

ON THE RELATIONSHIP BETWEEN THE STRUCTURES OF Cu(II) COMPLEXES AND THE COURSE OF THEIR THERMAL DECOMPOSITION

XV. Thermal decomposition of complexes $\text{Cu}_4\text{O}(\text{Cl}+\text{Br})_6(\text{OPPh}_3)_4$

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Abstract

Thermal decomposition of $[\text{Cu}_4\text{O}(\text{Cl}+\text{Br})_6(\text{OPPh}_3)_4]$, starts at temperatures about 200°C. The decomposition proceeds in several steps. The intermediate formed in the first decomposition step (weight loss 2–4%) is a new crystalline phase with slightly different structure but with preserved central unit Cu_4O . The only crystalline phases found in the further decomposition products was CuBr in all cases when the bromine atoms were present, the presence of CuCl was only observed at the decomposition of the hexachlorocomplex.

Keywords: complexes, Cu(II) complexes, structures, thermal decomposition

Introduction

The title compounds possess rather rare structure moiety, namely the central Cu_4O tetrahedron [1]. The Cu^{II} atoms are bridged by anions Cl and Br and the coordination polyhedron of Cu^{II} is completed to a trigonal bipyramid by one neutral ligand [1]. It was shown that this structure type exhibits a stabilizing effect on the oxidation state II of copper atoms, while complexes with strongly reductive ligands were prepared and characterised [2, 3]. According to our previous results [4] and literature data [1–3], the thermal and redox stability of these compounds depends strongly on the bonding properties of neutral ligands *L*. Therefore we continued our studies on these compounds and now we report the results, gained for complexes $[\text{Cu}_4\text{OCl}_6(\text{OPPh}_3)_4]$, $[\text{Cu}_4\text{OCl}_3\text{Br}_3(\text{OPPh}_3)_4]$,

[Cu₄OCIBr₅(OPPh₃)₄] and [Cu₄OBr₆(OPPh₃)₄] with the aim to compare their thermal properties with those containing N-donor ligands [4].

Experimental

Synthesis of compounds proceeded according to the procedure, described in [4]. The compounds were checked analytically for their composition using methods, given in [4]. The results are summarized in Table 1.

Thermal decomposition of all studied compounds was carried out on a derivatograph OD 102 (MOM Hungary). The sample mass was 100 mg, the heating rate 10 deg·min⁻¹. The temperature was measured by Pt, Pt–Rh thermocouples, the α-Al₂O₃ was used as inert material. The intermediates were prepared by isothermal decomposition of the compounds at temperatures indicated on the derivatograms.

The infrared spectra of the starting compounds and of the decomposition intermediates were taken in nujoll suspension in the region of 400–3800 cm⁻¹ on a spectrometer Specord IR-75 (Carl Zeiss Jena) and in the region 200–1600 cm⁻¹ on a Philips Analytical PU 9800 FTIR spectrometer.

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

Results and discussion

Detailed information on the spectral and magnetic properties of the studied complexes were given in [5]. These compounds, unlike those containing piperidine or morpholine as ligands does not contain solvent molecules in their structures in most cases. Those which contain solvent molecules are easily desolvated without expressive changes in their structures, as it was confirmed by X-ray powder diffractograms for solvated and desolvated [Cu₄OBr₆(OPPh₃)₄] (Table 2). Also in their IR spectra all absorption bands, significant for the basic compound structure features were retained (ν_{Cu4O} at 545, ν_{P=O} at 1120 cm⁻¹). Studied compounds exhibit very similar crystal structures (Table 3), the interlayer distances are growing with increasing bromide content in the compound. From the X-ray powder patterns it may also be seen that the compound [Cu₄OCIBr₃(OPPh₃)₄] is not a mechanical mixture of [Cu₄OCIBr₆(OPPh₃)₄] and [Cu₄OBr₆(OPPh₃)₄] complexes. The recent crystal structure solution of the [Cu₄OCIBr₃(OPPh₃)₄] [6] indicates, however the presence of two completely different complex molecules in the elementary cell,

