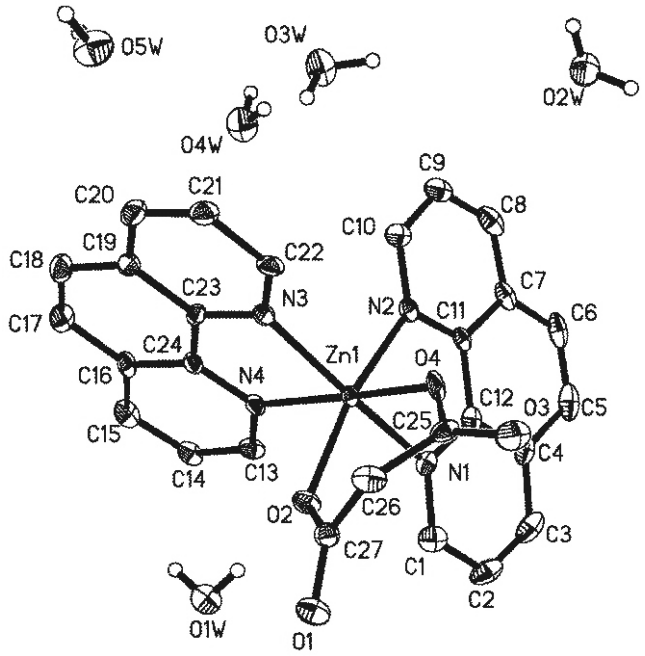
Crystal structure of bis(1,10-phenanthroline-κ^2N,N')-(malonato-κ^2O^1,O^3)zinc(II) pentahydrate, $Zn(C_{12}H_8N_2)_2(C_3H_2O_4) \cdot 5H_2O$

Xue Nie* and Jing-Nian Qu

Hengyang Normal University, Department of Chemistry and Materials Science, Hengyang 421008, Hunan, P. R. China

Received January 4, 2011, accepted and available on-line June 17, 2011; CCDC no. 1267/3354



Abstract

$C_{27}H_{28}N_4O_9Zn$, triclinic, $P\bar{1}$ (no. 2), a = 10.380(2) Å, b = 10.580(3) Å, c = 13.059(2) Å, α = 84.682(2)°, β = 76.965(3)°, γ = 72.834(2)°, V = 1334.4 Å^3, Z = 2, $R_{gt}(F)$ = 0.040, $wR_{ref}(F^2)$ = 0.097, T = 291 K.

Source of material

A mixture of $ZnSO_4 \cdot 7H_2O$ (0.029 g, 0.1 mmol), malonic acid (H_2L, 0.011 g, 0.1 mmol), NaOH (0.041 g, 0.1 mmol), 1,10-phenanthroline (0.019 g, 0.1 mmol), CH_3CH_2OH (4 mL) and H_2O (6 mL) was sealed in a 15 ml Teflon-lined stainless steel reactor, which was heated at 393 K for 72 h and then it was cooled to room temperature. Colorless block-shaped crystals of the title compound were collected.

Experimental details

Hydrogen atoms were placed geometrically and treated as riding with d(C—H) = 0.93 Å (aromatic) or 0.97 Å (acyclic), d(O—H) = 0.85 Å and U_{iso}(H) = 1.2 U_{eq}(C,O).

Discussion

There is considerable interest in the study of transition complexes containing carboxylate ligands due to their novel topology and excellent properties [1-6]. Furthermore, zinc, as one of the most important trace elements, plays a versatile role in biological systems caused by its structural and catalytic role in enzymes [7,8]. Therefore, many efforts have been made on the study of synthetic analogues of zinc enzymes in the hope of clarifying the mechanism of their action.

In the title crystal structure, the Zn(II) ion is six-coordinated by four N atoms from two phen molecules and two carboxylate O atoms from one L^{2-} ligands in a slightly distorted octahedral coordination with O4 and N4 at the apical positions. Other two carboxylate O atoms are not coordinating. The bond lengths d(Zn—N) and d(Zn—O) are in the normal ranges.

In the crystal structure, there are abundant strong O–H···O hydrogen bonds between the uncoordinated O atoms of carboxyl groups and water molecules, which link single complex into a three-dimensional framwork.

Table 1. Data collection and handling.

