

Copper–zinc oxide catalyst. Part II. Preparation, IR characterization and thermal properties of novel bimetallic precursors

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Abstract

Four new bimetallic model precursors of copper–zinc oxide catalysts for methanolization were prepared: $\text{Zn}(\text{NH}_3)_2\text{Cu}(\text{CN})_3$ (ZCA), $[\text{Zn}(\text{en})_3]_6[\text{Cu}_5(\text{CN})_{17}] \cdot n\text{H}_2\text{O}$ ($n = 8.4$) (ZCE3), $\text{Zn}(\text{en})\text{Cu}(\text{CN})_3$ (ZCE1) and $[\text{Zn}_{1-x}\text{Cu}_x(\text{en})][\text{Cu}(\text{CN})_3]$ (ZCCE1). The new compounds were characterized by elemental analysis, IR spectroscopy, and thermal analysis under dynamic conditions. Thermal stability increases in the order ZCE3 (65) < ZCA (120) < ZCE1 or ZCCE1 (155°C). Thermal decomposition in air proceeds via the following steps: dehydration (if water molecules are present), deamination, redox decomposition of the cyano groups with formation of metallic copper and ZnO, and finally re-oxidation of copper to CuO. In the case of en-containing compounds an unexplained phase transition was observed at 800°C.

Keywords: Bimetallic precursors of catalysts; Copper–zinc oxide catalysts; Methanol synthesis; IR; TG–DTA; Thermal analysis

1. Introduction

Copper–zinc oxide are well known catalysts for the synthesis of methanol from syngas ($\text{CO} + \text{H}_2$ mixture) [1], but they can also be used for other catalytic reactions such as the synthesis of higher alcohols with cobalt-promoted samples [2], the water gas shift reaction [3] or the hydrogenation of alkenes [4]. Most publications deal with

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the characterization of the active centres or the intermediates by various methods, or with the catalytic properties, but few focus on the preparation of the solid catalysts and how this influences their activity [5].

Conventional preparations are based on the coprecipitation of copper and zinc nitrates with different basic reagents such as Na_2CO_3 and NaHCO_3 [6], NaOH or NH_4HCO_3 [7], followed by calcination. During this preparation, different copper (II)- and zinc(II)-containing phases have been observed (gerhardtite, zinc malachite [5], aurichalcite and copper hydroxynitrate [6]) which led to different types of CuO-ZnO mixtures on calcination. Another way to obtain such catalysts is the formation of Raney copper in the presence of zinc, by leaching an Al-Zn-Cu alloy with a solution of zincate ions in aqueous alkali metal hydroxide [8].

The $\text{CO} + \text{H}_2$ atmosphere of the methanol process leads to reduction of the copper(II) oxide (CuO) obtained from the former method, with the formation of zero-valent copper. The intermediate formation of monovalent copper has been claimed by different authors on the basis of X-ray diffraction [9] or X-ray photoelectron spectroscopy [10] but in contrast intermediate Cu_2O has not been detected by in situ techniques, as was substantiated by another group [11, 12].

One of the crucial points in this type of preparation is the requirement to produce the finest possible interdispersion of the metallic elements. This need arises from the observation that the activity of such catalysts depends on the interaction between both metals [1]. As this elemental interdispersion at the atomic level has already been accomplished in bimetallic complexes, these compounds are good candidates as bimetallic catalyst precursors.

Surprisingly few Zn-Cu bimetallic complexes with known crystal structure are described in the literature. A search of the Cambridge Crystallographic Database [13] indicates that the crystal structure of only 14 complexes containing both copper and zinc have been studied; these mostly contain large organic ligands which render them unsuitable as precursors, e.g. picolinaldehyde *N*-oxide = L in $(\text{CuLZnCl}_4)_2$ [14]. Among the compounds with smaller ligands are $\text{CuZn}(\text{HCOO})_4 \cdot 4\text{H}_2\text{O}$ [15] and $[(\text{CH}_3)_4\text{N}][\text{ZnCu}(\text{CN})_4]$ — the later being one of the few structures containing copper in the oxidation state (I) [16].

