Spectroscopic and Magnetic Properties of Two Ferromagnetically Coupled Nickel(II) Dimers $[\{Ni(terpy)(NCX)_2\}_2]$ (terpy = 2,2′:6′,2″-terpyridine, X = S or Se). Crystal Structure of the Thiocyanate†

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Two new binuclear nickel(II) complexes $[\{Ni(terpy)(NCX)_2\}_2]$ (X = S or Se) have been prepared from 2,2′:6′,2″-terpyridine (terpy) ligand. The crystal structure of $[\{Ni(terpy)(NCS)_2\}_2]$ **1** was solved by direct methods and refined by least-squares analysis to a discrepancy factor of 0.050. The crystals are triclinic, space group $P\bar{1}$, with lattice constants a = 8.822(2), b = 9.569(1), c = 10.906(1) Å, and α = 74.35(1), β = 85.19(2), γ = 78.75(2)°. The dimer, whose halves are related by a crystallographic inversion centre, consists of two nickel atoms co-ordinated to two terpy ligands, two terminal NCS ligands and two end-to-end NCS bridging ligands. Each Ni^{II} has a distorted-octahedral environment. The Ni···Ni distance is 5.633(3) Å and the bridging angles are 100.0(8) and 159(2)°. The complex $[\{Ni(terpy)(NCSe)_2\}_2]$ **2** was found to be isomorphous [a = 8.867(3), b = 9.592(4), c = 11.047(3) Å, α = 73.64(3), β = 83.44(3) and γ = 76.67(2)°]. Magnetic susceptibility data, measured from 2 to 300 K, were fitted to the Ginsberg equation, giving the parameters J = +4.9 cm^{-1}, D = −4.3 cm^{-1} and $z'J'$ = +0.02 cm^{-1} (NCS) and J = +10.1 cm^{-1}, D = −10.0 cm^{-1} and $z'J'$ = +0.01 cm^{-1} (NCSe). The magnetic behaviour of these and related complexes is discussed and some magnetostructural trends are given.

Exchange interactions that are propagated by discrete polyatomic bridging moieties (NCO, NCS, NCSe, N_3, *etc.*) between paramagnetic centres have been the subject of several papers.[1–3] In the case of the nickel(II) ion, the structural and magnetic properties of octahedrally co-ordinated dimers with two pseudohalide bridging ligands have been studied.[4–7]

A great number of structural parameters affect the superexchange mechanism in these sorts of dimers,[4–6] the ferromagnetic exchange arising from pathways with an orthogonal interaction. Kahn[8] has suggested that the exchange integral J is the sum of two antagonistic contributions favouring the antiferromagnetic and ferromagnetic interactions. Bencini and Gatteschi,[9] for end-to-end pseudohalide-bridged dimers, have shown that the antiferromagnetic contributions 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 magnetostructural relationships can be delineated.

In previous papers we have reported the magnetic properties of several octahedrally co-ordinated nickel(II) dimers with 2,2′:6′,2″-terpyridine (terpy) and pseudohalide ligands, which exhibit end-on bridging modes. The compounds show ferromagnetic exchange constants the magnitude of which seems to be correlated with the value of the bridging angle.[10,11]

In this work, we have determined the crystal structure of the complex $[\{Ni(terpy)(NCS)_2\}_2]$, where the thiocyanate ligands exhibit an end-to-end bridging mode. We also present the spectroscopic and magnetic properties of the isomorphous compound $[\{Ni(terpy)(NCSe)_2\}_2]$ and compare the structural and magnetic properties of several octahedrally co-ordinated nickel(II) dimers with pseudohalide ligands in order to determine the influence of some structural parameters on the strength of the exchange coupling.

