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Magnetostructural *D* Correlation in Nickel(II) Complexes: Reinvestigation of the Zero-Field Splitting

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The magnetostructural *D* correlation interrelates the zero-field-splitting parameter *D* withdrawn from the magnetic data with the structural tetragonality parameter D_{str}. This correlation allows the quantitative prediction that $D < 0$ occurs for the tetragonally compressed nickel(II) complexes.

The search for magnetostructural correlations, i.e., the relationship between the exchange-coupling constants and the structural parameters in dinuclear and/or oligonuclear complexes, has a long history. In the most widely used correlation, the bonding angle Cu−O−Cu along the superexchange path is usually used in the role of the structural parameter, although some other parameter sets also have been correlated.[1] All of the previous attempts can be comprehensively termed the magnetostructural *J* correlations because just the *J* parameter was under focus.

The discovery of single-molecule magnets opened a series of new questions, such as the possibility of tuning the barrier to magnetic tunneling.[2] The key parameter of interest is the axial zero-field-splitting parameter *D*, which dominates the single-ion magnetic anisotropy. The possibility of correlating the *D* values with the structural tetragonality parameter in nickel(II) complexes has been outlined gradually.[3] However, the preliminary achievements need some improvements. The most critical point is the sign assignment to the *D* parameter based upon the powder susceptibility and magnetization data. The theoretical explanation of such correlations is also of a great interest.

Structural Data. The complexes under investigation are listed in Table 1. All of them were structurally fully characterized and deposited in CCDC.[4a] According to the chromophore, 18 complexes can be classified into 4 groups.

The first group is covered by homoleptic complexes with the $\{\mathrm{NiN_6}\}$ chromophore.[3a] The geometry, however, is not octahedral but rather orthorhombic with three sets of Ni−N distances $\{d_x, d_y, d_z\}$. The two, most similar distances define the equatorial plane of the complex with $R_{\mathrm{eq}} = (d_x + d_y)/2$, whereas the remaining one refers to the axial position ($R_{\mathrm{ax}} = d_z$). Then the structural distortion is defined through a tetragonality parameter

$$D_{\mathrm{str}} = R_{\mathrm{ax}} - R_{\mathrm{eq}} \qquad (1)$$

With these definitions, the geometry of the coordination polyhedron varies from a slightly compressed tetragonal bipyramid ($D_{\mathrm{str}} = -5.2$ pm) to a slightly elongated bipyramid ($D_{\mathrm{str}} = +3.5$ pm).

The second class of complexes is represented by molecular units that contain two thiocyanato ligands in the axial position and four organic bases B in the equatorial plane. The chromophore refers to $\{\mathrm{NiN_4N'_2}\}$, where different N-donor sets occur. Unlike to the previous publication,[3b] the correction to the heterogeneity of the donor set is accounted for by considering different averaged distances $\overline{d}$[Ni−N(B)] and $\overline{d}$[Ni−N(NCS)]. The data from the crystallographic database gave $\overline{d} = 214.5$ pm as an average in $[\mathrm{Ni(NH_3)_6}]^{2+}$ complexes,[4b] and $\overline{d} = 207.0$ pm for the much more ionic Ni−N(NCS) bond. Then the displacement from the average distance $\Delta_i = (d_i - \overline{d}_i)$ allows the redefinition of the tetragonality parameter

$$D_{\mathrm{str}} = \Delta_z - (\Delta_x + \Delta_y)/2 \qquad (2)$$

Inspection of Table 1 reveals that within group II the tetragonality parameter D_{str} varies between −4.3 and +2.9 pm.

