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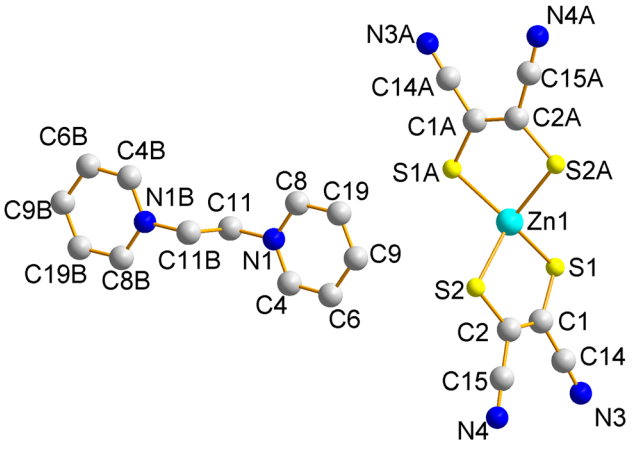
Crystal structure of 1,1′-(1,2-ethanediyl) bis(pyridin-1-ium) bis(1,2-dicyanoethene-1,2-dithiolato-κ^2*S*:*S*)zinc(II), $C_{20}H_{14}N_6ZnS_4$



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Abstract

$C_{20}H_{14}N_6ZnS_4$, monoclinic, *C*2/*c* (no. 15), a = 8.5063(13) Å, b = 12.3254(19) Å, c = 21.843(3) Å, β = 96.550(2)°, V = 2275.1(6) Å^3, Z = 4, $R_{gt}(F)$ = 0.0288, $wR_{ref}(F^2)$ = 0.0751, T = 293(2) K.

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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.

Source of material

All reagents and chemicals were purchased and used without further purification. The starting materials disodium maleonitriledithiolate and 1,1′-(1,2-ethanediyl) bis(pyridin-1-ium)bromide were synthesized following the literature procedures [4, 5]. An aqueous solution (15 mL) of 1,1′-(1,2-ethanediyl)bis(pyridin-1-ium) bromide (0.06872 g, 0.2 mmol) was added slowly to an aqueous solution (20 mL) of disodium maleonitriledithiolate (0.0751 g, 0.4 mmol) and $ZnCl_2$ (0.0277 g, 0.2 mmol). The mixture was stirred at room temperature for several minutes. A yellow precipitate was filtered off, washed by water and dried under vacuum. The precipitate was dissolved in DMF with ether diffusion. Two weeks later, yellow crystals were obtained.

Table 1: Data collection and handling.

Crystal:	Yellow block
Size:	0.25 × 0.22 × 0.18 mm
Wavelength:	MoKα radiation (0.71073 Å)
μ:	1.47 mm^{-1}
Diffractometer, scan mode:	φ and ω
θ_{max}, completeness:	28.3°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	8003, 2803, 0.030
Criterion for I_{obs}, $N(hkl)_{gt}$:	I_{obs} > 2 $\sigma(I_{obs})$, 2347
$N(param)_{refined}$:	141
Programs:	SHELX [1], Bruker [2], Olex2 [3]

Experimental details

Absorption corrections were applied by using multi-scan program. Hydrogen atoms were located in difference electron density maps, and treated as riding atoms. The U_{iso} values of the hydrogen atoms were set to 1.2U_{eq}(C).

Comment

The maleonitriledithiolate (mnt) complexes of transition metals are used as building units to construct molecule-based materials and therefore received extensive attention. Such compounds have potential applications in many areas [6–9]. Compared with the $[M(mnt)_2]^{n-}$ (M=Ni(II), Pd(II), etc.) complexes [10–15], the $[Zn(mnt)_2]^{2-}$ complexes are rarely studied. In our group we have

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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	0.3105 (2)	0.22106 (14)	0.02218 (9)	0.0480 (4)
H1A	0.258864	0.165748	0.044339	0.058*
H1B	0.387940	0.185819	−0.000463	0.058*
C2	0.52335 (19)	0.34949 (16)	0.05314 (9)	0.0495 (4)
H2	0.562609	0.334910	0.015969	0.059*
C3	0.6009 (2)	0.42103 (17)	0.09379 (9)	0.0548 (5)
H3	0.693464	0.454387	0.084614	0.066*
C4	0.5416 (2)	0.44325 (16)	0.14800 (9)	0.0526 (4)
H4	0.593911	0.491431	0.176097	0.063*
C5	0.4046 (2)	0.39398 (16)	0.16064 (8)	0.0536 (4)
H5	0.361924	0.409451	0.197014	0.064*
C6	0.3311 (2)	0.32185 (15)	0.11925 (8)	0.0491 (4)
H6	0.238678	0.287541	0.127800	0.059*
C7	0.6283 (2)	0.69776 (14)	0.37112 (9)	0.0480 (4)
C8	0.75635 (17)	0.65955 (14)	0.33999 (8)	0.0402 (3)
C9	0.86120 (18)	0.59011 (13)	0.37206 (7)	0.0396 (3)
C10	0.83284 (19)	0.56072 (15)	0.43318 (8)	0.0466 (4)
N1	0.39101 (15)	0.30020 (11)	0.06652 (7)	0.0409 (3)
N2	0.5274 (2)	0.72465 (17)	0.39775 (9)	0.0711 (5)
N3	0.8077 (2)	0.53589 (17)	0.48156 (8)	0.0690 (5)
S1	0.76266 (5)	0.70150 (5)	0.26494 (2)	0.05697 (14)
S2	1.02145 (5)	0.52863 (4)	0.34498 (2)	0.05630 (14)
Zn1	1.000000	0.61477 (3)	0.250000	0.04781 (11)

successfully obtained a series of complexes based on the maleonitriledithiolate (mnt) ligand. The preliminary work shows that it is important to select suitable cations to tune the stacking of the $[M(mnt)_2]^{n-}$ anion. Herein, we choose 1,1′-(1,2-ethanediyl)bis(pyridin- 1-ium) as organic divalent cation, to generate a new zinc(II) complex.

X-ray crystallography analyses reveal that the title complex shows a 3D framework linked through extensive hydrogen bonding interactions. The title complex crystallizes in the monoclinic space group *C*2/*c*. The asymmetric unit of complex consists of half of the $[Zn(mnt)_2]^{2-}$ and half of 1,1′-(1,2-ethanediyl)bis(pyridin-1-ium) dication. The Zn(II) ion is coordinated by four S atoms of mnt^{2-} ligands. The Zn(II) ion is in a slightly distorted tetrahedron. The Zn–S bond lengths range from 2.3190(6) to 2.3400(5) Å, and the S–Zn–S bond angles are in the range of 93.755(16)–125.64(3)° which are similar to the reported values [16, 17]. The anions and cations form segregated columns. The nearest distance between neighboring zinc(II) is different from that of the previously synthesized zinc(II) complexes [17], which could be caused by the different cations. C–H···N interactions are observed between anions and cations [18]. The three-dimensional supramolecular structure is formed by such weak interactions.

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