Experimental

Synthesis.—The compounds $[\{Ni(terpy)(NCX)_2\}_2]$ (X = S, **1**; or Se, **2**) were synthesised by adding a methanolic solution containing the $[Ni(terpy)Cl(H_2O)_2]Cl\cdot H_2O$ (0.40 g, 0.98 mmol), previously prepared,[12] to a warm aqueous solution of KNCS or KNCSe (3.0 mmol) respectively. The green precipitates were separated by vacuum filtration, washed with water and dried over P_2O_5 for 48 h. Green needle crystals of compound **1** suitable for X-ray analysis were obtained by recrystallization from methanol–water solutions. Several attempts to crystallize compound **2** have not yet been successful (Found: C, 49.9; H, 2.6; N, 17.2. Calc. for $C_{17}H_{11}N_5NiS_2$ **1**: C, 50.0; H, 2.7; N, 17.2. Found: C, 40.5; H, 2.3; N, 14.0. $C_{17}H_{11}N_5NiSe_2$ **2** requires C, 40.7; H, 2.2; N, 13.9%).

Physical Measurements.—Infrared spectra were obtained with KBr pellets in the 4000–250 cm^{-1} region, using a Perkin-Elmer 1430 spectrophotometer, reflectance spectra on a Perkin-Elmer lambda 9 spectrophotometer.

Magnetic susceptibility measurements were made in the temperature range 2–200 K using a Squid S.H.E. magnetometer working at 0.2 T. The susceptibilities were corrected for the diamagnetism of the constituent atoms [-220.6×10^{-6} (NCS) and -232.3×10^{-6} cm^3 mol^{-1} (NCSe)] and for temperature-independent paramagnetism (100×10^{-6} cm^3 mol^{-1}).

ESR spectra were recorded on a Bruker E.S.P. 300 spectrometer, equipped with a standard Oxford low-temperature device, operating at X-band, calibrated by an NMR probe for the

† Di-μ-thiocyanato-κ*N*:*S*; κ*S*′:*N*′-bis[(2,2′:6′,2″-terpyridine-κ^3*N*,*N*′,*N*″)thiocyanato-κ*N*-nickel(II)].

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1991, Issue 1, pp. xviii–xxii.

Non-SI unit employed: G = 10^{-4} T.

Table 1 Data collection and structure refinement of [{Ni(terpy)(NCS)$_2$}$_2$]

Formula	$C_{17}H_{11}N_5NiS_2$
Crystal dimensions/mm	0.45 × 0.12 × 0.07
M	413
System	Triclinic
Space group	$P\bar{1}$
a/Å	8.822(2)
b/Å	9.569(1)
c/Å	10.906(1)
α/°	74.35(1)
β/°	85.19(1)
γ/°	78.75(1)
U/Å^3	869(4)
Z	2
D_m/g cm^{-3}	1.56(2)
D_c/g cm^{-3}	1.58
μ(Cu-Kα)/cm^{-1}	38.8
F(000)	410
Measurements	
Radiation, λ(Cu-Kα)/Å	1.5418
Scan type	ω–2θ
θ Range (°)	1.5–65
Check reflections	−1–21, −1–31
No. measured reflections	3367
Interval h, k, l	±10, ±11, 12
Refinements	
No. variables	227
No. unique reflections with $I > 3\sigma(I)$, N_o	1077
p in weighting scheme	
$w = 1/[\sigma^2\|F_o\| + p\|F_o\|^2]$	0.0182
$R = (\Sigma\|\|F_o\| - \|F_c\|)/\Sigma\|F_o\|$	0.050
$R' = [\Sigma w(\|F_o\| - \|F_c\|)^2/\Sigma w\|F_o\|^2]^{\frac{1}{2}}$	0.057

magnetic field; the frequency was calibrated by using the signal of diphenylpicrylhydrazyl.

X-Ray Data and Crystal Structure Determination.—Crystals of [{Ni(terpy)(NCS)$_2$}$_2$] as green needles were mounted in an Enraf Nonius CAD4 automatic diffractometer with their long dimensions roughly parallel to the φ axis of the goniometer. The cell dimensions and orientation matrix were determined from the setting angles of 25 reflections with Cu-Kα radiation. Table 1 shows details of the data collection together with the structure refinement. Lorentz and polarization corrections were applied. The structure was solved using direct methods, MULTAN 84[13] and successive Fourier syntheses (SHELX 76[14]). Anisotropic thermal parameters were used for all atoms except hydrogen atoms whose thermal parameters were isotropic. The hydrogen positions were calculated [C–H 1.08(2) Å]. The final difference map revealed no significant regions of electron density with maximum 0.57 and minimum −0.26 e Å^{-3}.

