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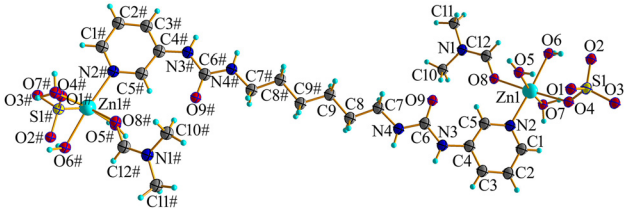
Crystal structure of Zn_2[(1,1′-(hexane-1,6-diyl) bis(3-(pyridin-3-yl)urea))·$(H_2O)_2$·$(DMF)_2$·$(SO_4)_2$], $C_{24}H_{50}N_8O_{18}S_2Zn_2$



https://doi.org/10.1515/ncrs-2023-0337
Received July 19, 2023; accepted October 25, 2023;
published online November 2, 2023

Abstract

$C_{24}H_{50}N_8O_{18}S_2Zn_2$, triclinic, $P\bar{1}$ (no. 2), a = 7.9797(5) Å, b = 10.4923(6) Å, c = 11.4835(7) Å, α = 97.512(2)°, β = 100.089(2)°, γ = 94.156(2)°, V = 933.98(10) Å^3, Z = 1, $R_{gt}(F)$ = 0.0382, $wR_{ref}(F^2)$ = 0.1202, T = 293(2) K.

CCDC no.: 2303478

The molecular 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.

1 Source of materials

Weigh 3-isocyanatopyridine (1.20 g, 10 mmol) and hexane-1,6-diamine (0.46 g, 4.0 mmol) and put it into a 50 mL round-bottom flask. Add 30 mL of ethanol solution, heat it and reflux for 12 h, cool to room temperature, separate out white solid, filter, wash with a small amount of ethanol for three times, dry in the vacuum, and obtain 1.07 g of white solid. The yield is 70 %. Weigh 1,1′-(hexane-1,6-diyl) bis(3-(pyridin-3-yl)urea) (0.18, 0.5 mmol) and dissolve it in 5 mL *N*,*N*–dimethylformamide. Weigh zinc(II) sulfate heptahydrate (0.29 g, 1 mmol) and dissolve it in 20 mL ethanol solution. Drop the ethanol solution into *N*,*N*–dimethylformamide, let it stand, evaporate naturally for 10 days, and separate out the crystal of X-ray diffraction with the suitable size.

Table 1: Data collection and handling.

Crystal:	Colourless block
Size:	0.20 × 0.17 × 0.14 mm
Wavelength:	Mo *K*α radiation (0.71073 Å)
μ:	1.48 mm^{-1}
Diffractometer, scan mode:	Bruker APEX-II, φ and ω
θ_{max}, completeness:	25.0°, 97 %
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	7866, 3200, 0.028
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\sigma(I_{obs})$, 2755
$N(param)_{refined}$:	255
Programs:	Olex2 [1], Bruker [2], SHELX [3], Diamond [4]

2 Experimental details

Crystal data, data collection and structure refinement details are summarized in Table 1. Using Olex2 [1], the structure was solved using Charge Flipping and refined with the ShelXL [3] refinement. All hydrogen atoms were positioned geometrically, with the d(C–H) = 0.97–0.99 Å, U_{iso}(H) = 1.2 times U_{eq}(C) and U_{iso}(H) = 1.5 times U_{eq}(O).

3 Comment

As a hydrogen bond donor, carbamido can provide the Y-type hydrogen bonding point (O–S–O) of diproton and Y-type anion such as (AcO^-) or tetrahedral anion (such as SO_4^{2-}), forming double hydrogen bonds [5]. At the same time, it is easy to form a hydrogen bond between carbamido and carbamido, and between carbamido and solvent molecules and assemble into the supramolecular compound with a novel structure [6]. Metal complexes containing carbamido are also an important category of anion receptors. It is possible to assemble simple monourea receptors into

