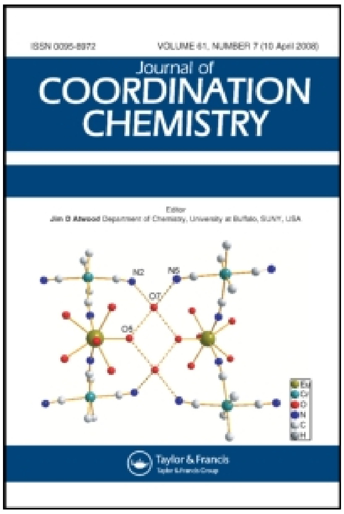

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Structure and magnetic behaviour of a 1-(4'-fluorobenzyl)quinolinium salt of the bis(maleonitriledithiolato)Ni(III) ion

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Structure and magnetic behaviour of a 1-(4′-fluorobenzyl)quinolinium salt of the bis(maleonitriledithiolato)Ni(III) ion

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A novel molecular solid, [FBzQl][Ni(mnt)$_2$] (**1**) ([FBzQl]$^+$ = 1-(4′-fluorobenzyl)quinolinium and mnt = maleonitriledithiolate) has been characterized and its structure determined by single-crystal X-ray methods. The complex is triclinic, space group $P\bar{1}$, with $a = 7.369(2)$, $b = 10.359(3)$, $c = 16.337(5)$ Å, $\alpha = 87.40(1)$, $\beta = 82.70(1)$, $\gamma = 74.97(1)°$, $V = 1194.6(6)$ Å^3, $Z = 2$. Ni(mnt)$_2^-$ anions and [FBzQl]$^+$ cations are alternately stacked and form 1D column *via* $\pi\cdots\pi$ interactions between the Ni(mnt)$_2$ plane and neighboring quinoline rings. Cation–cation and anion–anion $\pi\cdots\pi$ interactions, and hydrogen bonds between adjacent columns generate a 3D network. Magnetic susceptibility measurement for **1** in the temperature range 75–300 K show antiferromagnetic behaviour.

Keywords: Maleonitriledithiolate; 1-(4′-Fluorobenzyl)quinolinium; Nickel(III); X-ray structure; Magnetic properties

1. Introduction

Considerable attention has been devoted to magneto-structural studies of maleonitriledithiolate (mnt^{2-}) nickel(III) complexes [1–6]. This is mainly because some complexes exhibit unusual magnetic properties [1, 7–12], short Ni$\cdots$Ni, Ni$\cdots$S, S$\cdots$S, S$\cdots$N, and C$\cdots$N contact distances can play significant roles in super-exchange pathways and the Ni(III) ions in the solid state form a one-dimensional magnetic chain [13–18]. Magnetic coupling between Ni(mnt)$_2^-$ anions is very sensitive to not only the overlap of neighboring Ni(mnt)$_2^-$ anions but also intermolecular contacts, and small structural changes can result in large changes in properties due to the subtle interplay between ferromagnetic and antiferromagnetic components of intermolecular interactions [19, 20]. The topology and size of the cation in Ni(mnt)$_2^-$ salts may also play

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an important role in controlling the stacking pattern and further influence magnetic properties. Following previous work involving the 1-(4′-fluorobenzyl)quinolinium ion $[\mathrm{FBzQl}]^+$, we succeeded in synthesizing the $[\mathrm{FBzQl}][\mathrm{Ni(mnt)_2}]$ salt. Its preparation, structural characterization and magnetic properties are presented below.

2. Experimental

1-(4-Fluorobenzyl)quinolinium bromide and disodium maleonitriledithiolate were prepared following published procedures [21, 22]. A method similar to that used for preparing $[\mathrm{Bu_4N}]_2[\mathrm{Ni(mnt)_2}]$ which was used to make $[\mathrm{FBzQl}]_2[\mathrm{Ni(mnt)_2}]$ [22]. Other regents were of analytical grade and used without further purification. Elemental analyses were run on a Model 240 Perkin-Elmer instrument. IR spectra (KBr pellets) were recorded on an IF66V FT-IR (400–4000 $\mathrm{cm^{-1}}$ region) spectrophotometer. Magnetic susceptibility data for powder samples were collected over the temperature range 75–300 K using a Cahn 2000 Faraday-type magnetometer; diamagnetic corrections were made using Pascal's constants.

