Crystal structure of *bis*-(phenanthroline)-zinc(II) 5-(4-carboxy-2-nitrophenoxy)-isophthalic hydrate, $Zn(C_{15}H_9NO_9)(C_{12}H_8N_2)_2\cdot(H_2O)$, $C_{39}H_{25}N_5O_{10}Zn$

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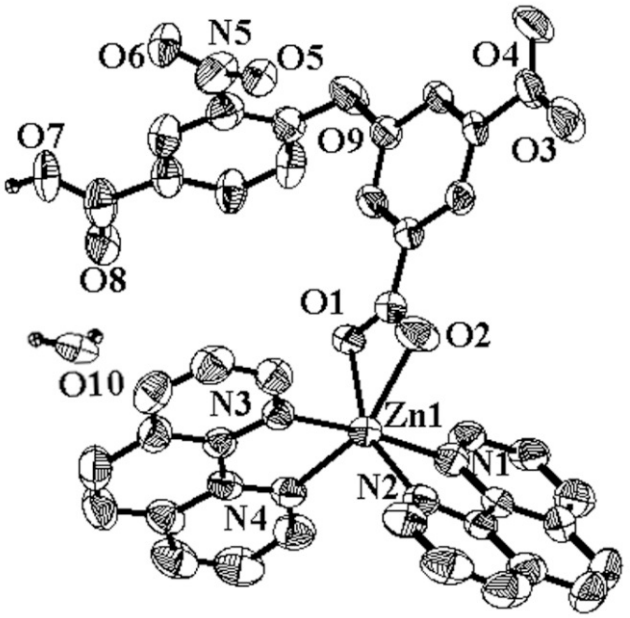

Abstract

$C_{39}H_{25}N_5O_{10}Zn$, monoclinic, $P2_1/c$ (no. 14), a = 11.4924(9) Å, b = 26.254(2) Å, c = 11.5760(9) Å, β = 101.839(1)°, V = 3418.5 Å^3, Z = 4, $R_{gt}(F)$ = 0.0454, $wR_{ref}(F^2)$ = 0.1354, T = 296 K.

Table 1. Data collection and handling.

Crystal:	colourless blocks, size 0.18×0.22×0.33 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	7.90 cm^{-1}
Diffractometer, scan mode:	CCD area detector, φ and ω
$2\theta_{max}$:	51°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	25867, 6364
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 4508
$N(param)_{refined}$:	497
Programs:	SHELXS-97 [10]

Source of material

A mixture of 5-(4-carboxy-2-nitrophenoxy) isophthalic anion (0.1 mmol, 34.7 mg), phen (0.2 mmol, 39.7 mg), $Zn(OAc)_2\cdot 2H_2O$ (0.1 mmol, 22.0 mg), NaOH (0.1 mmol), and H_2O (6.0 ml) were placed in a 23ml Teflon lined stainless steel reactor. The vessel was heated to 393K for 4 days, and then slowly cooled to room temperature. Colourless crystals were obtained, and further crystals were filtered off, washed with mother liquid, and dried under ambient conditions. Yield 43%.

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Discussion

The rational design and preparation of metal-organic coordination polymers has been attracted much attention for their promising applications of catalysis, gas sorption, magnetic, photoluminescent properties and so on [1-5]. In this regard, the selection of the structure of the spacer ligand is extremely important because changing the structure of the organic ligand can control and adjust the topology. Among various organic ligands, multicarboxylates have attracted considerable attention due to their various coordination modes to metal atoms [6,7]. On the other hand, the introduction of additional *N*-donor ligands to such synthetic systems can modify the structures and properties of the resulting materials [8,9]. The unit cell of the title complex consists of two 1,10-phenanthroline (phen) chelate molecules, one Zn ion, one 5-(4-carboxy-2-nitrophenoxy) isophthalic acid and one crystal water molecule. The Zn^{2+} ion is six-coordinated by four N atoms of two symmetry-related phen ligands and two oxygen atoms of one 5-(4-carboxy-2-nitrophenoxy) isophthalic anion adopting a bidentatly chelating mode. The Zn–N bond lengths are in the range of 2.118(3)-2.136(3) Å and the Zn–O bond lengths are 2.163(2) and 2.202(2) Å, respectively. The $[ZnO_2N_4]$ environment is best described as a distorted octahedron. In the complex, there are three kinds of weak interaction. Firstly, four hydrogen in two crystal water molecules as acceptor and the four carboxylate oxygen atoms in adjacent two unit cells as donors (O(10)–H(2W)···O(3)#1 distances are 2.864(5) Å and O(10)–H(1W)···O(2) distances are 3.329(5) Å), which extend the monomer to form a Zn dimer; Secondly, the hydrogen atom of O7 in 5-(4-carboxy-2-nitrophenoxy) isophthalic anion as acceptor and the carboxylate oxygen atom O4 of 5-(4-carboxy-2-nitrophenoxy) isophthalic anion in another Zn dimer as donors(O(7)–H(7)···O(4)#2 distances are 2.446(3) Å), which develop the dimer to form the 2D layer structure. Lastly, weak π–π stacking interactions (the face to face distance is 4.10 Å) existing between both aromatic rings of phen ligands from two adjacent 2D layers, result in 3D supermolecular structure. Clearly, hydrogen bonds and π–π stacking interactions play a vital role in the formation of 3D supermolecular structure.