Table 1 Analytical composition of the studied compounds

Compound	%Cu		%Cl		%Br		%C		%H	
	calc.	exp.	calc.	exp.	calc.	exp.	calc.	exp.	calc.	exp.
I	13.64	13.24	-	-	25.74	25.46	46.43	45.69	3.25	3.38
II	14.70	14.15	6.15	5.43	13.86	13.92	50.00	48.92	3.49	3.62
III	13.98	13.45	1.95	1.93	21.97	21.29	47.56	47.03	3.32	3.46
IV	15.92	15.28	13.33	13.06	-	-	54.18	53.19	3.79	3.73

Table 2 Powder patterns of solvated (A) and desolvated (B) $[\text{Cu}_4\text{OBr}_6(\text{OPPh}_3)_4]$

A			B		
2θ	$d/\text{\AA}$	I_r	2θ	$d/\text{\AA}$	I_r
6.12	14.4244	100	6.25	14.1172	99
10.07	8.7764	52	10.12	8.7303	58
11.85	7.4572	99	11.90	7.4281	100
12.37	7.1488	63	12.47	7.0917	74
15.59	5.6785	8	15.67	5.6496	6
18.60	4.7647	5			
21.20	4.1859	36	21.28	4.1703	40
21.47	4.1345	14			
22.67	3.9182	49	22.80	3.8956	52
23.50	3.7812	83	23.60	3.7654	88
24.87	3.5763	40	24.97	3.5623	46
25.67	3.4667	24	25.73	3.4578	24
26.87	3.3145	16	26.97	3.3024	21
27.60	3.2281	8	27.68	3.2189	12
28.79	3.0976	14	28.83	3.0927	17
29.67	3.0077	23	29.77	2.9978	30
30.57	2.9212	14	30.70	2.9088	19
31.20	2.8633	40	31.28	2.8562	49
32.87	2.7218	15	32.93	2.7165	20
36.03	2.4895	7	36.10	2.4851	9
36.93	2.4309	18	37.03	2.4246	18
37.47	2.3975	15	37.60	2.3893	14
39.07	2.3029	8	39.23	2.2935	12
39.80	2.2622	11	39.90	2.2567	16
41.13	2.1919	23	41.27	2.1851	31
41.63	2.1667	26	41.77	2.1601	31
42.50	2.1245	6			
43.00	2.1009	8			
44.07	2.0437	11	44.33	2.0408	12
45.03	2.0107	16	45.13	2.0065	18
45.50	1.9912	19	45.63	1.9856	20
46.79	1.9393	14	46.97	1.9323	19
47.47	1.9131	17	47.60	1.9081	20
48.00	1.8931	11	48.07	1.8906	18
48.67	1.8687	16	48.77	1.8651	23
52.17	1.7513	7	52.30	1.7471	10
52.53	1.7399	7	52.67	1.7358	13

Table 3 Powder patterns of [Cu₄OCl₆(OPPh₃)₄] (I), [Cu₄OCl₃Br₃(OPPh₃)₄] (II) and [Cu₄OBr₆(OPPh₃)₄] (III)

