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Dimethylmalonato Zinc Complexes as Molecular Precursors for Electronic Grade Zinc Oxide: Towards a Systematic Ligand Design by Understanding Molecular Decomposition Mechanisms

Rudolf C. Hoffmann^[a] and Jörg J. Schneider^{*[a]}

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Zinc complexes with dimethyl 2-hydroxyimino- and 2-nitromalonate (dmm-NOH and Hdmm-NO₂, respectively) were synthesized and examined as potential precursors for nanocrystalline zinc oxide. The functionalised 1,3-diketones are sufficiently acidic to allow direct synthesis from hydrozincite or zinc 2-propoxide as well as their full spectroscopic and analytical characterization. Their nominal elemental compositions of $[Zn_4O(dmm-NO)_6]$ and $[Zn_3(OH)_4(dmm-NO_2)_2]$ suggest the presence of multinuclear cage structures with oxo- or hydroxo-bridging ligands. This assumption is in ac-

Introduction

Molecular precursors for solution deposition of oxide thin films have to meet a number of specific requirements.^[1–3] Precursors which are typically employed in gasphase deposition routes, e.g. alkoxides, carboxylates or 1,3diketones^[4,5] and which often have advantages during gas phase deposition such as low conversion temperatures and low carbon residues in the final ceramic are, however, subject to limitations when employed in solution deposition routes. Precursors which are suited for solution deposition routes should allow for an appropriate wetting of substrates and should yield homogeneous layers after necessary drying and processing steps.^[6,7] Furthermore, partial sublimation of such precursors is undesired in a strict sense because ceramic materials with a defined multicomponent or multinary composition would therefore be inaccessible.^[8,9]

The 1,3-diketone ligand framework offers a range of possibilities for synthetic modifications especially in the 2-position (β -position) but also at the substituents of the carbonyl atoms (γ -position). This allows tuning their properties, thus rendering these ligand structures interesting for solution cordance with the obtained spectroscopic data. Thermogravimetry coupled with mass spectrometry and infrared spectroscopy (TG/MS and TG-IR) indicate the formation of dimethylcarbonate and methanol during the decomposition. Both precursors exhibit good film formation properties and the obtained zinc oxide was further characterized by XRD, SEM, TEM and PL. Finally, the semiconducting electronic behaviour of the obtained nanocrystalline ZnO was studied in a field-effect transistor (FET) device.

based molecular precursors.^[10] The introduction of such a tailored ligand substitution could offer a way to facilitate the decomposition process while avoiding unwanted sublimation of the metal oxide precursors. Moreover, metal complexes of 1,3-diketones can be synthesized by a large variety of methods.

The metathesis reaction using metal salts and the 1,3diketone in the presence of a suitable base is a commonly used procedure. Apart from that, the direct reaction of metal alkoxides, carbonates, carbonyls or acetates with sufficiently acidic 1,3-diketones has been described as a valuable route to these compounds. These routes seem particularly attractive because no contamination of the precursors by inorganic salt elimination reactions or other by-products is expected.^[11]

Our present study involved the synthesis and characterization of malonatozinc(II) complexes with functionalized dimethylmalonato molecules as ligands. To the best of our knowledge, this class of compounds has been neither previously described nor investigated for use as metal oxide precursors. The decomposition pathways into ZnO were investigated by in situ thermogravimetric analysis coupled with MS and IR. With respect to the influence of various residuals on the backbone of the malonic acid ester ligand and its subsequent thermal decomposition and ceramisation, we were keen to find a correlation between the substituent and decomposition process in order to allow a systematic molecular precursor design based on these ligand frameworks. Finally, the obtained nanoscale zinc oxide was

[[]a] Fachbereich Chemie, Eduard-Zintl-Institut für Anorganische und Physikalische Chemie, Technische Universität Darmstadt, Alarich-Weiss-Str. 12, 64287 Darmstadt, Germany E-mail: joerg.schneider@ac.chemie.tu-darmstadt.de http://www.chemie.tu-darmstadt.de/schneider/startseite_aks/ index.de.jsp

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characterized by microscopic (SEM, TEM), diffraction (XRD) as well as optical techniques (photoluminescence, PL) and was studied for its functional behaviour as a semiconductor material in a field-effect transistor (FET) device.