Our aims were: (i) to prepare new Zn-Cu bimetallic complexes, (ii) to ascertain their crystal structures, (iii) to study their thermal decomposition and properties, and (iv) to examine the catalytic properties of model catalysts prepared by calcination of such precursors. In previous work we described the crystal structure of two Zn-Cu complexes, $\text{Zn}(\text{NH}_3)_2\text{Cu}(\text{CN})_3$ and $[\text{Zn}(\text{en})_3]_6[\text{Cu}_5(\text{CN})_{17}] \cdot n\text{H}_2\text{O}$ ($n = 8.4$) [17]. We present here the preparation, IR characterization and derivatographic study of these compounds.

2. Experimental

2.1. Preparation

2.1.1. Preparation of $\text{Zn}(\text{NH}_3)_2\text{Cu}(\text{CN})_3$ (ZCA = zinc-copper-ammonia)

A solution of KCN (2.8 g in 25 cm^3 water) was added to a solution of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (5 g in 25 cm^3 of water). The CuCN precipitate thus formed was decanted and washed

with distilled water. It was then dissolved in KCN solution (2.8 g in 25 cm³ water), and the colourless to yellow solution (in the last case the colour due probably to dissolved (CN)₂) decolorized with active charcoal. The colourless solution containing [Cu(CN)₃]²⁻ and 2K⁺ was filtered and placed in a flask under nitrogen. Concentrated ammonia (25%, ca 10 cm³) was added to a solution of ZnSO₄·7H₂O in water (5.75 g in 25 cm³) until a clear solution was produced; this was filtered and added with vigorous stirring under nitrogen atmosphere to the cold solution of K₂Cu(CN)₃. The white crystalline precipitate formed was filtered off, washed first with small portions of cold dilute ammonia solution, then with ethanol and ether, and finally air-dried. The yield was 65%.

2.1.2. Preparation of [Zn(en)₃]₆[Cu₅(CN)₁₇]·nH₂O (n = 8.4) (ZCE3 = zinc-copper(I)-3 en)

To a fresh solution of K₂Cu(CN)₃ (2.20 g in 25 cm³ water) an aqueous solution of ethylenediamine (2.7 cm³ in 10 cm³) was added in a covered vessel under nitrogen atmosphere (to prevent oxidation of Cu(I)). A solution of ZnSO₄·7H₂O (2.87 g in 20 cm³ water; the Zn:en ratio was 1:4) was added with vigorous stirring. The white crystals were filtered off and dried in air. Yield: 43%.

2.1.3. Preparation of [Zn(en)][Cu(CN)₃] (ZCE1 = zinc-copper(I)-1 en)

The procedure described above was followed, but using 1.35 cm³ of ethylenediamine (Zn:en ratio 1:2). Yield: 67%.

2.1.4. Preparation of [Zn_{1-x}Cu_x(en)][Cu(CN)₃] (ZCCE1 = zinc-copper(I)-copper(II)-1 en)

The synthesis of this complex was as described above from the K₂Cu(CN)₃ solution but in the presence of air. Water (100 cm³) was added along with 2 cm³ of ethylenediamine (Zn:en ratio 1:3). Light green crystals separated. The value of x is of the order of 0.03. Yield: 28%.

2.2. Elemental analysis

The carbon, hydrogen and nitrogen content were analysed with a Hewlett-Packard, model 185 CHN analyzer. The sum of the metals was determined complexometrically and the copper content estimated iodometrically after mineralization of the samples with a mixture of 30% HNO₃ and 30% H₂SO₄. The results of these analyses are presented in Table 1.

2.3. Physico-chemical methods

Infrared spectra from 4000 to 200 cm⁻¹ were recorded as KBr pellets on a Nicolet 510 FTIR spectrometer.

Thermal analyses were performed with a Derivatograph OD-102 instrument (MOM Budapest). TG and DTA curves were recorded with the following experimental conditions: 100–300 mg; DTA sensitivity 1/5; air atmosphere; ceramic crucibles;

Table 1
Results of elemental analysis

Compound	M_r^a		C/%	H/%	N/%	Cu/%	Zn/%
ZCA	241.04	Found	15.04	2.65	28.65	25.70	26.57
		Calc.	14.95	2.51	29.05	26.36	27.12
ZCE3	2385.40 ($n = 8.4$)	Found	27.02	6.64	30.40	13.83	16.83
		Calc.	26.69	6.79	31.12	13.32	16.45
ZCE1	267.08	Found	22.65	2.91	26.20	22.93	24.52
		Calc.	22.49	3.02	26.22	23.79	24.48
ZCCE1	267.02 ($x = 0.03$)	Found	22.52	3.14	25.69	23.98	22.92
		Calc.	22.49	3.02	26.23	24.51	23.75

^a Molar mass.

heating rate 9°C min^{-1} ; max temp. 900°C . Intermediates were isolated by “freezing” or prepared by heating the initial compounds in an oven to the appropriate temperature.

