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Magnetostructural correlations in heteroleptic nickel(II) complexes

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Abstract

Heteroleptic nickel(II) complexes with the general formula Ni(L)_m(H₂O)_n(X)_k, have been synthesized and structurally characterized; L stands for neutral *N*-donor ligands: 4-benzofuropyridine (bzfupy), dimethylfuropyridine (Me_2fupy) and 1,2-dimethylimidazole (Me_2iz), X = acetate or Cl⁻. The structures of the complexes [Ni(bzfupy)₂(ac)₂(H₂O)₂], [Ni(Me_2fupy)₂(H₂O)₄](ac)₂ and [Ni(Me_2iz)₄(H₂O)₂]-Cl₂ · 3H₂O are formed from {NiO₂O'₂N₂}, {NiO₄N₂} and {NiN₄O₂} chromophores, respectively. These complexes and two other previously characterized complexes, [Ni(pz)₄(ac)₂], pz – pyrazole, and [Ni(L^{NN})₂(H₂O)₂], L^{NN} – bidentate chelating ligand, were subjected to magnetochemical investigation down to 2 K (susceptibility and magnetization measurements). They show magnetic behaviour typical for zero-field splitting systems. The axial parameter of the zero-field splitting, *D*, adopts either positive or negative values and correlates with the axial distortion of the coordination polyhedra.

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1. Introduction

The magnetism of mononuclear Ni(II) complexes is dominated by axial zero-field splitting (*D*-parameter) that appears on departure from an octahedral pattern towards a tetragonal bipyramid (D_{4h} symmetry). Of secondary importance is the rhombic component (*E*-parameter) on further symmetry descent to D_{2h} symmetry [1]. The splitting of the S = 1 manifold into the Γ_4 -singlet ($M_S = 0$) and Γ_5 -doublet ($M_S = \pm 1$) is typically $|D/hc| \sim 10 \text{ cm}^{-1}$ but also negligible values occur when the geometry of the coordination polyhedron is close to a regular octahedron. The appreciable value of the *D*-parameter is enhanced by a sizable spin–orbit coupling constant for the Ni(II) ion ($\xi/hc = 630 \text{ cm}^{-1}$, $\lambda/hc = -315 \text{ cm}^{-1}$) since the magnetic parameters, within the spin-Hamiltonian formalism, obey the relationships

$$D = \lambda^2 [4\kappa_x^2 / \Delta_{xy} ({}^3B_{1g} \to {}^3E_g) - 4\kappa_z^2 / \Delta_z ({}^3B_{1g} \to {}^3B_{2g})]$$
(1)

$$g_z = g_e - 2\lambda [4\kappa_z^2/\Delta_z({}^3\mathbf{B}_{1g} \to {}^3\mathbf{B}_{2g})] > g_e$$
(2)

$$g_x = g_e - 2\lambda [4\kappa_x^2/\Delta_{xy}({}^3B_{1g} \rightarrow {}^3E_g)] > g_e$$
(3)

$$\chi_{\rm TIP} = N_{\rm A} \mu_0 \mu_{\rm B}^2 (2/3) [2 \cdot 4\kappa_x^2 / \Delta_{xy} ({}^3{\rm B}_{1\rm g} \to {}^3{\rm E}_{\rm g}) + 4\kappa_z^2 / \Delta_z ({}^3{\rm B}_{1\rm g} \to {}^3{\rm B}_{2\rm g})]$$
(4)

where the first excitation energy (split due to the tetragonality) occurs. On further symmetry descent the following formulae hold true

$$D = \lambda^2 [2\kappa_x^2 / \Delta_x ({}^3\mathbf{A}_g \to {}^3\mathbf{B}_{3g}) + 2\kappa_y^2 / \Delta_y ({}^3\mathbf{A}_g \to {}^3\mathbf{B}_{2g}) - 4\kappa_z^2 / \Delta_z ({}^3\mathbf{A}_g \to {}^3\mathbf{B}_{1g})]$$
(5)

