Crystal structure of 2,2'-diamino-5,5'-dimethyl-4,4'-bithiazolium dibromide monohydrate, $[(C_4H_6N_2S)_2]Br_2 \cdot H_2O$

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Abstract

$C_8H_{14}Br_2N_4OS_2$, monoclinic, $P12_1/c1$ (no. 14), $a = 13.406(1)$ Å, $b = 9.028(1)$ Å, $c = 12.145(1)$ Å, $\beta = 94.171(5)^\circ$, $V = 1465.9$ Å³, $Z = 4$, $R_{gt}(F) = 0.033$, $wR_{ref}(F^2) = 0.075$, $T = 120$ K.

Source of material

The 2,2'-diamino-5,5'-dimethyl-4,4'-bithiazole ligand was prepared from 2,5-dibromo-3,4-hexandion and thiourea and recrystallized from $CHCl_3$. The single crystals suitable for X-ray analysis were then obtained by slow evaporation from a benzene/acetonitrile mixture at room temperature. The light brown crystals were filtered off, washed with cold methanol and ethyl ether and dried in vacuum over P_4O_{10} (yield 73 %, m.p. 467 K). Elemental analysis: found – C, 23.53 %; H, 3.43 %; N, 13.65 %; calc. for $C_8H_{14}Br_2N_4OS_2$ – C, 23.64 %; H, 3.44 %; N, 13.79 %.

Discussion

Bithiazole derivation are of interest in the area of organic conductors and as materials for nonlinear optics [1]. In the solid, bithiazoles take a planar or near planar configuration. In solution from

planarity can occur owing to a balance between conjugative and steric intramolecular interaction. Evidence of chain flexibility in solution comes from thermo chromic and solvato chromic studies. In our aim to correlate stereoactive of valence shell lone pairs ($6s^2$) and overcrowding [2] in the coordination environment of lead(II) [3,4], bismuth(III) [5] and thallium(I) [6] complexes were studied. Now, we prepared the 2,2'-diamino-5,5'-dimethyl-4,4'-bithiazole ligand.

The cations in the crystal structure of the title compound have approximately C_2 symmetry. The C4—C4' bond length of 1.468(3) Å is close to the standard value for a single bond between three-bonded carbon atoms. The C—N bond lengths in the bithiazole ring are in the range 1.393(4) Å – 1.399(4) Å, which is shorter than the single bond length of 1.48 Å and longer than the typical C=N distances of 1.28 Å indicating partial double-bond character. This can be interpreted in term of conjugation in the heterocycle [7]. The unit cell constituents form a 3D network through intermolecular N—H...Br, O—H...Br and N—H...O bonds.

Table 1. Data collection and handling.

Crystal:	light-brown prism, size 0.24 × 0.28 × 0.31 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ :	58.05 cm ⁻¹
Diffractometer, scan mode:	Bruker SMART 1000 CCD, ϕ/ω
$2\theta_{max}$:	58°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	13698, 3843
Criterion for I_{obs} , $N(hkl)_{gt}$:	$I_{obs} > 2 \sigma(I_{obs})$, 3231
$N(param)_{refined}$:	156
Programs:	SHELXTL [8], SHELXL-97 [9]

Table 2. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	x	y	z	U_{iso}
H(2W)	4e	0.7146	0.1848	0.5311	0.049
H(1W)	4e	0.7605	0.1514	0.4213	0.049
H(3)	4e	0.7139	-0.5479	0.6382	0.026
H(6A)	4e	0.6733	-0.1555	0.3950	0.042
H(6B)	4e	0.6161	-0.0626	0.4834	0.042
H(6C)	4e	0.5537	-0.1593	0.3918	0.042
H(7B)	4e	0.4878	-0.5476	0.7408	0.032
H(7A)	4e	0.5776	-0.6563	0.7334	0.032
H(3')	4e	0.7781	-0.5950	0.4189	0.027
H(6'A)	4e	0.8085	-0.1300	0.6019	0.046
H(6'B)	4e	0.8660	-0.0512	0.5069	0.046
H(6'C)	4e	0.9280	-0.1346	0.6060	0.046
H(7'B)	4e	0.9910	-0.5666	0.2769	0.035
H(7'A)	4e	0.9042	-0.6702	0.2929	0.035

