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3D supramolecular network constructed by intermolecular interactions in mixed ligand complex of zinc

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Abstract

New complex $[Zn(quin\text{-}2\text{-}c)_2(Him)_2]$ (quin-2-c = quinoline-2-carboxylate ion, Him = imidazole) was synthesized by self assembly and its structure was determined by X-ray analysis. The compound crystallizes in P21/c space group. Four independent molecules of complex are present in the structure. Strong hydrogen bonds create three different 1D chains which are collected in two different layers. The alternately packed layers form the 3D supramolecular structure. The interchain and interlayer contacts are of the C–H···O, π···π and C–H···π type. The influence of strong hydrogen bond on the vibrational characteristics of the monodentately coordinated carboxylate group in zinc complexes with quin-2-c ion is discussed.

Keywords: Zinc complex; Crystal structure; Supramolecular network; Hydrogen bonds; Infrared spectra

Carboxylates are efficient catalysts in the biological and chemical processes [1]. The carboxylate group offers a variety of coordination modes and many types of complexes are known [2]. The need for characterization of the metal enzyme centers as well as the searches for new catalytic or magnetic materials causes an incessant interest in carboxylate chemistry.

Quinoline-2-carboxylic acid is the biological compound involved in the metabolism of tryptophan [3]. It is a strong chelator providing the donor set similar to that responsible for binding metal ion in PQQ cofactor of quinoprotein family [4]. To date three zinc complexes with quin-2-c ion have been obtained and structurally characterized: [Zn(MEDA)(quin-2-c)] [5] (MEDA = *N*-(2-mercaptoethyl)picolylamine), $[Zn(quin\text{-}2\text{-}c)_2(1\text{-}Meim)_2]$ [6] and $[Zn(quin\text{-}2\text{-}c)_2(H_2O)]$ [7]. In these complexes, quin-2-c ion binds in a N,O chelate mode and the metal environment mimics the zinc enzyme centers. In the crystals of the mentioned compounds, strong hydrogen bonds and weak intermolecular interactions of the C–H···O, C–H···π and π···π type lead to the formations of 2D and 3D supramolecular frameworks.

As a continuation of our interest in quinoline-2-carboxylates, we have synthesized $[Zn(quin\text{-}2\text{-}c)_2(Him)_2]$ and studied its crystal structure. The significant differences in the hydrogen bonding systems in $[Zn(quin\text{-}2\text{-}c)_2(1\text{-}Meim)_2]$, $[Zn(quin\text{-}2\text{-}c)_2(H_2O)]$ and $[Zn(quin\text{-}2\text{-}c)_2(Him)_2]$ are expressively reflected in the vibrational characteristics of the monodentate carboxylate group.

cis-Bis(quinoline-2-carboxylato) bis imidazole zinc(II) was obtained from the reaction of $Zn(ClO_4)_2 \cdot 6H_2O$ with a twofold excess quinoline-2-carboxylic acid and five equivalents of imidazole in the form of the single crystals. Crystals are air stable and have very limited solubility in common organic solvents [8]. The crystal structure of the complex was determined by single-crystal X-ray diffraction [9,10].

In the crystal of $[Zn(quin\text{-}2\text{-}c)_2(Him)_2]$, four independent molecules of the complex have been found (**a**, **b**, **c** and **d**). A drawing of the molecular structure (Fig. 1) represents the molecule of the title complex.

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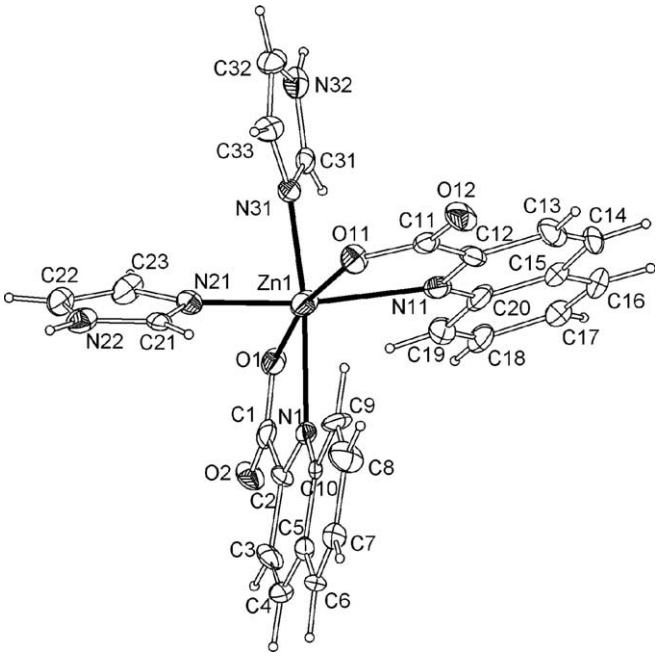

