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Crystal structure of dibromo-bis(1,3-imidazolidine-2-thione-*S*)zinc(II), $ZnBr_2(C_3H_6N_2S)_2$

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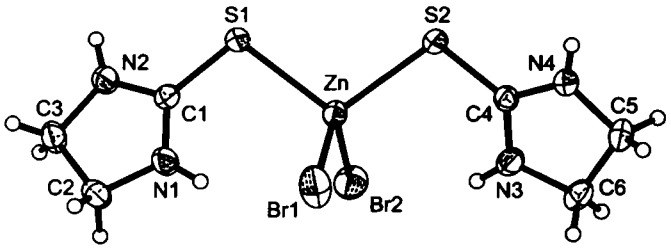

Abstract

$C_6H_{12}Br_2N_4S_2Zn$, monoclinic, $P12_1/n1$ (no. 14), a = 8.0984(5) Å, b = 13.4094(9) Å, c = 12.3230(8) Å, β = 100.983(1)°, V = 1313.7 Å^3, Z = 4, $R_{gt}(F)$ = 0.031, $wR_{ref}(F^2)$ = 0.074, T = 294 K.

Source of material

Zinc bromide was dissolved in minimum amount of water. Two molar equivalents of the thione were dissolved in methanol. The mixture of both solutions was refluxed for three hours and filtered. The filtrate was allowed to evaporate slowly and a white crystalline product was obtained (m.p. 175 °C).
Elemental analysis – found: C, 17.10 %; H, 2.68 %; N, 12.74 %; calc. for $C_6H_{12}N_4ZnBr_2S_2$: C, 16.77 %; H, 2.79 %; N, 13.08 %.

Experimental details

Hydrogen atoms were included at calculated positions using a riding model. An sp^2 hybridization was assumed for the nitrogen atoms of the NH groups.

Discussion

Complexes of heterocyclic ligands such as imidazolidine-2-thione (imt) and its derivatives with metal ions have been widely investigated in recent years. They are of special interest in bioinorganic chemistry because of the search for simple model compounds for metal-proteins [1-5]. These ligands exist in the N=C–SH and N–C=S forms exhibiting a thiol-thione equilibrium [6,7]. However, it has been established that the thione form dominates in the solid state [8]. We have studied extensively the interaction of metal ions with imidazolidine-2-thione and its derivatives [9-12].
In the title compound, the metal ion is bound to two bromide ions and the S atoms of two imidazolidine thione ligand molecules. The four-coordinate complex has a distorted tetrahedral geometry. The bond angles are in the range of 107.28(3)° – 111.60(2)° and the average Zn—S and Zn—Br bond lengths are 2.3450(8) Å and 2.3957(5) Å, respectively. The bond distances are in agreement with those reported for the complex dibromo-bis(1-*t*-butyl-4-imidazolidine-2-thione)zinc [13], the later being much more distorted (100.61(2)° – 121.48(2)°) probably due to the steric bulk of the ligand. The SCN_2 moieties of the two ligand molecules are essentially planar with the bond lengths of d(S1—C1) = 1.712(3) Å, d(C1—N1) = 1.315(4) Å, d(C1—N2) = 1.311(4) Å and d(S2—C4) = 1.715(3) Å, d(C4—N3) = 1.322(4) Å, d(C4—N4) = 1.313(4) Å. The corresponding bond lengths reported for the free ligand are d(S—C) = 1.688(3) Å, d(C—N) = 1.330(3) Å and 1.329(4) Å) [14]. The bromide ions have non-bonding contacts with the N atoms of the ligand molecules. The N···Br shortest distances are in the range of 3.392 Å – 3.485 Å, suggesting intra- and intermolecular hydrogen bonding. Such interactions are probably the main factor behind the distortion of the complex.

Table 1. Data collection and handling.