I			II			III		
2θ	d/Å	I _r	2θ	d/Å	I _r	2θ	d/Å	I _r
-	-	-	6.20	14.2385	100	6.12	14.4244	100
7.4	11.9320	80	-	-	-	-	-	-
10.40	8.4958	39	10.20	8.6620	72	10.07	8.7764	52
-	-	-	10.80	8.1821	21	-	-	-
-	-	-	11.33	7.7982	33	-	-	-
-	-	-	-	-	-	11.85	7.4572	99
-	-	-	12.00	7.3664	91	-	-	-
12.77	6.9257	65	12.53	7.0541	76	12.37	7.1488	63
14.73	6.0054	94	-	-	-	-	-	-
-	-	-	15.70	5.6377	13	15.59	5.6785	8
16.40	5.3986	100	-	-	-	-	-	-
17.95	4.9349	20	-	-	-	-	-	-
-	-	-	18.73	4.7311	5	18.60	4.7647	5
-	-	-	21.33	4.1600	34	21.20	4.1859	36
-	-	-	-	-	-	21.47	4.1345	14
21.73	4.0844	72	-	-	-	-	-	-
22.01	4.0330	88	-	-	-	-	-	-
-	-	-	22.83	3.8900	35	22.67	3.9182	49
23.19	3.8315	17	23.67	3.7549	78	23.50	3.7812	83
24.33	3.6535	13	24.53	3.6242	14	24.87	3.5763	40
25.41	3.5015	26	25.00	3.5576	33	-	-	-
-	-	-	25.83	3.4447	23	25.67	3.4667	24
-	-	-	27.07	3.2904	14	26.87	3.3145	16

Table 3 Continued

I			II			III		
2θ	$d/\text{\AA}$	I_r	2θ	$d/\text{\AA}$	I_r	2θ	$d/\text{\AA}$	I_r
27.43	3.2427	51	27.79	3.2068	9	27.60	3.2281	8
28.17	3.1644	16	-	-	-	-	-	-
30.30	2.9463	34	29.88	2.9867	23	28.79	3.0976	14
-	-	-	-	-	-	29.67	3.0077	23
-	-	-	30.75	2.9039	13	30.57	2.9212	14
31.23	2.8603	13	31.39	2.8467	35	31.20	2.8633	40
31.88	2.8038	20	-	-	-	-	-	-
32.08	2.7867	25	-	-	-	-	-	-
32.92	2.7175	7	32.40	2.7599	7	-	-	-
-	-	-	33.06	2.7058	17	32.87	2.7218	15
33.73	2.6538	13	33.88	2.6427	5	-	-	-
34.55	2.5932	20	-	-	-	-	-	-
36.13	2.4829	11	-	-	-	36.03	2.4895	7
36.88	2.4343	32	37.12	2.4191	22	36.93	2.4309	18
37.67	2.3853	18	37.67	2.3853	13	37.47	2.3975	15
38.39	2.3422	18	-	-	-	-	-	-
-	-	-	39.26	2.2917	9	39.07	2.3029	8
39.82	2.2611	27	39.87	2.2586	8	39.80	2.2622	11
40.60	2.2194	10	-	-	-	-	-	-
-	-	-	41.27	2.1851	25	41.13	2.1919	23
41.93	2.1519	20	41.85	2.1558	20	41.63	2.1667	26
42.63	2.1182	18	-	-	-	42.50	2.1245	6

Table 3 Continued

I			II			III		
2θ	$d/\text{\AA}$	I_r	2θ	$d/\text{\AA}$	I_r	2θ	$d/\text{\AA}$	I_r
43.30	2.0871	15	—	—	—	43.00	2.1009	8
44.57	2.0307	15	44.43	2.0364	8	44.27	2.0437	11
45.23	2.0023	17	45.13	2.0065	9	45.03	2.0107	16
45.93	1.9734	19	45.73	1.9815	11	45.50	1.9912	19
—	—	—	46.95	1.9329	11	46.79	1.9393	14
47.77	1.9018	32	47.60	1.9081	18	47.47	1.9131	17
—	—	—	—	—	—	48.00	1.8931	11
48.40	1.8784	23	48.63	1.8699	11	48.67	1.8687	16
49.57	1.8369	27	—	—	—	—	—	—
—	—	—	52.25	1.7486	9	52.17	1.7513	7
53.10	1.7227	16	52.73	1.7338	8	52.53	1.7399	7
53.63	1.7068	20	—	—	—	—	—	—
54.87	1.6713	15	—	—	—	—	—	—
55.35	1.6579	7	—	—	—	—	—	—
59.17	1.5597	7	—	—	—	—	—	—

