Preparation, structure and thermal properties of a zinc copper maleate precursor $Cu_{0.06}Zn_{0.94}C_4O_4H_2\cdot 2H_2O$ †

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A new Cu−Zn bimetallic precursor $Cu_{0.06}Zn_{0.94}C_4O_4H_2\cdot 2H_2O$ useful as a model catalyst for methanolation of syngas was prepared and identified. It crystallises in the monoclinic space group *Cc* with cell parameters $a = 5.725(1)$, $b = 16.251(2)$, $c = 6.825(1)$ Å, $\beta = 90.72(1)°$, $Z = 4$. The structure analysis shows a two-dimensional polymeric structure with layers containing metal atoms interconnected by tridentate maleate anions. The smallest ring in the layer contains 18 atoms among which are three metal atoms. These metal atoms are connected by two maleate ligands through the opposite carboxylic groups and the ring is completed by one *syn-anti* carboxylate bridge Zn−O−C−O−Zn. The metal atom is five-co-ordinated in the MO_2O_3 form through three oxygen atoms from three different maleate anions and two terminal water ligands. The packing of the structure is stabilised by intra- and inter-layer hydrogen bonds. Thermal decomposition begins with dehydration (75–170 °C) followed by decomposition of the maleate anions (190–635 °C). As final phases, zincite ZnO (major) and tenorite CuO (minor) were identified.

Copper–zinc oxide catalysts are industrially used for methanol synthesis from syngas ($CO + H_2$). It is accepted that copper, and its interaction with zinc oxide, play a prominent role,[2,3] but the precise nature of the active sites for this type of catalyst is still under debate and the oxidation state of copper is always a subject of discussion. Recently, Stirling *et al.*[4] have observed an enhanced catalytic activity for catalysts prepared from monophasic $Cu_xZn_{1-x}O$ solid solution with $x < 0.01$. The solid solution was prepared by calcination at 900 °C of the precipitate obtained from the reaction of sodium carbonate with the appropriate mixture of the respective nitrates. The precipitate was identified as a Cu-containing zinc carbonate hydroxide. Calcination at lower temperature (450 °C) did not lead to the formation of a solid solution. Similar results were obtained by Porta *et al.*[5] Other authors described the formation of a solid solution with defect structure and containing up to 10 atom % Cu ($x = 0.1$) after calcination of the precursor $(Cu_xZn_{1-x})_5(CO_3)_2(OH)_6$ at 350 °C.[6,7] They stated that, after calcination at temperatures above 700 °C, decomposition of the previous solid solution and segregation of CuO and ZnO phases occurred.

Coprecipitated copper zinc carbonate hydroxides represent the usual catalyst precursors.[2] An alternative way to achieve uniform interdispersion of both metallic elements in the precursor is to synthesize well characterised bimetallic compounds in the crystalline form.[5] In our previous papers we have reported the preparation, crystal structure analyses and characterisation of such new bimetallic compounds with variable Zn : Cu atomic ratio: 1 : 1 for $Zn(NH_3)_2Cu(CN)_3$ and Zn(en)-$Cu(CN)_3$ (en = ethane-1,2-diamine), 6 : 5 for $[Zn(en)_3]_6[Cu_5(CN)_{17}]\cdot nH_2O$ ($n = 8.4$) and 1 : 2 for $Zn(NH_3)_3Cu_2(CN)_4$.[1,8–10] Such Zn : Cu atomic ratios are out of the range (1–10 atom % Cu) reported as suitable for the preparation of monophasic solid solutions. Thus our goal was to prepare and characterise well defined bimetallic compounds but containing copper in the previously reported concentration range in order to verify the possibility of the formation of a $Cu_xZn_{1-x}O$ solid solution after calcination.

As model compounds we have chosen the maleate salts as both zinc and copper maleates have been described[11,12] but to our knowledge no mixed salts containing this anion had been studied. Here we report the preparation, characterisation, single-crystal X-ray analysis and thermal properties of the new Cu−Zn bimetallic compound $Cu_xZn_{1-x}C_4H_2O_4\cdot 2H_2O$ (zinc copper maleate hydrate) with $x = 0.06$.