Group III involves complexes with the $\{\mathrm{NiN_4O_2}\}$ chromophore. The correction to the heterogeneity of

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Table 1. Magnetic and Structural D Values for a Series of Nickel(II) Complexes

complex[a]	CCDC code	D_{str}/pm	D_{mag}/cm^{-1}
Group I, $\{\mathrm{NiN_6}\}$			
a $[\mathrm{Ni(iz)_6}](\mathrm{fm})_2$	KELMEU	−5.17	−3.43
b $[\mathrm{Ni(iz)_6}](\mathrm{Cl\text{-}ac})_2$	KELMAQ	−0.25	∼0
c $[\mathrm{Ni(iz)_6}](\mathrm{Cl\text{-}prop})_2$	LAKRIZ01	+2.03	+0.90[b]
d $[\mathrm{Ni(1\text{-}Meiz)_6}]\mathrm{Cl_2\cdot 2H_2O}$	SEHFAN01	+3.51	+1.96[b]
Group II, $\{\mathrm{NiN_4N'_2}\}$			
e $[\mathrm{Ni(fpy)_4(NCS)_2}]\cdot\mathrm{THF}$	ETOGEZ	+2.80	+2.70[b]
f $[\mathrm{Ni(Mefpy)_4(NCS)_2}]\cdot 1.29\mathrm{H_2O}$	YAWSOF	−2.60	−1.93[b]
g $[\mathrm{Ni(dmefpy)_4(NCS)_2}]\cdot 6.6\mathrm{H_2O}$	ETOGID	−4.3	−1.65[b]
h $[\mathrm{Ni(bzfpy)_4(NCS)_2}]\cdot 2\mathrm{H_2O}$	YAWSEV	+2.95	+1.15[b]
i $[\mathrm{Ni(iqu)_4(NCS)_2}]\cdot\mathrm{CH_2Cl_2}$	YAWSIZ	−0.70	−1.54[b]
Group III, $\{\mathrm{NiN_4O_2}\}$			
j $[\mathrm{Ni(pz)_4(ac)_2}]$	RAVQOV	+6.65	+3.88
k $[\mathrm{Ni(dmeiz)_4(H_2O)_2}]\mathrm{Cl_2\cdot 3H_2O}$	MIBWUQ	+11.35	+7.42
Group IV, $\{\mathrm{NiN_2O_2O'_2}\}$			
l $[\mathrm{Ni(2\text{-}Meiz)_2(fm)_2\,(H_2O)_2}]$	METMAA	−10.13	−6.00
m $[\mathrm{Ni(dmeiz)_2(fm)_2(H_2O)_2}]$	METMOO	−6.25	−7.70
n $[\mathrm{Ni(fpy)_2(ac)_2(H_2O)_2}]$	METMEE	−2.32	−5.00
o $[\mathrm{Ni(iqu)_2(ac)_2(H_2O)_2}]$	METMII	−4.97	−5.30
p $[\mathrm{Ni(bzfpy)_2(ac)_2\,(H_2O)_2}]$	MIBWIE	−2.85	−2.85
r $[\mathrm{Ni(Mefpy)_2(ac)_2\,(H_2O)_2}]$	756231	−3.70	−3.17
s $[\mathrm{Ni(Mefpy)_2\,(H_2O)_4}](\mathrm{ac})_2$	MIBWOK	−4.30	−3.22

[a] Abbreviations of ligands: $\mathrm{fm^-}$ = formato, $\mathrm{ac^-}$ = acetato, $\mathrm{Cl\text{-}ac^-}$ = chloroacetato, $\mathrm{Cl\text{-}prop^-}$ = 2-chloropropionato, iz = imidazole, 1-Meiz = 1-methylimidazole, 2-Meiz = 2-methylimidazole, dmeiz = 1,2-dimethylimidazole, pz = pyrazole, iqu = isoquinoline, fpy = furo[3,2-*c*]pyridine, Mefpy = 2-methylfuro[3,2-*c*]pyridine, dmefpy = 2,3-dimethylfuro[3,2-*c*]pyridine, bzfpy = benzo[4,5]furo[3,2-*c*]pyridine. [b] The D_{mag} sign was deduced from MO model.

the donor set refers to the average distance $\overline{d}(\mathrm{Ni{-}O})$ = 205.5 pm taken from a set of $[\mathrm{Ni(H_2O)_6}]^{2+}$ complexes. With these values, the geometry of the coordination polyhedron corresponds to an effectively elongated tetragonal bipyramid (D_{str} = +6.6 for **j** and +11.3 pm for **k**) despite the fact that the distance $d(\mathrm{Ni{-}O})$ = 206.6 pm in the axial direction is shorter than the equatorial one $d(\mathrm{Ni{-}N})$ = 208.9 pm for complex **k**.

