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**Two new 1-D dicyanamide bridged polymeric complexes
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[Ni(μ 1,5-dca)(TTA)](ClO $_4$) $_n$ (dca = dicyanamide, ;
salicyh = salicylic hydrazide; TTA =
triethylenetetramine): Synthesis, structures and
magnetic studies**

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Two new 1-D dicyanamide bridged polymeric complexes $[\text{Mn}(\mu_{1,5}\text{-dca})_2(\text{salicyh})_2]_n$ and $\{[\text{Ni}(\mu_{1,5}\text{-dca})(\text{TTA})](\text{ClO}_4)\}_n$ (dca = dicyanamide, $\text{N}(\text{CN})_2^-$; salicyh = salicylic hydrazide; TTA = triethylenetetramine) : Synthesis, structures and magnetic studies

Soma Sen, Pritha Talukder, Samiran Mitra, Georgina Rosair, Glenn Yap, Volker Gramlich, Jinkwon Kim, T. Matsushita, Cédric Desplanches and Jean-Pascal Sutter

Abstract

Two new dicyanamide bridged complexes $[\text{Mn}(\mu_{1,5}\text{-dca})_2(\text{salicyh})_2]_n$ (**1**) and $\{[\text{Ni}(\mu_{1,5}\text{-dca})(\text{TTA})](\text{ClO}_4)\}_n$ (**2**) (dca = dicyanamide, $\text{N}(\text{CN})_2^-$; salicyh = salicylic hydrazide; TTA = triethylenetetramine) have been synthesised and structurally characterised. Both the compounds **1** and **2** consist in 1-D coordination polymers. In **1** the manganese atoms are doubly bridged by $\mu_{1,5}$ -dca ligands, whereas in **2** the nickel atoms are bridged by a single $\mu_{1,5}$ -dca ligand. The magnetic measurements indicate that whereas intrachain interactions take place between the metal ions for compound **1** ($J = -0.26 \text{ cm}^{-1}$), no evidence for any exchange coupling is found for compound **2**.

1. Introduction

Dicyanamide $[\text{N}(\text{CN})_2]^-$, bridged polynuclear systems are a fast growing research field due to the large variety of topologies and magnetic properties that may be obtained from this ligand. The versatility of the dicyanamide as a ligand is well illustrated by its five structurally characterised coordination modes shown in Scheme 1 [1], [2], [3], [4], [5], [6], [7] and [8], monodentate coordination through nitrile nitrogen atom (1a), bis-monodentate bridging through one nitrile and one amide nitrogen atoms (1b), end-to-end bridging through two nitrile nitrogen atoms (1c), tris-monodentate bridging of three metal atoms (1d) [8] and rarer μ_4 coordination where one of the two nitrile nitrogen atoms is coordinated to two metal ions (1e).

Modification of structures and the magnetic properties of the coordination polymers of dca ligand is possible by incorporation of coligands into the structures. As for example, Escure et al. [9] reported two one dimensional dicyanamide bridged derivatives with formula $[\text{Mn}(\text{ac})(\text{terpy})(\mu_{1,5}\text{-dca})]_n$ and $[\text{Mn}(\text{pdz})_2(\mu_{1,5}\text{-dca})_2]_n$ {ac = acetate; terpy = 2,2':6'2"-terpyridine; pdz = pyridazine} having single and double dca bridges respectively. The first complex contains hepta coordinated manganese(II) central atom with MnN_5O_2 pentagonal bipyramid environment, whereas in the second complex manganese atom is hexacoordinated and both the complexes show weak antiferromagnetic coupling. Similarly, there are several reports of dca complexes of nickel where the geometry and magnetic properties of complexes depend on the nature of the coligand used [10], [11] and [12]. Among all possible coordination modes of dca, the $\mu_{1,5}$ -dca bridged complexes are very common [13], [14] and [15] and are generally characterised by antiferromagnetic interactions among the so-linked metal ions [9], [13], [16] and [17].