Experimental

Preparation

All chemicals were of analytical grade, from Lachema, Brno, Tschech Republic. Solutions of copper and zinc maleates were prepared following published methods with minor modifications:[11,12] $Na_2CO_3\cdot 10H_2O$ (14.6 g, 50 mmol) was added to $ZnSO_4\cdot 7H_2O$ (13.4 g, 47 mmol) dissolved in water (200 cm^3). After decantation the precipitate was dissolved in maleic acid (5.4 g, 47 mmol) in water (50 cm^3). The final volume was adjusted to 200 cm^3. From this solution zinc maleate can be isolated in the form of single crystals after standing. A solution of copper maleate was prepared by mixing three solutions: $CuSO_4\cdot 5H_2O$ (0.875 g, 3.5 mmol) in water (30 cm^3), maleic acid (0.70 g, 6 mmol) in water (20 cm^3) and $Na_2CO_3\cdot 10H_2O$ (1.0 g, 3.5 mmol) in water (20 cm^3), the final volume being 70 cm^3. The mixture of these two solutions (copper : zinc atomic ratio = 7 : 93) led upon slow isothermal evaporation at 60 °C on a water-bath to the separation of light blue parallelepipeds. The crystals were filtered off and washed with a small quantity of cold water. The elemental analysis (Carlo Erba CHN apparatus and metals by atomic absorption spectro-

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† Copper–zinc oxide catalysts. Part 5.[1] *Supplementary data available* (No. SUP 57266, 4 pp): IR spectra, X-ray powder diffraction data. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1997, Issue 1.

photometry) was consistent with the formula $Cu_{0.06}Zn_{0.94}C_4H_2O_4 \cdot 2H_2O$ [Found (Calc.): C, 22.02 (22.31); H, 2.70 (2.81); Cu, 1.87 (1.77); Zn, 28.91 (28.54)%].

Physicochemical methods

Energy-dispersive X-ray emission (EDX) measurements for copper and zinc were performed on a Philips CM 120 transmission electron microscope at 120 kV equipped with an EDX attachment (EDAX, Li-doped silicon). Single crystals were carefully ground to about 1 µm, dispersed in ethanol and deposited on an aluminium grid. The diameter of the electron beam was of the order of 500 nm.

Infrared spectra were taken on a Nicolet 750 FT-IR spectrophotometer using KBr discs in the range from 4000 to 400 cm^{-1} (Table 1); the measured infrared spectrum has been deposited (see SUP 57266) and the precise positions of the peaks are listed in Table 1. The UV/VIS spectra were obtained from a Specord M40 spectrophotometer using the reflectance method and $BaSO_4$ as standard.

Thermal analyses were made by using a Derivatograph OD-102 instrument (MOM, Budapest). The TG and DTA curves were recorded under the following experimental conditions: 100 mg, DTA sensitivity 1/5, static air atmosphere, ceramic crucibles, heating rate 9° min^{-1}, T_{max} 900 °C.

The powder X-ray diffraction pattern were recorded on a Siemens D500 Kristalloflex diffractometer with graphite-monochromatised Cu-Kα radiation ($\lambda = 1.5406$ Å).

Crystallography

Crystal data and data collection. $C_4H_6Cu_{0.06}O_6Zn_{0.94}$, $M = 215.36$, monoclinic, space group *Cc* (no. 9), $a = 5.725(1)$, $b = 16.251(2)$, $c = 6.825(1)$ Å, $\beta = 90.72(1)°$, $U = 634.9(2)$ $Å^3$ (by least-squares refinement on diffractometer angles from 25 reflections, $25 < 2\theta < 34°$), $T = 293$ K, graphite-monochromated Mo-Kα radiation, $\lambda = 0.710\,69$ Å, $Z = 4$, $D_m = 2.24$ Mg m^{-3}, (flotation in bromoform–chloroform), $D_c = 2.25$ Mg m^{-3}, $F(000) = 424$, light blue parallelepipeds, μ(Mo-Kα) = 3.937 mm^{-1}, crystal size = 0.15 × 0.20 × 0.32 mm.

Absorption correction using the program DIFABS,[13] transmission factors 0.72–1.15, Enraf-Nonius CAD4 diffractometer, ω–2θ scans, scan range = $(0.8 + 0.345 \tan\theta)°$, data collection range $2 < 2\theta < 70°$, $-9 < h < 9$, $0 < k < 26$, $0 < l < 11$, two standard reflections showed no significant variation in intensity, 1522 reflections measured, 1392 unique ($R_{int} = 0.052$), 1370 used in refinement [$F_o^2 > 3\sigma(F_o^2)$].