Group IV is covered by numerous examples with the $\{\mathrm{NiN_2O_2O'_2}\}$ chromophore. All of them refer to the effectively compressed tetragonal bipyramid because the structural tetragonality ranges between D_{str} = −10.1 and −2.3 pm. In this case, a significant rhombic component is also present.[3c,d]

To this end, the selected series of nickel(II) complexes is a representative set for which the compressed tetragonal bipyramid alters to an elongated form (D_{str} = −10 to +11 pm).

Magnetic Data. Magnetic susceptibility measurements were done using a SQUID magnetometer at B = 0.1 T between T = 2 and 300 K. Raw susceptibility data were corrected for underlying diamagnetism using the set of Pascal constants. In all cases, upon cooling from room temperature, the effective magnetic moment is invariable until low temperature, when it gradually drops down (typically below 50 K). This feature is a fingerprint of the zero-field splitting. At the same time, the magnetization per formula unit taken at low temperature (T = 2.0 K) saturates below a value $M_{\mathrm{mol}}/N_{\mathrm{A}} = 2\,\mu_{\mathrm{B}}$, which again confirms the presence of a sizable zero-field splitting.

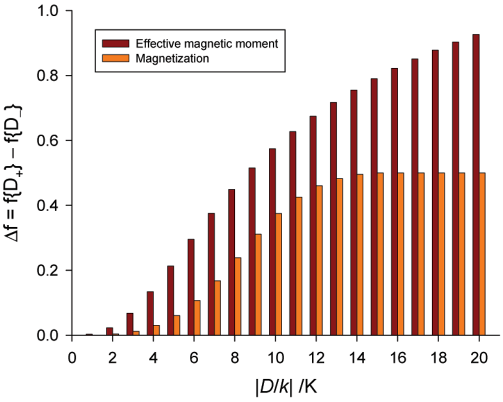

Figure 1. Relative sensitivity of the magnetic functions ($f = \mu_{\mathrm{eff}}$ and M_{mol}) on the sign of the D parameter at T = 2 K and B = 0.1 T (for the effective magnetic moment) and B = 6.0 T (for magnetization).

Two sets of magnetic data, $\chi(T)$ and $M(B)$, have been fitted using a common error functional

$$F = \sum_i (\chi_i^{\mathrm{c}} - \chi_i^{\mathrm{o}})/\chi_i^{\mathrm{o}} + \sum_j (M_j^{\mathrm{c}} - M_j^{\mathrm{o}})/M_j^{\mathrm{o}} \rightarrow 0 \qquad (3)$$

The susceptibility and magnetization data were calculated on the basis of the spin Hamiltonian (4)

$$\begin{aligned}\hat{H} &= \hbar^{-2}[D(\hat{S}_z^2 - \hat{S}^2/3) + E(\hat{S}_x^2 - \hat{S}_y^2)] \\ &\quad + \mu_{\mathrm{B}} B_{\mathrm{m}} \hbar^{-1}(g_x \sin\vartheta_k \cos\phi_l \hat{S}_x + g_y \sin\vartheta_k \sin\phi_l \hat{S}_y \\ &\quad + g_z \cos\vartheta_k \hat{S}_z) \qquad (4)\end{aligned}$$

where the Zeeman term is calculated and averaged for a number of grids over the polar angles ϑ_k and φ_l. The resulting magnetic parameters are presented in the Supporting Information; only the axial zero-field splitting D_{mag} is involved in Table 1. An important feature is that the magnetic data taken and their analysis have been done uniformly for the full set of compounds under study.

