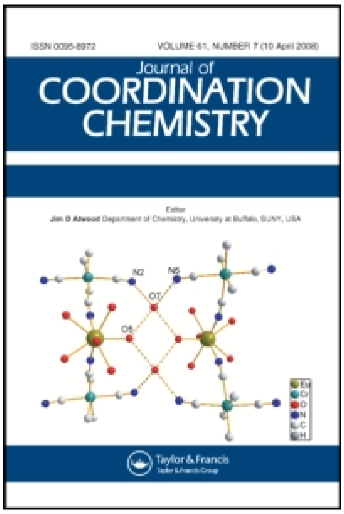

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Synthesis, crystal structure and magnetic properties of [1-(4'-bromobenzyl)-4-methylquinolinium] [Ni(mnt)$_2$] complex (mnt^2⁻=maleonitriledithiolate)

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SYNTHESIS, CRYSTAL STRUCTURE AND MAGNETIC PROPERTIES OF [1-(4′-BROMOBENZYL)-4-METHYLQUINOLINIUM] [Ni(MNT)$_2$] COMPLEX (MNT^{2-} = MALEONITRILEDITHIOLATE)

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A new ion-pair complex, [BrBzMeQl][Ni(mnt)$_2$] (**1**) ([BrBzMeQl]$^+$ = 1-(4′-bromobenzyl)-2-methylquinolinium; mnt^{2-} = maleonitriledithiolate), has been prepared and characterized. X-ray diffraction analysis shows that the Ni(mnt)$_2$ anion and [BrBzMeQl]$^+$ cations of **1** form completely segregated stacking columns, with the Ni$\cdots$Ni distances alternating between 3.717 and 4.466 Å in the Ni(mnt)$_2$ stacking column. The variable-temperature magnetic susceptibilities of **1** have been measured over the range 75–300 K and the results reveal that the complex exhibits antiferromagnetic behavior.

Keywords: 1-(4′-Bromobenzyl)-4-methylquinolinium; Bis(maleonitriledithiolate) nickelate(III) complex; X-ray structure; Magnetism

INTRODUCTION

In the past two decades, bis-1,2-dithiolene transition-metal complexes have attracted some interest because of their properties and application in many fields, including conducting and magnetic materials, nonlinear optics, catalysis and dyes [1,2]. Some of the most widely studied dithiolene complexes are the [M(mnt)$_2$]$^{n-}$ (M = Ni, Pd, Pt, mnt^{2-} = maleonitriledithiolate) complexes, which have a versatile set of structural, chemical and physical properties [3–5]. In particular, the discovery in 1996 of the ferromagnetic complex containing the Ni(mnt)$_2$ ion, $NH_4 \cdot Ni(mnt)_2 \cdot H_2O$, revived interest in Ni(mnt)$_2$ complexes as building blocks for new molecular magnets [6]. Recently, much of our attention has been directed at a new class of ion-pair complexes [RbzPy]$^+$[Ni(mnt)$_2$] ([RbzPy]$^+$ = derivatives of benzylpyridinium). These efforts are

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motivated by the desire to tune the stacking pattern of Ni(mnt)$_2$ complexes, and modulate the magnetic properties by the molecular conformation of the RbzPy$^+$ cation. In our previous papers, we found that [RbzPy]$^+$[Ni(mnt)$_2$] exhibits versatile magnetic properties such as ferromagnetic ordering at low temperature, magnetic transition from ferromagnetic coupling to diamagnetism, meta-magnetism and Spin-Peierls-like transitions [7–13]. To increase the scope of our research, in this article we describe the synthesis, crystal structure and magnetic behavior of the title complex. To the best of our knowledge, this is the first Ni(mnt)$_2$ complex containing a substituted benzyl-4-methylquinolinium cation.

EXPERIMENTAL

Reagents and Preparation of the Complex

4-Bromobenzyl bromide and 4-methylquinoline were purchased from Aldrich and were used without further purification. [1-(4′-Bromobenzyl)]-4-methylquinolinium bromide ([BrBzMeQl]Br) was prepared by the literature method [14]. Disodium maleonitriledithiolate (Na$_2$mnt) was synthesized by a published procedure, and a similar method to that used for the preparation of [Bu$_4$N][Ni(mnt)$_2$] was used to prepare [BrBzMeQl]$_2$[Ni(mnt)$_2$] [15].

