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CRYSTAL STRUCTURE OF BIS(ISO-MALEONITRILEDITHIOLATE)NICKEL(II) BENZYLPIPERIDINIUM

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Bis(iso-maleonitriledithiolate)nickel(II) benzylpiperidinium, $[BzPid]_2[Ni(i\text{-}mnt)_2]$ (**1**) is prepared and characterized by elemental analyses, UV, IR, molar conductivity, and single crystal X-ray diffraction. It is found that **1** crystallizes in the monoclinic space group $P2_1/n$ with $a = 9.551(1)$ Å, $b = 16.520(2)$ Å, $c = 11.004(1)$ Å, $\beta = 96.60(1)°$, $V = 1724.6(3)$ Å^3, $Z = 2$. Consolidate the stacking of the molecules The electrostatic interaction between $[Ni(i\text{-}mnt)_2]^{2-}$ anions and $[BzPid]^+$ cations consolidates the stacking of the molecules.

Keywords: bis(iso-maleonitriledithiolate)nickel(II) anion, benzylpiperidinium, crystal structure.

With the rapid development of coordination chemistry, studies on transition metal complexes are drawing widespread attention, especially in the field of 1,2-dithiolene ligands, due to their highly electronic extend systems, excellent properties and application in the conductive, superconductive and magnetic properties [1—8]. In addition, more and more relevant reports and researches have proven that a typical complex anion of the 1,2-dithiolene ligand $[M(mnt)_2]^{n-}$ (M = Ni, Pd, Pt, Cu; $n = 1$ or 2; mnt = maleonitriledithiolate) is a useful building block to find some molecular materials with unusual magnetic properties [7, 9—12]. Nevertheless, in the past years there was only a few findings concerning $M(i\text{-}mnt)^{n-}$. In fact, the planar geometry of i-mnt complexes also enables them to increase their coordination numbers by binding to molecules such as thiazole derivatives [13, 14]. Moreover, its metal complexes have shown many unusual properties and abundant coordination modes. The $[M(i\text{-}mnt)_2]^{n-}$ (i-mnt = iso-maleonitriledithiolate) segments are irreversible to both oxidation and reduction [15—19]. As a result, the important characteristics of the i-mnt ligand prompted us to synthesize and characterize a new ion-pair complex bis(iso-maleonitriledithiolate)nickel(II) benzylpiperidinium $[BzPid]_2[Ni(i\text{-}mnt)_2]$ (**1**). The crystal structure, weak interactions and the stacking mode of **1** have systematically been investigated.

Experimental. Synthesis. Benzyl bromide, piperidine, nickel(II) chloride hexahydrate and solvents were purchased from commercial sources and used as received. 1-[Benzylpiperidium] bromide (BzPidBr) and disodium iso-maleonitriledithiolate ($K_2(i\text{-}mnt)\cdot H_2O$) were synthesized following the literature procedures [20, 21]. $[BzPid]_2[Ni(i\text{-}mnt)_2]$ (**1**) was prepared by the direct combination of $NiCl_2\cdot 6H_2O$, $K_2(i\text{-}mnt)\cdot H_2O$, and [BzPid]Br in the 1:2:2 molar ratio. The brown precipitate formed was filtered off, washed with diethyl ether, and dried under vacuum. Yield: 88 %. Microanalyses for C, H and N were obtained from a Perkin Elmer 240C CHN elemental analyser. IR spectra (4000—400 cm^{-1}) were recorded with an IF66V FT—IR spectrophotometer using KBr pellets. Electrospray mass spectra (ESI-MS) were determined on a Finnigan LCQ mass spectrograph and the sample con-

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Table 1

Main crystallographic parameters and running characteristics of the X-ray diffraction experiment for **1**

Parameter	Value
Empirical formula	$C_{32}H_{36}NiN_6S_4$
Formula weight	691.62
Wavelength, Å	0.71073
Crystal system, space group	Monoclinic, $P2_1/n$
a, b, c, Å	9.551(1), 16.520(2), 11.004(1)
β, deg.	96.60(1)
V, Å^3; Z	1724.6(3); 2
D_c, g/cm^3	1.332
μ, mm^{-1}	0.836
$F(000)$	724
Crystal size, mm	0.23×0.17×0.11
θ data collection range, deg.	2.23—25.00
Intervals of reflection indices	$-11 \le h \le 11$, $-17 \le k \le 19$, $-12 \le l \le 13$
Measured reflections	12133
Independent reflections	3038 [R(int) = 0.023]
Completeness, %	99.9
S	1.040
R fators over $I > 2\sigma(I)$	$R1 = 0.0275$, $wR2 = 0.0706$
R fators over all the reflections	$R1 = 0.0323$, $wR2 = 0.0727$
Residual electron density (max / min), e/Å^3	0.210 / –0.230

