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Crystal structure of *catena*-poly[(μ_2 -1,5-dimethyl-2-phenyl-4-((pyridin-4-ylmethylene)amino)-1,2-dihydro-3*H*-pyrazol-3-one- κ^2 N:O)-bis(nitrato- κ^1 O)zinc(II)], $C_{17}H_{16}N_6O_7Zn$

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Abstract

$C_{17}H_{16}N_6O_7Zn$, orthorhombic, *Pbca* (no. 61), $a = 16.8032(17)$ Å, $b = 13.2780(13)$ Å, $c = 17.9636(18)$ Å, $V = 4007.9(7)$ Å³, $Z = 8$, $R_{gt}(F) = 0.0269$, $wR_{ref}(F^2) = 0.0879$, $T = 100(2)$ K.

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A part of the title crystal structure is shown in the figure. Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

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Table 1: Data collection and handling.

Crystal:	Yellow block
Size:	0.16 × 0.15 × 0.15 mm
Wavelength:	Mo K α radiation (0.71073 Å)
μ :	1.28 mm ⁻¹
Diffractometer, scan mode:	Broker APEX-II, φ and ω -scans
θ_{max} , completeness:	26°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int} :	24554, 3947, 0.024
Criterion for I_{obs} , $N(hkl)_{gt}$:	$I_{obs} > 2 \sigma(I_{obs})$, 3304
$N(param)_{refined}$:	282
Programs:	Broker programs [1], SHELX [2, 3]

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²).

Atom	<i>x</i>	<i>y</i>	<i>z</i>	U_{iso}^*/U_{eq}
Zn1	0.01196(2)	0.36781(2)	0.28615(2)	0.03709(10)
N1	0.17087(10)	0.55165(11)	0.25845(8)	0.0344(3)
N2	0.18554(10)	0.63572(11)	0.21560(8)	0.0342(4)
N3	0.11139(9)	0.47132(11)	0.07602(8)	0.0321(3)
N4	0.03749(10)	0.21868(12)	−0.12389(8)	0.0378(4)
N5	−0.06208(11)	0.34829(14)	0.15986(10)	0.0461(4)
N6	−0.10034(12)	0.49778(15)	0.33356(10)	0.0505(4)
O1	0.11776(8)	0.39324(9)	0.24269(7)	0.0352(3)
O2	−0.04930(10)	0.43697(12)	0.17667(9)	0.0537(4)
O3	−0.03998(11)	0.28103(11)	0.20754(8)	0.0518(4)
O4	−0.09325(13)	0.32321(16)	0.10212(10)	0.0792(6)
O5	−0.02440(10)	0.50181(13)	0.32944(10)	0.0616(5)
O6	−0.13077(13)	0.41371(15)	0.32587(11)	0.0775(6)
O7	−0.13777(13)	0.57356(15)	0.34608(12)	0.0822(6)
C1	0.18438(11)	0.54754(13)	0.33745(9)	0.0333(4)
C2	0.24915(14)	0.49464(17)	0.36296(11)	0.0497(5)
H2	0.2847	0.4629	0.3292	0.060*
C3	0.26149(15)	0.4886(2)	0.43904(12)	0.0593(6)
H3	0.3057	0.4519	0.4578	0.071*
C4	0.21009(15)	0.5352(2)	0.48754(11)	0.0553(6)
H4	0.2192	0.5314	0.5397	0.066*
C5	0.14616(14)	0.58685(18)	0.46101(11)	0.0515(5)
H5	0.1107	0.6185	0.4949	0.062*
C6	0.13217(12)	0.59383(16)	0.38542(11)	0.0424(5)
H6	0.0875	0.6298	0.3670	0.051*
C7	0.13952(11)	0.47760(13)	0.21547(9)	0.0293(4)
C8	0.13689(10)	0.51642(13)	0.14179(9)	0.0294(4)
C9	0.16589(12)	0.61454(13)	0.14528(10)	0.0331(4)
C10	0.17634(15)	0.68871(15)	0.08397(11)	0.0483(5)
H10A	0.1594	0.7555	0.1010	0.072*

Table 2 (continued)

