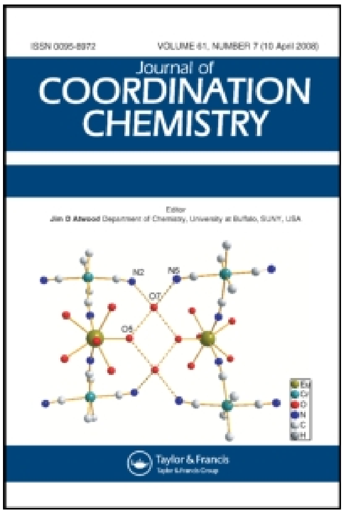

Journal of Coordination Chemistry

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

Preparation, thermal decomposition, and crystal structure of Zn(II) 2-chlorobenzoate complex with nicotinamide

L. Findoráková[a]; K. Győryová[a]; M. Melník[b]; M. Koman[b]; Faten A. Nour El-Dien[c]
[a] Department of Inorganic Chemistry, P. J. Šafarik University, SK-041 54 Košice, Slovak Republic [b] Department of Chemistry, Slovak Technical University, Bratislava, Slovak Republic [c] Department of Chemistry, Faculty of Science, Cairo University Giza, 126 13 A.R., Egypt

First published on: 25 August 2010

To cite this Article Findoráková, L. , Győryová, K. , Melník, M. , Koman, M. and Nour El-Dien, Faten A.(2010) 'Preparation, thermal decomposition, and crystal structure of Zn(II) 2-chlorobenzoate complex with nicotinamide', Journal of Coordination Chemistry, 63: 19, 3348 — 3355, First published on: 25 August 2010 (iFirst)

To link to this Article: DOI: 10.1080/00958972.2010.512083

URL: http://dx.doi.org/10.1080/00958972.2010.512083

Journal of Coordination Chemistry
Vol. 63, No. 19, 10 October 2010, 3348–3355

Preparation, thermal decomposition, and crystal structure of Zn(II) 2-chlorobenzoate complex with nicotinamide

L. FINDORÁKOVÁ*†, K. GYŐRYOVÁ†, M. MELNÍK‡,
M. KOMAN‡ and FATEN A. NOUR EL-DIEN§

†Department of Inorganic Chemistry, P. J. Šafarik University,
Moyzesova 11, SK-041 54 Košice, Slovak Republic
‡Department of Chemistry, Slovak Technical University,
Radlinského 9, SK-812 37, Bratislava, Slovak Republic
§Department of Chemistry, Faculty of Science,
Cairo University Giza, 126 13 A.R. Egypt

(*Received 22 November 2009; in final form 8 June 2010*)

A new Zn(II) 2-chlorobenzoate complex, $[Zn(2\text{-}ClC_6H_4COO)_2(nad)_2]$ (nad = nicotinamide), was synthesized and characterized by elemental analysis, infrared (IR) spectroscopy, mass spectrometry, thermal analysis, and X-ray structure determination. The mechanism of thermal decomposition of the complex was studied by TG/DTG, DTA, IR spectroscopy, and mass spectrometry. The thermal decomposition is characterized as a two-step process. Zinc oxide was found as the final product of the thermal decomposition performed up to 900°C. Mass spectrometry was used to determine the volatiles released during thermal decomposition. The IR spectrum indicates that carboxylate is coordinated to zinc in monodentate coordination. $[Zn(2\text{-}ClC_6H_4COO)_2(nad)_2]$ crystallizes in the monoclinic system, space group *Pn*, $a = 10.376(2)$ Å, $b = 10.100(1)$ Å, $c = 12.604(1)$ Å, $\beta = 100.79(1)°$. The zinc is tetrahedrally coordinated by two nitrogens of nicotinamide and two oxygens of 2-chlorobenzoate.

