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Crystal structure of bis[2-(1-(3-ethylpyrazin-2-yl) ethylidene)-1-tosylhydrazin-1-ido- κ^3 - N,N',O] copper(II), $C_{30}H_{34}N_8O_4S_2Cu$

Table 1: Data collection and handling.

Crystal:	Black block
Size:	0.20 × 0.15 × 0.14 mm
Wavelength:	Mo K α radiation (0.71073 Å)
μ :	0.86 mm ⁻¹
Diffractometer, scan mode:	CCD area detector, φ and ω
$\theta_{\max}$, completeness:	25.0°, 99%
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	16652, 11301, 0.032
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 6571
$N(\text{param})_{\text{refined}}$:	861
Programs:	Bruker [1], SHELX [2, 3]

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

Atom	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
Cu1	0.81054(4)	0.23205(3)	0.24996(3)	0.03989(15)
Cu2	0.70602(4)	0.74506(3)	0.25084(3)	0.04097(15)
S1	0.95449(8)	0.38096(7)	0.21701(6)	0.0456(3)
S2	0.95179(8)	0.04580(7)	0.25839(6)	0.0452(3)
S3	0.57061(8)	0.59510(7)	0.27652(6)	0.0452(3)
S4	0.55504(9)	0.92912(7)	0.24711(7)	0.0496(3)
N1	0.6969(3)	0.19204(19)	0.34899(19)	0.0434(8)
N2	0.5165(3)	0.1892(3)	0.4615(2)	0.0621(10)
N3	0.8105(2)	0.32217(19)	0.31840(18)	0.0363(8)
N4	0.8822(3)	0.3807(2)	0.30373(18)	0.0450(9)
N5	0.7104(3)	0.3029(2)	0.16641(19)	0.0459(9)
N6	0.5642(3)	0.3698(3)	0.0639(2)	0.0721(12)
N7	0.8092(2)	0.13939(19)	0.18532(18)	0.0369(8)
N8	0.8667(3)	0.05418(19)	0.19886(19)	0.0448(9)
N9	0.8210(3)	0.78957(19)	0.15680(18)	0.0417(8)
N10	1.0096(3)	0.7968(2)	0.0549(2)	0.0556(10)
N11	0.7140(2)	0.65769(19)	0.17867(18)	0.0377(8)
N12	0.6410(3)	0.5997(2)	0.18895(19)	0.0464(9)
N13	0.8122(2)	0.6761(2)	0.33369(18)	0.0424(8)
N14 ^a	0.9632(8)	0.6163(8)	0.4371(8)	0.063(3)
N15	0.6985(2)	0.83577(19)	0.31935(18)	0.0383(8)
N16	0.6420(3)	0.9205(2)	0.30538(19)	0.0458(9)
O1	0.9358(2)	0.31050(19)	0.17718(15)	0.0574(8)
O2	0.9443(2)	0.47107(19)	0.17291(18)	0.0718(10)
O3	0.9388(2)	0.12712(18)	0.29425(15)	0.0529(8)
O4	0.9523(2)	−0.03874(19)	0.31271(17)	0.0693(9)
O5	0.5914(2)	0.66279(19)	0.31954(15)	0.0582(8)
O6	0.5810(2)	0.50443(19)	0.31933(18)	0.0705(9)
O7	0.5710(2)	0.85079(19)	0.20675(16)	0.0601(8)
O8	0.5498(2)	1.01650(19)	0.19771(18)	0.0727(10)
N14A ^b	0.9186(13)	0.6004(14)	0.4605(13)	0.057(5)

<https://doi.org/10.1515/ncrs-2019-0909>

Received December 12, 2019; accepted January 31, 2020; available online March 5, 2020

Abstract

$C_{30}H_{34}N_8O_4S_2Cu$, triclinic, $P\bar{1}$ (no. 2), $a = 12.9537(9)$ Å, $b = 15.2802(10)$ Å, $c = 17.1041(11)$ Å, $\alpha = 78.748(1)^\circ$, $\beta = 79.684(1)^\circ$, $\gamma = 79.270(1)^\circ$, $V = 3226.4(4)$ Å³, $Z = 4$, $R_{\text{gt}}(F) = 0.0488$, $wR_{\text{ref}}(F^2) = 0.1178$, $T = 296$ K.

