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# Crystal structure of chlorido-tris(3-amino-5-phenyl-*1H*-pyrazole-$N^2$)zinc(II) chloride, $[ZnCl(C_9H_9N_3)_3]Cl$

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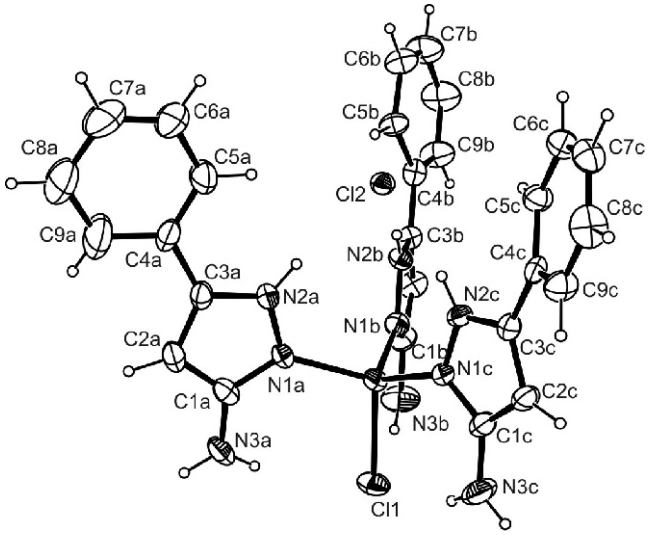


**Abstract**

$C_{27}H_{27}Cl_2N_9Zn$, tetragonal, $P\bar{4}2_1c$ (no. 114), $a$ = 17.522(2) Å, $c$ = 18.583(3) Å, $V$ = 5705.4 Å$^3$, $Z$ = 8, $R_{gt}(F)$ = 0.040, $wR_{ref}(F^2)$ = 0.114, $T$ = 293 K.

**Source of material**

A mixture of 3-amino-5-phenylpyrazole (0.16 g, 1 mmol) and $ZnCl_2$ (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 $d$(C—H) = 0.93 Å, $d$(N—H) = 0.86 Å and $U_{iso}$(H) = 1.2 $U_{eq}$(C,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 $d$(Zn—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, $d$(C3—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 $d$(N3···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 ($d$(N2···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···Cl2 interactions engaging the phenyl C as donor with $d$(C5···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···Cl2 ($d$(N3···Cl2) = 3.422(5) Å, symmetry code: $x$+½,$y$–½,$z$+½) 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 $\pi$ systems presented in this crystal structure mutually interact through numerous C–H···$\pi$ interactions. There is, however, only one $\pi$···$\pi$ interaction which is realized between the pz ring of ligand *b* and ph ring of ligand *c*. The distance between centoids of the adjacent rings is 3.622(4) Å, symmetry code: –$x$+½,–$y$+½,$z$+⅗.

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**Table 1.** Data collection and handling.

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

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

| Atom | Site | $x$ | $y$ | $z$ | $U_{iso}$ |
|---|---|---|---|---|---|
| H(2A) | 8*e* | 0.3543 | 0.7579 | 1.0402 | 0.085 |
| H(5A) | 8*e* | 0.4110 | 0.6927 | 0.8053 | 0.129 |
| H(6A) | 8*e* | 0.5157 | 0.6236 | 0.7784 | 0.150 |
| H(7A) | 8*e* | 0.6015 | 0.5965 | 0.8606 | 0.237 |
| H(8A) | 8*e* | 0.5791 | 0.6363 | 0.9838 | 0.318 |
| H(9A) | 8*e* | 0.4742 | 0.7191 | 1.0061 | 0.268 |
| H(2B) | 8*e* | 0.1841 | 1.0955 | 0.7383 | 0.088 |
| H(5B) | 8*e* | 0.3540 | 0.9135 | 0.6668 | 0.085 |
| H(6B) | 8*e* | 0.4330 | 0.9358 | 0.5678 | 0.107 |
| H(7B) | 8*e* | 0.4218 | 1.0471 | 0.5045 | 0.142 |
| H(8B) | 8*e* | 0.3317 | 1.1379 | 0.5378 | 0.152 |
| H(9B) | 8*e* | 0.2473 | 1.1115 | 0.6272 | 0.121 |
| H(2C) | 8*e* | –0.0099 | 0.6189 | 0.7638 | 0.097 |
| H(5C) | 8*e* | 0.1929 | 0.6692 | 0.6186 | 0.085 |
| H(6C) | 8*e* | 0.2342 | 0.5814 | 0.5373 | 0.096 |
| H(7C) | 8*e* | 0.1931 | 0.4586 | 0.5389 | 0.096 |
| H(8C) | 8*e* | 0.1094 | 0.4216 | 0.6233 | 0.118 |
| H(9C) | 8*e* | 0.0663 | 0.5054 | 0.7110 | 0.095 |
| H(2A1) | 8*e* | 0.3081 | 0.7590 | 0.8357 | 0.070 |
| H(3A1) | 8*e* | 0.1763 | 0.8602 | 1.0219 | 0.099 |
| H(3A2) | 8*e* | 0.2289 | 0.8335 | 1.0796 | 0.099 |
| H(2B1) | 8*e* | 0.2506 | 0.8864 | 0.7307 | 0.067 |
| H(3B1) | 8*e* | 0.0819 | 0.9957 | 0.8849 | 0.133 |
| H(3B2) | 8*e* | 0.0885 | 1.0746 | 0.8557 | 0.133 |
| H(2C1) | 8*e* | 0.1852 | 0.7201 | 0.7381 | 0.068 |
| H(3C1) | 8*e* | –0.0044 | 0.7716 | 0.8953 | 0.152 |
| H(3C2) | 8*e* | –0.0566 | 0.7089 | 0.8728 | 0.152 |

