cu_4O units. The wavenumbers for $\nu(Cu_4O)$ are not influenced by the ligand L. All the studied compounds were found thermogravimetrically to contain a small amount of solvent (methanol or diethyl ether). The solvent

Table 2 The X-ray powder patterns of complexes $Cu_4O(X+Y)_6P_4$

$Cu_4OBr_6P_4$		$Cu_4OBr_4Cl_2P_4$		$Cu_4OBr_3Cl_3P_4$		$Cu_4OBr_2Cl_4P_4$		$Cu_4OCl_6P_4$	
2θ	I_r	2θ	I_r	2θ	I_r	2θ	I_r	2θ	I_r
8.25	100	9.10	100	9.10	100	9.20	100	9.15	100
10.00	65	10.40	14	10.40	10	10.60	14	10.50	14
11.20	92			11.20	8	11.50	11	11.30	11
12.90	33	12.50	19						
13.20	36	13.70	22			14.00	13	14.00	13
14.20	42	14.30	29			14.85	16	14.50	16
		15.70	35			15.50	17	15.50	17
						15.85	20		
						16.00	14	16.00	14
17.30	14								
17.80	34	17.85	80	17.90	12	18.00	21	18.00	21
20.00	8	20.00	11						
		21.30	12						
22.80	80	21.80	14	22.60	3	22.65	6	22.40	6
23.00	35	23.10	61	23.30	10				
23.70	21								
		24.80	31	24.60	17	24.15	12	24.10	20
				24.90	15	24.85	9	24.50	8
26.00	45	26.90	11			25.15	13	25.10	13
26.20	45					25.80	5	25.60	5
29.30	22	29.40	32	28.90	4				
				29.70	9				
30.60	33	30.80	47	30.70	8	30.30	7	30.20	7
30.70	33								
31.20	14	31.70	35	31.40	7	31.50	11	31.30	11
31.70	22					31.70	12	31.40	12
32.25	23	32.30	41						
32.60	21								
34.30	21	34.40	14	33.80	6	34.30	6	34.20	6
36.90	29	37.00	12	37.85	5	37.60	6	37.10	7
								37.30	4
39.00	21	39.20	29			39.90	11	39.60	10

Table 3 The X-ray powder patterns of complexes $Cu_4O(X+Y)_6M_4$

$Cu_4OBr_6M_4$		$Cu_4OBr_4Cl_2M_4$		$Cu_4OBr_3Cl_3M_4$		$Cu_4OCl_6M_4$	
2θ	I_r	2θ	I_r	2θ	I_r	2θ	I_r
7.50	20	7.40	90	7.30	82	7.20	50
7.70	100	8.30	100	8.30	83	7.60	40
						8.10	51
		9.07	68			8.60	38
9.50	57	9.80	67	9.70	63	9.80	42
10.10	63	10.10	35	10.20	100	10.40	100
10.70	66			10.70	78		
		11.10	68	11.10	72	11.10	92
						11.30	62
						11.70	40
12.10	64	12.30	40	12.10	43	12.30	79
				12.60	32		
				13.30	15		
14.10	31					14.20	23
15.10	28	15.00	28	15.00	43	15.35	57
				15.70	40		
16.10	25	16.00	23	16.10	37		
16.30	25			16.90	25		
17.70	12					18.00	62
		18.40	18	18.30	28	18.30	65
19.00	32					18.70	57
19.20	32	19.30	22	19.30	22		
20.40	13	20.00	21	20.00	32		
20.70	13						
21.50	37	21.10	12				
		21.60	22			21.30	23
		22.10	23	22.20	54	22.70	26
23.70	44	23.80	41			24.00	32
24.30	63	24.10	45				
24.70	60	24.80	66				
25.30	43						
26.30	51	26.60	37			26.50	45
28.50	15			28.00	31	27.30	37
						28.00	26
30.20	17	30.30	37	30.40	24	30.70	25

Table 4 The wavenumbers of $\nu(Cu_4O)$ in the starting compounds and in the intermediates of their thermal decomposition

Compound	$\nu(Cu_4O)$		
	r.t.	140°C	360°C
$Cu_4OBr_6M_4$	535, s 505, sh	(570)	–
$Cu_4OCl_3Br_3M_4$	550, s	580, m 560, w	–
	510, sh	525, vw 510, vw	
$Cu_4OCl_6M_4$	570, s 515, sh	546, m	–
$Cu_4OBr_6P_4$	530, s 505, sh	546, m	–
$Cu_4OCl_3Br_3P_4$	550, s 510, sh	560, vw 545, w	–
$Cu_4OCl_6P_4$	570, s 515, m	570, w 540, vw 530, sh	–

molecules are probably trapped in the crystal structure cavities, because their removal from the sample does not lead to marked changes in the crystal structure of the sample (Fig. 1). The courses of the thermal decompositions of the studied complexes were very similar for all the studied compounds (Fig. 2). The processes start at temperatures only slightly higher

