Ligand-Field Calculations on Pseudo-Tetragonal Ni(II) Compounds

Interpretation of Magnetic Measurements and Ligand-field Spectra in a Single Model

A. Vermaas and W. L. Groeneveld

Department of Coordination Chemistry, Gorlaeus Laboratories, State University,
P.O. Box 75, Leiden, The Netherlands

and J. Reedijk

Department of Chemistry, Delft University of Technology, Delft, The Netherlands

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Magnetic susceptibility, magnetic saturation, ligand field and EPR measurements are reported for the compounds Ni(5-methyl pyrazole)$_4$X$_2$, (X = Cl, Br, I). All data are interpreted using ligand-field calculations, yielding parameters Dq, Ds, Dt, B, C, $g_{||}$, $g_{\perp}$, D, $\zeta_{||}$, $\zeta_{\perp}$ and k.

All data fit with a single set of parameters. The zero-field splittings and g values are determined from the magnetic measurements, whereas the excited state splittings are determined from the ligand-field spectra.

In studying the relation between the zero-field splitting of the Ni(II) ion and both the spin-orbit coupling and spectroscopic energy parameters, a description using an anisotropic spin-orbit coupling gave the most reliable fit.

In addition, known ligand-field spectra and D values of Ni(pyrazole)$_4$X$_2$, (X = Cl, Br, I) were considered. The derived energy parameters of the corresponding pyrazole and 5-methyl pyrazole compounds are very similar.

Introduction

Nickel(II) ions in octahedral symmetry posses a $^3A_{2g}$ ground state and three threefold orbitally degenerate excited states with spin multiplicity three. When the symmetry is lowered, the threefold spin-degenerate ground state splits by second-order spin-orbit interaction with the excited states that exhibit an orbital splitting[1]. Therefore, the magnitude of the ground state splitting parameter(s) will depend upon the orbital splittings of the excited states.

In the past Gerloch et al.[2] have calculated crystal-field and Racah parameters from experimental data, and calculated the zero-field splitting in a tetragonal case for sets of crystal-field and Racah parameters; however, no measurements to obtain the zero-field splitting for the compounds under investigation were reported. Several other workers[3–6] also calculated crystal-field and Racah parameters from their optical measurements.

In order to determine the relation between the ground state splitting and the orbital splittings of the excited states, we determined both the ground state splittings and the energies of the excited states for three compounds with formula Ni(mpz)$_4$X$_2$, where mpz stands for 5-methyl pyrazole and X = Cl, Br or I. In addition, earlier measurements on Ni(pz)$_4$X$_2$ that have relevance to this subject were reinvestigated. In this formula pz stands for pyrazole. The magnitude of the ground-state splitting was determined by magnetization measurements and EPR spectra, and the energies of the excited states were obtained from diffuse reflectance spectra.

Experimental Section

The compounds Ni(mpz)$_4$X$_2$ have been synthesized as described previously[7]. Magnetization measurements of powdered samples were performed by means of a PAR vibrating sample magnetometer, model 150. For each compound both magnetic saturation from 0 to 52,400 Oersted at distinct temperatures, and magnetic susceptibility in the 2 to 80 K region at fields of about 5000 Oersted were measured.

Diffuse reflectance spectra were obtained with a Beckman DK-2A spectrophotometer in the 325 to 2000 nm region, using magnesium oxide as a reference. A low temperature attachment was used, as described by Fackler and Holah[8].

Paramagnetic resonance spectra of powdered samples were recorded both at X-band and Q-band frequencies on Varian instruments by methods described previously[9, 10].