Table 4 Thermal decomposition of the studied compounds

Compound	$\nu(\text{Cu}_4\text{O})/\text{cm}^{-1}$	1. decomposition step		2. decomposition step		3. decomposition step	
		$T_d/^\circ\text{C}$	Weight loss/%	$T_d/^\circ\text{C}$	Weight loss/%	$T_d/^\circ\text{C}$	Weight loss/%
I	545	240	3 endo	280	51 endo	500-680	77 exo
II	560	230	2 endo	270	50 endo	500-740	75 exo
III		190	3 endo	260	50 endo	525-680	77 exo
IV	585	260	3 endo	280	57 endo	480-650	76 exo

Abbreviations: I - $[\text{Cu}_4\text{OBr}_6(\text{OPPh}_3)_4]$, II - $[\text{Cu}_4\text{OCl}_3\text{Br}_3(\text{OPPh}_3)_4]$, III - $[\text{Cu}_4\text{OClBr}_5(\text{OPPh}_3)_4]$, IV - $[\text{Cu}_4\text{OCl}_6(\text{OPPh}_3)_4]$

namely $[\text{Cu}_4\text{OCl}_6(\text{OPPh}_3)_4]$ and $[\text{Cu}_4\text{OBr}_6(\text{OPPh}_3)_4]$. Anyway, the vibration $\nu(\text{Cu}_4\text{O})$, which is very sensitive to the kind of anion, coordinated to the central atom does not exhibit any splitting.

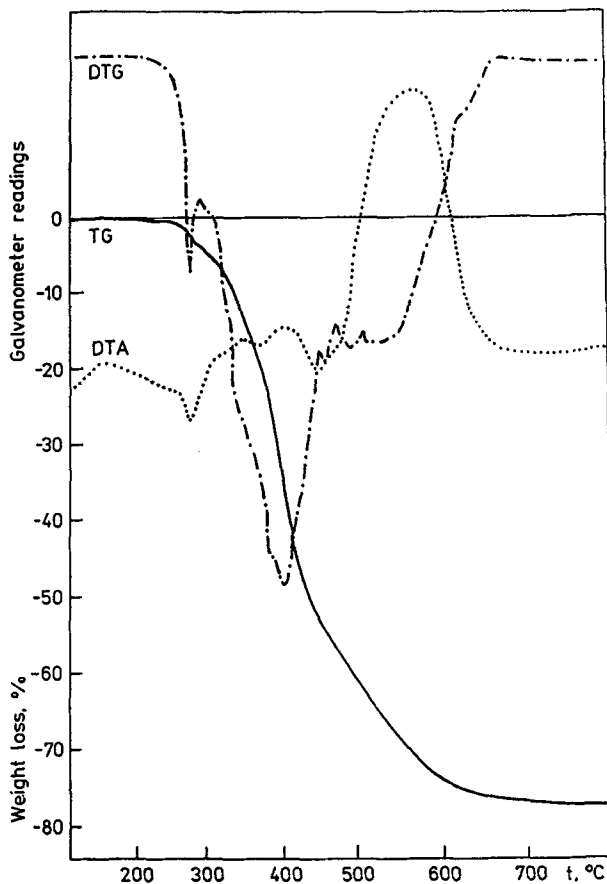


Fig. 1 Thermal decomposition of $[\text{Cu}_4\text{OCl}_6(\text{OPPh}_3)_4]$

The thermal decomposition of the compounds under study starts at considerably higher temperatures than it was found for complexes with N-donor ligands [4] (Table 4). The decomposition temperatures depend on the composition of the anionic part of coordination sphere, being the higher, the more chlorine anions are present. In the first decomposition step of the complexes $[\text{Cu}_4\text{O}(\text{Cl}+\text{Br})_6(\text{OPPh}_3)_4]$ only 2–3% of the sample mass are evolved (Fig. 1), the reaction being slightly endothermic. Investigation of the intermediate of this decomposition step of $[\text{Cu}_4\text{OCl}_3\text{Br}_3(\text{OPPh}_3)_4]$ showed that according to X-ray powder pattern a new phase was formed (Table 5). The compound do not melt