CCDC no.: 1981138

One of two crystallographically independent complexes 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.

Source of material

4-Methylbenzenesulfonyl hydrazide (0.188 g, 1 mmol) and 3-ethyl-2-aceto-pyrazine (0.150 g, 1 mmol) were dissolved in methanol (20 mL). The reaction mixture was refluxed for

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Table 2 (continued)

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso} */ <i>U</i> _{eq}
C1	0.6430(4)	0.1249(3)	0.3605(3)	0.0560(12)
H1A	0.6631	0.0800	0.3286	0.067*
C2	0.5555(4)	0.1212(3)	0.4210(3)	0.0652(14)
H2	0.5233	0.0697	0.4335	0.078*
C3	0.5693(3)	0.2602(3)	0.4471(2)	0.0507(11)
C4	0.6664(3)	0.2574(2)	0.3951(2)	0.0397(10)
C5	0.5129(4)	0.3409(3)	0.4845(3)	0.0699(14)
H5A	0.5240	0.3307	0.5404	0.084*
H5B	0.5446	0.3935	0.4570	0.084*
C6	0.3965(4)	0.3609(3)	0.4813(3)	0.0894(18)
H6A	0.3847	0.3773	0.4261	0.134*
H6B	0.3650	0.4099	0.5098	0.134*
H6C	0.3649	0.3082	0.5060	0.134*
C7	0.7415(3)	0.3221(2)	0.3841(2)	0.0381(10)
C8	0.7461(3)	0.3803(3)	0.4439(2)	0.0514(11)
H8A	0.8186	0.3765	0.4515	0.077*
H8B	0.7046	0.3599	0.4943	0.077*
H8C	0.7182	0.4418	0.4241	0.077*
C9	1.0882(3)	0.3541(3)	0.2339(2)	0.0434(10)
C10	1.1435(4)	0.4193(3)	0.2395(3)	0.0715(14)
H10	1.1104	0.4791	0.2366	0.086*
C11	1.2499(4)	0.3961(4)	0.2497(3)	0.0867(17)
H11	1.2870	0.4412	0.2540	0.104*
C12	1.3013(4)	0.3096(4)	0.2537(3)	0.0714(15)
C13	1.2437(4)	0.2459(4)	0.2462(3)	0.0812(16)
H13	1.2773	0.1864	0.2468	0.097*
C14	1.1381(4)	0.2669(3)	0.2378(3)	0.0675(14)
H14A	1.1006	0.2217	0.2348	0.081*
C15	1.4177(4)	0.2868(5)	0.2638(3)	0.120(2)
H15A	1.4462	0.3416	0.2592	0.180*
H15B	1.4561	0.2533	0.2228	0.180*
H15C	1.4246	0.2511	0.3160	0.180*
C16	0.6654(4)	0.3889(3)	0.1592(3)	0.0628(13)
H16A	0.6806	0.4263	0.1911	0.075*
C17	0.5961(4)	0.4224(3)	0.1041(3)	0.0793(17)
H17	0.5711	0.4841	0.0951	0.095*
C18	0.6065(4)	0.2816(3)	0.0732(3)	0.0529(12)
C19	0.6866(3)	0.2488(2)	0.1209(2)	0.0403(10)
C20	0.5534(4)	0.2242(3)	0.0345(3)	0.0716(15)
H20A	0.5963	0.2148	−0.0167	0.086*
H20B	0.5530	0.1655	0.0686	0.086*
C21	0.4434(4)	0.2614(4)	0.0200(3)	0.104(2)
H21A	0.4206	0.2253	−0.0117	0.156*
H21B	0.4408	0.3224	−0.0083	0.156*
H21C	0.3972	0.2608	0.0707	0.156*
C22	0.7522(3)	0.1581(2)	0.1273(2)	0.0376(9)
C23	0.7600(3)	0.0941(3)	0.0704(2)	0.0530(12)
H23A	0.8312	0.0619	0.0629	0.079*
H23B	0.7425	0.1271	0.0194	0.079*
H23C	0.7114	0.0520	0.0920	0.079*
C24	1.0759(3)	0.0380(3)	0.1961(2)	0.0408(10)
C25	1.0905(4)	0.0992(3)	0.1260(3)	0.0637(14)
H25	1.0349	0.1438	0.1112	0.076*
C26	1.1893(4)	0.0938(3)	0.0774(3)	0.0708(15)
H26	1.1995	0.1362	0.0308	0.085*

