Crystal Structure and Magnetic Properties of [Ni(terpy)(N$_3$)$_2$]$_2$·2H$_2$O, a Nickel(II) Dinuclear Complex with Ferromagnetic Interaction

M. ISABEL ARRIORTUA*

Departamento de Mineralogía-Petrología, Facultad de Ciencias, Universidad del País Vasco, Apartado 644, 48080 Bilbao (Spain)

A. ROBERTO CORTES, LUIS LEZAM, TEOFILO ROJO

Departamento de Química Inorgánica, Facultad de Ciencias, Universidad del País Vasco, Apartado 644, 48080 Bilbao (Spain)

XABIER SOLANS and MERCEDES FONT-BARDIA

Departamento de Cristalografía-Mineralogía, Universidad de Barcelona, Barcelona (Spain)

Abstract

The crystal structure of dimeric [Ni(C$_{15}$H$_{11}$N$_3$)-(N$_3$)$_2$]$_2$·2H$_2$O has been determined at room temperature. Crystal data are as follows: $P2_1/a$, $Z = 2$, $a = 15.628(3)$, $b = 9.798(2)$, $c = 10.322(2)$ Å, $\beta = 92.32(2)°$, $R = 0.049$ for 1137 reflections. The complex consists of isolated centrosymmetric [Ni-(terpy)(N$_3$)$_2$]$_2$·2H$_2$O dimeric units, where the two metallic centers are linked through the N-end of two azide bridging groups. The Ni(II) atom displays a distorted octahedral coordination, being linked to three N atoms from the terpyridine ligand and three N atoms of three azide ligands. Magnetic susceptibility measurements have shown the existence of ferromagnetic exchange between nickel centers ($J = +20.1$ cm^{-1}, $D = -12.5$ cm^{-1}). The magnetic behavior of this and others related complexes is discussed and some magneto-structural trends are given.

Introduction

The structural and magnetic properties of octahedrally coordinated nickel dimers with two (pseudo)halide bridging ligands have been the subject of numerous papers [1–8]. Ferromagnetic interactions are prevailing in every such dimer with halide or end-on pseudohalide bridges [1, 7, 8]. Both, ferromagnetic and antiferromagnetic behavior have been found in Ni(II) dimers with end-to-end pseudohalide bridges [2–6]. For octahedral nickel dimers bridged by more complex polynuclear units, such as oxalate, squarate, biimidazolate or chloranilate groups, the dominant interaction is invariably antiferromagnetic [9–11].

The larger number of structural parameters which affect the superexchange mechanism in these sorts of dimers has precluded the clear identification of the relevant magnetic-structural correlations. The general understanding is that ferromagnetic superexchange will arise from pathways which have an orthogonal interaction. In the orbital model of the exchange interaction proposed by Kahn [12] the J exchange integral is considered as the sum of two antagonistic contributions J_{AF} and J_F favoring the antiferromagnetic and the ferromagnetic interactions, respectively. Theoretical calculations have been performed on the superexchange in the Ni$_2$X$_2$ unit (X = Cl, Br) by Barraclough and Brookes [13]. They concluded that the exchange was ferromagnetic for a 90° bridging angle and was quite sensitive to variations of bridging angle and distortion around the nickel ion which would mix the d orbitals. The nature of the bridging atom is also important: the contribution made by the s orbitals may be negligible for an oxide or fluoride atom but certainly it must be considered for chlorides and bromides. On the other hand, for dimers with end-to-end pseudohalide bridges, Bencini and Gatteschi [14] have shown that the antiferromagnetic contributions to the exchange integral increase as the metal ion is moved out of the plane formed by the pseudohalide groups. Continued study of these systems is in order so that the relevant magneto-structural relationships can be delineated.

In this paper, the crystal structure of a bis(μ-azido) nickel(II) complex of formula [Ni(terpy)(N$_3$)$_2$]$_2$·2H$_2$O (terpy = 2,2′:6′2″-terpyridine), where the azide ligands bridge in an end-on fashion, is described. We shall also compare its magnetic properties with those observed in other octahedrally coordinated nickel(II) dimers in order to determine the influence of some structural parameters in the strength of the exchange coupling.

