Synthesis, Crystal Structure, and Magnetic Properties of the Two-Dimensional Nickel(II) Complex via Covalent and Hydrogen Bonds: [Ni(L)(H$_2$O)$_2$][Ni$_2$(L)(NTA)$_2$]·6H$_2$O (L = 3,14-dimethyl-2,6,13,17-tetra-azatricyclo[14,4,0$^{1.18}$,0$^{7.12}$]docosane, NTA = Nitrillotriacetate)

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Abstract

A new compound [Ni(L)(H$_2$O)$_2$][Ni$_2$(L)(NTA)$_2$]·6H$_2$O (**1**) (L = 3,14-dimethyl-2,6,13,17- tetraazatricyclo[14,4,0$^{1.18}$,0$^{7.12}$]-docosane, NTA = nitrillotriacetate) was prepared and its structure was determined by the X-ray diffraction method. Complex **1** crystallizes in the monoclinic space group $P2_1/c$ with $a = 11.217(2)$ Å, $b = 18.048(5)$ Å, $c = 15.393(3)$ Å, $\beta = 90.78(2)°$, $V = 3115.9(12)$ Å^3, and $Z = 2$, Each nickel atom in complex **1** has a distorted octahedral coordination geometry with an inversion center. Magnetic susceptibility measurement showed a weak intramolecular antiferromagnetic interaction between two Ni(1) and Ni(2) centers with a J value of $-0.93(1)$ cm^{-1}. The intermolecular hydrogen-bonding interaction gives rise to a two-dimensional network.

Introduction

In recent years, there has been increasing interest in the self-assembly and self-organization of the infinite metal complexes with specific network topologies because of their potential properties in supramolecular chemistry and crystal engineering [1–8]. It has been widely observed that the type and topology of the product generated from the self-assembly of inorganic metal species and organic ligands can be influenced by the choice of the metal and organic ligand species, metal-to-ligand ratio, solvent system, and inorganic counterion [9–12]. Among organic ligands, 1,3,5-benzenetricarboxylate (BTC^{3-}) has been proved to offer special structural features due to the rigidity and stability of the resulting porous framework [13]. The two-dimensional network [Ni(L)]$_3$[BTC]$_2$·18H$_2$O (L = 1,8-bis(2-hydroxyethyl)-1,3,6,8,10,13-hexaazacyclotetradecane) results in a brick wall structure, while a honeycomb structure is obtained for [Ni(L)]$_3$[BTC]$_2$·18H$_2$O·2C$_5$H$_5$N. The different molecular topologies in complexes arise from the different coordination mode of the organic BTC ligand.

In the present work, we report the structure and magnetic properties of a chain compound [Ni(L)(H$_2$O)$_2$][Ni$_2$(L)(NTA)$_2$]·6H$_2$O (**1**) (L = 3,14-dimethyl-2,6,13,17-tetraazatricyclo[14,4,0$^{1.18}$, 0$^{7.12}$]docosane, NTA = nitrillotriacetate). This compound is formed by the reaction of NiCl$_2$·6H$_2$O, macrocyclic ligand L, and the tridentate organic ligand NTA. All reactions were performed in methanol solution with a metal: ligands ratio of 1 : 1 : 1.

Experimental

Materials and physical measurements

All chemicals and solvents used in the synthesis were of reagent grade and were used without further purification. The macrocyclic ligand L was prepared according to the literature method [14]. IR spectra were recorded with a Perkin-Elmer Paragon 1000 FT-IR spectrophotometer using KBr pellets. Uv/vis diffuse reflectance spectra were recorded with a Shimadzu UV2401 PC/DRS spectrophotometer. Magnetic susceptibility data on powder samples were collected in the temperature range 2–300 K in an applied field of 1 T with the use of a Quantum Design MPMS7 SQUID magnetometer. The diamagnetic corrections were estimated from Pascal's constants. Elemental analyses were carried out by the Korea Research Institute of Chemical Technology, Taejon, Korea.