Reprint requests to Dr. A. Vermaas, Gorlaeus Lab. k 414, State University, P.O. Box 75, *Leiden/Netherlands.*

Starting Points and Theory

Model

Discussing the relation between the ground state splitting and the energies of the excited states, we will use calculations that involve the diagonalization of the complete d^8 manifold, perturbed by interelectronic repulsion, crystal-field and spin-orbit coupling effects and the Trees correction [11–13] under the Hamiltonian.

$$\hat{H} = \sum_{i<j}^{2} e^2/r_{ij} + \hat{V}_{\text{c.f.}} + \hat{H}_{\text{s.o.}} + \alpha L(L+1) \,. \qquad (1)$$

Structural Details

To set up an expression for the crystal-field Hamiltonian, we used known crystal structures of pyrazole and 5-methylpyrazole compounds. The crystal structures of $\mathrm{Ni(pz)_4Cl_2}$ and $\mathrm{Ni(pz)_4Br_2}$ have been published [14, 15]. These crystals are both monoclinic and have space group C2/c with four molecules per unit cell. The only rigorous molecular symmetry element in these molecules is a centre of symmetry on the nickel ion, and thus the rigorous point group is C_i. For the $\mathrm{Ni(N)_4X_2}$ unit, however, the point symmetry appears to be close to D_{4h}: the Ni – N distances of the two types of different pyrazole rings are nearly the same, and the deviation of the X – Ni – X line with the normal to the plane through the four coordinating nitrogen atoms (the basal plane) is less than 0.5 degrees. For the $\mathrm{Ni(pz)_4X_2}$ unit, the pyrazole rings are only slightly tilted from a position perpendicular to the basal plane, so that an axis perpendicular to that plane is nearly a fourfold axis, as far as the arrangements of the atoms in the rings are not considered.

For the compounds $\mathrm{Ni(mpz)_4X_2}$ no crystal structures are known. The crystal structure of $\mathrm{Mn(mpz)_4Br_2}$ [16], however, has been reported. The X-ray diffraction patterns of the powders of $\mathrm{Mn(mpz)_4Br_2}$ and $\mathrm{Ni(mpz)_4Br_2}$ appeared to be very similar both in *d* values and intensities [7]. Therefore, we assumed that the compounds $\mathrm{Ni(mpz)_4X_2}$ have the same crystal and molecular structure as $\mathrm{Mn(mpz)_4Br_2}$. This latter compound has space group $P\bar{1}$ with one molecule per unit cell. The only rigorous symmetry element is a centre of symmetry on the Mn(II) ion and thus the rigorous point group is C_i. However, the point symmetry appears to be close to C_{2h}. As in the pyrazole compounds, the Mn – N distances of the two types of different pyrazole rings are nearly the same and, furthermore, the deviation of the Br – Mn – Br line from the normal to the plane through the four coordinating nitrogens (the basal plane) is less than 1.5 degrees. Contrary to the pyrazole compounds however, the methyl pyrazole rings are tilted much more from a position perpendicular to the basal plane. The values of the tilt angles for the two rings are nearly equal. The consequence of this feature is that, besides the rigorous symmetry element of inversion, the only pseudo-symmetry elements are a twofold axis in the basal plane, and a plane of symmetry perpendicular to that axis. This results in a point symmetry close to C_{2h}. We assume in the following sections that the chloride and iodide compounds have similar point symmetry.

Calculations

The crystal-field Hamiltonian we have chosen for the pyrazole compounds is one that agrees with the point group D_{4h}. With the aid of the method given by Hutchings [17] and after evaluating the radial parts of the matrix elements a one-electron crystal-field Hamiltonian is obtained that is acting on the angular parts of the wave functions:

$$V'_{\text{c.f.}} = D\,q^{xy} \cdot (O_4{}^0 + 5 \cdot O_4{}^4)/12 + D\,s \cdot O_2{}^0/3 - D\,t \cdot O_4{}^0/12 \qquad (2)$$

where $D\,q^{xy}$, $D\,s$ and $D\,t$ have their usual meaning [1].

The theory of spin-orbit coupling effects in crystal fields of lower symmetry has been thoroughly investigated by Lulek [18].

For our purpose the spin-orbit coupling Hamiltonian is simplified to

$$\hat{H}_{\text{s.o.}} = -\sum_{i=1}^{2} [\zeta_{\parallel}\, \mathrm{l}_{iz}\, s_{iz} + \zeta_{\perp} (\mathrm{l}_{ix}\, s_{ix} + \mathrm{l}_{iy}\, s_{iy})] \qquad (3)$$

where $\zeta_{\parallel}$ and $\zeta_{\perp}$ are the spin-orbit coupling parameters.

