Crystal structure of bis[*N′*-(4-chlorobenzoyl)picolinohydrazide]zinc(II) — methanol — water (1:0.5:0.5), $Zn(C_{13}H_9ClN_3O_2)_2 \cdot 0.5CH_3OH \cdot 0.5H_2O$

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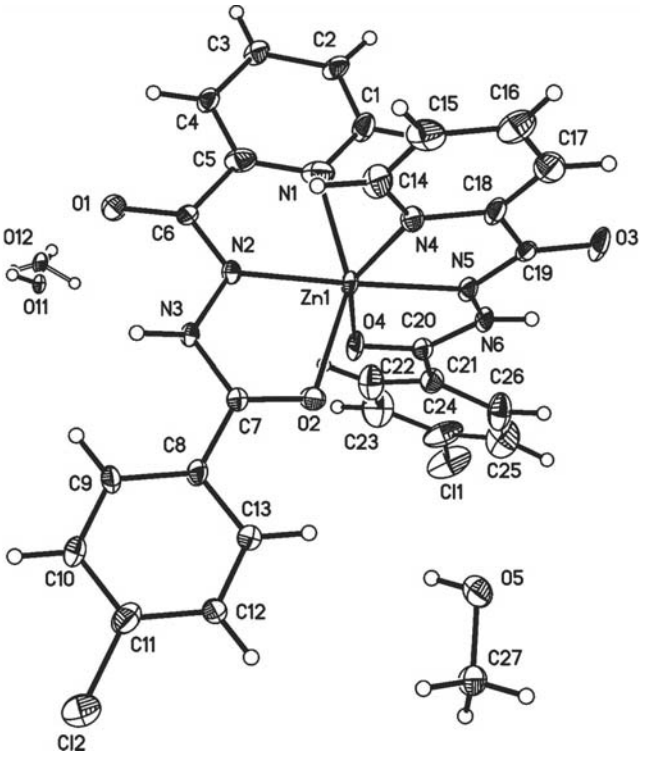

Abstract

$C_{53}H_{42}Cl_4N_{12}O_{10}Zn_2$, monoclinic, *C*12/*c*1 (no. 15), a = 25.558(3) Å, b = 14.523(2) Å, c = 18.525(2) Å, β = 124.912(2)°, V = 5638.7 Å^3, Z = 4, $R_{gt}(F)$ = 0.058, $wR_{ref}(F^2)$ = 0.155, T = 173 K.

Source of material

All reagents and solvents were used as obtained commercially without further purification. Zn(II) acetate dihydrate (0.044 g, 0.2 mmol) was dissolved in 6 ml deionized water, giving a transparent solution, and 10 ml methanol solution of *N′*-(4-chlorobenzoyl)picolinohydrazide (0.110 g, 0.4 mmol) was added dropwise for 0.5 h. After stirring for 8 h, the solution was filtered. Colorless single crystals of the title compound were obtained from the filtrate after 2 weeks. Elemental analysis — found: C, 49.45 %; H, 3.29 %; N, 13.19 %; calculated for $C_{53}H_{42}Cl_4N_{12}O_{10}Zn_2$: C, 49.35 %; H, 3.19 %; N, 13.28 %.

Experimental details

Hydrogen atoms bonded to carbon atoms were placed geometrically and treated as riding with d(C—H) = 0.95Å, U_{iso}(H) = 1.2 U_{eq}(C) for the CH while U_{iso}(H) = 1.5 U_{eq}(C) for the CH_3 groups of CH_3OH molecule. Hydrogen atoms bonded to nitrogen and oxygen atoms were located from difference Fourier maps and restrained with d(N—H) = 0.88 Å, U_{iso}(H) = 1.2 U_{eq}(N) and d(O—H) = 0.85 Å and U_{iso}(H) = 1.2 U_{eq}(O). The methanol and water molecules are both disordered about two-fold rotation axis, respectively. The two-fold axis pass the O11 and O12 atoms of the disordered water molecule and the site occupancy factors of O11 and O12 are 0.50(11) and 0.50(12), respectively, while another two-fold axis pass the C27 atom of methanol molecule and the O5 atom locates 0.273 Å near the two-fold axis. The occupancy of O5 was set to 0.50 according to the special position of C27 atom.

