Crystal Structure of a Carboxylate-bridged Chain and a Mononuclear Complex of Nickel and the Magnetic Behaviour of $[Ni(dtma)(Him)]_n[ClO_4]_n$ (Hdtma = diethylenetriamine-*N*′-acetic acid, Him = imidazole)†

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The molecular structures of a carboxylate-bridged chain and a mononuclear complex of nickel(II) with dtma (Hdtma = diethylenetriamine-*N*′-acetic acid) and Him (Him = imidazole) ligands were determined by single-crystal X-ray analysis. The complex $[Ni(dtma)(Him)]_n[ClO_4]_n$ **1** crystallizes in the monoclinic system, space group $P2_1/c$, with a = 8.255(1), b = 16.918(3), c = 11.114(1) Å and β = 104.77(1)° and the complex $[Ni(dtma)(Him)_2]ClO_4{\cdot}H_2O$ **2** in the orthorhombic system, space group $P2_12_12_1$, with a = 9.940(3), b = 12.917(3) and c = 14.602(3) Å. The crystal structure of complex **1** contains chains of carboxylate-bridged nickel(II) metal ions. Its variable-temperature (1.8–300 K) magnetic susceptibility was determined. The carboxylate bridge in complex **1** could only mediate a very weak ferromagnetic exchange interaction and the magnetic behaviour is better explained by single-ion anisotropy.

Tripodal ligands are usually used to synthesize oxo-, hydroxo-, carboxylate- and imidazolate-bridged bi- or poly-nuclear complexes as model compounds for some metalloproteins and metalloenzymes.[1–3] In most of the known bi- or poly-nuclear complexes with such ligands the tripodal ligand is normally a terminal ligand binding to a metal atom, and only in a few complexes,[4–6] such as $[Mn_2O_2(tren)_2]^{2+}$, $[Mn_{10}O_{14}(tren)_6]^{8+}$ and $[Fe_6(\mu_4\text{-}O)_2(\mu_2\text{-}OMe)_8(OMe)_4(tren)_2]^{2+}$ [tren = tris(2-aminoethyl)amine], do some of the donor atoms of the ligand co-ordinate to one metal atom, with other donor atoms co-ordinating to a second metal atom. However, a one-dimensional compound with a tripodal ligand acting as both a terminal and a bridging ligand has not been known until now.

We report herein the synthesis, crystal structure and magnetic behaviour of a one-dimensional nickel(II) complex with the tripodal ligand dtma [Hdtma = diethylenetriamine-*N*′-acetic acid, $N(CH_2CH_2NH_2)_2(CH_2CO_2H)$], where the three nitrogen donors of each dtma bind to one nickel(II) ion and its carboxylate group bridges the neighbouring two nickel(II) ions forming a chain structure. We report also the crystal structure and spectral properties of a mononuclear nickel(II) complex with dtma.

Experimental

Synthesis of the Complexes.—All reagents were reagent grade. Diethylenetriamine-*N*′-acetic acid, was prepared as described previously.[7]

$[Ni(dtma)(Him)]_n[ClO_4]_n$ **1**. Aqueous solutions of Hdtma, $Ni(ClO_4)_2{\cdot}6H_2O$ and imidazole (Him) were mixed in a 1:1:1 molar ratio and a saturated solution of $NaClO_4$ was added. After the pH of the solution was adjusted to 3, a blue polycrystalline powder was soon formed and redissolved in water. The solution was allowed to evaporate at about 70 °C until a blue crystalline product separated. Yield 45% (Found: C, 27.50; H, 4.75; N, 18.10; Ni, 15.05. Calc. for $C_9H_{18}ClN_5NiO_6$: C, 27.95; H, 4.70; N, 18.10; Ni, 15.20%).

$[Ni(dtma)(Him)_2]ClO_4{\cdot}H_2O$ **2**. To a warm (50 °C) stirred solution of complex **1** in water was added dropwise an aqueous solution of Him in a 1:1.1 molar ratio. The solution soon turned purple. The mixture was allowed to cool to room temperature and the purple crystals were filtered off and air-dried. Yield 82% (Found: C, 31.00; H, 5.05; N, 21.05; Ni, 12.70. Calc. for $C_{12}H_{24}ClN_7NiO_7$: C, 30.50; H, 5.10; N, 20.75; Ni, 12.40%).