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Table 3. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	x	y	z	U ₁₁	U ₂₂	U ₃₃	U ₁₂	U ₁₃	U ₂₃
Br(1)	4e	0.65610(2)	0.09225(3)	0.69969(2)	0.0210(1)	0.0275(2)	0.0279(2)	0.0014(1)	0.0040(1)	−0.0008(1)
Br(2)	4e	0.86024(2)	0.05937(3)	0.28002(2)	0.0197(1)	0.0297(2)	0.0306(2)	0.0004(1)	0.0033(1)	−0.0037(1)
O(1W)	4e	0.7210(2)	0.2261(3)	0.4574(2)	0.051(1)	0.030(1)	0.044(1)	0.004(1)	0.022(1)	0.003(1)
S(1)	4e	0.51848(5)	−0.33069(8)	0.59065(6)	0.0182(3)	0.0216(4)	0.0261(3)	0.0034(2)	0.0042(2)	−0.0019(3)
C(2)	4e	0.5817(2)	−0.4817(3)	0.6477(2)	0.019(1)	0.021(1)	0.022(1)	0.001(1)	0.0032(9)	−0.005(1)
N(3)	4e	0.6718(2)	−0.4948(3)	0.6099(2)	0.017(1)	0.023(1)	0.025(1)	0.0046(8)	0.0037(8)	0.002(1)
C(4)	4e	0.6955(2)	−0.3822(3)	0.5371(2)	0.019(1)	0.024(2)	0.020(1)	0.001(1)	0.0026(9)	0.000(1)
C(5)	4e	0.6208(2)	−0.2836(3)	0.5159(2)	0.020(1)	0.023(2)	0.022(1)	0.001(1)	0.0021(9)	−0.002(1)
C(6)	4e	0.6155(2)	−0.1542(4)	0.4401(2)	0.026(1)	0.028(2)	0.029(1)	0.001(1)	0.001(1)	0.005(1)
N(7)	4e	0.5457(2)	−0.5738(3)	0.7192(2)	0.023(1)	0.024(1)	0.034(1)	0.0028(9)	0.011(1)	0.003(1)
S(1')	4e	0.95833(5)	−0.32323(8)	0.40987(6)	0.0215(3)	0.0226(4)	0.0275(3)	−0.0034(2)	0.0079(2)	−0.0013(3)
C(2')	4e	0.9014(2)	−0.4898(3)	0.3754(2)	0.020(1)	0.023(2)	0.024(1)	−0.000(1)	0.0025(9)	0.001(1)
N(3')	4e	0.8163(2)	−0.5050(3)	0.4243(2)	0.0164(9)	0.022(1)	0.030(1)	−0.0018(8)	0.0044(8)	−0.003(1)
C(4')	4e	0.7924(2)	−0.3836(3)	0.4882(2)	0.018(1)	0.023(1)	0.022(1)	0.002(1)	0.0028(9)	0.000(1)
C(5')	4e	0.8615(2)	−0.2752(3)	0.4926(2)	0.021(1)	0.024(2)	0.023(1)	0.001(1)	0.0034(9)	−0.002(1)
C(6')	4e	0.8664(2)	−0.1360(4)	0.5573(3)	0.029(1)	0.030(2)	0.033(2)	−0.003(1)	0.004(1)	−0.008(1)
N(7')	4e	0.9375(2)	−0.5896(3)	0.3095(2)	0.023(1)	0.027(1)	0.038(1)	−0.0043(9)	0.012(1)	−0.007(1)

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