These interesting properties of dca complexes prompted us to prepare two new dca bridged polymeric complexes $[\text{Mn}(\mu_{1,5}\text{-dca})_2(\text{salicyh})_2]_n$ (**1**) and $\{[\text{Ni}(\mu_{1,5}\text{-dca})(\text{TTA})](\text{ClO}_4)\}_n$ (**2**). Here, in case of manganese, we chose a different type of ligand, salicylichydrazide (salicyh), to examine the variation in geometry and magnetic property of the complex with this ligand. But for nickel we used triethylenetetramine as coligand. Březina et al. [18] reported some new mononuclear dca complexes of Ni(II) using triethylenetetramine and some other tetramines as coligands. They measured the temperature dependence magnetic susceptibility of one complex $\{[\text{Ni}(\text{TTA})\{\text{N}(\text{CN})_2\}](\text{ClO}_4)\}$; TTA = triethylenetetramine} and no antiferromagnetic interaction was detected. Here, our aim was to prepare a polymeric Ni(II) complex using this tetramine by changing the reaction condition and monitor the magnetic behaviour of the polymeric complex.

The present report describes the synthesis, spectral characterisation, crystal structure and magnetic behaviour of two new one dimensional dca bridged polymeric complexes $[\text{Mn}(\text{salicyh})_2(\text{dca})_2]_n$ (**1**) and $\{[\text{Ni}(\mu_{1,5}\text{-dca})(\text{TTA})](\text{ClO}_4)\}_n$ (**2**). The coordination modes of the dca in both the complexes is end-to-end, by means of nitrile nitrogen atoms. To the best of our knowledge, complex **2** is the first reported dca bridged polymeric Ni(II) complex containing tetramine as coligand (according to CSD version 5.26 +1 update, November 2004 released).

2. Experimental

2.1. Materials

Manganese nitrate tetrahydrate, nickel perchlorate hexahydrate, salicylichydrazide, triethylenetetramine, and sodium dicyanamide (Fluka) were used as received. The solvents used were of reagent grade.

Caution. Perchlorate salts are potentially explosive and should be used in small quantity with much care.

2.2. Physical measurements

The infrared spectra were recorded on a Perkin–Elmer FT-IR spectrophotometer with a KBr disc. The electronic spectrum was recorded on a Perkin–Elmer Lambda 40 (UV–Vis) spectrophotometer in acetonitrile. Elemental analyses were carried out using a Perkin–Elmer 2400 II elemental analyser.

Magnetic susceptibility measurement of **1** was carried out with a Quantum Design MPMS-5S SQUID magnetometer under an applied magnetic field of 5000 Oe whereas the magnetic susceptibility measurement of **2** was carried out with a Nichaim SQUID magnetometer under an applied magnetic field of 5000 Oe. The temperature dependence of the molar magnetic susceptibility, χ_M , for complexes **1** and **2** was measured on polycrystalline samples in the temperature range 2–300 K. Diamagnetic corrections were estimated from Pascal tables and magnetic data were corrected for diamagnetic contributions of the sample holder.

2.3. Synthesis of complexes

2.3.1. Synthesis of $[\text{Mn}(\text{salicyh})_2(\text{dca})_2]_n$ (**1**)

To the solution of $\text{Mn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (0.251 g., 1 mmol) in 20 ml methanol, added methanolic solution (5 ml) of salicylichydrazide (0.152 g, 1 mmol) followed by the addition of a solution of sodium dicyanamide (0.178 g, 2 mmol) in minimum volume of water into the mixture with continuous stirring. The resulting solution was filtered and the filtrate was kept at room temperature. After 10 days, very light pink hexagonal crystals suitable for X-ray analysis were formed. Yield 54%. *Anal.* Calc. for $\text{C}_{18}\text{H}_{16}\text{N}_{10}\text{O}_4\text{Mn}$: C, 43.96; H, 3.25; N, 28.49. Found: C, 43.61; H, 2.98; N, 28.41%.