Crystals of both complexes suitable for an X-ray diffraction study were grown by slow evaporation of an aqueous solution at room temperature.

Physical Measurements.—Infrared spectra were recorded with a Perkin Elmer 283 grating spectrophotometer on KBr plates. Electronic spectra were performed in the range 200–1500 nm with a UV-3100 UV/VIS/NIR recording spectrophotometer. Magnetic-susceptibility measurements of complex **1** in the temperature range 1.8–300 K were made on a model CF-1 vibrating-sample magnetometer with the Faraday method. Data were corrected for diamagnetism estimated from Pascal's constants[8] at -138.5×10^{-6} emu mol^{-1} and temperature-independent paramagnetism estimated at 100×10^{-6} emu mol^{-1} per nickel(II) ion.

X-Ray Crystallography.—Cell parameters and reflection intensities for both complexes were measured at room temperature on a Nicolet R3M/E four-circle X-ray diffractometer with graphite-monochromated Mo-Kα radiation. A summary of crystal data, intensity measurements and structure solution and refinement data is given in Table 1. Intensity data were corrected for Lorentz-polarization effects but no absorption corrections were made owing to the low absorption coefficients and the fairly uniform dimensions of the crystals. The structures were solved using direct methods. The atomic coordinates of the nickel and chlorine atoms were obtained first.

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1993, Issue 1, pp. xxiii–xxviii.

Non-SI units employed: emu = SI × $10^6/4\pi$, $\mu_B = 9.274 \times 10^{-24}$ J T^{-1}.

Table 1 Crystal and refinement data

Complex	1	2
Formula	$C_{19}H_{18}ClN_5NiO_6$	$C_{12}H_{24}ClN_7NiO_7$
M	386.43	472.52
Space group	$P2_1/c$	$P2_12_12_1$
a/Å	8.255(1)	9.940(3)
b/Å	16.918(3)	12.917(3)
c/Å	11.114(1)	14.602(3)
β/°	104.77(1)	90
$U/Å^3$	1500.9(8)	1874.8(8)
$D_c/g\ cm^{-3}$	1.71	1.63
F(000)	780	960
Crystal dimensions/mm	0.32 × 0.44 × 0.54	0.20 × 0.24 × 0.24
Intensity variation (%)	< 2.0	< 2.4
μ/cm^{-1}	15.11	12.27
Standard reflections	0 −3 3, −2 5 2	0 5 1, −1 0 6
h k l	0–11, 0–22, −15 to 15	0–13, 0–17, 0–19
No. of independent reflections	3661	4559
No. of observed [$I \geqslant 3\sigma(I)$] reflections	2893	3774
R, *R′*	0.0366, 0.0366	0.0381, 0.0381
Largest shift/e.s.d.	−0.247	−0.137
Residual extrema in difference map/e $Å^{-3}$	0.438, −0.318	0.651, −0.538

Details in common: $Z = 4$, $\lambda = 0.710\ 73$ Å, θ–2θ scan type, 5° min^{-1} scan rate, 2θ range = 2–54°.

Table 2 Atomic coordinates for complex **1**

Atom	*x*	*y*	*z*
Ni	−1214(1)	2805(1)	875(1)
Cl	6892(1)	5679(1)	2195(1)
N(1)	−2928(3)	1855(1)	642(2)
N(2)	289(3)	1938(2)	343(2)
N(3)	−3341(4)	3470(2)	990(2)
N(4)	660(3)	3631(2)	1331(2)
N(5)	2478(4)	4546(2)	1214(4)
O(1)	−848(3)	2505(1)	2740(2)
O(2)	−1922(3)	1756(1)	4004(2)
O(3)	5529(4)	5456(2)	1177(3)
O(4)	6540(4)	5484(2)	3343(3)
O(5)	8355(4)	5293(3)	2112(3)
O(6)	7098(5)	6499(2)	2147(4)
C(1)	−2483(4)	1320(2)	−274(3)
C(2)	−617(5)	1182(2)	52(3)
C(3)	−4603(4)	2212(2)	208(3)
C(4)	−4725(4)	2924(2)	1002(3)
C(5)	−2714(4)	1459(2)	1868(3)
C(6)	−1755(4)	1953(2)	2955(2)
C(7)	1800(5)	3724(2)	2969(3)
C(8)	2917(5)	4291(2)	2401(4)
C(9)	1131(5)	4138(2)	605(4)