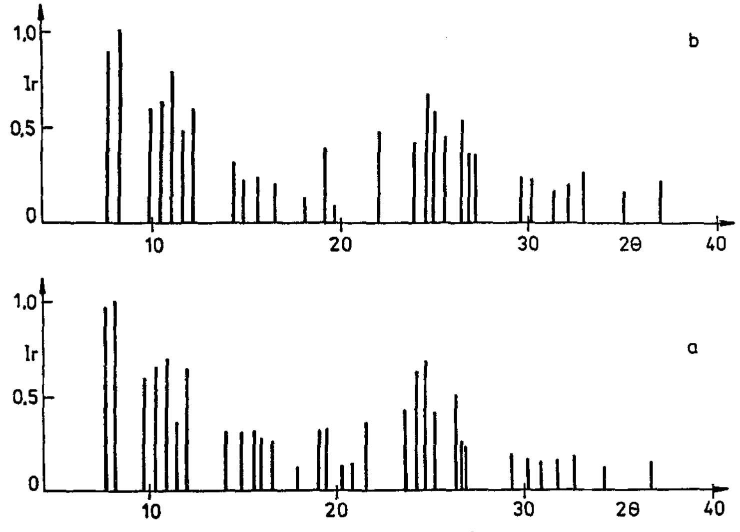

Fig. 1 X-ray powder patterns of *a*) solvated, *b*) desolvated $Cu_4OBr_6M_4$

than room temperature, and in the first decomposition step the small amount of solvent is released. The next decomposition step (Table 5) is connected with a marked exo effect, and the weight losses are in most cases only slightly higher than the oxygen content (1.45–1.97%) in the studied compounds (Table 5). The intermediates formed are viscous liquids, which did not crystallize even after they were cooled down to room temperature. The IR spectra of these intermediates were taken after their dissolution in acetone or ethanol. The results indicated that the Cu_4O unit was completely decomposed in this reaction (Table 4). The exothermicity of the reaction (al-

