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Preparation, characterization and crystal structure of dinuclear zinc(II) carboxylate complex with 1-(pyridin-4-yl)ethanone and 4-methylbenzoate based ligands

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ABSTRACT

The centrosymmetric binuclear complex, $[Zn_2(C_8H_7O_2)_4(C_7H_7NO)_2]$, has been synthesized and characterized by FT-IR and NMR methods. The obtained Zn(II) metal complex has been also characterized by a single crystal X-ray diffraction study. Crystal data for $C_{46}H_{42}N_2O_{10}Zn_2$: Monoclinic, Space group $P2_1/c$ (no. 14), a = 10.4827(3) Å, b = 8.6141(2) Å, c = 24.7582(6) Å, β = 101.066(1) °, V = 2194.07(10) Å^3, Z = 4, D_{calc} = 1.383 g/cm^3, 22545 reflections measured (3.96° ≤ 2Θ ≤ 52.74°), 4465 unique (R_{int} = 0.0388, R_{sigma} = 0.0333) which were used in all calculations. The final R_1 was 0.0489 (I ≥ 2σ(I)) and wR_2 was 0.1533 (all data). The four nearest oxygen atoms around each zinc ion form a distorted square-planar arrangement, and the distorted square-pyramidal coordination is completed by the nitrogen atom of the 1-(pyridin-4-yl)ethanone compound.

1. Introduction

The zinc ion is of essential importance for biological processes due to the presence of zinc-containing enzymes in biological systems. These enzymes can contain one, two or three zinc ions at the active binding sites, further the two zinc ions can connected to each other via the Zn···Zn bond, and the distance between them are generally in the range of 3.0-3.5 Å [1-6].

Zinc compounds supported by carboxylate ligands which structurally similar to zinc enzyme, are of great interest owing to their role in biochemical systems [7-11]. At the same time, zinc carboxylates are attracting attention as highly active catalysts for the polymerization or copolymerization of a wide range of organic monomers [12-15].

Carboxylates constitute an important class of ligands in the formation of coordination compounds [16-24]. Because ambidentate nature of their can display a wide variety of metal coordination modes such as monodentate terminal, chelating, bidentate bridging and monodentate bridging modes (Figure 1), which lead to several types of compounds [25-27]. The

nature of the bridging environment between adjacent zinc ions varies significantly in the structures and often several different environments exist within the same structure.
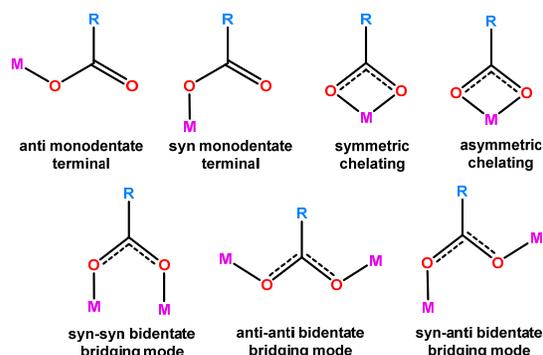
Figure 1. Carboxylate binding modes in metal complexes.
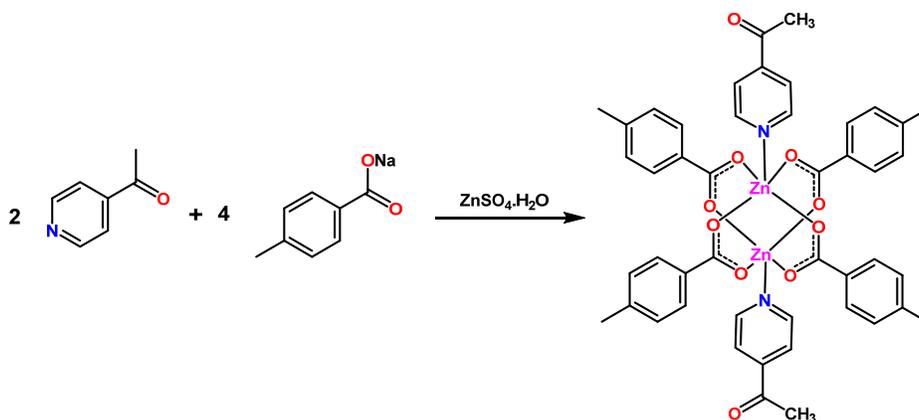
Scheme 1