Fig. 1. The molecular structure of the title complex (**a**) with the atom numbering scheme. The displacement ellipsoids are drawn at the 50% probability level.

The selected bond distances and angles for **a**, **b**, **c** and **d** are collected in Table 1. Table 2 lists the hydrogen bonds of N–H···O and C–H···O type. The geometry of the molecules **a**, **b**, **c** and **d** is the same but the molecular parameters display significant differences (see Table 1). The Zn^{2+} ion is six coordinated with the O_2N_4 donor set. The quin-2-c ion binds to zinc in a chelate mode, through the carboxylate O atom and the quinoline N atom. The carboxylate group is monodentate. The chelate rings are almost coplanar with the quinoline rings, the medium angle between quinoline rings in **a**, **b**, **c** and **d** equals 113.8(1)°. Two molecules of imidazole connected with zinc by aromatic nitrogen atoms are located in *cis* position. The medium value of $Zn–N_{Him}$ distance, 2.116(4) Å, is very close to that found for $[Zn(quin\text{-}2\text{-}c)_2(1\text{-}Meim)_2]$ [6] and is a little longer than the typical value observed for octahedral complexes (2.084 Å) [11]. Zinc–oxygen bond lengths in the studied complex are close to the literature data [5–7,11]. The zinc–quinoline nitrogen distances in **a**, **b**, **c** and **d** are very long (2.354(4) Å – medium value) when compared with those observed for other complexes of Zn with quin-2-c ion as well as in the octahedral complexes of zinc with pyridine ligands (2.111 Å) [11]. The geometry around zinc ion is severely distorted. The bite angle of the chelating ligand is very small in the studied compound. Its medium value equals 75.93(4)°, whereas the relevant values are 79.5° and 78.33° for $[Zn(quin\text{-}2\text{-}c)_2(H_2O)]$ [7] and 77.9° for $[Zn(quin\text{-}2\text{-}c)_2(1\text{-}Meim)_2]$ [6]. The intramolecular hydrogen bond of the C–H···O type stabilizes the molecules of **a**, **b**, **c** and **d**, see Table 2.

Table 1
Selected bond lengths (Å) and angles (°) for $Zn(quin\text{-}2\text{-}c)_2(Him)_2$

Bond distances	**a**	**b**	**c**	**d**
Zn(1)–O(11)	2.047(3)	2.030(3)	2.014(3)	2.020(3)
Zn(1)–O(1)	2.048(3)	2.052(3)	2.045(3)	2.043(3)
Zn(1)–N(21)	2.109(4)	2.115(4)	2.104(4)	2.088(4)
Zn(1)–N(31)	2.117(4)	2.131(4)	2.133(4)	2.135(4)
Zn(1)–N(1)	2.329(4)	2.293(4)	2.353(4)	2.399(4)
Zn(1)–N(11)	2.375(4)	2.418(4)	2.354(4)	2.399(4)
Bond angles				
O(11)–Zn(1)–N(21)	95.85(15)	95.15(12)	96.10(14)	96.22(15)
O(1)–Zn(1)–N(21)	92.84(15)	95.42(13)	92.21(14)	91.13(14)
O(11)–Zn(1)–N(31)	91.63(15)	90.92(13)	93.68(14)	94.64(14)
O(1)–Zn(1)–N(31)	95.70(15)	96.47(12)	95.01(14)	95.79(14)
N(21)–Zn(1)–N(31)	90.56(16)	89.66(14)	89.92(15)	91.01(15)
O(11)–Zn(1)–N(1)	96.64(14)	96.39(12)	96.62(14)	95.06(14)
O(1)–Zn(1)–N(1)	76.64(14)	76.38(12)	75.62(14)	75.10(13)
N(21)–Zn(1)–N(1)	85.45(15)	89.47(14)	83.78(15)	84.40(15)
O(11)–Zn(1)–N(11)	75.43(14)	74.99(11)	76.42(13)	76.86(14)
O(1)–Zn(1)–N(11)	96.36(14)	95.65(12)	95.55(13)	96.18(14)
N(31)–Zn(1)–N(11)	85.61(15)	81.43(13)	88.15(14)	86.95(14)
N(1)–Zn(1)–N(11)	99.52(14)	100.64(13)	99.36(13)	98.73(14)

