

Structure and magnetic behaviour of the one-dimensional $[\{\text{Ni}_2(\text{Medien})_2(\mu_{1,1}\text{-N}_3)_2(\mu_{1,3}\text{-N}_3)\}_n][\text{ClO}_4]_n$ compound with unusually strong ferro-antiferromagnetic alternating interactions

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A new monodimensional μ -azido-nickel(II) complex of formula $[\{\text{Ni}_2(\text{Medien})_2(\mu_{1,1}\text{-N}_3)_2(\mu_{1,3}\text{-N}_3)\}_n][\text{ClO}_4]_n$ **1** [Medien = bis(2-aminoethyl)methylamine] has been synthesized and crystallographically characterised. The nickel atom is placed in an octahedral environment bridged by two end-on azido ligands and one end-to-end azido bridge to the neighbouring nickel atoms, giving an alternated 1-D system. The magnetic behaviour corresponds to an alternating ferro-antiferromagnetic chain. The superexchange parameters have been calculated as $J_{\text{AF}} = -34.7 \text{ cm}^{-1}$ and $J_{\text{FM}} = +38.2 \text{ cm}^{-1}$, $a = 1.10$, by means of an improved analytical expression for the magnetic susceptibility of the isotropic ferro-antiferromagnetic $S = 1$ Heisenberg chain in terms of the alternation parameter $a = J_{\text{FM}}/|J_{\text{AF}}|$. Magnetic properties have been correlated to the structural data.

Introduction

One-dimensional magnetic materials have attracted increasing interest, and have been thoroughly studied from both experimental and theoretical points of view mostly due to their position between high nuclearity clusters and extended 3-D lattices, which opens up new possibilities for understanding phenomena that cannot be explained in a higher dimension.¹⁻⁴

In recent years the azide bridge has been shown to be able to generate systems from discrete molecules⁵ with different nuclearity to 3-D compounds,⁶ and specifically for nickel(II) a large number of one-dimensional systems have been reported.⁷ The most common topologies for the 1-D nickel-azide system consist of homogeneous chains with a single end-to-end bridge, with four co-ordination sites of the nickel environment occupied by four polyamine ligands or the double end-to-end bridge with the two remaining co-ordination sites occupied by two diamine blocking ligands.⁷ The end-to-end kind of compound has been extensively studied from synthetic and magnetic points of view and suitable models were proposed to explain and predict the magnitude of the antiferromagnetic coupling as a function of the bond parameters in the bridge region.^{5c,8} Less common are the examples of end-on ferromagnetic chains and the alternating systems.⁹ This latter kind of unusual system may be classified in several types: alternating end-to-end systems, alternating end-to-end/end-on systems and complex alternance of bridges, for which the magnetic analysis becomes more complicated or impossible in some cases. Continuing with our work in this field we report the syntheses and magnetic behaviour of the compound $[\{\text{Ni}_2(\text{Medien})_2(\mu_{1,1}\text{-N}_3)_2(\mu_{1,3}\text{-N}_3)\}_n][\text{ClO}_4]_n$ [Medien = bis(2-aminoethyl)methylamine] which shows the single end-to-end/double end-on alternance, giving a ferro-antiferromagnetic alternating system. To fit our experimental data an improved expression built on the basis of the increasing ring system calculations has been developed and checked.

Experimental

Synthesis

The complex $[\{\text{Ni}_2(\text{Medien})_2(\mu_{1,1}\text{-N}_3)_2(\mu_{1,3}\text{-N}_3)\}_n][\text{ClO}_4]_n$ was synthesized by the addition of 15 ml of an aqueous solution of sodium azide (0.23 g, 4 mmol) to an aqueous solution obtained by mixing 0.73 g (2 mmol) of nickel perchlorate and 0.24 g (2 mmol) of the Medien ligand. Slow evaporation of the blue resulting solution provided blue crystals suitable for X-ray determination. Yield 60%. [Calc. (Found) for $\text{C}_{10}\text{H}_{30}\text{ClN}_{15}\text{-Ni}_2\text{O}_4$: C, 20.8 (20.8); H, 5.2 (5.3); N, 36.4 (36.4)%]. The IR spectrum shows the typical absorptions corresponding to the Medien ligand, the perchlorate counter anion and the characteristic $\nu(\text{N}_3)$ at 2090, 2028 and 2055 (sh) cm^{-1} .