Here, we report the synthesis and characterization of dinuclear zinc(II) complex, *tetrakis*(μ-4-methylbenzoato-$\kappa^2O{:}O'$)-*bis*[(μ-acetylpyridine-κN^1)-zinc(II), supported by carboxylate ligands. Structural characterization of complex was achieved by single crystal X-ray diffraction technique.

2. Experimental

2.1. Instrumentation

Infrared measurement was recorded in the range 400-4000 cm^{-1} on a Perkin Elmer Spectrum 100 series FT-IR/FIR/NIR Spectrometer Frontier, ATR Instrument. The NMR spectra were recorded in DMSO-d_6 solvent on Bruker Avance III 400 MHz NaNoBay FT-NMR spectrophotometer using tetramethyl silane as an internal standard. Crystallographic measurements of the compound were carried out at 296(2) K using a Bruker APEX-II CCD area-detector diffractometer. The intensity data were collected using graphite monochromated Mo-Kα radiation, λ = 0.71073 Å. Absorption corrections were applied with the program SADABS [28]. The structure was solved by direct methods SHELXS-97 [29], and refined by full-matrix least-squares techniques on F^2 using SHELXL-97 with refinement of F^2 against all reflections. Hydrogen atoms were constrained by difference maps and were refined isotropically, and all non-hydrogen atoms were refined anisotropically. The molecular structure plots were prepared using PLATON [30] and ORTEP III [31]. The anisotropic thermal parameters and structure factors (observed and calculated), full list of bond distances, bond angles and torsional angles are given in supplementary materials. The geometric special details: all e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

2.2. Synthesis

A solution of 1-(pyridin-4-yl)ethanone (0.61 g, 5 mmol) in H$_2$O (10 mL) and sodium 4-methylbenzoate (1.58 g, 10 mmol) in H$_2$O (250 mL) was added dropwise ZnSO$_4$.H$_2$O (0.90 g, 5 mmol) in H$_2$O. The reaction mixture was stirred for 30 min in room temperature. The mixture was filtered and crystals were formed within five days at room temperature (Scheme 1).

Tetrakis(μ-4-methylbenzoato-κ^2O: O')- *bis*[(μ-acetylpyridine-κN^1)-zinc(II)]: FT-IR (ATR, ν cm^{-1}): 1630 ν(C=C)$_{ring}$, 1562 ν(COO$^-$)$_{asym}$, 1401 ν(COO$^-$)$_{sym}$, 1032 ν(C-N)$_{py}$, 2920 ν(C-H)$_{aliphatic}$,

475 ν(Zn-N). ^{1}H NMR (400 MHz, DMSO-d_6, δ, ppm): 8.82 (dd, 4H, Ar-H), 7.85 (s, 4H, Ar-H), 7.83 (ddd, 8H, Ar-H), 7.21 (dd, 8H, Ar-H), 2.63 (s, 6H, CO-CH$_3$), 2.34 (s, 12H, Ph-CH$_3$). ^{13}C NMR (100 MHz, DMSO-d_6, δ, ppm): 198.08, 171.84, 150.78, 142.65, 140.62, 131.90, 129.58, 128.46, 121.36, 26.88, 21.02.

3. Results and discussion

The dinuclear Zn(II) complex was obtained from the reaction with ZnSO$_4$.H$_2$O metal salt of 1-(pyridin-4-yl) ethanone and sodium 4-methylbenzoate compounds in water at room temperature and characterized by various spectroscopic techniques and also by X-ray crystallography. All the characterization data of the synthesized complex confirm the proposed structures. Scheme 1 outlines the synthesis of the complex.