centrations were 1.0×10^{-5} mol·l^{-1}. Electronic spectra were recorded on a SHIMADZU UV-4000 spectrophotometer and the solution concentrations were 1.0×10^{-5} mol·l^{-1} in MeCN. Anal. Calc. for $C_{32}H_{36}NiN_6S_4$: C, 55.57; H, 5.25; N, 12.15 %. Found: C, 55.66; H, 5.72; N, 12.01 %. IR spectrum (cm^{-1}): 3064(w), 2946(w), 2872(w), 2208(s), 1636(s), 1466(m), 1451(m), 1404(s), 1306(w), 1088(w), 937(m), 892(m), 868(w), 757(m), 703(m), 609(w), 569(m), 521(m). ESI-MS (MeCN): 177.1.

Single crystal XRD. Brown single crystals suitable for the X-ray structural analysis were obtained by evaporating a solution of **1** in a mixed solution of MeCN and *i*-PrOH (*v*/*v* = 1:2). Crystallographic data for **1** were collected using graphite-monochromated MoK_α radiation (λ = 0.71073 Å) by the ϕ—ω scan mode on a Smart APEX CCD area detector. The structures were solved by direct methods and refined on F^2 by full-matrix least-squares, employing Bruker's SHELXTL [22]. All non-hydrogen atoms were refined with anisotropic thermal parameters. All H atoms were placed in calculated positions, assigned fixed isotropic displacement parameters 1.2 times the equivalent isotropic U value of the attached atom, and allowed to ride on their respective parent atoms. The CIF file with complete information about the structure was deposited at CCDC (No. 837307), from which it is available free of charge on request at www.ccdc.cam.ac.uk/data_request/cif. Crystal data are summarized in detail in Table 1. Selected bond lengths and bond angles are listed in Table 2.

Results and discussion. IR spectra of both **1** are in line with their formulations. The bands at 3064 cm^{-1}, 2946 cm^{-1}, and 2872 cm^{-1} are due to the stretching vibrational frequencies of C—H in the aromatic ring and the methylene group. Compounds **1** respectively show one strong band at 2208 cm^{-1}, which are the CN stretching bands from the i-mnt ligand [23, 24]. The band at 892 cm^{-1}, 868 cm^{-1} result from ν(C—S), and the bands at 1636 cm^{-1}, 1466 cm^{-1} for **1** are attributable to ν(C=C) stretching bands for phenyl rings or the naphthalene ring. The ν(C=C) band of i-mnt^{2-} is at 1451 cm^{-1} [24]. The positive-ion ESI-MS spectra of **1** in a MeCN solution show the mass spectra dominated by 177.1 peaks, which is assigned to [BzPid]$^+$.

Table 2

Selected bond lengths (*d*, Å) *and bond angles* (ω, deg.) for **1**

Bond	*d*	Bond	*d*	Angles	ω	Angles	ω
Ni(1)—S(1)	2.2151(6)	N(3)—C(16)	1.509(3)	S(1)—Ni(1)—S(2)	101.18(2)	N(1)—C(3)—C(2)	179.1(2)
Ni(1)—S(2)	2.2022(5)	C(1)—C(2)	1.382(3)	S(1)—Ni(1)—S(2) #1	78.82(2)	N(2)—C(4)—C(2)	178.9(2)
S(1)—C(1)	1.7219(18)	C(2)—C(3)	1.436(3)	S(1)—C(1)—S(2) #1	109.17(10)	C(11)—N(3)—C(12)	111.77(16)
N(1)—C(3)	1.131(3)	C(2)—C(4)	1.414(3)	S(1)—C(1)—C(2)	126.02(14)	C(12)—N(3)—C(16)	110.36(17)
N(2)—C(4)	1.149(3)			S(2)—C(1)—C(2) #1	124.82(14)		

Symmetry transformations used to generate equivalent atoms: #1 $-x+1, -y, -z+1$; #2 $-x, -y+1, -z+1$.

The UV-Vis absorption spectra of **1** in MeCN from 200 nm to 800 nm are attributed to [Ni(i-mnt)$_2$]$^{2-}$ of the title complex. The characteristic bands at 450 nm, 335 nm, 290 nm, and 264 nm are assigned as L(π) → M, L(σ) → M, L(σ) → M, L → L* and L → M respectively, which is basically similar to the observations of those in [(n-C$_4$N$_9$)$_4$N]$_2$[Ni(i-mnt)$_2$] [23]. The molar conductivity of **1** with the concentration of 1.0×10^{-3} mol·l^{-1} in MeCN being 227.1 S·cm^2·mol^{-1} indicates that two salts are 2:1 electrolytes [25].