Results and Discussion

The reactions of the functionalised dimethyl malonates, dimethyl 2-hydroxyimino- and 2-nitromalonate (dmm-NOH and Hdmm-NO₂, respectively), with various zinc compounds were investigated (Figure 1). The addition of hydrozincite to Hdmm-NO₂ in water led to the formation of $[Zn_3(OH)_4(dmm-NO_2)_2]$ (1). The corresponding reaction with dmm-NOH, however, only resulted in a sparingly soluble compound with unsatisfactory yields. In a second series of reactions under inert conditions, the addition of zinc 2propanolate to Hdmm-NO₂ led to a moisture sensitive product which rapidly decomposed after exposure to air. The reaction of zinc 2-propanolate with dmm-NOH in THF yielded $[Zn_4O(dmm-NO)_6]$ (2) which, in contrast, was stable under ambient conditions and could be characterized accordingly. Both (1) and (2) are readily soluble in alcohols (up to 5 wt.-%) and very soluble in aprotic polar solvents such as N,N'-dimethylformamide or dimethyl sulfoxide (> 10 wt.-%).



Figure 1. Schematic presentation of the synthesis and thermal decomposition of complexes $[Zn_3(OH)_4(dmm\text{-}NO_2)_2]$ (1) and $[Zn_4O(dmm\text{-}NO)_6]$ (2).

Bekermann et al. reported the synthesis of bis(dimethylmalonato)zinc (3) from diethylzinc and dimethyl malonate in hexane by heating to reflux for several hours or stirring for a prolonged period of time.^[12] The electronegative residues in dmm-NOH and Hdmm-NO₂ lead to higher acidity of the 1,3-diketones and allowed fast complex formation even at room-temperature. In contrast to the well known zinc acetylacetonate, the homologous complex (3) is moisture sensitive and rapidly hydrolyses under ambient conditions. This supports the suggestion that (1) and (2) are multinuclear complexes which display an oxo- or hydroxobridging situation between the metal centres. The latter can be easily identified by means of IR (Figure S1) and NMR spectroscopy (see Experimental Section). Nominal compositions could be derived from the elemental analysis and residual mass of the thermogravimetric measurements (Figure 1). Based on these analytical and spectroscopic data, the structures of the new compounds were assigned to be like those of frequently found and well established tri- and tetranuclear zinc complexes.^[13–16]

In order to understand the decomposition pathway in the formation of ZnO we conducted in situ TG-MS and TG-IR studies. The course of the thermal decomposition is presented in Figure 2. The decay of both (1) and (2) proceeds in a stepwise manner. The decomposition of (1) starts at about 140 °C and is complete at about 400 °C. In the case of (2), the decomposition begins at about 170 °C and extends over a temperature range up to 450 °C. In both cases only the first step resulted in a sharp maximum of the Gram-Schmidt signal, which was positioned at 180 °C and 220 °C, respectively. The corresponding IR spectra are shown in Figure 3 and indicate a mixture of various gaseous decomposition products. The signals at 670 and 2370 cm⁻¹ could be attributed to carbon dioxide^[17] and additional peaks around 2220 cm⁻¹ were assigned to carbon monoxide.^[18] The presence of a carbonyl compound was revealed by the signal at 1780 cm⁻¹ (Figure 3, a–b). In combination with signals in the region between 500–2000 cm⁻¹ (fingerprint region), this signal pattern could be clearly attributed to dimethyl carbonate (Figure 3c; Figure S2). Moreover, the signal at about 1030 cm⁻¹ was assigned to methanol (Figure 3, d; Figure S2). The identification of decomposition products resulting from the nitro and hydroxyimino functionalities was less clear, since only weaker signals remained unassigned so far. In the case of (1), a small peak at about 1600 cm⁻¹ was attributed to nitrogen dioxide, whereas broader signals at 1350 and 1700 cm⁻¹



Figure 2. Thermogravimetric mass loss and corresponding Gram–Schmidt signal of (a) $[Zn_3(OH)_4(dmm-NO_2)_2]$ (1) and (b) $[Zn_4O(dmm-NO)_6]$ (2).



might indicate nitric acid (Figure 3, a).^[19,20] For (**2**), no signals revealing the decay of the hydroxyimino group could be clearly assigned (Figure 3, b).