Discussion

Hydrazides form an important class of organic compounds with many applications in organic synthesis and in industry. They are useful starting materials for the synthesis of biologically active heterocycles. However, acyl, aroyl and heteroaroyl hydrazide have an additional O-donor atom from the carbonyl group, which introduces a wider range of properties than those of hydrazides. Therefore, these compounds may function as polydentate ligands and some reports of their complexes have appeared to date [1-3].

In the crystal structure of the title compound, Zn(II) ion is coordinated by two O atoms and four N atoms from two ligands. The coordination polyhedron around the Zn(II) ion can be described as a distorted octahedron. The average Zn—O bond length is 2.211(2) Å, and the Zn—N bond lengthes range from 1.986 (2) to 2.201(3) Å. Both are comparable to those found in other Zn(II) complexes [4,5]. The packing of the molecules is governed by the large number of O–H···O and N–H···O hydrogen bonds which link the complexes into a chain.

Table 1. Data collection and handling.

Crystal:	colorless block, size 0.20 × 0.22 × 0.26 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	11.09 cm^{-1}
Diffractometer, scan mode:	Bruker Smart Apex CCD, φ/ω
$2\theta_{max}$:	52°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	15369, 5527
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 3995
$N(param)_{refined}$:	378
Programs:	SHELXS-97, SHELXL-97, SHELXTL [6]

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

Atom	Site	Occ.	*x*	*y*	*z*	U_{iso}
H(1A)	8*f*		0.2606	0.6785	0.2707	0.043
H(2A)	8*f*		0.3159	0.8088	0.2831	0.040
H(3A)	8*f*		0.3397	0.8356	0.1788	0.037
H(4A)	8*f*		0.3087	0.7230	0.0694	0.036
H(9A)	8*f*		0.1848	0.3023	–0.1166	0.044
H(10A)	8*f*		0.1541	0.1650	–0.1971	0.052
H(12A)	8*f*		0.0946	0.0643	–0.0515	0.049
H(13A)	8*f*		0.1253	0.2015	0.0290	0.044
H(14A)	8*f*		0.0748	0.5729	–0.0264	0.051
H(15A)	8*f*		–0.0193	0.6397	–0.0609	0.057
H(16A)	8*f*		–0.0345	0.6627	0.0532	0.058
H(17A)	8*f*		0.0436	0.6101	0.1953	0.051
H(22A)	8*f*		0.4156	0.4257	0.3558	0.057

Table 2. Continued.

Atom	Site	Occ.	*x*	*y*	*z*	U_{iso}
H(23A)	8*f*		0.5142	0.3863	0.4788	0.073
H(25A)	8*f*		0.4344	0.3229	0.6061	0.077
H(26A)	8*f*		0.3354	0.3696	0.4853	0.060
H(27A)	8*f*	0.50	–0.0335	0.3939	0.2557	0.059
H(27B)	8*f*	0.50	–0.0122	0.3996	0.1915	0.059
H(27C)	8*f*	0.50	0.0383	0.3796	0.2917	0.059
H(3B)	8*f*		0.1977	0.4210	–0.0527	0.035
H(6A)	8*f*		0.2611	0.4710	0.3844	0.030
H(5A)	8*f*		0.0404	0.5286	0.2620	0.053
H(1E)	8*f*	0.25(6)	0.9716	0.7260	0.1951	0.038
H(1F)	8*f*	0.25	1.0121	0.7738	0.2730	0.038
H(1K)	8*f*	0.25	1.0320	0.7443	0.2476	0.042
H(1L)	8*f*	0.25	1.0076	0.7265	0.2966	0.042

