Crystal structure of bis[5-methyl-1-(2′-pyridyl)pyrazol-3-carboxamide]-nitratozinc(II) nitrate perchlorate monohydrate, $[Zn(C_{10}H_{10}N_4O)_2NO_3][(NO_3)_{0.6}(ClO_4)_{0.4}] \cdot H_2O$, *an unusual zinc(II) complex*

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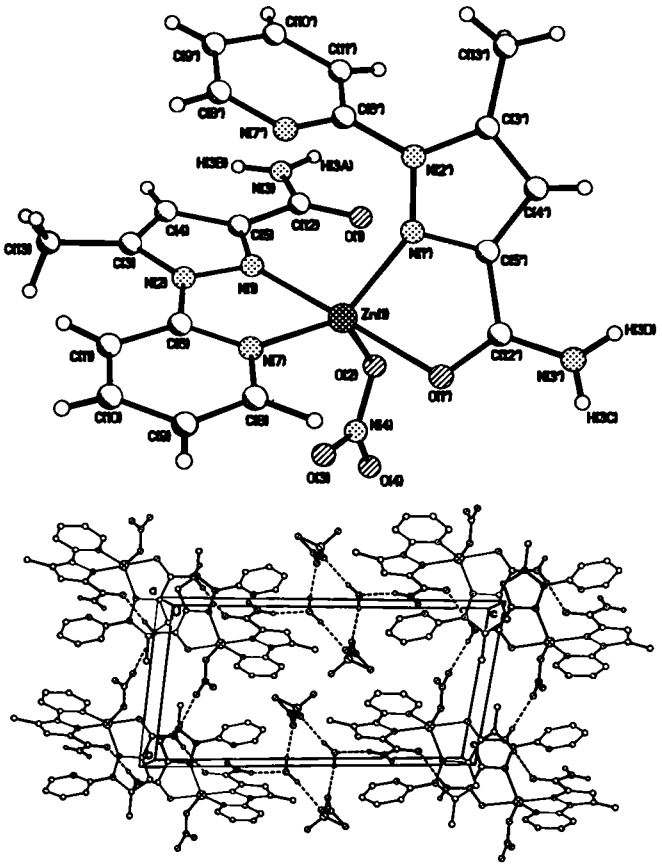

Abstract

$C_{20}H_{22}Cl_{0.4}N_{9.6}O_{9.4}Zn$, triclinic, $P\bar{1}$ (No. 2), $a = 7.588(1)$ Å, $b = 9.688(2)$ Å, $c = 18.538(4)$ Å, $\alpha = 95.38(2)°$, $\beta = 98.87(2)°$, $\gamma = 106.31(2)°$, $V = 1278.8$ Å^3, $Z = 2$, $R_{gt}(F) = 0.056$, $wR_{ref}(F^2) = 0.153$, $T = 293$ K.

Source of material

The ligand (L) was prepared by procedure described in [1]. Preparation of the complex $[Zn(L)_2NO_3]^+[(NO_3)_{0.60}(ClO_4)_{0.40}]^- \cdot H_2O$: To a magnetically stirred solution of ligand (0.404 g, 2 mmol) in ethanol (95%) (10 ml) was added dropwise a mixture of $Zn(NO_3)_2 \cdot 6H_2O$ (0.297 g, 1 mmol) and $NaClO_4 \cdot H_2O$ (0.421 g, 3 mmol) in ethanol (95%) (20 ml) at room temperature over 10 min. The reaction mixture was stirred for 24 h at room temperature. The white powder was filtered off, washed with cold ethanol (95%; 5 ml), diethyl ether (5 ml) and dried in vacuum over silica gel at room temperature. The product was then dried in vacuum over P_4O_{10} at 323 K (mp 493 K; yield: 0.46 g, 73%). A single crystal suitable for X-ray analysis was obtained by slow evaporation of acetonitrile solution of the product at room temperature. Analysis: calculated for $C_{20}H_{22}Cl_{0.40}N_{9.60}O_{9.40}Zn$: C, 38.32%; H, 3.54%; N, 21.45%; found: C, 38.4%; H, 3.6%; N, 21.5%.

Experimental details

Our efforts to improve the model of the disordered perchlorate and nitrate molecules by splitting the overlapped oxygen atoms (O(1s), O(2s) and O(3s)) failed, due to severe correlations among the involved parameters.