Spectral and magnetic measurements

Infrared spectra (4000–400 cm^{-1}) were recorded from KBr pellets on a Nicolet 520 FTIR spectrophotometer. Magnetic measurements were carried out with a DSM8 pendulum susceptometer, working in the temperature range 300–4 K. The applied external magnetic field was 1.5 T. Diamagnetic corrections were estimated from Pascal tables.

Crystallographic data collection and refinement

The single crystal data were collected on a modified STOE four-circle diffractometer (crystal size $0.55 \times 0.35 \times 0.30 \text{ mm}$). The crystallographic data, conditions retained for the intensity data collection, and some features of the structure refinement are listed in Table 1. The accurate unit-cell parameters were determined from automatic centring of 25 reflections ($12 < \theta < 18^\circ$) and refined by least-squares methods. Intensities were collected with graphite-monochromated Mo-K α radiation, using the ω -scan technique. 5462 Reflections were collected in the range $2.90 < 2\theta < 27.40^\circ$ (4917 independent reflections, R_{int} 0.0242).

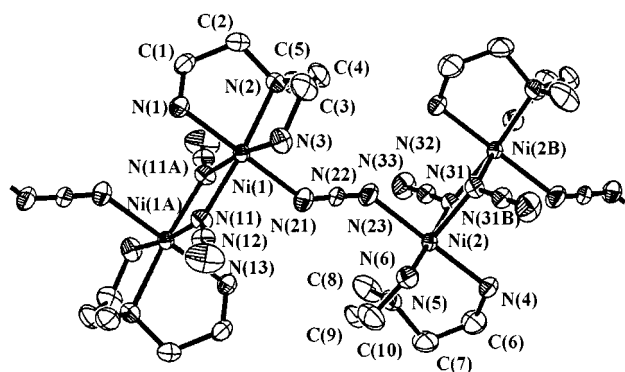


Fig. 1 An ORTEP¹³ drawing of $[\{Ni_2(Medien)_2(\mu_{1,1}-N_3)_2(\mu_{1,3}-N_3)\}_n][ClO_4]_n$ with the atom-labelling scheme. Thermal ellipsoids are at the 50% probability level.

No intensity decay of 3 control reflections ($-1\ 3\ -1$; $-1\ 4\ -3$; $0\ -2\ -4$), collected every hour, was observed. Corrections were applied for Lorentz-polarisation effects but not for absorption (range of transmission: 0.650–1.000). The structure was solved by direct methods using the SHELXS 86¹⁰ computer program, and refined by full-matrix least-squares methods on F^2 using SHELXL 93¹¹ incorporated in the SHELXTL/PC V 5.03 program package.¹² Fourier-difference maps indicated two split orientations of one partially disordered Medien ligand and the perchlorate counter anion. Refinement of the corresponding population parameters gave values of 0.60(1) and 0.40(1) for the Medien ligand and 0.67(1) and 0.33(1) for the perchlorate. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were located on calculated positions and assigned six common isotropic displacement factors (one for each type of parent C and N atom in each Medien ligand). The final R factor was 0.0398 ($wR2 = 0.0999$). The number of parameters refined was 378. Goodness of fit 1.048. Maximum shift/e.s.d. = 0.05. Maximum and minimum peaks in the final difference synthesis were 0.614 and $-0.546\ e\ \text{\AA}^{-3}$, respectively. Significant bond parameters are given in Table 2.