$$E = \lambda^2 [2\kappa_y^2 / \Delta_y({}^3\mathbf{A}_g \to {}^3\mathbf{B}_{2g}) - 2\kappa_x^2 / \Delta_x({}^3\mathbf{A}_g \to {}^3\mathbf{B}_{3g})]$$
(6)

$$g_z = g_e - 2\lambda [4\kappa_z^2 / \Delta_z ({}^3\mathrm{A_g} \to {}^3\mathrm{B_{1g}})]$$
⁽⁷⁾

$$g_x = g_e - 2\lambda [4\kappa_x^2 / \Delta_x ({}^3\mathrm{A}_\mathrm{g} \to {}^3\mathrm{B}_{3\mathrm{g}})]$$
(8)

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$$g_{y} = g_{e} - 2\lambda [4\kappa_{y}^{2}/\Delta_{y}(^{3}A_{g} \rightarrow {}^{3}B_{2g})]$$
(9)
$$\chi_{\text{TIP}} = N_{A}\mu_{0}\mu_{B}^{2}(2/3)[4\kappa_{x}^{2}/\Delta_{x}(^{3}A_{g} \rightarrow {}^{3}B_{3g}) + 4\kappa_{y}^{2}/\Delta_{y}(^{3}A_{g} \rightarrow {}^{3}B_{2g}) + 4\kappa_{z}^{2}/\Delta_{z}(^{3}A_{g} \rightarrow {}^{3}B_{1g})]$$
(10)

These spin-Hamiltonian parameters are frequently understood as internal characteristics of the complex under study (molecular constants) and fixed by fitting the experimental data (magnetic susceptibility, magnetization, heat capacity, INS, ESR, MCD and FAR-IR spectra). However, all of them originate in the electronic structure of the complex and they can be reconstructed with the help of the more principal electronic-structure parameters [2]: the Racah parameters B and C (electron repulsion), the crystal-field strengths Dq, Ds, ... (or more exactly the crystal-field poles for each ligand $F_2(L)$ and $F_4(L)$), the spin-orbit coupling constant ξ , and the orbital reduction factors κ (which could be anisotropic, κ_z , κ_x). With a tetragonal compression (negative structural tetragonality), the ground state is the Γ_5 multiplet, and D is negative. On tetragonal elongation (positive structural tetragonality) the ground state is Γ_4 multiplet, and D is positive. Such a general forecast, however, is tuned by the orbital reduction factors κ_z and κ_x .

Three publications preceded the present communication [3-5] where the axial zero-field parameter D (subtracted from the susceptibility and magnetization data sets) has been correlated with the structural anisotropy parameter $D_{\rm str}$ that characterizes the degree of the tetragonality. The complexes involved in such a correlation were either homoleptic (imidazole and its derivative, ${NiN_6}$ -chromophore), *N*-donor only of the $[Ni(base)_4(NCS)_2]$ type (possessing the ${NiN_4N_2}$ -chromophore), or heteroleptic complexes of the type $[Ni(base)_2(carboxylate)_2(H_2O)_2]$ having the $\{NiN_2 O_2O_2'$ -chromophore. We prepared and structurally characterized some more members of the above series with the ${NiO_4N_2}$, and ${NiN_4O_2}$ chromophores, respectively (three complexes). Five complexes were subjected to magnetochemical studies and involved in the above mentioned correlation.

Because the present paper is, in fact, a continuation of our previous work on heteroleptic Ni(II) complexes [5], we have kept numbering of the previously characterized complexes as follows: $[Ni(Meiz)_2(HCOO)_2(H_2O)_2]$ (1), $[Ni(Me_2iz)_2(HCOO)_2(H_2O)_2]$ (2), $[Ni(iqu)_2(CH_3COO)_2 (H_2O)_2]$ (3), $[Ni(fupy)_2(CH_3COO)_2(H_2O)_2]$ (4). The new complexes under study are: $[Ni(bzfupy)_2(ac)_2(H_2O)_2]$ (5), $[Ni(Me_2fupy)_2(H_2O)_4](ac)_2$ (6), $[Ni(Me_2iz)_4(H_2O)_2]Cl_2 \cdot$ $3H_2O$ (7), $[Ni(pz)_4(ac)_2]$ (8) and $[Ni(L^{NN})_2(H_2O)_2]$ (9).