Atom	x	y	z	U _{iso} [*] /U _{eq}
H10B	0.1440	0.6684	0.0411	0.072*
H10C	0.2325	0.6911	0.0694	0.072*
C11	0.23397(13)	0.71827(15)	0.24446(11)	0.0469(5)
H11A	0.2901	0.6983	0.2444	0.070*
H11B	0.2173	0.7341	0.2954	0.070*
H11C	0.2270	0.7778	0.2129	0.070*
C12	0.10160(12)	0.37604(13)	0.07382(10)	0.0358(4)
H12	0.1098	0.3375	0.1177	0.043*
C13	0.07787(11)	0.32475(14)	0.00473(10)	0.0345(4)
C14	0.05882(13)	0.37414(14)	−0.06070(10)	0.0394(4)
H14	0.0590	0.4456	−0.0624	0.047*
C15	0.03959(13)	0.31984(15)	−0.12331(10)	0.0395(4)
H15	0.0273	0.3552	−0.1678	0.047*
C16	0.05525(15)	0.17038(16)	−0.06032(12)	0.0508(6)
H16	0.0541	0.0988	−0.0599	0.061*
C17	0.07507(15)	0.22029(15)	0.00403(11)	0.0492(5)
H17	0.0868	0.1834	0.0480	0.059*

Source of materials

The title compound was synthesized by mixing 0.156 g (0.5 mmol) L4 (1,5-dimethyl-2-phenyl-4-((pyridin-4-ylmethylene)amino)-1,2-dihydro-3H-pyrazol-3-one), which was prepared according to the literature [4]): 0.196 g (0.65 mmol) Zn(NO₃)₂·6H₂O, 9 mL ethanol, 0.5 mL 2-propanol and 1 mL dichloromethane were poured in a 25 mL reactor. After shaking, the mixture was sealed and placed in an oven at 80° C. After 7 days, yellow granular crystals were grown with a yield of 90.45%. **Elemental Analysis** Data (% , measured/theoretical): C, 42.38/42.37; H, 3.33/3.30; N, 17.46/17.30. **IR** spectrum (cm^{−1}, KBr pellet): 3054(w), 1622(s), 1597(s), 1564 (s), 1477(s), 1427(versus), 1384(w), 1301(w), 1201(w), 1137(w), 1057(w), 1021(m), 947(m), 915(w), 823(s), 767(versus), 751(w), 732(w), 656(versus), 624(s), 597(w), 570(s), 531(m), 505(m), 470(w), 433(m).

Comment

Zinc(II) is an essential component of various metabolic enzymes and plays a very important role in catalysis and gene expression [5, 6]. Studies have shown that zinc (II) has a strong affinity for nitrogen and oxygen in biological systems, which attracts the interest in the coordination of zinc(II) [7–9].

Due to the biological activity and special chemical and physical properties, schiff base of 4-aminoantipyrine and its complexes are widely used in the fields of medicine, catalysis, analysis and materials. However, only a small number of metal complexes and structural characterization data of 4-aminoantipyrine based ligands have been reported, which makes the ligand coordination chemistry still have a great space for exploration.

The asymmetric unit of the title complex consists of one Zn(II) atom, one ligand L4, and two nitrate ligands (see the figure). In the coordination of the complex, the metal zinc(II) center adopts a tetrahedral coordination by the O and one N atom (see the figure). The coordinating atoms are derived from two nitrate ligands and one L4. Primarily both nitrate ligands coordinate in a monodentate mode. But there are two more weak Zn(II)···O interactions (see dashed lines in the figure). Thus a [4+2] coordination is detected. The bond length of Zn1-N4 is 2.0284(15) Å, which is similar to the bond lengths in other reports [10–14]. The bond length of Zn1-O1 is 1.9709(14) Å, and the bond length of Zn1-O3 is 2.0207(15) Å. The bond lengths and bond angles of the ligand L4 are in the normal range [9, 13, 14]. The distance between the two metal centers bridged by the L4 ligand is 9.51 Å.