2.3.2. Synthesis of $\{[\text{Ni}(\mu_{1,5}\text{-dca})(\text{TTA})](\text{ClO}_4)\}_n$ (**2**)

Methanolic solution of the ligand TTA (1 mmol) was added to the solution of $\text{Ni}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (0.365 g., 1 mmol) in 25 ml methanol followed by the dropwise addition of a solution of sodium dicyanamide (0.089 g, 1 mmol) in minimum volume of water into the mixture with constant stirring at a temperature of 313 K; stirring was continued further for 30 min. The resulting solution was filtered and the filtrate was kept at room temperature. After several days, purple coloured hexagonal crystals suitable for X-ray analysis were formed. Yield 62%. *Anal.* Calc. for $\text{C}_8\text{H}_{16}\text{N}_7\text{Ni} \cdot \text{ClO}_4$: C, 26.05; H, 4.34; N, 26.59. Found: C, 25.89; H, 4.32; N, 26.50%.

2.4. X-ray data collection and structure refinement

The determination of unit cell and the data collection for **1** was performed on a Bruker AXS APEX diffractometer equipped with a graphite crystal monochromated Mo K α radiation source. The structure was solved by direct methods followed by successive different Fourier syntheses. Hydrogen atoms were not included in the calculations. The structure was refined in full-matrix least-squares. All non-hydrogen atoms were refined with anisotropic thermal parameters in the final cycles. The details of data collection and refinement for **1** are given in Table 1.

The determination of the unit cell and the data collection for purple coloured crystal of **2** was performed on a Rigaku AFC7 four circle serial diffractometer. Data were corrected for absorption empirically by means of multi-scans (SADABS). The structure was solved by direct and difference Fourier methods and refined by full-matrix least-squares on F^2 . All non-hydrogen atoms were refined with anisotropic displacement parameters. The perchlorate ion was disordered and the Cl atom with three of the O atoms are situated on a mirror plane. The fourth O atom lies off the mirror plane and was assigned an occupancy of 0.75. Crystallographic computing was performed using SHELXTL [19] programs. Further details are given in Table 1.

3. Results and discussion

3.1. Description of crystal structures

3.1.1. Crystal structure of 1

A labelled ORTEP plot of the molecular structure of **1** is shown in Fig. 1. Selected bond lengths and angles are given in Table 2. The crystal structure of **1** consists of chains of manganese atoms bridged by means of double end-to-end $\mu_{1,5}$ -dca bridge, two salicyh ligands are additionally coordinated at the manganese centre giving octahedral metal sites. The manganese atoms are octahedrally coordinated by means of two nitrogen atoms from two molecules of salicyh ligand in *trans* arrangement and four nitrile nitrogen atoms of the four dca ligands. Two of the dca ligands act as end-to-end bridging ligands with one neighbouring manganese atom and the other two act as end-to-end bridging ligands to other neighbouring manganese atom, giving a uniform one dimensional system (Fig. 2). The distorted octahedral metal site is located on an inversion centre, where the donor nitrogen atoms from four bridging dca ligands [N1, N1A, N3, N3A] form the equatorial plane with angle subtended by the Mn(II) ion varying from 87.24(10) to 92.69(7) $^\circ$ (Table 2). Two nitrogen atoms from the two molecules of the salicyh ligand occupy the axial position with N4–Mn–N4A angle being 178.19(10) $^\circ$. The equatorial Mn–N bond distances [Mn–N3 = 2.2118(19) Å, Mn–N3A = 2.212(2) Å, Mn–N1 = Mn–N1A = 2.226(2) Å] are comparable to similar systems [9]. The axial Mn–N distance [2.282(2) Å] is slightly longer than the equatorial distances. As depicted in Fig. 1, the bridging array Mn–NCNCN–Mn adopts a “V”-type conformation because of the sp^2 hybridisation of the middle nitrogen atom of the dca, where C–N–C angle [C1–N2–C2] is 120.2(2) $^\circ$ [20]. $[\text{N}(\text{CN})_2]^-$ has pseudo C_{2v} symmetry with average C–N and C=N bond lengths of 1.302(3) and 1.160(3) Å, respectively, as commonly observed in $[\text{N}(\text{CN})_2]^-$ anions [21], [22], [23], [24], [25], [26], [27], [28], [29], [30], [31], [32] and [33]. The carbon atoms of the dca ligand are sp hybridised, with N–C–N angles (173.5(2) and 175.2) $^\circ$ are almost linear [16], while the C–N–Mn angle 159.56(18) $^\circ$ is deviated from linearity. Intramolecular H-bonding is present in the complex between N1–H, O1 of the salicyh moiety (Fig. 2). In the crystal, the chains are packed by O–H...O and N–H...N hydrogen bonds (Fig. 2) in one direction and by a six membered ring stacking in the other (Fig. 3). The infinite chain propagates along *b*-axis. The distance between two adjacent manganese centres within the same chain is 7.57(2) Å. The minimum distance between two manganese centres in the successive chains is 7.34 Å (see Table 3).