2. Experimental

2.1. Synthesis

The starting materials (1,2-dimethylimidazole, NiCl₂ · $6H_2O$ and CH₃COOK) were purchased from commercial sources and were used as received. The syntheses of 2,3-dimethylfuro[3,2-*c*]pyridine (abbr. *Me*₂*fupy*) and benzo-

[4,5]furo[3,2-*c*]pyridine (abbr. *bzfupy*) have been conducted in accordance with published recipes [6–9].

Nickel(II) acetate was synthesized by adding potassium acetate to a nickel(II) chloride ethanol solution. Elemental analysis (C, H, N) was performed on an elemental analyzer Eager 300 (Carlo Erba). The nickel content was determined chelatometrically using murexide as indicator.

The two complexes $[Ni(bzfupy)_2(ac)_2(H_2O)_2]$ (5) and $[Ni(Me_2fupy)_2(H_2O)_4](ac)_2$ (6) were prepared from nickel acetate. Into the solution of nickel acetate a stoichiometric amount of ligand was added and stirred for half hour. After 2 days the solid complexes were collected. Single crystals were grown from the ethanol solution. The complex $[Ni(Me_2iz)_4(H_2O)_2]Cl_2 \cdot 3H_2O$ (7) was prepared by reacting nickel(II) chloride with a four-fold excess of 1,2-dimethy-limidazole in warm ethanol over a 4 h reflux. The single crystals of (7) were obtained by slow evaporation at room temperature. Syntheses of compounds **8** and **9** are described elsewhere [11,12].

Anal. Calc. for (5) $C_{26}H_{24}N_2NiO_8$: C, 56.66; H, 4.39; N, 5.08. Found: C, 56.09; H, 4.52; N, 5.04%. Calc. for (6) $C_{22}H_{32}N_2NiO_{10}$: C, 48.65; H, 5.94; N, 5.16. Found: C, 48.30; H, 6.17; N, 5.47%. Calc. for (7) $C_{20}H_{42}Cl_2N_8NiO_5$: C, 39.76; H, 7.01; N, 18.55. Found: C, 40.0; H, 7.05; N, 18.5%.

2.2. Physical measurements

Single-crystal X-ray diffraction experiments for all complexes have been performed using an Xcalibur CCD apparatus (Oxford Diffraction). Data reduction and empirical absorption correction were performed by SHELXS-97.

Electronic spectra were measured using the DRIFT method on a Magna FTIR 750 spectrometer (Nicolet) in the region $5000-11\,000$ cm⁻¹ and in Nujol mull on a Specord 200 (Analytical Jena) in the range $50\,000-10\,000$ cm⁻¹.

Magnetic susceptibility and magnetization measurements were done using a SQUID magnetometer (Quantum Design) between 2 and 300 K at B = 0.1 T. The magnetization data until B = 5.5 T were taken at T = 2.0 and 4.6 K, respectively. Raw susceptibility data were corrected for underlying diamagnetism using a set of Pascal constants [10]. The effective magnetic moment has been calculated as usual: $\mu_{eff}/\mu_B = 798(\chi'T)^{1/2}$ when SI units are employed.

3. Results and discussion

3.1. Molecular and crystal structure

Crystal data for compounds 5 through to 7 are collected in Table 1. The molecular structure is viewed in Fig. 1.

