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Crystal structure of 1,1'-(methylene)bis(pyridin-1-ium) bis(1,2-dicyanoethene-1,2-dithiolato- $\kappa^2S:S$) nickel(II), $C_{42}H_{30}N_{14}Ni_2S_8$

<https://doi.org/10.1515/ncrs-2021-0434>

Received November 9, 2021; accepted January 13, 2022;

published online February 2, 2022

Abstract

$C_{42}H_{30}N_{14}Ni_2S_8$, triclinic, $P\bar{1}$ (no. 2), $a = 9.5083(17)$ Å, $b = 10.744(2)$ Å, $c = 12.188(2)$ Å, $\alpha = 80.109(4)^\circ$, $\beta = 84.876(4)^\circ$, $\gamma = 88.758(3)^\circ$, $V = 1221.7(4)$ Å³, $Z = 1$, $R_{gt}(F) = 0.0268$, $wR_{ref}(F^2) = 0.0701$, $T = 296.15$ K.

CCDC no.: 2141881

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'-(methylene)bis(pyridin-1-ium)bromide were synthesized following the literature procedures [3, 4]. An aqueous

Table 1: Data collection and handling.

Crystal:	Red block
Size:	0.23 × 0.20 × 0.18 mm
Wavelength:	Mo K α radiation (0.71073 Å)
μ :	1.16 mm ⁻¹
Diffractometer, scan mode:	φ and ω
θ_{max} , completeness:	27.7°, 99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int} :	14,613, 5581, 0.027
Criterion for I_{obs} , $N(hkl)_{gt}$:	$I_{obs} > 2 \sigma(I_{obs})$, 4890
$N(param)_{refined}$:	302
Programs:	SHELX [1], Bruker [2]

solution (10 mL) of 1,1'-(methylene)bis(pyridin-1-ium) bromide (0.0661 g, 0.2 mmol) was added slowly to an aqueous solution (15 mL) of disodium maleonitriledithiolate (0.0712 g, 0.4 mmol) and $NiCl_2 \cdot 6H_2O$ (0.0463 g, 0.2 mmol), and the mixture was stirred at room temperature for several minutes. A red precipitate was filtered off, washed by water and dried under vacuum. The precipitate was dissolved in acetonitrile and dimethylformamide with ether diffusion. Fourteen days later red crystals were obtained.

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 $1.2U_{eq}$ (C).