---

*Author to whom correspondence should be addressed.

Experimental

Synthesis

The [Ni(terpy)(N$_3$)$_2$]$_2$·2H$_2$O compound was synthesized by adding a methanolic solution containing 0.15 g (0.38 mmol) of the [Ni(terpy)Cl(H$_2$O)$_2$]Cl·H$_2$O complex, previously prepared [15], to a warm ethanolic solution of NaN$_3$ (2.3 mmol). The resulting green precipitate was separated by vacuum filtration, washed with ethanol and dried over P$_2$O$_5$ for 48 h. Green prismatic crystals suitable for X-ray analysis were obtained by recrystallization from methanol/water solutions. *Anal.* Calc. for C$_{15}$H$_{13}$N$_9$ONi: C, 45.7; H, 3.3; N, 32.0; Ni, 14.9. Found: C, 45.7; H, 3.2; N, 32.4; Ni, 14.6%.

X-ray and Structure Determination

Preliminary cell dimensions and space group symmetry were obtained from Weissenberg and oscillation photographs. A prismatic crystal (0.1 × 0.1 × 0.2 mm) was selected and mounted on a Phillips PW 1100 four circle diffractometer. Unit cell parameters $4 \leqslant \theta \leqslant 12°$ were determined from 25 reflections and refined by least-squares method. Intensities were collected with graphite monochromatized Mo Kα radiation, using the $\omega/2\theta$ scan technique, with scan width 1° and scan speed 0.03° s^{-1}.

Crystallographic data for [Ni(terpy)(N$_3$)$_2$]$_2$·2H$_2$O are reported in Table 1. A total of 1435 reflections were measured in the range $2 \leqslant \theta \leqslant 25°$, of which 1137 were assumed as observed applying the condition $I \geqslant 2.5\sigma(I)$. Three reflections were measured every two hours as orientation and intensity control, no significant intensity decay was observed. Lorentz polarization but no absorption corrections were applied. The structure was solved by direct methods, using the MULTAN 84 [16] system, and refined by full-matrix least-squares, using the SHELX 76 [17] program. The function minimized was $\Sigma w[|F_o| - |F_c|]$, where $w = [\sigma^2(F_o) + 0.00015(F_o)]^{-1}$. Positions of the hydrogen atoms were refined with overall

TABLE 1. Crystal data for [Ni(terpy)(N$_3$)$_2$]$_2$·2H$_2$O

Formula	Ni$_2$C$_{30}$H$_{26}$N$_{18}$O$_2$
System	monoclinic
M_r (g mol^{-1})	394.04
Space group	$P2_1/a$
Z	2
D_{calc} (g cm^{-3})	1.655
a (Å)	15.628(3)
b (Å)	9.798(2)
c (Å)	10.332(2)
β (°)	92.32(2)
V (Å^3)	1580.8(5)
$F(000)$	808
λ(Mo Kα) (Å)	0.71069
μ(Mo Kα) (cm^{-1})	12.56

TABLE 2. Final atomic coordinates ($\times 10^4$, $\times 10^5$ for Ni) and equivalent isotropic temperature factors (Å^2) with e.s.d.s in parentheses of the [Ni(terpy)(N$_3$)$_2$]$_2$·2H$_2$O complex