Structure solution and refinement. The structure was solved by the heavy-atom method and refined anisotropically, by full-matrix least squares using the CRYSTALS software package.[14] As the use of DIFABS[13] is not free of criticism and can take into account kinds of systematic errors other than absorption, a comparison between the results obtained before and after DIFABS gave the following outcomes: expected decrease of the *R* and *R′* factors (0.041, 0.044 before) but non-significant change in bond distances and angles and very small change for the ellipsoid parameters; the largest variations were 0.006 Å on the Zn–O(6) bond length and 0.5° on the O(3)–C(4)–O(4) angle. Thus the final results obtained after DIFABS use were retained. The positions of hydrogen atoms were refined with a common isotropic thermal parameter with the exception of H(2) which was placed in the calculated position. Unit weights and empirical extinction corrections ($p = 70 \times 10^{-6}$) were used. The final values of *R*, *R′* and *S* for 117 variables were 0.022, 0.026 and 5.9, respectively. Maximum and minimum values of $\Delta\rho$ were 0.37 and −0.36 e $Å^{-3}$. Selected geometrical parameters are given in Table 2 and possible hydrogen bonds in Table 3. The figures of the structures were drawn using the programs MOLDRAW[15] and ORTEP.[16]

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Table 1 Infrared spectral data (cm^{-1}) for the original compound $Cu_{0.06}Zn_{0.94}C_4H_2O_4 \cdot 2H_2O$, after dehydration (170 °C) and of maleic acid.

Assignment	$Cu_{0.06}Zn_{0.94}C_4H_2O_4 \cdot 2H_2O$	$Cu_{0.06}Zn_{0.94}C_4H_2O_4 \cdot 2H_2O$ (170 °C)	Maleic acid
ν(OH)	3511m		
	3404m	3440m (br)	2900–2000m (br)
	3229m		
ν(=C−H)	3031vw	3050vw	3050w
ν_{asym}(C=O)	1656m (sh)	1646m (sh)	1704s
ν(C=C)			1640s
ν_{asym}(C=O)	1555s	1586vs	1568vs
		1539vs	1575vs
ν_{sym}(C=O)	1421s	1437s	1460s
			1432s
ν_{sym}(C−C)	1323s	1320m	1264vs
ν_{asym}(=C−CO_2)	1196m	1208w	1220m
ν_{asym}(C−C)	984m	987w	992w
		929w	928w
β_s(CO_2^-)	862m	868m	864m
γ(=C−H)	829m	835m	784w
γ(CO_2^-)			
ρ(H_2O)	762w		
γ(CO_2^-)			
γ(=C−H)	706m	677m	
δ(C−C=C)	647m	619m	632m
			608m
?	532m		
τ(C−C=C−C)	471w	497w	404m

Results and Discussion

Preparation and spectroscopic characterisations

The experiments have shown that only single crystals of one specific composition (Cu : Zn = 6 : 94) separated. When the copper to zinc ratio differed (up to 15 : 85) a mixture of different crystals was obtained but easy to separate optically. Similar behaviour was observed for the compound $[Cu_{0.83}Zn_{0.17}(OMe)(tcp)(MeOH)]_4$ (tcp = 2,4,6-trichlorophenolate).[17] On the other hand, copper zinc formates form a continuous range of solid solutions.[18] It is worth noting that from solutions containing only zinc maleate we obtained single crystals upon standing (structure under study), in contrast to Allan *et al.*[11] who reported only the formation of powdered zinc maleate.

To corroborate the simultaneous presence of copper and zinc in the crystals, we carried out EDX analysis on a few ground single crystals. Four different specimens were checked and the atomic Cu : (Cu + Zn) ratio is 0.075(10) : 1 which agrees very well with the chemical analysis (0.063 : 1); thus the crystals correspond to one Cu-doped phase.