Keywords: Zn(II) 2-chlorobenzoate; Nicotinamide; Thermal decomposition; X-ray structure

1. Introduction

Chlorinated benzoic acids are environmental contaminants that result from industrial and agricultural activity, as well as from partial biotic and abiotic degradation of chlorinated aromatic compounds in the environment. Chlorinated benzoates can be biodegraded under aerobic conditions by a number of bacteria; however, when aerobic biodegradation occurs in the presence of benzoate it often results in the formation of toxic metabolic products, thereby killing or severely inhibiting the microbial community [1]. Metal complexes of biologically important ligands are sometimes more effective than free ligands [2]. Nicotinamide as a neutral ligand is a part of the pyridine nucleotides such as NAD^+ and $NADP^+$, which takes part in redox reactions [3]. Carboxylate can coordinate with metal ions with synergetic or antagonistic effects on

---

*Corresponding author. Email: lenka.piknova@upjs.sk

Journal of Coordination Chemistry
ISSN 0095-8972 print/ISSN 1029-0389 online © 2010 Taylor & Francis
DOI: 10.1080/00958972.2010.512083

biological activity. Recently, we studied interactions of 2-chlorobenzoic acid with zinc. Zinc and its complexes have antibacterial and antiviral activities [4, 5] and are used in the treatment of several diseases [6], for example, Zn(II) acetate with erythromycin has been used successfully in clinical medicine for acne therapy [7], and some aliphatic carboxylic acid Zn(II) complexes containing additional N-donor ligands have been found to exhibit some biological activity [8]. Benzoic acid is studied as a replacement of growth-promoting antibiotics for farm animals. Its antimicrobial effect is well-known [9]. However, the influence of aromatic zinc carboxylates (benzoate, salicylate) on the probiotic and pathogenic bacteria is poorly known. Zn(II) benzoates with bioactive ligands are also interesting for inorganic chemistry. The thermal, spectral, and structural behaviors of several aliphatic and aromatic Zn(II) carboxylate complexes with nicotinamide was investigated by Győryová *et al.* and by Zeleňák *et al.* [10–12].

The structure of aromatic carboxylates with nicotinamide was studied by many authors, such as Zeleňák *et al.* [13], who investigated the structure of Zn(II) benzoate with nicotinamide. They found that the structure is formed by a centrosymmetric linear array of three zinc ions, which are coordinated by six benzoate anions and two neutral nicotinamide ligands. Necefoglu *et al.* [14] studied the structure of Zn(II) 4-hydroxybenzoate with nicotinamide. They found that the compound crystallizes as mononuclear molecules with distorted trigonal-bipyramidal zinc coordination. One of the 4-hydroxybenzoate ions is coordinated to zinc as a bidentate ligand, while the other is monodentate. Moncol *et al.* [15] solved the structure of Cu(II) 2-bromobenzoate with nicotinamide, where Cu^{2+} is coordinated by two pairs of oxygens from the asymmetric bidentate 2-bromobenzoate anions and by a pair of pyridine nitrogens from the monodentate nicotinamide in *trans* positions, forming an extremely elongated bipyramid.

In this article Zn(II) 2-chlorobenzoate with nicotinamide has been prepared, characterized by elemental analysis, infrared (IR) spectroscopy, mass spectrometry, and the structure was determined by X-ray crystallography. Thermal behavior of the complex was also investigated by TG/DTG and DTA techniques.

2. Experimental

2.1. Synthesis of $Zn(2\text{-}ClC_6H_4COO)_2(nad)_2$

For preparation of $[Zn(2\text{-}ClC_6H_4COO)_2(nad)_2]$, A.R. grade chemicals were used: $ZnCO_3$ (Lachema Neratovice), 2-chlorobenzoic acid 98% (Aldrich), nicotinamide (Farmakon Hlohovec). A mixture of $ZnCO_3$ (0.4180 g, 3.33 mmol) and 2-chlorobenzoic acid (1.0438 g, 6.66 mmol) in water–ethanol was stirred at room temperature for 1 h and then filtered. A water solution of nicotinamide (0.8142 g, 6.66 mmol) was added to the filtrate and the mixture was stirred for 3 h. The resulting clear solution was allowed to stand in air at room temperature for several days, yielding colorless crystals. The crystals were separated and dried at ambient temperature. Yield = 1.96 g (95%). Anal. Calcd for $[Zn(2\text{-}ClC_6H_4COO)_2(nad)_2]$ (%): C, 50.31; H, 3.25; N, 9.03; Zn, 10.53. Found (%): C, 50.18; H, 3.29; N, 9.15; Zn, 10.21.