Table 2
Hydrogen bonds for $Zn(quin\text{-}2\text{-}c)_2$ (Him) (Å), (°)

D–H···A	*d*(D–H)	*d*(H···A)	*d*(D···A)	∠(DHA)
N(22)–H(22) ... O(12)$^{(i)}$	0.88	1.85	2.728(6)	172
N(22A)–H(22B) ... O(2A)$^{(ii)}$	0.88	1.85	2.728(5)	171
N(22B)–H(22C) ... O(2C)	0.88	1.85	2.722(6)	169
N(22C)–H(22D) ... O(2B)$^{(iii)}$	0.88	1.85	2.723(6)	168
N(32)–H(32) ... O(2)$^{(iv)}$	0.88	1.85	2.722(6)	170
N(32A)–H(32B) ... O(12A)$^{(v)}$	0.88	1.89	2.767(5)	172
N(32B)–H(32C) ... O(12C)$^{(vi)}$	0.88	1.87	2.733(5)	168
N(32C)–H(32D) ... O(12B)	0.88	1.85	2.726(6)	174
C(9A)–H(9AA) ... O(11A)	0.95	2.20	3.078(5)	152
C(32A)–H(32B) ... O(2C)$^{(vii)}$	0.95	2.44	3.164(7)	133
C(9)–H(9A) ... O(11)	0.95	2.23	3.107(7)	154
C(9B)–H(9BA) ... O(11B)	0.95	2.27	3.141(6)	152
C(22B)–H(22C) ... O(12A)$^{(viii)}$	0.95	2.55	3.186(7)	124
C(19)–H(19A) ... O(1)	0.95	2.28	3.160(7)	154
C(19A)–H(19B) ... O(1A)	0.95	2.33	3.208(5)	153
C(19B)–H(19C) ... O(1B)	0.95	2.26	3.133(6)	152
C(19C)–H(19D) ... O(1C)	0.95	2.24	3.113(6)	152
C(9C)–H(9CA) ... O(11C)	0.95	2.27	3.147(6)	153
C(22)–H(22A) ... O(2B)$^{(ix)}$	0.95	2.52	3.196(7)	128
C(22C)–H(22D) ... O(12)$^{(viii)}$	0.95	2.49	3.186(7)	130

Symmetry transformations used to generate equivalent atoms: (i) $-x,-y,-z+2$; (ii) $x,-y-1/2,z-1/2$; (iii) $x,y,z+1$; (iv) $4-x,-y,-z+1$; (v) $x,-y-1/2,z-3/2$; (vi) 6 $x,y,z-1$; (vii) $x-1,-y-1/2,z-3/2$; (viii) $x+1,y,z$; (ix) $-x+1,-y,-z+1$.

Various intermolecular interactions organize the supramolecular structure of the crystal. The strong hydrogen

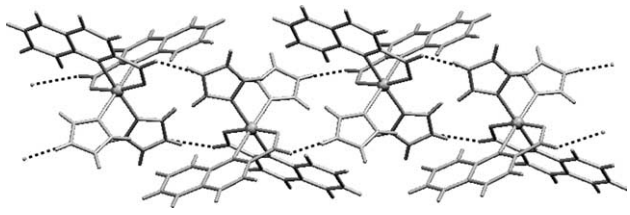

Fig. 2. Chain of molecules of $[Zn(quin\text{-}2\text{-}c)_2(Him)_2]$ connected by strong hydrogen bonds extending along *c*-axis.