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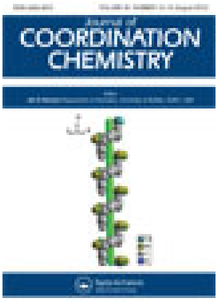

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Complicated weak interactions in a hybrid material containing tetra(isothiocyanate)cobalt(II) and 1,1′-ethylene-2,2′-dipyridinium: synthesis, crystal structure, and magnetic properties

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Complicated weak interactions in a hybrid material containing tetra(isothiocyanate)cobalt(II) and 1,1′-ethylene-2,2′-dipyridinium: synthesis, crystal structure, and magnetic properties

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A new inorganic–organic hybrid material, [EtdiPy][Co(NCS)$_4$] (**1**) ([EtdiPy]$^{2+}$ = 1,1′-ethylene-2,2′-dipyridinium), was synthesized and characterized by elemental analysis, IR spectrum, UV-Vis spectrum, ESI-MS, and single-crystal X-ray diffraction. Compound **1** is monoclinic, space group $P2_1/n$, with $a = 21.691(5)$ Å, $b = 8.639(2)$ Å, $c = 21.748(5)$ Å, $\beta = 90.124(3)^\circ$, $V = 4075.1(16)$ Å^3, $D_c = 1.550$ g cm^{-3}, $Z = 8$, $F(000) = 1928$, and $R_1 = 0.0435$. The C–H$\cdots$S hydrogen bond, short S$\cdots$C, S$\cdots$N interactions, p$\cdots\pi$, and $\pi\cdots\pi$ interactions observed in the solid state of **1** give a 3-D structure. Magnetic measurements from 2 to 300 K have shown weak antiferromagnetic exchange with $\theta = -0.892$ K in **1**.

Keywords: 1,1′-Ethylene-2,2′-dipyridinium; Tetra(isothiocyanate)cobalt(II); Weak interactions; Crystal structure; Magnetic properties

1. Introduction

Metal coordination complexes play an important role in crystal engineering and supramolecular chemistry due to applications in host-guest chemistry, electrical conductivity, molecular magnets, crystal bending effect, and catalysis [1–9]. Inorganic–organic hybrid materials with complex anions such as [M(CN)$_6$]$^{n-}$ (M = Cr^{3+}, Mn^{3+}, Fe^{2+}, Fe^{3+}, Co^{3+}; $n = 3$ or 4) [10], [Ni(dimt)$_2$]$^-$ (dmit^{2-} = 2-thioxo-1,3-dithiole-4,5-dithiolate) [11] and [M(mnt)$_2$]$^{n-}$ (M = Ni^{3+}, Pd^{3+}, Pt^{3+}, Cu^{2+}; mnt^{2-} = maleonitriledithiolate; $n = 1$ or 2) [12–15] have attracted much interest as these anions are very useful building blocks for molecular materials. In contrast, there are few examples of inorganic–organic hybrid materials containing tetra(isothiocyanate)cobalt(II) and organic cations [16–18]. The aim of our research was to find multifunctional organic cations in order to tune the stacking modes of the anions and the cations of the hybrid materials and understand the influence of weak

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interactions on structures and physical properties. We employed a substituted dipyridinium, $[EtdiPy]^{2+}$ ($[EtdiPy]^{2+}$ = 1,1′-ethylene-2,2′-dipyridinium), as multifunctional cation and $[Ni(i\text{-}mnt)_2]^{2-}$ as a building block to develop new hybrid materials, and found that $[Ni(i\text{-}mnt)_2]^{2-}$ form a 1-D chain by $\pi\cdots\pi$ stacking interactions between the CN groups and a ring structure through S···N short interactions [19]. In order to widen our research, we introduced $[EtdiPy]^{2+}$ into the system containing $[Co(NCS)_4]^{2-}$ and obtained $[EtdiPy][Co(NCS)_4]$ (**1**), and spectra, crystal structure, and magnetic properties were investigated. Complicated weak interactions such as C–H···S hydrogen bonds, short S···C, S···N interactions, $p\cdots\pi$, and $\pi\cdots\pi$ interactions observed in the solid state of **1** are discussed.