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Results and discussion

Crystal structure

The labelled diagram for complex **1** together with a chain perspective are shown in Fig. 1. The structure consists of $Ni(Medien)$ units bridged by azido ligands, giving a monodimensional compound and perchlorate counter anions. Two azide co-ordination modes are present in an alternating form along the chain: each nickel atom has a double end-on bridge with one of the neighbouring nickel atoms whereas the bridge with a second nickel atom consists of a single end-to-end azido linkage. Each $Ni(1)-Ni(1A)$ and $Ni(2)-Ni(2B)$ subunit has an inversion centre, and the structure may thus be envisaged as two non-equivalent $Ni(\mu_{1,1}-N_3)_2Ni$ planar units bridged by one $\mu_{1,3}-N_3$ ligand. The environments of $Ni(1)$ and $Ni(2)$ are quite similar, with the tridentate Medien ligand in *fac* co-ordination. Bond distances to the N atoms of the end-on bridge [$Ni(1)-N(11)$ 2.110(2), $Ni(1)-N(11A)$ 2.116(3), $Ni(2)-N(31)$ 2.113(3) and $Ni(2)-N(31B)$ 2.112(3) Å] are very similar, and slightly shorter than the bond distances to the N atoms of the end-to-end azido bridge [$Ni(1)-N(21)$ 2.159(3) and $Ni(2)-N(23)$ 2.142(3) Å]. The $Ni(1)-N(11)-Ni(1A)$ 100.8(1) and $Ni(2)-N(31)-Ni(2B)$ 98.9(1)° bond angles are smaller than the common bond angles found in previous dimeric $Ni(\mu_{1,1}-N_3)_2Ni$ entities, which show values between 101 and 104°.^{14–17} The end-to-end bridge shows asymmetric co-ordination as is normal for this ligand, $Ni(1)-N(21)-N(22)$ 138.1(2) and $N(22)-N(23)-Ni(2)$ 125.7(2)°. The τ torsion angle, defined as the dihedral between $Ni(1)-N(21)-N(22)-N(23)$ and $N(21)-N(22)-N(23)-$

Table 1 Crystal data and structure refinement for $[\{Ni_2(Medien)_2(\mu_{1,1}-N_3)_2(\mu_{1,3}-N_3)\}_n][ClO_4]_n$

Formula	$C_{10}H_{30}ClN_{15}Ni_2O_4$
Formula weight	577.36
Crystal system	Triclinic
Space group	$P\bar{1}$ (no. 2)
$a/\text{\AA}$	7.421(1)
$b/\text{\AA}$	12.339(3)
$c/\text{\AA}$	14.171(5)
$\alpha/^\circ$	113.35(2)
$\beta/^\circ$	100.80(3)
$\gamma/^\circ$	96.45(2)
$V/\text{\AA}^3$	1144.9(6)
Z	2
$T/^\circ\text{C}$	25(2)
$\lambda(\text{Mo-K}\alpha)/\text{\AA}$	0.71069
$D_c, D_m/\text{g cm}^{-3}$	1.675, 1.66(3)
$\mu(\text{Mo-K}\alpha)/\text{mm}^{-1}$	1.813
R	0.0398
$wR2$	0.0999

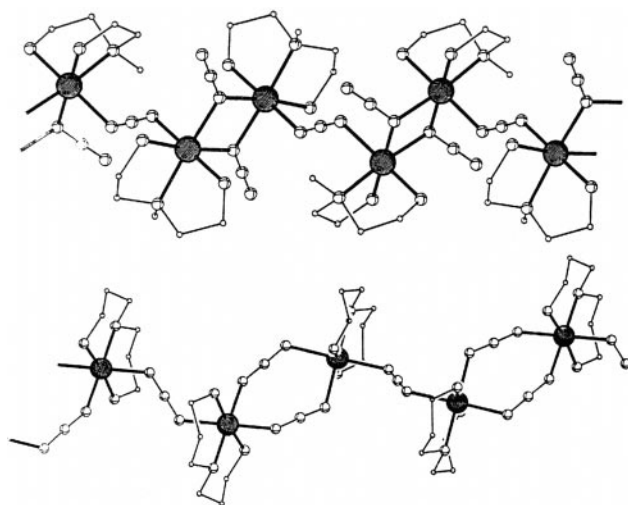


Fig. 2 Perspective view of $[\{Ni_2(Medien)_2(\mu_{1,1}-N_3)_2(\mu_{1,3}-N_3)\}_n][ClO_4]_n$ and comparison with the related $[\{Ni_2(dpt)_2(\mu_{1,1}-N_3)_2(\mu_{1,3}-N_3)\}_n][ClO_4]_n$ compound.