2.2. *Methods of sample characterization*

The IR spectrum was recorded on a Perkin-Elmer spectrophotometer from 4000 to 400 cm^{-1} using KBr pellets. The C, H, and N content of the complex were determined with a Perkin-Elmer 2400 CHN analyzer and zinc content complexometrically using Complexone III (disodium salt of EDTA) as an agent and Eriochrome black as an indicator. The thermal properties TG/DTG and DTA were carried out using a NETZSCH STA 409 PC/PG Thermoanalyzer (Germany). The sample (21.384 mg) was placed in Al_2O_3 crucible and heated at 10°C min^{-1} in an air flow. Hewlett-Packard mass spectrometer model MS-5988 was used for determination of volatile products of thermal decomposition. Diffraction intensity data for $[Zn(2\text{-}ClC_6H_4COO)_2(nad)_2]$ were collected using a Siemens P4 diffractometer with graphite-monochromated Mo-Kα radiation at 293 K [16]. The diffraction intensities were corrected for Lorentz and polarization effects [17]. Absorption corrections were applied using XEMP [18]. The structure was solved by direct methods using SHELXS-97 and refined by full-matrix least-squares on all F^2 using SHELXL-97 [19]. Geometrical analysis was performed using SHELXL-97. The structure was drawn by ORTEP-3 for Windows. The Single Crystal Suite WinGX was used as an integrated system for all crystallographic programs and software for preparing materials for publication [20].

3. Results and discussion

$[Zn(2\text{-}ClC_6H_4COO)_2(nad)_2]$ is very soluble in CH_3OH, soluble in H_2O, slightly soluble in C_2H_5OH, and insoluble in $(C_2H_5)_2O$, $(CH_3)_2CO$, $CHCl_3$, and CCl_4.

3.1. *IR spectra*

The FT-IR spectrum of the complex shows the presence of coordinated 2-chlorobenzoate and nicotinamide. In the IR spectrum of free 2-chlorobenzoic acid there is a single strong absorption band at 1693 cm^{-1} (COOH group). In the IR spectrum of the prepared compound, this absorption disappears, forming asymmetrical (COO^-) vibration ν_{as} at 1578 cm^{-1} and symmetrical vibration ν_s at 1382 cm^{-1}. The $\Delta\nu$ value is 196 cm^{-1}, which is higher than the value of $\Delta\nu$ (183 cm^{-1}) for the sodium salt of 2-chlorobenzoic acid [21]. From these values we suggest monodentate coordination of carboxylate group for compound. This was confirmed by X-ray analysis. The ν(C=N) shifts from 1619 cm^{-1} for uncoordinated ligand to 1632 cm^{-1} in the complex. The presence of nicotinamide is evident from the presence of strong absorption of the carbonyl ν(C=O) at 1692 cm^{-1}. Aromatic ν(C–H) is observed at 3075 cm^{-1}. Comparison of the most important absorption bands of the prepared compound and nicotinamide are summarized in table 1. The absorption bands were identified in accordance with literature data [21, 22].

3.2. *Thermal analysis*

$[Zn(2\text{-}ClC_6H_4COO)_2(nad)_2]$ starts to decompose by melting at 185°C, which is indicated by an endothermic effect on the DTA curve (Supplementary material). In the

Table 1. Characteristic absorptions (v cm^{-1}).