Atom	x/a	y/b	z/c	B_{eq} [a]
Ni	50148(7)	41637(13)	36280(12)	2.20(6)
N(1)	4539(5)	5737(8)	2452(7)	2.11(37)
N(2)	5901(5)	4338(9)	2340(7)	2.31(40)
N(3)	5853(5)	2578(8)	4197(8)	2.17(40)
C(1)	3775(7)	6385(11)	2558(11)	3.09(60)
C(2)	3522(7)	7421(12)	1744(12)	3.56(63)
C(3)	4045(7)	7825(11)	787(11)	3.56(61)
C(4)	4824(7)	7156(11)	673(10)	3.12(59)
C(5)	5043(7)	6117(8)	1505(10)	2.21(47)
C(6)	5841(6)	5302(11)	1442(9)	2.35(51)
C(7)	6483(8)	5515(11)	591(10)	3.14(58)
C(8)	7199(7)	4685(12)	694(11)	3.38(61)
C(9)	7263(6)	3709(11)	1644(11)	3.00(56)
C(10)	6598(6)	3525(10)	2459(9)	2.11(48)
C(11)	6552(6)	2517(10)	3478(10)	2.66(53)
C(12)	7171(6)	1523(11)	3724(11)	2.96(57)
C(13)	7035(7)	543(10)	4641(11)	3.54(61)
C(14)	6308(7)	582(11)	5338(11)	3.38(59)
C(15)	5743(8)	1617(14)	5062(10)	2.85(64)
N(4)	4251(5)	4362(9)	5169(8)	2.70(47)
N(41)	3879(6)	3436(10)	5705(8)	2.72(49)
N(42)	3495(6)	2619(10)	6245(10)	4.67(58)
N(5)	4215(5)	2806(10)	2631(9)	3.41(50)
N(51)	4506(6)	1734(11)	2300(8)	3.14(52)
N(52)	4763(7)	699(11)	1928(11)	5.80(66)
OW(1)	3620(6)	722(11)	-1424(10)	6.24(57)

[a] $B_{eq} = 8\pi^2[(U_{11} + U_{22} + U_{33})/3]$.

isotropic thermal parameters; the remaining atoms were refined anisotropically. The final R was 0.049 ($R_w = 0.043$) for all observed reflections. Maximum shift/e.s.d. = -0.3 in U_{12} of N(3). Maximum and minimum peaks in the final difference synthesis were 0.4 e Å^{-3} to 1.63 Å for C(15) and -0.3 e Å^{-3}, respectively.

Final atomic coordinates for non-H atoms and the equivalent isotropic temperature factors are given in Table 2.

Scattering factors were taken from the International Tables of X-ray Crystallography [18]. All calculations were carried out on a MicroVAX VT220 computer at the computer centre of the Basque University. The geometric calculations were performed with XANADU [19] and molecular illustrations were drawn with PLUTO [20]. See also 'Supplementary Material'.

Physical Measurements

Infrared spectra were obtained with KBr pellets in the 4000–250 cm^{-1} region, using a Perkin-Elmer spectrophotometer. Magnetic susceptibility measurements were performed on powdered samples in the temperature range 2–100 K using a SQUID SHE

magnetometer. Experimental susceptibilities were corrected for diamagnetic contributions and for the temperature independent paramagnetism estimated to be 100×10^{-6} cm^3 mol^{-1} per nickel(II) ion.

Results and Discussion

Description of the Structure

The structure of the title compound consists of isolated centrosymmetric [Ni(terpy)(N$_3$)$_2$]$_2$·2H$_2$O dimeric units, where the two metallic centers are linked through the N-end of two azide bridging groups (see Fig. 1). The main interatomic distances and angles of this compound are listed in Table 3.

Each Ni(II) ion has a distorted octahedral coordination. The equatorial positions are occupied by the three nitrogen atoms from the terpy ligand (Ni–N(1), N(2), N(3); 2.081(8), 1.966(8), 2.101(8) Å) and a nitrogen atom from a bridging azide group (Ni–N(4); 2.038(6) Å). Two nitrogen atoms, one from the terminal azide ligand (Ni–N(5); 2.071(9) Å) and the other from the azide bridging group, belonging to the other half of the dimer and which is Ni–N(4)^i 2.198(8) Å (i = $\frac{1}{2} - x$, $\frac{1}{2} - y$, $\frac{1}{2} - z$) distant from the Ni(II) ion, complete the coordination sphere. The four equatorial atoms are coplanar in the range -0.12 to 0.09 Å. The nickel ion is displaced 0.12 Å from the equatorial least-squares plane. The cis N–Ni–N angles range from 77.6(3) to 103.3(3)° while the largest deviation from linearity in the trans angles is observed for N(1)–Ni–N(3) (156.2(3)°).