The structure of complex 5 consist of $[Ni(bzfupy)_2(ac)_2-(H_2O)_2]$ monomeric units in which the central Ni(II) atom has a distorted octahedral configuration. The coordination around the Ni(II) atom is defined by two aqua ligands (w), two acetate ligands (a) and two neutral benzo[4,5]furo-[3,2-c]pyridine (b). The Ni–O(a) distances are 2.060(2) Å, the Ni–O(w) distances are 2.073(2) Å and the Ni–N(b) dis-

Table 1			
Summary	of X-ray	crystallographic	data

Compound	5	6	7
Formula	C ₂₆ H ₂₄ N ₂ NiO ₈	C ₂₂ H ₃₂ N ₂ NiO ₁₀	C ₂₀ H ₄₂ Cl ₂ N ₈ NiO ₅
Formula weight	551.17	543.21	604.23
Crystal system	monoclinic	triclinic	orthorhombic
Space group	P21/c	$P\overline{1}$	P ₂₁₂₁₂₁
Cell parameters			
<i>a</i> (Å)	12.228(4)	7.260(2)	9.387(4)
b (Å)	7.8460(10)	7.679(3)	10.069(4)
c (Å)	12.5980(10)	11.418(2)	29.611(9)
α (°)	90	97.53(2)	90
β (°)	93.75(2)	90.87(2)	90
γ (°)	90	98.08(1)	90
$V(Å^3)$	1206.1(4)	624.4(3)	2798.8(18)
Z	4	1	4
Density, D_{calc} (g cm ⁻³)	1.518	1.445	1.434
Absorption coefficient (mm^{-1})	0.860	0.834	0.929
<i>F</i> (000)	572	286	1280
Reflections collected	8272	6496	18682
Refinement method	full-matrix least-squares or	$1 F^2$	
Data/restraints/parameters	2430/3/175	2278/6/172	5694/12/424
Final <i>R</i> indices	$R_1 = 0.0297$	$R_1 = 0.0468$	$R_1 = 0.0480$
	$wR_2 = 0.0867$	$wR_2 = 0.1274$	$wR_2 = 0.0951$
CCDC deposit numbers	622567	622568	622569



Fig. 1. Molecular structure of complexes 5–7, along with two previously characterized complexes 8 [11] and 9 [12] (hydrogen atoms are deleted for clarity).

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Table 2 Selected bond lengths $(Å)^a$

Contact	5	6	7		
Nil-N1	2.128	2.168	2.100		
Ni1-N2	2.128	2.168	2.065		
Ni1–N3			2.077		
Nil-N4			2.063		
Ni1-O1	2.073 ^w	2.194 ^w	2.095 ^w		
Ni1–O2	2.073 ^w	2.194 ^w	2.106 ^w		
Ni1–O3	2.060	2.048^{w}			
Nil–O4	2.060	2.048^{w}			

^a w, the aqua ligand.

tances are 2.128(2) Å (see Table 2). Two oxygen atoms from water molecules and two oxygen atoms from acetate groups form the equatorial plane and two nitrogen atoms from benzo[4,5]furo[3,2-c]pyridine are situated in the axial sites.

The molecular structure of complex **6** consists of discrete $[Ni(Me_2fupy)_2(H_2O)_4]^{2+}$ monomeric units with the Ni(II) atom in a distorted octahedral configuration defined by four equatorial aqua (w) ligands and two axial 2,3-dimeth-ylfuro[3,2-*c*]pyridine (b) ligands. The Ni–O(w) distances are 2.194 and 2.048 Å and the Ni–N(b) distances are 2.168(2) Å. Such a geometry predisposes that the usual assumption |D| > 3E is no longer valid for this {Ni(O₂-O'₂)_{eq}N₂} chromophore.

The $[Ni(Me_{2i}z)_4(H_2O)_2]^{2+}$ monomeric units represent the structure of compound 7. The central Ni(II) atom possesses a distorted octahedral configuration formed by two aqua ligands and four neutral 1,2-dimethylimidazole (b) ligands. The distances inside the chromophore are Ni–O(w) 2.095 and 2.106 Å, Ni–N(b) 2.100, 2.065, 2.077 and 2.063 Å, respectively.

For compounds 8 and 9, whose structures have been published elsewhere, we refer to the original sources [11,12].