2. Experimental

2.1. *Materials and physical measurements*

1,1′-Ethylene-2,2′-dipyridinium bromide ($[EtdiPy]Br_2$) was synthesized following published procedures [20]. All other reagents were commercially available and used as received. Elemental analyses (C, H, and N) were determined on a Model 240 Perkin Elmer instrument. UV-Vis spectrum of the complex in HPLC grade CH_3CN ($3.3 \times 10^{-5}\,\mathrm{mol\,L^{-1}}$) from 200–700 nm was recorded in 1 cm quartz cells on a Shimadzu UV-2500 spectrophotometer. IR spectrum (KBr pellets) was recorded on an IF66V FT-IR spectrophotometer from 4000–400 $\mathrm{cm^{-1}}$. The crystal structure determination was performed on a Bruker SMART APEX CCD diffractometer equipped with graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å). The electrospray mass spectrum (ESI-MS) of a MeCN solution of **1** was obtained with a Finnigan LCQ mass spectrograph. Magnetic data were collected using a Quantum Design MPMS superconducting quantum interference device (SQUID) magnetometer. Crushed single-crystal sample of the salt was packed into a small gelatin capsule and temperature-dependent magnetic susceptibility data were collected from 2 to 300 K at an applied magnetic field of 2000 Oe. Diamagnetic correction was made with Pascal's constants for all constituent atoms, and the temperature-independent paramagnetic correction for cobalt was applied to the data sets.

2.2. *Synthesis of $[EtdiPy][Co(NCS)_4]$ (1)*

$[EtdiPy][Co(NCS)_4]$ (**1**) was prepared by the combination of 1 : 1 : 4 mol equiv of $[EtdiPy]Br_2$, $CoCl_2$, and KSCN in methanol. A blue precipitate was filtered off, washed by cool ether and dried under vacuum with yield of 82%. Blue block crystals suitable for X-ray diffraction analysis were obtained from CH_3CN by slow evaporation of the solvent for two weeks. Anal. Calcd for $C_{16}H_{12}N_6CoS_4$ (%): C, 40.42; H, 2.54; N, 17.67. Found: C, 40.37; H, 2.65; N, 17.58. IR (KBr, $\mathrm{cm^{-1}}$): 3056(w), 2993(w), 2933(w), 2854(w), 2067(vs), 1630(w), 1611(m), 1528(w), 1496(m), 1465(w), 1431(w), 1360(w), 1326(w), 1288(w), 1232(w), 1190(w), 1142(w), 764(w), 710(w), 474(w). UV-Vis spectrum (nm) ($\log\varepsilon$): 315(4.78), 625(3.61).

Table 1. Crystallographic data of **1**.

Compound	**1**
Empirical formula	$C_{16}H_{12}N_6S_4Co$
Formula weight	475.49
Temperature (K)	291(2)
Crystal system	Monoclinic
Space group	$P2_1/n$
Unit cell dimensions (Å, °)	
a	21.691(5)
b	8.639(2)
c	21.748(5)
β	90.124(3)
Volume (Å^3), Z	4075.1(16), 8
Calculated density (g cm^{-3})	1.550
Absorption coefficient (mm^{-1})	1.266
$F(000)$	1928
Crystal size (mm^3)	0.11 × 0.14 × 0.21
θ range for data collection (°)	1.87–25.00
Reflections collected/unique	28,542/7159
Independent reflection	6403 [$R(\text{int}) = 0.046$]
Data/restraints/parameters	7159/0/476
Goodness-of-fit on F^2	1.086
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0435$, $wR_2 = 0.1088$
R indices (all data)	$R_1 = 0.0513$, $wR_2 = 0.1142$
Largest difference peak and hole (e Å^{-3})	1.212 and −0.622

2.3. *Determination of crystal structure*

A blue block crystal of **1** having approximate dimensions 0.11 × 0.14 × 0.21 mm was selected and mounted on a glass fiber. All measurements were made on a Bruker Siemens Smart CCD diffracrometer equipped with graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å). A total of 7159 reflections was collected by ω–ω scan technique at 291(2) K from $1.87 \leq \theta \leq 25.00$ with index range of $-23 \leq h \leq 25$, $-10 \leq k \leq 10$, and $-25 \leq l \leq 25$, of which 6403 were independent ($R_{\text{int}} = 0.046$). The structure was solved by direct methods using SHELXS-2000 and refined with SHELXL-2000 [21]. All non-hydrogen atoms were refined anisotropically by full-matrix least-squares. Hydrogen atoms were included in structure factor calculation in idealized positions. A summary of crystallographic data and refinement parameters is given in table 1.