By the action of the complete D_{4h} perturbation Hamiltonian, the ground state which is $^3A_{2g}$ in an octahedron, splits into a non-degenerate and a twofold degenerate level. Concerning the excited states, the three orbital triplet states in octahedral field, all split into two states if spin-orbit coupling effects are neglected. This splitting has been observed in the polarized single crystal spectra for the two excited triplet states that are lowest in energy [6].

The diffuse reflectance spectra of the 5-methyl pyrazole compounds are very similar to those of the pyrazole compounds. The additional splitting of excited states by the descending of symmetry from point group D_{4h} to C_{2h} could not be detected, being apparently too small with respect to the experimental resolution.

Since the primary purpose of this investigation is an interpretation of both optical and magnetic measurements within the same model, a perturbation Hamiltonian appropriate to D_{4h} symmetry, i. e.

$$H = \sum_{i<j}^{2} e^2/r_{ij} - \sum_{i=1}^{2} V'_{\text{c.f.}}(i) + H_{\text{s.o.}} + \alpha\, L(L+1) \qquad (4)$$

will also be used for the mpz compounds. In (4) the summation over i is the summation over the two electron holes.

Calculated matrix elements of the 45×45 matrix for a D_{4h} Hamiltonian with isotropic spin-orbit interaction have been reported before[20, 21]: Perumareddi[20] used a set of symmetry adapted eigenvectors; Mooney and Smith[21] used a set of basic functions in $|L, L_z, S, S_z\rangle$ quantization. However, some of the matrix elements used by Mooney and Smith are incorrectly printed.

The correct expressions for these matrix elements are:

$$\begin{aligned}
A(2,11) &= A(8,29) = \zeta/2\,,\\
A(12,12) &= A(28,28)\\
&= -3\,Dq - 3\,\zeta/2 + Ds + 3\,Dt + 12\,\alpha\,,\\
A(4,19) &= A(6,21) = 5\,\zeta/\sqrt{70}\,,\\
A(16,16) &= A(24,24)\\
&= -Dq + \zeta/2 - 3\,Ds/5 + Dt + 12\,\alpha\,,\\
A(19,19) &= A(20,20) = A(21,21)\\
&= -6\,Dq - 4\,Ds/5 + 6\,Dt + 12\,\alpha\,,\\
A(19,32) &= A(21,34) = -\sqrt{(12/35)}\,\zeta\,,\\
A(45,45) &= 22\,B + 7\,C
\end{aligned}$$

Results and Discussion

Ligand-field Spectra and Calculations Concerning Excited State Energies

Room temperature ligand-field spectra of $Ni(mpz)_4X_2$ where X is a halide have been published before[19]. We have now also measured the diffuse reflectance spectra at lower temperature. The shapes of these spectra are very similar to those published before. The spectra show small shifts to higher energy as usually observed upon cooling. The absorption bands have been fit with values calculated with the Hamiltonian in (4). The assignment of the peaks was taken analogous to that in the pz compounds[6].

Furthermore, some transitions in the 20,000 cm^{-1} region could be assigned to triplet-singlet transitions. These transitions were not assigned by Reimann[6]. Using these assignments we are able to calculate the value of the Racah parameter C.

The observed absorption bands as well as the calculated values are presented in Table I. For the experimental absorption bands of $Ni(pz)_4Cl_2$ and $Ni(pz)_4Br_2$ we used the data given by Reimann[6]. Because of the resolution of our spectrophotometer and band broadening due to vibrations, only band splittings larger than about 500 cm^{-1} could be detected, so that no spin-orbit splittings could be detected. The reported calculated values are the average values over a number of levels originating from the same orbital terms and are rounded on multiples of 100 cm^{-1}.

The spectrochemical parameters that give the best fit within our assignment are listed in Table II. In the calculations, the spin-orbit coupling parameters were chosen such that they are in agreement with the zero field splitting (vide infra) and α was fixed at 75 cm^{-1}. This value of α means a reduction with respect to the free ion value as is usually observed in nickel (II) compounds[21]. Neglecting the Trees correction (thus, $\alpha = 0$) yields poorer fits. In that case the calculated B values are in general 50 cm^{-1} smaller.