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

Atom	Site	Occ.	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(1)	8*f*		0.2703(2)	0.6887(3)	0.2290(2)	0.046(2)	0.040(2)	0.025(2)	–0.008(2)	0.023(2)	–0.001(2)
C(2)	8*f*		0.3031(2)	0.7661(3)	0.2369(2)	0.045(2)	0.029(2)	0.018(2)	–0.004(2)	0.013(2)	0.004(1)
C(3)	8*f*		0.3176(2)	0.7817(3)	0.1761(2)	0.040(2)	0.029(2)	0.014(2)	–0.006(2)	0.010(2)	–0.001(1)
C(4)	8*f*		0.2985(2)	0.7156(3)	0.1110(2)	0.040(2)	0.029(2)	0.021(2)	–0.005(2)	0.018(2)	0.001(1)
C(5)	8*f*		0.2646(2)	0.6389(3)	0.1073(3)	0.041(2)	0.025(2)	0.038(2)	–0.008(2)	0.017(2)	–0.003(2)
C(6)	8*f*		0.2444(2)	0.5669(2)	0.0383(2)	0.033(2)	0.020(2)	0.021(2)	0.006(1)	0.016(2)	0.005(1)
C(7)	8*f*		0.1766(2)	0.3499(3)	0.0173(2)	0.039(2)	0.024(2)	0.026(2)	–0.001(2)	0.023(2)	–0.001(1)
C(8)	8*f*		0.1579(2)	0.2648(3)	–0.0362(2)	0.043(2)	0.030(2)	0.020(2)	–0.006(2)	0.021(2)	–0.003(2)
C(9)	8*f*		0.1665(2)	0.2540(3)	–0.1034(3)	0.059(3)	0.035(2)	0.032(2)	0.013(2)	0.036(2)	0.006(2)
C(10)	8*f*		0.1482(2)	0.1724(3)	–0.1512(3)	0.072(3)	0.040(2)	0.036(2)	0.005(2)	0.041(2)	0.008(2)
C(11)	8*f*		0.1214(2)	0.1017(3)	–0.1319(3)	0.045(2)	0.041(2)	0.042(2)	0.005(2)	0.028(2)	0.014(2)
C(12)	8*f*		0.1129(2)	0.1126(3)	–0.0647(3)	0.072(3)	0.026(2)	0.042(2)	0.014(2)	0.043(2)	0.010(2)
C(13)	8*f*		0.1311(2)	0.1941(3)	–0.0169(3)	0.060(3)	0.027(2)	0.038(2)	0.002(2)	0.036(2)	0.002(2)
C(14)	8*f*		0.0677(2)	0.5801(3)	0.0183(3)	0.054(3)	0.047(3)	0.018(2)	–0.006(2)	0.016(2)	–0.006(2)
C(15)	8*f*		0.0123(2)	0.6206(3)	–0.0024(3)	0.053(3)	0.035(2)	0.036(2)	–0.011(2)	0.015(2)	–0.013(2)
C(16)	8*f*		0.0030(2)	0.6335(3)	0.0653(3)	0.047(3)	0.043(3)	0.045(3)	–0.015(2)	0.020(2)	0.001(2)
C(17)	8*f*		0.0490(2)	0.6032(3)	0.1490(3)	0.049(3)	0.038(2)	0.039(2)	–0.006(2)	0.025(2)	–0.005(2)
C(18)	8*f*		0.1029(2)	0.5629(3)	0.1641(2)	0.043(2)	0.031(2)	0.023(2)	–0.008(2)	0.022(2)	0.000(2)
C(19)	8*f*		0.1563(2)	0.5308(2)	0.2552(2)	0.034(2)	0.017(2)	0.019(2)	–0.005(1)	0.017(2)	–0.001(1)
C(20)	8*f*		0.3042(2)	0.4350(2)	0.3289(2)	0.034(2)	0.024(2)	0.023(2)	–0.002(1)	0.019(2)	–0.002(1)
C(21)	8*f*		0.3649(2)	0.4065(3)	0.4075(3)	0.035(2)	0.033(2)	0.033(2)	–0.003(2)	0.022(2)	–0.001(2)