3. Results and discussion

3.1. *IR, UV-Vis, and MS spectra*

Bands at 3056, 2993, 2933, and 2854 cm^{-1} are due to stretching frequencies of C–H in the aromatic ring and ethylidene. The very strong $C \equiv N$ absorption of thiocyanate is at 2067 cm^{-1}, larger than that (2053 cm^{-1}) of ionic thiocyanate in KSCN, indicative of bonding to the metal *via* nitrogen [22]. Bands at 1630, 1611, 1528, and 1496 cm^{-1} are attributable to $\nu(C=N)$ and $\nu(C=C)$ stretches of the dipyridinium rings. Compound **1** exhibits a weak C–S stretch near 831 cm^{-1}; compared to that (837 cm^{-1}) of $[NEt_4]_2[Co(NCS)_4]$ [22], the bond is shifted to lower frequency as a result of weak interactions such as C–H···S hydrogen bond between $[EtdiPy]^{2+}$ and $[Co(NCS)_4]^{2-}$, short S···C, and S···N interactions between anions of **1** described below. UV-Vis absorption spectra of **1** in HPLC grade CH_3CN from 200–700 nm are attributed to $[Co(NCS)_4]^{2-}$. The M → L and L* → L bands of **1** are at 625 and 315 nm, respectively, similar to those of $[Co(NCS)_4]^{2-}$ [23]. The positive-ion ESI-MS spectrum of **1** in CH_3CN is dominated by the 92.2 peak due to $[EtdiPy]^{2+}$.

3.2. *Crystal structure*

$[EtdiPy][Co(NCS)_4]$ (**1**) crystallizes in the monoclinic system with $P2_1/n$ space group, and the asymmetric unit in a cell consists of two $[Co(NCS)_4]^{2-}$ anions and two $[EtdiPy]^{2+}$ cations as shown in figure 1. Selected bond distances and angles are shown in table 2. For $[Co(NCS)_4]^{2-}$ containing Co(1), the coordination geometry of Co(II) could be described as a slightly distorted tetrahedron; the average Co–N bond distance is 1.956 Å and the N–Co–N bond angles vary from 104.00 to 114.06°. For $[Co(NCS)_4]^{2-}$ containing Co(2), the average Co–N bond distance is 1.966 Å and the N–Co–N bond angles vary from 106.49–113.54°; these values are in agreement with those found in complexes containing $[Co(NCS)_4]^{2-}$ [16, 24]. The carbons on two methylenes of $[EtdiPy]^{2+}$ are tipped out of the planes of the pyridine rings. In $[EtdiPy]^{2+}$ containing N(9), deviations of C(19) are 0.015 Å for the pyridine plane containing N(9) and −0.884 Å for the pyridine plane containing N(10), while deviations of C(20) are 0.966 Å

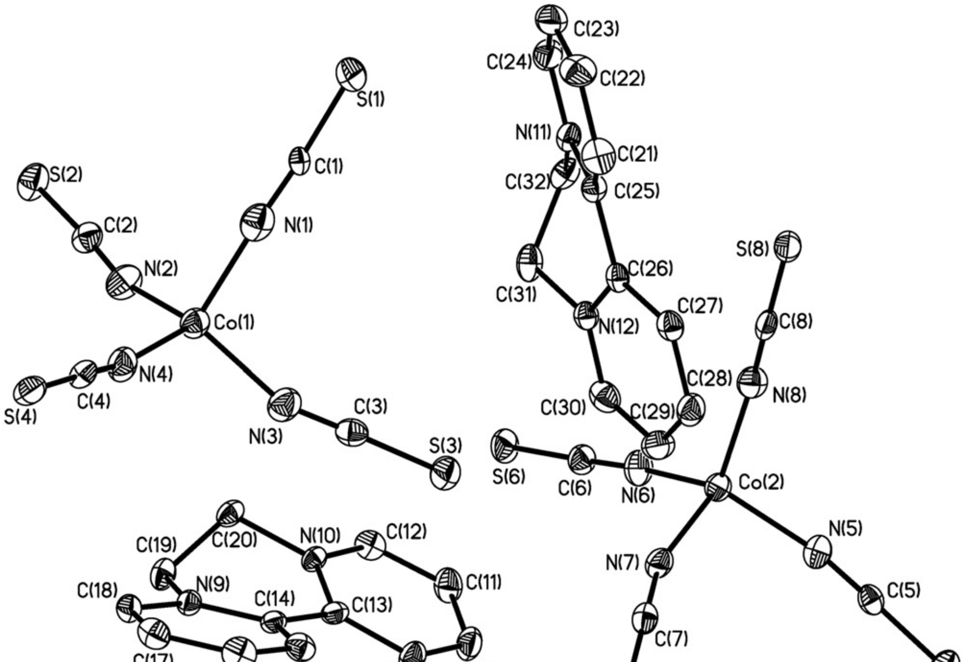

Figure 1. Molecular structure of **1**.

and −0.011 Å, respectively. Two pyridine rings twist with dihedral angle of 24.1°. In $[EtdiPy]^{2+}$ containing N(11), deviations of C(31) are −0.878 Å for the pyridine plane containing N(11) and 0.017 Å for the pyridine plane containing N(12), while deviations of C(32) are 0.0245 Å and 0.935 Å, respectively, and the dihedral angle between pyridine rings is 21.9°.