Figure 3. Gas phase IR spectra corresponding to the maximum of the Gram–Schmidt signal in Figure 1 of (a) $[Zn_3(OH)_4(dmm-NO_2)_2]$ (1) and (b) $[Zn_4O(dmm-NO)_6]$ (2) as well as reference spectra of (c) dimethyl carbonate and (d) methanol. (Spectra showing the range from 4000 to 500 cm⁻¹can be found in Figure S2).

The gaseous decomposition products mentioned which were already identified by means of IR spectroscopy could be further confirmed by additional experiments using TG-MS (Figure S3). Thus, besides the masses of species less specific than carbon dioxide $(m/z^+ = 44)$, carbon monoxide $(m/z^+ = 28)$, water $(m/z^+ = 18)$ or methanol $(m/z^+ = 32)$, the characteristic fragmentation pattern of dimethylcarbonate (m/z = 90, 59, 45, 31, 29) could be identified. For the decomposition of (1), the masses of nitrogen dioxide $(m/z^+ =$ 46) and nitrogen monoxide NO $(m/z^+ = 30)$ were found, whereas there was no indication of nitric acid $(m/z^+ = 63)$ or nitrous acid $(m/z^+ = 47)$. During the decomposition of (2), a mass of m/z^+ of 27 was detected, attributable to hydrogen cyanide. This finding is in accordance with a Beckmann fragmentation of the ligand framework responsible for the decay of the (CNO) moiety and an N-O bond cleavage.^[21] Although uncoordinated a-hydroxyketoximes can undergo several types of rearrangement and fragmentation reactions,^[22,23] the presence of neighbouring quaternary carbonyl carbon atoms should favour the latter.^[24,25] Detailed studies on 2-hydroxyimino 1,3-diketones are currently not available for comparison.

The decomposition of (1) and (2) leads to the formation of dimethyl carbonate and methanol (Figure 1). The course of the reaction could proceed by means of a pericylic process as well as by defined intermediates.^[26] Interestingly, the decomposition of the zinc^[12] and zirconium complexes^[27] of dialkyl malonates follows a different mechanism, whereby the elimination of the alkyl or alkoxy side groups occurs first. Thereby the scaffold of the 1,3-diketones initially remains intact and can indeed be identified by means of mass spectroscopy.^[12,27] In the investigations described herein, once again no specific decomposition products of uncoordinated dimethyl malonate (e.g. keto compounds^[28,29]) were identified. The introduction of strong electron-withdrawing groups into the framework of dimethyl malonate in (1) and (2) led to a decrease of the decomposition temperature in comparison with (3), i.e. about 180 °C.^[12] A direct comparison between (1), (2) and (3) remains difficult, though, due to differences in structure and the varying number of oxo- or hydroxo co-ligands.

The solid residues which were obtained by the decomposition of (1) and (2) were analysed by means of gracing incidence XRD (GI-XRD). The diffractograms of such thin films fabricated by spincoating of the molecular precursors on quartz and subsequent annealing at various temperatures are shown in Figure 4. Films deposited at lower temperatures (250 °C) were found to be amorphous, whereas at higher temperatures (350 and 450 °C) crystalline films of zincite (JCPDS 36-1451) were formed. The XRD measurements indicated preferential growth on the substrate normal to the (002) plane of the zincite structure. The formation of this type of texture in zinc oxide thin films is well known for sol-gel processes as well as solution deposition.^[30] Thus, the decomposition of zinc acetate to zinc oxide is frequently used for the formation of seed layers for epitactic growth of ZnO on different substrates.^[31,32] For ZnO films obtained by Chemical Bath Deposition (CBD), preferential orientation of zincite might occur directly near the substrate but can be lost with greater distance from the substrate surface, i.e. with increasing film thickness.^[33] The nanocrystallinity



Figure 4. GI-XRD of films obtained by spincoating solutions of (a) $[Zn_3(OH)_4(dmm-NO_2)_2]$ (1) and (b) $[Zn_4O(dmm-NO)_6]$ (2) followed by calcination at various temperatures. The broad signal at 20 of about 22° refers to the quartz substrate.



of the ZnO formed by ceramisation of complexes (1) and (2) was also confirmed by means of HRTEM. The ZnO particles are highly crystalline with a mean diameter of about 10–15 nm for those derived from 2 and slightly larger (20–30 nm) for those from complex 1 (see Figure 5 and Figure S4).



