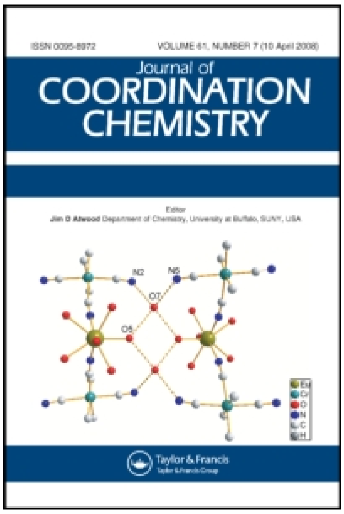

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Two complexes crystallizing from the aqueous system Ni^{2+}-<i>tacn</i>-[Ni(CN)$_4$]$^{2-}$(<i>tacn</i> = 1,4,7-triazacyclononane)

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Two complexes crystallizing from the aqueous system Ni^{2+}-*tacn*-$[Ni(CN)_4]^{2-}$(*tacn* = 1,4,7-triazacyclononane)

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Two new complexes $[Ni(tacn)_2][Ni(CN)_4]\cdot 2H_2O$ (**1**) and $Ni(tacn)Ni(CN)_4\cdot H_2O$ (**2**) (*tacn* = 1,4,7-triazacyclononane) have been synthesized from water and characterized by chemical analysis and infrared spectroscopy. Single-crystal X-ray structure analysis of **1** revealed an ionic structure built up of $[Ni(tacn)_2]^{2+}$ and $[Ni(CN)_4]^{2-}$ complex ions without coordinated water. While cationic Ni(II) atom is octahedrally coordinated by two tridentate *tacn* ligands with Ni–N bonds from 2.101(3)–2.118(3) Å, the anionic Ni(II) atom is square planar with Ni–C bonds from 1.866(4) to 1.880(3) Å. An extended hydrogen bonding system connects complex cations, complex anions and water yielding hydrogen-bonded layers. Magnetic study of **1** revealed a decrease of the effective magnetic moment from 2.90 (300 K) to 2.43 μ_B at 1.8 K due to zero-field splitting. Fitting of the susceptibility data yielded $g = 2.05$, $D/hc = 3.82\,\mathrm{cm}^{-1}$ and $E/hc = 0.23\,\mathrm{cm}^{-1}$. IR spectral data indicate the presence of bridging cyano ligands in the structure of **2**.

Keywords: Tetracyanonickellate; Nickel; Crystal structure; 1,4,7-Triazacyclononane; Zero-field splitting

1. Introduction

Tetracyanonickellate complexes [1, 2] have nitrogens in the square $[Ni(CN)_4]^{2-}$ anion to form additional coordination bonds enhancing dimensionality of the structure [2, 3]. Thus tetracyanonickellates form ionic (connectivity 0), oligonuclear, one-dimensional (1D), 2D as well as 3D (connectivities 1–4) structures [4–8]. The ability of the tetracyanonickellate anion to form oligo- and polynuclear compounds was mainly exploited in connection with their ability to form Hofmann-type and analogous clathrates [9]. Tetracyanonickellates exhibiting especially low-dimensional structures for magnetic applications attract the interest of chemists and physicists [7, 10, 11].

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The preparation of tetracyanonickellates with desired dimensionality can be based on the so called "brick and mortar" method [12], in which complex cation coordinated by suitable *N*-donor ligands ("brick") and tetracyanonickellate anion ("mortar") are used as building blocks. The nature of the formed structure can be tuned to a certain extent by the character of the *N*-donor ligands (denticity, number) used. Formation of 1D structure can be expected when four coordination sites from six (or three from five) around the cationic central atom are occupied by *N*-donor ligands like two molecules of *en* (*en* = 1,2-diamminoethane). This approach was used in preparation of several low-dimensional tetracyanonickellates, e.g. Ni(*bipy*)$_2$Ni(CN)$_4$ (*bipy* = 2,2′-bipyridine) [13]. Using the definition of Janiak [14], these compounds can be classified as organic-inorganic hybrid materials.