3. Results and discussion

As can be seen from Table 1 the chemical analyses were consistent with the compounds' formulae except for the ZCCE1 complex which was prepared in air and contained some copper(II) also. It was a light green colour. The composition of the complexes ZCA and ZCE3 was also consistent with their X-ray single crystal analysis [17] which showed that ZCA was three-dimensional in structure with zinc and copper atoms joined together by bridging cyano groups. Both atoms exhibit deformed tetrahedral coordination. The copper atom was coordinated to four cyano groups (CuC_3N coordination sphere) and the zinc atom to two cyano groups and two molecules of ammonia (ZnN_4). The structure of ZCE3 is ionic and contains discrete complex cations and anions: $[\text{Zn}(\text{en})_3]^{2+}$, $[\text{Cu}(\text{CN})_3]^{2-}$ and $[\text{Cu}_2(\text{CN})_7]^{5-}$. Water molecules are also present [17].

3.1. IR spectra

The IR spectra of all the complexes show the presence of amine or ammonia and cyano ligands, as well as the presence of water molecules in the ZCE3 complex. The cyano groups exhibit strong sharp absorption bands in the region of about 2100 cm^{-1} due to the stretching vibration of the CN group (Fig. 1). In the spectrum of ZCA (Table 2) there is a strong band at 2120 and a doublet at 2102 and 2097 cm^{-1} . These bands correspond to the stretching vibrations of the four stereochemically different bridging cyano groups found in the structure of this complex. The shoulder at 2077 cm^{-1} could be attributed to the stretching vibration of cyano groups containing ^{13}C (calc. 2076 cm^{-1}). These values are higher than the $\nu(\text{CN})$ value corresponding to