Synthesis of [Ni(L)(H$_2$O)$_2$][Ni$_2$(L)(NTA)$_2$]·6H$_2$O (**1**)

To a methanol (20 mL) solution of NiCl$_2$·6H$_2$O (238 mg, 1 mM) was added L (337 mg, 1 mM) and sodium nitrillotriacetate (275 mg, 1 mM). The mixture was refluxed

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for 2 h and then cooled to room temperature. The solution was filtered and left at room temperature until the violet crystals formed. The products were filtered off, washed with diethyl ether and dried in air. Yield: 62%. Calcd. for $C_{52}H_{108}N_{10}Ni_3O_{20}$: C, 45.60; H, 7.95; N, 10.23%. Found: C, 45.53; H, 7.92; N, 10.31%. IR (ν_{max}, cm^{-1}): 3416(s), 3354(m), 3055(s), 2934(s), 1618(s), 1467(m), 1396(s), 1307(s), 1275(m), 1224(w), 1188(w), 1128(m), 1111(m), 1093(s), 1050(m), 1020(m), 992(m), 952(w), 924(w), 894(m), 783(m), 730(w), 614(m), 515(w) (KBr). UV/VIS (diffuse reflectance spectrum, λ_{max}): 530 nm.

X-ray crystallography

The crystallographic data, conditions used for the intensity collection, and some features of the structure refinement are listed in Table 1. Data were collected on an Enraf-Nonius CAD4 diffractometer equipped with graphite-monochromated Mo-Kα radiation ($\lambda = 0.71069$ Å) in the $\omega - 2\theta$ scan mode. The intensity data were corrected for Lorentz and polarization effects. An empirical absorption correction based on ψ-scan was applied. The structure was solved by direct methods [15] and the least-squares refinement of the structure was performed by the program SHELXL97 [16]. All non-hydrogen atoms were refined with anisotropic thermal parameters. All hydrogen atoms except for the water hydrogen atoms were placed in calculated positions with isotropic displaced parameters. Final atomic coordinates and equivalent isotropic displacement parameters are given in Table 2.

Results and discussion

Description of the structure

An ORTEP diagram of [Ni(L)(H$_2$O)$_2$][Ni$_2$(L)(NTA)$_2$]·6H$_2$O (**1**) with the atomic numbering scheme is shown in Figure 1. The selected bond distances and angles are listed in Table 3. The crystallographically independent nickel(II) cations are located at centers of inversion. The coordination environment of Ni(1) is described as a tetragonally distorted octahedron with four carboxylate oxygen atoms (O(1), O(6), O(1)′, and O(6)′) of two NTA ligands that comprise the equatorial plane, whereas the axial positions are filled by two nitrogen atoms (N(1) and N(1)′) of two NTA ligands. The Ni(1)—N bond distance of 2.117(5) Å is slightly longer than the Ni(1)—O distances (2.040(5) and 2.061(4) Å). The coordination geometry of Ni(2) and Ni(3) ions reveals a distorted octahedron with secondary amines of macrocycles in which two *trans* carboxylate oxygens of NTA ligands and two *trans* water molecules have assembled around each metal center. The average Ni—N (secondary amines) distances (Ni(2)—N$_{av}$ = 2.072(4) and Ni(3)—N$_{av}$ = 2.067(4) Å) are similar to those observed for high-spin octahedral nickel(II) complexes with 14-membered tetraaza macrocyclic ligands [17–21]. Furthermore, the Ni—N distances in the Ni(2)N$_4$ and Ni(3)N$_4$ planes are shorter than the axial Ni—O distances (Ni(2)—O(2) = 2.161(4) and Ni(3)—Ow(1) =

Table 1. Crystal data and structure refinement for **1**

Compound	[Ni(L)(H$_2$O)$_2$][Ni$_2$(L)(NTA)$_2$]·6H$_2$O
Color/shape	Light violet/block
Chemical formula	$C_{52}H_{108}N_{10}Ni_3O_{20}$
Formula weight	1369.61
Temperature	293 K
Crystal system	Monoclnic
Space group	$P2_1/c$
Unit cell dimensions	$a = 11.217(2)$ Å $\alpha = 90°$
	$b = 18.048(5)$ Å $\beta = 90.78(2)°$
	$c = 15.393(3)$ Å $\gamma = 90°$
Volume	3115.9(12) Å^3
Z	2
Density (calculated)	1.460 mg/m^3
Absorption coefficient	0.977 mm^{-1}
Diffractometer/scan	Enraf-Nonius CAD4/$\omega - 2\theta$
Radiation/wavelength	Mo-$K\alpha$(graphite monochrom.)/0.71069 Å
$F(000)$	1468
Crystal size	$0.30 \times 0.26 \times 0.17$ mm
θ range for data collection	2.14 to 22.50
Index ranges	$0 \leq h \leq 12, 0 \leq k \leq 19, -16 \leq l \leq 16$
Reflections collected	4317
Independent reflections	4072 [R(int) = 0.0686]
Absorption correction	ψ-scan
Max. and min. transmission	0.85 and 0.74
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	4072/0/394
Goodness of fit on F^2	1.045
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.0725P)^2$ $+5.5841P]$ with $P = (F_o^2 + 2F_c^2)/3$
Final R indices [$I > 2\sigma(I)$]	$R1^a = 0.0592$, $wR2^b = 0.1336$
R indices (all data)	$R1^a = 0.1148$, $wR2^b = 0.1629$
Largest diff. peak and hole	0.676 and -0.673 eÅ^{-3}