Complicated short S⋯C and S⋯N interactions were observed between adjacent anions: (1) short $S(2)\cdots C(1^{i})$ and $S(2)\cdots N(1^{i})$ (symmetry code: $i = x, y+1, z$) interactions with distances of 3.631 and 3.526 Å, respectively, and short $S(4)\cdots C(2^{ii})$ and $S(4)\cdots N(2^{ii})$ (symmetry code: $ii = -x, -y-1, -z$) interactions with distances of 3.642 and 3.680 Å between adjacent anions containing Co(1) (figure 2a); (2) short $S(6)\cdots C(7^{i})$ and $S(6)\cdots N(7^{i})$ interactions with distances of 3.329 and 3.436 Å, and short $S(8)\cdots N(6^{iii})$ and $S(8)\cdots N(8^{iii})$ (symmetry code: $iii = -x+1, -y-1, -z$) interactions with distances of 3.658 and 3.676 Å between adjacent anions containing Co(2) (figure 2b); (3) short $S(1)\cdots C(5^{iv})$ (symmetry code: $iv = -x+1, -y, -z$), $S(3)\cdots N(7)$, $S(7)\cdots C(3^{v})$ and $S(7)\cdots N(3^{v})$ (symmetry code: $v = -x+3/2, y+3/2, -z+1/2$) interactions with distances of 3.600, 3.622, 3.533, and 3.456 Å between adjacent anions containing Co(1) or Co(2) (figure 2c and d). These short interactions are similar to short S⋯S [25–27] or C⋯N

Table 2. Selected bond lengths (Å) and angles (°) for **1**.

Co(1)–N(1)	1.939(6)	N(9)–C(19)	1.483(6)
Co(1)–N(2)	1.958(4)	N(10)–C(12)	1.361(6)
Co(1)–N(3)	1.962(5)	N(10)–C(13)	1.369(6)
Co(1)–N(4)	1.964(4)	N(10)–C(20)	1.486(6)
Co(2)–N(5)	1.971(4)	N(11)–C(24)	1.342(8)
Co(2)–N(6)	1.949(4)	N(11)–C(25)	1.356(6)
Co(2)–N(7)	1.994(4)	N(11)–C(32)	1.482(6)
Co(2)–N(8)	1.945(4)	N(12)–C(26)	1.376(6)
S(1)–C(1)	1.606(5)	N(12)–C(30)	1.331(8)
S(2)–C(2)	1.610(6)	N(12)–C(31)	1.503(6)
S(3)–C(3)	1.627(5)	N(1)–C(1)	1.189(7)
S(4)–C(4)	1.618(7)	N(2)–C(2)	1.173(7)
S(5)–C(5)	1.624(5)	N(3)–C(3)	1.160(6)
S(6)–C(6)	1.622(5)	N(4)–C(4)	1.176(8)
S(7)–C(7)	1.640(5)	N(5)–C(5)	1.161(6)
S(8)–C(8)	1.616(6)	N(6)–C(6)	1.169(7)
N(9)–C(14)	1.367(6)	N(7)–C(7)	1.147(6)
N(9)–C(18)	1.367(6)	N(8)–C(8)	1.172(8)
N(1)–Co(1)–N(2)	104.0(2)	C(12)–N(10)–C(20)	120.6(4)
N(1)–Co(1)–N(3)	104.5(2)	C(13)–N(10)–C(20)	118.6(4)
N(1)–Co(1)–N(4)	109.28(19)	C(24)–N(11)–C(25)	120.7(4)
N(2)–Co(1)–N(3)	113.5(2)	C(24)–N(11)–C(32)	120.8(4)
N(2)–Co(1)–N(4)	110.77(18)	C(25)–N(11)–C(32)	118.6(4)
N(3)–Co(1)–N(4)	114.06(19)	C(26)–N(12)–C(30)	121.9(4)
N(5)–Co(2)–N(6)	108.41(18)	C(26)–N(12)–C(31)	117.9(4)
N(5)–Co(2)–N(7)	106.49(18)	C(30)–N(12)–C(31)	120.2(4)
N(5)–Co(2)–N(8)	112.09(18)	Co(1)–N(1)–C(1)	174.7(4)
N(6)–Co(2)–N(7)	107.57(18)	Co(1)–N(2)–C(2)	162.7(5)
N(6)–Co(2)–N(8)	113.54(18)	Co(1)–N(3)–C(3)	160.3(4)
N(7)–Co(2)–N(8)	108.41(18)	Co(1)–N(4)–C(4)	167.3(4)
C(14)–N(9)–C(18)	121.4(4)	Co(2)–N(5)–C(5)	170.4(4)
C(14)–N(9)–C(19)	118.7(4)	Co(2)–N(6)–C(6)	170.4(4)
C(18)–N(9)–C(19)	119.9(4)	Co(2)–N(7)–C(7)	162.3(4)
C(12)–N(10)–C(13)	120.8(4)	Co(2)–N(8)–C(8)	168.9(4)