Table 2. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	x	y	z	U_{iso}
H(7)	4*e*	–0.1123	0.3661	0.2557	0.120
H(1W)	4*e*	0.4884	0.0642	0.5500	0.215
H(2W)	4*e*	0.5846	0.0631	0.4915	0.215
H(2)	4*e*	0.0715	0.1281	0.4922	0.053
H(4)	4*e*	0.2707	0.0014	0.5509	0.049
H(6)	4*e*	–0.0055	0.0087	0.2756	0.053
H(11)	4*e*	–0.0020	0.2587	0.2113	0.066

Table 2. continued.

Atom	Site	x	y	z	U_{iso}
H(13)	4*e*	–0.2108	0.2334	0.4407	0.079
H(14)	4*e*	–0.1877	0.1468	0.4216	0.075
H(16)	4*e*	0.1061	0.1110	0.8427	0.081
H(17)	4*e*	0.0109	0.0582	0.9535	0.097
H(18)	4*e*	0.1191	0.0148	1.1109	0.094
H(20)	4*e*	0.3219	–0.0080	1.2345	0.097
H(21)	4*e*	0.5207	–0.0011	1.2662	0.097
H(23)	4*e*	0.7044	0.0348	1.2029	0.092
H(24)	4*e*	0.7825	0.0841	1.0755	0.089
H(25)	4*e*	0.6563	0.1247	0.9208	0.073
H(41)	4*e*	0.3155	0.3474	0.9422	0.084
H(42)	4*e*	0.2418	0.2016	0.9878	0.069
H(43)	4*e*	0.2193	0.2866	1.0300	0.086
H(46)	4*e*	0.5752	0.3410	0.6846	0.079
H(47)	4*e*	0.4570	0.3686	0.8052	0.082
H(49)	4*e*	0.5709	0.1266	0.6605	0.065
H(50)	4*e*	0.6775	0.1803	0.5634	0.077
H(51)	4*e*	0.6608	0.2670	0.5852	0.076