The IR spectrum of the copper–zinc compound (Table 1) is almost identical with that of the pure zinc compound (not listed); the spectral data for maleic acid are also given for comparison. The formation of hydrogen bonds is indicated by the very broad shape and by the shift to lower wavenumbers of the absorption bands due to ν(OH) vibrations. The ν(C−H) vibrations are manifested by a weak absorption band at 3031 cm^{-1}. The stretching vibration of the C=C double bond leads to a medium sharp shoulder at 1656 cm^{-1}. The very strong absorption bands due to asymmetric and symmetric stretching vibrations of the carboxylic groups ν(COO) are at 1555 (multiplet) and 1421 cm^{-1}. The band due to the δ(H_2O) vibration may be hidden by the peak due to the asymmetric ν(COO) vibration. A tentative assignment of the other observed absorption bands was made on the basis of literature data.[19]

The partial substitution of the Zn^{II} by the Cu^{II} in the studied compound is in line with its light blue colour. The UV/VIS spectrum exhibits a maximum at 779 nm with a shoulder at 446 nm. Assuming an idealised C_{4v} geometry of the CuO_5 chromophore (see below) these absorption bands may be attributed

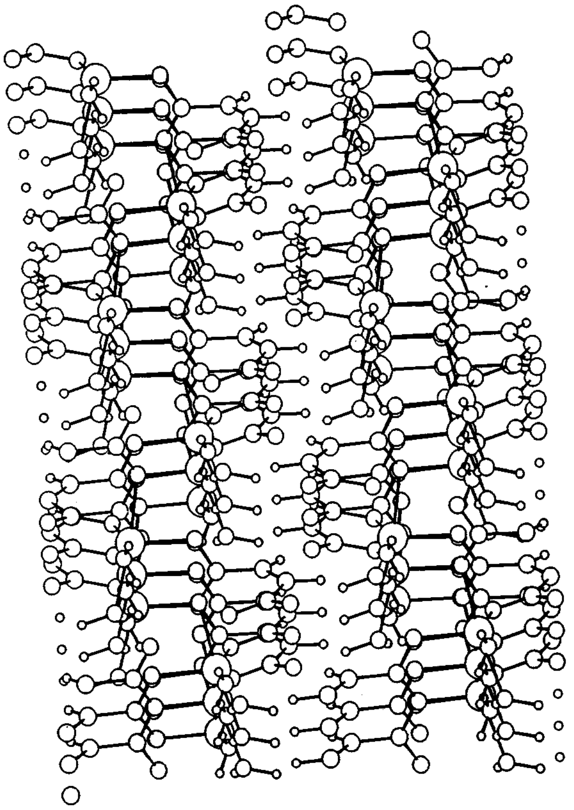

Fig. 1 View of the layered structure along the *y* direction

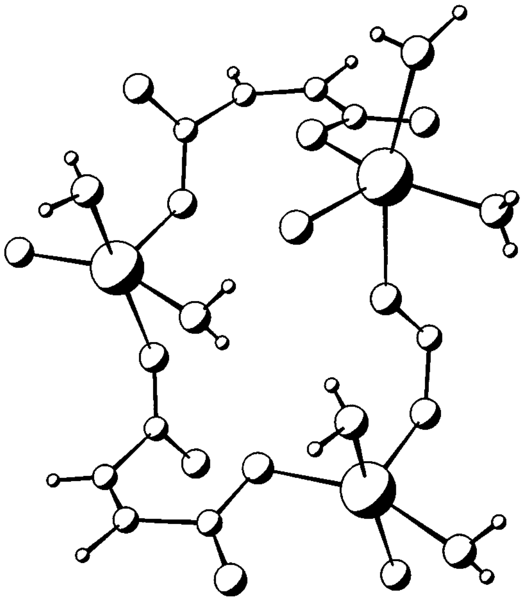

Fig. 2 View of the 18-membered ring displaying the co-ordinative properties of the maleate ligand. The atoms with decreasing radii are metal, oxygen, carbon, hydrogen

respectively to the $^2B_2 \longleftarrow {}^2B_1$ and $^2E \longleftarrow {}^2B_1$ transitions. For five-co-ordinated copper complexes the band at higher energy usually exhibits higher intensity;[20] this is not the case here.

Crystal structure

The structure analysis shows a two-dimensional structure with layers extending in the *a* and *c* directions (Fig. 1). The layers are built up of metal atoms interconnected by crystallographically equivalent tridentate maleate anions and display a rather complicated bonding array. In the layer the smallest ring contains 18 atoms formed by three metal atoms and only bridging maleate ligands. These metal atoms are connected by two maleate ligands through the opposite carboxylic groups and the ring is completed by one *syn-anti* carboxylate bridge Zn–O–C–O–Zn (Fig. 2). Such a two-dimensional structure with hydrogen bonds between layers was also found in copper maleate hydrate but with seven-membered rings;[21] to our knowledge the structure of the pure zinc maleate has not yet been described.