[a] $R1 = \|F_o| - |F_c\|/\Sigma|F_o|$.
[b] $wR2 = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$.

2.177(5) Å), giving an axially elongated octahedron. Also, the axial Ni(2)—O(2) and Ni(3)—Ow(1) bonds are bent slightly off the perpendicular to the NiN$_4$ plane by 1.2–4.1° and 2.3–5.9°, respectively. On the other hand, the Ni(1) and Ni(2) centers are connected by NTA ligands through the carboxylate oxygen atoms into a one-dimensional zig-zag chain. The dihedral angle between two neighboring Ni(1)N$_2$O$_2$ and Ni(2)N$_4$ planes is 26.9(2)°. The coordination of the carboxylate bridge is strongly asymmetrical; the two Ni(1)—O(1)—C(2) and Ni(2)—O(2)—C(2) angles are 114.6(4) and 135.6(4)°. The intramolecular Ni(1)···Ni(2) distance (5.609(1) Å) is significantly elongated compared to [(pyrazolate)Ni$_2$(μ-OAc)(acetone)$_2$](ClO$_4$)$_2$ (4.161 Å) [22]. This fact may be due to the steric hindrance imposed by the macrocyclic ligand L. In addition, the Ni(1) and Ni(3) atoms in compound **1** are linked by an intermolecular hydrogen bond involving the uncoordinated carboxylate oxygen of the NTA unit and the coordinated water molecule (O(4)···Ow(1) = 2.651(7) Å) connecting to an adjacent chain (Figure 1). This intermolecular hydrogen-bonding interaction gives rise to a two-dimensional layered arrangement (Figure 2). The carboxylate oxygen atoms of NTA

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{Å}^2 \times 10^3$) for **1**. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

Atom	x	y	z	U(eq)
Ni(1)	5000	5000	5000	24(1)
Ni(2)	10000	5000	5000	26(1)
Ni(3)	5000	10000	5000	30(1)
O(1)	6826(4)	4986(3)	4868(3)	36(1)
O(2)	8439(4)	5700(3)	5045(3)	35(1)
O(3)	5546(6)	7480(3)	6303(4)	73(2)
O(4)	3801(5)	7793(3)	5764(3)	64(2)
O(5)	6005(5)	4899(3)	7505(3)	54(2)
O(6)	5252(4)	4584(3)	6221(3)	41(1)
N(1)	5407(4)	6028(3)	5596(3)	23(1)
N(2)	9847(5)	5094(3)	3654(3)	35(1)
N(3)	11034(5)	5938(3)	4898(4)	32(2)
N(4)	3305(5)	10232(3)	4501(4)	39(2)
N(5)	4624(5)	10818(3)	5877(4)	38(2)
C(1)	6532(5)	6250(3)	5191(4)	28(2)
C(2)	7336(6)	5596(4)	5035(4)	26(2)
C(3)	4459(6)	6585(4)	5457(5)	32(2)
C(4)	4615(7)	7337(4)	5895(5)	38(2)
C(5)	5579(7)	5862(4)	6527(5)	43(2)
C(6)	5627(6)	5048(4)	6763(4)	34(2)
C(7)	10764(7)	5638(4)	3367(5)	43(2)
C(8)	10550(7)	5941(5)	2451(5)	62(3)
C(9)	11515(9)	6492(7)	2200(7)	86(4)
C(10)	11616(10)	7107(6)	2870(8)	87(4)
C(11)	11822(7)	6810(5)	3769(6)	61(3)
C(12)	10845(6)	6260(5)	4029(5)	40(2)
C(13)	10939(6)	6466(4)	5628(5)	46(2)
C(14)	11232(7)	6095(5)	6496(5)	51(2)
C(15)	9711(7)	4406(5)	3126(5)	48(2)
C(16)	10846(9)	3991(6)	2970(7)	85(3)
C(17)	2684(6)	10693(4)	5144(5)	44(2)
C(18)	1584(7)	11096(5)	4773(6)	67(3)
C(19)	1016(8)	11583(5)	5466(7)	81(3)
C(20)	1900(8)	12130(5)	5853(7)	74(3)
C(21)	2991(7)	11735(4)	6214(6)	57(2)
C(22)	3583(6)	11249(4)	5523(5)	38(2)
C(23)	5662(7)	11288(4)	6144(5)	45(2)
C(24)	6648(7)	10814(5)	6529(6)	60(3)
C(25)	2585(7)	9626(5)	4090(6)	56(2)
C(26)	1949(8)	9146(5)	4749(7)	78(3)
Ow(1)	4415(5)	9202(3)	5965(3)	47(1)
Ow(2)	4962(19)	3144(13)	6928(12)	99(6)
Ow(2)[a]	4410(30)	3280(20)	7220(20)	99(6)
Ow(3)	7366(6)	5693(5)	2912(5)	113(3)
Ow(4)	7760(50)	7760(30)	7020(50)	270(20)
Ow(4)[a]	7250(80)	8190(60)	7000(80)	270(20)