3.1.2. Crystal structure of complex 2

A labelled ORTEP plot of the structure of **2** is shown in Fig. 4. The relevant bond angles are given in Table 2. The structure consists of chains of nickel(II) atoms bridged by means of single end-to-end $\mu_{1,5}$ -dca bridge (Fig. 4). Each nickel(II) atom is octahedrally surrounded by four nitrogen atoms from TTA ligand and two nitrile nitrogen atoms from two dicyanamide ligands. Two nitrogen atoms of the TTA ligand and two nitrogen atoms of the dca ligand form the equatorial plane, the deviations of these two types of nitrogen atoms from this equatorial plane are –0.1419, 0.1419, 0.1567, and –0.1567 Å for N1, N1A, N7 and N7A, respectively. The central nickel(II) ion (Ni1) lies on the equatorial plane. The other two nitrogen atoms N4 and N4A of TTA ligand occupy the axial position with *trans* axial angle N4–Ni–N4A = 177.55(19) $^\circ$. The equatorial angles range from 82.40(13) to 95.76(14) $^\circ$. The equatorial bond distances [2.114(14)–2.116(3) Å] are nearly equal to the axial bond distances [2.119(3) Å]. Similar to **1** in this complex also, the bridging array Ni–NCNCN–Ni adopts a V-type conformation because of sp^2 hybridisation of middle nitrogen atom of the dca ligand, where C–N–C angle [C2–N2–C2B] is 122.1(5) $^\circ$ [20]. $[\text{N}(\text{CN})_2]^-$ has pseudo C_{2v} symmetry with average C–N and C=N bond lengths of 1.302(5) and 1.146(5) Å, respectively, as commonly observed in $[\text{N}(\text{CN})_2]^-$ anions [21], [22], [23], [24], [25], [26], [27], [28], [29], [30], [31], [32] and [33]. The carbon atoms of the dca ligand are sp hybridised, with N–C–N angles 173.5(5) $^\circ$ are almost linear [16], while the C–N–Ni angle 151.8(3) $^\circ$ is deviated from linearity. The distance between two nickel centres bridged by single $\mu_{1,5}$ -dca ligand is 7.508 Å. One perchlorate ion for each asymmetric unit is present in the lattice.

3.2. Infrared spectra

The IR spectra of complexes **1** and **2** show the characteristic stretching vibration bands of dicyanamide ligand. The solid state of complexes depict several ν_{CN} bands at 2303, 2240, 2172 cm^{-1} for **1** and 2306, 2229, 2160 cm^{-1} for **2** which are attributed to $\nu_{\text{sym}} + \nu_{\text{asym}}(\text{CN})$, $\nu_{\text{asym}}(\text{CN})$ and $\nu_{\text{sym}}(\text{CN})$ modes. All data are in good agreement with the literature [23], [34], [35], [36], [37], [38] and [39]. Relative to $\nu(\text{N}(\text{CN})_2)$ values of the free ligand (2287, 2229 and 2181 cm^{-1}), those of complex **1** and complex **2** show higher frequency shifts, due to the bridging coordination mode of dca in the complexes. For complex **1** compared with the free salicylic hydrazide ligand, the bands at 3177–3279 cm^{-1} attributed to PhO–H

group remain nearly unchanged after complexation indicates the presence of uncoordinated phenolic-OH group in the complex [40].