**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(1) | 8*e* | 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) | 8*e* | 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) | 8*e* | 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) | 8*e* | 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) | 8*e* | 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) | 8*e* | 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) | 8*e* | 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) | 8*e* | 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) | 8*e* | 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) | 8*e* | 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) | 8*e* | 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) | 8*e* | 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) | 8*e* | 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) | 8*e* | 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) | 8*e* | 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) | 8*e* | 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) | 8*e* | 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) | 8*e* | 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) | 8*e* | 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) | 8*e* | 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) | 8*e* | 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) | 8*e* | 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) | 8*e* | 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) | 8*e* | 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) | 8*e* | 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) | 8*e* | 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) | 8*e* | 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) | 8*e* | 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) | 8*e* | 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) | 8*e* | 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) | 8*e* | 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) | 8*e* | 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) | 8*e* | 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) | 8*e* | 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) | 8*e* | 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) | 8*e* | 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) | 8*e* | –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) | 8*e* | 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) | 8*e* | 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) |

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## References

1. Mukherjee, R.: Coordination chemistry with pyrazole-based chelating ligands: molecular structural aspects. Coord. Chem. Rev. **203** (2000) 151-218.
2. Marchetti, F.; Pettinari, C.; Pettinari, R.: Acylpyrazolone ligands: Synthesis, structures, metal coordination chemistry and applications. Coord. Chem. Rev. **249** (2005) 2909-2945.
3. Holló, B., Tomić, Z. D., Pogány, P., Kovács, A., Leovac, V. M., Mészáros Szécsényi, K.: Transition metal complexes with pyrazole-based ligands. Part 28. Synthesis, structural, DFT and thermal studies of cadmium(II) halides and zinc(II) chloride complexes with 3,5-dimethylpyrazole-1-carboxamidine. Polyhedron **28** (2009) 3881-3889.
4. Jaćimović, Ž. K.; Leovac, V. M.; Francuski, D. D.; Drašković; B. M.; Bogdanović, G. A.: Crystal structure of dicholoro-(3,5-dimethyl-1*H*-pyrazole-1-carboxamidine-*N*,*N'*)copper(II), $Cu(C_6H_{10}N_4)Cl_2$. Z. Kristallogr. NCS **224** (2009) 569-570.
5. Jaćimović, Ž. K.; Leovac, V. M.; Tomić, Z. D.: Crystal structure of hexakis($\mu_2$-chloro)-$\mu_4$-oxo-tetrakis((3,5-dimethylpyrazole)copper(II))ethanol tetrasolvate, $Cu_4OCl_6(C_5H_8N_2)_4 \cdot 4C_2H_5OH$. Z. Kristallogr. NCS **222** (2007) 246-248.
6. Mészáros Szécsényi, K.; Leovac, V. M.; Jaćimović, Ž. K.; Češljević, V. I.; Kovács, A.; Pokol, G.; Gál, S.: Transition metal complexes with pyrazole-based ligands. Part 8. Characterization and thermal decomposition of zinc(II) complexes with di- and trisubstituted pyrazoles. J. Therm. Anal. Calorim. **63** (2001) 723-732.
7. Jaćimović, Ž. K.; Tomić, Z. D.; Bogdanović, G. A.; Ivegeš, E. Z.; Leovac, V. M.: Transition metal complexes with pyrazole-derived ligands. X. $[Zn(CH_3COO)_2L_2] \cdot 2MeOH$ (L = 3-amino-5-phenylpyrazole). Acta Crystallogr. **C55** (1999) 1769-1771.
8. Day, J.; Marriott, K. E. R.; Kilner, C. A.; Halcrow, M. A.: The effect of different ligand substituents on the chemistry of a zinc–pyrazole anion host. New J. Chem. **34** (2010) 52-60.
9. Bondi, A.: van der Waals Volumes and Radii. J. Phys. Chem. **68** (1964) 441-451.
10. Sheldrick, G. M.: A short history of SHELX. Acta Crystallogr. **A64** (2008) 112-122.
11. Farrugia, L. J.: ORTEP-3 for Windows - a version of ORTEP-III with a Graphical User Interface (GUI) J. Appl. Crystallogr. **30** (1997) 565.
12. Farrugia, L. J.: WinGX suite for small-molecule single-crystal crystallography. J. Appl. Crystallogr. **32** (1999) 837-838.
13. Spek, A. L.: Single-crystal structure validation with the program PLATON. J. Appl. Crystallogr. **36** (2003) 7-13.