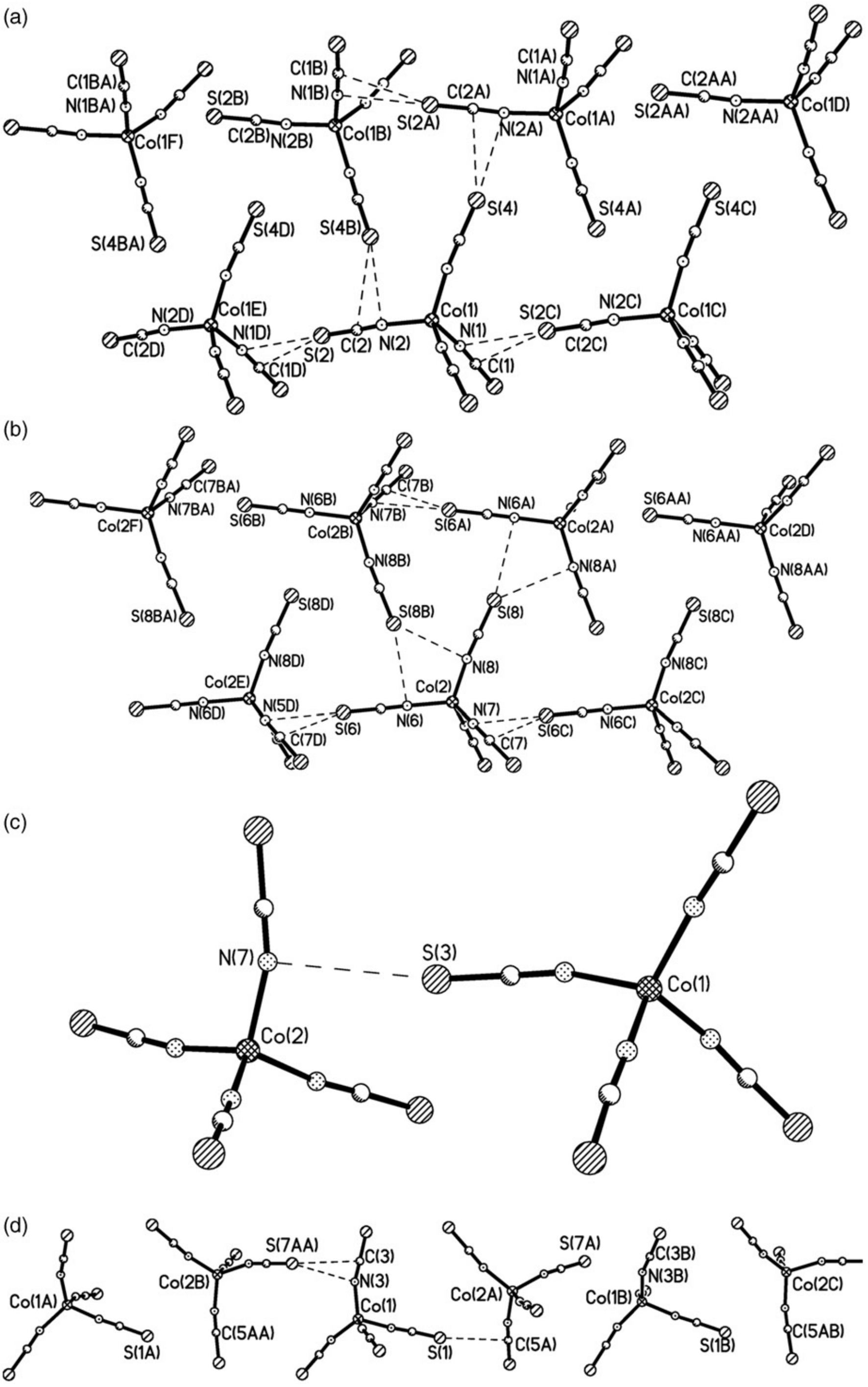

Figure 2. (a) Short S···C and S···N interactions between adjacent anions containing Co(1) for **1**. (b) Short S···C and S···N interactions between adjacent anions containing Co(2) for **1**. (c) and (d) Short S···C and S···N interactions between adjacent anions containing Co(1) or Co(2) for **1**.