Concerning the values of the crystal field parameters the following remarks can be made:

i. The Dq^{xy} values are all very close to each other; in agreement with the proposed structure the Dq^{xy} of the pyrazole compounds is nearly the same as that of the corresponding 5-methyl pyrazole compounds. The Dq^{xy} values increase with decreasing temperature, except for $Ni(mpz)_4I_2$. The increase in Dq^{xy} is a feature that is generally observed[6, 22] and is thought to be caused by the compression of the crystal with decreasing temperature. The deviating behaviour of $Ni(mpz)_4I_2$ may be due to the fact that the two absorptions near 11,000 cm^{-1} could not be detected separately and, furthermore, the spin-allowed band highest in energy was not observed because of a charge transfer absorption in that region.

Table I. Observed and calculated ligand-field transitions of Ni(II) compounds.

Compound	$Ni(pz)_4Cl_2$		$Ni(pz)_4Br_2$		$Ni(mpz)_4Cl_2$				Assignment [a]
Temperature (K)	295		295		110		295		
Absorption frequencies (cm^{-1})	obs.	calc.	obs.	calc.	obs.	calc.	obs.	calc.	
	8000	8000	7240	7250	8100	8100	7900	7900	$^3E_g(^3T_{2g}(F)) \leftarrow {}^3B_{1g}$
	10950	10950	10900	10900	11100	11100	11000	11000	$^3B_{2g}(^3T_{2g}(F)) \leftarrow$
	13100	13100	12000	12000	13300	13300	13100	13100	$^3A_{2g}(^3T_{1g}(F)) \leftarrow$
	13500	13700	—	13600	—	13600	—	13500	$^1B_{1g}(^1E(D)) \leftarrow$
	16400	16400	15900	15900	16600	16500	16200	16200	$^3E_g(^3T_{1g}(F)) \leftarrow$
	21000*	21000	—	20100	21100	21100	20800	20800	$^1E_g(^1T_{2g}(D)) \leftarrow$
	23200*	23800	—	23200	23400	23900	—	23700	$^1B_{2g}(^1T_{2g}(D)) \leftarrow$
	26500	26500	25800	25800	26600	26600	25900	25900	$^3E_g, {}^3A_{2g}(^3T_{1g}(P)) \leftarrow$

Compound	$Ni(mpz)_4Br_2$				$Ni(mpz)_4I_2$				Assignment [a]
Temperature (K)	125		295		135		295		
Absorption frequencies (cm^{-1})	obs.	calc.	obs.	calc.	obs.	calc.	obs.	calc.	
	7500	7500	7400	7400	6500	6500	6200	6200	$^3E_g(^3T_{2g}(F)) \leftarrow {}^3B_{1g}$
	11000	11000	10800	10800	10800	10800	10900	10900	$^3B_{2g}(^3T_{2g}(F)) \leftarrow$
	12100	12000	11900	11900	—	—	—	—	$^3A_{2g}(^3T_{1g}(F)) \leftarrow$
	—	13800	—	13400	—	13400	—	13500	$^1B_{1g}(^1E_g(D)) \leftarrow$
	16300	16300	15900	15900	15600	15500	15200	15200	$^3E_g(^3T_{1g}(F)) \leftarrow$
	20500	20500	20000	20000	19200	19200	19000	19000	$^1E_g(^1T_{2g}(D)) \leftarrow$
	—	22600	—	22400	—	—	—	—	$^1B_{2g}(^1T_{2g}(D)) \leftarrow$
	26100	26100	25500	25500	—	—	—	—	$^3E_g, {}^3A_{2g}(^3T_{1g}(P)) \leftarrow$

* At 77 K⁰.

[a] The given representations are irreducible representations of the D_{4h} point group. In parentheses are the representations of the splitted octahedral point group and the free ion multiplets.

Table II. Spectrochemical parameters of Ni(II) compounds (in cm^{-1}).

