

Crystal structure of chlorido-tris(3-amino-5-phenyl-1*H*-pyrazole-*N*²)zinc(II) chloride, [ZnCl(C₉H₉N₃)₃]Cl

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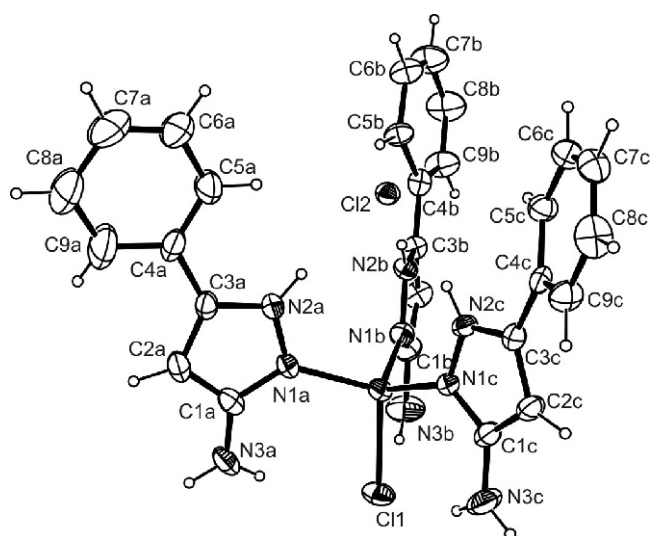
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Received March 7, 2011, accepted and available on-line July 12, 2011; CCDC no. 1267/3429



Abstract

C₂₇H₂₇Cl₂N₉Zn, tetragonal, $P\bar{4}2_1c$ (no. 114), $a = 17.522(2)$ Å, $c = 18.583(3)$ Å, $V = 5705.4$ Å³, $Z = 8$, $R_{\text{gt}}(F) = 0.040$, $wR_{\text{ref}}(F^2) = 0.114$, $T = 293$ K.

Source of material

A mixture of 3-amino-5-phenylpyrazole (0.16 g, 1 mmol) and ZnCl₂ (0.08 g, 0.5 mmol) was dissolved under heating in ethanol (4 ml). After three days the colourless crystals were obtained.

Experimental details

All H atoms were included in calculated positions and treated as riding with $d(\text{C}—\text{H}) = 0.93$ Å, $d(\text{N}—\text{H}) = 0.86$ Å and $U_{\text{iso}}(\text{H}) = 1.2 U_{\text{eq}}(\text{C}, \text{N})$.

Discussion

The complexing properties of pyrazole derivatives have been the subject of extensive research [1,2].

In the title crystal structure, Zn(II) has a tetrahedral surrounding defined by three N atoms of the monodentate pyrazole ligands and Cl ligand. This monocationic unit is neutralized with the anionic Cl. The distances $d(\text{Zn}—\text{N})$ range from 2.013(3) to 2.028(5) Å. The bonds within the pyrazole parts are of normal lengths, intermediate between those characteristic for single and