$Ni(2)$ mean planes is 162.8(4)°. The $Ni\cdots Ni$ distance in the end-on units is 3.257(1) Å for $Ni(1)-Ni(1A)$ and 3.203(1) Å for $Ni(2)-Ni(2B)$, whereas the $Ni(1)\cdots Ni(2)$ distance is greater, 6.060(2) Å, due to the end-to-end co-ordination of the bridge. The structure of the $[\{Ni_2(Medien)_2(\mu_{1,1}-N_3)_2(\mu_{1,3}-N_3)\}_n][ClO_4]_n$ compound shows the same double/single bridge alternance as the previously reported^{9b} $[\{Ni_2(dpt)_2(\mu_{1,1}-N_3)_2(\mu_{1,3}-N_3)\}_n][ClO_4]_n$, dpt = bis(3-aminopropyl)amine, Fig. 2. The difference between the two systems lies in the kind of bridge, alternating double end-on/single end-to-end for the present compound and only end-to-end bridges for the previous complex. From the synthetic and magnetic points of view, these compounds are a nice example of the extreme versatility of the azido ligand in providing uncommon magnetic systems on the basis of simple synthetic procedures.

The model and calculation

Ferro-antiferromagnetic systems have attracted much attention in the past few years, mainly focused on their complicated magnetic behaviour derived from the simultaneous exchange coupling interactions. One of the consequences has been the development of suitable models to explain their magnetic properties. For the $S = 5/2$ system, which permits the treatment as a classical vector, appropriate equations have been proposed,¹⁸ whereas for lower S values several authors have solved numerically the magnetic exchange expressions for the alternating anti-

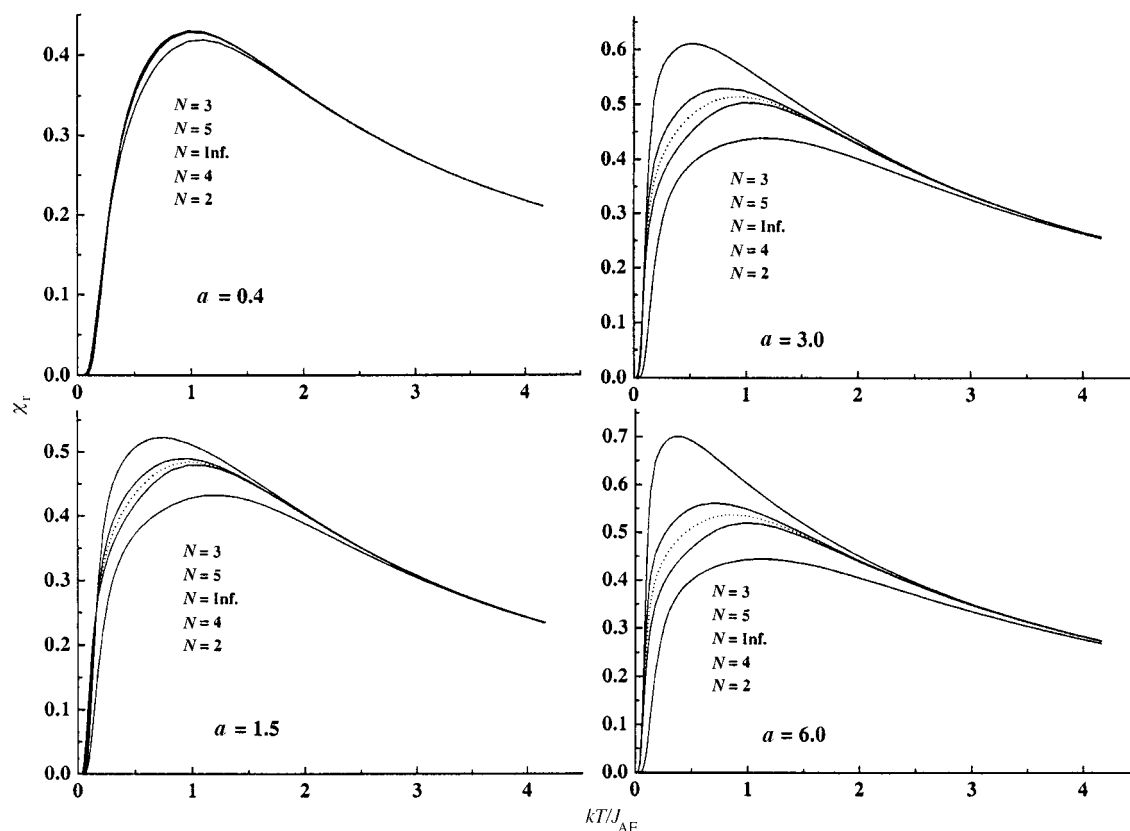


Fig. 3 Temperature dependence of χ_T versus T_r for $N = 2, 3, 4, 5$ rings (solid lines) and $N =$ infinite (dashed line) for the alternating parameter $a = 0.4, 1.5, 3.0$ and 6.0 .