Assignment	nad	Zn(2-Clbenz)$_2$(nad)$_2$
$\nu_{as}(NH_2)_{nad}$	3368vs	3369s
$\nu_{s}(NH_2)_{nad}$	3161s	3215m
$\nu(C–H)_{ar}$	3060w	3075w
$\nu(C{=}O)_{nad}$	1697sh	1692s
$\nu(C{=}N)_{nad}$	1619vs	1632vs
$\nu_{as}(COO^-)$	–	1578vs
$\nu_{s}(COO^-)$	–	1382vs
Δ	–	196
$\delta(NH_2)_{nad}$	1618vs	1604vs
$\rho(NH_2)_{nad}$	1153m	1143m
$\nu(C–Cl)$	–	698s
$\gamma(C–H)$	–	762s
$\nu(Zn–O)$	–	468w

nad – nicotinamide; ar – aromatic; vs – very strong; s – strong; m – medium; w – weak.

temperature range 200–350°C two nicotinamides and one CO_2 are released (Calcd mass loss 46.44%, found 46.13%) accompanied with an endothermic effect on the DTA curve at 300°C. The release of nicotinamide was confirmed by mass spectrum ($m/z = 122$) measured up to 270°C (Supplementary material). Thermal decomposition continued with the release of $(C_6H_4Cl)_2CO$ in the temperature range 350–704°C (Calcd mass loss 40.45%, found 40.09%); $(C_6H_4Cl)_2CO$ decomposed to two free radicals $(C_6H_4Cl)CO^\bullet$ and $C_6H_4Cl^\bullet$ (for $(C_6H_4Cl)CO^\bullet$ $m/z = 139$; $C_6H_4Cl^\bullet$ $m/z = 112$) (Supplementary material). ZnO resulted as the final product of the thermal decomposition (Calcd residual mass 13.11%, found 13.78%). The following reaction is proposed for the thermal decomposition of $[Zn(2\text{-}ClC_6H_4COO)_2(nad)_2]$:

$$\left[Zn(2\text{-}ClC_6H4COO)_2(nad)_2\right] \longrightarrow 2nad + CO_2 + (C_6H_4Cl)_2CO + ZnO$$
$$(C_6H_4Cl)_2CO \longrightarrow (C_6H_4Cl)CO + C_6H_4Cl^\bullet$$

3.3. *Crystal structure determination*

The crystal data and structure refinement for $[Zn(2\text{-}ClC_6H_4COO)_2(nad)_2]$ are listed in table 2. The structure consists of isolated $[Zn(2\text{-}ClC_6H_4COO)_2(nad)_2]$ units (figure 1). Zn(II) is coordinated by two nitrogens from two nicotinamides and two oxygens from two 2-chlorobenzoates in a very distorted tetrahedron (ZnO_2N_2). The mean Zn–N and Zn–O bond distances are 2.074(6) and 1.954(6) Å, respectively. The angles with most deviation from ideal tetrahedral (109.5°) are O(3)–Zn–O(1) and N(1)–Zn–N(2) at 135.02(12) and 97.73(9)°. The remaining four O–Zn–N bond angles vary from 102.2(3) to 107.5(3)°. A reason for the deviations is a weak bond (semi-coordination) Zn–O(2), 2.580 Å and Zn–O(4), 2.644 Å. The Zn(II) lies on a crystallographic two-fold rotation axis. The crystal structure of the complex consists of 3-D sheets. The layers are situated in the *abc* directions and consist of molecules linked by strong and weak hydrogen bonds (table 3). The details of hydrogen-bonding network and hydrogen-bonding geometry along the *b*-axis are shown in figures 2 and 3, respectively.

Table 2. Crystal data and structure refinement details for [Zn(2-ClC$_6$H$_4$COO)$_2$(nad)$_2$].