Compound	Temp. (K)	Dq^{xy}	Ds	Dt	B	C	α	Dq^z
$Ni(pz)_4Cl_2$	295	1095	1040	285	940	3400	75	595
$Ni(pz)_4Br_2$	295	1090	1250	345	920	3400	75	490
$Ni(mpz)_4Cl_2$	110	1110	1000	290	935	3400	75	600
$Ni(mpz)_4Cl_2$	295	1100	950	300	900	3450	75	580
$Ni(mpz)_4Br_2$	125	1100	1350	320	905	3525	75	540
$Ni(mpz)_4Br_2$	295	1080	1250	320	890	3400	75	520
$Ni(mpz)_4I_2$	135	1080	1500	390	900	3400	75	400
$Ni(mpz)_4I_2$	295	1090	1400	440	900	3400	75	320

ii. The tetragonal distortion parameters Ds and Dt are large, indicating a large difference in coordinating properties between the pyrazole ligands and the halide ions.

iii. The Ds and Dt values of the corresponding pz and mpz complexes are close to each other; the methyl substituent does not seem to influence the tetragonal distortion parameter very much.

iiii. The Dq^z values which can be obtained by the relation

$$Dq^z = Dq^{xy} - \tfrac{7}{4} Dt \qquad (5)$$

are much lower than the Dq values of the compounds NiX_2 [23].

As concluded earlier, this is a manifestation of the unusually long metal-halide distance [14–16].

Experiments and Calculations Concerning the Ground State

A) Electron Paramagnetic Resonance

Attempts were made to obtain EPR powder spectra for the compounds $Ni(pz)_4X_2$ and $Ni(mpz)_4X_2$. The compounds $Ni(pz)_4X_2$ showed no EPR spectra. This feature is expected for tetragonal compounds with large zero field splittings; the magnetic fields for obtaining such spectra should be higher than is experimentally available. For the compounds $Ni(mpz)_4X_2$ the zero field splitting is also large (vide infra). According to the structure determination [16] these compounds have a symmetry lower than tetragonal. This lowering of symmetry with respect to the pyrazole compounds has also been detected in measurements on the powder isomorphic $Fe(mpz)_4X_2$ compounds [24]. By the action of the part of the Hamiltonian that reflects this lower symmetry the double degenerate ground state doublet Γ_5 (D_{4h}) is split. For a certain range of such splittings an EPR absorption at experimental magnetic fields is possible, due to a change of the energy level pattern with respect to the tetragonal case and, furthermore, mixing of the levels takes place so that now all possible transitions are allowed. Nevertheless, no EPR spectra were obtained for all three $Ni(mpz)_4X_2$ compounds, either at X-band or at Q-band frequencies. Therefore, we can conclude that the splitting of Γ_5 is very small so that either the situation is too alike the tetragonal case or that the splitting of Γ_5 is so large that even no Q-band transitions are possible. We believe that because of the structural data the first situation is the more probable one.

B) Magnetic Susceptibility

For all three $Ni(mpz)_4X_2$ compounds magnetization measurements for varying magnetic fields at various temperatures were recorded as well as magnetic measurements for varying temperatures at a magnetic field of about 5000 Oersted. Calculations were carried out to fit these experimental data. We performed the calculations for purely paramagnetic compounds and used an ab initio method as given before [25]. Moreover, a corrected method [26, 27] was applied to obtain the average magnetization of a powder. The spin Hamiltonian used in the calculations only involves tetragonal terms. This is because the lower symmetry splitting for the mpz compounds