Table 2 Selected bond lengths (Å) and angles (°) for $[\{\text{Ni}_2(\text{Medien})_2(\mu_{1,1'}-\text{N}_3)_2(\mu_{1,3'}-\text{N}_3)\}_n][\text{ClO}_4]_n$

Ni(1)–Ni(1)	2.065(3)	Ni(2)–Ni(4)	2.081(3)
Ni(1)–Ni(2)	2.145(3)	Ni(2)–Ni(5)	2.118(3)
Ni(1)–Ni(3)	2.076(3)	Ni(2)–Ni(6)	2.081(3)
Ni(1)–Ni(11)	2.110(2)	Ni(2)–Ni(23)	2.142(3)
Ni(1)–Ni(11A)	2.116(3)	Ni(2)–Ni(31)	2.113(3)
Ni(1)–Ni(21)	2.159(3)	Ni(2)–Ni(31B)	2.112(3)
N(11)–N(12)	1.179(3)	N(22)–N(23)	1.165(4)
N(12)–N(13)	1.152(4)	N(31)–N(32)	1.194(3)
N(21)–N(22)	1.163(4)	N(32)–N(33)	1.149(4)
N(1)–Ni(1)–N(2)	82.7(1)	N(4)–Ni(2)–N(5)	82.9(1)
N(1)–Ni(1)–N(3)	98.0(1)	N(4)–Ni(2)–N(6)	96.1(1)
N(1)–Ni(1)–N(11)	91.8(1)	N(4)–Ni(2)–N(31)	86.5(1)
N(1)–Ni(1)–N(11A)	86.8(1)	N(4)–Ni(2)–N(31B)	91.6(1)
N(1)–Ni(1)–N(21)	174.0(1)	N(4)–Ni(2)–N(23)	172.8(1)
N(2)–Ni(1)–N(3)	83.7(1)	N(5)–Ni(2)–N(6)	83.4(1)
N(2)–Ni(1)–N(11)	174.1(1)	N(5)–Ni(2)–N(31)	100.4(1)
N(2)–Ni(1)–N(11A)	102.5(1)	N(5)–Ni(2)–N(31B)	174.1(1)
N(2)–Ni(1)–N(21)	96.0(1)	N(5)–Ni(2)–N(23)	94.3(1)
N(3)–Ni(1)–N(11)	95.0(1)	N(6)–Ni(2)–N(31)	175.6(1)
N(3)–Ni(1)–N(11A)	172.6(1)	N(6)–Ni(2)–N(31B)	95.0(1)
N(3)–Ni(1)–N(21)	87.7(1)	N(6)–Ni(2)–N(23)	90.1(1)
N(11)–Ni(1)–N(11A)	79.2(1)	N(31)–Ni(2)–N(31B)	81.4(1)
N(11)–Ni(1)–N(21)	89.7(1)	N(23)–Ni(2)–N(31)	87.5(1)
N(11A)–Ni(1)–N(21)	87.8(1)	N(23)–Ni(2)–N(31B)	91.4(1)
N(12)–N(11)–Ni(1)	124.8(2)	N(32)–N(31)–Ni(2)	125.8(2)
N(12)–N(11)–Ni(1A)	134.3(2)	N(32)–N(31)–Ni(2B)	121.0(2)
Ni(1)–N(11)–Ni(1A)	100.8(1)	Ni(2)–N(31)–Ni(2B)	98.9(1)
N(22)–N(21)–Ni(1)	138.1(2)	N(22)–N(23)–Ni(2)	125.7(2)
N(11)–N(12)–N(13)	179.7(3)	N(31)–N(32)–N(33)	177.8(3)
N(21)–N(22)–N(23)	178.1(3)		

ferromagnetic chain and alternating ferro-antiferromagnetic systems of spins $S = 1/2$.¹⁹ Recently, an expression to fit ferro-antiferromagnetic $S = 1$ chains was proposed by Borrás

Almenar *et al.*,²⁰ assuming that the ring of $N = 5$ pairs of $S = 1$ spins describes the chain behaviour satisfactorily. In this section, therefore, we felt it appropriate to extend those calculations and attempt to develop such an expression for the $N =$ infinite extrapolation, in order to improve the expression for large $a = J_{\text{FM}}/|J_{\text{AF}}|$ values.