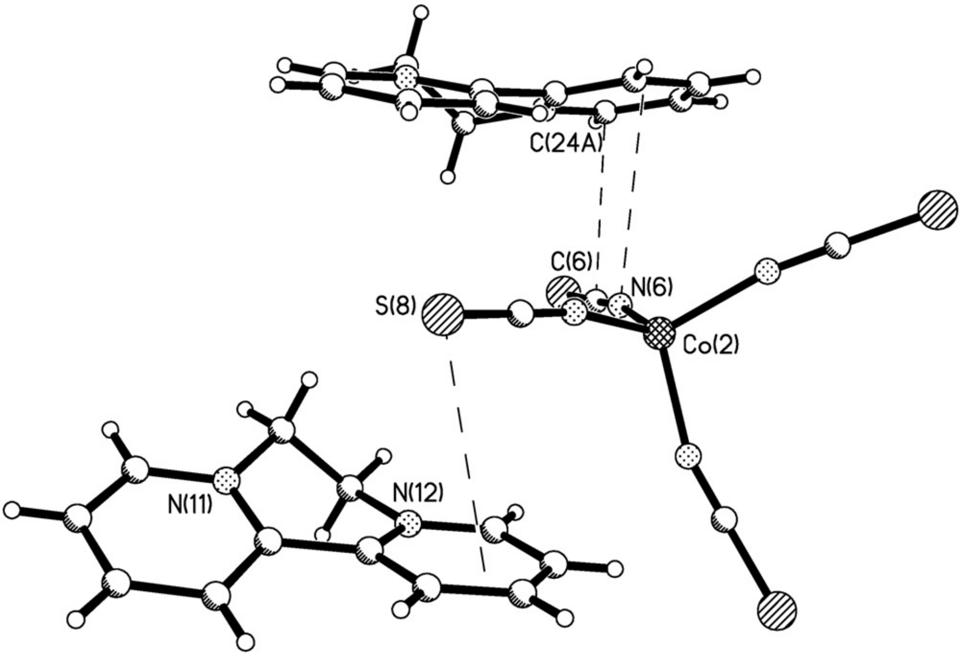

Figure 3. The p· · ·π and π· · ·π packing interactions for **1**.

interactions [28–30]. Two weak interactions were observed between cations and anions (figure 3): (1) the p· · ·π stacking interaction [31, 32] between S(8) of NCS and the pyridine ring containing N(12) with a perpendicular distance of 3.500 Å; (2) the π· · ·π stacking interaction between C$\equiv$N of NCS and the pyridine ring containing C(24) with C(6)· · ·C(24^{iv}) distance of 3.292 Å. These weak interactions are uncommon for complexes containing $[Co(NCS)_4]^{2-}$. In addition, one C–H· · ·N and nine C–H· · ·S hydrogen bonds are found between adjacent anions and cations (figure 4), and the bond parameters are summarized in table 3.

In the family of hybrid materials containing $[Co(NCS)_4]^{2-}$ and cations, the crystal stacking modes are affected by size and topology of the countercation and dominated by weak interactions such as p· · ·π and π· · ·π, C–H· · ·S hydrogen bonds, and S· · ·C, S· · ·N, or S· · ·S interactions. When the countercation is $[Ru(phen)_3]^{2+}$ (phen:1,10-phenanthroline), the S· · ·S interactions build up a 1-D helical chain through $[Co(NCS)_4]^{2-}$ [18]. When $[4,4'\text{-bipyH}_2]^+$ (4,4′-bipy = 4,4′-bipyridine) is used, the $[Co(NCS)_4]^{2-}$ anions form 2-D and highly wavy networks [16]. While $[EtdiPy]^{2+}$ is used, the combination of electrostatic force between the anion and cation and the complicated weak interactions such as C–H· · ·N and C–H· · ·S hydrogen bonds, short S· · ·C and S· · ·N interactions, p· · ·π, and π· · ·π interactions result in a 3-D network structure (figure 4).