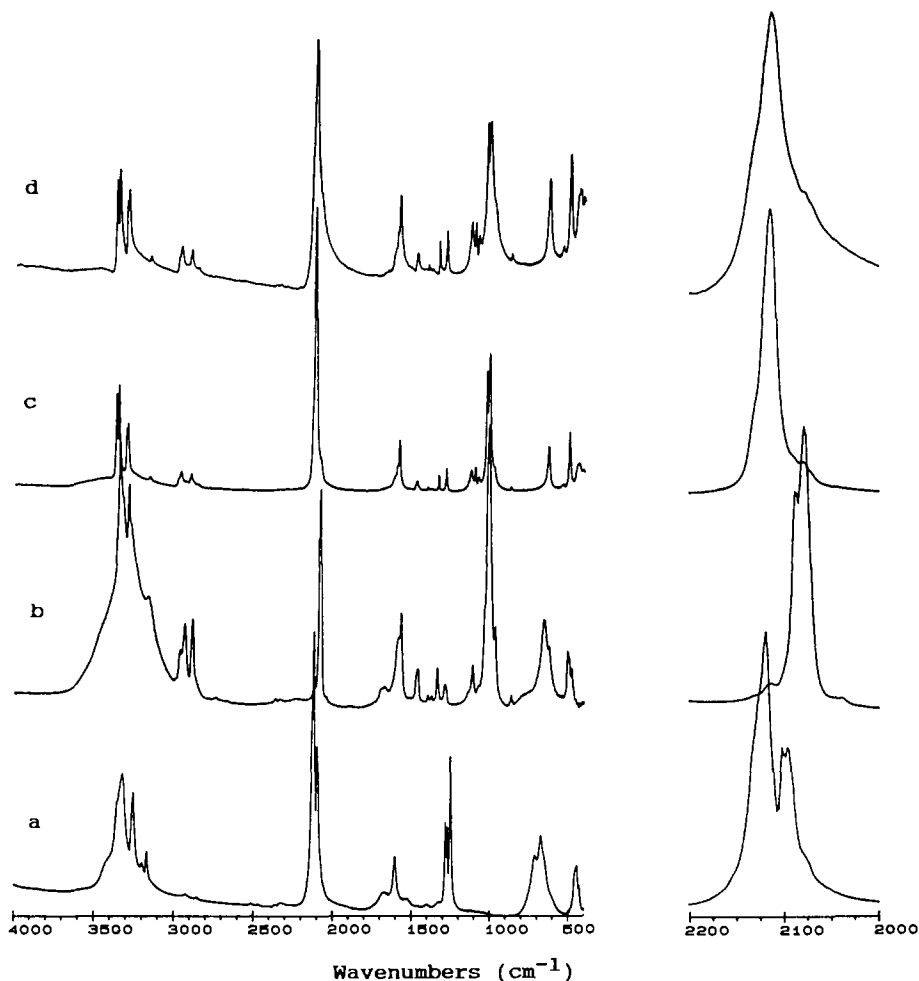


Fig. 1. IR spectra of (a) ZCA; (b) ZCE3; (c) ZCE1; (d) ZCCE1. An expansion of the range of the ν (CN) stretching vibrations is displayed on the right.

terminal CN groups in the tetrahedral $[\text{Cu}(\text{CN})_4]^{3-}$ anion in aqueous solution (2076 cm^{-1}) [18]. The bridging character of cyano groups in the structures of ZCE1 and ZCCE1 (Table 3) (the spectra of these two complexes are almost identical) was evidenced by the presence of only one very intense peak at 2116 cm^{-1} accompanied by a shoulder at 2080 cm^{-1} (^{13}C , calc. 2072). On the other hand, three peaks are present in the spectrum of ZCE3; these correspond to the symmetry-allowed ν (CN) vibrations: a weak peak at 2099 and two at 2089 (strong) and 2079 cm^{-1} (very strong). This observation is in line with the presence of different cyano groups as revealed by the crystal structure of this complex (Fig. 1): (i) the weak peak could be attributed to the

Table 2
IR spectra of ZCA and its intermediates after heating in air at 140 and 200°C^a

Assignment	ZCA/cm ⁻¹	ZCA(140)/cm ⁻¹	ZCA(200)/cm ⁻¹
ν(OH)	–	3623vw	–
	–	3553vw	–
	–	3433wsh	–
ν(NH ₂)	3324s	3371m	–
	3256s	3356m	–
	3200wsh	3283m	–
	3169w	3213w	–
ν(C≡N)	–	3186w	–
	2127ssh	2155ssh	2218m
	2120vs	2137vs	2174ssh
	2107s	2128vs	2157vs
	2097s	–	–
δ(OH ₂)	–	1694vwb	–
δ _a (NH ₂)	1604m	1610w	–
δ _s (NH ₂)	1282m	1269msh	1251vvw
	1269m	1247s	–
	1249s	–	–
ρ(NH ₃)	713m	695wsh	–
	675m	636m	–
?	444m	485m	492s
	429wsh	405w	461s
	344vw	–	345w

^a s, strong; m, medium; w, weak; sh, sharp; b, broad; v, very.

ν(CN) vibration of the bridging cyano group in the [Cu₂(CN)₇]⁵⁻ anion; (ii) the peak at 2089 cm⁻¹ to the vibration of terminal cyano groups in the [Cu(CN)₃]²⁻ anion, the corresponding value in aqueous solution being 2094 cm⁻¹ [18], (iii) the peak at 2079 cm⁻¹ to the vibration of terminal cyano groups in the [Cu₂(CN)₇]⁵⁻ anion, the corresponding value in the tetrahedral [Cu(CN)₄]³⁻ anion being 2076 cm⁻¹ [18].

The presence of the ammine ligands in ZCA is manifested by various absorption bands which are given in Table 2; the assignment of observed absorption bands to different types of vibration was made by following the procedure described in Ref. [18]. It is worth noting that in the spectrum we observed also the presence of weak ν(OH) and δ(OH₂) bands; their presence could be explained by the hygroscopic behaviour of the sample.