3.3. Electronic spectrum

As the solution of complex **1** is almost colourless, electronic spectrum was not recorded for this complex. The peaks in the electronic spectrum of complex **2** in acetonitrile exhibit the d-d maxima of octahedral Ni^{II}. The bands at 245, 382 and 640 nm are assigned to the spin allowed transitions ${}^3A_{2g} \rightarrow {}^3T_{2g}$, ${}^3A_{2g} \rightarrow {}^3T_{1g}$, ${}^3A_{2g} \rightarrow {}^3T_{1g}(P)$, respectively. The last transition appeared as shoulder [41].

3.4. Magnetic studies

The magnetic behaviour for compound **1** is shown in the form of $\chi_M T$ versus T plot (Fig. 5). At 300 K, the $\chi_M T$ value is $4.4 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$ in good agreement with that expected for an isolated spin $S = 5/2$ ($4.37 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$). The $\chi_M T$ values remain constant from 300 K down to ca. 50 K, then decrease rapidly to $1.6 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$ at 2 K, suggesting the occurrence of antiferromagnetic interactions between the Mn(II) ions. This experimental behaviour has been analysed with a model appropriate for a chain derived from the spin Hamiltonian

$$H = -J \sum_{i=1}^{n-1} S_{A_i} \cdot S_{A_{i+1}},$$

where the summation runs over the n sites of the chain. For large values of the spin, $S = 5/2$ in our case, it is possible to treat the spin as a classical vector resulting in the following expression for $\chi_M T$ [42] and [43]:

The best fit of this expression to the experimental data leads to an intrachain exchange parameter of $J = -0.26 \text{ cm}^{-1}$ with $g = 2.02$ (Fig. 5). These values are in good agreement with some previously reported Mn(II)-dicyanamido complexes. With one exception ($J = +1.6 \text{ cm}^{-1}$), in all other cases the exchange interaction is very weak antiferromagnetic [17].

The magnetic behaviour for compound **2** is shown in Fig. 6. For this compound, $\chi_M T$ is invariant over the whole temperature range except a sharp decrease observed below 5 K. The $\chi_M T$ value between 10 and 300 K is $1.16 \text{ cm}^3 \text{ K mol}^{-1}$, which is consistent with a $S = 1$ spin for a d^8 electronic configuration in an octahedral geometry. The observed magnetic behaviour in the low temperature domain might be ascribed either to very weak antiferromagnetic interactions between the metal ions within a chain as found for **1**, or to the effect of zero-field splitting on the Ni ions in the absence of any exchange interaction mediated by the dca ligand. In order to evaluate the two hypotheses, the magnetic behaviour was first analysed by considering exchange interaction among the Ni ions. The spin Hamiltonian that applies is the same as that for **1** but the Fisher solution relevant only for larger spins was replaced by the Weng equation [44]. The expression for $\chi_M T$ appropriate to compound **2** is given below

$$\chi_M T = \frac{Ng^2\beta^2}{k} \frac{2 + A\delta + B\delta^2}{3 + C\delta + D\delta^2 + E\delta^3} \quad \text{with}$$

$$A = 0.019, B = 0.777, C = 4.346, D = 3.232, E = 5.834 \text{ and}$$

$$\delta = |J|/kT.$$

The fit of this expression to the experimental data yielded an intrachain exchange parameter of $J = -0.14 \text{ cm}^{-1}$ with $g = 2.16$ but agreement between the experimental and calculated behaviour is poor (Fig. 6), suggesting that the observed behaviour does not result from antiferromagnetic interactions.