during this reaction and the original colour is retained. The comparison of the IR spectra of the reaction product, and of the initial compound shows (Table 6) that the structure moiety Cu_4O does not break down in this reaction step, but some changes do occur in the region of Cu-X, Cu-O and ligand vibrations at low wave numbers. This indicates small changes in the structure units arrangement, however what escapes from compound is not clear. Thermal decomposition of the compound $[\text{Cu}_4\text{OCl}_3\text{Br}_3(\text{OPPh}_3)_4]$ in its early stages differs, according to the DTG curve from the decomposition of other compounds under study, the weight loss of 4% being achieved in two subsequent steps (Fig. 2). This would mean that the different complex molecules $[\text{Cu}_4\text{OX}_6(\text{OPPh}_3)_4]$ are decomposed at different temperatures.

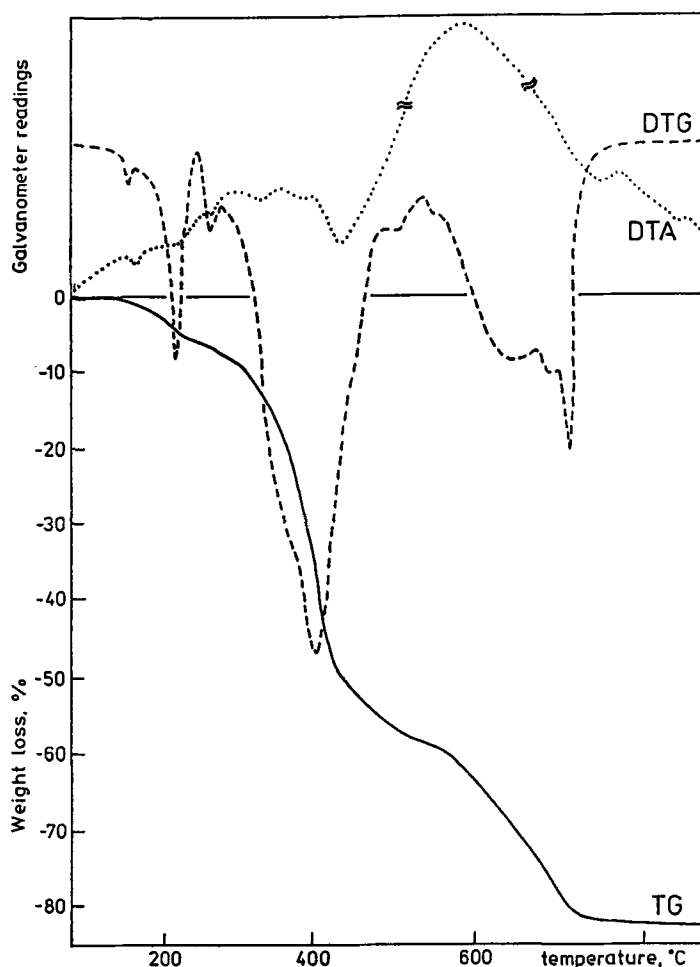


Fig. 2 Thermal decomposition of $[\text{Cu}_4\text{OCl}_3\text{Br}_3(\text{OPPh}_3)_4]$

Table 5 Powder patterns of $[\text{Cu}_4\text{OCl}_3\text{Br}_3(\text{OPPh}_3)_4]$ and of the first decomposition reaction product (weight loss 4%)