Previously we examined the effect of acyclic 3*N*-donor blocking ligands *dien* (1,4,7-triazaheptane, diethylenetriamine) and *aepn* (1,4,8-triazaoctane, *N*-(2-aminoethyl)-1,3-diaminopropane) on the dimensionality of the formed structures of tetracyanonickellates [15–17]. We have also used cyclic 3*N*-donor ligand 1,4,7-triazacyclononane (*tacn*) which forms three coordination bonds with the same central atom affording *fac* coordination [18, 19]. Here we report the results of our study on synthesis, chemical, spectral, structural and magnetic characterization of two new compounds.

2. Experimental

2.1. *Materials*

Ligand *tacn* as trihydrogenbromide was prepared according to literature procedures [20, 21]. $Ni(NO_3)_2 \cdot 6H_2O$ (Lachema, p.a.) was used as received without further purification. $K_2[Ni(CN)_4] \cdot H_2O$ was prepared from nickel sulfate heptahydrate (p.a., Lachema Brno) and potassium cyanide (p.a., Lachema Brno) following the literature [22].

2.2. *Synthesis*

2.2.1. Tetracyanonickellate(II)-*bis*(1,4,7-triazacyclononane) nickel(II)-dihydrate [Ni(*tacn*)$_2$][Ni(CN)$_4$] • 2H$_2$O (1). An aqueous solution of $Ni(NO_3)_2$ (0.5 cm^3, 0.5 mmol) was mixed with 10 cm^3 of water and 0.372 g (1 mmol) of *tacn* · 3HBr. Some drops of conc. aqueous ammonia (w = 0.26) were added to neutralize the hydrogenbromide. After dropwise addition of 5 cm^3 of 0.1 M $K_2[Ni(CN)_4]$ (0.5 mmol) under stirring, pink microcrystalline precipitate was formed which was partly dissolved by addition of 30 cm^3 of aqueous ammonia. The remaining precipitate was removed by filtration. Within a few days pink crystals crystallized from the filtrate at room temperature, these were filtered off and dried in air. The subsequent IR spectra revealed identical composition of the precipitate and crystals. Yield (crystals): 19%. Anal. (CHN by Fisons Instrument, nickel gravimetrically as dimethylglyoximato complex after mineralization of the sample), found: C, 37.45; H, 6.54; N, 27.14; Ni, 22.89%. Calcd (M_r = 515.9): C, 37.25; H, 6.64;

N, 27.15; Ni, 22.75%. IR (cm^{-1}): 3640s, 3583vs, 3441vs, 3323vs, 3297vs, 3250vs, 2980w, 2936s, 2875s, 2122vs, 1625w, 1472s, 1451m, 1103s, 1040m, 933vs, 861m, 581w, 413s.

2.2.2. Tetracyanonickellate(II)-(1,4,7-triazacyclononane) nickel(II)-hydrate, Ni(*tacn*) $Ni(CN)_4 \cdot H_2O$ (2). An aqueous solution of $Ni(NO_3)_2$ (0.5 cm^3, 0.5 mmol) was mixed with 10 cm^3 of water and 0.186 g (0.5 mmol) *tacn* · 3HBr. The amine solution was neutralized with some ammonia drops. 5 cm^3 of 0.1 M solution of $K_2[Ni(CN)_4]$ (0.5 mmol) was slowly added dropwise under stirring. The formed pink precipitate was dissolved in 5 cm^3 of ammonia (w = 0.26). The formed pink solution was filtered and kept for crystallization at room temperature. Within two days light pink crystals were separated by filtration and dried in air. Yield: 46%. Anal. (Fisons Instrument), found: C, 32.18; H, 4.62; N, 26.83; Ni, 31.42%. Calcd ($M_r = 368.7$): C, 32.58; H, 4.65; N, 26.59; Ni, 31.84%. IR (cm^{-1}): 3445b, vs, 3373vs, 3289vs, 2977w, 2934w, 2882w, 2151vs, 2123vs, 1620m, 1486w, 1456m, 1103s, 1009w, 940s, 867w, 617w, 424m.