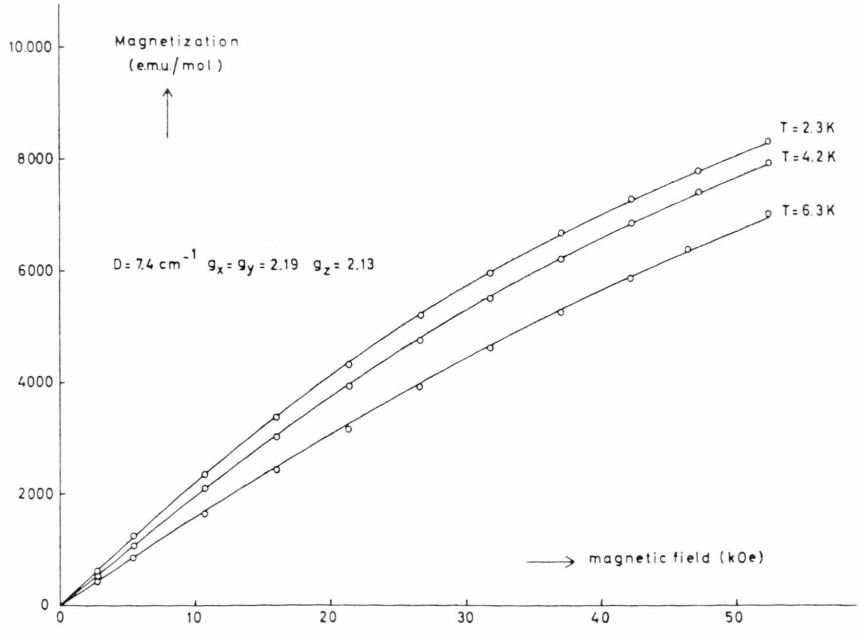

Fig. 1. Calculated saturation magnetization curves for $D = 7.4\ cm^{-1}$, $g_x = g_y = 2.19$ and $g_z = 2.13$ at temperatures of 2.3, 4.2 and 6.3 K. Measurements for $Ni(mpz)_4Cl_2$ are shown as circles.

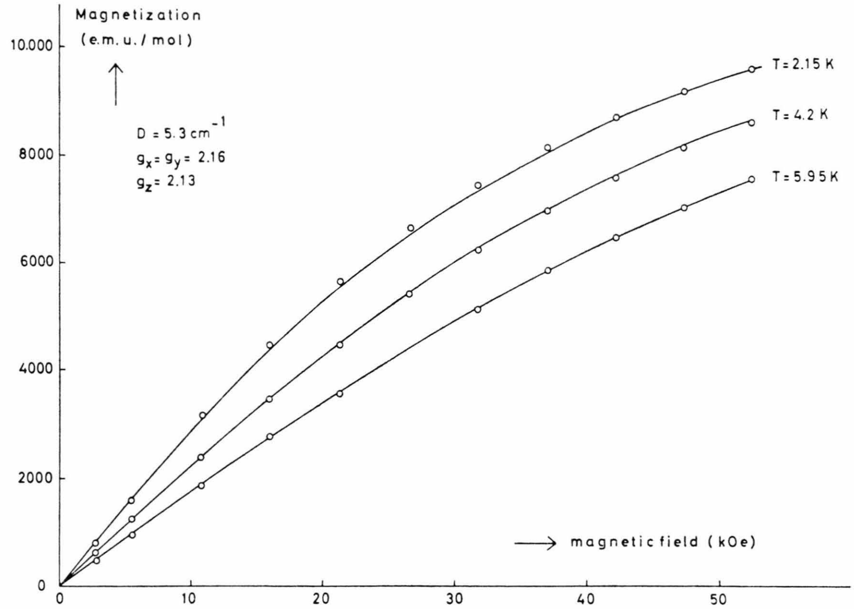

Fig. 2. Calculated saturation magnetization curves for $D=5.3$ cm^{-1}, $g_x=g_y=2.16$ and $g_z=2.13$ at temperatures of 2.15, 4.2 and 5.95 K. Measurements for Ni(mpz)$_4$Br$_2$ are shown as circles.