FT-IR spectral analysis confirms the presence of characteristic groups in the Zn(II) complex. The main vibrational bands of the complex are given in the experimental section. The stretching vibrations of ν(CH) groups are observed in the region above 3000 cm^{-1}. The stretching vibrations of aliphatic ν(CH) groups of 1-(pyridin-4-yl)ethanone are at 2952 cm^{-1}. The ν(C=O) stretching vibration band belong to 1-(pyridin-4-yl)ethanone ligands are showed at 1672 and 1707 cm^{-1}, respectively.

The potential carboxylate binding modes for zinc complex can determine by infrared spectroscopy. For the IR spectra of carboxylates, the stretching vibrations of the carboxylate group ν_{asym}(COO) and ν_{sym}(COO) are characteristic. But, stretching vibrations belong to aromatic rings in both benzoate and N-donor ligands can observe in the same region of the spectrum as the stretching vibrations of the carboxylate group. The value of $\Delta_\nu[\nu_{asym}$(COO)$-\nu_{sym}$(COO)] can provide structural insight into the coordination mode of the carboxylate group [32,33]. These values are applied to assign the type of the carboxylate coordination in inorganic complexes [34-38].

The Δ values determined from the IR spectra of the synthesized zinc complex. The synthesized complex has stretching ν_{asym}(COO) at 1562 cm^{-1} and ν_{sym}(COO) at 1401 cm^{-1} (Figure 1). The experimental Δ_ν value 161 cm^{-1} which suggested, that zinc complex forms the paddle-wheel centrosymmetric dimmer with four *syn-syn* carboxylato bridges [39]. In the synthesized dinuclear zinc complex, the Δ_ν value (161 cm^{-1}) is consistent with the coordination modes of the carboxylate group observed in the complex.

The NMR spectrum of complex was recorded in DMSO-d_6. The NMR data of the obtained complex is given in the experimental section and are consistent with the structural results.
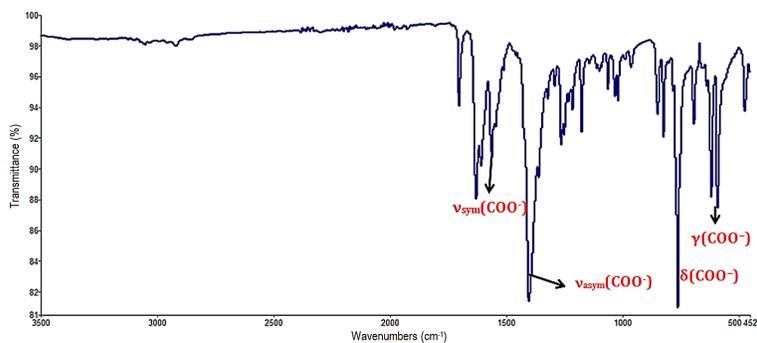
Figure 1. Infrared spectrum of the zinc complex.
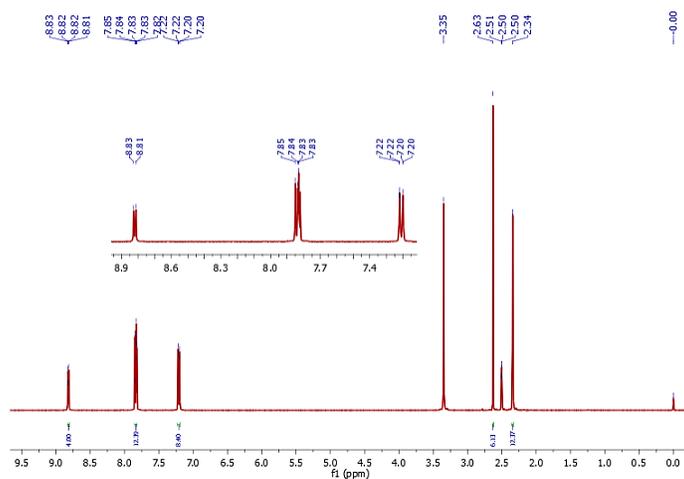
Figure 2. ¹H NMR spectrum of the zinc complex.
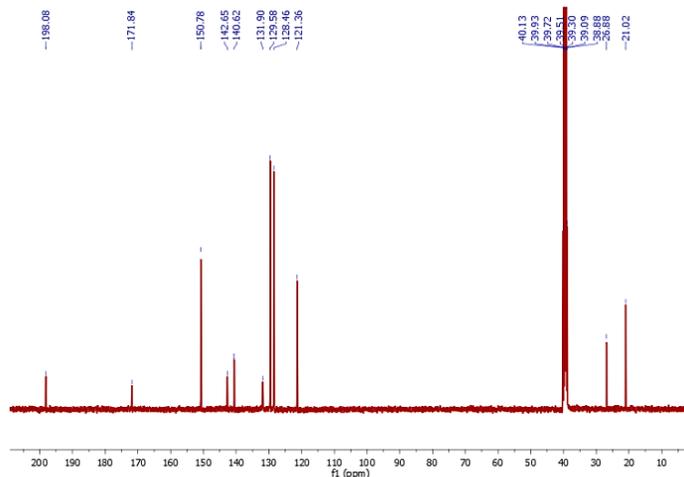
Figure 3. ¹³C NMR spectrum of the zinc complex.

