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Crystal structure of bis(3-bromo-*N*-(1-(3-methylpyrazin-2-yl)ethylidene)benzohydrazonato- $\kappa^3 O,N,N'$)cadmium(II) hemihydrate, $C_{28}H_{25}N_8O_{2.5}Br_2Cd$

<https://doi.org/10.1515/ncrs-2020-0071>

Received February 04, 2020; accepted March 20, 2020; available online April 10, 2020

Abstract

$C_{28}H_{25}N_8O_{2.5}Br_2Cd$, triclinic, $P\bar{1}$ (no. 2), $a = 8.7233(16)$ Å, $b = 11.655(2)$ Å, $c = 15.374(3)$ Å, $\alpha = 82.225(4)^\circ$, $\beta = 86.125(3)^\circ$, $\gamma = 76.300(3)^\circ$, $V = 1503.6(5)$ Å³, $Z = 2$, $R_{gt}(F) = 0.0459$, $wR_{ref}(F^2) = 0.1102$, $T = 296$ K.

CCDC no.: 1991684

The molecular structure is shown in the figure (Hydrogen atoms are omitted for clarity). 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:	0.18 × 0.15 × 0.10 mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ :	3.43 mm ^{−1}
Diffraction, scan mode:	SMART, φ and ω
θ_{max} , completeness:	25.0°, 99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int} :	7570, 5260, 0.027
Criterion for I_{obs} , $N(hkl)_{gt}$:	$I_{obs} > 2 \sigma(I_{obs})$, 3313
$N(param)_{refined}$:	394
Programs:	Bruker [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}
Cd1	0.77249(5)	0.15841(4)	0.16443(3)	0.05310(17)
Br1	0.38586(13)	0.26730(9)	−0.32635(5)	0.1218(4)
Br2	1.22454(10)	0.52398(7)	0.45293(5)	0.0891(3)
O1	0.6185(5)	0.2768(3)	0.0614(2)	0.0603(11)
O2	0.9739(5)	0.2417(4)	0.1786(2)	0.0609(11)
O3 ^a	−0.029(2)	0.0385(18)	0.4804(16)	0.228(9)
N1	0.9074(6)	−0.0466(4)	0.1925(3)	0.0603(13)
N2	1.0829(8)	−0.2755(6)	0.2110(5)	0.0939(19)
N3	0.7687(5)	0.0582(4)	0.0476(3)	0.0464(11)
N4	0.6740(5)	0.1166(4)	−0.0207(3)	0.0489(12)
N5	0.5519(5)	0.1127(4)	0.2506(3)	0.0556(13)
N6	0.2994(6)	0.0656(5)	0.3526(4)	0.0716(15)
N7	0.7552(6)	0.2225(4)	0.2991(3)	0.0490(12)
N8	0.8674(5)	0.2805(4)	0.3167(3)	0.0513(12)
C1	0.9807(9)	−0.0949(7)	0.2657(4)	0.085(2)
H1	0.9746	−0.0495	0.3117	0.102*
C2	1.0643(10)	−0.2091(8)	0.2751(5)	0.104(3)
H2	1.1100	−0.2416	0.3285	0.125*
C3	1.0108(7)	−0.2298(6)	0.1362(5)	0.0647(17)
C4	0.9169(6)	−0.1128(5)	0.1263(4)	0.0481(14)
C5	1.0461(8)	−0.3125(6)	0.0673(5)	0.081(2)
H5A	1.1457	−0.3676	0.0781	0.122*
H5B	1.0509	−0.2675	0.0105	0.122*
H5C	0.9645	−0.3554	0.0692	0.122*
C6	0.8223(6)	−0.0546(5)	0.0502(3)	0.0440(13)
C7	0.7779(8)	−0.1232(6)	−0.0169(4)	0.075(2)
H7A	0.6780	−0.0814	−0.0405	0.112*
H7B	0.7703	−0.2007	0.0105	0.112*
H7C	0.8573	−0.1310	−0.0635	0.112*
C8	0.6063(6)	0.2271(5)	−0.0061(3)	0.0474(14)
C9	0.4997(6)	0.2985(5)	−0.0749(3)	0.0454(14)
C10	0.4951(7)	0.2581(5)	−0.1556(3)	0.0534(15)
H10	0.5624	0.1871	−0.1682	0.064*
C11	0.3909(8)	0.3235(6)	−0.2164(3)	0.0613(17)