2.1. *Preparation of [FBzQl][Ni(mnt)₂]*

A MeCN solution (20 $\mathrm{cm^3}$) of I_2 (200 mg, 0.79 mmol) was slowly added to a MeCN solution (50 $\mathrm{cm^3}$) of $[\mathrm{FBzQl}]_2[\mathrm{Ni(mnt)_2}]$(816 mg, 1 mmol) and the mixture stirred for 3 h. MeOH (90 $\mathrm{cm^3}$) was then added, and the mixture allowed to stand overnight; 515 mg of black microcrystals that formed were filtered off, washed with MeOH and dried

Table 1. Crystallographic data for **1**.

Chemical formula	$\mathrm{C_{24}H_{13}FN_5NiS_4}$
Formula weight	577.36
T (K)	293(2)
Wavelength (Å)	0.71073
Space group	$P\bar{1}$
Unit cell dimensions	
a (Å)	7.369(2)
b (Å)	10.359(3)
c (Å)	16.337(5)
α (°)	87.40(1)
β (°)	82.70(1)
γ (°)	74.97(1)
V (Å^3)	1194.6(6)
Z	2
D_{Calcd} (g cm^{-3})	1.605
μ (Mo-Kα) (mm^{-1})	1.194
F(000)	586
θ range for data collection (°)	2.41–26.18
Index ranges	$-8 \le h \le 8$, $-12 \le k \le 10$, $-19 \le l \le 15$
Reflections collected	5923
Independent reflections	4134 ($R_{\mathrm{int}} = 0.022$)
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	4134/0/316
Goodness-of-fit on F^2	1.023
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0391$, $wR_2 = 0.0769$
R indices (all data)	$R_1 = 0.0564$, $wR_2 = 0.0802$
Largest diff. peak and hole (e Å^{-3})	0.45 and −0.30

Table 2. Atomic coordinates and equivalent isotropic displacement parameters (Å^2) for **1**.

Atom	x/a	y/b	z/c	U_{eq}
Ni(1)	0.18292(5)	0.85754(3)	0.17002(2)	0.0406(1)
S(1)	0.20600(11)	0.86277(7)	0.29855(5)	0.0474(3)
S(2)	0.10542(11)	1.07106(7)	0.15929(5)	0.0492(3)
S(3)	0.16545(12)	0.84843(7)	0.04052(5)	0.0499(3)
S(4)	0.25537(11)	0.64416(7)	0.18386(5)	0.0493(3)
N1	0.1858(4)	1.0912(3)	0.46581(18)	0.0713(12)
N2	0.0381(5)	1.3729(3)	0.28561(18)	0.0837(13)
N3	0.2222(4)	0.5973(3)	−0.12255(18)	0.0757(14)
N4	0.3219(4)	0.3381(3)	0.06304(17)	0.0703(11)
N5	0.7517(3)	0.7621(2)	0.27185(15)	0.0466(9)
F1	0.0965(3)	0.5974(2)	0.49461(13)	0.0975(10)
C1	0.1702(4)	1.0666(3)	0.4009(2)	0.0495(11)
C2	0.1574(4)	1.0306(3)	0.31843(18)	0.0422(10)
C3	0.1117(4)	1.1214(3)	0.25743(18)	0.0437(10)
C4	0.0705(5)	1.2626(3)	0.2722(2)	0.0557(12)
C5	0.2906(4)	0.4500(3)	0.07374(18)	0.0488(11)
C6	0.2505(4)	0.5910(3)	0.08650(17)	0.0430(10)
C7	0.2133(4)	0.6799(3)	0.02359(17)	0.0425(10)
C8	0.2162(5)	0.6352(3)	−0.0582(2)	0.0535(11)
C9	0.4892(5)	0.7453(3)	0.45641(18)	0.0536(12)
C10	0.3180(5)	0.7225(3)	0.4908(2)	0.0626(16)
C11	0.2647(5)	0.6187(4)	0.4616(2)	0.0648(16)
C12	0.3694(6)	0.5381(3)	0.4011(2)	0.0683(16)
C13	0.5393(5)	0.5621(3)	0.3673(2)	0.0593(14)
C14	0.6002(4)	0.6664(3)	0.39427(19)	0.0453(11)
C15	0.7817(4)	0.6947(3)	0.35364(17)	0.0503(11)
C16	0.7755(4)	0.6830(3)	0.2072(2)	0.0569(12)
C17	0.7376(5)	0.7324(4)	0.1300(2)	0.0623(14)
C18	0.6737(4)	0.8660(3)	0.11858(19)	0.0586(14)
C19	0.6505(4)	0.9532(3)	0.18469(18)	0.0448(11)
C20	0.5880(4)	1.0915(3)	0.1747(2)	0.0614(12)
C21	0.5673(5)	1.1730(3)	0.2390(2)	0.0655(14)
C22	0.6099(4)	1.1187(3)	0.3157(2)	0.0590(12)
C23	0.6714(4)	0.9848(3)	0.32957(18)	0.0504(11)
C24	0.6916(4)	0.8986(3)	0.26314(18)	0.0414(10)