The signals belong to the Ph-CH_3 and CO-CH_3 groups of the ligands were observed in the most upfield as a singlet at δ 2.34 and 2.63 ppm in the ¹H NMR spectrum, respectively. The protons of the aromatic rings are observed in the region approximately at δ ~7-8 ppm (Figure 2). The ¹³C NMR spectra displayed signals corresponding to the characteristic quaternary carbonyl and carboxylate groups at δ 198.08 and 171.84 ppm, respectively (Figure 3).

The structure of complex was confirmed by the result of single crystal X-ray diffraction determination. The synthesized dinuclear zinc complex has a paddle-wheel type structure with two 1-(pyridin-4-yl)ethanone ligands at axial positions and in each case there are four carboxylate ligands bridging the two zinc centers (Figure 4). Asymmetric unit contains half of whole molecule, and there is an inversion center in the middle of Zn–Zn bond.

Table 1. Crystallogrphic data for the Zn(II) complex.

Parameters	$[Zn_2(C_8H_7O_2)_4(C_7H_7NO)_2]$
Empirical formula	$C_{23}H_{21}NO_5Zn$
Formula weight	456.78
Temperature (K)	296(2)
Crystal system	Monoclinic
Space group	$P2_1/c$
a, (Å)	10.4827(3)
b, (Å)	8.6141(2)
c, (Å)	24.7582(6)
β, (°)	101.0660(10)
Volume (Å³)	2194.07(10)
Z	4
D_{calc} (g cm⁻¹)	1.383
M (mm⁻¹)	1.152
F(000)	944.0
Crystal size (mm³)	0.25 × 0.25 × 0.25
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection (°)	3.96-58.92
Index ranges	-14 ≤ h ≤ 14, -10 ≤ k ≤ 11, -34 ≤ l ≤ 34
Reflections collected	22545
Independent reflections	5872 [R_{int} = 0.0388, R_{sigma} = 0.0333]
Data/restraints/parameters	5872/0/274
Goodness-of-fit on F^2	1.048
Final R indexes (I≥2σ (I))	R_1 = 0.0472, wR_2 = 0.1470
Final R indexes (all data)	R_1 = 0.0733, wR_2 = 0.1613
Largest diff. peak/hole / e Å⁻³	0.44-0.28
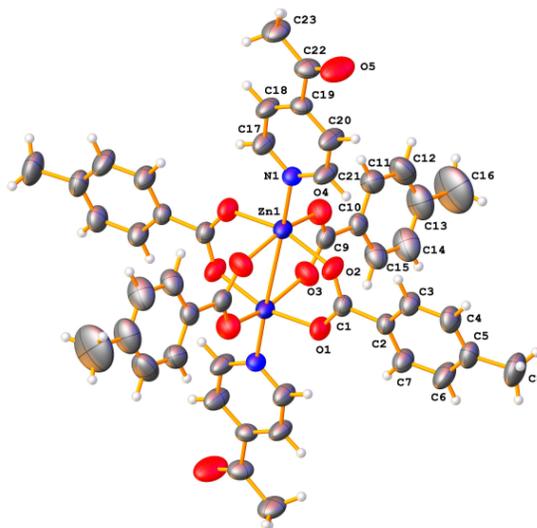
Figure 4. Crystal structure of dinuclear Zn(II) complex.