Table 2 Selected geometric parameters (bond lengths in Å, angles in °) for $Cu_{0.06}Zn_{0.94}C_4H_2O_4{\cdot}2H_2O$

Zn–O(1)	1.988(3)	O(2)–C(1)	1.240(4)
Zn–O(3)	2.125(2)	O(3)–C(4)	1.247(3)
Zn–O(4)	2.022(2)	O(4)–C(4)	1.278(3)
Zn–O(5)	2.109(3)	C(1)–C(2)	1.487(4)
Zn–O(6)	1.999(3)	C(2)–C(3)	1.328(4)
O(1)–C(1)	1.281(4)	C(3)–C(4)	1.486(4)
O(1)–Zn–O(3)	94.5(1)	Zn–O(1)–C(1)	107.7(2)
O(1)–Zn–O(4)	98.2(1)	Zn–O(3)–C(4)	136.8(2)
O(1)–Zn–O(5)	95.6(1)	Zn–O(4)–C(4)	121.9(2)
O(1)–Zn–O(6)	157.3(1)	O(1)–C(1)–O(2)	122.1(3)
O(3)–Zn–O(4)	83.06(9)	O(1)–C(1)–C(2)	117.8(3)
O(3)–Zn–O(5)	165.4(1)	O(2)–C(1)–C(2)	120.2(3)
O(3)–Zn–O(6)	84.1(1)	C(1)–C(2)–C(3)	125.1(2)
O(4)–Zn–O(5)	105.9(1)	C(2)–C(3)–C(4)	125.6(2)
O(4)–Zn–O(6)	104.1(1)	O(3)–C(4)–O(4)	122.8(2)
O(5)–Zn–O(6)	82.5(1)	O(3)–C(4)–C(3)	120.1(2)
		O(4)–C(4)–C(3)	117.0(2)

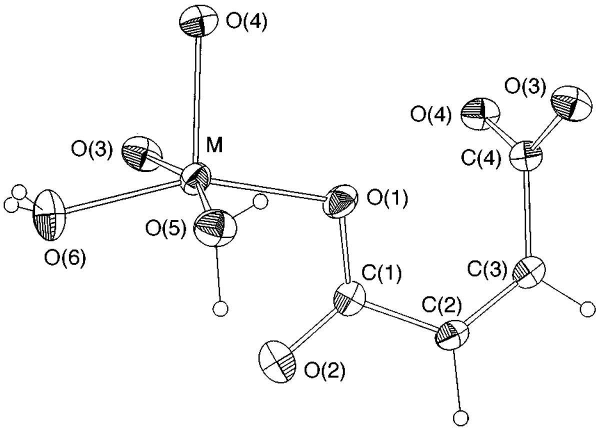

Fig. 3 An ORTEP view of the metal atom co-ordination along with atom numbering scheme

Despite the complexity of the structure, only one independent metal atomic position is present in the unit cell. The metal atom is five-co-ordinated in the form MO_2O_3 by three oxygen atoms from three different maleate anions and two terminal water ligands (Fig. 3). The partial occupancy of zinc sites by copper atoms is too small to observe variation of bond distances (Table 2). An ideal square pyramid gives a value for the distortion parameter $\tau = 0$ on the basis of the interbond angles;[22] in our case, the calculated value is 13.5 and thus discloses a slightly deformed square pyramid with the O(4) atom at the apex and the two water ligands in *cis* positions. The metal atom is shifted by 0.249(5) Å toward the O(4) atom, from the mean plane defined by the four basal oxygen atoms. With regard to the Zn–O bond lengths, we can distinguish two sets with mean values at 2.00 [O(1), O(4) and O(6)] and at 2.11 Å [O(3) and O(5)]. Thus we can propose an alternative way to describe the co-ordination geometry as a deformed trigonal bipyramid: the three shortest Zn–O distances correspond then to the ligands in equatorial positions and the two longer ones to axial positions. Although the five-co-ordination of zinc (as a major component of the metal site) is less common than octahedral or tetrahedral co-ordination, it is important and 69 five-co-ordinated zinc compounds are listed in a recently published review.[23] It should be noted that in the direction of the sixth position defined by an octahedral co-ordination geometry one can find an O(2) oxygen atom with a Zn–O distance of

Table 3 Possible hydrogen bonds (distances in Å, angles in °)