It needs be mentioned that the quality of the fitting procedure is a little sensitive to the sign of the D parameter when $|D| < 2$ K. This well-known feature is quantitatively expressed in Figure 1: here the sign-discrimination function Δf is plotted relative to the absolute D value (when D is large enough, then Δf is also well determined). The correct sign for critical cases has been assigned with the help of the molecular orbital (MO) model (see below).

The fitted magnetic data, D_{mag}, have been plotted versus the D_{str} parameters, and the observed correlation (termed the magnetostructural D correlation) is displayed in Figure 2. The correlation equation is

$$D_{\mathrm{mag}} \approx 2\{25.8[1 - \exp(-0.014 D_{\mathrm{str}})]\} \qquad (5)$$

This equation can be used in the prediction of the sign and approximate estimation of the magnitude of the zero-field-splitting parameter D_{mag} by knowing only the metal−ligand distances.[5] Thus, a rational tuning of the magnetic

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[5] Small argument allows an expansion of the exponentials $\exp(-bx) \approx 1 - bx$, and thus the correlation function collapses to a couple of straight lines, providing $D_{\mathrm{mag}} = 0$ for $D_{\mathrm{str}} = 0$.

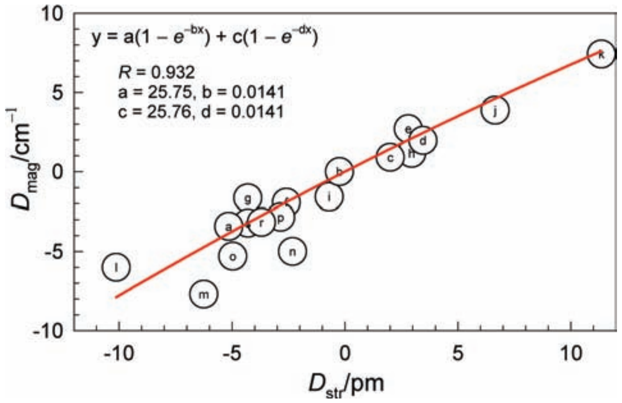

Figure 2. Magnetostructural *D* correlation for nickel(II) complexes.

anisotropy, at least in nickel(II) complexes, seems be a realistic task.

Electronic Structure Data. The observed magnetostructural *D* correlation opens a number of questions about its origin and limits. The simple crystal-field theory predicts that for nickel(II) complexes the *D* value is given by the excitation energies $\Delta_{xy}({}^3B_{1g} \rightarrow {}^3E_g)$ and $\Delta_z({}^3B_{1g} \rightarrow {}^3B_{2g})$ from the ground electron term and the orbital reduction factors κ

$$D = 4(\xi/2S)^2({\kappa_{xy}}^2{\Delta_{xy}}^{-1} - {\kappa_z}^2{\Delta_z}^{-1}) \qquad (6)$$

where ξ stands for the spin–orbit coupling constant and $S = 1$. For a regular octahedron, the two contributions cancel exactly and then $D = 0$. For a compressed bipyramid, $\Delta_z < \Delta_{xy}$ holds true, and with $\kappa_z \sim \kappa_{xy}$, the value of D is negative; for an elongated bipyramid, obviously $D > 0$. However, different covalencies/ionicities of the M–L bond cause a tuning of the *D* values via the orbital reduction factors.

