Crystal structure of carbonatobis(1,10-phenanthroline-*N*,*N*′)zinc(II) heptahydrate, $Zn(C_{12}H_8N_2)_2CO_3 \cdot 7H_2O$

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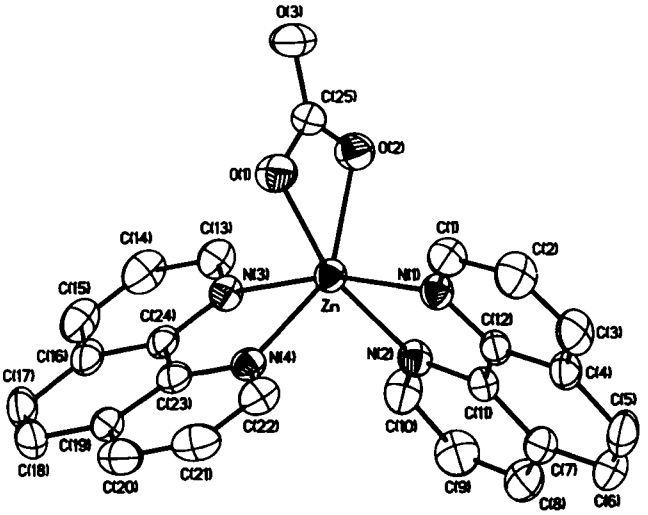
Received September 21, 2001, accepted and available on-line February 21, 2002; CCDC-No. 1267/732



Abstract

$C_{25}H_{30}N_4O_{10}Zn$, monoclinic, $P12_1/c1$ (No. 14), $a = 9.932(1)$ Å, $b = 26.400(2)$ Å, $c = 10.568(1)$ Å, $\beta = 105.746(6)°$, $V = 2667.0$ Å^3, $Z = 4$, $R_{gt(F)} = 0.041$, $wR_{ref(F^2)} = 0.164$, $T = 293$ K.

Source of material

Reactions of equimolar freshly-prepared $ZnCO_3$ and phenanthroline monohydrate in 20 ml CH_3OH/H_2O (1:1 v/v) containing an appropriate amount of α,ω-dicarboxylic acid such as succinic acid and suberic acid at pH = 10–11 afforded well-shaped colorless crystals in high yields.

Discussion

Consisting of the $[Zn(phen)_2CO_3]$ complex molecules and lattice H_2O molecules, the title compound is isostructural with $Ni(phen)_2CO_3 \cdot 7H_2O$ [1]. Within the $[Zn(phen)_2CO_3]$ complex molecule, the Zn atom is coordinated by two phen ligands and one carbonate ligand to complete a severely distorted ZnN_4O_2 octahedron with d(Zn—O) = 2.089 Å, 2.124 Å and d(Zn—N) = 2.147 Å – 2.182 Å. The complex molecules are arranged in such ways that the symmetry-related neighboring phen ligands involving N1 and N2 atoms parallelly face the opposite directions in pairs with an interplanar distance of 3.62 Å and the phen ligands involving N3 and N4 atoms are each anti-parallelly sandwiched by two symmetry-related neighbors with the interplanar distances of 3.32 Å and 3.35 Å. It is clear that the above intermolecular π-π stacking interactions assemble the complex molecules into corrugated supramolecular layers parallel to (100). Among the seven crystallographically distinct lattice H_2O molecules which are sandwiched between the layers, five water molecules are hydrogen bonded into coplanar pentagonal rings and the other two into rhombic rings. Along the [001] direction, the pentagonal rings are then interlinked through hydrogen bonds to generate 1D chains with alternative pentagonal and rhombic rings. The chains are further bridged by the former rhombic rings, forming hydrogen bonded 2D open networks parallel to (100). Four crystallographically different water molecules of the hydrogen bonded networks donate hydrogen atoms to carbonato O atoms of the complex molecules to form hydrogen bonds with d(O···O) = 2.664 Å – 2.691 Å and ∠O–H···O = 168° – 176°, which are slightly stronger than those within the hydrogen bonded networks (d(O···O) = 2.748 Å – 2.949 Å and ∠O–H···O = 150° – 178°). The carbonate group exhibits a considerable deviation from the D_{3h} symmetry due to coordination and site effects and the C—O bonds to the chelating O atoms are 1.285 Å and 1.297Å, respectively, longer than that to the non-coordinating one (1.257 Å).