The dimer sits on an inversion center, hence the Ni$_2$N$_2$ bridging unit is planar. The bridging Ni–N distances are significantly different (Δd = 0.160 Å) from a crystallographic viewpoint. The interior N(4)–Ni–N(4)^i angle of the bridging arrangement is 78.7(3)° while the Ni–N(4)–Ni bridging angle is 101.3(3)°. The Ni–Ni^i distance is 3.276(1) Å, which is significantly larger than the sum of the two nickel radii (1.56 for Ni(II)) and precludes any direct Ni–Ni bonding.

Both, bridging and terminal azide groups are quasi-linear, with N–N–N angles of 175(1) and 176(1)°, respectively.

The interatomic bond distances and angles of the terpyridine ligand are similar to those found in other related compounds [7, 21–24]. The terpy ligand is planar within ±0.1 Å. Because of the rigidity of the terpyridine rings the angles N(2)–Ni–N(1) and N(2)–Ni–N(3) deviate from 90° by about 12° and the Ni–N(2) bond length is smaller than Ni–N(1), N(3) by ≈0.1 Å.

The water molecules are connected to two azide groups, belonging to two different dimeric units, by hydrogen bonds (OW(1)–H(W1)······N(42)^{ii} and
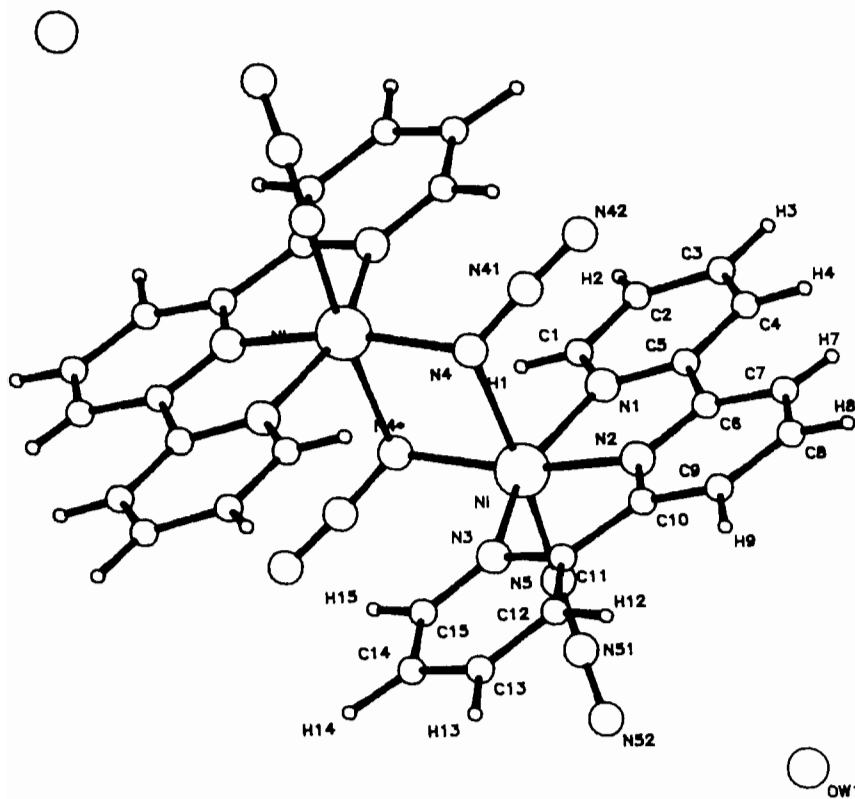

Fig. 1. Perspective view of the [Ni(terpy)(N$_3$)$_2$]$_2$·2H$_2$O dimeric complex with the numbering system.