An acetone solution (10 cm^3) of I$_2$ (160 mg, 0.62 mmol) was slowly added to an acetone solution (50 cm^3) of [BrBzMeQl]$_2$[Ni(mnt)$_2$] (966 mg, 1 mmol) and the mixture was stirred for 1 h. MeOH (90 cm^3) was then added, and the mixture allowed to stand overnight; the 520 mg of black microcrystals formed were filtered off, washed with MeOH and dried in a vacuum (yield: 79.8%). Anal. Calcd. $C_{25}H_{15}N_5NiBrS_4$(%): C, 46.03; H, 2.32; N, 10.74. Found: C, 45.96; H, 2.41; N, 10.57.

Black single crystals suitable for X-ray structure analysis were obtained by evaporating a MeCN and *i*-PrOH (v/v = 1 : 1) solution of **1** after about 2 weeks at room temperature.

Physical Methods

Elemental analyses were run on a Model 240 Perkin Elmer CHN instrument. IR spectra were recorded on an IF66V FT-IR (400–4000 cm^{-1} region) spectrophotometer in KBr pellets. Magnetic susceptibilities were determined down to liquid nitrogen temperature on a CAHN-2000 Faraday-type magnetometer; diamagnetic corrections for the constituent atoms were made with Pascal's constants.

Crystallography

Measurement of complex **1** was performed on a Siemens Smart CCD area detector using graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) and ω scan mode within the angular range $1.91 < \theta < 26.0$. The structure was solved by direct methods and refined on F^2 by full-matrix least-squares, using Bruker's SHELXTL [16]. 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

TABLE I Crystal data and structure refinement for **1**

CCDC deposit no.	227478
Color/shape	Black/block
Chemical formula	$C_{25}H_{15}N_5NiBrS_4$
Formula weight	652.28
Temperature (K)	293(2)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	$P2_1/n$
Unit cell dimensions	
a (Å)	9.218(1)
b (Å)	21.352(3)
c (Å)	16.928(2)
β (°)	99.61(1)
Volume (Å)^3	2569.2(6)
Z	4
Density (calculated) (mg m^{-3})	1.686
Absorption coefficient (mm^{-1})	2.661
Diffractometer/scan	Simens SMART/CCD area detector
F(000)	1308
θ range for data collection	1.91–26.00
Index ranges	$-8 \leq h \leq 8$, $-25 \leq k \leq 26$, $-17 \leq l \leq 20$
Reflections collected	13 677
Independent reflections	5025 ($R_{\text{int}} = 0.005$)
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	5025/0/326
Goodness of fit on F^2	1.095
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0594$, $wR_2 = 0.0965$
R indices (all data)	$R_1 = 0.0975$, $wR_2 = 0.1143$
Largest diff. peak and hole (e Å^{-3})	0.29 and −0.44

their respective parent atoms. The crystal data and details of crystal structure determination are summarized in Table I and atomic coordinates and equivalent isotropic displacement parameters are listed in Table II. Selected bond lengths and angles are listed in Table III. Full details of the crystallographic data are available from the authors upon request.

RESULTS AND DISCUSSION

Structure of the Complex

Complex **1** crystallizes in the monoclinic space group $P2_1/n$. An ORTEP drawing with nonhydrogen atomic labeling of the asymmetric unit is shown in Fig. 1. The molecular structure of the Ni(mnt)$_2$ anion consists of two mnt^2 ligands symmetrically chelated to the nickel atom, which adopts the expected square-planar coordination geometry. The five-membered nickel-containing rings are slightly puckered. The average Ni–S bond distance is 2.140(2) Å, and the average S–Ni–S bond angle within the five-membered rings is 90.0(5)°, which compares well with those found in Ni(mnt)$_2$ complexes [17]. It is worth noting that the Ni–S and C–S bond distances within the anion are slightly longer than those of Ni(mnt)$_2^2$ complexes [18]. The CN groups of Ni(mnt)$_2$ are tipped slightly out of the plane; the deviations from the plane are −0.0918 Å for

TABLE II Atomic coordinates and equivalent isotropic displacement parameters (Å^2) for **1**