2.3. *Spectral methods*

Infrared spectra of the prepared compounds were recorded on FT-IR Avatar 330 Thermo-Nicolet instrument using KBr pellets in the range 4000–400 cm^{-1}.

2.4. *Magnetic measurements*

Susceptibility of the powdered sample of **1** (31.0 mg) was measured in SQUID magnetometer (Quantum Design). A magnetic field 0.1 T was applied during the susceptibility measurement and the background contribution arising from the varnish, gelcap and straw is negligible below 20 K. The obtained values of magnetic susceptibility were corrected for diamagnetic contribution ($-2.875600 \times 10^{-4} cm^3 mol^{-1}$) [23].

2.5. *X-ray crystallography*

Crystal data and data collection conditions for $[Ni(tacn)_2][Ni(CN)_4] \cdot 2H_2O$ are presented in table 1. For data collection ($T = 120$ K) a KUMA-KM4 diffractometer (Mo-Kα radiation, $\lambda = 0.71073$ Å) equipped with a CCD area detector and graphite monochromator were used. The structures were solved by heavy atom method using SHELXS-97 (Sheldrick, 1997) [24]. Refinement based on intensities was performed using the SHELXL-97 program [25]. All atoms except hydrogen were refined anisotropically. Hydrogen atoms of the water molecules were found in the difference map and their positions were refined using common isotropic thermal parameter. The hydrogen atoms in *tacn* ligands were placed in calculated positions and their common group isotropic thermal parameters were refined.

Selected geometric parameters are displayed in table 2 and possible hydrogen bonds are gathered in table 3. For geometric calculations (hydrogen bonds geometry) the program PARST95 [26] was used. The figures were drawn with DIAMOND programme [27].

Table 1. Crystal and X-ray experimental data for **1**.

Summary	$C_{16}H_{34}N_{10}Ni_2O_2$
Formula weight	515.904
Temperature (K)	120
Crystal system	Monoclinic
Space group	$C2/c$
Unit cell dimensions (Å, °)	
a	29.485(6)
b	11.714(2)
c	14.590(3)
α	90
β	115.97(3)
γ	90
V (Å^3)	4530.4(15)
Z	8
D_{Calcd} (g cm^{-3})	1.744
μ (mm^{-1})	3.462
$F(000)$	2448
2θ range (°)	2.89–25.00
Index range (h, k, l)	$-32 \le h \le 34$ $-9 \le k \le 9$ $-17 \le l \le 11$
No. parameters	271
No. of reflections collected	3433
Observed [$I > 2\sigma(I)$]	2454
R_1 [$I > 2\sigma(I)$]	0.0332
R_1 (all)	0.0574
wR_2 [$I > 2\sigma(I)$]	0.0762
wR_2 (all)	0.0832
Goodness-of-fit	0.987
$\Delta\rho_{min,max}$ (e Å^{-3})	−0.281; 0.567

Table 2. Selected geometric parameters (Å, °) for **1**.

Ni1–N1	2.117(3)	N1–Ni1–N2	82.7(1)
Ni1–N2	2.112(3)	N2–Ni1–N3	82.6(1)
Ni1–N3	2.118(3)	N1–Ni1–N3	81.8(1)
Ni1–N4	2.109(3)	N4–Ni1–N5	82.1(1)
Ni1–N5	2.110(2)	N5–Ni1–N6	82.2(1)
Ni1–N6	2.101(3)	N4–Ni1–N6	82.7(1)
Ni2–C21	1.866(4)	Ni2–C21–N21	178.7(3)
Ni2–C22	1.880(3)	Ni2–C22–N22	178.3(3)
Ni2–C23	1.867(4)	Ni2–C23–N23	177.6(3)
Ni2–C24	1.874(4)	Ni2–C24–N24	178.1(3)