The geometric calculations were performed with XANADU[15] and molecular illustrations were drawn with SCHAKAL.[16]

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

For the selenocyanate compound the cell dimensions were calculated by the program LSUCRE[17] using its powder diagram and the lattice constants of the thiocyanate compound, giving: a = 8.867(3), b = 9.592(4), c = 11.047(3) Å; α = 73.64(3), β = 83.44(3), γ = 76.67(2)°; Z = 2.

Results and Discussion

The analysis of the crystal data for the two complexes indicates that both are isomorphous phases with triclinic cells and space group $P\bar{1}$.

Fig. 1 shows a view of the dimeric complex [{Ni(terpy)(NCS)$_2$}$_2$]. Final positional parameters for the non-hydrogen atoms are listed in Table 2, bond distances and angles in Table 3. The structure consists of discrete [{Ni(terpy)(NCS)$_2$}$_2$] entities. The two nickel(II) atoms are bridged by two thiocyanate ions in an end-to-end fashion, the other two thiocyanate groups acting as terminal ligands. As Fig. 1 illustrates, the co-ordination around the nickel(II) ions can be described as distorted octahedral, with the terpy ligand [Ni–N 1.97(1)–2.09(1) Å] and the nitrogen atom from one bridging NCS group [Ni–N(4) 1.99(2) Å] in the equatorial plane, while the nitrogen atom of the terminal NCS group [Ni–N(5) 2.04(2) Å] and the sulphur atom of the second NCS bridging group [Ni–S(1^I) 2.625(5) Å] occupy the axial positions. The four equatorial atoms are coplanar with deviations in the range 0.018 for N(4) to 0.023 Å for N(3). The nickel(II) ion is practically in this mean plane (deviation −0.06 Å).

The distances and angles in the terpyridine ligand are as found in other related compounds; the ligand is planar and shows its habitual rigidity.[10,18,19]

The two thiocyanate ligands of the bridging unit are coplanar being related by an inversion centre. The two nickel(II) ions are above and below this plane (deviation ±0.56 Å). The bridging angles Ni–N(4)–C(16) and Ni–S(1^I)–C(16^I) are 159(2) and 100.0(8)° respectively, the NCS bridging groups being quasi-linear [N(4)–C(16)–S(1) 178(2)°]. The nickel(II) ions are separated from each other by 5.633(3) Å. In the terminal NCS groups the distances N(5)–C(17) and C(17)–S(2) are 1.15(3) and 1.61(2) Å, respectively. The ligand is quasi-linear with a N(5)–C(17)–S(2) angle of 177(2)°.

The distortion of the co-ordination polyhedron around the Ni^{II} from octahedral to trigonal prismatic has been calculated by the Muetterties and Guggenberger model.[20] The resulting value of Δ = 0.05 indicates that the polyhedron is close to octahedral geometry (see Table 4).

Infrared Spectroscopy.—The interest in the infrared spectra of these compounds lies mainly in the bands due to the thiocyanate and selenocyanate groups. The position of the bands corresponding to the ν(CN) stretching vibrations of these groups can illustrate the mode of co-ordination to the metal ions, because its energy depends on the degree of symmetry of these groups. The infrared spectrum of the thiocyanate compound shows two bands corresponding to the ν(CN) stretching vibrations at 2130 and 2105 cm^{-1}.[21] The high frequencies are characteristic of normal 'end-to-end' NCS bridges, in good agreement with the structural results. In the case of the selenocyanate compound the IR spectrum exhibits two bands at 2120 and 2100 cm^{-1} due to the ν(CN) stretching vibrations. The high frequencies of these vibrations suggest the presence of 'end-to-end' bridges. The band corresponding to the stretching vibration ν(CSe) appears at 700 cm^{-1}, while the δ(NCSe) mode is observed at 410 cm^{-1}.