Discussion

Numerous zinc complexes with nitrogen or oxygen donor ligands have been synthesized and studied [2-5]. Some of these complexes are as structural models for the active site in enzymes [3]. The well-documented bio-activity of pyrazole derivatives is often related to the chelation phenomena with trace metal ions; this has generated substantial work on the coordination chemistry of pyrazole-derived ligands [1], especially, the synthesis and spectroscopic characterisation of copper (II) complexes with 5-methyl-1-(2′-pyridyl)pyrazole-3-carboxamid (L) together with the crystal structure of $[Cu(L)_2(H_2O)](ClO_4)_2$.

In the crystal structure of $[Zn(L)_2NO_3]^+[(NO_3)_{0.60}(ClO_4)_{0.40}]^- \cdot H_2O$, the two molecules of the ligand (L) are coordinated in different ways. They are both bidentate, however one of them coordinates the Zn(II) ion by the pyrazole nitrogen and carboxamide oxygen atoms, whereas another ligand is coordinated via its pyrazole and pyridyl nitrogen atoms. Coordination environment around the Zn(II) ion is distorted trigonal bipyramide [ZnN$_3$O(carboxamidic)O(nitrate anion)]. The atoms N(1) and O(1′) are axial with a N(1)–Zn(1)–O(1′) angle of 177.41(14)° and the atoms N(1′), N(7) and O(2) are in the distorted equatorial plane with angles ∠O(2)–Zn(1)–N(1′) = 115.39(15)°, ∠O(2)–Zn(1)–N(7) = 128.19(15)°, and ∠N(1′)–Zn(1)–N(7) = 116.22(16)°. It is also found that the crystal along with the perchlorate and nitrate anions. Moreover, there are two crystallographically independent NO_3^- anions in the structure, one of them coordinates the Zn atom via one of its oxygen atoms; another one is disordered and in fact shares one crystallographic position with the ClO_4^- anion. Final refinement showed that 40% of these positions in the crystal are occupied by ClO_4^- and 60% of positions contain NO_3^-. The crystal structure shows a high degree of stabilization through extensive hydrogen bonding.

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Table 1. Data collection and handling.

Crystal:	colorless prism, size 0.1 × 0.2 × 0.2 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	10.74 cm^{-1}
Diffractometer, scan mode:	Siemens P3/PC, $\omega/2\theta$
$2\theta_{max}$:	52.12°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	4617, 4219
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 3435
$N(param)_{refined}$:	443
Programs:	SHELXTL-97 [7], SHELXTL [8], SADABS [9]

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

Atom	Site	x	y	z	U_{iso}
H(3B)	2*i*	0.510(8)	0.066(6)	0.321(4)	0.05(2)
H(3A)	2*i*	0.54(1)	0.001(7)	0.244(4)	0.07(2)
H(4)	2*i*	0.334(8)	0.147(6)	0.397(3)	0.04(1)
H(8)	2*i*	–0.376(9)	0.379(7)	0.155(4)	0.06(2)
H(9)	2*i*	–0.492(8)	0.480(6)	0.253(3)	0.04(2)
H(10)	2*i*	–0.385(8)	0.476(6)	0.372(3)	0.05(2)
H(11)	2*i*	–0.152(7)	0.376(6)	0.408(3)	0.04(1)
H(13C)	2*i*	0.1755	0.2515	0.4967	0.06(2)
H(13B)	2*i*	–0.0366	0.2240	0.4641	0.07(2)
H(13A)	2*i*	0.1056	0.3793	0.4703	0.16(5)
H(3D)	2*i*	–0.310(8)	0.095(6)	–0.096(3)	0.04(2)
H(3C)	2*i*	–0.289(7)	0.233(5)	–0.078(3)	0.02(1)
H(4')	2*i*	–0.298(8)	–0.146(6)	–0.047(3)	0.04(2)
H(8')	2*i*	–0.260(9)	–0.077(7)	0.337(4)	0.06(2)
H(9')	2*i*	–0.038(8)	–0.210(6)	0.376(3)	0.05(2)
H(10')	2*i*	0.089(9)	–0.278(7)	0.295(3)	0.05(2)
H(11')	2*i*	0.047(8)	–0.237(6)	0.174(3)	0.04(1)
H(13F)	2*i*	–0.3138	–0.3920	0.0897	0.07(2)
H(13E)	2*i*	–0.1367	–0.3727	0.0533	0.08(2)
H(13D)	2*i*	–0.3350	–0.4071	0.0036	0.07(2)
H(1W)	2*i*	0.3714	–0.1183	0.5336	0.132
H(2W)	2*i*	0.4661	0.0265	0.5758	0.132