3. Results and discussion

From aqueous systems of Ni^{2+}-*tacn*-$[Ni(CN)_4]^{2-}$ two complexes $[Ni(tacn)_2][Ni(CN)_4] \cdot 2H_2O$ (**1**) and $Ni(tacn)Ni(CN)_4 \cdot H_2O$ (**2**) were isolated. Their compositions were checked by elemental analyses and infrared spectroscopy. Single crystals of X-ray quality were formed only by **1**. The composition was tuned by the M : *tacn* ratios in the reaction mixture, ratio 1 : 2 led to coordination of two tridentate

Table 3. Possible hydrogen bonds (Å, °) for **1**.

D–H $\cdots$ A	d(D–H)	d(D $\cdots$ A)	d(H $\cdots$ A)	D–H $\cdots$ A
O1–H2O1 $\cdots$ N24$^{\text{i}}$	0.850	2.876(5)	2.032	172
O1–H1O1 $\cdots$ N24	0.850	3.014(3)	2.627	109
O2–H1O2 $\cdots$ N21$^{\text{i}}$	0.850	3.352(5)	2.678	137
O2–H2O2 $\cdots$ N24$^{\text{i}}$	0.850	3.217(3)	2.372	173
N1–H1 $\cdots$ N21$^{\text{ii}}$	0.910	3.285(5)	2.402	164
N2–H2 $\cdots$ O1	0.910	2.990(4)	2.294	133
N2–H2 $\cdots$ N22	0.910	3.383(4)	2.742	128
N3–H3 $\cdots$ N23$^{\text{iii}}$	0.910	3.295(3)	2.675	126
N4–H4 $\cdots$ O2	0.910	2.904(4)	2.011	166
N5–H5 $\cdots$ N22	0.910	3.084(3)	2.269	149
N6–H6 $\cdots$ N23$^{\text{iii}}$	0.910	2.995(4)	2.165	151

Equivalent positions: i: $-x+1/2+2$, $-y+1/2$, $-z+2$; ii: $x+1/2$, $-y+1/2$, $z+1/2$; iii: $-x+1/2+2$, $-y+1/2$, $-z+3$.

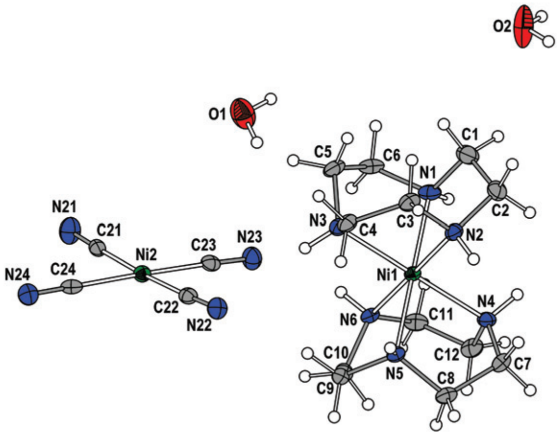

Figure 1. The crystal structure of **1**.

tacn ligands to Ni and zero connectivity of the complex cation, while lowering the M : *tacn* ratio to 1 : 1 yielded [Ni(*tacn*)]$^{2+}$.

The structure of [Ni(*tacn*)$_2$][Ni(CN)$_4$] $\cdot$ 2H$_2$O is ionic, composed of isolated [Ni(*tacn*)$_2$]$^{2+}$ cations, [Ni(CN)$_4$]$^{2-}$ anions and two crystallographically independent lattice water molecules (figures 1 and 2). Upon the search in CSDS [28] only five compounds containing [Ni(*tacn*)$_2$]$^{2+}$ were structurally characterized, e.g. with perchlorate [18] or 7,7,8,8-tetracyanoquinodimethane [29] anions, respectively. In [Ni(*tacn*)$_2$]$_2$(S$_2$O$_6$)$_3$ $\cdot$ 7H$_2$O, [Ni(*tacn*)$_2$]$^{3+}$ was found [30]. On the other hand, ionic tetracyanonickellates with *N*-donor ligands are numerous, as examples [Ni(*dien*)$_2$][Ni(CN)$_4$] or [Ni(*bipy*)$_3$][Ni(CN)$_4$] $\cdot$ 6H$_2$O $\cdot$ 0.5*bipy* can be mentioned [31, 32].