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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	0.42192 (18)	0.75001 (15)	0.93099 (13)	0.0370 (3)
C2	0.56160 (17)	0.76129 (15)	0.89510 (13)	0.0360 (3)
C3	0.63737 (19)	0.66774 (17)	0.84277 (16)	0.0446 (4)
C4	0.3417 (2)	0.64191 (18)	0.92029 (16)	0.0471 (4)
C5	0.88675 (17)	0.33807 (16)	0.80122 (15)	0.0385 (4)
H5	0.839258	0.413493	0.778913	0.046*
C6	0.97260 (18)	0.32824 (18)	0.88625 (16)	0.0468 (4)
H6	0.983144	0.396523	0.922421	0.056*
C7	1.04376 (18)	0.2163 (2)	0.91831 (16)	0.0494 (5)
H7	1.102710	0.208706	0.976057	0.059*
C8	1.02670 (18)	0.11634 (18)	0.86416 (16)	0.0476 (4)
H8	1.074516	0.040672	0.884728	0.057*
C9	0.93922 (17)	0.12861 (16)	0.78002 (15)	0.0401 (4)
H9	0.926818	0.060871	0.743592	0.048*
C10	0.78502 (17)	0.25269 (17)	0.65288 (13)	0.0383 (4)
H10A	0.829266	0.313223	0.591997	0.046*
H10B	0.780618	0.172223	0.627467	0.046*
C11	0.60006 (19)	0.41425 (16)	0.64345 (16)	0.0443 (4)
H11	0.662705	0.469753	0.597527	0.053*
C12	0.4644 (2)	0.45276 (18)	0.67121 (18)	0.0529 (5)
H12	0.434572	0.534344	0.644006	0.063*
C13	0.3736 (2)	0.3695 (2)	0.73947 (17)	0.0528 (5)
H13	0.282155	0.394997	0.759577	0.063*
C14	0.41792 (19)	0.2488 (2)	0.77794 (16)	0.0542 (5)
H14	0.356604	0.191682	0.823429	0.065*
C15	0.55263 (17)	0.21350 (17)	0.74883 (14)	0.0411 (4)
H15	0.583398	0.131821	0.774577	0.049*
C16	0.5872 (3)	0.1532 (2)	0.40578 (19)	0.0627 (6)
C17	0.6025 (3)	0.0519 (2)	0.34180 (19)	0.0719 (6)
H17A	0.681454	0.068627	0.286663	0.108*
H17B	0.518129	0.045836	0.305326	0.108*
H17C	0.618162	−0.026201	0.390825	0.108*
C18	0.8358 (2)	−0.12958 (18)	0.57556 (16)	0.0477 (4)
C19	0.90563 (17)	−0.24751 (15)	0.56991 (14)	0.0364 (3)
C20	1.00398 (17)	−0.29073 (15)	0.64180 (14)	0.0366 (3)
C21	1.0363 (2)	−0.22038 (18)	0.72606 (17)	0.0477 (4)
N1	0.2746 (2)	0.55663 (18)	0.91448 (18)	0.0706 (5)
N2	0.70046 (19)	0.59504 (17)	0.79991 (17)	0.0633 (5)
N3	0.64128 (13)	0.29584 (12)	0.68320 (10)	0.0313 (3)
N4	0.87062 (13)	0.23871 (12)	0.74947 (11)	0.0320 (3)
N5	0.7818 (2)	−0.03458 (17)	0.58174 (18)	0.0729 (6)
N6	1.0604 (2)	−0.16311 (19)	0.79275 (18)	0.0725 (6)
N7	0.5744 (3)	0.2312 (2)	0.4567 (2)	0.0927 (7)
Ni1	0.500000	1.000000	1.000000	0.02856 (7)
Ni2	1.000000	−0.500000	0.500000	0.03001 (8)
S1	0.33334 (4)	0.86928 (4)	0.98950 (4)	0.03823 (10)
S2	0.65479 (4)	0.89470 (4)	0.90973 (3)	0.03589 (10)
S3	0.86132 (4)	−0.33534 (4)	0.47093 (4)	0.03766 (10)
S4	1.08996 (4)	−0.43333 (4)	0.63615 (4)	0.03938 (10)

Comment

Much effort has been devoted to the study of square-planar $[M(\text{mnt})_2]^{n-}$ complexes because of their structures and

properties in conducting and magnetic materials, dyes, non-linear optics and catalysis [5–10]. Recently, mal-eonitriledithiolate complexes have been obtained by selecting different divalent cations [11–14]. These salts generally consist of $[M(\text{mnt})_2]^{n-}$ ($M = \text{Ni(II)}, \text{Pd(II)}, \text{Zn(II)}$, etc.) anions and cationic counterions. It is interesting to note that different cations or metals lead to significantly different stacking patterns. Herein, we choose 1,1'-(methylene)bis(pyridin-1-ium) as organic divalent cation to obtain the title salt. The title complex crystallizes in the triclinic space group $P\bar{1}$, with two half of $[\text{Ni}(\text{mnt})_2]^{2-}$, one 1,1'-(1,2-ethanediy)bis(pyridin-1-ium) dication and one acetonitrile molecule in the asymmetric unit (see the figure). The presence of acetonitrile molecule is obviously different from the compounds previously synthesized [12–14]. Each Ni(II) ion is coordinated by four sulfur atoms, and exhibits a square-planar coordination geometry. The Ni–S bond lengths and S–Ni–S bond angles are in agreement with reported values [12]. It should be noted the title structure possesses segregated stacking column. The C–H...N interactions are observed between anions and cations [15]. The three-dimensional supramolecular structure is formed by such weak interactions.

Author contributions: All the authors have accepted responsibility for the entire content of this submitted manuscript and approved submission.

Research funding: This study was financially supported by Scientific and Technological Research Projects of Henan Province (182102311077).

Conflict of interest statement: The authors declare no conflicts of interest regarding this article.

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