Atom	*x/a*	*y/b*	*z/c*	U_{eq}^{a}
Ni(1)	0.78077(9)	0.04486(3)	0.00339(4)	0.0455(2)
Br(1)	−0.33973(7)	0.97683(2)	0.62855(3)	0.0459(2)
S(1)	0.71925(17)	−0.05327(6)	−0.00059(7)	0.0461(4)
S(2)	0.78436(17)	0.04896(6)	0.13000(7)	0.0461(4)
S(3)	0.84220(17)	0.14311(6)	0.00670(7)	0.0456(4)
S(4)	0.77934(17)	0.03957(5)	−0.12307(7)	0.0457(4)
N(1)	0.6233(5)	−0.18588(19)	0.1209(2)	0.0451(14)
N(2)	0.7101(6)	−0.04853(17)	0.2972(3)	0.0471(16)
N(3)	0.9229(5)	0.27387(19)	−0.1255(2)	0.0470(12)
N(4)	0.8863(5)	0.13610(17)	−0.2905(2)	0.0468(14)
N(5)	0.2805(5)	0.79958(17)	0.4470(2)	0.0454(12)
C(1)	0.6581(7)	−0.1342(2)	0.1127(3)	0.0445(17)
C(2)	0.7013(7)	−0.0702(2)	0.0969(3)	0.0458(17)
C(3)	0.7249(7)	−0.0254(2)	0.1528(3)	0.0471(17)
C(4)	0.6980(7)	−0.0362(2)	0.2332(3)	0.0459(17)
C(5)	0.8914(7)	0.2235(2)	−0.1095(3)	0.0476(17)
C(6)	0.8571(7)	0.1596(2)	−0.0911(3)	0.0458(17)
C(7)	0.8340(6)	0.1151(2)	−0.1472(3)	0.0457(17)
C(8)	0.8592(7)	0.1264(2)	−0.2278(3)	0.0463(17)
C(9)	0.1378(7)	0.7651(2)	0.4572(3)	0.0457(17)
C(10)	0.0928(7)	0.7106(2)	0.4134(3)	0.0464(17)
C(11)	0.1947(7)	0.6922(2)	0.3573(3)	0.0449(17)
C(12)	0.4766(6)	0.7102(2)	0.2940(3)	0.0466(17)
C(13)	0.6290(7)	0.7438(2)	0.2892(3)	0.0454(17)
C(14)	0.6742(7)	0.7967(2)	0.3356(3)	0.0469(17)
C(15)	0.5640(7)	0.8146(2)	0.3874(3)	0.0463(17)
C(16)	0.3997(7)	0.7815(2)	0.3960(3)	0.0471(17)
C(17)	0.3552(7)	0.7268(2)	0.3478(3)	0.0457(17)
C(18)	0.1416(7)	0.6344(2)	0.3079(3)	0.0455(17)
C(19)	0.3141(6)	0.8620(2)	0.4876(3)	0.0455(17)
C(20)	0.1518(7)	0.8870(2)	0.5228(3)	0.0452(17)
C(21)	0.1577(7)	0.8894(2)	0.6045(3)	0.0447(17)
C(22)	0.0104(7)	0.9166(2)	0.6343(3)	0.0465(17)
C(23)	−0.1458(7)	0.9392(2)	0.5851(3)	0.0449(17)
C(24)	−0.1506(7)	0.9377(2)	0.5037(3)	0.0452(17)
C(25)	−0.0045(7)	0.9115(2)	0.4732(3)	0.0471(17)

[a] U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

N(1), −0.0820 Å for N(2), −0.0158 Å for N(3) and 0.3266 Å for N(4). The [BrBzMeQl]$^+$ cation adopts a conformation where both the phenyl ring and quinoline ring are twisted to the C(20)–C(19)–N(5) reference plane. The phenyl ring and the quinoline ring are planar. The deviation of Br from the phenyl ring is 0.0432 Å, and the deviation of C(18) from the quinoline ring is −0.0285 Å. The dihedral angles that the quinoline ring and the phenyl ring make with the reference plane are 16.5° and 107.3°, respectively. The phenyl ring and the quinoline ring make a dihedral angle of 106.4°. The plane defined by S(1)S(2)S(3)S(4) with the phenyl ring and the quinoline ring make dihedral angles of 75.4° and 49.6°, respectively.