The cationic Ni(II) (Ni1) is six coordinate by two chelate bonded *tacn* ligands in *s-fac* fashion. Both chelate rings (ring 1 includes N1, N2 and N3 donor atoms, ring 2 includes N4, N5 and N6 donor atoms) are in chair parallel, λ conformations (figure 1). The NiN$_6$ octahedron is quite regular as the Ni–N coordination bonds are from 2.101(3)–2.118(3) Å (table 2). Similar values in the range 2.108(3)–2.127(3) Å were found in [Ni(*tacn*)$_2$](ClO$_4$)$_2$ $\cdot$ H$_2$O [18]. The intrachelate N–Ni–N angles in both

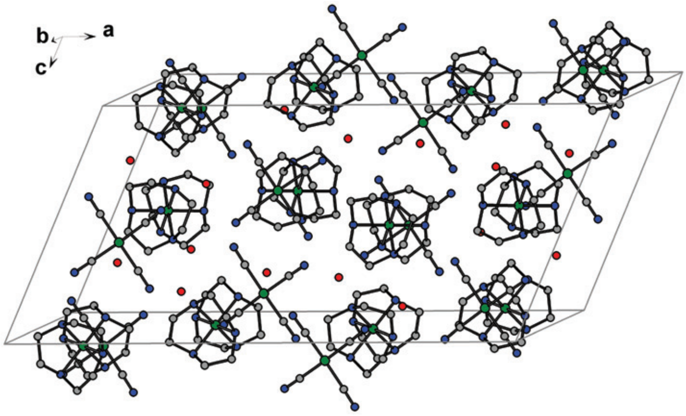

Figure 2. The unit cell packing diagram for **1**; hydrogen atoms are omitted for the sake of clarity.

tacn ligands range from 81.8(1) to 82.7(1)°; almost the same values were found in the perchlorate complex [18].

The Ni(II) (Ni2) in square tetracyanonickellate anion is coordinated by four terminal cyano groups *via* carbon atoms with Ni–C distances from the range 1.866(4)–1.880(3) Å. The Ni–C–N arrangement is almost linear with highest deviation from the linearity observed for Ni2–C23–N23 (177.6(3)°). All these geometric parameters are normal [8]. The closest distance between Ni(II) atoms in the complex cation and anion is 5.942(1) Å.

The most interesting feature of the structure is its hydrogen bonding system. Complex cations and complex anions connect *via* hydrogen bonds of the N–H $\cdots$ N(C) type giving a hydrogen-bonded double chain running perpendicularly to (011) plane with alternating cations and anions (figure 3, table 3). Between these double chains within the (101) plane are water molecules with each water forming three hydrogen bonds, two of the O–H $\cdots$ N(C) type with two crystallographically different complex anions and one of the N–H $\cdots$ O type with the complex cation; as a result a hydrogen-bonded hydrophilic layer is formed (figures 3 and 4). One hydrogen bond, O1–H1O1 $\cdots$ N24, exhibits rather low (109°) O1–H1O1–N24 angle, but we have included it in table 3 for the sake of completeness of all contacts assuming also that the positions of hydrogen atoms are of lower precision. There is no hydrogen bond interaction perpendicular to the above mentioned hydrogen bonded layer as the outer sides of the layers are occupied by hydrophobic methylene hydrogens. As a consequence, there are van der Waals contacts between the layers and Coulombic forces. Such packing of ions is unique among compounds containing $[\mathrm{Ni}(\mathit{tacn})_2]^{2+}$.