The intermolecular O–H···O hydrogen bonds for **5** $[H \cdot \cdot O = 1.834 \text{ and } 1.934 \text{ Å}$, and O–H···O = 165 and 163°] are formed through aqua-ligand OH groups to uncoordinated acetate-ligand O-atoms from a neighboring molecule, and they are situated in the equatorial plane. In the crystal structure of this complex, the secondary N-atoms are not involved in the hydrogen bonds; consequently only a two-dimensional network is formed (Fig. 2).

The registered intermolecular contacts for **6** are O–H···O [H···O = 1.683, 1.821, 1.918 and 2.184 Å, O–H···O = 161°, 166°, 171° and 176°]. They are formed by aqua-ligand OH groups to the O atom from an uncoordinated acetate molecule in the equatorial plane. Thus, these hydrogen bonds form a two-dimensional network because the N-atoms are not involved in the hydrogen bonds.

For complex 7 the O–H···O hydrogen bonds [H···O = 2.688, 2.767 and 2.784 Å, Cl···O = 3.146, 3.125, 3.096, 3.142 and 3.110 Å, O–H···O = 161°, 171° and 167° and O–H···Cl = 162°, 170°, 174°, 160° and 167°] are formed through coordinated water OH groups to crystal-water



 $[Ni(Me_{2}iz)_{4}(H_{2}O)_{2}]Cl_{2}\cdot 3H_{2}O, 7$

Fig. 2. The hydrogen bonds in complexes 5, 6 and 7.

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Election spectra for the helefoliphic ru(n)complexes							
Complex	Chromophore, bipyramid ^a	Spin allowed transition, (E/hc) (cm ⁻¹)					
	Compressed	${}^{3}B_{2g} \leftarrow {}^{3}B_{1g} = 10Dq$	${}^{3}E_{g} \leftarrow {}^{3}B_{1g}$	${}^{3}E_{g} \leftarrow {}^{3}B_{1g}$			
	Octahedral Elongated	${}^{3}E_{g} \leftarrow {}^{3}B_{1g}$ ${}^{3}T_{2g} \leftarrow {}^{3}A_{2g} = 10Dq$ ${}^{3}E_{g} \leftarrow {}^{3}B_{1g}$ ${}^{3}B_{2g} \leftarrow {}^{3}B_{1g} = 10Dq$	${}^{3}A_{2g} \leftarrow {}^{3}B_{1g}$ ${}^{3}T_{1g}(F) \leftarrow {}^{3}A_{2g}^{b}$ ${}^{3}A_{2g} \leftarrow {}^{3}B_{1g}$ ${}^{3}E_{g} \leftarrow {}^{3}B_{1g}$	${}^{3}A_{2g} \leftarrow {}^{3}B_{1g}$ ${}^{3}T_{1g}(P) \leftarrow {}^{3}A_{2g}$ ${}^{3}A_{2g} \leftarrow {}^{3}B_{1g}$ ${}^{3}E_{g} \leftarrow {}^{3}B_{1g}$			
1, [5]	${NiO_2O_2N_2}, c$	9400	15300 (13531)	26000			
2, [5]	$\{NiO_2O_2N_2\}, c$	10893	16207 (13642)	26525			
3, [5]	$\{NiO_2O_2N_2\}, c$	9611	15764 (13740)	26000			
4, [5]	$\{NiO_2O_2N_2\}, c$	9945	15968 (13800)	26870			
5, This work	$\{NiO_2O_2N_2\}, c$	9720	15670 (13673)	26380			
6, This work	$\{NiO_4N_2\}, c$	9890	15900 (13878)	26500			
7, This work	$\{NiN_4O_2\}, e$	10450	16000 (13696)	25800			
8, This work	${\rm NiN_4O_2}$, e	10397	16681 (13603)	27004			

Table 3 Electron spectra for the heteroleptic Ni(II)complexes

^a Bipyramid: c, compressed; e, elongated; based upon relative structural tetragonality.