Table 3 Atomic coordinates for complex **2**

Atom	*x*	*y*	*z*
Ni	3 219(1)	376(1)	8 712(1)
Cl	6 231(1)	179(1)	5 570(1)
N(1)	3 918(3)	−888(2)	9 475(2)
N(2)	3 892(3)	−498(2)	7 585(2)
N(3)	1 390(3)	−457(3)	8 696(3)
N(4)	2 266(3)	1 609(2)	8 093(2)
N(5)	927(4)	2 935(3)	7 907(3)
N(6)	5 058(3)	1 209(2)	8 735(2)
N(7)	6 457(4)	2 459(3)	9 099(2)
O(1)	2 862(2)	884(2)	10 081(2)
O(2)	3 771(3)	739(2)	11 473(2)
O(3)	5 480(5)	−627(3)	5 116(4)
O(4)	5 257(5)	823(3)	6 005(3)
O(5)	6 892(5)	739(3)	4 894(3)
O(6)	7 057(5)	−330(4)	6 187(4)
O_w	9 234(16)	461(15)	7 405(11)
C(1)	4 958(4)	−1 408(3)	8 907(3)
C(2)	4 530(5)	−1 471(3)	7 900(3)
C(3)	2 731(4)	−1 555(3)	9 685(3)
C(4)	1 668(5)	−1 534(3)	8 950(3)
C(5)	4 469(4)	−465(3)	10 330(2)
C(6)	3 625(3)	460(3)	10 664(2)
C(7)	2 492(4)	2 043(3)	7 261(3)
C(8)	1 675(5)	2 873(3)	7 142(3)
C(9)	1 303(5)	2 168(4)	8 456(3)
C(10)	6 317(4)	995(3)	8 378(3)
C(11)	7 164(4)	1 766(3)	8 596(3)
C(12)	5 180(4)	2 099(3)	9 157(3)

Table 4 Selected bond lengths (Å) and angles (°)

Complex **1**			
Ni–N(1)	2.114(2)	Ni–N(2)	2.101(3)
Ni–N(3)	2.116(3)	Ni–N(4)	2.050(3)
Ni–O(1)	2.081(2)	Ni–O(2b)	2.144(2)
O(1)–C(6)	1.258(4)	O(2)–C(6)	1.254(3)
O(2)–Ni(a)	2.144(2)		
N(1)–Ni–N(2)	81.9(1)	N(1)–Ni–N(3)	82.7(1)
N(2)–Ni–N(3)	161.2(1)	N(1)–Ni–N(4)	171.2(1)
N(2)–Ni–N(4)	94.7(1)	N(3)–Ni–N(4)	102.0(1)
N(1)–Ni–O(1)	81.9(1)	N(2)–Ni–O(1)	99.4(1)
N(3)–Ni–O(1)	88.9(1)	N(4)–Ni–O(1)	90.6(1)
N(1)–Ni–O(2b)	97.8(1)	N(2)–Ni–O(2b)	90.2(1)
N(3)–Ni–O(2b)	81.3(1)	N(4)–Ni–O(2b)	90.3(1)
O(1)–Ni–O(2b)	170.2(1)	Ni–O(1)–C(6)	115.3(1)
C(6)–O(2)–Ni(a)	137.9(1)	O(1)–C(6)–O(2)	125.9(1)
Complex **2**			
Ni–N(1)	2.095(3)	Ni–N(2)	2.105(3)
Ni–N(3)	2.113(3)	Ni–N(4)	2.061(3)
Ni–N(6)	2.121(3)	Ni–O(1)	2.134(3)
N(1)–Ni–N(2)	83.8(1)	N(1)–Ni–N(3)	83.9(1)
N(2)–Ni–N(3)	89.5(1)	N(1)–Ni–N(4)	170.9(1)
N(2)–Ni–N(4)	102.6(1)	N(3)–Ni–N(4)	89.6(1)
N(1)–Ni–N(6)	95.8(1)	N(2)–Ni–N(6)	90.6(1)
N(3)–Ni–N(6)	179.7(1)	N(4)–Ni–N(6)	90.6(1)
N(1)–Ni–O(1)	78.3(1)	N(2)–Ni–O(1)	161.9(1)
N(3)–Ni–O(1)	91.4(1)	N(4)–Ni–O(1)	95.6(1)
N(6)–Ni–O(1)	88.4(1)		

Symmetry operation: a, $x, \frac{1}{2} - y, \frac{1}{2} + z$; b, $x, \frac{1}{2} - y, -\frac{1}{2} + z$.