Figure 5. (a) and (b) HRTEM images at different magnifications of nanocrystalline zinc oxide obtained from the precursor $[Zn_4O(dmm-NO)_6]$ (2) after processing at 350 °C. (c) Corresponding SAED pattern.

For further characterisation, photoluminescence (PL) spectra of ZnO films on quartz slides obtained from the decomposition of [Zn₄O(dmm-NO)₆] were recorded (Figure S5). The amorphous film from the decomposition at 250 °C showed intense fluorescence which seems, however, to be unrelated to zinc oxide. The films obtained at higher temperatures both exhibited a peak at about 380 nm and a further very broad signal with maxima at 584 and 597 nm. The first is commonly attributed to the e-/h exciton, whereas the latter refers to structural point defects within the zincite structure.^[34-36] These findings also support the view that significant amounts of organic residues are still present at lower calcination temperatures. The topography of the zinc oxide thin films from the decomposition of (1) and (2) was further analysed by means of AFM (Figure 6). Solutions of the precursors display excellent wetting of the substrate which results in complete surface coverage. After annealing, the ceramic films are uniform and exhibit low surface roughness. The formation of nitrogen oxides from (1) or hydrogen cyanide from (2) was not recognizable during the thermal processing and posed no problems.



Figure 6. AFM topographies of films obtained by spincoating of solutions of (a) $[Zn_3(OH)_4(dmm-NO_2)_2]$ (1) and (b) $[Zn_4O(dmm-NO)_6]$ (2) and subsequent annealing at 350 °C [film thickness about 10 nm, RMS values (a) 0.3 nm and (b) 0.2 nm].

Functional Properties of the Precursor Derived Semiconductor ZnO Films

A series of FETs with bottom gate/bottom contact setup (Figure 7) were fabricated by spincoating solutions of $[Zn_4O(dmm-NO)_6]$ in methoxyethanol on prefabricated substrates (support/gate highly n-doped silicon, dielectric silicon dioxide and interdigital gold electrodes) followed by



Figure 7. (a) Schematic setup of FET device. (b) SEM micrograph showing a top-view of the FET device structure at the intersection from the channel area (left) to the gold electrode (right).



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annealing on a hotplate at temperatures from 250 to 450 °C. Prior to the FET measurement in a glove box, an additional annealing step was carried out under an argon atmosphere at 150 °C. This treatment served to eliminate adsorbed oxygen and/or water.

No performance was observed for a processing temperature of the ZnO films of 250 °C. This was in accordance with the before-mentioned findings from GI-XRD and PLspectroscopy which indicated the presence of amorphous ZnO films still containing some organic residues. However, the FET characteristics obtained by annealing the films at 350 °C are shown in Figure 8 with characteristic values of $\mu = 5.2 \times 10^{-2} \text{ cm}^2/\text{V} \text{ s}$, $I_{\text{On/off}} \approx 245,000$ and a threshold voltage $V_{\rm th}$ = +6.3 V. Based on these values the transistor behaviour showed both a reasonable saturation and $I_{\text{on/off}}$ ratio. Moreover, no hysteresis was observed. Processing at 450 °C lead to even better charge carrier mobility above $0.3 \text{ cm}^2/\text{V}\text{ s}$ but resulted in a decrease in the $I_{\text{on/off}}$ ratio by one order of magnitude($\mu = 0.307 \text{ cm}^2/\text{V} \text{ s}$, $I_{\text{On/off}} \approx 10,000$, $V_{\rm th}$ +5.9 V). The observed values and behaviour are thus comparable with earlier reports for solution derived nanocrystalline zinc oxide.^[6,37]



Figure 8. Performance of an FET derived from $[Zn_4O(dmm-NO)_6]$ (1) by annealing at 350 °C in air and subsequently at 150 °C in argon. (a) Output characteristics obtained from variation of the drain-source voltage from 0–25 V for gate-source voltages from 0–25 V in 5 V steps. Data were acquired for increasing as well as decreasing drain-source voltages. (b) Transfer characteristics for constant drain-source voltage of 25 V. ($\mu = 5.2 \times 10^{-2} \text{ cm}^2/\text{V}\text{ s}$; $I_{\text{On/off}} \approx 245,000$; $V_{\text{th}} = +6.3 \text{ V}$).