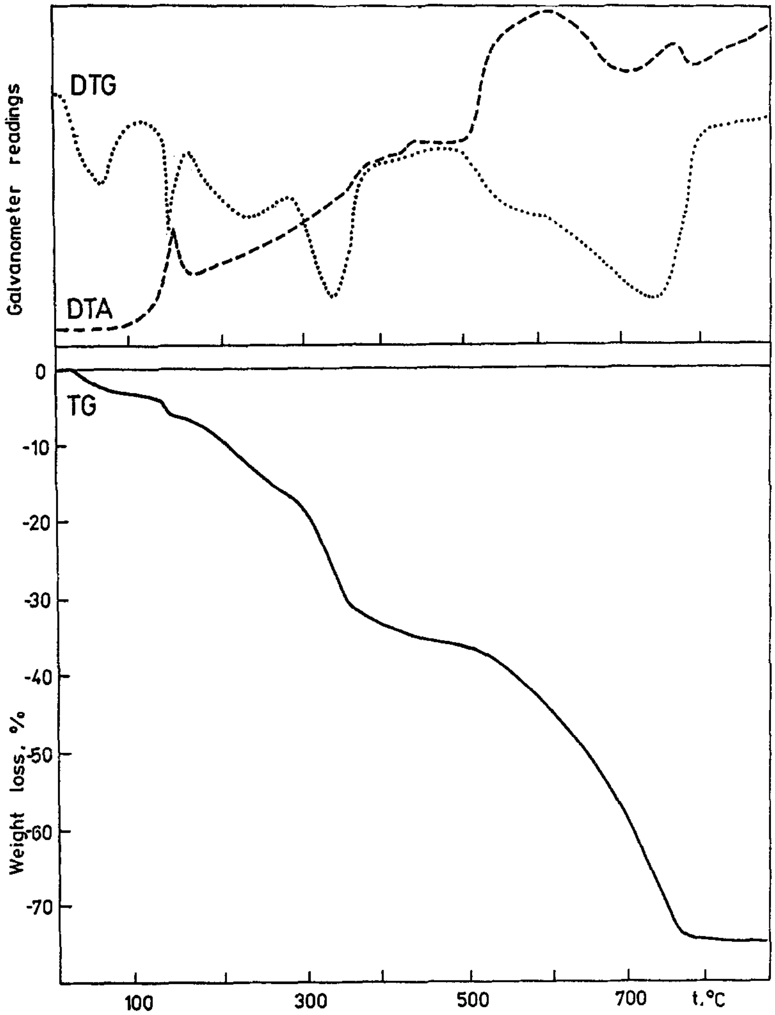

Fig. 2 The overall course of the thermal decomposition of $Cu_4OCl_2Br_4M_4$

Table 5 Thermal decomposition of compounds $Cu_4O(X+Y)_6L_4$

Compound	2. decomp. step		3. decomp. step		4. decomp. step	
	T_d, °C	Weight loss, %	T_d, °C	Weight loss, %	T_d, °C	Weight loss, %
$Cu_4OBr_6 \cdot 4M$	140	1.5	140–420	38	420–860	79
$Cu_4OCl_2Br_4 \cdot 4M$	140	2.0	140–460	35	460–845	75
$Cu_4OCl_3Br_3 \cdot 4M$	138	2.5	140–450	40	450–900	80
$Cu_4OCl_4Br_2 \cdot 4M$	150	2.0	150–460	33	460840	80
$Cu_4OCl_6 \cdot 4M$	160	2.5	160–460	40	460–840	75
$Cu_4OBr_6 \cdot 4P$	120	2.0	120–485	33	490–840	83
$Cu_4OCl_2Br_4 \cdot 4P$	120	5.0	120–480	33	480–840	83
$Cu_4OCl_3Br_3 \cdot 4P$	130	2.5	130–460	29	460–840	77
$Cu_4OCl_4Br_2 \cdot 4P$	130	3.0	130–460	33	460–840	83
$Cu_4OCl_6 \cdot 4P$	150	3.0	150–460	36	460–840	77

though melting of the sample took place as well) suggests the simultaneous reduction of Cu(II) to Cu(I). The decomposition temperature of the complexes depends on the ligand L and on the ratio of chlorine and bromine atoms present. Generally, the complexes containing morpholine as ligand decompose at higher temperatures than those containing piperidine as ligand. In both studied series of complexes, the decomposition temperature is the lower, the higher the content of bromine atoms (Table 5). This behaviour of the complexes can be explained if it is supposed that the molecular structure of these compounds is the same as found for pyridine and picoline derivatives [2], in which trigonal-bipyramidal surroundings of the Cu(II) are characteristic, with heterogeneous occupation of the axial trans coordinate. The four-fold coordinated oxygen atom must attract the electrons from the copper(II) atoms, which saturate their electron needs by abstracting the coordinating donor electron pair from the nitrogen atom of the piperidine or morpholine and/or from the coordinated halide atoms. Both neutral ligands used in this study are good σ-donors ($pK_{\text{piperidine}} = 2.80$, $pK_{\text{morpholine}} = 5.3$). Nevertheless, complexes of a more common composition with these ligands, e.g. CuX_2L_2, are rather scarce [8] and their composition is in fact not sure [9]. Moreover, it has been found that in benzene solutions of CuX_2 ($X^- = Br, Cl, NO_3, ClO_4$) the Cu(II) is reduced to Cu(I) in the presence of piperidine [10], the rate of reaction being strongly dependent on the nature of X and on the molar ratio of the anions present. Although we are aware that two completely different systems are being compared, some common features can be found. Of the complexes under study, the complexes with X = Br or with mixed anionic ligands are less stable against decomposition; this is connected with the redox reaction. The literature data indicate that the complexes $Cu_4OX_6L_4$ with X = Br are always less stable than those with X = Cl [1, 4] for the same neutral ligand L. On further heating of the intermediates, the organic products of the redox reaction evaporate and CuBr crystallizes from the samples containing only bromine anions (Fig. 3) and from compounds which simultaneously contain chlorine and bromine atoms. The crystalline product of the decomposition of $Cu_4OCl_2Br_4P_4$, for example, was found to correspond to γ-CuBr (found interplanar distances 3.25, 2.00 and 1.77 Å, tabulated distances 3.25, 2.00 and 1.72 Å). CuCl was found as a decomposition product merely for compounds originally containing only chlorine anions. This result is interesting because, according to the tabulated data, CuCl is thermally more stable than CuBr.