under vacuum. Yield: 89%. Anal. Calcd for $C_{24}H_{13}FN_5NiS_4$ (%): C, 49.93; H, 2.27; N, 12.13. Found: C, 49.87; H, 2.38; N, 12.02. IR (cm^{-1}): 3087(m), 3059(m), 2210(m), 1632(s), 1608(s), 1581(s), 1525(s), 1484(vs), 1162(s). Black single crystals suitable for X-ray structure analysis were obtained by evaporating an MeCN/*i*-PrOH (1 : 1, v/v) solution of **1** for two weeks at room temperature.

2.2. *X-ray crystallography*

A crystal ($0.45 \times 0.32 \times 0.30\,\mathrm{mm}^3$) of **1** was mounted on a Bruker Smart APEX CCD area detector and used for data collection. Diffraction data were collected at 293(2) K using graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) by ω-scan mode in the angular range $2.0 < \theta < 25.0°$. Space group, lattice parameters, and other relevant crystallographic information are listed in table 1 while atomic coordinates for non-hydrogen atoms are listed in table 2. The structure was solved by direct methods and refined on F^2 by full-matrix least-squares techniques using SHELXTL [23]. All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen 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.

3. Results and discussion

3.1. *Crystal structure of 1*

An ORTEP diagram of **1** together with the atom numbering scheme is shown in figure 1. The asymmetric unit includes one $\mathrm{Ni(mnt)_2^-}$ anion and one $\mathrm{[FBzQl]^+}$ cation,

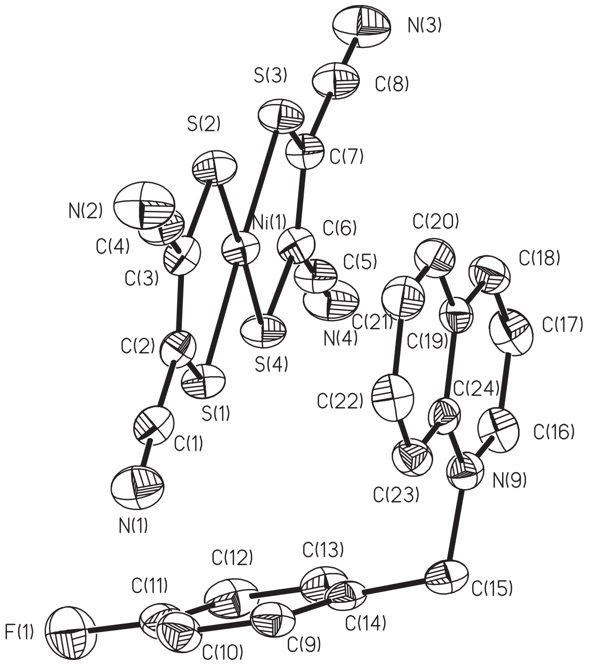

Figure 1. ORTEP plot (30% probability ellipsoids) showing the molecular structure of **1**.

Table 3. Selected bond parameters for **1**.

Ni(1)–S(1)	2.132(1)
Ni(1)–S(2)	2.141(1)
Ni(1)–S(3)	2.133(1)
Ni(1)–S(4)	2.144(1)
S(1)–C(2)	1.719(3)
S(2)–C(3)	1.718(3)
S(3)–C(7)	1.717(3)
S(4)–C(6)	1.714(3)
S(1)–Ni(1)–S(2)	92.53(3)
S(1)–Ni(1)–S(4)	86.32(3)
S(2)–Ni(1)–S(3)	88.49(3)
S(3)–Ni(1)–S(4)	92.67(3)