The coordinates of the other atoms, including the hydrogen atoms, were gradually obtained by Fourier-difference syntheses except H(5), H(7a) and H(9) of complex **2** which were added at calculated positions. All non-hydrogen atoms were refined anisotropically to a minimum of $\Sigma w(|F_o| - |F_c|)^2$, in which a unit weight was used for both refinements, while hydrogen atoms were included in the structure-factor calculations with a common thermal parameter. All calculations were performed on an Eclipse/S140 computer with programs of the SHELXTL[9] system as implemented on a Nicolet R3M/E structure determination system. Neutral atomic scattering factors were taken from ref. 10. Final refined atomic coordinates are listed in Tables 2 and 3. Selected bond lengths and angles for both complexes are reported in Table 4.

Additional material available for both structures from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

Results and Discussion

Description of the Crystal Structure.—The structure of complex **1**, which is shown in Fig. 1, consists of a –Ni(dtma)(Him)– chain isolated by ClO_4^-. In the chain

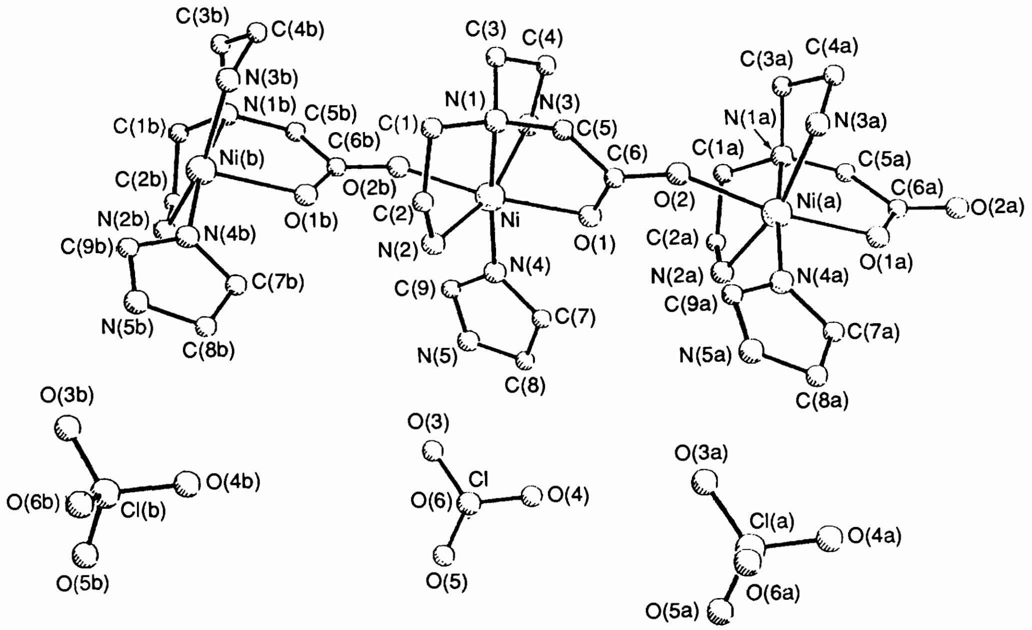

Fig. 1 Chain structure of complex **1**

structure, each nickel(II) ion is octahedrally co-ordinated by three nitrogen and one oxygen donor atoms of the dtma ligand, a nitrogen atom from the imidazole ligand and an oxygen atom of the carboxylate from another dtma ligand. The carboxylate groups bridge the nickel(II) ions along the *c* axis. The intrachain separations of Ni $\cdots$ Ni(a) [or Ni $\cdots$ Ni(b)] and Ni(a) $\cdots$ Ni(b) are 5.652(1) and 11.114(2) Å, respectively, while the minimum Ni $\cdots$ Ni interchain separation is 13.075(2) Å. The best plane formed by the N(1)–N(4) atoms was calculated and the deviation of the Ni atom from this plane is 0.016 Å. The dihedral angle between the N(1)–N(4) and the N(1a)–N(4a) planes is 29.0°. In addition, the angle between the N(1)–Ni–N(4) and N(1a)–Ni(a)–N(4a) axes is 54.9°.