Crystal:	colorless bolck, size 0.14 × 0.20 × 0.24 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	9.83 cm^{-1}
Diffractometer, scan mode:	Bruker Smart APEX CCD, φ/ω
$2\theta_{max}$:	52°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	13993, 5236
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 4851
$N(param)_{refined}$:	370
Program:	SHELXTL [9]

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

Atom	Site	x	y	z	U_{iso}
H(1A)	2*i*	0.9374	0.0280	0.6714	0.045
H(2A)	2*i*	1.0580	–0.1720	0.5906	0.053
H(3A)	2*i*	0.9417	–0.2926	0.5343	0.054
H(5A)	2*i*	0.7120	–0.3134	0.5062	0.051
H(6A)	2*i*	0.4798	–0.2431	0.5461	0.046
H(8A)	2*i*	0.2604	–0.0678	0.6259	0.048
H(9A)	2*i*	0.1622	0.1309	0.7064	0.045
H(10A)	2*i*	0.3002	0.2489	0.7422	0.038
H(13A)	2*i*	0.7381	–0.0279	0.8743	0.035
H(14A)	2*i*	0.7184	–0.0742	1.0514	0.036
H(15A)	2*i*	0.5760	0.0869	1.1695	0.042
H(17A)	2*i*	0.3955	0.3090	1.1974	0.044
H(18A)	2*i*	0.2722	0.5014	1.1299	0.045
H(20A)	2*i*	0.2241	0.6489	0.9678	0.042
H(21A)	2*i*	0.2692	0.6745	0.7893	0.042
H(22A)	2*i*	0.4223	0.5052	0.6864	0.035
H(26A)	2*i*	0.7076	0.4980	0.6369	0.041
H(26B)	2*i*	0.8433	0.4731	0.5507	0.041
H(1X)	2*i*	0.8963	0.2004	0.8401	0.048
H(1Y)	2*i*	0.8802	0.1636	0.9460	0.048

* Correspondence author (e-mail: xuehuanie@126.com)

Table 2. Continued.

Atom	Site	x	y	z	U_{iso}
H(2X)	2*i*	0.0151	0.3453	0.1366	0.065
H(2Y)	2*i*	0.1286	0.2722	0.0667	0.065
H(3X)	2*i*	0.0796	0.4957	0.6727	0.056
H(3Y)	2*i*	0.1389	0.5629	0.7266	0.056

Table 2. Continued.

Atom	Site	x	y	z	U_{iso}
H(4X)	2*i*	0.1009	0.3840	0.8602	0.063
H(4Y)	2*i*	0.0423	0.2945	0.9240	0.063
H(5X)	2*i*	1.0299	–0.0188	0.8783	0.061
H(5Y)	2*i*	1.0258	–0.1433	0.9203	0.061