double ones. In each organic ligand, $d(\text{C3}—\text{C4})$ are the longest (ranging from 1.449(9) to 1.473(10) Å) and allow for free rotation of the corresponding pyrazole (pz) and phenyl (ph) rings. The differences in the dihedral angles formed by pz and ph mean planes (7.5(5), 15.5(5) and 29.4(4)° in *a*, *b* and *c* ligands, respectively) represent the most significant structural difference between the three ligands. The amino substituents of each pyrazole are engaged in three intramolecular hydrogen bonds to coordinating chlorine with $d(\text{N3} \cdots \text{Cl1}) = 3.267(6)$, 3.187(7) and 3.179(9) Å for *a*, *b* and *c* ligands, respectively, while the three pyrazole (N2–H) fragments interact with the ionic chlorine ($d(\text{N2} \cdots \text{Cl2}) = 3.174(5)$, 3.187(4) and 3.145(5) Å for *a*, *b* and *c* ligands, respectively). These interactions favour the edge-on orientation of the ligands regarding the two Cl atoms. Similar orientation of the ligands has been observed in the complex of Zn(II) with the monosubstituted 3(5)-phenylpyrazole [8]. In the case of the ligands *a* and *b* the above interactions to the ionic Cl2 are accompanied by weak C5–H $\cdots$ Cl2 interactions engaging the phenyl C as donor with $d(\text{C5} \cdots \text{Cl2}) = 3.782(9)$ and 3.680(6) Å, respectively. The similar contact is missing for ligand *c* where the twisting of ph ring is the most pronounced. The three ligands considerably differ in the manner of further engagement in the intermolecular interactions. The interaction N3a–H3a2 $\cdots$ Cl2 ($d(\text{N3} \cdots \text{Cl2}) = 3.422(5)$ Å, symmetry code: $x+1/2, y-1/2, z+1/2$) involves the amino substituent and the ionic Cl and arranges the molecules in [001] direction. An analogue interaction for ligand *c* is much weaker, while for ligand *b* significantly exceeds the sum of van der Waal's radii for Cl and H [9]. The six π systems presented in this crystal structure mutually interact through numerous C–H $\cdots$ π interactions. There is, however, only one $\pi \cdots \pi$ interaction which is realized between the pz ring of ligand *b* and ph ring of ligand *c*. The distance between centroids of the adjacent rings is 3.622(4) Å, symmetry code: $-x+1/2, -y+1/2, z+1/2$.

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Table 1. Data collection and handling.

Crystal:	colourless prism, size 0.20 × 0.23 × 0.26 mm
Wavelength:	Mo K_{α} radiation (0.71073 Å)
μ :	10.82 cm ⁻¹
Diffractometer, scan mode:	Enraf-Nonius CAD-4, $\omega/2\theta$
$2\theta_{\max}$:	51.94°
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$:	6024, 3087
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 1898
$N(\text{param})_{\text{refined}}$:	346
Programs:	SHELXS-97, SHELXL-97 [10], ORTEP-3 [11], WinGX [12], PLATON [13]

Table 2. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso}
H(2A)	8e	0.3543	0.7579	1.0402	0.085
H(5A)	8e	0.4110	0.6927	0.8053	0.129
H(6A)	8e	0.5157	0.6236	0.7784	0.150
H(7A)	8e	0.6015	0.5965	0.8606	0.237
H(8A)	8e	0.5791	0.6363	0.9838	0.318

Table 2. Continued.

Atom	Site	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso}
H(9A)	8e	0.4742	0.7191	1.0061	0.268
H(2B)	8e	0.1841	1.0955	0.7383	0.088
H(5B)	8e	0.3540	0.9135	0.6668	0.085
H(6B)	8e	0.4330	0.9358	0.5678	0.107
H(7B)	8e	0.4218	1.0471	0.5045	0.142
H(8B)	8e	0.3317	1.1379	0.5378	0.152
H(9B)	8e	0.2473	1.1115	0.6272	0.121
H(2C)	8e	−0.0099	0.6189	0.7638	0.097
H(5C)	8e	0.1929	0.6692	0.6186	0.085
H(6C)	8e	0.2342	0.5814	0.5373	0.096
H(7C)	8e	0.1931	0.4586	0.5389	0.096
H(8C)	8e	0.1094	0.4216	0.6233	0.118
H(9C)	8e	0.0663	0.5054	0.7110	0.095
H(2A1)	8e	0.3081	0.7590	0.8357	0.070
H(3A1)	8e	0.1763	0.8602	1.0219	0.099
H(3A2)	8e	0.2289	0.8335	1.0796	0.099
H(2B1)	8e	0.2506	0.8864	0.7307	0.067
H(3B1)	8e	0.0819	0.9957	0.8849	0.133
H(3B2)	8e	0.0885	1.0746	0.8557	0.133
H(2C1)	8e	0.1852	0.7201	0.7381	0.068
H(3C1)	8e	−0.0044	0.7716	0.8953	0.152
H(3C2)	8e	−0.0566	0.7089	0.8728	0.152