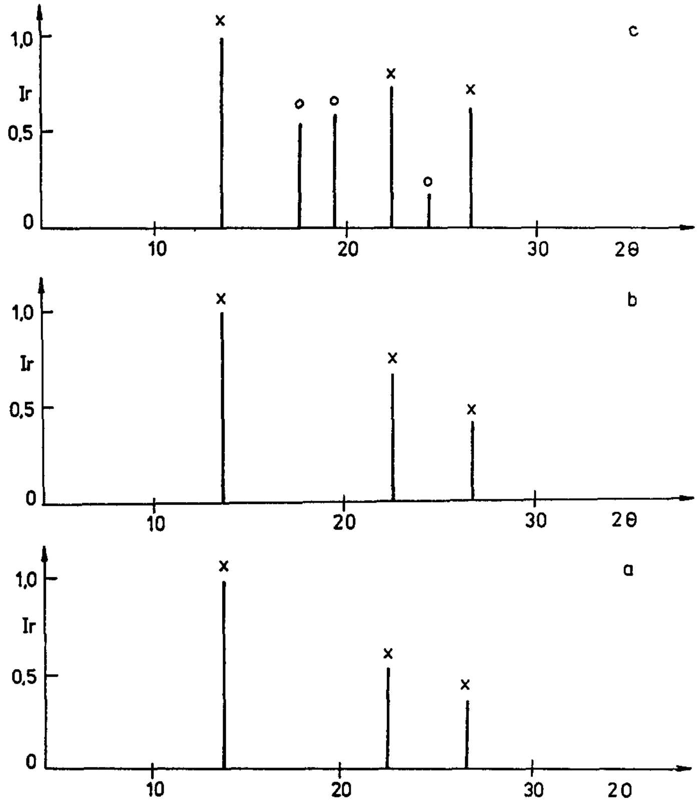

Fig. 3 X-ray patterns of the intermediates of the thermal decomposition of $Cu_4OBr_6P_4$ at *a*) 250, *b*) 300 and *c*) 400°C (x: CuBr, o: CuO)

The reaction intermediates were in each case black, and their powder patterns showed that a considerable amount of unidentified amorphous phase was present as well. The course of decomposition was found to be the same in nitrogen. However, when the decomposition was carried out in the air, the CuBr was oxidized to CuO at higher temperatures, and a mixture of CuBr and CuO was identified in the powder diffraction patterns (Fig. 3). The overall weight loss was in all cases much higher than corresponded to the formation of copper(I) halides, and was even higher than the Cu content in the complexes (Table 6). We presume that compounds of copper halides with products of organic ligand decomposition are lost from the systems during their heating.

Table 6 Calculated contents of oxygen, ligands *L*, CuX and Cu in the studied compounds

Compound	M.w., g mol^{-1}	%0	%*L*	%CuX
$Cu_4OBr_6P_4$	1030.21	1.46	31.24	52.26
$Cu_4OBr_4Cl_2P_4$	1001.30	1.59	34.02	
$Cu_4OBr_3Cl_3P_4$	956.85	1.67	35.59	
$Cu_4OBr_2Cl_4P_4$	912.39	1.75	37.33	
$Cu_4OCl_6P_4$	823.48	1.97	41.36	48.00
$Cu_4OBr_6M_4$	1098.09	1.45	31.47	52.25
$Cu_4OBr_4Cl_2M_4$	1009.18	1.58	39.54	
$Cu_4OBr_3Cl_3M_4$	969.13	1.65	36.11	
$Cu_4OBr_2Cl_4M_4$	920.27	1.73	37.73	
$Cu_4OCl_6M_4$	931.36	1.92	41.54	

To conclude, we can say that the thermal stabilities of the complexes $Cu_4O(X+Y)_6L_4$ depend strongly on the nature of both anionic and neutral ligands in the Cu(II) coordination sphere. Till now, only compounds containing N-donor ligands or strongly reducing O-ligands have been investigated to our knowledge. To obtain more information on the influence of the neutral ligand and its donor atom upon these properties of complexes, compounds containing non-reducing O-donor ligands will be investigated.

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Zusammenfassung — Bei der thermischen Zersetzung von Komplexen der Formel $Cu_4O(X+Y)_6L_4$ mit X, $Y =$ Cl bzw. Br und $L =$ Piperidin oder Morpholin wurde der Einfluß der Zusammensetzung der Cu(II)-Koordinationssphäre auf den Verlauf der thermischen Zersetzung untersucht. Als thermisch schwächstes Glied des Komplexes wurde die tetraedrische Einheit Cu_4O mit dem Sauerstoffatom im Zentrum befunden. Die Zersetzungstemperaturen der Komplexe werden durch die Anionen X und Y sowie durch die Liganden L wesentlich beeinflußt. Die Temperatur, bei der die Zersetzung einsetzt liegt um so niedriger, je mehr Chloridanionen durch Bromidanionen ersetzt werden. Komplexe mit Piperidin als Ligand zeigen höhere Zersetzungstemperaturen als mit dem Ligand Morpholin. Die Zersetzung aller Komplexe ist von Redoxreaktionen begleitet. Die einzigen Verbindungen, die unter den Zersetzungsprodukten mittels Röntgendiffraktion identifiziert wurden, waren Kupfer(I)-halogenide. Kupfer(I)-bromid unterliegt bei weiterem Erhitzen einer Oxidation und man erhält letztendlich ein Gemisch aus CuO und CuBr als Zersetzungsprodukt.