Table 2 (continued)

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso} */ <i>U</i> _{eq}
C27	1.2712(3)	0.0277(3)	0.0967(3)	0.0594(13)
C28	1.2539(4)	−0.0329(3)	0.1665(3)	0.0749(16)
H28	1.3089	−0.0786	0.1808	0.090*
C29	1.1568(4)	−0.0280(3)	0.2164(3)	0.0639(13)
H29	1.1472	−0.0698	0.2636	0.077*
C30	1.3793(4)	0.0214(4)	0.0449(3)	0.0861(17)
H30A	1.3726	0.0546	−0.0082	0.129*
H30B	1.4069	−0.0408	0.0415	0.129*
H30C	1.4267	0.0462	0.0685	0.129*
C31	0.8734(4)	0.8574(3)	0.1503(3)	0.0528(12)
H31	0.8486	0.9015	0.1827	0.063*
C32	0.9649(4)	0.8630(3)	0.0958(3)	0.0589(12)
H32	0.9963	0.9147	0.0874	0.071*
C33	0.9599(3)	0.7246(3)	0.0640(2)	0.0449(10)
C34	0.8589(3)	0.7250(2)	0.1103(2)	0.0377(10)
C35	1.0238(4)	0.6458(3)	0.0268(3)	0.0615(13)
H35A	0.9918	0.5922	0.0498	0.074*
H35B	1.0207	0.6578	−0.0307	0.074*
C36	1.1376(4)	0.6277(4)	0.0395(4)	0.107(2)
H36A	1.1712	0.6789	0.0135	0.160*
H36B	1.1733	0.5753	0.0170	0.160*
H36C	1.1413	0.6174	0.0962	0.160*
C37	0.7866(3)	0.6592(2)	0.1158(2)	0.0371(9)
C38	0.7905(3)	0.6035(3)	0.0522(2)	0.0507(11)
H38A	0.8312	0.5450	0.0665	0.076*
H38B	0.8233	0.6328	0.0014	0.076*
H38C	0.7197	0.5968	0.0478	0.076*
C39	0.4357(3)	0.6254(3)	0.2620(2)	0.0433(10)
C40	0.4042(4)	0.6862(3)	0.1980(3)	0.0752(15)
H40	0.4544	0.7088	0.1567	0.090*
C41	0.2962(4)	0.7142(4)	0.1948(3)	0.0872(18)
H41	0.2749	0.7552	0.1507	0.105*
C42	0.2213(4)	0.6831(3)	0.2547(3)	0.0661(14)
C43	0.2539(4)	0.6227(3)	0.3191(3)	0.0689(14)
H43	0.2038	0.6012	0.3610	0.083*
C44	0.3603(4)	0.5933(3)	0.3225(3)	0.0591(13)
H44	0.3813	0.5514	0.3662	0.071*
C45	0.1047(4)	0.7168(4)	0.2513(3)	0.0971(19)
H45A	0.0955	0.7785	0.2246	0.146*
H45B	0.0663	0.7128	0.3050	0.146*
H45C	0.0780	0.6804	0.2220	0.146*
C46	0.8642(3)	0.5925(3)	0.3399(3)	0.0529(12)
H46	0.8571	0.5559	0.3042	0.064*
C47	0.9284(4)	0.5589(3)	0.3979(3)	0.0720(15)
H47 ^a	0.9487	0.4968	0.4110	0.086*
H47 ^b	0.9784	0.5073	0.3933	0.086*
C48 ^a	0.9123(7)	0.7029(5)	0.4283(6)	0.044(2)
C48 ^b	0.8632(13)	0.6823(10)	0.4610(8)	0.051(4)
C49	0.8240(3)	0.7286(3)	0.3851(2)	0.0473(11)
C50 ^a	0.9605(6)	0.7624(5)	0.4671(5)	0.055(3)
H50A ^a	1.0369	0.7518	0.4512	0.065*
H50B ^a	0.9352	0.8248	0.4458	0.065*
C50A ^b	0.8677(13)	0.7210(9)	0.5341(8)	0.081(6)
H50C ^b	0.8087	0.7697	0.5406	0.097*
H50D ^b	0.8606	0.6746	0.5815	0.097*