^b Values in parentheses are the positions of the band-arms.

molecules and one of these three hydrogen bonds is formed between two crystal-water molecules. These hydrogen bonds form a two-dimensional network.

3.2. Electron spectra

The electron spectra of the studied complexes show three principal d-d bands (${}^{3}T_{2g} \leftarrow {}^{3}A_{2g}$, ${}^{3}T_{1g}(F) \leftarrow {}^{3}A_{2g}$ and ${}^{3}T_{1g}(F) \leftarrow {}^{3}A_{2g}$, characteristic for the octahedral geometry) in the region 9400–10893 cm⁻¹, 15300–16681 cm⁻¹ and 26000–27004 cm⁻¹, which are split due to the symmetry lowering of the crystal field (Table 3). The splitting is evidenced as an arm and is well visible for the second principal transition; this refers to the transition ${}^{3}A_{2g} \leftarrow {}^{3}B_{1g}$ within the point-group D_{4h} . A weak feature with a maximum at ~13600 cm⁻¹ can be assigned to the spin-forbidden transition (${}^{1}A_{1g} \leftarrow {}^{3}B_{1g}$) arising from the ${}^{1}D$ term.

3.3. Magnetic data

Magnetic data for the complexes under study are shown in Fig. 3. This figure displays the temperature dependence of the effective magnetic moment and the field dependence of the molar magnetization at two temperatures. The effective magnetic moment keeps an almost constant value except at very low temperatures when its decrease reflects a zero-field splitting. The ZFS is also responsible for deviation of the magnetization from the Brillouin-function behaviour.

The experimental data were fit using the spin-Hamiltonian

$$\widehat{H} = \widehat{H}^{\text{zfs}} + \widehat{H}^{\text{Z}} \tag{11}$$

where the first contribution is the zero-field splitting term

$$\widehat{H}^{zfs} = \hbar^{-2} D(\widehat{S}_z^2 - \widehat{S}^2/3) + \hbar^{-2} E(\widehat{S}_x^2 - \widehat{S}_y^2)$$
(12)

describing the axial and rhombic magnetic anisotropy. The Zeeman term entering the spin-Hamiltonian is expressed through the grids of polar angles ϑ_k and φ_l as

$$\widehat{H}^{Z}(\vartheta_{k},\varphi_{l}) = \mu_{B}B_{m}\hbar^{-1}(g_{x}\sin\vartheta_{k}\cos\varphi_{l}\widehat{S}_{x} + g_{y}\sin\vartheta_{k}$$
$$\times \cos\varphi_{l}\widehat{S}_{y} + g_{z}\cos\vartheta_{k}\widehat{S}_{z})$$
(13)

In order to reduce the free parameters, the zero-field splitting parameters were restricted according to the constraints offered by the spin-Hamiltonian formalism

$$D = (\lambda/2)[g_z - (g_x + g_y)/2]$$
(14)

$$E = (\lambda/4)(g_x - g_y) \tag{15}$$

Two experimental data-sets (M versus T at 0.1 T, and M versus B at 2.0 and 4.6 K) have been treated simultaneously. The average magnetization data have been calculated as a correct powder average using a random spherical distribution of the magnetic-field vector [13]

$$M_{\rm av} = \frac{1}{4\pi} \int_0^\pi \int_0^{2\pi} M(\vartheta, \varphi) \sin \vartheta \, \mathrm{d}\vartheta \, \mathrm{d}\varphi \tag{16}$$

The free parameters to be optimized are g_x , g_y , g_z and α_{TIP} (temperature-independent paramagnetism).

The calculated magnetic parameters are listed in Table 4. The acquired data for compounds **5–9** show that the *D*-parameters adopt values between -3 and $+11 \text{ cm}^{-1}$. Enhancement of the magnetic anisotropy in these complexes is caused by the different crystal-field strengths in the axial and equatorial positions.

