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Crystal structure of 1,1'-(1,2-ethanediyl)bis(pyridin-1-ium) bis(1,2-dicyanoethene-1,2-dithiolato- $\kappa^2S:S$)nickel(II), $C_{20}H_{14}N_6NiS_4$

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Abstract

$C_{20}H_{14}N_6NiS_4$, triclinic, $P\bar{1}$ (no. 2), $a = 8.519(3)$ Å, $b = 8.5956(16)$ Å, $c = 8.6531(17)$ Å, $\alpha = 116.404(3)^\circ$, $\beta = 94.574(4)^\circ$, $\gamma = 103.031(4)^\circ$, $V = 541.0(2)$ Å³, $Z = 1$, $R_{\text{gt}}(F) = 0.0445$, $wR_{\text{ref}}(F^2) = 0.1147$, $T = 296.15$ 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.

Source of material

All reagents and chemicals were purchased from commercial sources 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 [3, 4]. An aqueous solution (10 mL) of 1,1'-(1,2-ethanediyl)bis(pyridin-1-ium)bromide (0.068 g, 0.2 mmol) was added slowly to an aqueous solution (20 mL) of disodium maleonitriledithiolate (0.074 g, 0.4 mmol) and $NiCl_2 \cdot 6H_2O$ (0.048 g, 0.2 mmol), and the mixture was stirred at room temperature

Table 1: Data collection and handling.

Crystal:	Red block
Size:	$0.25 \times 0.21 \times 0.17$ mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ :	1.30 mm^{-1}
Diffractometer, scan mode:	φ and ω
θ_{max} , completeness:	28.5° , 99%
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	3974, 2708, 0.027
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 2157
$N(\text{param})_{\text{refined}}$:	142
Programs:	SHELX [1], Bruker [2]

for several minutes. A red precipitate was filtered off, washed by water and dried under vacuum. The precipitate was dissolved in DMF with ether diffusion. Two weeks later yielded red crystals.

Experimental details

Absorption corrections were applied by using multi-scan program. The structure was refined based on F^2 with the SHELXL software package. Hydrogen atoms were treated as riding atoms. The U_{iso} values of the hydrogen atoms were set to $1.2U_{\text{eq}}$ (C).

Comment

The development of polythiophene complexes have captured much attention because of their variable structures and properties on molecular conductors, magnets, catalysts, and nonlinear optical, etc. [5–9]. The maleonitriledithiolate (mnt) ligand is one of the most popular ligands in this area. It is crucial to design and prepare suitable multifunctional salts to achieve new molecular arrangements, resulting in developing unique stacking schemes of $[M(\text{mnt})_2]^{2-}$ anions and properties. Recently, our effort have been devoted to maleonitriledithiolate complexes using different cations [10–12].

The title complex crystallizes in triclinic $P\bar{1}$ space group, with one half of $[\text{Ni}(\text{mnt})_2]^{2-}$ dianion and one half of

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Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ($\text{\AA}^2$).