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}
C(1)	2*i*	0.8893(3)	–0.0210(3)	0.6477(2)	0.035(2)	0.036(2)	0.039(2)	–0.012(1)	–0.007(1)	0.007(1)
C(2)	2*i*	0.9626(3)	–0.1418(3)	0.5995(3)	0.030(2)	0.036(2)	0.051(2)	0.006(1)	0.003(1)	0.004(1)
C(3)	2*i*	0.8934(3)	–0.2128(3)	0.5667(3)	0.047(2)	0.031(2)	0.041(2)	–0.001(1)	0.010(1)	–0.005(1)
C(4)	2*i*	0.7496(3)	–0.1694(2)	0.5801(2)	0.050(2)	0.019(1)	0.019(1)	–0.003(1)	–0.004(1)	0.0031(9)
C(5)	2*i*	0.6684(4)	–0.2373(3)	0.5447(2)	0.083(2)	0.023(1)	0.022(1)	–0.016(2)	–0.013(1)	0.006(1)
C(6)	2*i*	0.5299(4)	–0.1932(3)	0.5660(2)	0.077(2)	0.031(1)	0.019(1)	–0.030(2)	–0.017(1)	0.010(1)
C(7)	2*i*	0.4589(3)	–0.0738(3)	0.6176(2)	0.049(2)	0.027(1)	0.021(1)	–0.020(1)	–0.018(1)	0.014(1)
C(8)	2*i*	0.3162(3)	–0.0214(3)	0.6421(2)	0.050(2)	0.053(2)	0.030(1)	–0.034(2)	–0.019(1)	0.020(1)
C(9)	2*i*	0.2576(3)	0.0969(3)	0.6895(2)	0.029(1)	0.056(2)	0.028(1)	–0.016(1)	–0.009(1)	0.017(1)
C(10)	2*i*	0.3413(3)	0.1664(3)	0.7123(2)	0.028(1)	0.044(2)	0.021(1)	–0.011(1)	–0.005(1)	0.015(1)
C(11)	2*i*	0.5355(3)	0.0041(2)	0.6465(2)	0.032(1)	0.027(1)	0.014(1)	–0.013(1)	–0.0097(9)	0.0068(9)
C(12)	2*i*	0.6836(3)	–0.0471(2)	0.6290(2)	0.038(1)	0.024(1)	0.017(1)	–0.009(1)	–0.007(1)	0.0071(9)
C(13)	2*i*	0.6790(3)	0.0354(3)	0.9213(2)	0.026(1)	0.034(1)	0.027(1)	–0.008(1)	–0.011(1)	0.012(1)
C(14)	2*i*	0.6684(3)	0.0069(3)	1.0273(2)	0.035(1)	0.036(1)	0.025(1)	–0.017(1)	–0.013(1)	0.014(1)
C(15)	2*i*	0.5817(3)	0.1018(3)	1.0975(2)	0.045(2)	0.045(2)	0.022(1)	–0.023(1)	–0.011(1)	0.014(1)
C(16)	2*i*	0.5016(3)	0.2219(3)	1.0581(2)	0.036(1)	0.037(1)	0.013(1)	–0.019(1)	–0.005(1)	0.0024(9)
C(17)	2*i*	0.4076(3)	0.3224(3)	1.1248(2)	0.039(2)	0.052(2)	0.021(1)	–0.023(1)	0.003(1)	0.001(1)
C(18)	2*i*	0.3351(3)	0.4380(3)	1.0847(2)	0.036(2)	0.051(2)	0.026(1)	–0.019(1)	0.003(1)	–0.010(1)
C(19)	2*i*	0.3548(3)	0.4622(3)	0.9741(2)	0.023(1)	0.032(1)	0.032(1)	–0.010(1)	–0.004(1)	–0.009(1)
C(20)	2*i*	0.2867(3)	0.5812(3)	0.9265(2)	0.030(1)	0.033(1)	0.041(2)	–0.006(1)	–0.002(1)	–0.014(1)
C(21)	2*i*	0.3131(3)	0.5961(3)	0.8210(2)	0.027(1)	0.030(1)	0.046(2)	0.000(1)	–0.013(1)	–0.006(1)
C(22)	2*i*	0.4062(3)	0.4940(3)	0.7592(2)	0.022(1)	0.027(1)	0.036(1)	0.001(1)	–0.015(1)	0.002(1)
C(23)	2*i*	0.4500(2)	0.3641(2)	0.9057(2)	0.020(1)	0.021(1)	0.020(1)	–0.0065(9)	–0.0009(9)	–0.0048(9)
C(24)	2*i*	0.5217(2)	0.2419(2)	0.9492(2)	0.024(1)	0.029(1)	0.017(1)	–0.009(1)	–0.0076(9)	0.0005(9)
C(25)	2*i*	0.7182(2)	0.3692(3)	0.5295(2)	0.020(1)	0.029(1)	0.025(1)	0.001(1)	–0.0003(9)	0.008(1)
C(26)	2*i*	0.7806(3)	0.4298(3)	0.5965(2)	0.031(1)	0.024(1)	0.047(2)	–0.007(1)	–0.011(1)	0.010(1)
C(27)	2*i*	0.8586(3)	0.3378(2)	0.6726(2)	0.026(1)	0.025(1)	0.032(1)	–0.008(1)	–0.007(1)	–0.004(1)
N(1)	2*i*	0.7535(2)	0.0252(2)	0.6604(2)	0.029(1)	0.026(1)	0.021(1)	–0.0063(9)	–0.0011(8)	–0.0016(8)
N(2)	2*i*	0.4776(2)	0.1201(2)	0.6932(2)	0.029(1)	0.027(1)	0.019(1)	–0.0094(9)	–0.0083(8)	0.0022(8)
N(3)	2*i*	0.4729(2)	0.3804(2)	0.8016(2)	0.024(1)	0.024(1)	0.019(1)	–0.0035(8)	–0.0090(8)	0.0031(8)
N(4)	2*i*	0.6074(2)	0.1510(2)	0.8820(2)	0.024(1)	0.028(1)	0.018(1)	–0.0070(8)	–0.0096(8)	0.0022(8)
O(1)	2*i*	0.9787(2)	0.3391(2)	0.6713(2)	0.035(1)	0.044(1)	0.050(1)	–0.0188(9)	–0.0134(9)	0.003(1)
O(2)	2*i*	0.7984(2)	0.2653(2)	0.7356(2)	0.0279(9)	0.032(1)	0.033(1)	–0.0140(8)	–0.0112(8)	0.0077(8)
O(3)	2*i*	0.7436(2)	0.3892(2)	0.4339(2)	0.036(1)	0.071(2)	0.029(1)	–0.009(1)	–0.0051(9)	0.024(1)
O(4)	2*i*	0.6369(2)	0.3009(2)	0.5741(1)	0.044(1)	0.046(1)	0.0104(8)	–0.0196(9)	–0.0109(7)	0.0050(7)
O(1W)	2*i*	0.9384(2)	0.1693(2)	0.8897(2)	0.044(1)	0.034(1)	0.043(1)	–0.0116(9)	–0.0145(9)	0.0064(9)
O(2W)	2*i*	0.0797(3)	0.2733(3)	0.1285(2)	0.049(1)	0.071(2)	0.043(1)	–0.017(1)	–0.007(1)	–0.009(1)
O(3W)	2*i*	0.0798(2)	0.5202(2)	0.7328(2)	0.057(1)	0.060(1)	0.035(1)	–0.036(1)	–0.005(1)	0.004(1)
O(4W)	2*i*	0.1087(3)	0.3290(2)	0.9118(2)	0.057(1)	0.059(2)	0.049(1)	–0.032(1)	–0.007(1)	–0.000(1)
O(5W)	2*i*	1.0707(2)	–0.1012(2)	0.8743(2)	0.050(1)	0.034(1)	0.067(2)	–0.012(1)	–0.008(1)	–0.001(1)
Zn(1)	2*i*	0.62469(3)	0.21697(3)	0.72004(2)	0.0219(2)	0.0209(2)	0.0128(1)	–0.0068(1)	–0.0044(1)	