Table 2 (continued)

Atom	x	y	z	U_{iso}^*/U_{eq}
C51 ^a	0.9381(11)	0.7504(15)	0.5566(7)	0.078(4)
H51A ^a	0.8627	0.7609	0.5735	0.117*
H51B ^a	0.9706	0.7925	0.5752	0.117*
H51C ^a	0.9665	0.6899	0.5789	0.117*
C51A ^b	0.969(2)	0.756(3)	0.5278(17)	0.172(17)
H51D ^b	0.9819	0.7950	0.4769	0.258*
H51E ^b	1.0268	0.7062	0.5316	0.258*
H51F ^b	0.9651	0.7892	0.5708	0.258*
C52	0.7558(3)	0.8188(2)	0.3775(2)	0.0392(10)
C53	0.7463(4)	0.8839(3)	0.4324(2)	0.0609(13)
H53A	0.7913	0.9284	0.4087	0.091*
H53B	0.7674	0.8528	0.4828	0.091*
H53C	0.6739	0.9131	0.4414	0.091*
C54	0.4325(3)	0.9285(3)	0.3116(2)	0.0455(11)
C55	0.3913(4)	0.8506(3)	0.3426(3)	0.0592(13)
H55	0.4275	0.7959	0.3289	0.071*
C56	0.2953(4)	0.8529(3)	0.3946(3)	0.0661(13)
H56	0.2671	0.7997	0.4139	0.079*
C57	0.2413(4)	0.9323(3)	0.4180(3)	0.0579(12)
C58	0.2846(4)	1.0100(3)	0.3861(3)	0.0704(15)
H58	0.2490	1.0645	0.4005	0.084*
C59	0.3789(4)	1.0094(3)	0.3335(3)	0.0629(13)
H59	0.4061	1.0628	0.3130	0.076*
C60	0.1376(4)	0.9347(4)	0.4742(3)	0.0923(18)
H60A	0.0807	0.9390	0.4439	0.138*
H60B	0.1264	0.9861	0.5009	0.138*
H60C	0.1396	0.8804	0.5135	0.138*

^aOccupancy: 0.618(11), ^bOccupancy: 0.382(11).

1h and cooled to room temperature. Then nickel(II) acetate tetrahydrate (0.124 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 [4]. The moiety involving the atoms N14, C48, C50, and C51 shows a disorder occupying two positions, with the occupancy value of N14/N14A, C48/C48A, C50/C50A or C51/C51A being 0.62/0.38. The hydrogen atoms were placed at calculated positions and refined as riding atoms with calculated isotropic displacement parameters.

Comment

Schiff bases, including hydrazones [1], semicarbazones [2] and thiosemicarbazones [3] derived from 2-aceto-pyrazine and their metal complexes have been widely investigated due to their excellent biological activities. However, sulfonyl hydrazones has been paid much less attention [4, 5]. In this work, the title complex was synthesized and characterized by X-ray diffraction.

In the title complex, the asymmetric unit contains two independent complex molecules. In each complex a six-coordinated Cu(II) ion adopts a distorted octahedron geometry with the donor sets of four nitrogen and two oxygen atoms from two sulfonyl hydrazone ligands. The structure is similar as those reported pyrazine sulfonyl hydrazone complexes [6–8]. As expected, there exist no classical hydrogen bonds in the crystal.

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