Carboxylate ligands are known to assume *syn–syn*, *anti–anti* and *syn–anti* types of bridging conformations.[11–13] It is seen from Fig. 1 that complex **1** contains *syn–anti* type bridges. The carboxylate group formed by the O(1), O(2), C(5) and C(6) atoms shows good planar conformation. While the constituent atoms of the bridge all lie within ± 0.007 Å of the best mean plane, the Ni and Ni(a) atoms, both on the same side of the plane are at 0.384 and 0.176 Å, respectively, out of the plane. In addition, the dihedral angles of this bridging plane with the mean plane formed by the N(1)–N(4) atoms around the Ni atom and with the mean plane formed by the N(1a)–N(4a) atoms around the Ni(a) atom are 74.0 and 92.2°, respectively.

For complex **2**, the structure consists of one complex ion, $[Ni(dtma)(Him)_2]^+$, one ClO_4^- anion and one water molecule. In the cation, the nickel(II) ion is co-ordinated by a tetradentate dtma ligand and two monodentate imidazole ligands in a slightly distorted octahedral fashion similar to complex **1**. The molecular structure is shown in Fig. 2. Both imidazole rings with a dihedral angle of 77° occupy the equatorial and axial positions respectively. The Ni–N bond length of the imidazole ligand in the equatorial plane [2.121(3) Å] is larger than that for the ligand in the axial position [2.061(3) Å]. The internal geometry of the imidazole ligand is normal and so will not be discussed further.[3] All the bond distances and angles of the ligands are also within normal ranges.

Spectroscopic and Magnetic Data.—In the IR spectra, the carboxylate antisymmetric and symmetric stretching frequencies, $\nu_{asym}(CO_2^-)$ and $\nu_{sym}(CO_2^-)$, are located at 1596 and 1412 cm^{-1} for complex **1** and at 1627 and 1402 cm^{-1} for complex **2**, respectively (Table 5). The $\nu_{asym}(CO_2^-) - \nu_{sym}(CO_2^-)$ separation is 184 and 225 cm^{-1} for complexes **1** and **2**, respectively. These values mean that the carboxylate of the tripod ligand in complex **1** co-ordinates to two nickel(II) ions in a bridging form and in complex **2** co-ordinates to one nickel(II) ion as a monodentate ligand.[14] This result is consistent with the structural data. Additional strong and sharp peaks at 1102 and 1052 cm^{-1} in the IR spectrum of complex **1** are attributable to ionic perchlorate. For complex **2** the corresponding assignments appear as broad bands at 1112 and 1079 cm^{-1}.

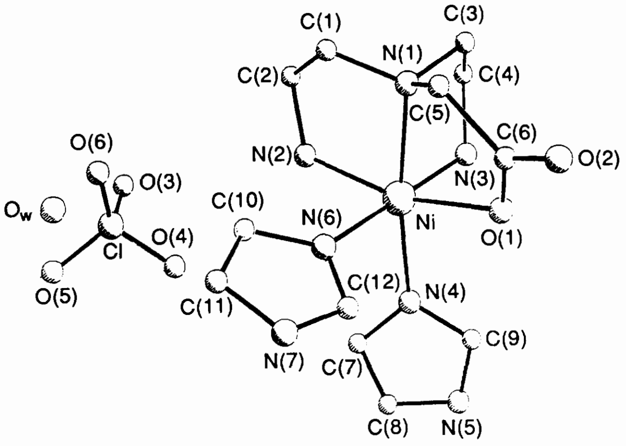

Fig. 2 Molecular structure of complex **2**

The electronic spectra of both complexes were recorded in aqueous solution and absorption maxima in the visible region are listed in Table 5 along with suggested assignments. Their electronic spectral features are quite similar. In the range 300–1000 nm both nickel(II) complexes exhibit the expected three spin-allowed ligand-field bands which are typical of a high-spin six-co-ordinated octahedral nickel(II) ion and correspond to transitions from the $^3A_{2g}$ ground state to the $^3T_{2g}$, $^3T_{1g}$ and $^3T_{1g}(P)$ excited states.[15] The extent of the distortion from an ideal octahedral geometry is reflected in the intensity and occasional splitting of these bands. For complexes which are octahedral or only slightly distorted from octahedral, molar absorption coefficients lie below 30 dm^3 mol^{-1} cm^{-1}.[16] The