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}
Zn(1)	2*i*		–0.03980(8)	0.24127(6)	0.16006(3)	0.0463(5)	0.0339(3)	0.0265(3)	0.0179(3)	0.0071(2)	0.0017(2)
N(1)	2*i*		0.0924(6)	0.2109(4)	0.2619(2)	0.037(3)	0.040(2)	0.026(2)	0.020(2)	0.010(2)	0.002(2)
O(1)	2*i*		0.2743(5)	0.0754(4)	0.1718(2)	0.056(3)	0.046(2)	0.029(2)	0.028(2)	0.010(2)	0.006(1)
N(2)	2*i*		0.0283(6)	0.2610(4)	0.3202(2)	0.034(3)	0.047(2)	0.027(2)	0.022(2)	0.007(2)	–0.001(2)
N(3)	2*i*		0.4629(7)	0.0462(6)	0.2721(3)	0.049(3)	0.069(3)	0.035(2)	0.037(3)	0.010(2)	0.006(2)
C(3)	2*i*		0.1232(8)	0.2389(7)	0.3851(3)	0.046(4)	0.076(4)	0.026(2)	0.031(3)	0.007(2)	0.001(2)
C(4)	2*i*		0.2494(8)	0.1730(7)	0.3667(3)	0.041(4)	0.071(4)	0.031(2)	0.034(3)	0.005(2)	0.009(2)
C(5)	2*i*		0.2269(7)	0.1574(5)	0.2900(2)	0.034(3)	0.040(2)	0.028(2)	0.018(2)	0.007(2)	0.005(2)
C(6)	2*i*		–0.1185(7)	0.3250(5)	0.3046(3)	0.035(3)	0.039(2)	0.035(2)	0.017(2)	0.008(2)	–0.001(2)
N(7)	2*i*		–0.1795(6)	0.3217(4)	0.2330(2)	0.039(3)	0.036(2)	0.033(2)	0.018(2)	0.006(2)	0.003(2)
C(8)	2*i*		–0.3190(8)	0.3800(6)	0.2133(3)	0.042(4)	0.043(3)	0.049(3)	0.019(2)	0.003(2)	0.001(2)
C(9)	2*i*		–0.3971(9)	0.4412(6)	0.2641(3)	0.044(4)	0.051(3)	0.059(3)	0.028(3)	0.005(3)	0.003(3)
C(10)	2*i*		–0.334(1)	0.4441(7)	0.3374(3)	0.054(4)	0.061(4)	0.057(4)	0.032(3)	0.019(3)	–0.004(3)
C(11)	2*i*		–0.1909(9)	0.3854(7)	0.3591(3)	0.049(4)	0.065(3)	0.036(3)	0.032(3)	0.010(2)	–0.004(2)
C(12)	2*i*		0.3236(7)	0.0886(5)	0.2394(2)	0.041(3)	0.034(2)	0.032(2)	0.017(2)	0.011(2)	0.004(2)
C(13)	2*i*		0.089(1)	0.277(1)	0.4609(3)	0.085(7)	0.164(9)	0.027(3)	0.083(6)	0.013(3)	0.012(4)
O(1')	2*i*		–0.1899(6)	0.2731(3)	0.0552(2)	0.066(3)	0.034(2)	0.032(2)	0.023(2)	0.003(2)	0.002(1)
N(1')	2*i*		–0.1712(6)	0.0331(4)	0.1059(2)	0.041(3)	0.029(2)	0.028(2)	0.017(2)	0.009(2)	0.005(1)
N(2')	2*i*		–0.1769(6)	–0.1040(4)	0.1176(2)	0.044(3)	0.031(2)	0.028(2)	0.018(2)	0.011(2)	0.007(2)
N(3')	2*i*		–0.2836(7)	0.1639(5)	–0.0631(2)	0.061(3)	0.038(2)	0.029(2)	0.024(2)	0.006(2)	0.007(2)
C(3')	2*i*		–0.2329(7)	–0.1983(5)	0.0530(2)	0.036(3)	0.030(2)	0.035(2)	0.010(2)	0.014(2)	–0.000(2)