An interesting structural feature of the complex is the presence of completely segregated columns of Ni(mnt)$_2$ anions, each flanked by four columns of cations, as revealed by the projection along the crystallographic *a*-axis in Fig. 2. As depicted in Fig. 3, the Ni$\cdots$Ni distances alternate between 3.717 and 4.466 Å in the Ni(mnt)$_2$ stacking column; the nearest Ni$\cdots$S and S$\cdots$S distances are 3.606 and 3.691 Å, respectively, values that are larger than the sums of the van der Waals radii of the corresponding

TABLE III Selected bond lengths (Å) and angles (°) for **1**

Bond length		*Bond angles*	
Ni(1)–S(1)	2.138(2)	S(1)–Ni(1)–S(2)	92.25(5)
Ni(1)–S(2)	2.141(1)	S(3)–Ni(1)–S(4)	92.53(5)
Ni(1)–S(3)	2.140(2)	S(1)–Ni(1)–S(4)	87.17(5)
Ni(1)–S(4)	2.142(1)	S(2)–Ni(1)–S(3)	88.05(5)
S(1)–C(2)	1.715(5)	C(2)–S(1)–Ni(1)	102.97(16)
S(2)–C(3)	1.704(5)	C(3)–S(2)–Ni(1)	103.14(18)
S(3)–C(6)	1.713(5)	C(6)–S(3)–Ni(1)	102.81(16)
S(4)–C(7)	1.724(4)	C(7)–S(4)–Ni(1)	102.98(16)
N(1)–C(1)	1.144(6)	N(1)–C(1)–C(2)	176.2(5)
N(2)–C(4)	1.104(7)	N(2)–C(4)–C(3)	167.0(6)
N(3)–C(5)	1.140(6)	N(3)–C(5)–C(6)	177.9(5)
N(4)–C(8)	1.130(6)	N(4)–C(8)–C(7)	177.2(5)
C(1)–C(2)	1.435(6)		
C(2)–C(3)	1.335(7)		
C(3)–C(4)	1.425(7)		
C(5)–C(6)	1.429(6)		
C(6)–C(7)	1.333(7)		
C(7)–C(8)	1.427(7)		

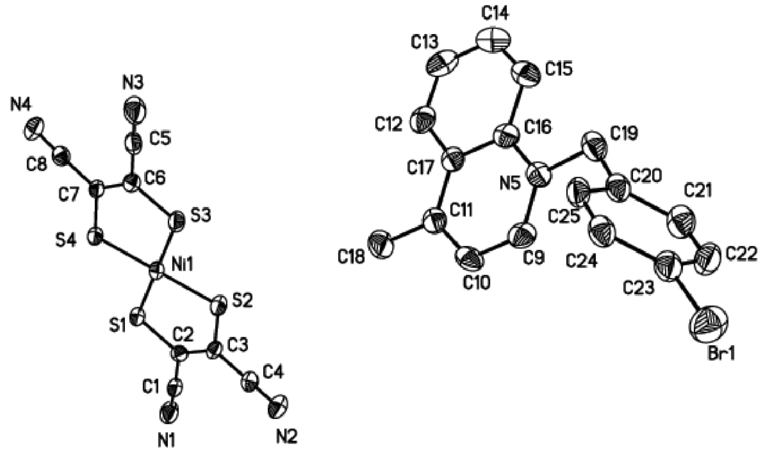

FIGURE 1 ORTEP plot (30% probability ellipsoids) showing the molecule structure of **1**.

atoms. The closest Ni···Ni separation between anion columns is 13.093 Å, significantly longer than the Ni···Ni separation within a column. Hence, there are clearly intermolecular interactions between neighboring Ni(mnt)$_2$ anions within an anion column. Thus, each Ni(mnt)$_2$ anion can be considered as a one-dimensional alternating magnetic chain via the shorter intermolecular interactions from the viewpoint of the crystal structure. The slipped zigzag configuration of Ni(mnt)$_2$ anions is displayed in Fig. 3. Intermolecular hydrogen bonds between anions and cations were observed in the crystal and molecular structure as shown in Fig. 4. The intermolecular contact is N(3) with the C(19) ($3/2-x$, $1/2-y$, $1/2-z$) atom at 3.332 Å. The hydrogen atom associated with these atoms has contact with N(3)···H(19) at 2.550 Å. At this distance significant van der Waals interactions would be expected, and these contacts play important roles in crystal packing.