In the complexes ZCE3, ZCE1 and ZCCE1 the presence of ethylenediamine molecules (en) is demonstrated by peaks collected in Table 3 along with tentative assignment which was made on the basis of published data [19, 20]. The chelate bonding of en molecules is revealed by the presence of absorption band at about 500 cm⁻¹ which could be attributed to the bending vibration of the chelate ring

Table 3
IR spectra of complexes containing en. ZCE3(T) denotes heating at $T^{\circ}\text{C}$ in air for 1 h^a

Assignment	ZCE3	ZCE3 (100)	ZCE3 (170)	ZCE3 (200)	ZCE1	ZCCE1
$\nu(\text{OH})$	3451msh	–	–	–	–	–
$\nu(\text{NH}_2)$	3343vs 3320ssh 3285vs 3271ssh 3166m	3343s 3326vs 3266s – 3169m	3370m 3353m 3304w 3295w 3156vm	– – 3312m 3268w –	3370m 3353m 3304m 3294m 3157vw	3370m 3352m 3303m 3294m 3155vw
$\nu(\text{CH}_2)$	2962w 2985m 2885m	2959m 2941m 2887m	– 2962vw 2898vw	– 2957vw 2894vww	– 2963w 2899w	– 2961w 2898w
$\nu(\text{CN})$	2099w 2089s 2079vs	2113shw 2104wsh 2092vs 2089vs	– 2216vw – 2117vs	– 2218w 2143vs –	– – – 2116vs	– – – 2116vs
$\delta(\text{OH}_2)$	1674	–	–	–	–	–
$\delta(\text{NH}_2)$	1583shm 1568m	1587m –	1592vwsh 1581w	1601w 1577w	1594wsh 1581m	1593shw 1580m
$\delta(\text{CH}_2)$	1462w	1459m	1467vw	1466vw	1469vw	1468w
?	–	–	–	1125m	–	–
$\nu(\text{C-N})$	1007vs 967m	1013vs 1003vs	1024m 1008m	– 1001m	1024s 1006s	1025s 1008s
$\rho(\text{CH}_2)$	867vw	863vw	867vww	–	867vw	867vw
$\rho(\text{NH}_2)$	656m 623shm	649m 630msh	626w –	– 613m	626m –	624m –
$\delta(\text{NCCN})$	504m 494msh 479w	509m 498msh 473w	494w – –	490m – 461wsh	493m – –	492m – –
?	–	–	444bw	–	431w	430m
?	–	385w	–	–	405w	404w

^a Symbols as for Table 2.

$\delta(\text{NCCN})$. This is in line with the known crystal structure of ZCE3 and indicates the same type of en coordination in ZCE1 and ZCCE1 complexes. In the literature the crystal structure of $\text{Cd}(\text{en})\text{Cd}(\text{CN})_4$ is described; it is three-dimensional and consists of CdC_4 tetrahedra and CdN_6 octahedra joined together by bridging cyano groups [21]. On the basis of stereochemical considerations and measured IR spectra, similar structures could be formed by the two complexes under study.

The water molecules present in the structure of ZCE3 are manifested by a sharp shoulder at 3451 (hydrogen bonds) and a $\delta(\text{OH}_2)$ peak at 1674 cm^{-1} .

3.2. Thermal decomposition under dynamic conditions

3.2.1. ZCA

The decomposition of ZCA (Fig. 2) begins at 120°C, relatively high for an ammonia-containing compound. Its higher thermal stability could be explained by its polymeric structure. The loss of two ammonia molecules proceeds in two endothermic steps (minima on DTA curve are at 195 and 300°C) corresponding to weight losses of 7.7 and 7.5% (calculated for two ammonia molecules, 14.2%). The IR spectrum of the intermediate formed after the liberation of the first ammonia molecule indicates the presence of bridged cyano groups, ammonia and a few water molecules whose presence could be explained by rehydration during pellet preparation. The intermediate formed after liberation of the second ammonia ligand contains only cyano ligands as revealed by the IR spectrum (Table 2).

A strong internal exothermic redox reaction between cyanide ligands and copper(I) proceeds in the temperature range between 385 and 780°C ($DTA_{max} = 635^{\circ}C$). The observed weight loss (25.3%) is in agreement with the formation of Cu and ZnO (calculated 25.7%). The XRD of samples prepared by the “freezing” method