TABLE 3. Selected bond distances (Å) and angles (°) in the [Ni(terpy)(N₃)₂]₂·2H₂O complex

Distance/angle		Distance/angle	
Nickel coordination sphere			
Ni−N(1)	2.081(8)	Ni−N(2)	1.966(8)
Ni−N(3)	2.101(8)	Ni−N(4)	2.038(8)
Ni−N(5)	2.071(9)	Ni−Niⁱ	3.276(1)
Ni−N(4)ⁱ	2.198(8)		
N(1)−Ni−N(2)	77.6(3)	N(1)−Ni−N(4)	100.3(3)
N(2)−Ni−N(4)	166.3(3)	N(3)−Ni−N(4)	103.3(3)
N(3)−Ni−N(2)	78.8(3)	N(2)−Ni−N(5)	98.4(3)
N(1)−Ni−N(3)	156.2(3)	N(4)−Ni−N(5)	95.1(3)
N(1)−Ni−N(5)	89.5(3)	N(3)−Ni−N(5)	91.2(3)
N(4)ⁱ−Ni−N(1)	90.5(3)	N(4)ⁱ−Ni−N(2)	87.7(3)
N(4)ⁱ−Ni−N(3)	91.3(3)	N(4)ⁱ−Ni−N(4)	78.7(3)
Ni−N(4)−Niⁱ	101.3(3)		
Average values in the terpyridine			
C−N	1.341(22)	C−C(intracycle)	1.375(18)
C−C(intercycle)	1.466(26)	C−H	0.97(12)
C−C−C(intracycle)	121(3)	C−C−C(intercycle)	125(2)
C−C−N(intracycle)	122(2)	C−C−N(intercycle)	114(1)
C−N−C	119(2)		
Azide			
N(4)−N(41)	1.222(13)	N(41)−N(42)	1.157(14)
N(5)−N(51)	1.200(14)	N(51)−N(52)	1.162(15)
Ni−N(4)−N(41)	126.0(7)	N(4)−N(41)−N(42)	175.8(11)
Ni−N(5)−N(51)	118.4(7)	N(5)−N(51)−N(52)	176.8(11)
Niⁱ−N(4)−N(41)	118.6(6)		

Symmetry code: i = $\frac{1}{2} - x, \frac{1}{2} - y, \frac{1}{2} - z$.

OW(1)−H(W2)·····N(52)ⁱⁱⁱ). The d_{ON} distances are 3.04(1) and 2.94(1) Å and the d_{HN} distances 2.19(9) and 2.22(9) Å, respectively (symmetry code: ii = 1 − x, 1 − y, −z and iii = 1 − x, −y, −z).

Distortion from an octahedron to a trigonal prism (Δ) for the title complex has been examined using the Muetterties and Guggenberger [25] description by comparison of the observed dihedral angles (δ) formed by the normal to adjacent polytopal faces with those of the ideal octahedron (Δ = 0) (see Table 4). The value Δ = 0.04 indicates that the [NiN₆] polyhedron is close to octahedral geometry.

Infrared Spectroscopy

The interest of the IR spectra of the title compound lies mainly in the bands due to the azide groups. The coordination of azides to transition metals can easily be detected by an intense infrared absorption band which occurs about 2000 cm⁻¹. This band is associated with the azide antisymmetric stretch, $\nu_{as}(N_3)$, and its energy depends, to a first approximation, only on the configuration of the bonded azide, that is, on the degree of its symmetry. The [Ni(terpy)(N₃)₂]₂·2H₂O complex presents two intense absorption bands at 2050 and 2020 cm⁻¹. Considering the difference between the two N−N distances (Δd) in each azide group, the signal at 2050 cm⁻¹ can be ascribed to the azide bridging group (Δd = 0.065 Å) and the other to the terminal azide (Δd = 0.038 Å). For the azide symmetric stretch, $\nu_s(N_3)$, a similar result could be expected, however only a weak signal at about 1300 cm⁻¹ was observed because this region is obscured by the terpyridine characteristic absorption bands. Two signals at 600 and 615 cm⁻¹, corresponding to the azide bending vibrations, δ, can also be observed.

A broad signal centered at 3500 cm⁻¹ has been observed; apparently it corresponds to the stretching vibration for the water molecule but it could be associated with the N−H stretching vibrations expected considering the existence of hydrogen bonds between the water molecules and the azide groups.