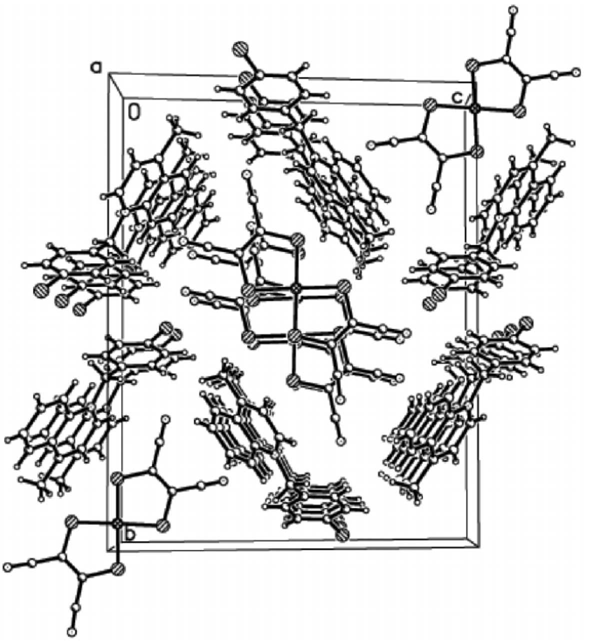

FIGURE 2 The packing diagram of a unit cell of **1** as viewed along the *c*-axis.

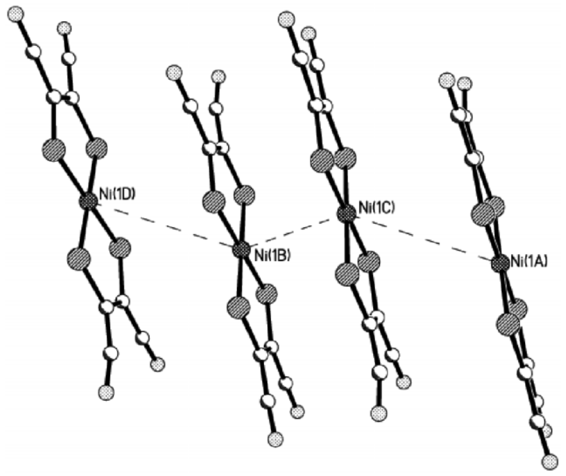

FIGURE 3 Side view of the anion stack of **1** showing the alternating space linear chain of [Ni(mnt)$_2$].

IR Spectra

In the IR spectra of **1**, a very strong ν(C≡N) band appears at 2208 cm^{-1}. The band at 3060 cm^{-1} is assigned to the stretching frequency of C–H in the aromatic rings. The ν(C=N) and ν(C=C) bands for the quinoline and phenyl rings are located at 1621(m), 1606(s), 1591(m) and 1529(s) cm^{-1}. The bands at 573(w) and 520(w) cm^{-1} originate from ν(Br–C). The ν(C=C) of mnt^{2-} is at 1487(s) cm^{-1} and the band at 864(m) cm^{-1} results from ν(C–S).

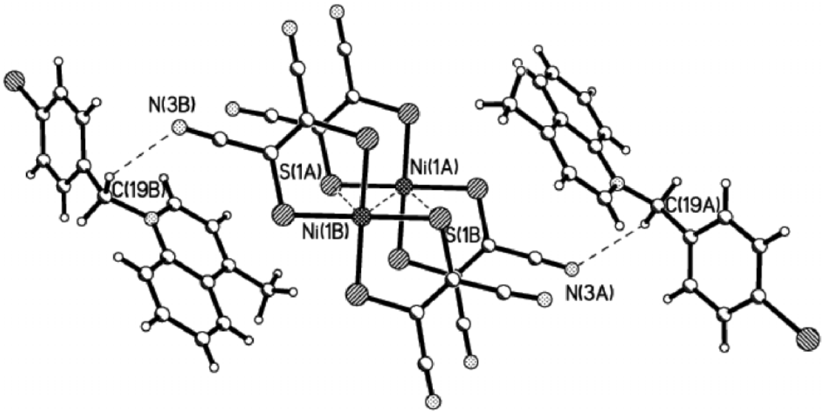

FIGURE 4 The intermolecular contacts between anions and cations of **1**.

