Crystal structure of dihydrogenpimelato(1,10-phenanthroline-*N,N'*)zinc(II), $\text{Zn}(\text{C}_{12}\text{H}_8\text{N}_2)_2[\text{OOC}(\text{CH}_2)_5\text{COOH}]_2$

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Received November 19, 2001, accepted and available on-line February 21, 2002; CCDC-No. 1267769

Abstract

$\text{C}_{26}\text{H}_{30}\text{N}_2\text{O}_8\text{Zn}$, monoclinic, $C12/c1$ (No. 15), $a = 13.533(2)$ Å, $b = 9.854(2)$ Å, $c = 19.461(3)$ Å, $\beta = 100.84(1)^\circ$, $V = 2548.9$ Å³, $Z = 4$, $R_{\text{gt}}(F) = 0.054$, $wR_{\text{ref}}(F^2) = 0.108$, $T = 293$ K.

Source of material

Addition of 1.0 ml (1 M) Na_2CO_3 to 1.0 ml (1 M) ZnCl_2 yielded white precipitate, which was separated out and washed with doubly-distilled water for several times until no detectable Cl^- anions were present. The white precipitate was added to 20 ml $\text{CH}_3\text{OH}/\text{H}_2\text{O}$ (1:1 v/v) dissolving 0.206 g (1.00 mmol) phenanthroline monohydrate and 0.162 g (1.00 mmol) pimelic acid. The resulting solution was then allowed to stand at room temperature. Slow evaporation for several days afforded a small amount of colorless crystals.

Discussion

The crystal structure of the title compound is built up of the $[\text{Zn}(\text{phen})(\text{C}_7\text{H}_{11}\text{O}_4)_2]$ complex molecules. The Zn atoms are each surrounded by two N atoms from one chelating phen ligand [$d(\text{Zn}-\text{N}) = 2.078(3)$ Å ($2\times$)] and two carboxylate O atoms from different hydrogenpimelato ligands to form distorted tetrahedra [$d(\text{Zn}-\text{O}) = 1.968(2)$ Å ($2\times$)]. The N–Zn–N($1-x, y, 3/2-z$) angle is of $80.8(2)^\circ$ and the O1–Zn–O1($1-x, y, 3/2-z$) angle of $128.4(2)^\circ$ while the N–Zn–O1 bond angles are $109.1(1)^\circ$ and $109.7(1)^\circ$, respectively, close to the value for an ideal tetrahedron. The carboxylic group of the monodentate hydrogenpimelato ligand donate the hydrogen atom to the uncoordinated carboxylate O2 atom of the hydrogenpimelato ligand of the neighboring complex molecule to form strong intermolecular hydrogen bonds [$d(\text{O3}\cdots\text{O2}(-x+3/2, -y+3/2, -z+1)) = 2.658$ Å, $\angle \text{O3-H}\cdots\text{O2}(-x+3/2, -y+3/2, -z+1) = 175^\circ$], resulting in 1D chains with hydrogen bonded 20-membered rings. The formed polymeric chains extend along the [101] direction and approach one another so that the carboxylic group of the hydrogenpimelato ligand orientates

nearly parallelly to one chelating phen plane belonging to an adjacent chain with an interplanar distance of 3.56 Å, suggesting π - π stacking interactions between the carboxylic group and the phen ligand. Based on such π - π stacking interactions, the polymeric chains are assembled into 2D layers parallel to (111). Careful examination shows that the supramolecular assembly of the 2D layers could result from the interlayer π - π stacking interactions between the carboxylic group and the phen ligand to meet the requirements of close packing in the crystal structure. Under the influence of the π - π stacking interactions, the hydrogenpimelato group is twisted with a torsion angle of $63.4(1)^\circ$ for C7–C8–C9–C10 chain.

Table 1. Data collection and handling.

Crystal:	colorless block, size $0.13 \times 0.13 \times 0.24$ mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ :	10.16 cm^{-1}
Diffractometer, scan mode:	Bruker P4, θ/θ
$2\theta_{\text{max}}$:	54.98°
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$:	3666, 2912
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2\sigma(I_{\text{obs}})$, 1873
$N(\text{param})_{\text{refined}}$:	175
Programs:	SHELXS-97 [1], SHELXL-97 [2]