We also tested the hypothesis about the sign reversal for the *D*-parameter, since it is problematic to fix the sign of the *D*-parameter from powder data alone when |D| is small. The sign reversal always led to a worse fit of magnetic data with an enlarged *R*-factor. Some other techniques could also be applied in detecting the zero-field splitting (e.g., high-field/ high-frequency ESR, frequency-domain spectroscopy) but these are less common and hardly accessible for routine usage [1]. Nevertheless, a simultaneous utilization of the susceptibility and magnetization data-sets helps substantially in a reliable determination of the sign of the *D*-parameter.

The fitting procedure results in appreciable values of the axial zero-field splitting parameter *D*. These magnetic data



Fig. 3. Temperature dependence of the effective magnetic moment and field dependence of the magnetization (right panel) for **5–9**. Filled circles, fitted data.

were used in correlation with the structural *D*-values subtracted from the X-ray structure data. The latter parameter, in the case of the heteroleptic complexes, is defined as

$$D_{\rm str} = \Delta_z - (\Delta_y + \Delta_x)/2 \tag{17}$$

where $\Delta_a = (d_a - \bar{d}_i)$ for a = x, y, z is a shift relative to the mean distance \bar{d}_i for a given bond (i = N, O). For the N-and O-donor ligands these values have been taken from

complexes containing the $[Ni(NH_3)_6]^{2+}$ and $[Ni(H_2O)_6]^{2+}$ units, respectively; $\overline{d}(Ni-N) = 2.145$ Å and $\overline{d}(Ni-O) = 2.055$ Å [14]. As seen from Fig. 4, the correlation of the magnetic D_{mag} values versus the relative structural tetragonality parameters D_{str} is fairly good. However, three notes need to be added: (i) the magnetic as well as structural data bring evidence also for the rhombic anisotropy, which has not been included into the correlation; (ii) the correlation

Table 4 Fitted magnetic parameters for heteroleptic complexes^a

Compound ^b	g_x	g_y	g_z	$D/hc \ (\mathrm{cm}^{-1})^{\mathrm{c}}$	$E/hc \ (\mathrm{cm}^{-1})$	$\alpha_{TIP}/10^9 \ (m^3 \ mol^{-1})$	$R^{0/0}$	$D_{\rm str}~({\rm pm})$	$E_{\rm str}~({\rm pm})$
1, [5]	2.000	2.000	2.038	-6.0	+0.7	+0.49	2.4	-9.9	+1.1
2, [5]	2.139	2.140	2.190	-7.7	+2.0	-1.12	1.8	-6.2	+1.9
3, [5]	2.094	2.104	2.139	-5.3	+1.2	+0.61	0.7	-5.0	+1.4
4, [5]	2.147	2.149	2.179	-5.0	+0.5	-2.25	0.5	-2.25	+1.0
5, This work	2.200	2.203	2.310	-2.85	+0.68	+0.13	0.67	-2.85	+0.7
6, This work	2.218	2.219	2.249	-3.22	+0.74	+1.40	0.91	-8.8	+7.3
7, This work	2.100	2.118	2.079	+7.42	+0.49	-1.08	1.69	+11.45	+0.7
8, This work	2.170	2.181	2.142	+3.88	+0.01	-0.36	1.37	+6.6	+0.4
9, This work	2.103	2.159	2.000	+11.23	+1.46	+3.46	2.89	+15.5	+3.1

^a Estimated errors: 0.01 for g-factors, 0.1 for ZFS parameters.