We have then neglected the exchange contribution between the Ni ions and introduced axial zero-field splitting using the Hamiltonian $H = D[S_z^2 - S(S+1)/3]$, the resulting expression for the susceptibility is given by [44]

$$\chi_M T = (\chi_{M,i} + 2\chi_{M,c})T/3$$

$$= \frac{2Ng^2\beta^2}{3k} \frac{\exp(-y) + 2[1 - \exp(-y)]/y}{1 + 2\exp(-y)} \quad \text{with } y = D/kT.$$

Best fit to the experimental data yielded a zero-field splitting parameter $|D| = 2.16 \text{ cm}^{-1}$ and a Landé factor $g = 2.17$. The obtained D parameter is in the range of those usually found for Ni(II) ions. For instance, for six-coordinated Ni(II) ions linked by oxalate-bridges into a chain organisation, a D value of 1.87 cm^{-1} has been deduced using high-field/high-frequency EPR spectroscopy [45]. The calculated behaviour considering a D parameter closely follows the experimental data, especially in the low temperature domain (Fig. 5). Consequently, the decrease of $\chi_M T$ observed below 10 K for **2** can be attributed to the single-ion anisotropy rather than to exchange among the Ni(II) ions.

4. Concluding remarks

In case of compound **1**, using a different coligand we do not get any remarkable variation in the geometry compared to that of previously reported dca bridged Mn(II) polymers whereas compound **2** is the first reported dca bridged polynuclear Ni(II) complex having tetramine as coligand. On the magnetic point of view, the weak antiferromagnetic interaction found for compound **1** is perfectly in line with the behaviour usually found for $\mu_{1,5}$ -dca bridged Mn(II) ions. When Ni(II) ions are involved instead of Mn(II), it is rather surprising that no exchange interaction is detected. In the reported compound **2**, the experimental behaviour was best analysed by considering only the contribution of the zero-field splitting on the Ni(II) ion, confirming the very poor ability of the dca linker to mediate the magnetic interaction for this ion. For such $S = 1$ chain compounds with antiferromagnetic interactions, a peculiar behaviour known as Haldane gap [46] is anticipated, however for compound **2** the weakness of the exchange interaction precludes the observation of this gap.

5. Supplementary material

CCDC – 266438 (**1**) and 266439 (**2**) – contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk [or from Cambridge Crystallographic Data Center, 12, Union Road, Cambridge CB2 1EZ, UK; e-mail: deposit@ccdc.cam.ac.uk].

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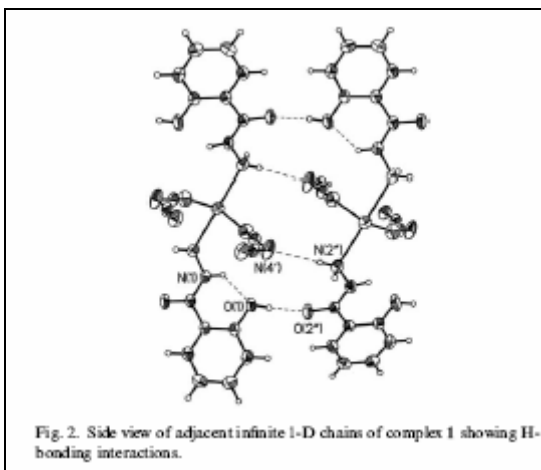
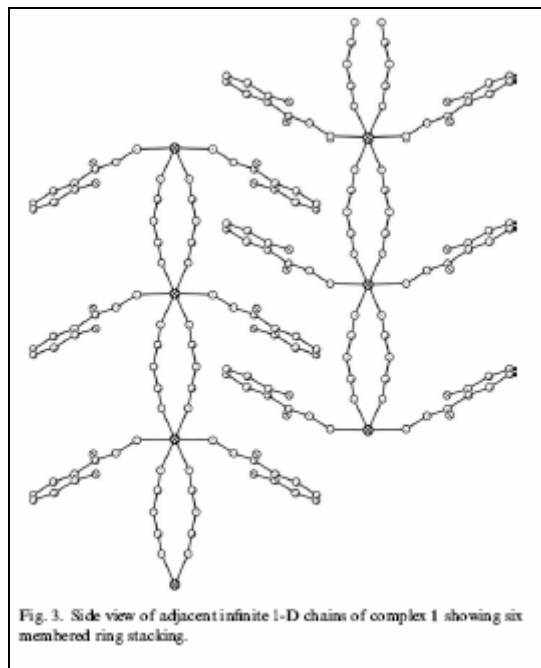
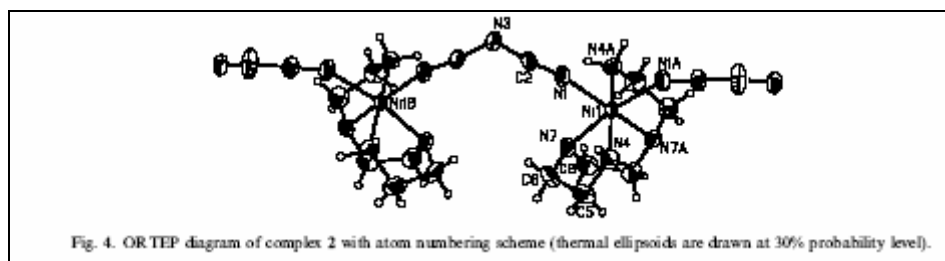