The Hamiltonian for the Heisenberg alternating ferro-antiferromagnetic chain can be written as in eqn. (1) where N is

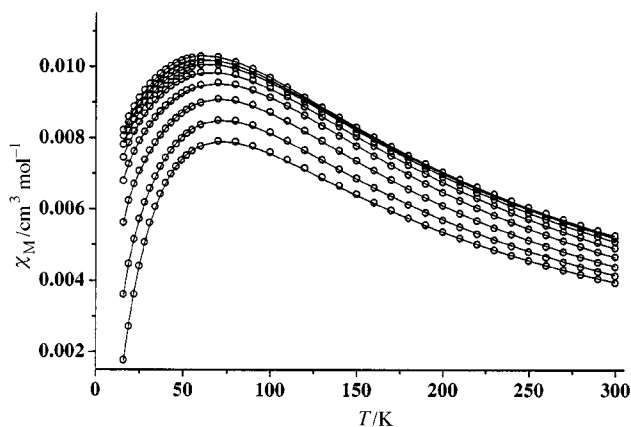
$$H = - \sum_{i=1}^{N-1} J_{\text{AF}} S_{2i} S_{2i+1} + J_{\text{FM}} S_{2i} S_{2i-1} \quad (1)$$

the number of spin pairs, J_{AF} and J_{FM} are the nearest neighbour antiferro- and ferro-magnetic exchange interactions. By using the usual computational technique, based on the calculation of the properties of finite rings of increasing size, we have determined the magnetic susceptibility of alternating ferro-antiferromagnetic chains for various a values. The series of calculations were made using the computer program CLUMAG, which uses the irreducible tensor operator (ITO) formalism.²¹

Owing to the difficulties associated with the large dimensions of the calculations and the required computing times, our calculations were only achieved up to 10 spins ($N = 5$), and by the same reason the influence in the low temperature region of the zero field splitting parameter D has not been considered. Fig. 3 reports the reduced magnetic susceptibility curves of the chains $N = 2, 3, 4$ and 5 for $a = 0.4, 1.5, 3$ and 6 . Closer examination shows that when a is low (0.4) the two curves $N = 4$ and 5 are indistinguishable throughout the temperature range, whereas significant differences become observable when a increases especially at low temperature (below the reduced temperature, $T_r = 1.3$ for $a = 1.5$, 1.6 for 3 and 1.8 for 6), and the maximum deviation becomes 2.9% for $a = 6$. Nevertheless, it seems clear that the unique sequence ($N =$ infinite) will appear in the intermediate region bracketed by the curves for odd N and those for even N , exactly between $N = 5$ and 4 , which led us to assume that the curves of half of the sum between $N = 5$ and 4 ,

Table 3 Coefficients for the polynomials for $0 \leq a \leq 2$ and $2 \leq a \leq 6$

	<i>A</i>	<i>B</i>	<i>C</i>	<i>D</i>	<i>E</i>
$0 \leq a \leq 2$					
a_0	0.610392	b_0 0.141083	c_0 1.17598	d_0 1.26115	e_0 0.282429
a_1	-2.56528	b_1 0.503112	c_1 -3.14941	d_1 -1.584444	e_1 -1.15824
a_2	3.3881	b_2 -0.687456	c_2 3.18665	d_2 3.30872	e_2 0.896513
a_3	-1.68187	b_3 0.331817	c_3 -1.49803	d_3 1.86917	e_3 -0.383948
a_4	0.310599	b_4 -0.0547117	c_4 0.269656	d_4 0.369253	e_4 0.0743106
$2 \leq a \leq 6$					
a_0	38.728	b_0 16.4703	c_0 32.1303	d_0 18.3973	e_0 57.5268
a_1	-51.9772	b_1 -21.8691	c_1 -42.9283	d_1 -23.3778	e_1 -76.6243
a_2	25.4004	b_2 10.4464	c_2 20.6105	d_2 12.0541	e_2 36.553
a_3	-5.38647	b_3 -2.1991	c_3 -4.3098	d_3 -2.66954	e_3 -7.6135
a_4	0.454228	b_4 0.185766	c_4 0.357483	d_4 0.236077	e_4 0.630971

**Fig. 4** Temperature dependence of χ_m (theoretical) versus T for $N =$ infinite. The solid lines are the best fits calculated for different values of the alternating parameter $a = 0.2, 0.6, 1.2, 2.0, 3, 4, 5$ and 6 ($J_{AF} = -50 \text{ cm}^{-1}$ and $g = 2.35$).