In the already mentioned $[\mathrm{Ni}(\mathit{bipy})_3][\mathrm{Ni(CN)_4}] \cdot 6\mathrm{H_2O} \cdot 0.5\mathit{bipy}$ compound a 3D extended hydrogen-bonded system leads to formation of a host-guest system in which the hydrophobic part of the structure (complex cations and not coordinated *bipy* molecules) are enclosed in the hydrophilic part of the structure (complex anions, water molecules of crystallization) [32].

The temperature dependence of the magnetic susceptibility of a powdered sample of **1** was studied from 300 to 1.8 K in a magnetic field of 1 kG (1000 Oe). As can be seen in figure 5, the observed behavior is described by the Curie–Weis law ($\chi = C/(\mathrm{T}\text{-}\Theta)$).

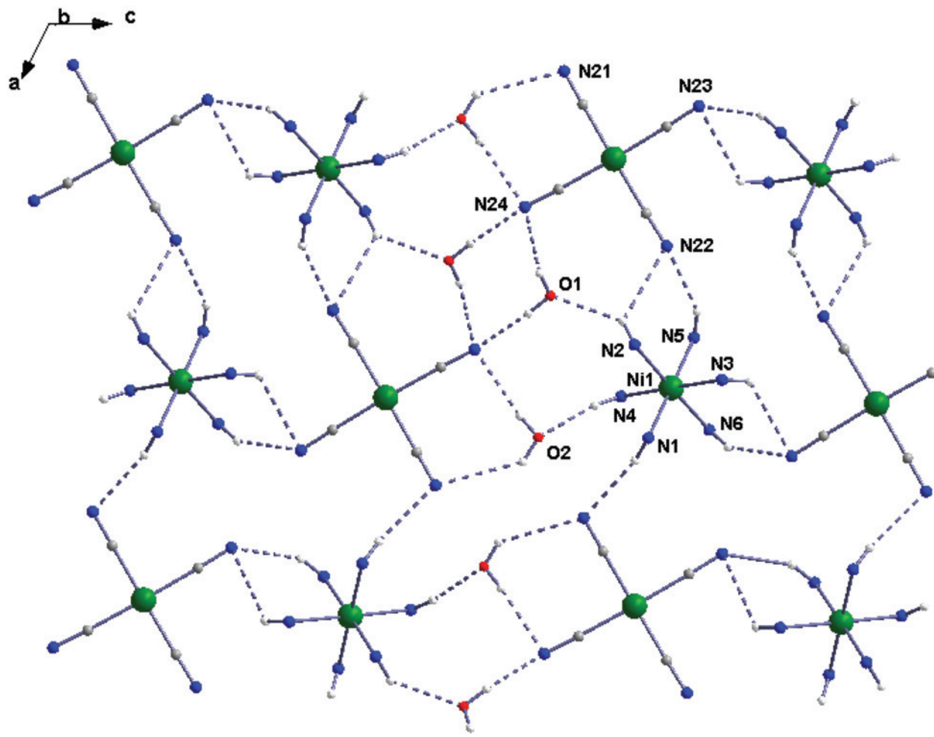

Figure 3. Hydrogen bonding system in **1**; methylene groups from the *tacn* ligands are omitted for the sake of clarity.