C(22)	8*f*		0.4192(2)	0.4075(4)	0.4077(3)	0.041(2)	0.065(3)	0.041(2)	–0.007(2)	0.026(2)	–0.006(2)
C(23)	8*f*		0.4776(2)	0.3832(5)	0.4801(4)	0.032(2)	0.086(4)	0.064(3)	–0.007(2)	0.026(2)	–0.003(3)
C(24)	8*f*		0.4834(2)	0.3544(3)	0.5546(3)	0.036(2)	0.040(3)	0.052(3)	–0.013(2)	0.006(2)	0.012(2)
C(25)	8*f*		0.4306(3)	0.3468(5)	0.5555(3)	0.066(3)	0.082(4)	0.026(2)	–0.025(3)	0.016(2)	–0.016(2)
C(26)	8*f*		0.3717(2)	0.3735(4)	0.4834(3)	0.048(3)	0.075(4)	0.033(2)	–0.022(2)	0.027(2)	–0.015(2)
C(27)	4*e*		0	0.4127(4)	¼	0.059(4)	0.037(3)	0.024(3)	0	0.025(3)	0
Cl(1)	8*f*		0.55782(6)	0.3258(1)	0.64635(9)	0.0517(7)	0.0641(9)	0.0463(7)	–0.0182(6)	–0.0021(6)	0.0139(6)
Cl(2)	8*f*		0.09552(7)	0.00255(9)	–0.1941(1)	0.0670(8)	0.0433(7)	0.0606(8)	0.0069(5)	0.0369(7)	0.0118(5)
N(1)	8*f*		0.2510(2)	0.6263(2)	0.1657(2)	0.049(2)	0.027(2)	0.037(2)	–0.001(2)	0.018(2)	–0.001(1)
N(2)	8*f*		0.2150(2)	0.4983(2)	0.0493(2)	0.049(2)	0.026(2)	0.014(1)	0.003(1)	0.020(1)	0.000(1)
N(3)	8*f*		0.1964(2)	0.4217(2)	–0.0062(2)	0.052(2)	0.027(2)	0.013(1)	0.006(1)	0.021(1)	0.004(1)
N(4)	8*f*		0.1117(2)	0.5505(2)	0.0992(2)	0.042(2)	0.028(2)	0.019(1)	–0.002(1)	0.018(1)	–0.003(1)
N(5)	8*f*		0.2031(2)	0.4918(2)	0.2555(2)	0.035(2)	0.026(2)	0.017(1)	–0.008(1)	0.017(1)	–0.005(1)
N(6)	8*f*		0.2573(2)	0.4666(2)	0.3342(2)	0.036(2)	0.029(2)	0.013(1)	–0.005(1)	0.016(1)	–0.003(1)
O(1)	8*f*		0.2564(1)	0.5727(2)	–0.0173(2)	0.045(2)	0.035(2)	0.022(1)	0.013(1)	0.018(1)	0.009(1)
O(2)	8*f*		0.1744(1)	0.3545(2)	0.0828(2)	0.050(2)	0.024(1)	0.020(1)	0.004(1)	0.019(1)	0.001(1)
O(3)	8*f*		0.1523(2)	0.5429(2)	0.3184(2)	0.055(2)	0.051(2)	0.026(1)	–0.019(2)	0.030(1)	–0.005(1)
O(4)	8*f*		0.2973(1)	0.4337(2)	0.2560(2)	0.043(2)	0.044(2)	0.020(1)	–0.002(1)	0.023(1)	0.002(1)
O(5)	8*f*	0.50	0.0108(6)	0.5111(4)	0.2668(5)	0.063(9)	0.047(3)	0.025(7)	0.022(4)	0.026(6)	0.010(3)
O(11)	4*e*	0.50(11)	0	0.721(3)	¼	0.057(7)	0.03(1)	0.023(5)	0	0.029(5)	0
O(12)	4*e*	0.50(12)	0	0.752(3)	¼	0.058(7)	0.03(2)	0.012(6)	0	0.019(5)	0
Zn(1)	8*f*		0.20590(2)	0.49163(3)	0.14865(3)	0.0486(3)	0.0278(3)	0.0198(2)	–0.0012(2)	0.0259(2)	–0.0003(2)

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