$N_\infty = [(N = 4 + N = 5)/2]$, should describe the behaviour of the infinite chain with negligible uncertainty (dashed curves on Fig. 3).

Based on this proposition, and applying the same strategy reported in the literature, it is possible to generate an expression of χ_r , which depends on T_r and a , by fitting all the infinite theoretical susceptibility curves, eqn. (2) where $\chi_r = 3\chi_m|J_{AF}|$

$$\chi_r = \frac{T_r^2 + AT_r + B}{T_r^3 + CT_r^2 + DT_r + E} \quad (2)$$

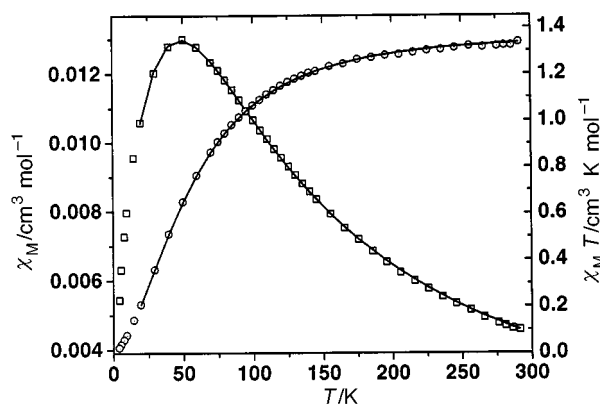
$2Ng^2\mu_B^2$ and the reduced temperature T_r is given by $kT/|J_{AF}|$; A – E are the fitting coefficients, which depend on a , and such dependence can be described by the use of a polynomial expression (3) to the fourth degree in a . (In eqn. (3) x_0 etc. corre-

$$X = x_0 + x_1a + x_2a^2 + x_3a^3 + x_4a^4 \quad (3)$$

spond to a_0 – e_0 from Table 3.) Two sets of coefficients have been proposed according to the value of a , Table 3. The reduced susceptibility expression can be converted into magnetic susceptibility in the habitual form to give eqn. (4) where

$$\chi_m = \frac{2Ng^2\mu_B^2}{3kT} \frac{1 + Ax + Bx^2}{1 + Cx + Dx^2 + Ex^3} \quad (4)$$

$x = |J_{AF}|/kT$. The expression with the two sets of A – E coefficients is valid for $kT/|J_{AF}| \geq 0.22$, as shown in Fig. 4, which gives the calculated magnetic susceptibility of the infinite chain with good approximation ($R = 1.5 \times 10^{-5}$), even for high values of a .

**Fig. 5** Molar magnetic susceptibility and the $\chi_m T$ product vs. temperature for $[\{\text{Ni}_2(\text{Medien})_2(\mu_{1,1}\text{-N}_3)_2(\mu_{1,3}\text{-N}_3)\}_n][\text{ClO}_4]_n$. Solid lines show the best fit obtained by applying eqn. (3) (see text).