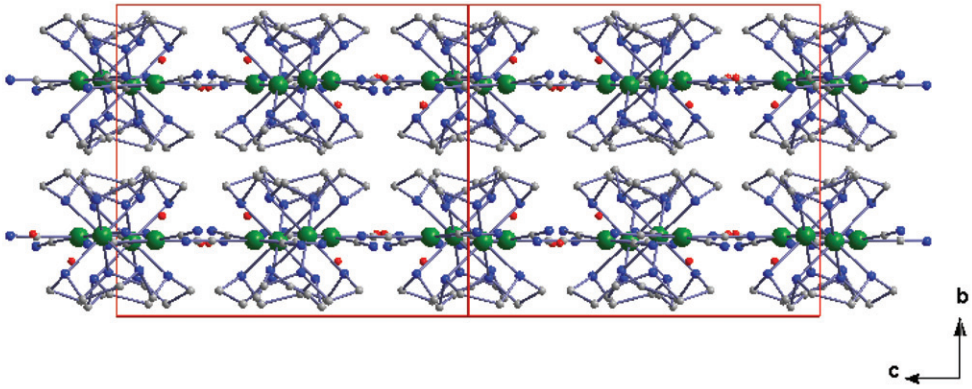

Figure 4. View on the structure of **1** perpendicular to the (011) plane showing formation of hydrogen bonded layers of complex ions and water molecules. Hydrogen atoms are omitted for the sake of clarity.

Analysis yields the Curie constant, $C = [N(g\mu_B)^2 S(S+1)]/3k_B = 1.0464\,K$, Weiss constant $\Theta = -0.77\,K$, a gyromagnetic parameter $g = 2.05$, and an effective magnetic moment, $\mu_{eff} = 2.90\,\mu_B$. On cooling, the effective magnetic moment decreases very slowly from 2.90 (300 K) to $2.85\,\mu_B$ (15 K), then somewhat more rapidly to $2.82\,\mu_B$ at 6 K. At this temperature the magnetic moment drops rapidly to $2.43\,\mu_B$ at 1.8 K,

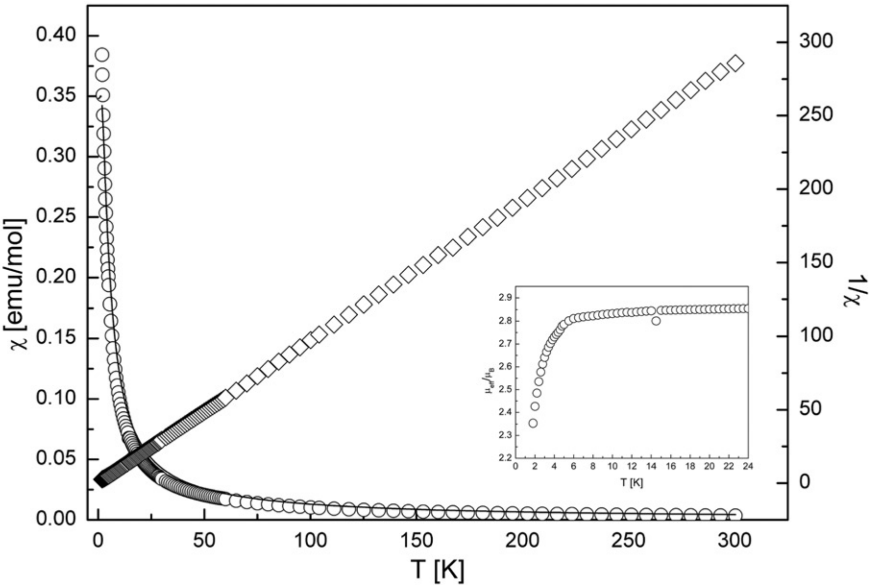

Figure 5. Temperature dependence of effective magnetic moment (empty circles in the inset), susceptibility (empty circles) and inverse susceptibility for **1** (empty squares). The solid line represents the fit using the strong coupling theory [33]. See text for more detailed discussion.