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

Atom	*x*	*y*	*z*	U_{iso}*/U_{eq}
C1	0.2052 (5)	−0.4475 (4)	0.5896 (4)	0.0425 (10)
H1	0.0954	−0.4273	0.5610	0.051*
C2	0.2347 (5)	−0.5778 (4)	0.5857 (4)	0.0425 (10)
H2	0.1470	−0.6433	0.5554	0.051*
C3	0.3960 (5)	−0.6048 (4)	0.6276 (4)	0.0400 (10)
H3	0.4182	−0.6906	0.6276	0.048*
C4	0.5280 (5)	−0.5089 (4)	0.6702 (3)	0.0316 (8)
C5	0.4864 (5)	−0.3818 (4)	0.6707 (3)	0.0320 (9)
H5	0.5725	−0.3147	0.6988	0.038*
C6	0.8346 (5)	−0.4657 (4)	0.7694 (3)	0.0320 (9)
C7	1.1257 (5)	−0.4551 (4)	0.8785 (4)	0.0359 (9)
H7A	1.0999	−0.4003	0.9467	0.043*
H7B	1.1717	−0.3995	0.8281	0.043*
C8	1.2589 (5)	−0.5405 (4)	0.9221 (4)	0.0380 (9)
H8A	1.2782	−0.6010	0.8554	0.046*
H8B	1.2190	−0.5897	0.9795	0.046*
C9	1.4272 (5)	−0.4587 (4)	0.9809 (4)	0.0395 (10)
H9A	1.4611	−0.4044	0.9252	0.047*
H9B	1.4086	−0.4026	1.0507	0.047*
C10	0.7090 (6)	−0.1217 (5)	0.9892 (4)	0.0495 (12)
H10A	0.8070	−0.0984	1.0521	0.074*
H10B	0.6120	−0.1477	1.0226	0.074*
H10C	0.7317	−0.1920	0.9336	0.074*
C11	0.7904 (7)	0.1065 (5)	0.9626 (5)	0.0627 (15)
H11A	0.8761	0.0955	1.0295	0.094*
H11B	0.8442	0.1231	0.8969	0.094*
H11C	0.7282	0.1780	0.9847	0.094*
C12	0.5438 (5)	−0.0197 (4)	0.8374 (3)	0.0348 (9)
H12	0.5293	0.0510	0.7967	0.042*
N1	0.6728 (4)	−0.0108 (3)	0.9273 (3)	0.0386 (8)
N2	0.3258 (4)	−0.3525 (3)	0.6321 (3)	0.0322 (7)
N3	0.6893 (4)	−0.5447 (3)	0.7129 (3)	0.0359 (8)
H3A	0.7000	−0.6262	0.7029	0.043*
N4	0.9696 (4)	−0.5265 (3)	0.8119 (3)	0.0358 (8)
H4	0.9629	−0.6094	0.7992	0.043*
O1	0.3017 (3)	−0.1835 (2)	0.3221 (2)	0.0332 (6)
O2	0.1760 (3)	0.0086 (2)	0.3853 (2)	0.0311 (6)
O3	−0.0024 (3)	−0.1750 (3)	0.2652 (2)	0.0352 (6)
O4	0.1210 (3)	−0.1854 (2)	0.4695 (2)	0.0288 (6)
O5	0.4951 (4)	−0.1289 (3)	0.5568 (3)	0.0333 (6)
H5A	0.4633	−0.1374	0.4806	0.050*
O6	0.2550 (4)	0.0506 (3)	0.6395 (3)	0.0321 (6)
H6A	0.1720	0.0833	0.6811	0.048*
O7	0.0580 (3)	−0.1626 (3)	0.7150 (2)	0.0348 (6)
H7C	0.0078	−0.2409	0.7029	0.052*
H7D	−0.0185	−0.1194	0.6783	0.052*
O8	0.4399 (3)	−0.1170 (3)	0.8035 (2)	0.0334 (6)
O9	0.8409 (4)	−0.3468 (2)	0.7824 (3)	0.0402 (7)
S1	0.14856 (11)	−0.13440 (8)	0.35894 (8)	0.0251 (2)
Zn1	0.27788 (5)	−0.15537 (4)	0.63905 (4)	0.02635 (17)
H6B	0.222 (5)	0.050 (4)	0.577 (4)	0.019 (11)*
H5B	0.581 (6)	−0.092 (4)	0.576 (4)	0.032 (13)*