Electronic Spectra.—The reflectance spectra exhibit three bands at 10 600, 17 200 and 24 300, and at 10 700, 17 200 and 23 900 cm^{-1} for the NCS and NCSe compounds respectively. These values are in agreement with those given in the literature for octahedral nickel(II) compounds.[22] The bands have been ascribed to d ⟶ d transitions in a symmetry near to O_h [$^3A_{2g}$ ⟶ $^3T_{2g}$, $^3A_{2g}$ ⟶ $^3T_{1g}$(F), $^3A_{2g}$ ⟶ $^3T_{1g}$(P)]. The calculated[23] nephelauxetic parameters β are 0.91 and 0.86 for the thiocyanate and selenocyanate compounds respectively.

Magnetic Measurements.—We previously reported magnetic susceptibility data for the dimeric complex [{Ni(terpy)(NCS)$_2$}$_2$], which exhibits ferromagnetic exchange interactions.[21]

The variation of the reciprocal molar magnetic susceptibility

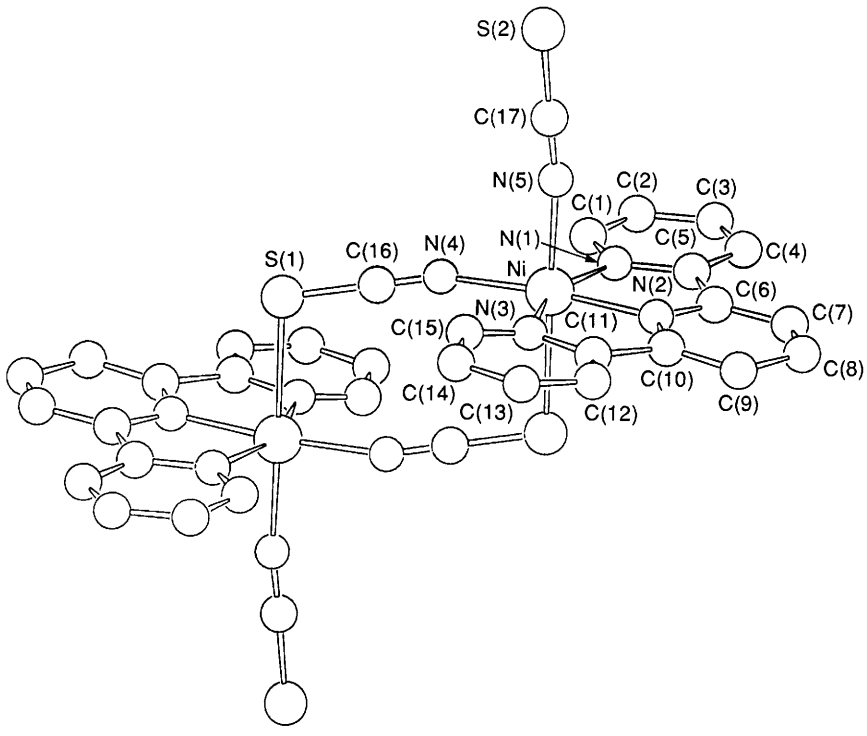

Fig. 1 Molecular structure of the dimeric compound $[\{Ni(terpy)(NCS)_2\}_2]$

Table 2 Fractional atomic coordinates ($\times 10^4$) of $[\{Ni(terpy)(NCS)_2\}_2]$

Atom	*X/a*	*Y/b*	*Z/c*
Ni	3554(3)	2348(2)	3057(2)
N(1)	1283(4)	2983(15)	3657(12)
N(2)	3260(17)	4517(15)	2464(12)
N(3)	5729(15)	2665(15)	2222(12)
C(1)	318(22)	2082(20)	4286(18)
C(2)	−1229(22)	2618(23)	4567(18)
C(3)	−1764(21)	4114(23)	4187(18)
C(4)	−796(23)	5047(20)	3555(16)
C(5)	736(20)	4463(18)	3306(15)
C(6)	1880(21)	5348(19)	2656(15)
C(7)	1668(21)	6868(20)	2318(17)
C(8)	2910(26)	7565(21)	1733(19)
C(9)	4317(24)	6687(21)	1529(17)
C(10)	4483(21)	5165(18)	1890(15)
C(11)	5859(22)	4092(20)	1739(15)
C(12)	7225(23)	4490(21)	1105(17)
C(13)	8458(23)	3403(24)	993(18)
C(14)	8331(23)	1943(22)	1486(18)
C(15)	6928(23)	1629(21)	2090(17)
N(4)	3960(19)	174(19)	3776(14)
C(16)	4654(21)	−1026(24)	4192(17)
S(1)	5586(5)	−2695(4)	4813(4)
N(5)	2794(16)	2106(15)	1418(16)
C(17)	2458(19)	1800(18)	539(19)
S(2)	2028(7)	1435(6)	−736(5)