Identification code	mk20
Empirical formula	$C_{26}H_{20}C_{12}N_4O_6Zn$
Formula weight	620.73
Temperature (K)	293(2)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	*Pn*
Unit cell dimensions (Å, °)	
a	10.376(2)
b	10.100(1)
c	12.604(1)
α	90
β	100.79(1)
γ	90
Volume, *Z*	1297.5(3), 2
Calculated density (Mg m^{-3})	1.589
Absorption coefficient (mm^{-1})	1.202
F(000)	632
Crystal size (mm^3)	0.35 × 0.39 × 0.43
θ range for data collection	2.02–30.00°
Limiting indices	$-1 \le h \le 14$; $-1 \le k \le 14$; $-17 \le l \le 17$
Reflections collected (unique)	4729/4297 [*R*(int) = 0.0292]
Completeness to $\theta = 30.00$ (%)	98.6
Absorption correction	psi-scan
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	4297/2/353
GOF on F^2	1.021
R_1, wR_2 [$I > 2\sigma(I)$]	0.0375, 0.0893
R_1, wR_2 indices (all data)	0.0542, 0.0981
Absolute structure parameter	0.05(2)
Extinction coefficient	0.0202(15)
Largest difference peak and hole (e Å^{-3})	0.311 and −0.276

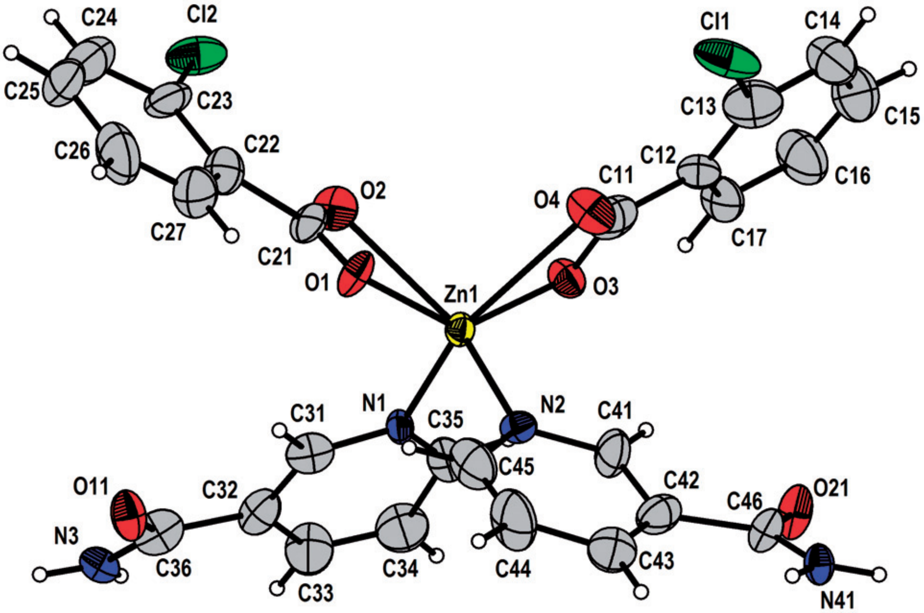

Figure 1. The crystal structure of [Zn(2-ClC$_6$H$_4$COO)$_2$(nad)$_2$] with atom numbering.

Table 3. Hydrogen bonds in [Zn(2-ClC$_6$H$_4$COO)$_2$(nad)$_2$].

D–H	(Å)	H···A	(Å)	D···A	(Å)	DHA	(°)
N3–N1	0.860	H1–O21^a	2.143	N3–O21^a	2.895	N3–H1–O21^a	145.85
N3–H2	0.860	H2–O4^b	2.132	N3–O4^b	2.981	N3–H2–O4^b	169.06
N41–H3	0.860	H3–O11^c	2.189	N41–O11^c	2.941	N41–H3–O11^c	146.01
N41–H4	0.860	H4–O2^d	2.140	N41–O2^d	2.962	N41–H4–O2^d	159.76

Symmetry codes: $^a x, y, 1+z$; $^b 0.5-x, -y, 0.5+z$; $^c x, y, 1-z$; $^d 0.5+x, -y, 0.5-z$.