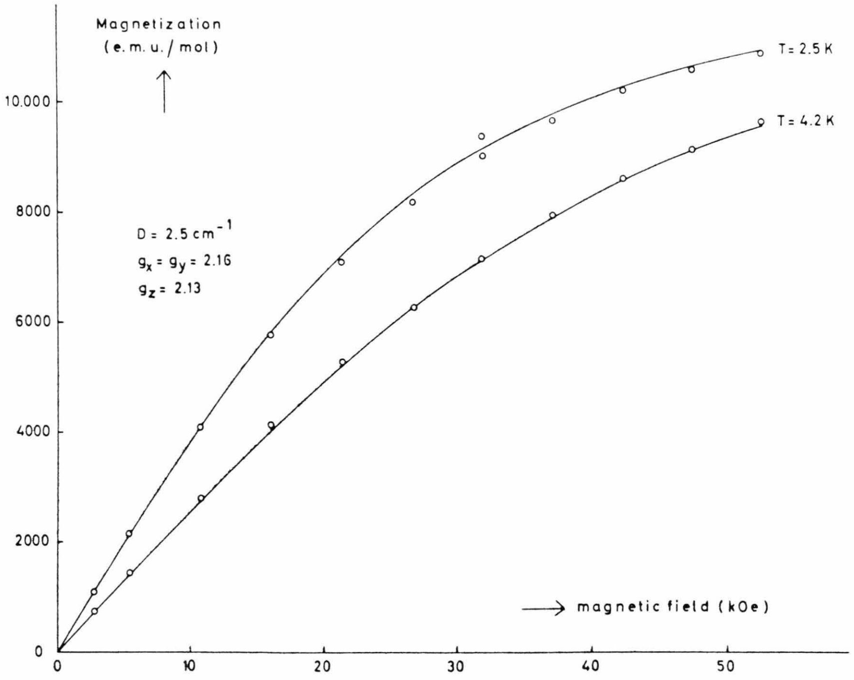

Fig. 3. Calculated saturation magnetization curves for $D=2.5$ cm^{-1}, $g_x=g_y=2.16$ and $g_z=2.13$ at temperatures of 2.5 and 4.2 K. Measurements for Ni(mpz)$_4$I$_2$ are shown as circles.

only influences the Γ_5 (D$_{4h}$) doublet which appears to be higher in energy (vide infra). It can be shown that the influence of this lower symmetry splitting on the magnetic behaviour will be negligible. In the calculations we used two kinds of g values: $g_{\parallel}$, that is the g value along the pseudo-tetragonal axis and $g_{\perp}$, the g value perpendicular to that axis. From our experimental results these two g values could not be determined separately. We, therefore, derived the average g value from our high temperature magnetic data and next determined the distinct g values by assuming that the orbital reduction factor k is

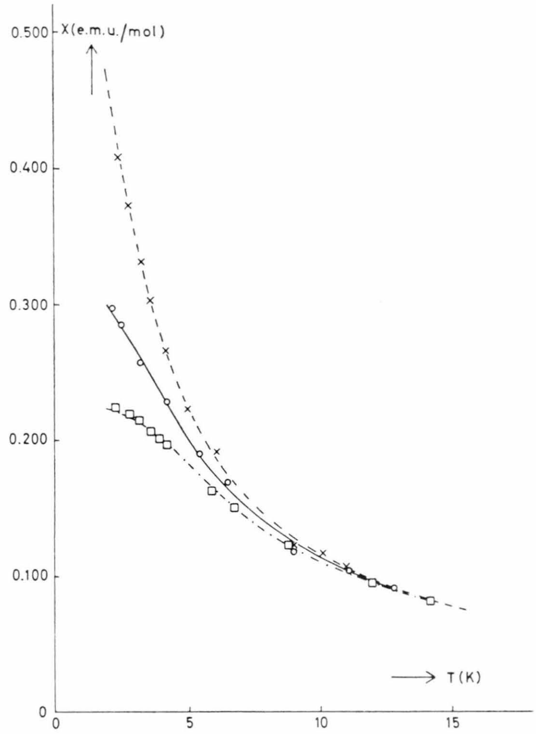

Fig. 4. Calculated curves for the powder paramagnetic susceptibility for
---- $D=2.5$ cm^{-1}, $g_x=g_y=2.16$, $g_z=2.13$,
——— $D=5.3$ cm^{-1}, $g_x=g_y=2.16$, $g_z=2.13$,
—·—· $D=7.4$ cm^{-1}, $g_x=g_y=2.19$, $g_z=2.13$.
Measurements are shown as
× for Ni(mpz)$_4$I$_2$, ○ for Ni(mpz)$_4$Br$_2$,
□ forNi(mpz)$_4$Cl$_2$.