The each Zn atom is one nitrogen and four oxygen donor atoms penta-coordinated to form square pyramidal geometry. The paddle-wheel type structure for dinuclear complex is similar with literature [40-42].

The coordination sphere around each Zn atom in the complex is shown in Figure 5. The details of crystallographic data and structure refinement parameters are summarized in Table 1. The metal ligand bond distances and angles are listed in Tables 2 and 3. In the geometry of the complex, it is observed that the orientation of the two planes of the 1-(pyridin-4-yl)ethanone rings are perpendicular to each other. Zn–O bond distances range from 2.0276(13) to 2.0512(15) Å, on an average, they are somewhat longer than values observed for a series of structurally characterised zinc benzoate complexes [43,44]. Zn–N bond distance is 2.0397(15) Å which is typical in Zn(II) complexes, and Zn–Zn distance is 2.9332(4) Å (Table 2).

The bond lengths of all C-O bonds of synthesized Zn(II) complex (C1-O1 1.252(2), C1-O2 1.252(2), O3-C9^i 1.250(3), O4-C9 1.250(3) Å, i: 2-x, 2-y, 2-z) are shorter than the normal C-O single bond and longer than normal C=O double bond. The bond angles of O2^i-Zn1-O1, O1-Zn1-N1, O4-Zn1-O3, O2 ^{i}-Zn1-

O4 and O4-Zn1-N1 are 159.84(6), 99.81(6), 159.85(6), 89.29(7) and 89.65(7) (i:2-x, 2-y, 2-z), respectively. The dihedral angle between Zn1-O1-O2-C1 and Zn-O3-O4-C2 planes is 86.33°. The dihedral angles between the planar carboxylate groups O1-O2-C1 and O3-O4-C2 are 75.45°.
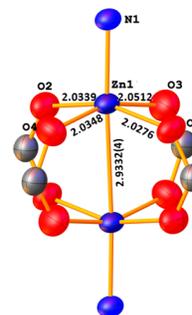
Figure 5. The coordination sphere around zinc atom in the complex.

Table 2. Selected bond distances for the Zn(II) complex.

Atom	Atom	Length (Å)	Atom	Atom	Length (Å)
Zn1	Zn1^i	2.9332(4)	C4	C5	1.376(3)
Zn1	O1	2.0276(13)	C5	C6	1.380(3)
Zn1	O2^i	2.0339(14)	C5	C8	1.506(3)
Zn1	O3	2.0512(15)	C6	C7	1.381(3)
Zn1	O4^i	2.0348(16)	C9	C10	1.497(3)
Zn1	N1	2.0397(15)	C10	C11	1.384(3)
O1	C1	1.252(2)	C10	C15	1.374(3)
O2	Zn1^i	2.0338(14)	C11	C12	1.376(4)
O2	C1	1.252(2)	C12	C13	1.377(4)
O3	C9	1.250(3)	C13	C14	1.370(5)
O4	Zn1^i	2.0347(15)	C13	C16	1.522(4)
O4	C9	1.250(3)	C14	C15	1.371(3)
O5	C22	1.201(3)	C17	C18	1.373(3)
N1	C17	1.322(3)	C18	C19	1.360(3)
N1	C21	1.330(3)	C19	C20	1.374(3)
C1	C2	1.495(3)	C19	C22	1.502(3)
C2	C3	1.385(3)	C20	C21	1.369(3)
C2	C7	1.373(3)	C22	C23	1.493(3)

^{i} 2-*x*, 2-*y*, 2-*z*.