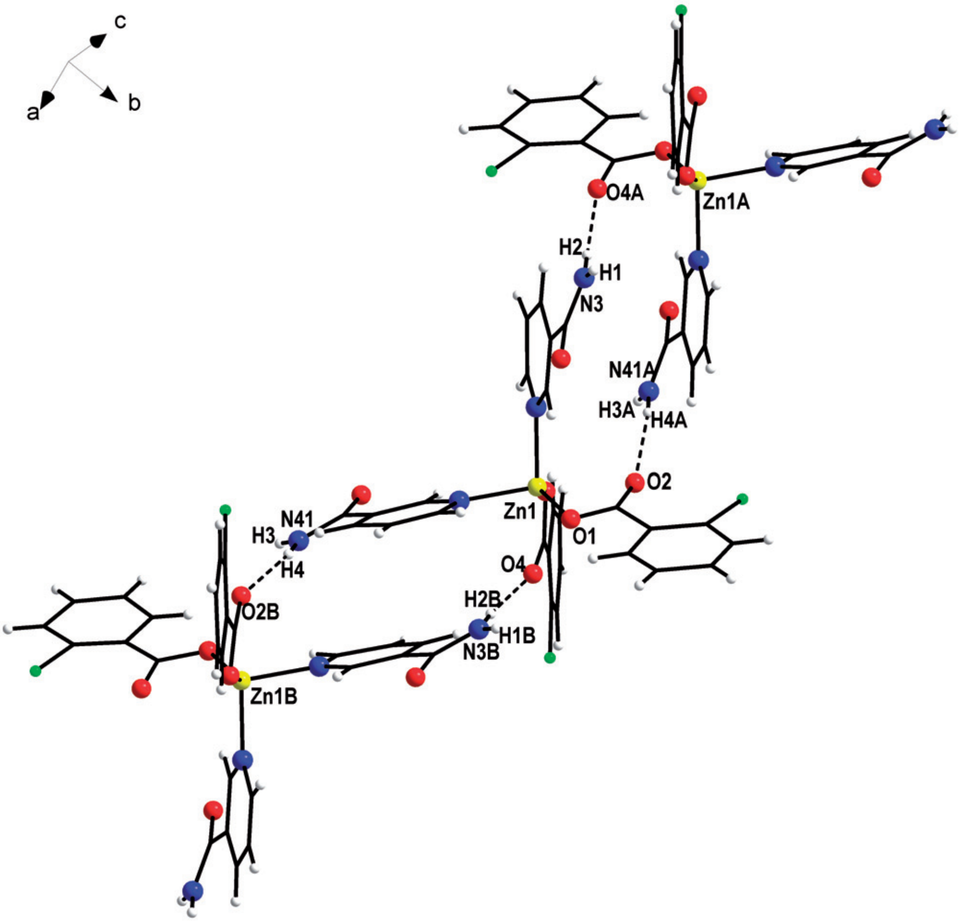

Figure 2. View of the hydrogen bonding network in the title compound. Symmetry codes: (A) $-0.5+x, -y, 0.5+z$; (B) $0.5+x, -y, -0.5+z$.

Some examples of Zn(II) complexes with coordination environments of zinc with two oxygens and two nitrogens are given in table 4. In each complex two pairs of unidentate ligands create a tetrahedral arrangement about Zn(II). As can be seen in [23–25], the homo L–Zn–L (L are O or N) bond angles deviate from the ideal tetrahedral angle only