3.3. *Magnetic properties*

The temperature dependence of the solid state magnetic susceptibilities of **1** was investigated from 2 to 300 K under an applied field of 2000 Oe. As shown in figure 5,

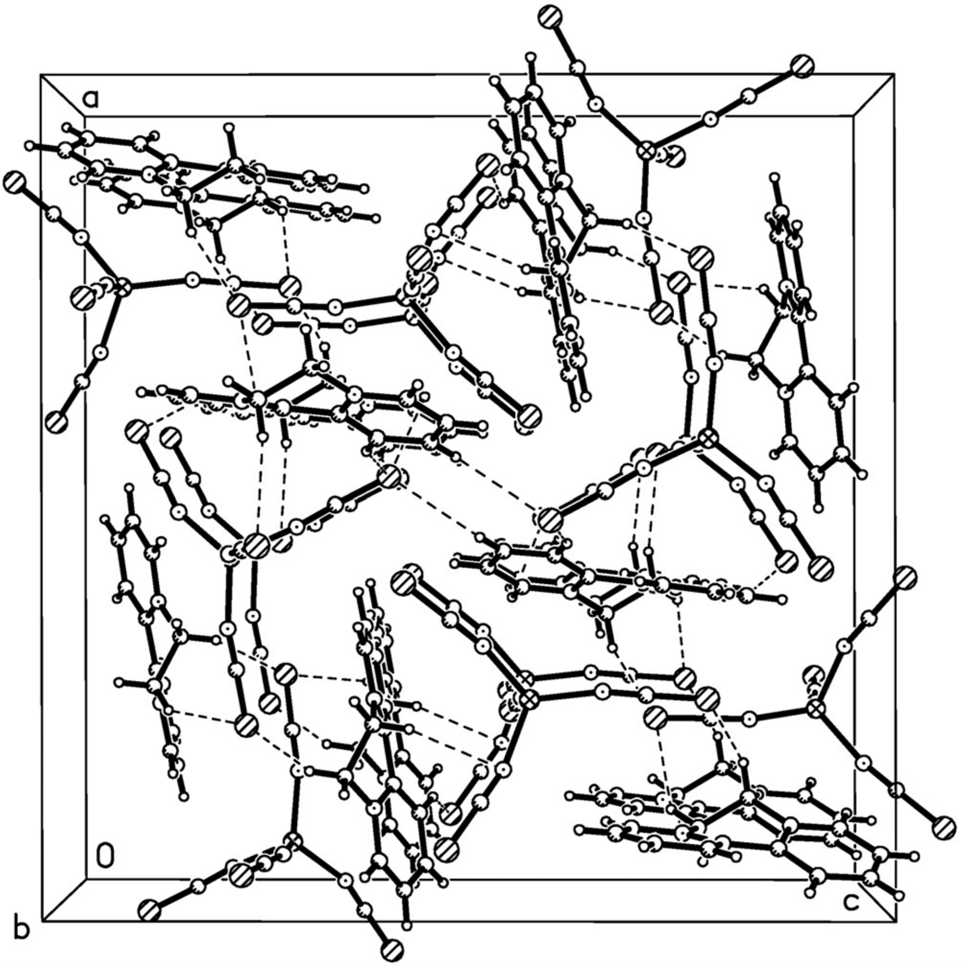

Figure 4. The packing diagram of a unit cell for **1**.

Table 3. Hydrogen bonds for **1** (Å and °).

D–H···A	*d*(D···H)	*d*(H···A)	*d*(D···A)	∠(DHA)
C(9)–H(9)···S(7)#1	0.930	2.860	2.633(5)	141.00
C(19)–H(19 A)···S(4)	0.970	2.720	3.546(5)	143.00
C(19)–H(19B)···N(7)#2	0.970	2.610	3.537(6)	161.00
C(20)–H(20B)···S(4)#3	0.970	2.770	3.619(5)	147.00
C(21)–H(21)···S(1)#4	0.930	2.830	3.671(5)	151.00
C(22)–H(22)···S(1)#5	0.930	2.850	3.585(7)	136.00
C(30)–H(30)···S(3)	0.930	2.870	3.724(6)	154.00
C(31)–H(31A)···S(2)#4	0.970	2.760	3.573(5)	142.00
C(31)–H(31B)···S(8)#6	0.970	2.800	3.597(5)	140.00
C(32)–H(32A)···S(8)	0.970	2.810	3.657(5)	147.00

Symmetry transformations used to generate equivalent atoms: #1 = $-x+1$, $-y$, $-z$; #2 = $-x+1$, $-y+1$, $-z$; #3 = $-x+1/2$, $y-1/2$, $-z+1/2$; #4 = x, $y-1$, z; #5 = $-x+1$, $-y+1$, $-z+1$; #6 = $-x+3/2$, $y+1/2$, $-z+1/2$.