Magnetic Properties

The magnetic behavior of the [Ni(terpy)(N₃)₂]₂·2H₂O compound is shown in Fig. 2, in the form of the variation of $\chi_m T$ versus the temperature T, χ_m

TABLE 4. Distortion Δ of the $[NiN_6]$ polyhedron in the $[Ni(terpy)(N_3)_2]_2 \cdot 2H_2O$ complex

Dihedral angle	Octahedron (°)	NiN$_6$ (°)		Trigonal prism
$\delta b_{1,1}$	70.5	59.8	$[N(5)-N(3)-N(4)-N(4)^i]$	0
$\delta b_{1,2}$	70.5	60.9	$[N(1)-N(4)^i-N(2)-N(3)]$	0
$\delta b_{1,3}$	70.5	79.0	$[N(2)-N(1)-N(5)-N(4)]$	0
$\delta b_{2,1}$	70.5	75.6	$[N(5)-N(1)-N(2)-N(4)^i]$	120
$\delta b_{2,2}$	70.5	70.0	$[N(4)-N(4)^i-N(3)-N(2)]$	120
$\delta b_{2,3}$	70.5	80.0	$[N(3)-N(5)-N(4)-N(1)]$	120
δ_1	70.5	87.1	$[N(1)-N(4)^i-N(4)-N(3)]$	90
δ_2	70.5	68.0	$[N(4)-N(1)-N(4)^i-N(2)]$	90
δ_3	70.5	59.9	$[N(4)^i-N(1)-N(4)-N(5)]$	90
δ_4	70.5	76.4	$[N(5)-N(3)-N(2)-N(4)^i]$	90
δ_5	70.5	51.8	$[N(3)-N(2)-N(5)-N(1)]$	90
δ_6	70.5	80.4	$[N(2)-N(5)-N(3)-N(4)]$	90
Δ [a]	0	0.04		1

[a] Δ is calculated using the following formula: $\Delta = \sum \dfrac{[\delta b_1 - \delta b_{1oct}]}{846} \div \sum \dfrac{[\delta b_2 - \delta b_{2oct}]}{594} \div \sum \dfrac{[\delta_i - \delta_{oct}]}{234}$
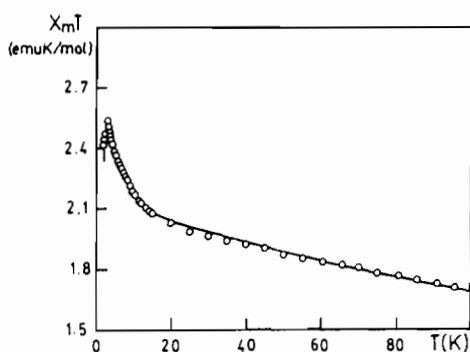

Fig. 2. Magnetic behavior of the $[Ni(terpy)(N_3)_2]_2 \cdot 2H_2O$ complex. The full line represents the calculated curve using the Ginsberg expression for a nickel(II) dimer.

being the molar magnetic susceptibility for the dinuclear unit. The main features of this curve are similar to those observed for several Ni(II) dimers [1, 2, 6]: the effective magnetic moment increases with decreasing temperature (down to 3.1 K) and decreases rapidly at lower temperatures. This behavior indicates the existence of an intradimeric ferromagnetic exchange associated to a large Ni(II) single-ion zero-field splitting. The experimental data were least-squares fitted to the analytic expression given by Ginsberg et al. [2] for a magnetically isotropic Ni(II) dimer, and the following parameters were obtained:

$J = +20.1$ cm^{-1}; $D = -12.5$ cm^{-1};

$Z'J' = 0.38$ cm^{-1}; $g = 2.26$

the agreement factor, defined as $Se = [\Phi/(n - K)]^{1/2}$, where n is the number of data points, K is the number of parameters, and $\Phi = \Sigma[\chi_m T_{obs} -$ $\chi_m T_{calc}]^2$ is the sum of the squares of the residuals, is equal to 5×10^{-3} [8].

In order to discuss the relationship between the strength of the exchange constant and the structural parameters in octahedrally coordinated nickel dimers with end-on bridging modes, we have compiled, in Table 5, the structural and magnetic properties of several of them. The first two entities correspond to the title compound and another Ni(II) dimer with terpyridine, which we have studied both magnetically and crystallographically [7]. The rest are bibridged nickel halide dimers which have received considerable study [1, 2, 26–29].