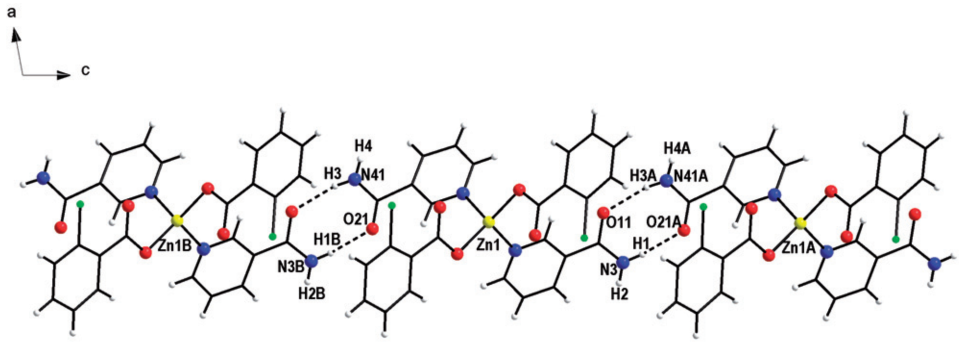

Figure 3. Hydrogen bonding geometry along the *b*-axis in the title compound. Symmetry codes: (A) *x*, *y*, $1+z$; (B) *x*, *y*, $-1+z$.

Table 4. Summary data of Zn(II) complexes with distorted tetrahedral ZnO_2N_2.

Compound	Zn–O[a] (Å)	Zn–N[a] (Å)	O–Zn–O (°)	N–Zn–N (°)	O–Zn–N[a] (°)	References
$Zn(ac)_2(im)_2$	1.972(1, 15)	2.003(2, 3)	104.8	109.9	110.3(–, 14.4)	[23]
$Zn(pr)_2(im)_2$	1.956(2, 18)	2.009(2, 3)	108.4	110.3	109.5(–, 13.1)	[24]
$Zn(3\text{-}OHbz)_2(py)_2$	2.01(1, 2)	2.08(2, 0)	107.9(5)	108.5(6)	108.5(6, 17.5)	[25]
$Zn(2\text{-}Clbz)_2(nad)_2$	1.954(6, 5)	2.074(6, 1)	135.0	97.7	104.6(3, 7.3)	[This work]

ac = acetate, im = imidazole, pr = propionate, 3-OHbz = 3-hydroxybenzoate, 2-Clbz = 2-chlorobenzoate, py = pyridine, nad = nicotinamide

[a]Mean values. The first number in parenthesis is e.s.d. and the second is maximum deviation from the mean.

slightly (maximum 4.7° [26]), while our complex deviates by 25.5°. Deviations in the remaining four O–Zn–N angles [23–25] are much higher than in our complex.

The mean Zn–O and Zn–N bond distances of 1.964 and 2.006 Å reported previously [23, 24] with alkylcarboxylates are somewhat shorter than those found in an arylcarboxylate [25] (1.982 and 2.077 Å). The O–Zn–O bond angles are in the order: 104.8° (acetate) <107.9° (3-hydroxybenzoate) <108.4° (propionate) <135.0° (2-chlorobenzoate). There is a tendency between the sum of Zn–L[Zn–O(x2) plus Zn–N(x2)] bond distance and the deviation of the L–Zn–L bond angle from ideal tetrahedron. Distortion increases with the increasing sum of the bond distance about Zn(II).

4. Conclusions

$[Zn(2\text{-}ClC_6H_4COO)_2(nad)_2]$ on heating in air decomposes in two steps. In the first step, the release of nicotinamide and CO_2 takes place, followed by the thermal decomposition of $(C_6H_4Cl)_2CO$ to new free radicals. Zinc oxide was the final product of thermal decomposition. Monodentate coordination of carboxylate group is reflected from the IR spectrum ($\Delta\nu = 196\,\mathrm{cm}^{-1}$) and confirmed by X-ray analysis. Zn^{+2} is coordinated by two oxygens and two nitrogens in a distorted tetrahedron (ZnO_2N_2).

Supplementary material

Complete crystallographic data have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. 766630. These data can be obtained free of charge *via* http://www.ccdc.cam.ac.uk/deposit or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44 01223 336033; E-mail: deposit@ccdc.cam.ac.uk.