Table 2. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	x	y	z	U_{iso}
H(1)	8f	0.6935	0.9421	0.6853	0.074(6)
H(2)	8f	0.7734	1.1396	0.6614	0.074
H(3)	8f	0.7105	1.345	0.6851	0.074
H(5)	8f	0.5732	1.4797	0.7305	0.074
H(8A)	8f	0.4107	0.5585	0.5868	0.058(3)
H(8B)	8f	0.5152	0.5800	0.5647	0.058
H(9A)	8f	0.3508	0.7589	0.5282	0.058
H(9B)	8f	0.3823	0.6524	0.4765	0.058
H(10A)	8f	0.5078	0.8700	0.5319	0.058
H(10B)	8f	0.4371	0.8769	0.4584	0.058
H(11A)	8f	0.5297	0.7033	0.4176	0.058
H(11B)	8f	0.6000	0.6945	0.4913	0.058
H(12A)	8f	0.5892	0.9250	0.4037	0.058
H(12B)	8f	0.6611	0.9134	0.4766	0.058
H	8f	0.813(3)	0.861(5)	0.360(2)	0.09(2)

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Table 3. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	x	y	z	U ₁₁	U ₂₂	U ₃₃	U ₁₂	U ₁₃	U ₂₃
Zn	4e	1/2	0.86813(5)	3/4	0.0411(3)	0.0282(3)	0.0464(3)	0	0.0167(2)	0
N	8f	0.5841(2)	1.0288(3)	0.7225(1)	0.037(2)	0.036(2)	0.041(2)	−0.007(1)	0.013(1)	0.001(1)
C(1)	8f	0.6671(3)	1.0256(4)	0.6950(2)	0.043(2)	0.056(2)	0.053(2)	−0.013(2)	0.015(2)	0.004(2)
C(2)	8f	0.7154(3)	1.1443(5)	0.6805(2)	0.051(2)	0.087(3)	0.065(3)	−0.023(3)	0.020(2)	0.009(3)
C(3)	8f	0.6777(3)	1.2659(5)	0.6942(2)	0.073(3)	0.067(3)	0.052(2)	−0.038(3)	0.000(2)	0.016(2)
C(4)	8f	0.5895(3)	1.2744(4)	0.7222(2)	0.063(2)	0.038(2)	0.048(2)	−0.019(2)	−0.006(2)	0.007(2)
C(5)	8f	0.5431(3)	1.3974(4)	0.7377(2)	0.106(4)	0.033(2)	0.071(3)	−0.017(2)	−0.020(3)	0.008(2)
C(6)	8f	0.5458(2)	1.1513(3)	0.7360(2)	0.043(2)	0.033(2)	0.035(2)	−0.004(2)	0.000(1)	−0.001(2)
O(1)	8f	0.4268(2)	0.7811(2)	0.6644(1)	0.044(1)	0.053(2)	0.055(2)	−0.008(1)	0.024(1)	−0.015(1)
O(2)	8f	0.5817(2)	0.7112(3)	0.6727(1)	0.049(2)	0.050(2)	0.063(2)	0.001(1)	0.019(1)	0.001(1)
C(7)	8f	0.4925(3)	0.7110(3)	0.6416(2)	0.047(2)	0.032(2)	0.050(2)	−0.006(2)	0.025(2)	0.002(2)
C(8)	8f	0.4578(3)	0.6267(4)	0.5769(2)	0.057(2)	0.043(2)	0.059(2)	−0.015(2)	0.029(2)	−0.013(2)
C(9)	8f	0.4078(3)	0.7120(4)	0.5155(2)	0.047(2)	0.071(3)	0.056(2)	−0.004(2)	0.016(2)	−0.018(2)
C(10)	8f	0.4772(3)	0.8162(4)	0.4917(2)	0.054(2)	0.055(2)	0.046(2)	0.007(2)	0.011(2)	−0.005(2)
C(11)	8f	0.5601(3)	0.7560(4)	0.4583(2)	0.055(2)	0.050(2)	0.045(2)	0.004(2)	0.015(2)	−0.005(2)
C(12)	8f	0.6293(3)	0.8622(4)	0.4358(2)	0.053(2)	0.051(2)	0.046(2)	0.005(2)	0.016(2)	−0.000(2)
C(13)	8f	0.7093(3)	0.8022(4)	0.4013(2)	0.053(2)	0.050(2)	0.042(2)	0.002(2)	0.011(2)	0.001(2)
O(3)	8f	0.7663(2)	0.8942(3)	0.3783(2)	0.063(2)	0.054(2)	0.086(2)	0.008(2)	0.038(2)	0.009(2)
O(4)	8f	0.7225(2)	0.6815(3)	0.3955(2)	0.082(2)	0.051(2)	0.092(2)	0.002(2)	0.046(2)	−0.006(2)

Acknowledgments. The authors gratefully acknowledge the financial support of Zhejiang Provincial Natural Science Foundation of China (RC99034) and Municipal Natural Science Foundation of Ningbo (01J20130-1).

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