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Synthesis, structural characterization and thermochemical reactivity of tris(ethylenediamine)zinc tetracyanozincate, a precursor for nanoscale ZnO

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Dedicated to Prof. Wolfgang F. Hemminger on the occasion of his 65th birthday.

Abstract

The binuclear complex tris(ethylenediamine)zinc tetracyanozincate was prepared and characterized by single-crystal X-ray structure analysis. It consists of distorted $[Zn(en)_3]^{2+}$ octahedra and $[Zn(CN)_4]^{2-}$ tetrahedra. The thermolysis under air was studied by thermogravimetry, and the resulting product (ZnO) was characterized by X-ray diffraction and scanning electron microscopy, showing compact particles with a diameter of 100–300 nm.

Keywords: Zinc oxide; Coordination compounds; Crystal structure; Thermolysis; Scanning electron microscopy

1. Introduction

Zinc oxide nanostructures have been the subject of intense interest due to their potential wide-ranging applications [1,2]. Zinc oxide is a wide band gap semiconductor which is used, e.g., in electronics, photoelectrochemistry, and sensor technology [3–5]. In catalysis, a mixed catalyst containing copper and zinc oxide is used in methanol synthesis. Recent studies indicate that the Cu–ZnO interface plays an important role under reducing reaction conditions [6]. Nanostructured ZnO with various morphologies such as nanorods, nanowires, nanotubes, nanosheets and nanodiscs were prepared by different synthetic methods [7–12]. Vapour phase growth at high temperature is the major physical method to prepare ZnO nanostructures [13]. The wet-chemistry synthesis is generally carried out with solutions of zinc salts in water or alcohols, to which hydroxide is added which leads to the precipitation of ZnO [14]. The preparation of ZnO nanostructures by thermolysis of organometallic [15] or molecular precursors [16] was also reported.

Metal oxides can be obtained by thermolysis of metal cyanide coordination compounds under mild conditions [17–21]. In the work presented here, zinc oxide was prepared by thermolysis of $[Zn(en)_3][Zn(CN)_4]$, a new binuclear complex that decomposes to zinc oxide at moderate temperature under oxidizing conditions. This process was followed by thermogravimetry and the product was characterized with respect to its crystallinity and morphology. It was of interest whether the loss of the ligands would lead to a fine particulate ZnO phase which might be of interest, e.g., for heterogeneous catalysis. The neutral ligand ethylenediamine should be a good leaving group as well as the cyanide which may be released as cyanogen, $(CN)_2$ or undergo oxidative combustion [20].

2. Materials and methods

Single-crystal structure analysis was carried out with a Siemens SMART CCD area detector system and for calculations (solution and refinement) the program package Bruker AXS SHELXTL Version 6.12 was used.

Thermogravimetry was carried out with a Netzsch STA 409 TG-DTA apparatus. Samples were heated from room temperature to 1000 °C at a rate of 5 K min^{-1} under dynamic O_2 atmosphere at a flow rate of 50 mL min^{-1}.

IR characterization of the products was performed with a Bruker Vertex 70 instrument in KBr pellets. High-resolution

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X-ray powder diffractometry was carried out in transmission geometry at beamline B2 at HASYLAB/DESY, Hamburg, Germany, with a wavelength of $\lambda = 0.71$ Å. Scanning electron microscopy was carried out with a Leo 420 instrument on gold-sputtered samples.

3. Results and discussion

The binuclear coordination compound was prepared by coordinating Zn^{2+} (zinc nitrate) with ethylenediamine, giving a cationic complex, and by coordinating Zn^{2+} (zinc nitrate) with cyanide (KCN), giving an anionic complex, respectively. Mixing of both solutions in equal amounts led to a white precipitate of the title compound. The final concentration of zinc was 20 mmol in 50 mL of water, used in stoichiometric amounts according to Eqs. (1)–(3). All reactions were carried out in water at room temperature in high yield. Single crystals were isolated from the precipitate:

$$Zn^{2+} + 3en \rightarrow [Zn(en)_3]^{2+} \quad (1)$$

$$Zn^{2+} + 4CN^- \rightarrow [Zn(CN)_4]^{2-} \quad (2)$$

$$[Zn(en)_3]^{2+} + [Zn(CN)_4]^{2-} \rightarrow [Zn(en)_3][Zn(CN)_4] \downarrow$$
$$(en = H_2N–CH_2–CH_2–NH_2) \quad (3)$$

Elemental analysis gave 29.74% Zn (calculated: 31.50%), 28.14% C (calculated: 28.93%), 5.37% H (calculated: 5.83%), and 32.39% N (calculated: 33.74%). Zn was determined by atomic absorption spectroscopy, and carbon, hydrogen and nitrogen by combustion analysis.