Conclusions

Molecular zinc(II) complexes of 1,3-diketones which are functionalised in the 2-position are suitable precursors for the preparation of zinc oxide thin films. If employed in a solution deposition route they are certainly advantageous over their unfunctionalised counterparts. The multinuclear complexes which were synthesised in this work show good solubility in organic solvents and can be employed under ambient conditions (air and light). Moreover, they can be cleanly converted into zinc oxide by thermal annealing without any sign of sublimation. The functionalisation of 1,3-diketones in the 2-position thus offers a valuable way to introduce a predefined bonding breaking point into the ligand framework of such zinc complexes ("molecular zipper"). The variation of the side groups in the 1- and 3positions of the malonic acid ester allows further tailoring of the solubility and decomposition behaviour of the corresponding zinc complexes. This ligands of this class are therefore promising candidates for the synthesis of various other metal oxide precursors.

Experimental Section

Ligand Synthesis: Dimethyl 2-(hydroxyimino)malonate (dmm-NOH) was obtained by the reaction of dimethyl malonate with sodium nitrite in acetic acid.^[38] The crude liquid product contained some unreacted dimethyl malonate and was purified by fractional microdistillation (bp. of product fraction 95 °C at 0.3 mbar). The product solidifies after cooling to room temperature. $C_5H_7NO_5$ (161.1): calcd. C 37.27, N 8.69, H 4.38; found C 37.51, N 8.68, H 4.29. ¹H NMR (500 MHz, [D₃]chloroform, 25 °C): δ = 3.81, 3.84 (-CH₃), 10.68 (br., -OH) ppm. ¹³C{¹H} NMR(500 MHz, [D₃]chloroform, 25 °C): δ = 53.09, 53.37 (-CH₃); 143.71 (-C=NOH); 160.55, 161.04 ppm (-COO) as mixture of two *E*/*Z*-diastereomers.

Dimethyl 2-Nitromalonate (Hdmm-NO₂) was synthesized by the reaction of dimethyl malonate with fuming nitric acid.^[39,40] No side products or contamination were observed and a pure product was obtained after distillation (bp. 82 °C at 0.4 mbar). C₅H₇NO₆ (177.1): calcd. C 33.91, N 7.91, H 3.98; found C 34.46, N 7.85, H 3.97. ¹H NMR (500 MHz, [D₃]chloroform, 25 °C): δ = 3.85 (-CH₃); 5.81 [-C(NO₂)H]. ¹³C{¹H} NMR(500 MHz, [D₃]chloroform, 25 °C): δ = 54.35 (-CH₃); 87.82 [-C(NO₂)H]; 159.87 (-COO).

Zinc Oxide Precursor Synthesis: Synthesis of dimethyl 2-nitromalonate-Zn^{II} $[Zn_3(OH)_4(dmm-NO_2)_2]$ (1): Hdmm-NO₂ (10 g, 56.8 mmol) was added to distilled water (200 mL). After addition of hydrozincite (10 g, 91.1 mmol Zn), a yellow suspension was obtained which was stirred overnight. After removal of solid residues by filtration, the solvent was completely removed with a rotary evaporator (65 °C, 130 mbar). The remaining yellow oil was dissolved in dichloromethane (50 mL) and added to dropwise to methyl-tert-butyl ether (200 mL). The product was collected by filtration, dried in vacuo and obtained in the form of a yellowish powder (6.4 g, 34.2%). Ceramic yield (CY) / elemental analysis (CHN): found CY 39.87%, C 19.86, N 4.50, H 2.78%. calcd. for Zn₃(OH)₄(C₅H₆NO₆)₂ CY 39.63%, C 19.49, N 4.54, H 2.62%. ¹H NMR (500 MHz, [D₆]dimethyl sulfoxide, 25 °C): δ = 3.57 (-CH₃), 3.40 (-OH) ppm. ${}^{13}C{}^{1}H$ NMR (500 MHz, [D₆]dimethyl sulfoxide, 25 °C): δ = 50.91 (-CH₃); 109.07 (-C-NO₂); 163.72 (-COO) ppm. IR: 3460 (v.br., vO–H) cm⁻¹.