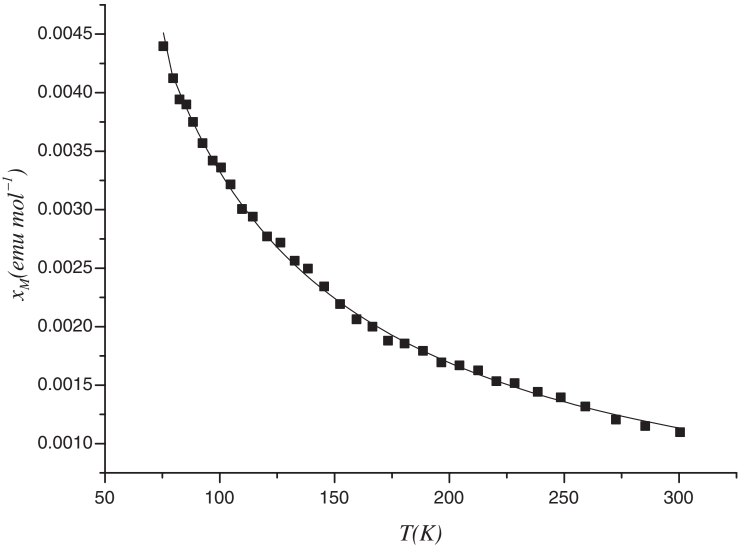

FIGURE 5 Plot of χ_M *vs.* T for **1**.

Magnetic Susceptibility

The magnetic behavior of **1** was studied in the range 300–75 K. The molar magnetic susceptibility, χ_m, as a function of T is shown in Fig. 5. Corrections for the diamagnetism of **1** are estimated from Pascal's constants to be -261.12×10^{-6} emu mol^{-1}. The effective magnetic moment of **1** is 1.717 μB at 300 K, which is slightly less than the calculated spin-only value of 1.732 μB for a system composed of noninteracting $g = 2$, $s = 1/2$ spin sites, and drops to 1.577 μB at 75 K. The effective magnetic moment of **1** decreases with temperature decrease, which suggests that weak antiferromagnetic interactions between adjacent $s = 1/2\,\mathrm{Ni}^{\mathrm{III}}$ spin magnetic centers exist within the anion chain. The magnetic susceptibility data for the complex can be interpreted in terms of a one-dimensional antiferromagnetic Heisenberg alternating chain mode

($H=-J\sum[S_{2i}S_{2i-1}+\alpha S_{2i}S_{2i+1}]$, where α is the alternating parameter) [19,20]. The best-fit parameters obtained by least-squares fit are: $J=-3.57\,\mathrm{cm}^{-1}$, $\alpha J=-2.39\,\mathrm{cm}^{-1}$ and $R=4.6\times10^{-5}$. The model provides an excellent fit (the solid line Fig. 5), as indicated by the low value of R. We recently reported an ion-pair complex of Ni(mnt)$_2$ containing the large cation [NO$_2$BzQl]$^+$ (NO$_2$BzQl = 1-(4′-nitrobenzyl)quinolinium) that exhibits diamagnetic behavior at 75–300 K [21]. Hence, it is clearly inferred that adding the Br in the para-position of the benzyl ring and Me in the 4-position of quinoline of the cation has significantly influenced the crystal packing pattern and the magnetic properties of the complex.

Summary

A novel ion-pair complex [BrBzMeQl][Ni(mnt)$_2$] exhibiting antiferromagnetic behavior has been prepared and its single-crystal structure analysis shows that the Ni(mnt)$_2$ anions of the complex form one-dimensional alternating magnetic chains via the shorter intermolecular interactions. This work further reveals that the topology and size of the counter cation in Ni(mnt)$_2$ complexes play an important role in controlling the stacking pattern of the anions and cations, which further influences the magnetic properties of these complexes.

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