Table 3. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Zn(1)	4*e*	0.37572(3)	0.13552(1)	0.82335(3)	0.0502(2)	0.0444(2)	0.0366(2)	–0.0058(2)	0.0026(2)	–0.0014(2)
O(1)	4*e*	0.2285(2)	0.13674(8)	0.6732(2)	0.061(1)	0.037(1)	0.038(1)	–0.001(1)	0.003(1)	–0.0035(9)
O(2)	4*e*	0.3523(2)	0.07281(9)	0.6944(2)	0.066(2)	0.054(2)	0.065(2)	0.013(1)	–0.022(1)	–0.013(1)
O(3)	4*e*	0.2419(3)	–0.08153(9)	0.4365(3)	0.085(2)	0.036(1)	0.092(2)	0.013(1)	–0.015(2)	–0.003(1)
O(4)	4*e*	0.1053(3)	–0.07126(9)	0.2719(2)	0.090(2)	0.038(1)	0.075(2)	0.003(1)	–0.017(2)	–0.017(1)
O(5)	4*e*	0.1288(4)	0.1336(2)	0.2026(4)	0.175(5)	0.121(4)	0.144(4)	0.063(3)	0.078(4)	0.003(3)
O(6)	4*e*	0.0825(5)	0.1954(2)	0.0990(5)	0.190(5)	0.136(4)	0.179(5)	0.030(3)	0.134(4)	0.026(3)
O(7)	4*e*	–0.0894(3)	0.3365(1)	0.2570(3)	0.081(2)	0.039(2)	0.122(3)	0.008(1)	0.026(2)	0.026(2)
O(8)	4*e*	–0.1850(4)	0.3285(1)	0.4044(4)	0.143(3)	0.068(2)	0.136(3)	0.045(2)	0.068(3)	0.002(2)
O(9)	4*e*	–0.0687(2)	0.09843(8)	0.2957(2)	0.080(2)	0.034(1)	0.078(2)	0.011(1)	–0.036(2)	–0.005(1)
O(10)	4*e*	0.5124(3)	0.0550(2)	0.4885(4)	0.098(3)	0.180(4)	0.143(4)	0.019(3)	0.003(3)	–0.078(3)
N(1)	4*e*	0.2690(3)	0.0963(1)	0.9246(2)	0.052(2)	0.054(2)	0.045(2)	–0.013(1)	0.000(1)	0.001(1)
N(2)	4*e*	0.5064(2)	0.1019(1)	0.9579(2)	0.051(2)	0.046(2)	0.043(2)	–0.003(1)	–0.001(1)	–0.005(1)
N(3)	4*e*	0.4930(2)	0.1780(1)	0.7386(2)	0.049(2)	0.041(2)	0.039(1)	0.005(1)	0.009(1)	–0.003(1)
N(4)	4*e*	0.3503(2)	0.2106(1)	0.8803(2)	0.047(2)	0.051(2)	0.038(2)	–0.004(1)	0.010(1)	–0.009(1)
N(5)	4*e*	0.0661(4)	0.1695(2)	0.1754(3)	0.129(4)	0.078(3)	0.069(3)	0.048(3)	0.036(2)	0.007(2)
C(1)	4*e*	0.0227(3)	0.0731(1)	0.3709(3)	0.048(2)	0.035(2)	0.046(2)	0.004(1)	–0.007(2)	0.004(1)
C(2)	4*e*	0.0893(3)	0.0954(1)	0.4701(3)	0.052(2)	0.030(2)	0.047(2)	0.001(1)	0.001(2)	–0.003(1)
C(3)	4*e*	0.1834(3)	0.0685(1)	0.5368(3)	0.043(2)	0.034(2)	0.039(2)	–0.003(1)	0.005(1)	0.001(1)
C(4)	4*e*	0.2074(3)	0.0193(1)	0.5058(3)	0.042(2)	0.033(2)	0.045(2)	0.001(1)	0.001(1)	0.006(1)
C(5)	4*e*	0.1367(3)	–0.0035(1)	0.4070(3)	0.050(2)	0.026(2)	0.048(2)	–0.005(1)	0.008(2)	0.002(1)
C(6)	4*e*	0.0433(3)	0.0238(1)	0.3406(3)	0.051(2)	0.032(2)	0.044(2)	–0.005(1)	–0.004(2)	–0.001(1)
C(7)	4*e*	0.2590(3)	0.0942(1)	0.6413(3)	0.053(2)	0.039(2)	0.038(2)	–0.004(2)	0.002(2)	0.000(1)
C(8)	4*e*	0.1646(3)	–0.0567(1)	0.3708(3)	0.057(2)	0.029(2)	0.064(2)	–0.004(2)	0.004(2)	–0.000(2)
C(9)	4*e*	–0.0774(3)	0.1505(1)	0.3090(3)	0.056(2)	0.038(2)	0.053(2)	0.011(2)	–0.013(2)	0.003(2)
C(10)	4*e*	–0.0200(3)	0.1849(1)	0.2480(3)	0.059(2)	0.050(2)	0.051(2)	0.015(2)	0.009(2)	0.003(2)
C(11)	4*e*	–0.0384(3)	0.2363(1)	0.2552(3)	0.055(2)	0.047(2)	0.063(2)	0.008(2)	0.014(2)	0.014(2)