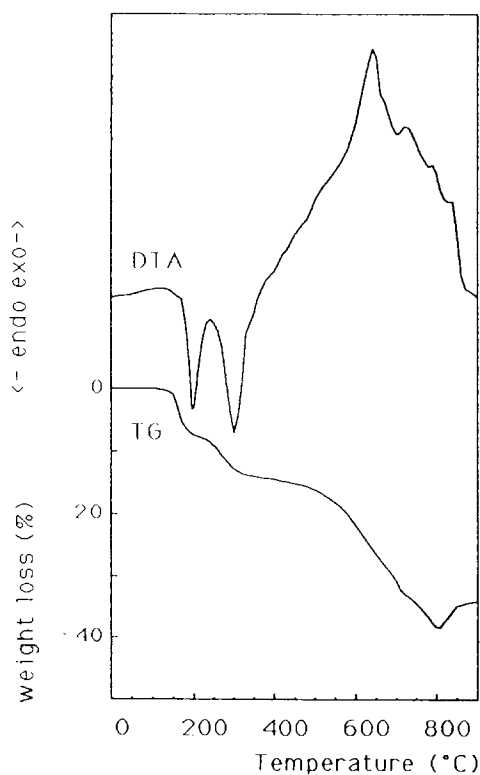


Fig. 2. Thermal curves (TG, DTA) for ZCA.

(dynamic conditions) at different stages has confirmed the presence of metallic copper, $\text{Zn}(\text{CN})_2$ which is later transformed into ZnO . The copper thus formed is then reoxidized to CuO via Cu_2O as could be seen from the weight increase of 6.3% indicated by the TG curve in the temperature range 780–860°C; this process was also evidenced by XRD study of calcination products [22]. It should be noted that the amount of sample (300 mg) limits oxygen penetration during the first stages of decomposition. The final weight loss (34.2%) is in agreement with the formation of both oxides (calc. 33.3%).

3.2.2. ZCE3

The thermal decomposition of ZCE3 is rather complicated (Fig. 3) as could be expected on the basis of the known crystal structure. The endothermic ($\text{DTA}_{\text{min}} = 90^\circ\text{C}$) first step of decomposition in the temperature range between 65 and 100°C presents a 9.0% weight loss on the TG curve which is more than that calculated for total water content (8.4 molecules, 6.8%). This higher weight loss may suggest that the dehydration step is accompanied by a loss of one en molecule (calc. 9.3%). The IR absorption bands due to water molecules disappear and some $\nu(\text{CN})$ vibrations are

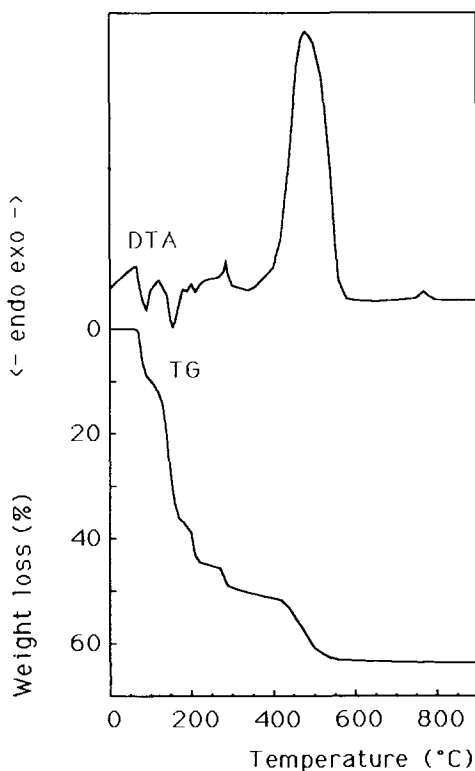


Fig. 3. Thermal curves (TG, DTA) for ZCE3.

shifted to higher wavenumbers (Table 3) owing to the formation of a $-\text{CN}-$ bridge in the structure.

The next endothermic step ($\text{DTA}_{\text{min}} = 155^\circ\text{C}$) may be explained by liberation of a major part of the en molecules from the coordination spheres of the zinc atoms. The observed weight loss of 27.0% corresponds to 11 en molecules of the 17 remaining (calculated 27.5%). IR measurement indicates the formation of an intermediate displaying the same features as ZCE1 (Table 3). An additional weak peak at 2216 cm^{-1} indicates the presence of another compound which can be related to the difference in the atomic Cu:Zn ratio between compounds ZCE3 (5:6) and ZCE1 (1:1).

The decomposition is followed by two endothermic processes ($\text{DTA}_{\text{min}} = 190, 210^\circ\text{C}$). The observed weight losses of 2.5 and 6.0% in the temperature range $170\text{--}220^\circ\text{C}$ may correspond to further partial liberation of en molecules (respectively 1 and 2.5). The intermediate prepared by the freezing method suggests the presence of zinc cyanide and another compound containing en molecules and cyano groups.