Table 2 (continued)

Atom	x	y	z	U_{iso}^*/U_{eq}
C12	0.2910(8)	0.4296(6)	−0.2020(4)	0.0689(18)
H12	0.2209	0.4723	−0.2442	0.083*
C13	0.2976(8)	0.4710(5)	−0.1232(4)	0.0672(18)
H13	0.2326	0.5437	−0.1122	0.081*
C14	0.4000(7)	0.4060(5)	−0.0597(4)	0.0574(16)
H14	0.4017	0.4349	−0.0063	0.069*
C15	0.4537(7)	0.0592(6)	0.2212(4)	0.0633(17)
H15	0.4704	0.0365	0.1649	0.076*
C16	0.3279(8)	0.0364(6)	0.2713(5)	0.078(2)
H16	0.2594	−0.0009	0.2482	0.093*
C17	0.3994(7)	0.1203(5)	0.3835(4)	0.0567(16)
C18	0.3582(9)	0.1505(7)	0.4758(4)	0.089(2)
H18A	0.3234	0.2352	0.4747	0.134*
H18B	0.4496	0.1220	0.5109	0.134*
H18C	0.2753	0.1134	0.5006	0.134*
C19	0.5284(7)	0.1466(5)	0.3321(4)	0.0509(15)
C20	0.6453(7)	0.2096(5)	0.3567(4)	0.0567(16)
C21 ^b	0.663(5)	0.231(5)	0.4491(12)	0.115(12)
H21A ^b	0.7711	0.2025	0.4646	0.173*
H21B ^b	0.5978	0.1896	0.4883	0.173*
H21C ^b	0.6302	0.3148	0.4535	0.173*
C21A ^c	0.606(5)	0.289(4)	0.434(2)	0.075(10)
H21D ^c	0.6405	0.2415	0.4883	0.112*
H21E ^c	0.4942	0.3213	0.4385	0.112*
H21F ^c	0.6596	0.3531	0.4228	0.112*
C22	0.9713(6)	0.2845(5)	0.2506(3)	0.0449(14)
C23	1.0977(6)	0.3463(5)	0.2630(3)	0.0441(13)
C24	1.1010(7)	0.3988(5)	0.3390(4)	0.0507(14)
H24	1.0236	0.3957	0.3834	0.061*
C25	1.2198(7)	0.4550(5)	0.3475(4)	0.0562(16)
C26	1.3364(8)	0.4613(5)	0.2845(4)	0.0654(17)
H26	1.4156	0.5000	0.2919	0.078*
C27	1.3338(7)	0.4087(5)	0.2098(4)	0.0623(17)
H27	1.4129	0.4109	0.1663	0.075*
C28	1.2147(7)	0.3528(5)	0.1989(4)	0.0564(16)
H28	1.2134	0.3189	0.1476	0.068*

^aOccupancy: 0.5, ^bOccupancy: 0.59(7), ^cOccupancy: 0.41(7).

Source of material

3-Bromo-benzoic acid hydrazide (0.214 g, 1 mmol) and 3-methyl-2-aceto-pyrazine (0.136 g, 1 mmol) was dissolved in methanol (20 mL). The reaction mixture was refluxed for 1 h and cooled to room temperature. Then cadmium(II) acetate tetrahydrate (0.125 g, 0.5 mmol) was added. After stirring for 1 h, the mixture was filtered and set aside to crystallize for several days, giving black block crystals.