Table 3. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> ₁₁	<i>U</i> ₂₂	<i>U</i> ₃₃	<i>U</i> ₁₂	<i>U</i> ₁₃	<i>U</i> ₂₃
Zn(1)	8e	0.14959(4)	0.83783(4)	0.86185(4)	0.0609(4)	0.0652(4)	0.0465(3)	0.0027(4)	0.0039(4)	−0.0046(3)
C(1A)	8e	0.2616(4)	0.8015(3)	0.9843(3)	0.088(5)	0.049(4)	0.047(3)	−0.022(4)	−0.001(4)	−0.007(3)
C(2A)	8e	0.3305(4)	0.7658(4)	0.9961(3)	0.082(5)	0.075(4)	0.055(4)	−0.017(4)	−0.021(4)	0.010(3)
C(3A)	8e	0.3570(4)	0.7443(4)	0.9296(3)	0.057(4)	0.069(4)	0.061(4)	−0.017(3)	−0.015(3)	0.015(3)
C(4A)	8e	0.4278(4)	0.7040(5)	0.9099(5)	0.051(4)	0.093(5)	0.094(6)	−0.010(4)	−0.019(4)	0.031(5)
C(5A)	8e	0.4447(5)	0.6805(6)	0.8422(5)	0.099(6)	0.147(9)	0.077(6)	0.048(6)	−0.020(5)	−0.010(5)
C(6A)	8e	0.5084(6)	0.6399(6)	0.8255(6)	0.089(6)	0.16(1)	0.121(8)	0.043(7)	−0.002(6)	0.017(8)
C(7A)	8e	0.5579(7)	0.624(1)	0.8728(9)	0.106(9)	0.30(2)	0.19(1)	0.09(1)	0.02(1)	0.03(2)
C(8A)	8e	0.5454(8)	0.650(1)	0.9473(9)	0.13(1)	0.49(3)	0.18(1)	0.15(2)	−0.04(1)	−0.03(2)
C(9A)	8e	0.4803(3)	0.6955(3)	0.9616(3)	0.13(1)	0.40(3)	0.15(1)	0.12(2)	−0.058(9)	−0.07(1)
C(1B)	8e	0.1525(3)	1.0015(3)	0.8031(3)	0.058(4)	0.059(4)	0.087(5)	0.010(4)	0.004(4)	−0.009(4)
C(2B)	8e	0.1901(3)	1.0439(3)	0.7485(3)	0.077(5)	0.043(3)	0.100(5)	0.008(3)	0.006(4)	−0.001(4)
C(3B)	8e	0.2354(3)	0.9949(4)	0.7150(3)	0.060(4)	0.045(3)	0.062(3)	−0.002(3)	0.001(3)	−0.001(3)
C(4B)	8e	0.2886(4)	1.0092(4)	0.6569(4)	0.069(4)	0.051(4)	0.077(5)	0.000(3)	−0.011(4)	−0.001(3)
C(5B)	8e	0.3475(4)	0.9574(3)	0.6393(4)	0.068(4)	0.062(4)	0.084(4)	−0.003(3)	0.018(4)	0.009(4)
C(6B)	8e	0.3962(4)	0.9715(4)	0.5808(5)	0.082(5)	0.074(5)	0.113(7)	0.001(4)	0.025(5)	0.004(5)
C(7B)	8e	0.3895(6)	1.0377(6)	0.5432(5)	0.129(8)	0.112(8)	0.115(7)	−0.004(7)	0.040(7)	0.040(6)
C(8B)	8e	0.3345(6)	1.0917(5)	0.5622(6)	0.152(9)	0.092(6)	0.136(8)	0.015(7)	0.039(8)	0.056(6)
C(9B)	8e	0.2851(5)	1.0760(5)	0.6165(5)	0.105(6)	0.080(5)	0.119(7)	0.016(5)	0.032(6)	0.031(5)
C(1C)	8e	0.0378(4)	0.7106(5)	0.8166(4)	0.049(4)	0.108(6)	0.078(5)	−0.011(4)	0.008(3)	−0.022(4)