Further heating causes an exothermic weight loss of 6.5% ($\text{DTA}_{\text{max}} = 285^\circ\text{C}$) which can be explained by the loss of remaining en molecules (calc. 6% for 2.5 molecules). At this step the intermediate is formed mainly by $\text{Zn}(\text{CN})_2$ and another unidentified cyanide. The cyano groups are decomposed in a strong exothermic process in the temperature range $370\text{--}550^\circ\text{C}$ yielding CuO (tenorite) and ZnO (zincite) as end products, as found by X-ray diffractometry [22] (total weight loss: 63.5%; calc. 63.0%).

The last feature of the thermal decomposition is a small exothermic peak at 800°C without weight change; this corresponds to a phase transition. The same phase transition was observed also during the thermal decomposition of the other two compounds containing en (Fig. 4). The nature of this process is not well understood at present and will be studied by high temperature XRD.

3.2.3. ZCE1 and ZCCE1

The thermal stability of these compounds is higher than for the previous samples. Because of the low copper content in the cationic positions the results are the same for both compounds, so we limit our discussion to the first. The first step of decomposition furnishes two endothermic peaks at 170 and 210°C (Fig. 4). The observed weight loss of 11.8% may be explained by liberation of half the en content (calc. 11.3%) and the IR spectrum of the intermediate indicates the presence of cyano groups and ethylenediamine. The remaining en content decomposes in the temperature range $250\text{--}380^\circ\text{C}$ (obs.: 10.5; calc.: 11.3%) and the intermediate contains only cyano groups as detected by IR spectroscopy. The process is complicated as indicated by the presence of a small exothermic peak at 280°C followed by an endothermic peak at 305°C .

The remaining cyano ligands are decomposed by internal redox reaction displaying a very strong exotherm and leading to the formation of metallic copper. Reoxidation of this copper by air in the temperature range of $675\text{--}730^\circ\text{C}$ is indicated by a weight increase of 3.5% (calc. for 1 oxygen: 6%). The final phase transition (see above) is observed in this case at 770°C . The total weight loss of 40.0% is in agreement with the formation of oxides (calc. 39.8%).

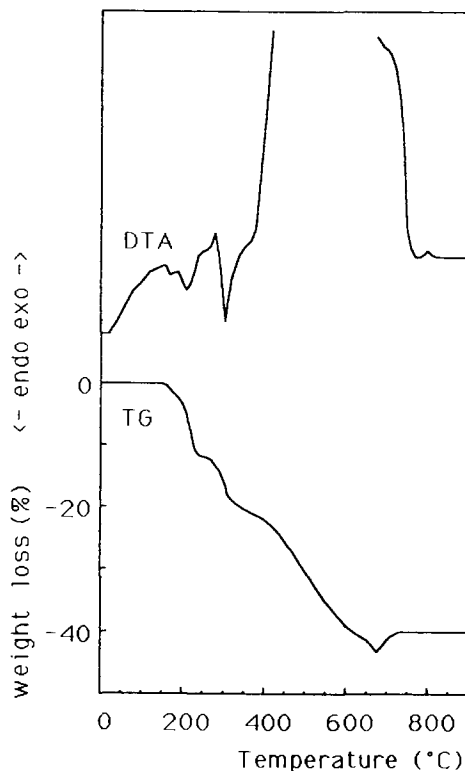
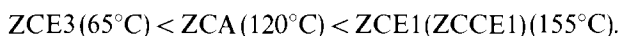


Fig. 4. Thermal curves (TG, DTA) for ZCE1.

4. Conclusion

The results obtained showed that the thermal stability of the compounds studied is:



This is in line with the crystal structures of these compounds, i.e. ionic structure containing water molecules (ZCE3), polymeric structure containing ammonia ligands (ZCA), and chelate-bonded en molecules (ZCE1 and ZCCE1).

From the course of the thermal decomposition of the compounds it follows that more volatile amine ligands are evolved preceded by the liberation of water molecules of crystallization (if present). The next process involves an internal redox reaction between cyano ligands and copper (I) resulting in formation of metallic copper. This copper is then reoxidized by air at the final stage of the heating, resulting in formation of a mixture of ZnO and CuO.

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