Experimental details

The structure was solved by direct methods and refined with the SHELX crystallographic software package [3]. The C21 atom occupied two positions, with the occupancy value of C21/C21A being 0.59/0.41. The hydrogen atoms for O3 atom of the crystal water are not added because of its occupancy value being 0.5. The other hydrogen atoms were placed at calculated positions and refined as riding atoms.

Comment

As one type of Schiff bases, hydrazones are ligands with interesting ligation properties due to the presence of several coordination sites, and are widely applied in many fields [4]. In particular, pyrazine-contained hydrazone have been used as fluorescent sensors for metal ions [4, 5]. In addition, metal complexes with pyrazine hydrazones have exhibited excellent biological activities [6, 7].

In the title structure, the asymmetric unit contains a neutral complex molecule and a half of a water molecule. The C=O bond of the hydrazone ligand is enolized, which could be confirmed by the bond length of C–O being 1.270(6)/1.277(6) Å [6, 7]. All bond distances and angles are in their normal ranges, and can be compared with those in previously reported complexes [8, 9]. The central Cd(II) ion with a distorted octahedral coordination geometry is surrounded by two anionic ligands with a ON₂ donor set, which is the most common coordination mode in pyrazine hydrazone-metals [6, 7].

References

1. Bruker. SMART and SAINT. Bruker AXS Inc., Madison, WI, USA (2007).
2. Sheldrick, G. M.: SHELXT-integrated space-group and crystal-structure determination. *Acta Crystallogr.* **A71** (2015) 3–8.
3. Sheldrick, G. M.: Crystal structure refinement with SHELX. *Acta Crystallogr.* **C71** (2015) 3–8.
4. Wang, Y.; Wang, W.-W.; Xue, W.-Z.; Wu, W.-N.; Zhao, X.-L.; Xu, Z.-Q.; Fan, Y.-C.; Xu, Z.-H.: A simple hydrazone as a fluorescent turn-on multianalyte (Al³⁺, Mg²⁺, Zn²⁺) sensor with different emission color in DMSO and resultant Al³⁺ complexes as a turn-off sensor for F[−] in aqueous solution. *J. Lumin.* **212** (2019) 191–199.
5. Li, C.-R.; Liao, Z.-C.; Qin, J.-C.; Wang, B.-D.; Yang, Z.-Y.: Study on 2-acetylpyrazine (pyridine-2-acetyl) hydrazone as a fluorescent sensor for Al³⁺. *J. Lumin.* **168** (2015) 330–333.
6. Hou, X.-F.; Zhao, X.-L.; Zhang, L.; Wu, W.-N.; Wang, Y.: Co(II)/Zn(II)/Cu(II) complexes containing hydrazone ligand bearing pyrazine unit: syntheses, crystal structures and fluorescence properties. *Chin. J. Inorg. Chem.* **34** (2018) 201–205.
7. Huang, W.; Li, Y.; Yong, J.; Liu, Y.; Wu, D.: Hydrazone-based cobalt complexes toward multielectron redox and spin crossover. *RSC Adv.* **8** (2018) 17159–17167.
8. Chang, H.-Q.; Jia, L.; Xu, J.; Xu, Z.-Q.; Chen, R.-H.; Wu, W.-N.; Bie, H.-Y.; Zhu, T.-F.; Ma, T.-L.; Wang, Y.: Syntheses, characterizations, antitumor activities and cell apoptosis induction of Cu(II), Zn(II) and Cd(II) complexes with hydrazone Schiff base derived from isonicotinohydrazide. *Inorg. Chem. Commun.* **57** (2015) 8–10.
9. Gao, X.-L.; Geng, R.-L.; Chen, P.: Crystal structure of bis[*N*-(1-pyrazin-2-ylethylidene)-cyanoacetic acid-hydrazone-*κ*³O, *N,N'*]zinc(II), C₁₈H₁₆N₁₀O₂Zn. *Z. Kristallogr. NCS* **235** (2020) 503–504.