Table 3. Selected bond angles for the Zn(II) complex.

Atom	Atom	Atom	Angle (°)	Atom	Atom	Atom	Angle (°)
O1	Zn1	Zn1^i	80.71(4)	C9	O3	Zn1	132.54(15)
O1	Zn1	O2^i	159.84(6)	C9	O4	Zn1^i	121.69(15)
O1	Zn1	O3	85.59(6)	C17	N1	Zn1	120.79(13)
O1	Zn1	O4^i	89.65(7)	C17	N1	C21	117.26(17)
O1	Zn1	N1	99.81(6)	C21	N1	Zn1	121.93(14)
O2^i	Zn1	Zn1^i	79.15(4)	C5	C4	C3	121.8(2)
O2^i	Zn1	O3	88.51(7)	C4	C5	C6	117.2(2)
O2^i	Zn1	O4^i	89.29(7)	C4	C5	C8	121.1(2)
O2^i	Zn1	N1	100.16(6)	C6	C5	C8	121.7(2)
O3	Zn1	Zn1^i	75.57(5)	C7	C6	C5	121.6(2)
O4^i	Zn1	Zn1^i	84.34(5)	C2	C7	C6	120.6(2)
O4^i	Zn1	O3	159.85(6)	O3	C9	O4	125.4(2)
O4^i	Zn1	N1	100.90(7)	O3	C9	C10	116.89(19)

^{i} 2-*x*, 2-*y*, 2-*z*.
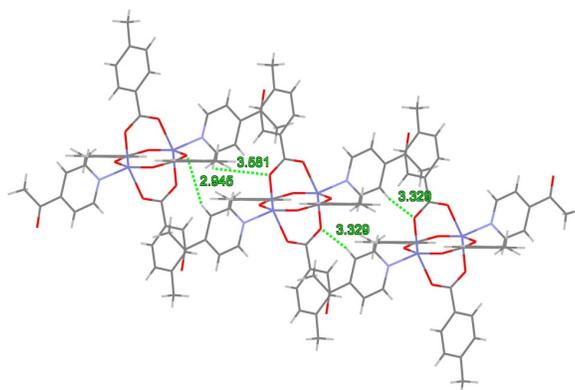
Figure 6. The intermolecular C–H···O interactions of dinuclear Zn(II) complex. The C–H···O interactions are shown as green dashed lines.

The dinuclear complex present in the crystal lattice of the self-assembly are held together by weak C–H···O interactions. The intermolecular C–H···O (C10-H8···O4, 3.581 Å; C11-H14···O4, 3.329 Å; C14-H14···O2, 2.945 Å) interactions of dinuclear Zn(II) complex is shown in Figure 6. The packing diagram of zinc complex is also shown in Figure 7.

4. Conclusions

A new class of compound formed by a dinuclear zinc carboxylate complex were prepared and characterized by IR, NMR spectroscopy and single crystal X-ray diffraction. Single crystal analysis and Δ values determined from the IR spectra revealed that the synthesized zinc complex forms the paddle-wheel centrosymmetric dimmer with four *syn-syn* carboxylato bridges. Also, the dinuclear complex present in the crystal lattice of the self-assembly are held together by weak C–H···O interactions.
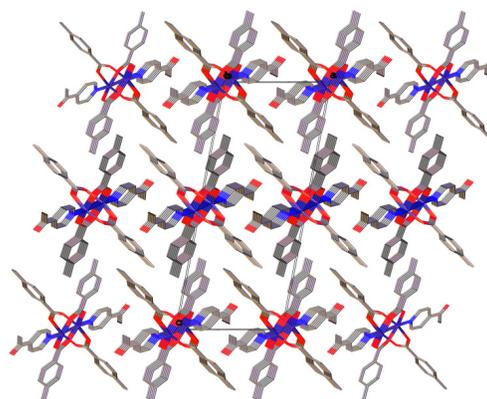
Figure 7. The packing diagram of Zn(II) complex.

Acknowledgements

Supplementary material

CCDC-1515549 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by e-mailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44(0)1223-336033.

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