C(12)	4*e*	–0.1102(3)	0.2550(1)	0.3269(3)	0.051(2)	0.037(2)	0.066(2)	0.009(2)	0.012(2)	0.008(2)
C(13)	4*e*	–0.1638(4)	0.2212(1)	0.3902(4)	0.068(2)	0.050(2)	0.088(3)	0.011(2)	0.037(2)	0.015(2)
C(14)	4*e*	–0.1489(3)	0.1692(1)	0.3800(4)	0.063(2)	0.047(2)	0.080(3)	0.003(2)	0.017(2)	0.023(2)
C(15)	4*e*	–0.1313(3)	0.3116(1)	0.3343(4)	0.056(2)	0.042(2)	0.092(3)	0.011(2)	0.012(2)	0.016(2)
C(16)	4*e*	0.1513(3)	0.0923(2)	0.9042(3)	0.056(2)	0.089(3)	0.054(2)	–0.021(2)	0.002(2)	–0.001(2)
C(17)	4*e*	0.0933(4)	0.0611(2)	0.9717(4)	0.070(3)	0.112(4)	0.062(3)	–0.043(3)	0.017(2)	–0.012(3)
C(18)	4*e*	0.1575(5)	0.0349(2)	1.0642(4)	0.104(4)	0.080(3)	0.056(3)	–0.042(3)	0.028(3)	–0.009(2)
C(19)	4*e*	0.2816(4)	0.0382(1)	1.0895(3)	0.093(3)	0.044(2)	0.050(2)	–0.017(2)	0.015(2)	–0.001(2)
C(20)	4*e*	0.3562(5)	0.0122(2)	1.1844(4)	0.126(4)	0.056(3)	0.062(3)	–0.005(3)	0.023(3)	0.016(2)
C(21)	4*e*	0.4742(5)	0.0161(2)	1.2029(4)	0.131(4)	0.053(2)	0.055(3)	0.019(3)	0.009(3)	0.013(2)
C(22)	4*e*	0.5303(4)	0.0460(1)	1.1277(3)	0.084(3)	0.046(2)	0.047(2)	0.018(2)	–0.001(2)	–0.008(2)
C(23)	4*e*	0.6541(4)	0.0515(2)	1.1413(4)	0.085(3)	0.075(3)	0.057(3)	0.034(2)	–0.013(2)	–0.005(2)
C(24)	4*e*	0.7006(4)	0.0805(2)	1.0661(4)	0.056(2)	0.087(3)	0.068(3)	0.015(2)	–0.012(2)	–0.020(2)
C(25)	4*e*	0.6238(3)	0.1053(2)	0.9734(3)	0.052(2)	0.070(3)	0.058(2)	–0.003(2)	0.005(2)	–0.013(2)
C(26)	4*e*	0.4599(3)	0.0728(1)	1.0341(3)	0.063(2)	0.036(2)	0.037(2)	0.003(2)	–0.001(2)	–0.007(1)
C(27)	4*e*	0.3336(3)	0.0692(1)	1.0160(3)	0.068(2)	0.036(2)	0.039(2)	–0.007(2)	0.006(2)	–0.007(1)
C(39)	4*e*	0.3975(3)	0.2988(1)	0.8483(3)	0.055(2)	0.047(2)	0.056(2)	0.008(2)	0.003(2)	–0.009(2)
C(40)	4*e*	0.4079(3)	0.2463(1)	0.8291(3)	0.041(2)	0.044(2)	0.038(2)	0.003(1)	–0.001(1)	–0.007(1)
C(41)	4*e*	0.3247(4)	0.3131(2)	0.9260(4)	0.074(3)	0.059(2)	0.076(3)	0.015(2)	0.012(2)	–0.024(2)
C(42)	4*e*	0.2819(3)	0.2260(2)	0.9526(3)	0.058(2)	0.068(2)	0.051(2)	–0.001(2)	0.020(2)	–0.011(2)
C(43)	4*e*	0.2674(4)	0.2771(2)	0.9781(4)	0.068(3)	0.082(3)	0.067(3)	0.012(2)	0.022(2)	–0.024(2)
C(44)	4*e*	0.4840(3)	0.2288(1)	0.7527(3)	0.040(2)	0.043(2)	0.036(2)	0.003(1)	0.000(1)	–0.000(1)
C(45)	4*e*	0.5458(3)	0.2642(1)	0.6976(3)	0.049(2)	0.049(2)	0.049(2)	–0.000(2)	0.006(2)	0.006(2)
C(46)	4*e*	0.5336(4)	0.3174(1)	0.7202(4)	0.073(3)	0.048(2)	0.076(3)	–0.004(2)	0.013(2)	0.013(2)
C(47)	4*e*	0.4631(4)	0.3338(1)	0.7920(4)	0.083(3)	0.037(2)	0.083(3)	0.003(2)	0.010(2)	0.000(2)
C(49)	4*e*	0.5639(3)	0.1616(1)	0.6699(3)	0.062(2)	0.052(2)	0.052(2)	0.008(2)	0.017(2)	–0.005(2)
C(50)	4*e*	0.6287(4)	0.1936(2)	0.6109(3)	0.068(3)	0.073(3)	0.056(2)	0.010(2)	0.026(2)	0.000(2)
C(51)	4*e*	0.6190(3)	0.2448(2)	0.6244(3)	0.061(2)	0.074(3)	0.058(2)	–0.002(2)	0.020(2)	0.015(2)

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