Table 3 Selected bond distances (Å) and angles (°) for $[\{Ni(terpy)(NCS)_2\}_2]$

Nickel co-ordination sphere			
Ni–N(1)	2.08(1)	Ni–N(2)	1.97(1)
Ni–N(3)	2.09(1)	Ni–N(4)	1.99(2)
Ni–N(5)	2.04(2)	Ni · · · Ni^I	5.633(3)
Ni–S(1^I)	2.625(5)		
N(1)–Ni–N(2)	77.8(6)	N(1)–Ni–N(4)	103.5(6)
N(2)–Ni–N(4)	175.0(7)	N(3)–Ni–N(4)	100.3(6)
N(3)–Ni–N(2)	78.3(6)	N(2)–Ni–N(5)	94.2(6)
N(1)–Ni–N(3)	156.1(5)	N(4)–Ni–N(5)	90.7(6)
N(1)–Ni–N(5)	90.4(6)	N(3)–Ni–N(5)	92.4(6)
S(1^I)–Ni–N(1)	87.3(4)	S(1^I)–Ni–N(2)	85.2(4)
S(1^I)–Ni–N(3)	89.6(4)	Ni–N(4)–C(16)	159(2)
Ni–S(1^I)–C(16^I)	100.0(8)		
Average values in terpyridine			
C–N	1.341(22)	C–C(intra ring)	1.375(18)
C–C(inter ring)	1.466(26)		
C–C–C(intra ring)	121(3)	C–C–C(inter ring)	125(2)
C–C–N(intra ring)	122(2)	C–C–N(inter ring)	114(1)
C–N–C	119(2)		
Thiocyanate			
N(4)–C(16)	1.18(2)	C(16)–S(1)	1.64(2)
N(5)–C(17)	1.15(3)	C(17)–S(2)	1.61(2)
Ni–N(4)–C(16)	159(2)	N(4)–C(16)–S(1)	178(2)
Ni–N(5)–C(17)	172(1)	N(5)–C(17)–S(2)	177(2)

Symmetry related position: I $1-x, -y, 1-z$.

data *versus* temperature for $[\{Ni(terpy)(NCSe)_2\}_2]$ is well described, for temperatures higher than 50 K, by a Curie–Weiss law: $\theta = +13.7$ K and $C = 1.16$ cm^3 K mol^{-1} ($\theta = +7.5$ K and $C = 1.10$ cm^3 K mol^{-1} for the thiocyanate compound). In Fig. 2 the data are plotted as $\chi_m T$ *versus* T ($\chi_m T = \mu_{eff}^2/8$) for the thiocyanate and selenocyanate compounds. The product $\chi_m T$ increases with decreasing temperature reaching a maximum of 1.58 cm^3 K mol^{-1} at 7.40 K (NCS) and 2.11 cm^3 K mol^{-1} at 3.2 K (NCSe), after which it rapidly decreases at lower temperatures. The susceptibility data were fitted by the expression given by Ginsberg *et al.*[5] for a magnetically isotropic nickel(II) dimer, based in the spin Hamiltonian (1), where J is

$$H = -2J\vec{S}_1\vec{S}_2 - D(\vec{S}_{1z}^2 + \vec{S}_{2z}^2) - g\mu H(\vec{S}_1 + \vec{S}_2) - z'J'\vec{S}_z\langle\vec{S}_z\rangle \quad (1)$$