The $[Ni(terpy)(NCO)(H_2O)]_2 \cdot (PF_6)_2$ compound exhibits a magnetic behavior analogous to that of the title compound, with the exchange integral $J = +4.6$ cm^{-1} and $D = -12.2$ cm^{-1} [7]. The NCO groups play the same role as the azide groups in the present complex. Both complexes exhibit approximately the same distortion from an octahedron to a trigonal prism, 4 and 5% for the N_3 and NCO complexes, respectively, and they have practically the same value for the Ni(II) zero-field splitting, as should be expected. Therefore, the distortion around the nickel atom is not the cause of the different strength for the exchange integral and it must be ascribed to the differences between the Ni–N–Ni angles. Considering these angles and the corresponding J values shown in Table 5, it could be seen that the orthogonality in a Ni–X–Ni bridge occurs for a value of the bridging angle larger than 101.3°. However, if one observes the J values calculated for the halide complexes, the orthogonality of the magnetic orbitals appears to be realized for a value of the Ni–X–Ni bridging angle close to 90°. This apparent contradiction can be easily explained considering the different contributions, with opposite signs, to the exchange integral,

TABLE 5. Structural and magnetic properties of octahedrally coordinated dihalide and end-on pseudohalide bridged nickel dimers

Compound[a]	Ni–X–Ni (°)	Ni–Ni (Å)	J (cm^{-1})	D (cm^{-1})	Reference
$[Ni(terpy)(N_3)_2]_2 \cdot 2H_2O$	101.3	3.27	+20.1	−12.5	this work
$[Ni(terpy)(NCO)(H_2O)]_2(PF_6)_2$	97.7	3.193	+4.6	−12.2	7
$[Ni_2(en)_4Cl_2]Cl_2$	96.6		+6.6	−3.7	26, 28
$[Ni_2(en)_4Br_2]Br_2$			+7.6		2, 27
$[Ni_2(en)_4Cl_2](ClO_4)$	95.4		+8.9	−4.2	26, 28
$[Ni_2(H_2O)_2Cl_8](PDA)_2$	95.05	3.606	+8.1	−3.4	1
$[Ni_2(EG)_4Br_2]Br_2$			+8.0		29
$[Ni_2(EG)_4Cl_2]Cl_2$	93.03	3.458	+9.0		29

[a]Abbreviations: en = ethylenediamine, PDA = 1,3-propylenediammonium, EG = ethylene glycol.

especially the antiferromagnetic contributions. Since the Ni–Ni distance is so great, it is clear that it does not play a significant role in determining the net magnetic interaction. In a bridging network as
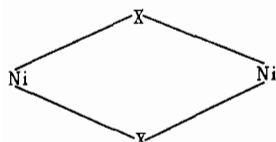
the main pathway for an antiferromagnetic coupling takes place via the s orbitals of the bridging group. This contribution is obviously less important in the case of the 2s orbitals for the azide and cyanate groups than for the 3s chloride orbitals, and it causes the different value in the bridging angle for the accidental orthogonality. This problem can also be treated in terms of the electronegativity of the X atom; when X is made less electronegative the orthogonality is realized for larger values of the Ni–X–Ni bridging angles [30].

A similar behavior has been pointed out by Kahn et al. [30] for copper(II) dimers. Extended Hückel-type calculations have shown that orthogonality is expected for Cu–X–Cu = 103° when X = N and 90° when X = Cl. At this stage of the investigation, it appears that a quantitative study using Extended Hückel calculations would be interesting for octahedrally coordinated Ni(II) dimers with this sort of bridge.

Supplementary Material

Further details of geometric calculations and molecular illustrations as well as thermal parameters, bond lengths and angles, mean average planes and structure factors are available from the authors on request.