Table 1. Data collection and handling.

Crystal:	colorless rhombohedron, size 0.311 × 0.333 × 0.622 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	9.85 cm^{-1}
Diffractometer, scan mode:	Bruker P4, $\theta/2\theta$
$2\theta_{max}$:	55°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	7431, 6093
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 4973
$N(param)_{refined}$:	362
Programs:	SHELXS-97 [2], SHELXL-97 [3]

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

Atom	Site	x	y	z	U_{iso}
H(1)	4*e*	0.3044	0.0937	0.5567	0.052
H(2)	4*e*	0.2050	0.0573	0.3478	0.053
H(3)	4*e*	0.3590	0.0348	0.2353	0.036
H(5)	4*e*	0.6175	0.0242	0.2228	0.086
H(6)	4*e*	0.8426	0.0260	0.3201	0.076
H(8)	4*e*	1.0355	0.0586	0.5031	0.055
H(9)	4*e*	1.0922	0.0858	0.7254	0.049
H(10)	4*e*	0.9383	0.1101	0.8286	0.060
H(13)	4*e*	0.8199	0.1116	1.0274	0.052
H(14)	4*e*	0.9385	0.1657	1.1931	0.046
H(15)	4*e*	0.9328	0.2504	1.1581	0.053
H(17)	4*e*	0.8309	0.3241	1.0133	0.079
H(18)	4*e*	0.6844	0.3497	0.8175	0.096
H(20)	4*e*	0.5196	0.1657	0.6043	0.045

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Table 2. Continued.

Atom	Site	x	y	z	U_{iso}
H(21)	4e	0.4084	0.2773	0.4371	0.050
H(22)	4e	0.4559	0.1892	0.4963	0.035
HA(W1)	4e	0.1387	0.1053	1.0608	0.040
HB(W1)	4e	0.2304	0.1166	1.0095	0.065
HA(W2)	4e	0.2884	0.1772	0.7362	0.097
HB(W2)	4e	0.1703	0.1973	0.7425	0.054
HA(W3)	4e	0.0947	0.1865	0.9249	0.074
HB(W3)	4e	0.0859	0.2374	0.8926	0.165

Table 2. Continued.

Atom	Site	x	y	z	U_{iso}
HA(W4)	4e	0.7243	–0.0135	0.0255	0.059
HB(W4)	4e	0.6963	0.0294	–0.0311	0.078
HA(W5)	4e	0.2464	0.1743	0.1970	0.068
HB(W5)	4e	0.2640	0.2172	0.2201	0.032
HA(W6)	4e	0.0981	0.0224	0.0948	0.056
HB(W6)	4e	–0.0469	0.0337	0.0934	0.055
HA(W7)	4e	0.1460	0.1918	0.4976	0.075
HB(W7)	4e	0.1664	0.1829	0.3873	0.109