C(4')	2*i*		–0.2624(8)	–0.1165(5)	–0.0020(3)	0.042(3)	0.038(2)	0.026(2)	0.014(2)	0.007(2)	0.001(2)
C(5')	2*i*		–0.2250(7)	0.0243(5)	0.0328(2)	0.030(3)	0.036(2)	0.027(2)	0.014(2)	0.006(2)	0.004(2)
C(6')	2*i*		–0.1415(7)	–0.1363(5)	0.1911(2)	0.040(3)	0.030(2)	0.031(2)	0.017(2)	0.013(2)	0.006(2)
N(7')	2*i*		–0.2352(7)	–0.0888(5)	0.2375(2)	0.056(3)	0.053(2)	0.034(2)	0.033(2)	0.020(2)	0.012(2)
C(8')	2*i*		–0.200(1)	–0.1176(7)	0.3066(3)	0.079(5)	0.072(4)	0.038(3)	0.044(4)	0.026(3)	0.016(3)
C(9')	2*i*		–0.080(1)	–0.1953(7)	0.3291(3)	0.080(5)	0.064(4)	0.033(3)	0.034(3)	0.015(3)	0.019(2)
C(10')	2*i*		0.011(1)	–0.2446(6)	0.2800(3)	0.066(5)	0.045(3)	0.049(3)	0.032(3)	0.006(3)	0.016(2)
C(11')	2*i*		–0.0183(8)	–0.2135(5)	0.2087(3)	0.049(4)	0.038(3)	0.037(2)	0.023(2)	0.015(2)	0.007(2)
C(12')	2*i*		–0.2307(7)	0.1640(5)	0.0080(2)	0.036(3)	0.039(2)	0.029(2)	0.018(2)	0.008(2)	0.006(2)
C(13')	2*i*		–0.2567(9)	–0.3565(5)	0.0496(3)	0.066(4)	0.028(2)	0.041(3)	0.012(2)	0.011(3)	0.002(2)
N(4)	2*i*		0.2171(7)	0.4834(4)	0.1348(2)	0.053(3)	0.035(2)	0.038(2)	0.020(2)	0.011(2)	0.008(2)
O(2)	2*i*		0.2038(6)	0.3479(4)	0.1281(2)	0.063(3)	0.036(2)	0.056(2)	0.026(2)	0.023(2)	0.019(2)
O(3)	2*i*		0.0937(7)	0.5210(5)	0.1578(3)	0.073(4)	0.053(2)	0.106(4)	0.032(2)	0.037(3)	–0.006(2)
O(4)	2*i*		0.3524(6)	0.5682(4)	0.1181(2)	0.065(3)	0.048(2)	0.070(3)	0.014(2)	0.022(2)	0.024(2)
O(1W)	2*i*		0.3863(8)	–0.0567(6)	0.5715(3)	0.110(5)	0.105(4)	0.059(3)	0.052(3)	0.015(3)	0.005(3)
N(1S)	2*i*	0.60	0.3556(6)	–0.3111(5)	0.4138(2)	0.015(4)	0.044(4)	0.016(3)	0.028(3)	–0.012(2)	0.010(3)
O(1S)	2*i*		0.319(1)	–0.4112(8)	0.3603(3)	0.168(7)	0.161(7)	0.107(5)	0.107(6)	0.002(5)	–0.027(5)
O(2S)	2*i*		0.227(1)	–0.293(1)	0.4454(5)	0.149(8)	0.33(2)	0.146(8)	0.124(9)	0.072(6)	–0.013(8)
O(3S)	2*i*		0.5245(8)	–0.2376(9)	0.4291(5)	0.172(9)	0.144(8)	0.179(9)	0.027(7)	0.040(7)	0.038(7)
Cl(1)	2*i*	0.40	0.3674(6)	–0.3464(4)	0.4325(2)	0.058(3)	0.069(3)	0.042(2)	0.036(2)	–0.003(2)	0.014(2)
O(4S)	2*i*	0.40	0.434(3)	–0.436(2)	0.478(1)	0.14(2)	0.16(2)	0.11(1)	0.03(1)	–0.02(1)	0.05(1)

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