polyurea receptors with a special spatial configuration and pre-organize associated points to enhance the recognition of anions. For anion receptors based on metal coordination, the central metal coordinates with ligand and plays the role of pre-organized functional hydrogen [7]. The metal ions in the *ds* area have the electron configuration of d^{10} and different coordination numbers. They can use different coordination modes in the process of coordination with organic ligands and build complexes with diversified structures [8]. The nitrogen atoms on the pyridine ring have strong nucleophilic ability and may coordinate with transition metal ions and form complexes easily [9]. Therefore, we synthesized compounds containing carbamido and pyridine ring as functional groups. The title ligand is coordinated with Zn (II) ions to obtain Zn (II) complexes. The bond length and bond angle of the complexes are within the normal range. Each ligand coordinates with two Zn (II) ions as a bidentate ligand. Each Zn (II) ion coordinates with a nitrogen atom on the pyridine ring of the ligand, three oxygen atoms of water molecules, an oxygen atom of sulfate radical, and oxygen atom of *N*,*N*–dimethylformamide, forming a dinuclear complex. Different from the complex structure reported in the literature [10], two pyridine rings in the complex are completely parallel and the whole chain has a serrated structure. The coordinated water molecules in the complex and sulfate ions form intramolecular hydrogen bonds of O5–H5A···O1, O6–H6B···O2, and O6–H6B···O4, and intermolecular hydrogen bonds of O6–H6A···O3, O7–H7C···O9, and O5–H5B···O2. Nitrogen atoms and sulfate ions of carbamido form intermolecular hydrogen bonds of N3–H3A···O1 and N4–H4···O3.

Conflict of interest statement: The authors declare no conflicts of interest regarding this article.

Author contribution: All the authors have accepted responsibility for the entire content of this submitted manuscript and approved submission.

Research funding:

References

1. Dolomanov O. V., Bourhis L. J., Gildea R. J., Howard J. A. K., Puschmann H. OLEX2: a complete structure solution, refinement and analysis program. *J. Appl. Cryst.* 2009, *42*, 339–341.
2. Bruker. *APEX2*, *SAINT and SADABS*; Bruker AXS Inc.: Madison, Wisconsin, USA, 2012.
3. Sheldrick G. M. Crystal structure refinement with SHELXL. *Acta Cryst.* 2015, *C71*, 3–8.
4. Brandenburg K. DIAMOND. *Visual Crystal Structure Information System. Ver. 4.0*; Crystal Impact: Bonn, Germany, 2015.

5. Zhang Q. L., Yu Q., Xie H. F., Yang X. S. Crystal structure of 3-(3-(4-carboxyphenyl)ureido)pyridin-1-iumperchlorate, $C_{26}H_{24}C_{l2}N_6O_{14}$. *Z. Kristallogr. N. Cryst. Struct.* 2020, *235*, 133–134.
6. Liu C. Y., Xu C. Q., Yu J. G., Pui Y. S., Chen H. J., Wang S., Zhu A. D., Li J., Qian F. Impact of a single hydrogen substitution by fluorine on the molecular interaction and miscibility between sorafenib and polymers. *Mol. Pharmaceutics* 2019, *16*, 318–326.
7. Liang L., Zhao W., Yang X. J., Wu B. Anion-coordination-driven assembly. *Acc. Chem. Res.* 2022, *55*, 3218–3229.
8. Ni B., Cao H. Z., Zhang C. K., Li S. L., Zhang Q., Tian X. H., Li D. D., Wu J. Y., Tian Y. P. Activated type I and type II process for two-photon promoted ROS generation: the coordinated Zn matters. *Inorg. Chem.* 2020, *59*, 13671–13678.
9. Rams M., Lohmiller T., Böhme M., Jochim A., Foltyn M., Schnegg A., Plass W., Näther C. Weakening the interchain interactions in one dimensional cobalt(II) coordination polymers by preventing intermolecular hydrogen bonding. *Inorg. Chem.* 2023, *62*, 10420–10430.
10. Wu B., Liang J. J., Zhao Y. X., Li M. R., Li S. G., Liu Y. Y., Zhang Y. P., Yang X. J. Sulfate encapsulation in three-fold interpenetrated metal-organic frameworks with bis(pyridylurea) ligands. *CrystEngComm* 2010, *12*, 2129–2134.