Synthesis of [2-Hydroxyimino-dimethylmalonato- Zn^{II}] [$Zn_4O(dmm-NO)_6$] (2): The following operations were carried out under inert conditions. Two separate solutions of zinc 2-propanolate (1.33 g,



7.2 mmol) and dmmNOH (3.50 g, 21.7 mmol) were prepared in tetrahydrofuran (10 mL, each). After cooling the zinc compound to 0 °C, the ligand was added dropwise, whereby a clear yellow solution was formed. During warming to room temperature precipitation occurred. The product was filtered and washed twice with methyl-*tert*-butyl ether (10 mL). After drying in high vacuum over several hours, a yellowish powder (1.84 g, 82.3%) was obtained. The product was stable under ambient conditions. Ceramic yield (CY)/elemental analysis (CHN): Found CY 26.50%, C 29.52, N 6.60, H 2.98. calcd. for Zn₄O(C₅H₆NO₅)₆ CY: 26.29%, C 29.10, N 6.79, H 2.92. ¹H NMR (500 MHz, [D₆]dimethyl sulfoxide, 25 °C): δ = 3.69, 3.72 (-CH₃) ppm. ¹³C{¹H} NMR (500 MHz, [D₆]dimethyl sulfoxide, 25 °C): δ = 51.62 (-CH₃); 143.36 (-C=NO); 162.70, 164.69 (-COO) ppm.

Zinc Oxide Film Preparation: Quartz slides $(2 \times 2 \text{ cm})$ were cleaned by ultrasonication in 2-propanol and distilled water. Substrates $(1.5 \times 1.5 \text{ cm})$ for FET devices (interdigital structure obtained from Fraunhofer IWS-Dresden) consisted of n-doped silicon with a 90 nm layer of SiO₂, on which gold electrodes were deposited with an intermediate adhesive layer of indium tin oxide (ITO). The channel width of source/drain electrodes was W = 10 mm with a channel length $L = 10 \text{ µm}.^{[6.37,41]}$ FET substrates were cleaned by consecutive ultrasonication in acetone, 2-propanol and deionised water for 5 min and dried by purging with argon. The deposited solutions contained 3 wt.-% of the precursor (1) or (2) in methoxyethanol. Films were produced by spincoating (6 s at 1000 rpm followed by 20 s at 2000 rpm) and heating on a hotplate in air for 4 min. Thicker films can be obtained by iteration of this coating procedure.

Materials Characterisation: TG/IR/MS measurements: TG 209N1 (Netzsch) coupled with a Nicolet iS10 spectrometer (Thermo-Scientific) and Aelos QMS 403C (Netzsch). IR: Nicolet 6700 (ThermoScientific). Samples were measured as liquids or powders with an attenuated total reflection (ATR) unit. XRD: STOE Stadi-P, Cu- K_{α} radiation. PL spectra: Fluorolog-3 (Horiba) with Xenon lamp. AFM: CP-II (Bruker-Veeco), 0.5 Hz, silicon cantilevers. SEM: JSM-7600F (Jeol). TEM: CM20 (Philips, FEI) operated at 200 kV. Samples were supported on a lacey-carbon copper grid (300 mesh).

FET characteristics were determined with an HP 4155A Semiconductor Parameter Analyzer (Agilent) in a glove box in the dark under an argon atmosphere. FET devices were stored in darkness for about 24 h prior to measurement. Charge carrier mobility μ_{SAT} and the threshold voltage V_{th} were derived from a linear fitting of the square root of the source drain current ($I_{\text{DS}}^{0.5}$) as a function of gate source voltage V_{GS} .^[6,37,41]

Supporting Information (see footnote on the first page of this article): IR spectra of zinc oxide precursors, gas phase IR spectra as well as mass spectra from TG coupling, additional TEM images and photoluminescence spectra of zinc oxide films.

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