C(2C)	8e	0.0314(4)	0.6518(5)	0.7690(4)	0.052(4)	0.112(6)	0.079(5)	−0.024(4)	0.011(3)	−0.030(5)
C(3C)	8e	0.0980(3)	0.6509(4)	0.7302(3)	0.051(3)	0.066(4)	0.062(4)	−0.007(3)	−0.005(3)	−0.005(3)
C(4C)	8e	0.1250(3)	0.5966(3)	0.6753(3)	0.039(3)	0.062(4)	0.066(4)	−0.004(3)	−0.011(3)	−0.004(3)
C(5C)	8e	0.1758(4)	0.6190(4)	0.6212(3)	0.069(4)	0.071(4)	0.072(4)	−0.013(4)	0.008(4)	−0.007(3)
C(6C)	8e	0.1997(4)	0.5664(5)	0.5726(4)	0.080(5)	0.088(6)	0.072(5)	0.005(4)	0.005(4)	−0.015(4)
C(7C)	8e	0.1756(5)	0.4932(5)	0.5731(4)	0.097(6)	0.066(5)	0.078(5)	0.018(4)	−0.004(4)	−0.014(4)
C(8C)	8e	0.1268(6)	0.4718(4)	0.6231(5)	0.129(7)	0.045(4)	0.121(7)	−0.004(4)	−0.015(6)	0.000(5)
C(9C)	8e	0.1003(4)	0.5221(4)	0.6759(4)	0.078(5)	0.067(5)	0.093(5)	−0.018(4)	0.010(4)	0.000(4)
N(1A)	8e	0.2451(3)	0.8038(3)	0.9144(2)	0.065(3)	0.055(3)	0.041(2)	−0.005(3)	−0.007(2)	−0.002(2)
N(2A)	8e	0.3047(3)	0.7667(3)	0.8813(2)	0.059(3)	0.068(3)	0.048(3)	−0.001(3)	−0.008(2)	0.000(2)
N(3A)	8e	0.2168(4)	0.8360(4)	1.0348(3)	0.110(5)	0.096(4)	0.040(3)	−0.016(4)	−0.003(3)	−0.001(3)
N(1B)	8e	0.1736(3)	0.9284(3)	0.7993(3)	0.062(3)	0.053(3)	0.062(3)	0.005(2)	0.001(3)	−0.010(2)
N(2B)	8e	0.2265(3)	0.9267(3)	0.7442(3)	0.064(3)	0.054(3)	0.049(3)	0.004(3)	0.005(3)	−0.006(2)
N(3B)	8e	0.1011(4)	1.0272(4)	0.8544(4)	0.120(6)	0.081(4)	0.131(6)	0.041(4)	0.048(5)	−0.009(4)
N(1C)	8e	0.1052(3)	0.7483(3)	0.8081(2)	0.045(3)	0.076(3)	0.048(3)	0.001(3)	0.001(2)	−0.007(3)
N(2C)	8e	0.1407(3)	0.7090(3)	0.7545(3)	0.043(3)	0.067(3)	0.059(3)	−0.003(2)	0.008(2)	−0.010(3)
N(3C)	8e	−0.0142(4)	0.7332(5)	0.8680(4)	0.060(4)	0.195(8)	0.125(6)	−0.031(5)	0.035(4)	−0.070(6)
Cl(1)	8e	0.0627(1)	0.8767(1)	0.94357(9)	0.095(1)	0.098(1)	0.068(1)	0.014(1)	0.029(1)	−0.012(1)
Cl(2)	8e	0.30430(8)	0.76621(8)	0.71046(8)	0.0533(8)	0.0559(8)	0.0511(7)	−0.0006(7)	0.0052(7)	−0.0062(7)

Acknowledgment. This work was financially supported by the Ministry for Science and Technological Development of the Republic of Serbia (Projects 172014 and 172035).

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