Acknowledgments

This work was supported by the Slovak Ministry of Education VEGA project No. 1/0353/08, 1/0122/08. The financial support is gratefully acknowledged.

References

[1] T. Deniz, Ö. Cinar, C.P.L. Grady. *Water Res.*, **38**, 4524 (2004).
[2] J.R.J. Sorenson. *Metal Ions in Biological Systems*, Marcel Dekker, New York (1982).
[3] H. Pasaoglu, S. Güven, Z. Heren, O. Büyükgüngör. *J. Mol. Struct.*, **794**, 270 (2006).
[4] B. Simo, L. Perello, R. Ortiz, A. Castineiras, J. Latorre, E. Canton. *J. Inorg. Biochem.*, **8**, 275 (2000).
[5] E.D. Clercq. *Met.-Based Drugs*, **4**, 173 (1997).
[6] S.C. Cunnane. *Zinc Clinical and Biochemical Significance*, CRC Press, Florida (1988).
[7] E.J. Van Hoogdalem. *J. Eur. Acad. Dermatol. Venereol.*, **11**, 13 (1998).
[8] V. Zeleňák, K. Győryová, D. Mlynárčik. *Met.-Based Drugs*, **8**, 269 (2002).
[9] H. Kluge, J. Brož, K. Eder. *J. Anim. Physiol. Anim. Nutr.*, **90**, 316 (2006).
[10] K. Győryová, V. Balek, M. Melník, F.A. Nour El-Dien. *J. Therm. Anal. Calorim.*, **53**, 577 (1998).
[11] K. Győryová, J. Chomič, E. Szunyogová, L. Piknová, V. Zeleňák, Z. Vargová. *J. Therm. Anal. Calorim.*, **84**, 727 (2006).
[12] V. Zeleňák, I. Císařová, M. Sabo, P. Llewellyn, K. Győryová. *J. Coord. Chem.*, **57**, 87 (2004).
[13] V. Zeleňák, M. Sabo, W. Massa, P. Llewellyn. *Inorg. Chim. Acta*, **357**, 2049 (2004).
[14] H. Necefoglu, T. Hökelek, C.C. Erdönmez. *Acta Cryst.*, **E58**, m758 (2002).
[15] J. Moncol, J. Maroszova, M. Koman, M. Melnik, M. Valko, M. Mazur, T. Lis. *J. Coord. Chem.*, **61**, 3740 (2008).
[16] Siemens (1990). *XEMP* (*Version 4.2*), *Siemens Analytical X-ray Instruments Inc.*, Madison, Wisconsin, USA.
[17] Siemens (1994). *Siemens Analytical X-ray Instruments Inc.*, Madison, Wisconsin, USA.
[18] G.M. Sheldrick. *Acta Cryst.*, **A46**, 467 (1990).
[19] G.M. Sheldrick. *SHELXL-97, Program for X-ray Crystal Structure Refinement*, University of Göttingen, Germany (1997).
[20] L.J. Farrugia. *J. Appl. Cryst.*, **30**, 565 (1997).
[21] K. Nakamoto. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, Wiley, Toronto (1997).
[22] R.C. Mehrotra, R. Bohra. *Metal Carboxylates*, Academic Press, London (1983).
[23] W.D. Horrocks, J.N. Ishley, B. Holmanist, J.S. Thomson. *J. Inorg. Biochem.*, **12**, 131 (1980).
[24] W.D. Horrocks, J.N. Ishley, R.R. Whitley. *Inorg. Chem.*, **21**, 3265 (1982).
[25] G.N. Nadzhafov, B.T. Usubaliev, I.R. Amiraslanov, Z.M. Movsumov, H.S. Mamedov. *Koord. Khim.*, **7**, 770 (1981).
[26] C. Brassy, M.C. Michaud, J. Delettre, J.P. Mornon. *Acta Cryst.*, **B30**, 2848 (1974).