^b Compounds: $\mathbf{1} = [Ni(2-Meiz)_2(HCOO)_2(H_2O)_2]; \ \mathbf{2} = [Ni(1,2-Me_2iz)_2(HCOO)_2(H_2O)_2]; \ \mathbf{3} = [Ni(iqu)_2(ac)_2(H_2O)_2]; \ \mathbf{4} = [Ni(fupy)_2(ac)_2(H_2O)_2]; \ \mathbf{5} = [Ni(bzfupy)_2(ac)_2(H_2O)_2]; \ \mathbf{6} = [Ni(Me_2fupy)_2(H_2O)_4](ac)_2; \ \mathbf{7} = [Ni(Me_2iz)_4(H_2O)_2] \cdot Cl_2 \cdot 3H_2O; \ \mathbf{8} = [Ni(pz)_4(ac)_2]; \ \mathbf{9} = [Ni(L^{NN})_2(H_2O)_2].$

^c Fits with a sign-reversed *D*-value (*R*-factor/%): **5**, +2.41 cm⁻¹ (0.98); **6**, +2.79 cm⁻¹ (1.10); **7**, -15.29 cm⁻¹ (6.72); **8**, -7.03 cm⁻¹ (6.60); **9**, -22.00 cm⁻¹ (40.0).



Fig. 4. Correlation of the magnetic vs. structural *D*-parameters. Broken lines, confidence intervals. $\mathbf{1} = [Ni(2-Meiz)_2(HCOO)_2(H_2O)_2]; \mathbf{2} = [Ni(1,2-Me_2iz)_2(HCOO)_2(H_2O)_2]; \mathbf{3} = [Ni(iqu)_2(ac)_2(H_2O)_2]; \mathbf{4} = [Ni(fupy)_2(ac)_2(H_2O)_2]; \mathbf{5} = [Ni(bzfupy)_2(ac)_2(H_2O)_2]; \mathbf{6} = [Ni(Me_2fupy)_2(H_2O)_4](ac)_2; \mathbf{7} = [Ni(Me_2iz)_4(H_2O)_2]Cl_2 \cdot 3H_2O; \mathbf{8} = [Ni(pz)_4(ac)_2]; \mathbf{9} = [Ni(L^{NN})_2(H_2O)_2].$

curve cannot be linear, since the compressed bipyramid cannot be extrapolated to zero metal-ligand distances; (iii) the magnetic parameters (*D*, *E*) are influenced by the orbital reduction factors via Eqs. (5) and (6). The last aspect manifests itself in the complex [Ni(imidazole)₄](acetate)₂: the structural distortion is extremely positive (strongly elongated bipyramid) whereas the axial zero-field splitting parameter, that measures the magnetic anisotropy, is extremely negative, $D/hc = -23 \text{ cm}^{-1}$ [15]. This apparent contradiction can be understood by inspecting Eq. (1): the orbital reduction factor for very long axial Ni···O contacts approaches a value of $\kappa_z = 1.0$ whereas that for the equatorial Ni–N bonds adopts normal values of $\kappa_x = 0.7$; this causes the sign reversal of the *D*-parameter.

It is recapitulated that in the solid state, the magnetic anisotropy for homoleptic Ni(II) complexes adopts small values: D/hc = -3.5 to +2.0 cm⁻¹ for $[Ni(iz)_6](car)_2$ type complexes [3] (car – carboxylate). In heteroleptic, but "effective octahedral" complexes of the $[Ni(N-base)_4(NCS)_2]$ · nH_2O type the registered magnetic anisotropy is not

enhanced significantly: D/hc = -3 to -1.5 cm^{-1} [4]. On passing to the heteroleptic complexes of the $[\text{Ni}(N-\text{base})_2(-H_2\text{O})_2(car)_2]$ type the magnetic anisotropy is enhanced substantially: D/hc = -8 to -5 cm^{-1} [5]. Two complexes of the present study (5 and 6) span this interval, which is typical for the {NiO₂O₂N₂} chromophore. The remaining complexes (7, 8 and 9) possessing the {NiN₄O₂} chromophore adopt positive values of D/hc = +4 to $+11 \text{ cm}^{-1}$.

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Appendix A. Supplementary material

CCDC 622567, 622568 and 622569 contains the supplementary crystallographic data for **5**, **6** and **7**. These data can be obtained free of charge via http://www.ccdc.ac.uk/ conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ ccdc.cam.ac.uk. Calculated magnetic data assuming only the tetragonal distortion are deposited. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.poly.2006.11.054.

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