Table 5 Spectral data for complexes **1** and **2**

Complex	λ_{max}/cm^{-1} (ε/dm^3 mol^{-1} cm^{-1})*	Assignment	$\tilde{\nu}$/cm^{-1}
1	10 750(16)	$^3A_{2g} \longrightarrow {}^3T_{2g}$	3399, 3365, 3314, 3278
	17 570(11)	$^3A_{2g} \longrightarrow {}^3T_{1g}$	3187, 3145, 1596, 1585
	27 320(16)	$^3A_{2g} \longrightarrow {}^3T_{1g}(P)$	1470, 1438, 1412, 1102, 1052
2	10 860(12)	$^3A_{2g} \longrightarrow {}^3T_{2g}$	3355, 3336, 3294, 3170
	17 740(9)	$^3A_{2g} \longrightarrow {}^3T_{1g}$	3143, 3126, 1627, 1575
	27 400(13)	$^3A_{2g} \longrightarrow {}^3T_{1g}(P)$	1540, 1491, 1465, 1402, 1112, 1079

* In water.

intensities of the three ligand-field bands observed for both complexes are consistent with their near-octahedral structure. Indeed, their structural data reveal that the nickel(II) ions are in a slightly distorted octahedral environment. From these spectra D_q splitting-parameter values of 1074 and 1086 cm^{-1} for complexes **1** and **2** are computed.

No ESR signals for either complex was observed at room temperature. However, isotropic g tensor values may be approximately estimated according to equation (1), where Δ is

$$g_{iso} = g_e - \frac{8\lambda}{\Delta} \quad (1)$$

the $A_{2g} - T_{2g}$ energy separation. Using the free nickel(II) ion value of $\lambda = 325$ cm^{-1}, g values of 2.244 and 2.242 for complexes **1** and **2** were obtained.

The magnetic behaviour of complex **1** is shown in Fig. 3 in the form of the temperature dependence of the effective magnetic moment [$\mu_{eff} = 2.828(\chi_M T)^{\frac{1}{2}}$]. In the temperature range 14–300 K, μ_{eff} (per nickel ion) increases slowly upon cooling with values essentially in the range usually observed for octahedral high-spin nickel(II) ($S = 1$) ions. Below 14 K, μ_{eff} drops rapidly. The drop-off is to 2.42 at 4.2 K and to 1.67 at 1.8 K. Such abnormal magnetic behaviour can be due to:[17] (1) a single-ion anisotropy with a low non-magnetic singlet state, *e.g.* zero-field splitting is observed for high-spin nickel(II) compounds, or (2) a magnetic-exchange coupling and dipolar interaction between the nickel(II) ions. Of course, the two effects can occur in the same compound.

In complex **1** the nickel(II) ions are bridged by carboxylates along the *c*-axis direction to form a chain structure. The magnetic behaviour, therefore, may be described by a Hamiltonian [equation (2)]. There is, however, no theoretical

$$\hat{H} = -J\sum_i S_i S_{i+1} - D\sum_i (S_{i,z}^2 - \tfrac{2}{3}) - g\mu_B H \sum_i S_i \quad (2)$$

analytical model available for complex **1** which involves both isotropic intrachain magnetic-exchange interaction and zero-field splitting. First, in order to estimate the intrachain magnetic-exchange interaction, the magnetic susceptibility can, regardless of zero-field splitting, be approximately expressed by equation (3) where $u = \coth(4J/kT) - (kT/4J)$.[18] Least-squares fit of the

$$\chi = \frac{2Ng^2\mu_B^2}{3kT}\,\frac{1+u}{1-u} \quad (3)$$

obtained susceptibility data for complex **1** to equation (3) was carried out at 1.8–300 K and results of $g = 2.51$ and $J = 0.63$ K (reliability factor, $R = 3.8 \times 10^{-3}$) were obtained. The g value is slightly larger than that usually observed in nickel(II) compounds. Since most nickel(II) complexes are known to have zero-field splitting, which easily influences susceptibilities at low temperatures, only the data for relatively high temperatures ($T > 20$ K) were used for refitting and this yielded a best fit of $g = 2.12$ and $J = 0.45$ K ($R = 4.9 \times 10^{-4}$). The results obtained indicate that the intrachain magnetic-exchange interaction in complex **1** is ferromagnetic, but very weak. In other words, the major factor effecting the low-temperature magnetic behaviour should be zero-field splitting.