Acknowledgements

References

1 C. P. Landee and R. D. Willet, *Inorg. Chem.*, 20 (1981) 2521.
2 A. P. Ginsberg, R. L. Martin, R. W. Brookes and R. C. Sherwood, *Inorg. Chem.*, 11 (1972) 2884.
3 D. M. Duggan and D. N. Hendrickson, *Inorg. Chem.*, 12 (1973) 2422.
4 D. M. Duggan and D. N. Hendrickson, *Inorg. Chem.*, 13 (1974) 2929.
5 D. M. Duggan and D. N. Hendrickson, *Inorg. Chem.*, 13 (1974) 2056.
6 T. Rojo, R. Cortés, L. Lezama, J. L. Mesa and G. Villeneuve, *Inorg. Chim. Acta*, 162 (1989) 11.
7 M. I. Arriortua, R. Cortés, J. L. Mesa, L. Lezama, T. Rojo and G. Villeneuve, *Transition Met. Chem.*, 13 (1989) 371.
8 T. Rojo, L. Lezama, R. Cortés, J. L. Mesa, M. I. Arriortua and G. Villeneuve, *J. Magn. Magn. Mater.*, 83 (1990) 519.
9 D. M. Duggan, E. K. Barefield and D. N. Hendrickson, *Inorg. Chem.*, 12 (1973) 985.
10 M. S. Haddad and D. N. Hendrickson, *Inorg. Chem.*, 17 (1978) 2622.
11 C. G. Pierpont, L. C. Francesconi and D. N. Hendrickson, *Inorg. Chem.*, 16 (1977) 2367.
12 O. Kahn, *Inorg. Chim. Acta*, 62 (1982) 3.
13 C. G. Barraclough and R. W. Brookes, *J. Chem. Soc., Faraday Trans.*, 2 (1974) 1364.
14 A. Bencini and D. Gatteschi, *Inorg. Chim. Acta*, 31 (1978) 11.
15 R. Cortés, M. I. Arriortua, T. Rojo, X. Soláns, C. Miravitlles and D. Beltrán, *Acta Crystallogr., Sect. C*, 41 (1985) 1733.
16 P. Main, G. Germain and M. M. Woolfson, *MULTAN 84*, a system of computer programs for the automatic solution of crystal structures from X-ray diffraction data, Universities of York, U.K. and Louvain, Belgium, 1984.
17 G. M. Sheldrick, *SHELX 76*, program for crystal structure determination, University of Cambridge, U.K., 1976.
18 *International Tables for X-ray Crystallography*, Vol. 4, Kynoch Press, Birmingham, 1974, pp. 72-99.

19 P. Roberts and G. M. Sheldrick, *XANADU,* program for torsion angle, mean plane and libration correction calculations, University of Cambridge, U.K., 1975.
20 W. D. S. Motherwell and W. Clegg, *PLUTO78,* program for plotting molecular and crystal structures, University of Cambridge, U.K., 1978.
21 T. Rojo, M. I. Arriortua, J. Ruiz, J. Darriet, G. Villeneuve and D. Beltrán, *J. Chem. Soc., Dalton Trans.,* (1987) 285.
22 T. Rojo, M. I. Arriortua, J. L. Mesa, R. Cortés, G. Villeneuve and D. Beltrán, *Inorg. Chim. Acta, 134* (1987) 59.
23 D. L. Kepert, E. S. Kucharski and A. H. White, *J. Chem. Soc., Dalton Trans.,* (1980) 1932.
24 M. I. Arriortua, J. L. Mesa, T. Rojo, T. Debaerdemaeker, D. Beltrán, H. Stratemeier and D. Reinen, *Inorg. Chem., 27* (1988) 2976.
25 E. L. Muetterties and J. L. Guggenberger, *J. Am. Chem. Soc., 96* (1974) 1748.
26 Y. Journeaux and O. Kahn, *J. Chem. Soc., Dalton Trans.,* (1979) 1575.
27 A. S. Antsyshkina and M. A. Porai-Koshits, *Dokl. Chem., (Engl. Transl.), 143* (1962) 105.
28 G. A. Bottomley, L. G. Glossop, C. L. Raston, A. H. White and A. C. Willis, *Aust. J. Chem., 31* (1978) 285.
29 D. Knetsch and W. L. Groeneveld, *Inorg. Nucl. Chem. Lett., 12* (1976) 27.
30 O. Kahn, S. Sikorav, J. Gouteron, S. Jeannin and Y. Jeannin, *Inorg. Chem., 22* (1983) 2877.