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	4e	0.59771(3)	0.12175(1)	0.74466(3)	0.0283(2)	0.0319(2)	0.0289(2)	–0.0015(1)	0.0068(1)	–0.0036(1)
N(1)	4e	0.4974(2)	0.08636(9)	0.5603(2)	0.032(1)	0.034(1)	0.032(1)	–0.0027(9)	0.0062(9)	–0.0040(9)
N(2)	4e	0.7728(2)	0.09270(9)	0.6784(2)	0.030(1)	0.035(1)	0.037(1)	–0.0019(9)	0.0068(9)	–0.0043(9)
N(3)	4e	0.7319(2)	0.16451(9)	0.9026(2)	0.028(1)	0.036(1)	0.031(1)	–0.0007(9)	0.0051(9)	–0.0035(9)
N(4)	4e	0.5706(2)	0.19834(9)	0.6684(2)	0.027(1)	0.037(1)	0.032(1)	–0.0008(9)	0.0097(9)	–0.0005(9)
C(1)	4e	0.3610(3)	0.0831(1)	0.5043(3)	0.032(1)	0.047(2)	0.042(2)	–0.004(1)	0.007(1)	–0.004(1)
C(2)	4e	0.3047(3)	0.0623(1)	0.3804(3)	0.038(2)	0.060(2)	0.045(2)	–0.007(1)	–0.002(1)	–0.009(2)
C(3)	4e	0.3939(4)	0.0454(1)	0.3108(3)	0.053(2)	0.050(2)	0.035(2)	–0.011(2)	–0.002(1)	–0.013(1)
C(4)	4e	0.5383(3)	0.0488(1)	0.3661(3)	0.049(2)	0.033(1)	0.033(1)	–0.003(1)	0.010(1)	–0.006(1)
C(5)	4e	0.6395(4)	0.0337(1)	0.2982(3)	0.065(2)	0.046(2)	0.042(2)	0.002(2)	0.016(2)	–0.016(1)
C(6)	4e	0.7759(4)	0.0388(1)	0.3539(4)	0.060(2)	0.046(2)	0.052(2)	0.004(2)	0.028(2)	–0.009(1)
C(7)	4e	0.8284(3)	0.0581(1)	0.4857(3)	0.043(2)	0.034(1)	0.048(2)	0.002(1)	0.021(1)	–0.004(1)
C(8)	4e	0.9719(3)	0.0641(1)	0.5513(4)	0.038(2)	0.048(2)	0.069(2)	0.007(1)	0.025(2)	–0.006(2)
C(9)	4e	1.0106(3)	0.0824(1)	0.6748(4)	0.030(2)	0.058(2)	0.068(2)	0.003(1)	0.010(2)	–0.004(2)
C(10)	4e	0.9085(3)	0.0963(1)	0.7372(3)	0.032(2)	0.053(2)	0.048(2)	0.002(1)	0.005(1)	–0.012(1)
C(11)	4e	0.7327(3)	0.0733(1)	0.5545(3)	0.035(1)	0.025(1)	0.034(1)	0.000(1)	0.010(1)	–0.002(1)
C(12)	4e	0.5853(3)	0.0694(1)	0.4923(3)	0.036(1)	0.026(1)	0.032(1)	–0.001(1)	0.009(1)	–0.003(1)
C(13)	4e	0.8110(3)	0.1477(1)	1.0157(3)	0.036(1)	0.046(2)	0.034(1)	0.003(1)	0.007(1)	–0.002(1)
C(14)	4e	0.8890(3)	0.1795(1)	1.1144(3)	0.034(2)	0.070(2)	0.031(1)	–0.000(1)	–0.000(1)	–0.006(1)
C(15)	4e	0.8817(3)	0.2300(1)	1.0944(3)	0.032(2)	0.068(2)	0.041(2)	–0.010(1)	0.008(1)	–0.020(2)
C(16)	4e	0.7970(3)	0.2497(1)	0.9762(3)	0.030(1)	0.044(2)	0.044(2)	–0.009(1)	0.017(1)	–0.017(1)
C(17)	4e	0.7801(4)	0.3029(1)	0.9477(4)	0.050(2)	0.041(2)	0.064(2)	–0.016(1)	0.026(2)	–0.027(2)
C(18)	4e	0.6938(4)	0.3199(1)	0.8351(4)	0.056(2)	0.031(2)	0.070(2)	–0.005(1)	0.034(2)	–0.012(1)