Atom	x	y	z	U_{iso}^*/U_{eq}
C1	0.2296 (4)	0.3660 (4)	0.5637 (4)	0.0185 (6)
C2	0.2905 (4)	0.5305 (4)	0.5563 (4)	0.0204 (7)
C3	0.3197 (4)	0.3216 (4)	0.6662 (4)	0.0175 (6)
C4	0.4793 (4)	0.4371 (4)	0.7693 (4)	0.0194 (7)
C5	1.0133 (4)	1.4167 (4)	0.9267 (4)	0.0187 (7)
H5A	1.006242	1.425756	0.818658	0.022*
H5B	1.121933	1.408168	0.957223	0.022*
C6	0.7543 (4)	1.1766 (4)	0.7662 (4)	0.0178 (6)
H6	0.744419	1.223846	0.689105	0.021*
C7	0.6339 (4)	1.0267 (4)	0.7451 (4)	0.0225 (7)
H7	0.541736	0.973156	0.653955	0.027*
C8	0.6501 (5)	0.9569 (5)	0.8581 (5)	0.0303 (8)
H8	0.569174	0.856050	0.843959	0.036*
C9	0.7887 (5)	1.0377 (5)	0.9949 (5)	0.0359 (10)
H9	0.801802	0.991621	1.072584	0.043*
C10	0.9051 (5)	1.1868 (5)	1.0116 (5)	0.0302 (8)
H10	0.998230	1.242254	1.101628	0.036*
N1	0.3333 (4)	0.6627 (4)	0.5477 (4)	0.0259 (6)
N2	0.6084 (4)	0.5299 (4)	0.8526 (4)	0.0288 (7)
N3	0.8864 (3)	1.2536 (4)	0.9002 (3)	0.0179 (6)
Ni1	0.000000	0.000000	0.500000	0.01449 (16)
S1	0.03407 (10)	0.22651 (11)	0.44255 (10)	0.01830 (19)
S2	0.24209 (10)	0.11917 (11)	0.67378 (10)	0.01782 (19)

1,1'-(1,2-ethanediyl)bis(pyridin-1-ium) dication in the asymmetric unit (see the Figure). Each Ni(II) ion is coordinated by four sulfur atoms, and exhibits a quasi-square planar coordination geometry. The Ni1–S bond lengths and S–Ni1–S bond angles are in 2.1787(10)–2.1798(9) Å and 88.12(3)–180.0°, respectively. These parameters are comparable to the reported $[Ni(mnt)_2]^{2-}$ complexes [11]. The anions and cations form segregated columns. The C–H···N interactions are observed between anions and cations [13]. The three-dimensional supramolecular structure is formed by such weak 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., rabinova 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.
- Coomber A. T., Beljonne D., Friend R. H., Brédas J. L., Charlton A., Robertson N., Underbill A. E., Kurmoo M., Day P. Intermolecular interactions in the molecular ferromagnetic $NH_4Ni(mnt)_2 \cdot H_2O$. *Nature* 1996, *380*, 144–146.
- Robertson N., Cronin L. Metal bis-1,2-dithiolene complexes in conducting or magnetic crystalline assemblies. *Coord. Chem. Rev.* 2002, *227*, 93–127.
- 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.
- Wang P. Crystal structure of $Mn(II)(H_2O)(2,13\text{-dimethyl-}3,6,9,12,18\text{-pentaazabicyclo}[12.3.1]\text{octadeca-}1(18),2,12,14,16\text{-pentaene})$ bis (maleonitriledithiolate)nickel(II), $C_{23}H_{25}MnN_9NiOS_4$. *Z. Kristallogr. N. Cryst. Struct.* 2012, *227*, 511–512.
- Perochon R., Barriere F., Jeannin O., Piekara-Sady L., Fourmigue M. A radical mixed-ligand gold bis(dithiolene) complex. *Chem. Commun.* 2021, *57*, 1615–1618.
- Yan W. H., Ji E. Y., Shen M. L., Li Z. Y., Li X., Xu X. L. Two ion-pair complexes constructed by $[M(mnt)_2]^{n-}$ ($M = Ni, Co$, $mnt =$ maleonitriledithiolate): syntheses, characterization and thermal stability. *Chin. J. Struct. Chem.* 2015, *34*, 306–312.
- 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. N. Cryst. Struct.* 2021, *236*, 107–108.
- Yan W. H., Liu X. G., Shen M. L., Pan H. Y. Crystal structure of 1,1'-(1,4-phenylenebis(methylene))bis(pyridin-1-ium) bis (1,2-dicyanoethene-1,2-dithiolato- $\kappa^2S:S$) zinc(II), $C_{26}H_{18}N_6ZnS_4$. *Z. Kristallogr. N. Cryst. Struct.* 2021, *236*, 533–535.
- Jeffrey G. A. Hydrogen-bonding: an update. *Crystallogr. Rev.* 2003, *9*, 135–176.