In terms of a simple MO approach, the *D* value can be expressed as follows:[6a]

$$D = 4(\xi/2S)^2\left[\frac{1}{16}\gamma^2(\alpha + 3\delta)^2{\Delta_{xy}}^{-1} - \alpha^2\beta^2{\Delta_z}^{-1}\right] \qquad (7)$$

where α, β, γ, and δ are coefficients of the d orbitals ($x^2 - y^2$, xy, $xz \sim yz$, and z^2) in appropriate MOs. The excitation energies upon symmetry lowering to D_{4h} can be expressed in terms of the MO energies. The relevant schematic diagrams and derived relationships are shown in Figure S2 in the Supporting Information. According of these expressions: for a compressed tetragonal bipyramid $\varepsilon(e_g) < \varepsilon(b_{2g})$, $\varepsilon(b_{1g}) < \varepsilon(a_{1g})$ holds true, then $\Delta_z < \Delta_{xy}$ and consequently the zero-field-splitting parameter is negative, $D < 0$. For an elongated tetragonal bipyramid, $\varepsilon(e_g) > \varepsilon(b_{2g})$, $\varepsilon(b_{1g}) > \varepsilon(a_{1g})$, then $\Delta_z > \Delta_{xy}$. Consequently, $D > 0$ applies. Upon involvement of the covalency effects, setting a moderate anisotropic covalency causes a shift of the *D* value without the sign reversal. However, much pronounced anisotropy (e.g., α, $\beta \sim 0.7$ and γ, $\delta \sim 1$) alters the sign of *D*. Simple MO calculations based on extended Hückel theory (EHT) were made to figure out one-electron orbital energies using the crystallographic coordinates of the complexes studied. Figure 3 compares the energies of the σ-type MOs $a_{1g}(d_{z^2})$ and $b_{1g}(d_{x^2-y^2})$ (in an approximation of the ideal D_{4h} symmetry) of all complexes and creates a suitable "springboard" for qualitative deduction. On the basis of the above considerations and the obtained MO-splitting scheme, a *D*-sign assignment can be done easily. Notice that orbital analysis confirmed a moderate anisotropy of the metal–ligand bond covalency (as could be expected from bond distances). Although this does not alter the sign of the *D* parameter, it moves the *D* values toward larger or smaller values.

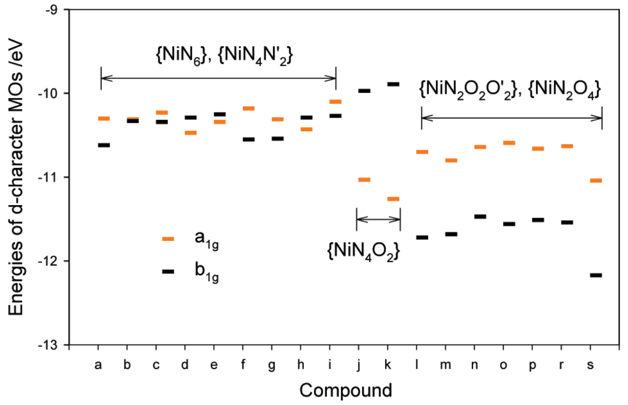

Figure 3. Comparison of one-electron MO energies (EHT) for the complexes studied.

In order to bring some light to the physical origin of the above correlation, we derive a crystal-field expression of the D_{str} parameter.[3e] A modeling of the magnetic *D* values (exact multiplet splitting)[6b] depending upon this transformed structural ordinate $D_{\mathrm{str}} = R_{\mathrm{ax}}X_{\mathrm{F}}$ is shown in Figure S3 in the Supporting Information. The important message is that such a dependence is generally nonlinear. Within the relevant experimental range, it can follow a nearly linear relationship. However, we found that the best-fit equation could be an exponential function (see Figure 2).

The presented correlation allows one to predict that $D < 0$ occurs for the tetragonally compressed nickel(II) complexes. However, the magnetic as well as structural data bring evidence also for the rhombic anisotropy, which has not been included in the correlation. As can be seen, the largest deviants are achieving values for $\{NiN_2O_2O'_2\}$-type complexes **l**, **m**, and **n**. Resolving this problem could eliminate the remaining inaccuracies.

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Supporting Information Available: Magnetic data, complete set of fitted spin-Hamiltonian parameters, orbital diagrams, and calculated D_{mag} as a function of the crystal-field strengths F_4 and the structural tetragonality. This material is available free of charge via the Internet at http://pubs.acs.org.

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