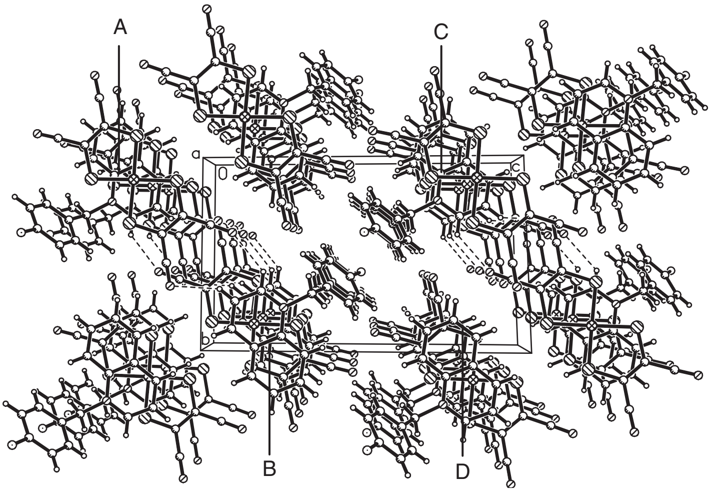

Figure 2. Packing diagram viewed along the *a* axis.

and the quinoline ring of the cation is nearly parallel with the plane of $Ni(mnt)_2^-$ anion (the dihedral angle is 4.8°). The $Ni(mnt)_2^-$ ion exhibits square planar coordination geometry. Ni–S bond distances and S–Ni–S angles (table 3) in the five-membered rings agree well with those found in [FBzPy][Ni(mnt)$_2$] ([FBzPy] = 1-(4′-fluorobenzyl)pyridinium) [9]. The cation adopts a conformation where both the phenyl and quinoline rings are twisted with respect to the C(14)–C(15)–N(5) reference plane. Dihedral angles that quinoline and phenyl rings make with the reference plane are 93.6 and 93.7°, respectively. $Ni(mnt)_2^-$ anions and $[FBzQl]^+$ cations are alternately stacked as revealed by a projection along the crystallographic *a* axis (figure 2) and form a column through $\pi\cdots\pi$ interactions between the quinoline rings and $Ni(mnt)_2^-$ ions (figure 3a). This stacking mode is obviously different from that of [FBzPy][Ni(mnt)$_2$] [9], indicating that the change from pyridine to quinoline in the cation plays an important role in stacking. The nearest distance between a quinoline ring and the Ni(III) ion in $Ni(mnt)_2^-$ ion is 3.645 Å. There are two types of significant interactions between column A and column B (figure 2). Short C⋯N interactions between $Ni(mnt)_2^-$ anions (the contacts C(5)⋯N(3A), C(8)⋯N(4A), are 3.680 and 3.476 Å) are as shown in figure 3(b). Two non-classical hydrogen bonds observed between anion and cation are as depicted in figure 3(c); one is between C(16) of $[FBzQl]^+$ cations and N(3) of the CN groups of the $Ni(mnt)_2^-$ anions, and the other is a hydrogen bond between C(17)–H(17) of the cation and N(4) atom of $Ni(mnt)_2^-$ ion. It should be noted that the $\pi\cdots\pi$ stacking interactions of benzene rings of cations between columns B and C are observed (figure 4a) with a contact distance from the centres of the rings being 3.687 Å. Between columns C and D (figure 4b), the C(15) atom of $[FBzQl]^+$ cation is hydrogen bonded to the N(2) atoms of $Ni(mnt)_2^-$ ion. Corresponding distances and angles are summarized in table 4. At these distances significant Van der Waals interactions would be expected, and the effect of the combination of π–π stacking, short C⋯N interactions and the hydrogen bonds generate a 3D network structure (figure 2), and provides a structural basis for antiferromagnetic interactions in **1**.