Table 4 Distortion Δ of the NiN_5S polyhedron in $[\{Ni(terpy)(NCS)_2\}_2]$

Dihedral angle	Octahedron (°)	NiN_5S (°)	Trigonal prism (°)
$\delta b_{1,1}$	70.5	55.7 [N(1)–N(2)–N(5)–N(3)]	0
$\delta b_{1,2}$	70.5	60.5 [N(5)–N(3)–N(4)–S(1^I)]	0
$\delta b_{1,3}$	70.5	79.3 [N(2)–N(1)–S(1^I)–N(4)]	0
$\delta b_{2,1}$	70.5	66.9 [N(5)–N(1)–N(2)–S(1^I)]	120
$\delta b_{2,2}$	70.5	74.1 [N(2)–N(3)–N(5)–N(4)]	120
$\delta b_{2,3}$	70.5	85.7 [N(1)–N(4)–S(1^I)–N(3)]	120
δ_1	70.5	81.6 [N(1)–N(5)–N(4)–N(3)]	90
δ_2	70.5	68.7 [N(5)–N(3)–N(4)–S(1^I)]	90
δ_3	70.5	56.1 [N(5)–N(1)–N(4)–S(1^I)]	90
δ_4	70.5	77.0 [N(2)–S(1^I)–N(3)–N(4)]	90
δ_5	70.5	63.7 [N(1)–N(2)–S(1^I)–N(3)]	90
δ_6	70.5	76.2 [N(2)–N(1)–N(5)–N(4)]	90
Δ*	0	0.05	1

* Calculated from $\Delta = \Sigma[(\delta b_i - \delta b_{i\,oct})/846] + \Sigma[(\delta b_2 - \delta b_{2oct})/594] + \Sigma[(\delta_i - \delta_{oct})/234]$.

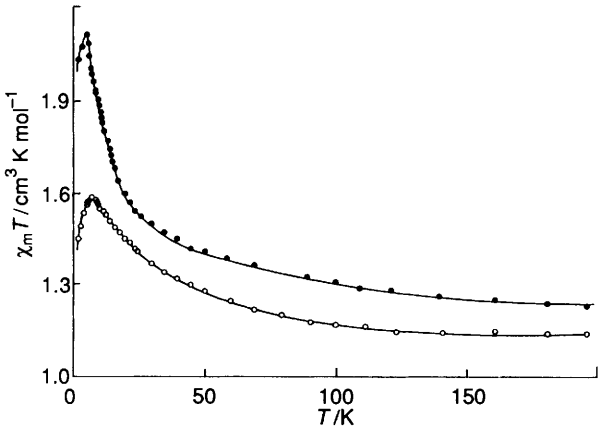

Fig. 2 Magnetic behaviour of the $[\{Ni(terpy)(NCX)_2\}_2]$ [X = NCS (○) or NCSe (●)] complexes. The full lines were calculated using the Ginsberg expression for a nickel(II) dimer

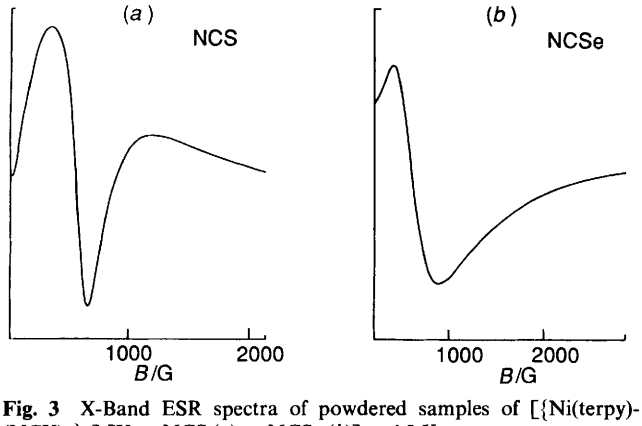

Fig. 3 X-Band ESR spectra of powdered samples of $[\{Ni(terpy)(NCX)_2\}_2]$ [X = NCS (*a*) or NCSe (*b*)] at 4.2 K