[BzPid]$_2$[Ni(i-mnt)$_2$] (**1**) crystallizes in the monoclinic space group $P2_1/n$. An ORTEP drawing of **1** in an symmetric unit is shown in Fig. 1 with one [Ni(i-mnt)$_2$]$^{2-}$ anion and two [BzPid]$^+$ cations. The nickel(II) ion of the [Ni(i-mnt)$_2$]$^{2-}$ anion is coordinated by four sulfur atoms of i-mnt^{2-} ligands and situated at the center of symmetry of a square planar complex in which two [BzPid]$^+$ ions are related to each other by the symmetry center. The [Ni(i-mnt)$_2$]$^{2-}$ anion is not completely planar and the terminal nitrogen atom of CN groups deflects from the coordination plane Ni(1)S(1)C(1)S(2) with the deviations from the plane being –0.262 Å for N(1) and 0.099 Å for N(2). The Ni(1)—S(1) and Ni(1)—S(2) bond distances are 2.215 Å and 2.202 Å, while the S—Ni—S bond angle within the four-membered ring is 101.18°, similar to the values found in other complexes containing the [Ni(i-mnt)$_2$]$^{2-}$ anion [26, 27]. The relevant bond lengths and angles are listed in Table 2. The [BzPid]$^+$ cation adopts a conformation in which the phenyl and piperidine rings are twisted to the reference plane defined by C(10)C(11)N(3) with a dihedral angle of 83.7° for the phenyl ring, and the piperdine ring adopts a classical *chair* conformation. The electrostatic interaction between the [Ni(i-mnt)$_2$]$^{2-}$ anions and the [BzPid]$^+$ cations consolidates the stacking of the molecules (Fig. 2).

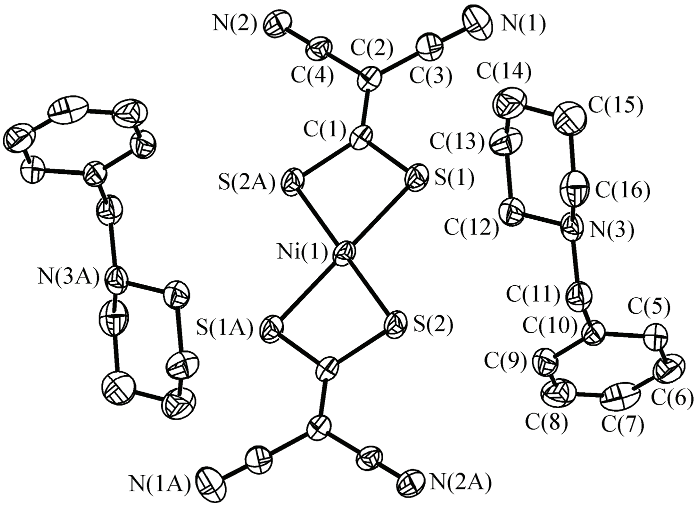

Fig. 1. Structure of **1**

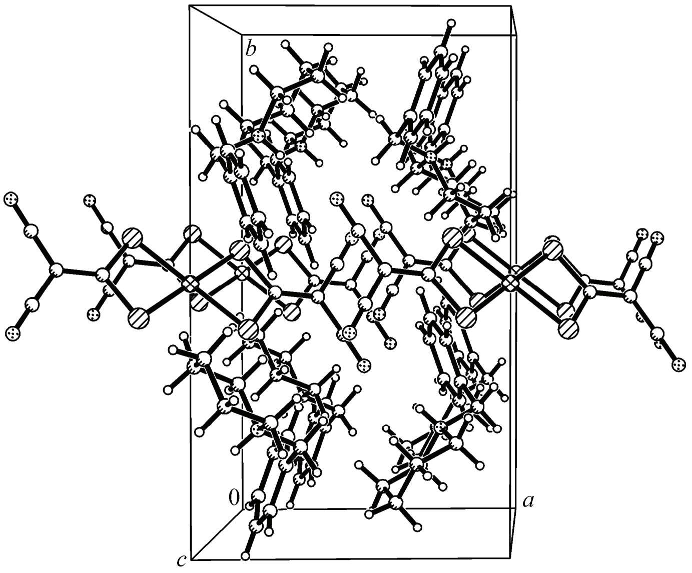

Fig. 2. Packing diagram for **1** as viewed along the *c* axis

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