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Crystal structure of 1,1'-(1,4-phenylenebis(methylene))bis(pyridin-1-ium) bis(1,2-dicyanoethene-1,2-dithiolato- $k^2S:S$) zinc(II), $C_{26}H_{18}N_6ZnS_4$

Table 1: Data collection and handling.

Crystal:	Yellow block
Size:	0.22 × 0.21 × 0.18 mm
Wavelength:	Mo K α radiation (0.71073 Å)
μ :	1.26 mm ⁻¹
Diffractometer, scan mode:	φ and ω
$\theta_{\max}$, completeness:	28.3°, >99%
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	9681, 6567, 0.093
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 5260
$N(\text{param})_{\text{refined}}$:	334
Programs:	SHELX [1], Bruker [2]

Source of material

All reagents and chemicals were purchased from commercial sources and used without further purification. The starting materials disodium maleonitriledithiolate and 1,4-bis(methylpyridinium benzene bromide) were synthesized following the literature procedures [3, 4]. An aqueous solution (10 mL) of 1,1'-(1,4-phenylenebis(methylene)) bis(pyridin-1-ium) dibromide (BisPyBr₂) (0.0842 g, 0.2 mmol) was added slowly to an aqueous solution (15 mL) of disodium maleonitriledithiolate (0.0741 g, 0.4 mmol) and ZnCl₂ (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 solved in DMF with ether diffusion yielding yellow crystals after two weeks.

Experimental details

Absorption corrections were applied by using the multi-scan method. 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 $1.2U_{\text{eq}}(\text{C})$.

Comment

The maleonitriledithiolate (mnt) ligand is most often used for special structures and has great potential in diversified

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Abstract

$C_{26}H_{18}N_6ZnS_4$, triclinic, $P\bar{1}$ (no. 2), $a = 9.4677(13)$ Å, $b = 12.0147(17)$ Å, $c = 13.571(3)$ Å, $\alpha = 102.907(3)^\circ$, $\beta = 102.302(3)^\circ$, $\gamma = 110.419(2)^\circ$, $V = 1336.7(4)$ Å³, $Z = 2$, $R_{\text{gt}}(F) = 0.0441$, $wR_{\text{ref}}(F^2) = 0.1202$, $T = 296(2)$ K.

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

Atom	x	y	z	U _{iso} */U _{eq}
C1	0.9451 (3)	0.2105 (2)	0.05814 (18)	0.0456 (5)
C2	0.9456 (2)	0.2330 (2)	0.16656 (17)	0.0416 (4)
C3	0.8896 (3)	0.3176 (2)	0.20736 (18)	0.0427 (5)
C4	0.8312 (3)	0.3768 (2)	0.13851 (19)	0.0517 (6)
C5	1.1081 (3)	0.1708 (2)	0.70883 (18)	0.0462 (5)
C6	1.0242 (3)	0.1611 (2)	0.60428 (16)	0.0398 (4)
C7	0.8665 (3)	0.08420 (19)	0.55806 (17)	0.0402 (4)
C8	0.7812 (3)	0.0135 (2)	0.61560 (19)	0.0456 (5)
C9	0.8185 (3)	0.3409 (3)	0.6839 (3)	0.0652 (7)
H9	0.9070	0.3806	0.6648	0.078*
C10	0.8384 (4)	0.3195 (3)	0.7798 (3)	0.0754 (9)
H10	0.9401	0.3441	0.8256	0.090*
C11	0.7076 (4)	0.2615 (3)	0.8076 (2)	0.0656 (7)
H11	0.7197	0.2483	0.8733	0.079*
C12	0.5599 (3)	0.2233 (3)	0.7382 (2)	0.0581 (6)
H12	0.4700	0.1823	0.7553	0.070*
C13	0.5450 (3)	0.2456 (2)	0.6431 (2)	0.0508 (5)
H13	0.4442	0.2188	0.5952	0.061*
C14	0.6497 (4)	0.3285 (3)	0.5137 (2)	0.0600 (7)
H14A	0.5848	0.2492	0.4569	0.072*
H14B	0.7521	0.3634	0.5030	0.072*
C15	0.5708 (3)	0.4173 (2)	0.50768 (19)	0.0458 (5)
C16	0.6505 (3)	0.5423 (2)	0.5690 (2)	0.0504 (5)
H16	0.7525	0.5712	0.6161	0.060*
C17	0.4190 (3)	0.3753 (2)	0.4385 (2)	0.0494 (5)
H17	0.3636	0.2911	0.3969	0.059*
C18	0.3202 (3)	0.3055 (3)	0.0460 (2)	0.0557 (6)
H18	0.2415	0.2608	-0.0198	0.067*
C19	0.3896 (4)	0.4352 (3)	0.0796 (3)	0.0688 (8)
H19	0.3565	0.4782	0.0372	0.083*
C20	0.5072 (3)	0.4997 (3)	0.1754 (3)	0.0641 (7)
H20	0.5559	0.5869	0.1986	0.077*
C21	0.5525 (3)	0.4348 (3)	0.2370 (2)	0.0611 (6)
H21	0.6326	0.4774	0.3025	0.073*
C22	0.4805 (3)	0.3087 (2)	0.20223 (18)	0.0516 (5)
H22	0.5109	0.2649	0.2448	0.062*
C23	0.2920 (3)	0.1048 (2)	0.0721 (2)	0.0613 (7)
H23A	0.1937	0.0736	0.0139	0.074*
H23B	0.2664	0.0767	0.1303	0.074*
C24	0.4017 (3)	0.0515 (2)	0.0355 (2)	0.0462 (5)
C25	0.4100 (3)	0.0389 (2)	-0.0667 (2)	0.0539 (6)
H25	0.3491	0.0643	-0.1124	0.065*
C26	0.4905 (3)	0.0118 (2)	0.1012 (2)	0.0540 (6)
H26	0.4841	0.0188	0.1696	0.065*
N1	0.6731 (2)	0.30538 (17)	0.61782 (15)	0.0449 (4)
N2	0.3663 (2)	0.24471 (17)	0.10803 (14)	0.0407 (4)
N3	0.7826 (3)	0.4239 (3)	0.0834 (2)	0.0769 (8)
N4	0.9460 (3)	0.1911 (3)	-0.02791 (18)	0.0636 (6)
N5	0.7066 (3)	-0.0423 (2)	0.6590 (2)	0.0623 (6)
N6	1.1847 (3)	0.1848 (2)	0.79231 (17)	0.0673 (6)
S1	1.01499 (8)	0.14502 (6)	0.23146 (5)	0.04983 (15)
S2	0.88203 (8)	0.35786 (6)	0.33647 (5)	0.05154 (16)
S3	1.14199 (6)	0.25819 (6)	0.54831 (5)	0.04838 (15)
S4	0.75176 (7)	0.06525 (6)	0.43227 (5)	0.04942 (15)
Zn1	0.95002 (3)	0.20276 (2)	0.38601 (2)	0.04353 (10)