the intradimer exchange parameter, D the 'zero-field splitting' of the $^3A_2$ ground state, and J' is the interdimer exchange parameter. The g value was fixed at 2.10 (NCS) and 2.15 (NCSe), as determined by the Curie–Weiss plot. Fig. 2 shows the excellent agreement between observed and calculated values of $\chi_m T$ obtained for both compounds with the parameters $J = +4.9$ cm^{-1}, $D = -4.3$ cm^{-1} and $z'J' = 0.02$ cm^{-1} (NCS) and $J = +10.1$ cm^{-1}, $D = -10.0$ cm^{-1} and $z'J' = 0.01$ cm^{-1} (NCSe). This behaviour indicates the existence of an intradimeric ferromagnetic exchange. Population of the molecular ground state $S = 2$ increases the value of $\chi_m T$ with decreasing

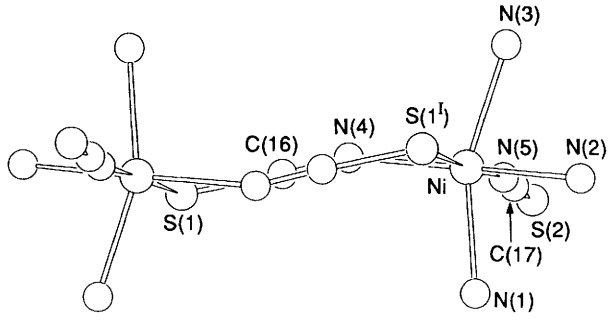

Fig. 4 Schematic diagram of the separation of the nickel atoms with respect to the bridging plane in $[\{Ni(terpy)(NCS)_2\}_2]$

temperature. The single-ion zero-field splitting causes a depopulation to a diamagnetic ground state and consequently a decrease in $\chi_m T$ at very low temperatures.

Electronic Spin Resonance.—The ESR spectra of polycrystalline samples of both compounds recorded at 4.2 K show strong signals at about 650 G (see Fig. 3). These signals can be ascribed, according to the magnetic measurements, to the allowed transition between the ground state $S = 2$, $M_s = 0$ and the first excited state $S = 2$, $M_s = 1$. The intensities of the absorption lines decrease with increasing temperature. Above 125 K the signals disappear probably because the spin–lattice relaxation time of Ni^{II} becomes too short.

In order to study the relationship between the strength and sign of the exchange constant and the structural parameters in octahedrally co-ordinated nickel(II) dimers with pseudohalide polynuclear bridges we have compiled data for several of them in Table 5. We notice that the molecular structures of all the compounds lie on an inversion centre. The terpyridine dimers $[\{Ni(terpy)(NCO)(H_2O)\}_2][PF_6]_2$ and $[\{Ni(terpy)(N_3)_2\}_2]\cdot 2H_2O$ contain polynuclear bridges of end-on type, showing ferromagnetic exchange constants of +4.6 and +20.1 cm^{-1}, respectively.[10,11] In the Ni_2N_2 bridging unit of these compounds orthogonality occurs for bridging angles larger than 101.3° (see Table 5). The difference in the strength of the exchange constants can probably be ascribed to the differences between the Ni–N–Ni angles.[11]

The last eight compounds in Table 5 contain end-to-end bridging modes. The thiocyanate-bridged dimer $[\{Ni(en)_2(NCS)\}_2]I_2$ (en = ethylenediamine) was found to be ferromagnetically coupled with $J = +4.5$ cm^{-1}.[24] Of the nickel(II) dimers with the 2,2′,2″-triaminotriethylamine (tren) ligand, of general formula $[\{Ni(tren)X\}_2][BPh_4]_2$ (X = NCS, NCSe, NCO, or N_3) the thiocyanate and selenocyanate compounds

Table 5 Structural and magnetic parameters of octahedrally co-ordinated di-pseudohalide(NXY)-bridged nickel(II) dimers (NXY = NCO, NCS, NCSe, or NNN)