Table 3
Hydrogen bonding interactions (\AA , $^\circ$) of complex 1

D-H...A	D-H	H...A	D...A	\angle D-H...A
N1-H2...O1	0.86(3)	1.94(3)	2.607(3)	133(3)
O1-H1...O2_S1	0.835(19)	1.81(2)	2.643(3)	173(4)
N2-H3...N4_S2	0.82(4)	2.51(4)	3.168(4)	137(4)

Symmetry code: S1, $X, 1 - Y, 0.5 + Z$; S2, $1 - X, 1 - Y, -Z$.



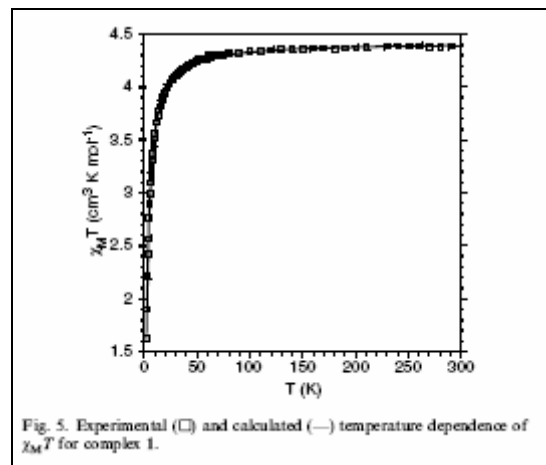


Fig. 5. Experimental (\square) and calculated (—) temperature dependence of $\chi_M T$ for complex 1.

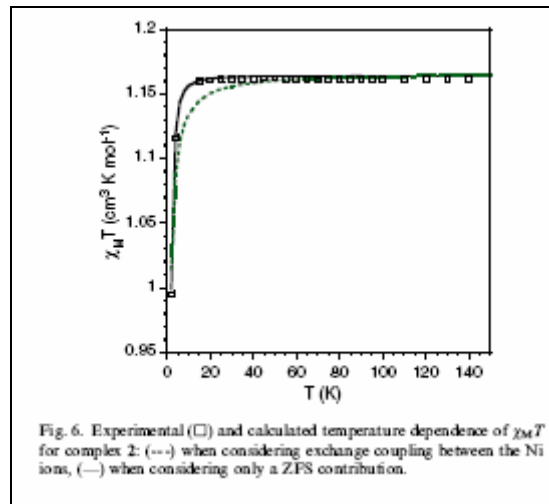


Fig. 6. Experimental (\square) and calculated temperature dependence of $\chi_M T$ for complex 2: (---) when considering exchange coupling between the Ni ions, (—) when considering only a ZFS contribution.