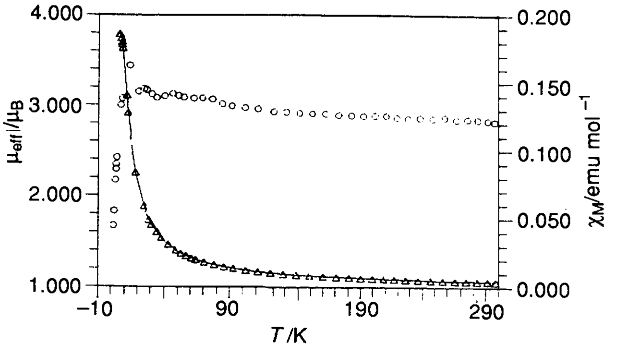

Fig. 3 Plots of μ_{eff} *vs.* T and χ_M *vs.* T for complex **1**. The solid line corresponds to the prediction by the single-ion anisotropy model [equation (5)]

Secondly, we neglected the intrachain exchange interaction and only considered the zero-field splitting. The susceptibility is then expressed in the form of equation (4),[17] with $B = D/kT$.

$$\chi = \frac{2Ng_B{}^2}{3kT}\,\frac{\frac{2}{B} - [2e^{-B}/(B + e^{-B})]}{1 + 2e^{-B}} \quad (4)$$

Using this model the data were analysed at 1.8–300 K giving $g = 2.24$ and $D = 6.71$ K ($R = 1.4 \times 10^{-4}$), a positive value for D indicating that the $M_s = 0$ state is the ground state. Fig. 3 shows the fitting results.

Finally, the data were analysed using an anisotropic intrachain-interaction model. Such as Ising-like exchange interaction involving zero-field splitting has been described in the literature[19] and leads to expression (5), where $F_\lambda =$

$$\chi = \frac{Ng^2\mu_B{}^2S(S+1)}{kT}\,\frac{e^{2d}(e^j\lambda_+ - 1 + e^j)}{F_\lambda} \quad (5)$$

$3\lambda_+{}^2 - 2\lambda_+\{1 + 2e^{j+2d} - [2e^{2d}(1 - e^j) - 2e^{4d}\sinh(2j)]\}$, $\lambda_+ = \frac{1}{2}(\alpha + \gamma + 1) + \frac{1}{2}[(\alpha + \gamma - 1)^2 + 8\beta^2]^{\frac{1}{2}}, \alpha = e^{(2J+D)/kT}$, $\gamma = e^{(-2J+D)/kT}$, $\beta = e^{D/kT}$, $j = 2J/kT$ and $d = D/2kT$. In the range 1.8–300 K, the best fit was obtained with $g = 2.24$, $J = 2.14$ and $D = 4.88$ K ($R = 0.06$) and for $T > 20$ K, the data yielded $g = 2.94$, $J = 0.33$ and $D = 3.93$ K ($R = 4 \times 10^{-4}$). The results are sensitive both to the temperature range utilized and the g values assumed. Unusually large g values and the variation in the parameters obtained show that the intrachain anisotropic model is not suitable for complex **1**.

The variable-temperature (4.2–300 K) magnetic susceptibility of complex **2** was also determined. The best fit of $g = 2.22$ and $D = 5.26$ K ($R = 8.3 \times 10^{-4}$) were obtained with equation (4). This result indicates that the magnetism of complex **2** has an origin of zero-field splitting normally observed for high-spin nickel(II) compounds, and also that the result obtained using equation (4) for complex **1** is reasonable.

All results obtained clearly indicate that although complex **1** has a chain structure, the ferromagnetic intrachain exchange coupling is very weak. The magnetic behaviour is better explained assuming single-ion anisotropy.

Acknowledgements

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