$[\text{Cu}_4\text{OCl}_3\text{Br}_3(\text{OPPh}_3)_4]$			Product of decomposition		
2θ	$d/\text{\AA}$	I_r	2θ	$d/\text{\AA}$	I_r
6.20	14.2385	100	6.00	14.7127	59
			6.27	14.0872	90
			7.20	12.2630	34
			8.27	10.6829	12
			8.75	10.0977	15
			9.13	9.6711	8
			9.47	9.3313	24
10.20	8.6620	72	10.17	8.6903	100
10.80	8.1821	21	10.80	8.1821	1
11.33	7.7982	33			
12.00	7.3664	91	11.92	7.4157	85
12.53	7.0541	76	12.47	7.0917	63
15.70	5.6377	13	15.60	5.6736	12
18.73	4.7311	5			
21.33	4.1600	34	20.95	4.2346	28
			21.23	4.1794	43
22.83	3.8900	35	22.73	3.9069	48
23.67	3.7549	78	23.53	3.7759	78
24.53	3.6242	14			
25.00	3.5576	33	24.93	3.5669	31
25.83	3.4447	23	25.59	3.4773	14
27.07	3.2904	14	26.87	3.3137	11
27.79	3.2069	9	27.67	3.2204	12
			28.80	3.0962	14
29.88	2.9867	23	29.73	3.0011	25
30.75	2.9039	13	30.68	2.9106	18
31.39	2.8467	35	31.27	2.8574	35
32.40	2.7599	7			
33.07	2.7058	17	32.90	2.7191	17
33.88	2.6427	5	33.87	2.6437	6
37.12	2.4191	22	36.99	2.4275	18
37.67	2.3853	13			
39.27	2.2917	9	38.98	2.3075	10
39.87	2.2586	8	39.73	2.2658	7
			40.23	2.2388	12
41.27	2.1851	25	41.20	2.1885	23

Table 5 Continued

[Cu ₄ OCl ₃ Br ₃ (OPPh ₃) ₄]			Product of decomposition		
2θ	d/Å	I _r	2θ	d/Å	I _r
41.85	2.1558	20	41.63	2.1667	24
44.43	2.0364	8			
			45.07	2.0093	17
45.13	2.0065	9			
45.73	1.9815	11	45.53	1.9898	18
46.95	1.9329	11	46.73	1.9414	16
47.60	1.9081	18	47.43	1.9144	18
48.63	1.8699	11			
52.25	1.7486	9			
52.73	1.7338	8			

Products of further quick, endothermic reaction were identified as single Cu^I halides, mostly as the low temperature γ -phases, containing in several cases a small admixture of high temperature β -phase (Table 6). For all complexes, containing bromine atoms, or bromine and chlorine atoms, the presence of merely CuBr was established. The CuCl was formed only at decomposition of compound Cu₄OCl₆(OPPh₃)₄ and as a small admixture of high temperature phase in the decomposition product of [Cu₄OCl₃Br₃(OPPh₃)₄]. Although the same result was found [4] for the decomposition of the compounds with morpholine or piperidine as ligands, it is surprising because of higher melting and boiling points of CuCl with respect to the CuBr [8]. The powder diffractograms indicate in either case a presence of significant amount of amorphous phases, which disappears at continuous heating. In the IR spectra of these intermediates absorption bands of C-H vibrations (2730, 2660, 1500–1580 cm⁻¹) and some others, which might correspond to some phosphor-oxygen compounds (910, 1073, 1110 cm⁻¹) [7] were found. The amorphous phases contain the largest part of organic residue, because only the last decomposition reactions, taking place between approximately 500°C and 700°C are exothermic. During this last reaction, however the crystalline phases do not change, and no crystallization of CuO was observed (Table 7) as it was the case at complexes with morpholine or piperidine ligands [4]. Because the overall weight loss is higher than the copper content in the reactants, we have to assume sublimation of compounds containing these atoms as well.