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References

1. Bruker. SMART and SAINT. Bruker AXS Inc., Madison, WI, USA (2007).
2. Sheldrick, G. M.: Crystal refinement with SHELX. *Acta Crystallogr.* **C71** (2015) 3–8.
3. Sheldrick, G. M.: SHELXT – Integrated space-group and crystal-structure determination. *Acta Crystallogr.* **A71** (2015) 3–8.
4. Zhang, Y.; Zhao, J.; Li, R.; Jiang, Z.; Tang, G.: Experimental and DFT studies on the vibrational and electronic spectra of 1, 5-dimethyl-2-phenyl-4-[(pyridin-4-ylmethylene)-amino]-1, 2-dihydro-pyrazol-3-one. *Spectrochim. Acta.* **A 77** (2010) 732–739.
5. Aslkhademi, S.; Noshiranzadeh, N.; Sadjadi, M. S.; Mehrani, K.; Farhadyar, N.: Synthesis, crystal structure and investigation of the catalytic and spectroscopic properties of a Zn(II) complex with coumarin-hydrazone ligand. *Polyhedron* **160** (2019) 115–122.
6. Sutar, A. K.; Das, Y.; Pattnaik, S.; Routaray, A.; Nath, N.; Rath, P.; Maharana, T.: Novel polystyrene-anchored zinc complex: Efficient catalyst for phenol oxidation. *Chin. J. Catal.* **35** (2014) 1701–1708.
7. Tyagi, M.; Chandra, S.; Tyagi, P.; Akhtar, J.; Kandan, A.; Singh, B.: Synthesis, characterization and anti-fungal evaluation of Ni(II) and Cu(II) complexes with a derivative of 4-aminoantipyrine. *J. Taibah Univ. Sci.* **11** (2017) 110–120.
8. Palanimurugan, A.; Kulandaisamy, A.: DNA, *in vitro* antimicrobial/anticancer activities and biocidal based statistical analysis of Schiff base metal complexes derived from salicylaldehyde-4-imino-2,3-dimethyl-1-phenyl-3-pyrazolin-5-one and 2-aminothiazole. *J. Organomet. Chem.* **861** (2018) 263–274.

9. Pang, H.; Zou, X.; Tao, D.; Li, J.; Zhang, J.; Zhang, H.: Crystal structure of catena-poly[dichlorido-(μ_2 -1,5-dimethyl-2-phenyl-4-((pyridin-4-ylmethylene)amino)-1,2-dihydro-3H-pyrazol-3-one- $\kappa^2N:O$)cobalt(II)]-methanol (1/1), $C_{18}H_{20}Cl_2Co_4O_2$. Z. Kristallogr. NCS **234** (2019) 125–126.
10. Syed Ali Fathima, S.; Paulpandiyan, R.; Nagarajan, E. R.: Expanding biological excellence of aminoantipyrine derived novel metal complexes: Combined DNA interaction, antimicrobial, free radical scavenging studies and molecular docking simulations. J. Mol. Struct. **1178** (2019) 179–191.
11. Saber, M. R.; Mautner, F. A.: Zinc and manganese complexes with 4-aminoantipyrine. J. Mol. Struct. **1020** (2012) 177–182.
12. Wang, X.; Chen, F.; Chen, L.; Chen, J.; Jiang, W.; Cai, T.; Deng, Q.: Crystal structures and fluorescent properties of two linear trinuclear zinc(II) complexes. J. Mol. Struct. **842** (2007) 75–80.
13. Pang, H.: Crystal structure of catena-poly[dibromido-(μ_2 -1,5-dimethyl-2-phenyl-4-((pyridin-4-ylmethylene)amino)-1,2-dihydro-3H-pyrazol-3-one- $\kappa^2N:O$)zinc(II)], $C_{34}H_{32}Br_4N_8O_2Zn_2$. Z. Kristallogr. NCS **234** (2019) 559–561.
14. Zhang, H.; Zou, X.; Feng, Q.; Xu, B.; Pang, H.: Crystal structure of catena-poly[diiodido-(μ_2 -1,5-dimethyl-2-phenyl-4-((pyridin-3-ylmethylene)amino)-1,2-dihydro-3H-pyrazol-3-one- $\kappa^2N:O$)zinc(II)], $C_{17}H_{16}I_2N_4OZn$. Z. Kristallogr. NCS **233** (2018) 1061–1063.