applications, such as conducting, magnetic materials, dyes and non-linear optics [5–8], and so on. Compared with the [Ni(mnt)₂]ⁿ⁻ complexes [9–11], the [Zn(mnt)₂]²⁻ complexes are less studied.

The title complex crystallizes in triclinic *P* $\bar{1}$ space group. The asymmetric unit of complex consists of one [Zn(mnt)₂]²⁻ and two halves of the BisPy dication. The Zn²⁺ ion is surrounded by four sulfur atoms from two mnt²⁻ ligands, and its coordination geometry is a slightly distorted tetrahedron. The Zn–S bond lengths range from 2.3222 (7) to 2.3561 (6) Å, and the S–Zn–S bond angles are in the range of 92.76 (2)–123.67 (3). All of these geometric parameters are comparable to that in the reported [Zn(mnt)₂]²⁻ complex [12]. The anions and cations form segregated columns. Weak C–H···N interactions are observed in the title structure [13]. A supramolecular network structure is thus constructed through weak intermolecular interactions.

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References

- Sheldrick G. M. Crystal structure refinement with SHELXL. *Acta Crystallogr.* 2015, *C71*, 3–8.
- Bruker. SMART APEX–II CCD; Bruker AXS Inc: Madison, WI, USA, 2006.
- Simmons H. E., Blomstrom D. C., Vest R. D. Thiocyanocarbons. II. chemistry of disodium dimercaptomaleonitrile. *J. Am. Chem. Soc.* 1962, *84*, 4756–4771.
- Musilek K., Komloova M., Zavadova V., Holas O., Hrabanova M., Pohanka M., Dohnal V., Nachon F., Dolezal M., Kuca K., Jung Y. S. Preparation and in vitro screening of symmetrical bispyridinium cholinesterase inhibitors bearing different connecting linkage-initial study for Myasthenia gravis implications. *Bioorg. Med. Chem. Lett.* 2010, *20*, 1763–1766.
- Mueller–Westerhoff U. T., Vance B., Ihl Yoon D. The synthesis of dithiolenes dyes with strong near-IR absorption. *Tetrahedron* 1991, *47*, 909–932.
- Tanaka H., Okano Y., Kobayashi H., Suzuki W., Kobayashi A. A three-dimensional synthetic metallic crystal composed of single-component molecules. *Science* 2001, *291*, 285–287.
- Bigoli F., Chen C. T., Wu W. C., Deplano P., Mercuri M. L., Pellinghelli M. A., Pilia L., Pintus G., Serpe A., Trogu E. F. [Ni(R₂pipdt)₂](BF₄)₂ (R₂pipdt = 1,4-disubstituted-piperazine-3,2-dithione) as useful precursors of mixed-ligand dithiolenes of interest for non-linear optics. *Chem. Commun.* 2001, 2246–2247; <https://doi.org/10.1039/b106064n>.

8. Robertson N., Cronin L. Metal bis-1,2-dithiolene complexes in conducting or magnetic crystalline assemblies. *Coord. Chem. Rev.* 2002, 227, 93–127.
9. Duan H. B., Ren X. M., Meng Q. J. One-dimensional (1D) $[Ni(mnt)_2]^-$ based spin–Peierls-like complexes: structural, magnetic and transition properties. *Coord. Chem. Rev.* 2010, 254, 1509–1522.
10. Wang P. Crystal structure of $Mn(II)(H_2O)(2,13\text{-dimethyl-3,6,9,12,18-pentaazabicyclo[12.3.1]octadeca-1(18),2,12,14,16-pentaene})\text{-bis(maleonitriledithiolate)nickel(II)}$, $C_{23}H_{25}MnN_9NiOS_4$. *Z. Kristallogr. NCS* 2012, 227, 511–512.
11. Yan W. H., Pan H. Y. Crystal structure of 1,4- bis(methylpyridinium benzene) bis(1,2-dicyanoethene-1,2-dithiolato- $\kappa^2S:S$)nickel(II), $C_{26}H_{18}N_6NiS_4$. *Z. Kristallogr. NCS* 2021, 236, 107–108.
12. Liu X., Liu J. L., Cai B., Ren X. M. A charge transfer salt consisted of bis(maleonitriledithiolato)zincate dianion and 1,1'-didecyl- 4,4'-bipyridinium exhibiting uncommon nematic mesophase behavior. *Inorg. Chem. Commun.* 2011, 14, 1428–1431.
13. Jeffrey G. A. Hydrogen-bonding: an update. *Crystallogr. Rev.* 2003, 9, 135–176.