Compound	Ni–Y–X/°	X–N–Ni/°	Ni···Ni/Å	Ni–N/Å	Ni–Y/Å	J/cm^{-1}	D/cm^{-1}	d^a/Å	Ref.
$[\{Ni(terpy)(NCO)(H_2O)\}_2][PF_6]_2$	97.7(3)		3.19(2)	2.04(2)	2.19(3)	+4.6	−12.2	0.01	10
$[\{Ni(terpy)(N_3)_2\}_2]\cdot 2H_2O$	101.3(3)		3.268	2.038(6)	2.198(8)	+20.1	−12.5	0.01	11
$[\{Ni(en)_2(NCS)\}_2]I_2$	100	167	5.78	2.04	2.61	+4.5	−3.3	0.05	24
$[\{Ni(tren)(NCS)\}_2][BPh_4]_2$	100	167	5.78	2.04	2.61	+2.4	−0.4	0.05	6
$[\{Ni(tren)(NCSe)\}_2][BPh_4]_2$						+1.6	−0.5		6
$[\{Ni(tren)(NCO)\}_2][BPh_4]_2$	117.1(5)	155.0(5)	5.385(1)	2.018(7)	2.336(5)	−4.4	−10.1	0.25	6, 27
$[\{Ni(tren)(N_3)\}_2][BPh_4]_2$	135.3(7)	122.3(3)	5.220(2)	2.069(8)	2.195(7)	−35.1	+6.8	0.52	25
$[\{NiL(N_3)_2\}_2]$	138.4(3)	124.4(2)		2.135(3)	2.167(3)	−90	0[b]	0.02	26
$[\{Ni(terpy)(NCS)_2\}_2]$	100.0(8)	159(2)	5.633(3)	2.04(2)	2.625(5)	+4.9	−4.3	0.56	This work
$[\{Ni(terpy)(NCSe)_2\}_2]$						+10.1	−10.0		This work

[a] Deviation of Ni from plane of bridging ligand. The first two complexes exhibit end-on bridging modes, the remainder end-to-end modes. [b] Magnetic susceptibility data have been analysed using the simple isotropic Heisenberg dimer model assuming a zero-field parameter $D = 0$.

were found to be ferromagnetic (J being +2.4 and +1.6 cm^{-1} respectively).[6] However, the cyanate and azide dimers are antiferromagnetically coupled with exchange constants of −4.4 and −35.1 cm^{-1} respectively[6,25] (see Table 5). The angles of the bridging units range from 100 to 167°. The different magnetic behaviour was ascribed by Landee and Willet[4] to the separation of the nickel(II) ions with respect to the planes formed by the bridging groups. In $[\{Ni(en)_2(NCS)\}_2I_2]$ and $[\{Ni(tren)(NCS)\}_2][BPh_4]_2$ the nickel(II) ions are practically in the planes formed by the thiocyanate groups (deviation 0.05 Å) while in $[\{Ni(tren)(NCO)\}_2][BPh_4]_2$ and $[\{Ni(tren)(N_3)\}_2][BPh_4]_2$ the nickel atoms lie significantly out of those planes (±0.25 and ±0.52 Å respectively), enhancing the antiferromagnetic contributions by movement of the metal ions out of the bridging planes.[9] However, in the azide-bridged dimer $[\{NiL(N_3)_2\}_2]$ (L = 1,5,9-triazacyclododecane) the eight-membered $Ni_2(\mu\text{-}N_3)_2$ ring is approximately planar and the compound exhibits the strongest antiferromagnetic behaviour ($J = -90$ cm^{-1}).[26] In the present thiocyanate compound the nickel ions lie ±0.56 Å out of the bridging plane (see Fig. 4), similar to the azide tren compound, and ferromagnetic behaviour is observed; nevertheless, the bridging angles in the compounds exhibiting ferromagnetic behaviour are very similar to each other and quite different to the corresponding ones in the antiferromagnetic compounds. In view of this the values of the bridging angles seem to play a significant role in determining the net magnetic interaction.

Acknowledgements

This work was financially supported in part by a grant from the Universidad del País Vasco (UPV/90) which we gratefully acknowledge.

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Received 3rd *January* 1991; *Paper* 1/00046B