Donor–H	Donor···Acceptor	H···Acceptor	Donor–H···Acceptor
O(5)–H(52)	O(5)···O(2^{i})	H(52)···O(2^{i})	O(5)–H(52)···O(2^{i})
1.06(6)	2.722(5)	1.66(7)	177(5)
O(5)–H(51)	O(5)···O(4^{ii})	H(51)···O(4^{ii})	O(5)–H(51)···O(4^{ii})
0.69(66)	3.084(4)	2.49(6)	146(7)
O(6)–H(61)	O(6)···O(1^{iii})	H(61)···O(1^{iii})	O(6)–H(61)···O(1^{iii})
0.64(6)	2.743(4)	2.18(6)	149(7)
O(6)–H(62)	O(6)···O(4^{iv})	H(62)···O(4^{iv})	O(6)–H(62)···O(4^{iv})
0.87(6)	2.839(4)	2.00(6)	164(5)

Equivalent positions: i $x, -y, z + \frac{1}{2}$; ii $x, y, z + 1$; iii $x - 1, y, z$; iv $x - 1, y, z + 1$.

2.682(3) Å which is too long to be considered as a bond. Such non-bonding interactions are common for zinc carboxylates with tetrahedral co-ordination.[24] In copper maleate hydrate also five-co-ordination in a square-pyramidal form was observed with one water ligand in the apical position (Cu–O 2.26 Å) and four oxygen atoms in the basal plane (mean Cu–O 1.99 Å); three different maleate anions are co-ordinated, one of them as a seven-membered chelate ring.[21]

The bond distances in the maleate anion are in line with those found in copper maleate hydrate.[21] The dihedral angle between the plane defined by the C(1) atom from the monodentate carboxylic group and the plane formed by the four carbon atoms is 34.4(2)°; the corresponding angle including the second bidentate carboxylic group is 77.66(9)°. These values are not favourable for a conjugation of the C(2)–C(3) double bond with the carboxylic groups. The two carboxylic groups form a dihedral angle of 75.3(3)°.

There are intra- and inter-layer hydrogen bonds and the shortest O–H···O distance corresponds to the interlayer type [Table 3, O(5)···O(2)]; other short distances involving both water molecules correspond to intralayer hydrogen bonds. An inspection of the geometric situation around water molecule O(5) disclosed the formation of a strong hydrogen bond with the non-co-ordinated O(2) atom (2.72 Å) and a weak one with the co-ordinated carboxylic oxygen atom O(4) (3.08 Å); the relevant angles Zn–O(5)–O(2), Zn–O(5)–O(4) and O(2)–O(5)–O(4) exhibit values of 120.1, 123.8 and 102.1°, respectively. The O(6) water molecule forms two hydrogen bonds with oxygen atoms O(1) (2.74 Å) and O(4) (2.84 Å) [thus O(4) is involved in two hydrogen bonds]; the corresponding angles Zn–O(6)–O(1), Zn–O(6)–O(4) and O(1)–O(6)–O(4) being 121.4, 125.7 and 110.6°, respectively. It should be noted that although the O(5)···O(3) and O(6)···O(3) distances (2.928 and 2.764 Å) are shorter than the O(5)···O(4) and O(6)···O(4) distances, they correspond only to non-bonding contacts as the corresponding angles Zn–O(5)–O(3) (74.5°) and Zn–O(6)–O(3) (49.9°) exclude the formation of a hydrogen bond. All other interatomic distances between oxygen and a non-hydrogen atom are greater than 3 Å, but it can be noted that there are further short contacts of the C–H···O type (shorter than the sum of the van der Waals radii, see Table 3). The existence of four different O···O contacts corresponding to hydrogen bonds in the range from 2.722 to 3.084 Å is manifested by the presence of several absorption bands corresponding to the ν(OH) vibrations in the range of 3229–3511 cm^{-1} (Table 1).

In order to verify the identity of the structure deduced from single-crystal data and that of the powdered sample, the X-ray powder diffraction pattern was measured (Fig. 4). By using the program DICVOL[25] the same unit-cell parameters were obtained; these were refined by the program LSUCRI.[26] They are in line with those found from single-crystal measurement and the powder is clearly monophasic (see SUP 57266).