Table 6 Wave numbers (cm^{-1}) of absorption bands in the IR spectra of $[\text{Cu}_4\text{OCl}_3\text{Br}_3(\text{OPPh}_3)_4]$ and of the decomposition products

	Initial compound	Weight loss	
		4%	50%
L	233 m	233 m	
$\nu(\text{M}-\text{X})$	245 w		
$\nu(\text{M}-\text{X})$	260 s		
$\nu(\text{M}-\text{X})$	295 s	299 m	
L	395 w	399 w	
L	425 w		
$\nu(\text{M}-\text{O})$	447 vs	447 m	
L	536 vs	536 vs	510 m
$\nu(\text{Cu}_4\text{O})$	560 m	567 m	
L	612 m	615 m	
L	625 w		
L	690 s	692 vs	690 br
L	742 m	748 m	
L	752 m	756 m	
L	846 m	846 m	
L	924 m	924 m	890–920 br
L	995 s	972 m	
		995 m	
L	1020 s	1028 m	
L	1070 s	1070 s	1070 br, sh
L	1090 s	1101 s	1110 br, m
$\nu(\text{P}-\text{O})$	1120 vs	1120 vs	

Abbreviations: L – ligand OPPh_3 , ν – very, w – weak, m – medium, s – strong, br – broad, sh – shoulder. The assignment was done according to [7]

The Cu^{I} halides, arising in the decomposition reactions have distorted crystal structures, which is reflected in the slightly different interlayer distances when compared to the data from ASTM tables (Table 8). These distortions are probably caused by impurities present in the samples, because all gained decomposition products, identified via X-ray powder patterns as CuX , were black. However, there is no dependence between the composition of the starting compounds and the lattice deformation degree.

Table 7 The products of the studied decomposition reactions

Compound	Temperature / °C	Weight loss / %		Identified phase
		calc. ^a	found	
Cu ₄ OCl ₆ (OPPh ₃) ₄	400	75.1	35	CuCl
	500	75.1	61	CuCl
Cu ₄ OCl ₃ Br ₃ (OPPh ₃) ₄	400	69.3	34	CuBr, CuCl ^b
	500	69.3	55	CuBr
Cu ₄ OClBr ₅ (OPPh ₃) ₄	400	70.9	50	CuBr
Cu ₄ OBr ₆ (OPPh ₃) ₄	500	69.2	54	CuBr
	600	69.2	65	CuBr

^acalculated for CuX formation, ^bonly traces of high temperature phase

Table 8 Tabeled and found interlayer distances for CuBr

	<i>d</i> ₁	<i>d</i> ₂	<i>d</i> ₃
ASTM	3.25	2.00	1.77
Cu ₄ OCl ₆ (OPPh ₃) ₄	3.29	2.01	1.72
Cu ₄ OCl ₃ Br ₃ (OPPh ₃) ₄ ^a	3.25	1.99	1.70
Cu ₄ OCl ₃ Br ₃ (OPPh ₃) ₄ ^b	3.27	2.01	1.72
Cu ₄ OBr ₆ (OPPh ₃) ₄	3.27	2.01	1.71

^aat 400°C, ^bat 500°C

Conclusion

We can conclude that compounds [Cu₄O(Cl+Br)₆(OPPh₃)₄] are thermally more stable than analogous compounds with morpholine or piperidine as ligands. The course of the thermal decomposition is different, because the central moiety Cu₄O is not decomposed in the first step. The only crystalline decomposition products are the Cu^I halides. The comparison of gained results with those on thermal decomposition of related complexes, containing N-donor ligands underlines the importance of coordination sphere composition and binding properties of ligands for the course of their thermal decomposition.

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Zusammenfassung — Die thermische Zersetzung von $[\text{Cu}_4\text{O}(\text{Cl}+\text{Br})_6(\text{OPPh}_3)_4]$ beginnt bei Temperaturen oberhalb 200°C . Die Zersetzung verläuft in mehreren Schritten. Das im ersten Zersetzungsschritt gebildete Intermediär (Gewichtsverlust 2–4%) ist eine neue kristalline Phase mit leicht adweichender Struktur, jedoch mit einer eingeschlossenen Zentraleinheit Cu_4O . Die im verlaufe der weiteren Zersetzungsschritte gefundene einzige kristalline Phase war in allen Fällen CuBr , wenn Bromatome vorhanden waren, die Gegenwart von CuCl wurde nur bei der Zersetzung des Hexachlorocomplexes beobachtet.