Magnetic properties and magneto-structural correlations

The $\chi_m T$ product and the molar magnetic susceptibilities vs. T in the 300–4 K range for $[\{\text{Ni}_2(\text{Medien})_2(\mu_{1,1}\text{-N}_3)_2(\mu_{1,3}\text{-N}_3)\}_n][\text{ClO}_4]_n$ 1 are plotted in Fig. 5, which shows an overall antiferromagnetic behaviour: $\chi_m T$ decreases on cooling from $1.34 \text{ cm}^3 \text{ K mol}^{-1}$ at 292 K and tends to zero at low temperature, showing a maximum of susceptibility at 50 K ($1.30 \times 10^{-2} \text{ cm}^3 \text{ mol}^{-1}$). The fit of the experimental data with the above equation gave the best parameters $J_{AF} = -34.7$, $J_{FM} = +38.2 \text{ cm}^{-1}$, $a = 1.10$, $g = 2.34$ and $R = 4.2 \times 10^{-5}$. The strong ferromagnetic contribution of J_{FM} to the global magnetic behaviour is reflected in the very slow decrease of $\chi_m T$ in the high temperature range 300–150 K. Despite the mathematic quality of the fit, the sign and magnitude of the calculated coupling constants should be chemically reasonable in comparison with those for ferro- or anti-ferromagnetic models or well established experimental data. The best known interaction is the antiferromagnetic superexchange through the single end-to-end azido bridge, which has been modelled as a function of the two Ni–N–N bond angles and the τ torsion angle defined as the angle between the mean planes Ni–N–N–N and N–N–N–Ni'.⁸ Analysis of published data indicates that the best fit J_{AF} value of -34.7 cm^{-1} , the Ni–N–N bond angles $138.1/125.7^\circ$ and the τ torsion angle of 162.8° are consistent with the J value expected for a compound with a medium τ angle. A useful comparison is offered by the $[\{\text{Ni}(\text{cyclam})(\mu_{1,3}\text{-N}_3)\}_n][\text{ClO}_4]_n$ homogeneous chain, which shows practically the same structural and magnetic parameters: Ni–N–N bond angles $140.7/128.2^\circ$, $\tau = 166.9^\circ$ and $J = -39.2 \text{ cm}^{-1}$.²²

Less systematized data are available for the double end-on kind of bridge, but the best fit J_{FM} lies in the typical range of J values for this kind of compound, for which J close to $+40$

Table 4 Bond angles and J superexchange parameters for the ferromagnetic [NiNi] pairs with a double end-on azido bridge and aliphatic blocking ligands {en = ethane-1,2-diamine, Medt = bis(3-aminopropyl)methylamine, 232-tet = N,N' -bis(2-aminoethyl)propane-1,3-diamine, $\text{Me}_3[12]\text{N}_3 = 2,4,4$ -trimethyl-1,5,9-triazacyclododec-1-ene}

Compound	Ni–N–Ni/ $^\circ$	J/cm^{-1}	Ref.
$[\text{Ni}_2(\text{en})_4(\mu\text{-N}_3)_2][\text{ClO}_4]_2$	104.3	43.4	14
$[\text{Ni}_2(\text{Medpt})_2(\text{N}_3)_2(\mu\text{-N}_3)_2][\text{ClO}_4]_2$	104.0	46.7	15
$[\text{Ni}_2(232\text{-tet})_2(\mu\text{-N}_3)_2][\text{ClO}_4]_2$	104.9	33.8	16
$[\text{Ni}_2(232\text{-tet})_2(\mu\text{-N}_3)_2][\text{PF}_6]_2$	104.6	34.3	17
$[\text{Ni}_2(\text{Me}_3[12]\text{N}_3)_2(\mu\text{-N}_3)_2]$	103.8	43.9	16
$\text{Ni}_2(\text{Medien})_2(\mu\text{-N}_3)_2$ fragment	100.8 98.9	38.2	This work

cm^{-1} is a normal value. The slightly lower Ni–N–Ni' bond angle is not expected to be relevant in the light of the data summarized in Table 4, which show a similar J value for all the reported compounds with Ni–N–Ni' bond angles between 100.8 and 104.9°. This result is also consistent with the calculations performed by Ruiz *et al.*²³ by means of density functional methods, which predict a maximum ferromagnetic coupling around the bond angle Ni–N–Ni' = 104° and a narrow range of this bond parameter ($\pm 8^\circ$ approximately), in which minor J differences should be expected.

Concluding remarks

A new structurally and magnetically alternating 1-D nickel(II)-azido system has been fully characterized and its superexchange coupling constants have been determined as $J_{\text{AF}} = -34.7$ and $J_{\text{FM}} = +38.2 \text{ cm}^{-1}$, $a = 1.1$. These results have been calculated by extrapolation of the expected properties for rings of increasing size up to $N = 5$ pairs of $S = 1$. The best fit parameters are consistent with the values that may be expected on the basis of the structural bond parameters in the bridging region, which confirm the validity of the sign and magnitude of the J values found. One of the most interesting aspects of the present work is the application for the first time of the theoretical expressions to a system in which the two superexchange interactions are strong, the results lying in the optimum range of a , which permits an accurate determination of the J values.

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