C(19)	4e	0.6178(3)	0.2852(1)	0.7367(3)	0.041(2)	0.032(1)	0.047(2)	0.000(1)	0.024(1)	–0.003(1)
C(20)	4e	0.5284(4)	0.3012(1)	0.6160(4)	0.048(2)	0.042(2)	0.066(2)	0.012(1)	0.029(2)	0.016(2)
C(21)	4e	0.4641(3)	0.2656(1)	0.5260(3)	0.041(2)	0.058(2)	0.047(2)	0.011(2)	0.014(1)	0.019(2)
C(22)	4e	0.4888(3)	0.2143(1)	0.5559(3)	0.035(1)	0.050(2)	0.035(1)	0.002(1)	0.008(1)	0.001(1)
C(23)	4e	0.6351(3)	0.2328(1)	0.7586(3)	0.027(1)	0.037(1)	0.036(1)	–0.001(1)	0.014(1)	–0.002(1)
C(24)	4e	0.7241(3)	0.2149(1)	0.8815(3)	0.028(1)	0.036(1)	0.034(1)	–0.002(1)	0.014(1)	–0.007(1)
C(25)	4e	0.4431(3)	0.0890(1)	0.8774(3)	0.041(2)	0.035(1)	0.040(1)	–0.008(1)	0.018(1)	–0.004(1)
O(1)	4e	0.4110(2)	0.12906(8)	0.8044(2)	0.038(1)	0.042(1)	0.053(1)	0.0097(9)	0.019(1)	0.0076(9)
O(2)	4e	0.5566(2)	0.06691(8)	0.8717(2)	0.045(1)	0.039(1)	0.047(1)	0.0063(9)	0.017(1)	0.0074(9)
O(3)	4e	0.3701(3)	0.0745(1)	0.9509(3)	0.084(2)	0.049(1)	0.092(2)	–0.003(1)	0.063(2)	0.007(1)
O(4)	4e	0.1850(3)	0.12765(9)	1.0400(3)	0.068(2)	0.050(1)	0.063(2)	0.005(1)	0.028(1)	–0.001(1)
O(5)	4e	0.2241(3)	0.2001(1)	0.6974(2)	0.063(2)	0.073(2)	0.048(1)	0.028(1)	0.021(1)	0.015(1)
O(6)	4e	0.0553(3)	0.2046(1)	0.8646(3)	0.056(2)	0.073(2)	0.051(1)	0.010(1)	0.018(1)	0.010(1)
O(7)	4e	0.7678(2)	0.00914(8)	0.0096(2)	0.035(1)	0.041(1)	0.064(2)	–0.0016(9)	0.008(1)	0.004(1)
O(8)	4e	0.2747(3)	0.1942(1)	0.2615(3)	0.073(2)	0.075(2)	0.052(2)	–0.006(2)	0.022(1)	–0.009(1)
O(9)	4e	0.0453(3)	0.0423(1)	0.1237(3)	0.049(1)	0.067(2)	0.075(2)	–0.005(1)	0.005(1)	–0.024(1)
O(10)	4e	0.1025(3)	0.1920(1)	0.4283(3)	0.056(2)	0.114(3)	0.051(2)	–0.000(2)	0.012(1)	–0.003(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).

References

1. Zheng, Y.-Q.; Lin, J.-L.; Sun, J.; Chen, W.-J.: Synthesis and crystal structure of the tris-bidentate carbonatobis(1,10-phenanthroline-*N*,*N'*) nickel(II), $[Ni(C_{12}H_8N_2)_2(CO_3)]$. Z. Anorg. Allg. Chem. **626** (2000) 1505-1507.
2. Sheldrick, G. M.: Phase Annealing in SHELX-90: Direct Methods for Larger Structures. Acta Crystallogr. A**46** (1990) 467-473.
3. Sheldrick, G. M.: SHELXL-97. Program for the Refinement of Crystal Structure University of Göttingen, Germany 1997.