presumably due to the zero-field splitting. The susceptibility data were in the first approximation analyzed using the strong coupling theory developed for $S = 1$ Heisenberg chains [33] in which the exchange coupling is treated as a perturbation. The fitting of the observed temperature dependence of susceptibility for $g = 2.05$ yields values of zero-field splitting parameter $D/hc = 3.82\,\text{cm}^{-1}$ and rhombic magnetic anisotropy parameter $E/hc = 0.23\,\text{cm}^{-1}$. The obtained results are consistent with the observed structural features, i.e. (1) the paramagnetic Ni1 atoms are rather distant to each other with shortest Ni1 ··· Ni1 distance of 7.692(2) Å, and (2) there are not direct covalent bonds between the paramagnetic Ni1 central atom which might mediate magnetic exchange interactions. The values of the crystal field parameters are not unusual for Ni(II) compounds [34]. For example, in a similar $\text{Ni}(tn)_2\text{Ag}_2(\text{CN})_4$ ($tn = 1$,3-diaminoethane) the corresponding values were: $g = 2.11$, $D/hc = 2.33\,\text{cm}^{-1}$, $E/hc = 0.52\,\text{cm}^{-1}$ [35]. On the other hand, for $\text{Ni}(dien)\text{Ni}(\text{CN})_4 \cdot \text{H}_2\text{O}$ compound exhibiting layered structure with bridging cyano ligands, and thus with possibility of magnetic exchange interactions *via* covalent bonds, it was concluded that weak magnetic exchange ($J/hc = -0.10\,\text{cm}^{-1}$) is the dominant term in the magnetic properties of this compound [7].

Dominant features in the IR spectra of both compounds are represented by strong and sharp well identifiable absorptions due to ν(CN) stretching vibrations. In line with the literature data [36] the band at higher wavenumbers $2151\,\text{cm}^{-1}$ in the spectrum of **2** indicates the presence of bridging cyano ligands, while the absorption bands situated at lower wavenumbers $2122\,\text{cm}^{-1}$ for **1** and $2123\,\text{cm}^{-1}$ for **2** were assigned to the terminal cyano groups. The absorption bands observed in the region 410–430 cm^{-1} arising from the deformation vibration δ(Ni–CN) are in line with the presence of tetracyanonickellate anions in **1** and **2**, respectively. These spectral features were confirmed by the crystal structure of **1**. In Ni(*dien*)Ni$(CN)_4 \cdot H_2O$, which is similar in composition with **2**, the corresponding ν(CN) absorption bands were observed at 2160 and 2133 cm^{-1} [7] indicating similarities in the structures of these compounds.

The presence of the *N*-donor ligand *tacn* is corroborated by several absorption bands due to stretching and deformation vibrations of the CH_2 and NH groups. Absorption bands due to ν(NH) of the *tacn* ligand are observed in the range 3441 to 3250 cm^{-1}, while those arising from $\nu(CH_2)$ are observed between 2980 to 2875 cm^{-1} in line with literature data [36].

The water of **1** displays ν(OH) at 3640 to 3583 cm^{-1} and of **2** at 3445 cm^{-1}. In the spectrum of **1** the absorption band assigned to the δ(OH) deformation vibration was found at 1625 cm^{-1} and of **2** at 1620 cm^{-1}.

Seven crystal structures containing $[Ni(tacn)]^{2+}$ have been reported but none with cyanocomplex anion [28]. In all reported structures *fac* coordination of the *tacn* ligand exists. The same type of coordination of the tridentate *dien* ligand was observed in Ni(*dien*)Ni$(CN)_4 \cdot H_2O$ in which due to hexacoordination of the paramagnetic Ni(II), a two-dimensional bilayer structure is formed [7]. The same type of bilayer was also observed in the analogous Cu(II) compounds Cu(*tn*)Ni$(CN)_4$ (*tn* = 1,3-diaminopropane, blue polymorph) in which Cu(II) is pentacoordinate [37]. Using similarities in the observed IR spectra of **2** and Ni(*dien*)Ni$(CN)_4 \cdot H_2O$ and on the basis of the known crystal structure of Ni(*dien*)Ni$(CN)_4 \cdot H_2O$ we suggest that **2** has a similar central atom coordination to that of Ni(*dien*)Ni$(CN)_4 \cdot H_2O$.

Supplementary material

Crystallographic data (excluding structure factors) for structure **1** in this article has been deposited with the Cambridge Crystallographic Data Centre [28] as supplementary publication No. CCDC 666287. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-(0)1223-336033 or Email: deposit@ccdc.cam.ac.uk).

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