[a] There is disorder in the two water molecules Ow(2) and Ow(4).

are also hydrogen-bonded to the secondary amines of macrocycles $(\text{O}(1)^i \cdots \text{N}(3) = 2.942(7)$ Å, 155.4°; $\text{O}(2) \cdots \text{N}(2) = 2.894(7)$ Å, 106.3°; $\text{O}(2)^i \cdots \text{N}(3) = 3.016(7)$ Å, 102.9°; $\text{O}(5)^{ii} \cdots \text{N}(5) = 3.082(8)$ Å, 170.2°; symmetry codes i: $-x+2, -y+1, -z+1$; ii: $-x+1, y+0.5, -z+1.5$).

Magnetic properties

The temperature dependency of the magnetic susceptibilities (χ_m) and the effective magnetic moments (μ_{eff}) per nickel(II) ion for compound **1** is shown in Figure 3. The magnetic moment per nickel(II) ion gradually decreases from 3.05 μ_B at around 301 K to 2.07 μ_B at 2 K, which is indicative of an antiferromagnetic interaction. In **1**, the
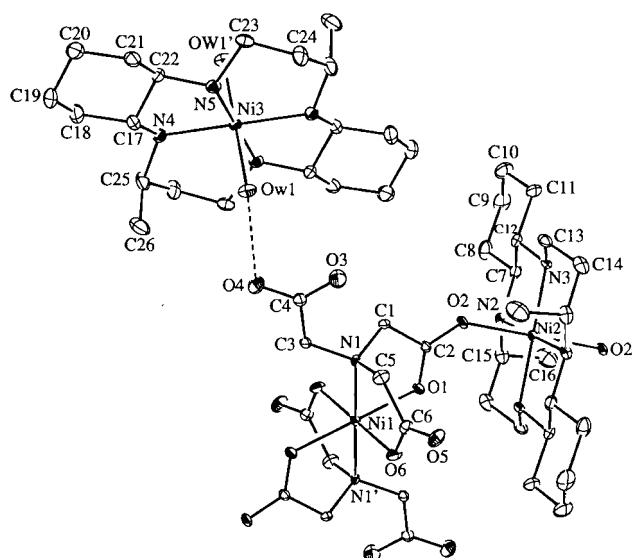

Figure 1. An ORTEP drawing of **1** with the atomic numbering scheme. The water molecules are omitted for clarity. The dotted line presents the hydrogen bond.

Table 3. Selected bond distances (Å) and angles (°) for **1**[*]