Acknowledgment. This work was supported by Hengyang Bureau of Science & Technology (grant no. 2009KJ28).

References

1. Batten, S. R.; Robson, R.: Interpenetrating Nets: Ordered, Periodic Entanglement. Angew. Chem., Int., Ed. **37** (1998) 1460-1494.
2. Kitagawa, S.; Kondo, M.: Functional Micropore Chemistry of Crystalline Metal Complex-Assembled Compounds. Bull. Chem. Soc. Jpn. **71** (1998) 1739-1753.
3. Kong, X. J.; Ren, Y. P.; Long, L. S.; Zheng, Z. P.; Huang, R. B.; Zheng, L. S.: A Keplerate Magnetic Cluster Featuring an Icosidodecahedron of Ni(II) Ions Encapsulating a Dodecahedron of La(III) Ions. J. Am. Chem. Soc. **129** (2007) 7016-7017.
4. Mrozinski, J.: New trends of molecular magnetism. Coord. Chem. Rev. **249** (2005) 2534-2548.
5. Wang, Y.; Huang, Y. Q.; Liu, G. X.; Okamuraz, T.-A.; Doi, M.; Sheng, Y. W.; Sun, W. Y.; Ueyama, N.: New Metal-Organic Frameworks with Large Cavities: Selective Sorption and Desorption of Solvent Molecules. Chem. Eur. J. **13** (2007) 7523-7531.
6. Zou, R. Q.; Sakurai, H.; Han, S.; Zhong, R. Q.; Xu, Q.: Probing the Lewis Acid Sites and CO Catalytic Oxidation Activity of the Porous Metal-Organic Polymer [Cu(5-methylisophthalate)]. J. Am. Chem. Soc. **129** (2007) 8402-8403.
7. Parkin, G.: Synthetic Analogues Relevant to the Structure and Function of Zinc Enzymes. Chem. Rev. **104** (2004) 699-768.
8. Vallee, B. L.; Auld, D. S.: Zinc coordination, function, and structure of zinc enzymes and other proteins. Biochemistry **29** (1990) 5647-5659.
9. Sheldrick, G. M.: A short history of SHELX. Acta Crystallogr. **A64** (2008) 112-122.