Crystal:	colorless parallelepiped, size 0.24 × 0.37 × 0.54 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	82.45 cm^{-1}
Diffractometer, scan mode:	Bruker SMART APEX CCD, ω/φ
$2\theta_{max}$:	56.56°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	11324, 3152
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 2719
$N(param)_{refined}$:	136
Program:	SHELXTL [15]

Table 2. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	x	y	z	U_{iso}
H(2A)	4e	0.6629	–0.0930	0.3597	0.054
H(2B)	4e	0.5621	–0.1834	0.2966	0.054
H(3A)	4e	0.5633	–0.2606	0.4572	0.050
H(3B)	4e	0.6684	–0.1715	0.5200	0.050
H(5A)	4e	–0.4772	0.2697	–0.0400	0.055
H(5B)	4e	–0.6072	0.1904	–0.0117	0.055
H(6A)	4e	–0.4672	0.0755	–0.0901	0.051
H(6B)	4e	–0.3179	0.1505	–0.0946	0.051
H(1)	4e	0.3759	–0.0409	0.2863	0.056
H(2)	4e	0.3869	–0.1661	0.5600	0.054
H(3)	4e	–0.2380	0.0255	0.0542	0.049
H(4)	4e	–0.4226	0.2567	0.1578	0.043

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Table 3. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Zn	4*e*	0.02748(4)	0.01578(3)	0.26250(3)	0.0295(2)	0.0340(2)	0.0300(2)	0.0025(1)	0.0026(1)	0.0029(1)
Br(1)	4*e*	0.22410(5)	0.11252(3)	0.18485(4)	0.0444(2)	0.0700(3)	0.0802(3)	0.0020(2)	0.0180(2)	0.0417(2)
Br(2)	4*e*	−0.05651(5)	−0.13168(3)	0.15567(3)	0.0625(2)	0.0409(2)	0.0478(2)	0.0029(2)	0.0014(2)	−0.0130(2)
S(1)	4*e*	0.1481(1)	−0.03512(7)	0.44181(6)	0.0351(4)	0.0574(5)	0.0279(4)	0.0162(4)	0.0088(3)	0.0071(3)
S(2)	4*e*	−0.2131(1)	0.10969(6)	0.27489(6)	0.0388(4)	0.0475(4)	0.0258(3)	0.0143(3)	0.0047(3)	0.0019(3)
C(1)	4*e*	0.3332(4)	−0.0895(2)	0.4258(2)	0.032(2)	0.033(1)	0.026(1)	0.002(1)	0.004(1)	−0.001(1)
C(2)	4*e*	0.5656(4)	−0.1359(3)	0.3563(3)	0.041(2)	0.051(2)	0.048(2)	0.014(2)	0.017(2)	0.006(2)
C(3)	4*e*	0.5685(4)	−0.1888(3)	0.4664(3)	0.034(2)	0.043(2)	0.049(2)	0.010(1)	0.007(1)	0.008(2)
C(4)	4*e*	−0.3076(3)	0.1333(2)	0.1406(2)	0.024(1)	0.034(1)	0.029(1)	−0.001(1)	0.005(1)	0.004(1)
C(5)	4*e*	−0.4888(4)	0.2068(3)	−0.0034(3)	0.037(2)	0.058(2)	0.039(2)	0.009(2)	−0.003(1)	0.008(2)
C(6)	4*e*	−0.3915(4)	0.1238(3)	−0.0482(3)	0.042(2)	0.051(2)	0.031(2)	−0.006(2)	−0.003(1)	−0.001(1)
N(1)	4*e*	0.4118(4)	−0.0782(2)	0.3426(2)	0.043(2)	0.060(2)	0.041(2)	0.021(1)	0.017(1)	0.019(1)
N(2)	4*e*	0.4176(4)	−0.1505(2)	0.4991(2)	0.045(2)	0.055(2)	0.036(1)	0.020(1)	0.014(1)	0.018(1)
N(3)	4*e*	−0.2954(4)	0.0796(2)	0.0525(2)	0.049(2)	0.043(2)	0.029(1)	0.011(1)	0.002(1)	−0.001(1)
N(4)	4*e*	−0.4073(3)	0.2101(2)	0.1128(2)	0.034(1)	0.040(1)	0.032(1)	0.009(1)	0.004(1)	0.001(1)

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