Thermal properties

The thermal decomposition curves (TG and DTA) are presented in Fig. 5. The first endothermic decomposition step with a minimum on the DTA curve at 135 °C corresponds to the dehydration. The corresponding weight loss in the temperature range 75–170 °C is 16.5% which corroborates the full dehydration of the sample (calculated 16.73%); the IR spec-

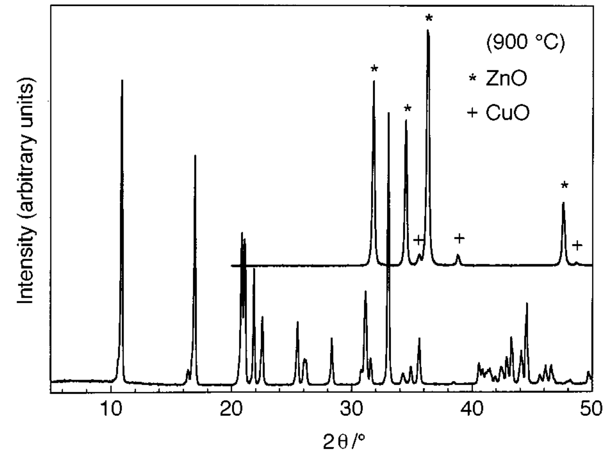

Fig. 4 X-Ray powder diffractogram of $Cu_{0.06}Zn_{0.94}C_4H_2O_4{\cdot}2H_2O$ (Cu-K$\alpha_{1,2}$, λ = 1.541 78 Å)

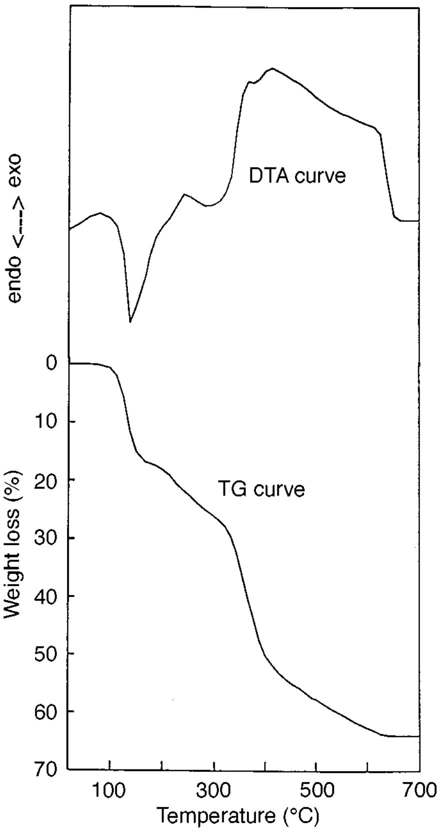

Fig. 5 The TG and DTA curves of $Cu_{0.06}Zn_{0.94}C_4H_2O_4{\cdot}2H_2O$

trum of the intermediate obtained by heating the sample to 170 °C displays clearly the disappearance of the ν(OH) broad absorption band and shifts of some carbonyl stretching vibration peaks (Table 1). On the basis of stereochemical considerations and knowledge of the structure of other carboxylate compounds, one may expect after dehydration the co-ordination of the fourth oxygen atom from the maleate anion.

The decomposition of the maleate groups takes place in the temperature range 190–635 °C. This is associated with three exothermic peaks on the DTA curve at 240, 360 and 405 °C indicating that decomposition includes three consecutive steps not well resolved on the TG curve. The exothermic behaviour of the ligand decomposition can be attributed to the oxidation in air. The total weight loss is 63.7%, which corresponds to the presence of the mixture of oxides ZnO and CuO (calc. 62.3%). The X-ray powder diffraction measurements indicate the presence of zincite ZnO with some tenorite CuO as minor phase. The phases were identified by using the PDF database.[27]

The thermal decomposition of zinc maleate measured for comparison is within experimental errors identical to that of the bimetallic compound, but the observed temperatures are shifted to higher values from those given for zinc maleate.[11] These differences may be explained by the use of different experimental conditions.

Conclusion

A new bimetallic copper–zinc compound was prepared from zinc maleate and copper maleate. The structure analysis has shown a five-co-ordination of the metal atom and a two-dimensional character. The thermal decomposition of the compound is similar to those found for the monometallic zinc compound. In the final product (900 °C) we have observed beside the zincite phase, the presence of tenorite CuO which indicates a limited solid solution and the segregation of copper from the ZnO lattice.

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