Ni(1)—N(1)	2.117(5)	Ni(1)—O(1)	2.061(4)
Ni(1)—O(6)	2.040(5)	Ni(2)—N(2)	2.084(5)
Ni(2)—N(3)	2.060(5)	Ni(2)—O(2)	2.161(4)
Ni(3)—N(4)	2.084(6)	Ni(3)—N(5)	2.049(6)
Ni(3)—Ow(1)	2.177(5)	O(1)—C(2)	1.266(8)
O(2)—C(2)	1.251(7)	O(3)—C(4)	1.238(8)
O(4)—C(4)	1.244(9)	O(5)—C(6)	1.243(8)
O(6)—C(6)	1.251(8)	Ni(1)$\cdots$Ni(2)	5.609(1)
O(1)—Ni(1)—N(1)	81.0(2)	O(1)—Ni(1)—N(1)^i	99.0(2)
O(6)—Ni(1)—N(1)	84.1(2)	O(6)—Ni(1)—N(1)^i	95.9(2)
O(1)—Ni(1)—O(6)	87.75(19)	O(1)—Ni(1)—O(6)^i	92.25(19)
N(2)—Ni(2)—N(3)	84.0(2)	N(2)—Ni(2)—N(3)^{ii}	96.0(2)
O(2)—Ni(2)—N(2)	85.9(2)	O(2)—Ni(2)—N(3)	88.8(2)
N(4)—Ni(3)—N(5)	84.4(2)	N(4)—Ni(3)—N(5)^{iii}	95.6(2)
Ow(1)—Ni(3)—N(4)	95.9(2)	Ow(1)—Ni(3)—N(5)	87.7(2)
Ni(1)—O(1)—C(2)	114.6(4)	Ni(1)—O(6)—C(6)	114.1(4)
Ni(2)—O(2)—C(2)	135.6(4)	O(1)—C(35)—O(2)	125.2(6)
O(1)—C(2)—C(1)	116.4(5)	O(2)—C(2)—C(1)	118.4(6)
O(3)—C(4)—O(4)	123.8(7)	O(3)—C(4)—C(3)	120.1(7)
O(4)—C(4)—C(3)	116.0(7)	O(5)—C(6)—O(6)	125.1(7)
O(5)—C(6)—C(5)	116.2(7)	O(6)—C(6)—C(5)	118.7(6)

[*] Symmetry codes: (i) $-x+1, -y+1, -z+1$; (ii) $-x+2, -y+1, -z+1$; (iii) $-x+1, -y+2, -z+1$.

intramolecular Ni(1)$\cdots$Ni(2) separation within the chain is 5.609(1) Å, while the intermolecular Ni(1)$\cdots$Ni(3) separation is 9.024(3) Å. The observed antiferromagnetic interaction is, therefore, due to the intrachain interaction. The magnetic susceptibility data was interpreted with Fisher's model [23, 24] for the classical-spin chain system ($S = 1$ and $H_{\text{chain}} = -J \sum S_i \cdot S_{i+1}$). The magnetic susceptibility χ_m can be expressed as

$$\chi_m = \frac{N\beta^2 g^2 S(S+1)}{3kT} \frac{(1+\mu)}{(1+\mu)} \quad (1)$$

with

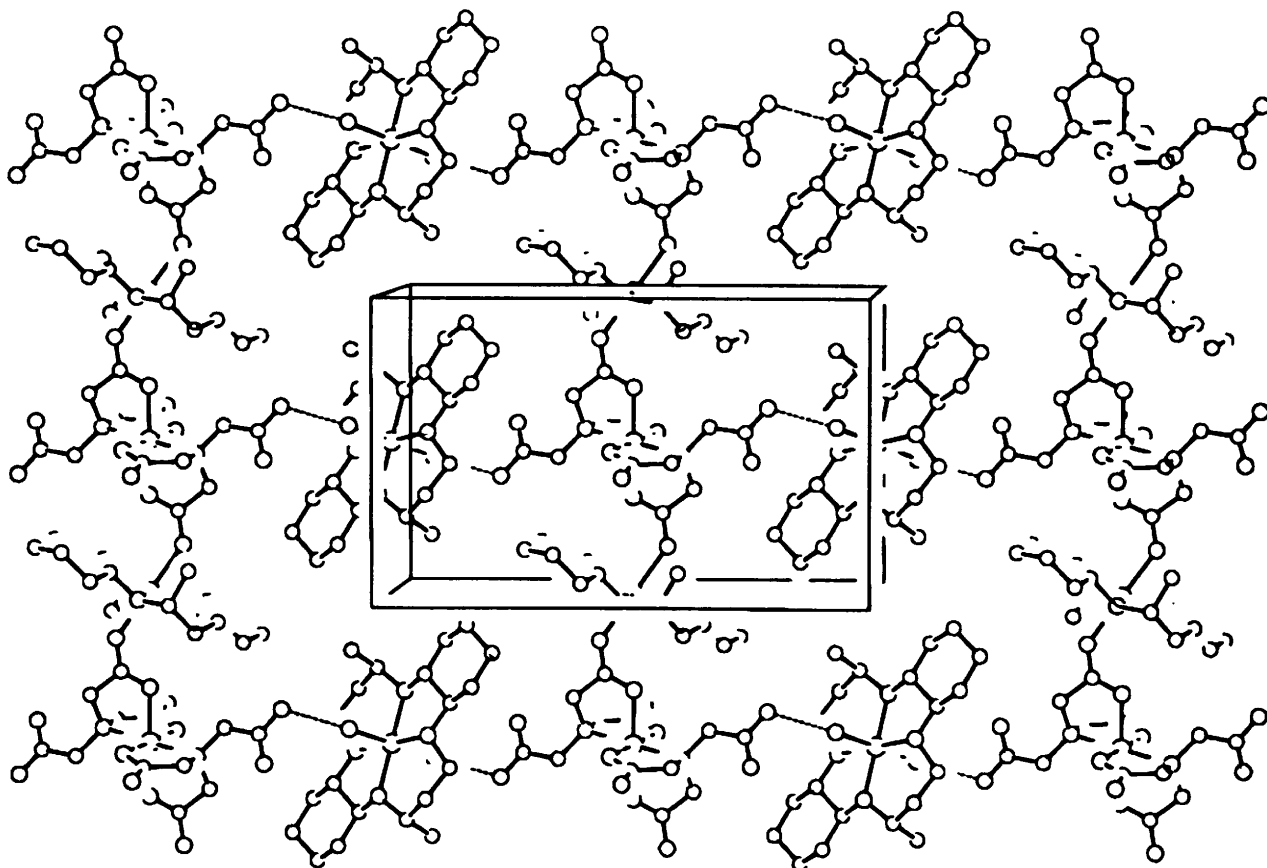$$\mu = \coth\left[\frac{JS(S+1)}{kT}\right] - \left[\frac{kT}{JS(S+1)}\right].$$