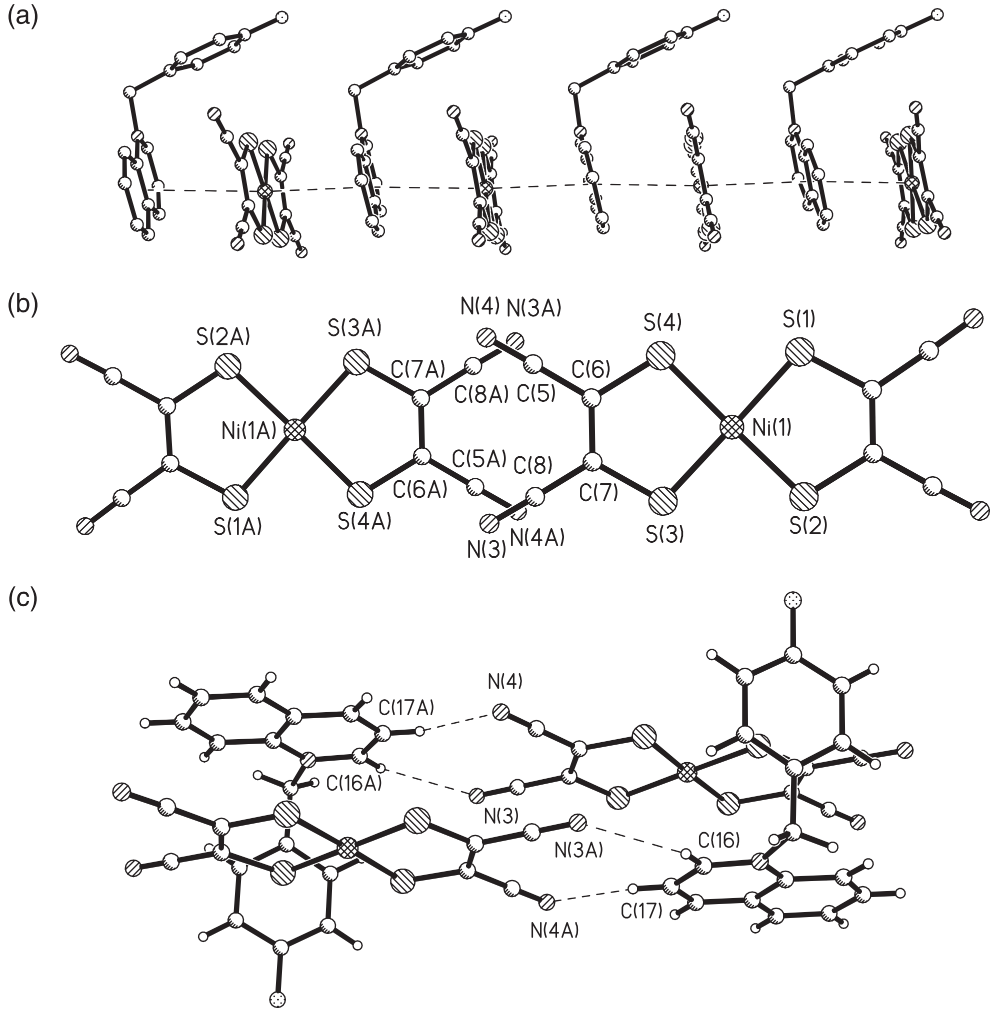

Figure 3. (a) $Ni(mnt)_2^-$ anions and $[FBzQl]^+$ cations are alternately stacked to form a column through $\pi\cdots\pi$ interactions between quinoline rings and the planes of $Ni(mnt)_2^-$ ions; (b) short C···N interactions of anions between columns A and B; (c) hydrogen bonds between columns A and B.

3.2. *IR and mass spectra, and magnetic properties*

The IR spectrum of **1** is consistent with the structural data presented above. Bands at 3087 and 3059 cm^{-1} are assigned to C–H stretching in the aromatic ring. A very strong $\nu(C{\equiv}N)$ band is observed at 2210 cm^{-1}. The $\nu(C{=}N)$ and $\nu(C{=}C)$ bands for the pyridine and phenyl rings are located at 1632(m), 1608(s), 1581(m) and 1525(s) cm^{-1}; $\nu(C{=}C)$ of mnt^{2-} is at 1484(s) cm^{-1} and the $\nu(C–F)$ band is at 1162 cm^{-1}. Negative- and positive-ion ESI-MS spectra of **1** in MeCN solution are dominated by the 238.2 peak due to $[FBzQl]^+$ and the peak at 340.3 is assigned to $[Ni(mnt)_2 + H]^-$.

Temperature-dependent molar magnetic susceptibilities of **1** were measured in a magnetic field of 5000 Oe in the range 75–300 K (figure 5). The $\chi_m T$ value at 300 K