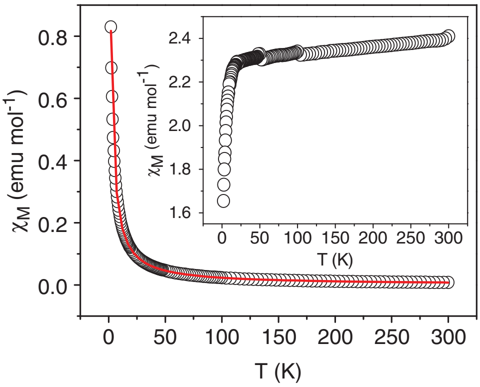

Figure 5. Plot of χ_m *vs.* T for **1** (inset: plot of $\chi_m T$ *vs.* T). The red solid line is reproduced from calculations and detailed fitting procedure described in the text.

$\chi_m T$ at 300 K is 2.410 emu K mol^{-1}, larger than the spin-only value of high-spin Co(II) ($S = 3/2$), 1.875 emu K mol^{-1}, indicating a contribution of the orbital momentum typical for the $^4T_{1g}$ ground state [33, 34]. As the temperature is lowered, $\chi_m T$ value of **1** slightly decreased to 2.197 emu K mol^{-1} at 10 K, then sharply decreased to 1.654 emu K mol^{-1} at 2 K, indicative of weak antiferromagnetic exchange. The magnetic susceptibility data can be fitted to the Curie-Weiss law (solid line in inset of figure 5) with $C = 2.36$ emu K mol^{-1}, $\theta = -0.892$ K, and $R = 4.4 \times 10^{-6}$ (R is the agreement factor defined as $\Sigma(\chi_m^{\text{Calcd}} - \chi_m^{\text{obsd}})^2/(\chi_m^{\text{obsd}})^2$).

There are some reports on magnetic properties of Co(II) complexes such as $[A]_2[CoX_4]$, where A is an organic cation and X is Cl^- or Br^- [35], and end-to-end thiocyanato-bridged dicobalt(II) complexes [36]. For $[A]_2[CoX_4]$ complexes, the magnetic properties are dominated by van der Waals contacts between the halide of $[CoX_4]^{2-}$, and the contacts are determined by the crystal packing which is affected by the organic cation. For example, when A is $[3\text{-MAPH}]^+$ (3-MAP = 2-amino-3-methylpyridine) $[CoCl_4]^{2-}$ forms chains through Cl···Cl contacts between Cl^- on the neighboring anion and the O–H···Cl hydrogen bonds occurring with water, while $[CoBr_4]^{2-}$ forms ladders through Br···Br contacts between the anions, and $[3\text{-MAPH}]_2[CoCl_4]$ and $[3\text{-MAPH}]_2[CoBr_4]$ exhibit different magnetic properties [35]. For thiocyanate-bridged $[Co(dien)(H_2O)(NCS)(\mu_{1,3}\text{-NCS})Co(dien)(NCS)_2]$ (dien = diethylenetriamine) [36], the Co(II) centers are coupled by weak ferromagnetic interaction. In **1**, $[Co(NCS)_4]^{2-}$ forms networks through weak short S···C and S···N interactions between anions, therefore, the difference in magnetic properties for these Co(II) complexes can be attributed to the difference in the weak interactions and the crystal packing modes of the anions and the organic cations.

4. Conclusions

Crystal structure and magnetic properties were presented for a new material, $[EtdiPy][Co(NCS)_4]$ (**1**) ($[EtdiPy]^{2+}$ = 1,1′-ethylene-2,2′-dipyridinium, NCS^- = isothiocyanate). The $[Co(NCS)_4]^{2-}$ exhibit 2-D net structures through short S···C and S···N interactions between the neighboring anions, and these short interactions together with the C–H···S hydrogen bond, p···π and π···π interactions in the solid state of the complex give rise to a 3-D structure. Magnetic susceptibility measurements show that **1** exhibits weak antiferromagnetic exchange with $\theta = -0.892\,\mathrm{K}$.

Supplementary material

Tables of atomic coordinates, isotropic thermal parameters, and complete bond distances and angles have been deposited at the Cambridge Crystallographic Data Center as supplementary publication No. CCDC-851712. Copies of the data may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; E-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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