Figure 2. Crystal packing of **1**, showing the intermolecular hydrogen bonds as dotted lines. The hydrogen atoms are omitted for clarity.

The parameters giving the best fit were obtained using a nonlinear regression analysis with $g = 2.24(2)$, $J = -0.93(1)$ cm^{-1}, and $R = 3.7 \times 10^{-3}$ ($R = [\Sigma(\chi_{obs} - \chi_{calc})_z / \Sigma \chi_{obs}^z]^{1/2}$). This result indicates that there exists a weak intramolecular antiferromagnetic interaction between two Ni(1) and Ni(2) centers, and also indicates that the interaction between the two nickel(II) ions through the bridging acetate moiety is not very strong. The J value of compound **1** is much smaller than that observed in [(pyrazolate)Ni$_2$(μ-OAc)(acetone)$_2$](ClO$_4$)$_2$ ($J = -2.6(1)$ cm^{-1}) [22]. This may be attributed to the longer intramolecular Ni(1)$\cdots$Ni(2) distance (5.609(1) Å) compared to that of the carboxylato bridged dinickel(II) system (4.161 Å) [22].

Spectroscopic properties

The infrared spectrum for complex **1** contains the antisymmetric and symmetric ν(OH) stretching bands at 3354 and 3416 cm^{-1}. The coordinated secondary ν(NH) stretching band at 3055 cm^{-1} and ν(COO) stretching band at 1618 cm^{-1} were also observed in the spectrum. The diffuse reflectance absorption spectrum of **1** shows maximum absorption at 530 nm, which is the characteristic spectrum expected for a high-spin d^8 nickel(II) ion in an octahedral environment [25].
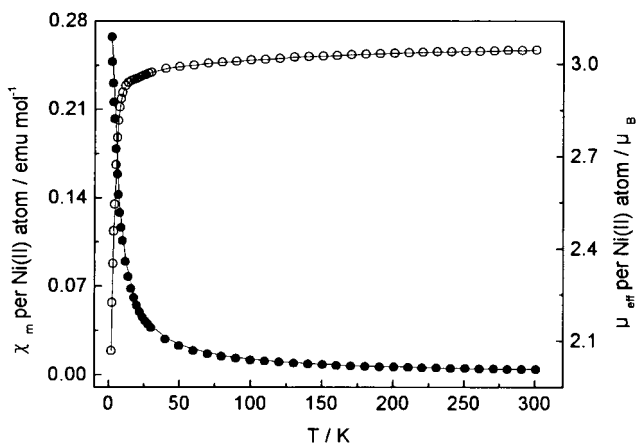
Figure 3. Plots of χ_m vs T($\bullet$) and μ_{eff} vs T($\circ$) for **1**. The solid line represents the best fit of the experimental data to Equation (1).

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