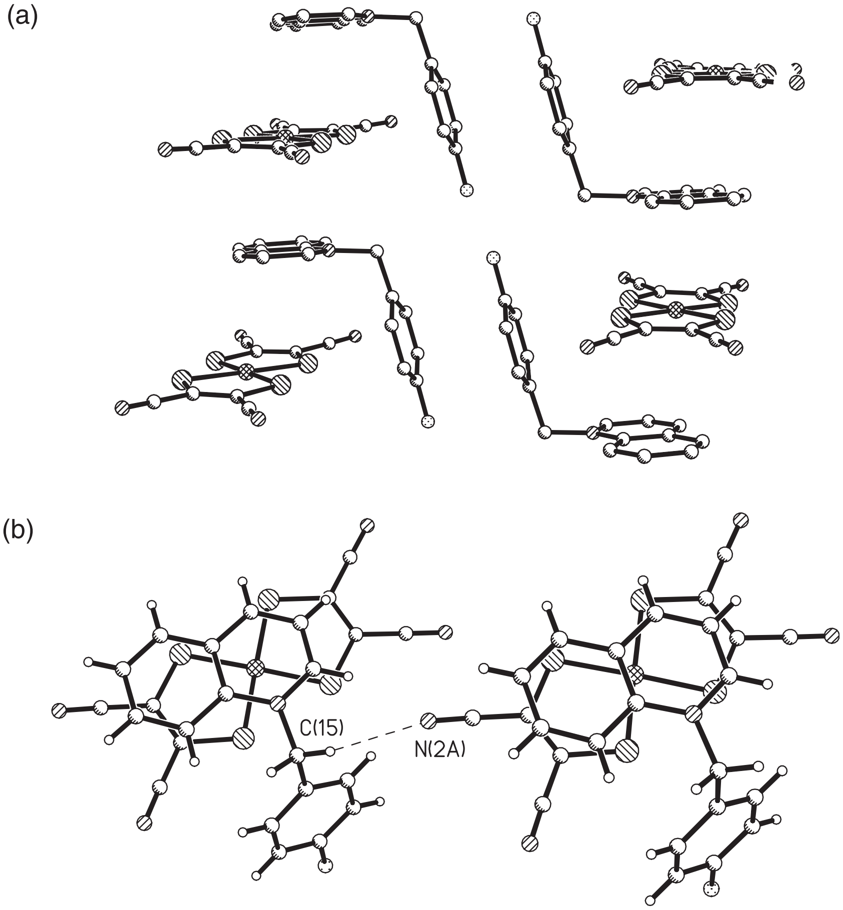

Figure 4. (a) Arrangement of $\pi\cdots\pi$ interactions involving phenyl rings of cations between columns B and C; (b) the hydrogen bond between columns C and D.

Table 4. Hydrogen bond details for **1** (Å and °).

D–H···A	d(D–H)	d(H···A)	d(D···A)	∠(DHA)
C(15)–H(15B)···N(2)#1	0.97	2.62	3.529(4)	155.0
C(16)–H(16)···N(3)#2	0.93	2.62	3.268(4)	127.0
C(17)–H(17)···N(4)#2	0.93	2.59	3.376(4)	143.0

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

is 0.372 emu K mol^{-1}, as expected for Ni(III) ($S=1/2$) being magnetically isolated. As the temperature is lowered, χ_mT smoothly decreases to 0.290 emu K mol^{-1} at 75 K. The drop in χ_mT as T decreases is characteristic of a magnetic system with dominant antiferromagnetic interactions between N(III) ions. The magnetic data can be fitted by the Curie–Weiss law. The best fit curve for **1** is gives $C=0.40\,\mathrm{cm^3\,K\,mol^{-1}}$, $\theta=-29.85$ K and $R=2.2\times10^{-5}$.

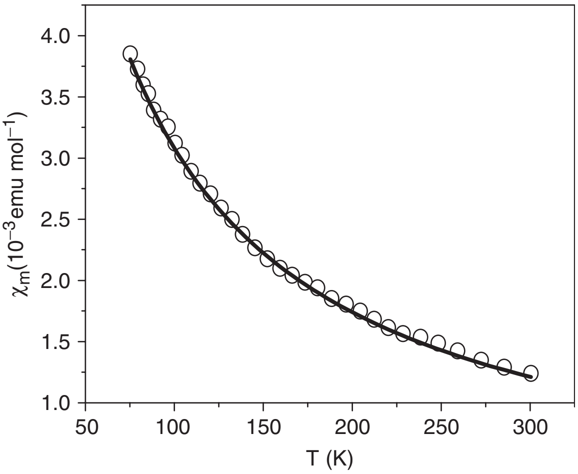

Figure 5. Plot of χ_m *versus* T in the range of 75–300 K, the solid line is reproduced from the theoretic calculation and detailed fitting procedure described in the text.

Supplementary material

Crystallographic data for **1** have been deposited at the Cambridge Crystallographic Data Centre as supplementary publication CCDC 294634. 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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