The structural elements of this coordination compound are shown in Fig. 1. At the cationic zinc site (Zn1), zinc is octahedrally coordinated by three bidentate ethylenediamine ligands, and on the anionic site (Zn11), it is tetrahedrally coordinated by four monodentate cyanide ligands. The octahedron around Zn1 is distorted as it has been reported earlier for $[Zn(en)_3]^{2+}$-complexes [22–25]. The tetrahedral $[Zn(CN)_4]^{2-}$ unit is also distorted. The proximity of the cyanide ligand (N13) to one of the hydrogen atoms of ethylendiamine at N2 (2.291 Å) seems to be responsible for the elongated bond between zinc (Zn11) and this cyanide ligand (C13–N13). The shortest Zn–Zn distances in the structure are 5.380 and 5.552 Å. The main crystallographic data are comprised in Tables 1 and 2.

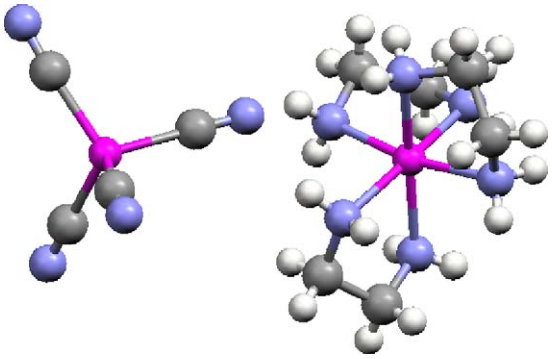

Fig. 1. The two structural elements, $[Zn(en)_3]^{2+}$ (central atom: Zn1) and $[Zn(CN)_4]^{2-}$ (central atom: Zn11), of the crystal structure of tris(ethylene diamine) zinc tetracyanozincate. Zinc: magenta; carbon: grey; nitrogen: blue; hydrogen: white.

Table 1
Crystallographic data of tris(ethylenediamine)zinc tetracyanozincate

Crystal structure data	
Calculated formula	$Zn_2C_{10}H_{24}N_{10}$
Calculated density	1.525 g cm^{-3}
Wavelength	0.71073 Å
Space group	$P2_1/n$
Crystal system	Monoclinic
a	10.7073 Å
b	15.2124 Å
c	11.1041 Å
β	91.967°
Z	4
Unit cell volume	1807.61 Å^3
Independent reflections	4514 [R(int) = 0.0187]
R indices [$I > 2\sigma(I)$]	$R_1 = 0.0158$ $wR_2 = 0.0426$
R indices (all data)	$R_1 = 0.0186$ $wR_2 = 0.0444$

Atomic coordinates

Atom	x	y	z	U (eq)
Zn1	8027	1704	2671	23
N1	7277	352	2676	29
C1	6076	360	3283	37
N2	6160	1955	3308	29
C2	5370	1195	2978	39
N3	7488	1918	768	29
C3	8635	1936	66	31
N4	9770	1368	1838	27
C4	9542	1242	536	31
N5	8626	3074	2948	34
C5	9534	3093	3981	39
N6	8883	1610	4498	31
C6	9065	2509	4971	41
Zn11	2825	4706	2272	27
C11	2226	5063	3905	36
N11	1919	5184	4865	56
C12	2924	5693	1048	33
N12	3064	6231	357	52
N13	5578	3909	2519	38
C13	4595	4201	2434	29
N14	1096	3179	1221	46
C14	1702	3735	1601	32

Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters (Å$^2 \times 10^3$) are given. U (eq) is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

The infrared spectrum of the zinc complex is shown in Fig. 2. All expected IR bands are visible: 3359/3365/3294 cm^{-1} (NH_2 valence), 2956/2893 cm^{-1} (CH_2 valence), 2144 cm^{-1} (C≡N valence), 1589 cm^{-1} (N–H deformation), 1467 cm^{-1} (C–H deformation), 1328/1278 cm^{-1} (C–H), and 1045/1001/959 cm^{-1} (C–C valence).

The thermolysis of $[Zn(en)_3][Zn(CN)_4]$ under oxygen occurs in a multi-step process (Fig. 3). First, probably a part of