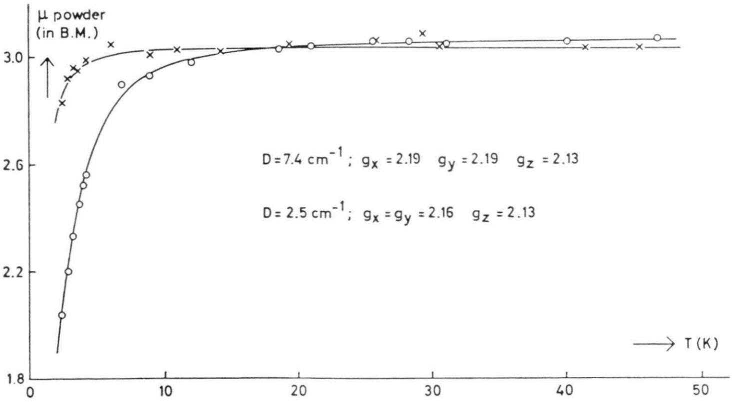

Fig. 5. Calculated curves of powder paramagnetic moment for $D=2.5$ cm^{-1}, $g_x=g_y=2.16$ $g_z=2.13$ (the higher one at low temperature) and $D=7.4$ cm^{-1}, $g_x=g_y=2.19$, $g_z=2.13$ (the lower one at low temperature). Measurements are shown as × for Ni(mpz)$_4$I$_2$, ○ for Ni(mpz)$_4$Cl$_2$.

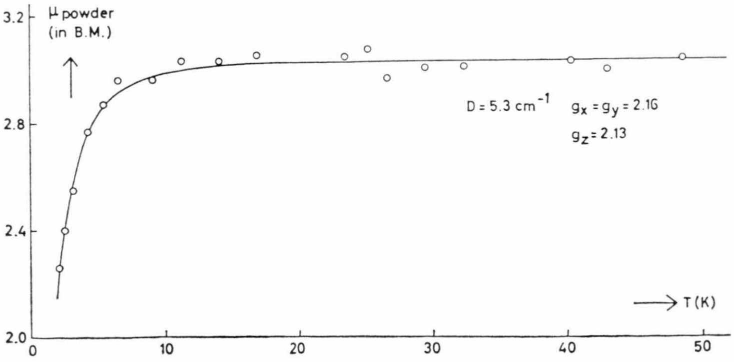

Fig. 6. Calculated curve of powder paramagnetic moment for $D=5.3$ cm^{-1}, $g_x=g_y=2.16$ and $g_z=2.13$. Measurements for Ni(mpz)$_4$Br$_2$ are shown as circles.

equal in the two distinct directions. For the calculation of the distinct g values the ground state eigenfunctions were used, obtained by the ligand field calculations for the lower temperature. With the g values determined in this way the zero field splitting was calculated by means of the results of magnetic measurements at low temperatures.

Table III. Ground state parameters of Ni(II) compounds.

Compound	D (cm^{-1})	$g_\perp$	$g_\parallel$	k
Ni(mpz)$_4$Cl$_2$	7.4(2) [a]	2.13(2) [b]	2.19(2)	0.85
Ni(mpz)$_4$Br$_2$	5.3(2)	2.13(2)	2.16(2)	0.65
Ni(mpz)$_4$I$_2$	2.5(3)	2.13(2)	2.16(2)	0.6
Ni(pz)$_4$Cl$_2$	7.2(1)	2.14(3)	2.21(3)	
Ni(pz)$_4$Br$_2$	5.4(1)	2.12(3)	2.20(3)	

[a] Uncertainties in the last digit are shown in parentheses.
[b] The uncertainties shown for the g values of the mpz compounds concern the average g value.

The calculated curves as well as the experimental data are shown in Figures 1 to 6. The two different types of magnetic measurements were fitted with the set of parameters D, $g_\parallel$, $g_\perp$ and k. In Table III the D, g and k values are listed for the compounds under investigation. The available data for two pyrazole compounds [25] have been listed for comparison. Both the D and g values of Ni(mpz)$_4$X$_2$ are close to those of the corresponding Ni(pz)$_4$X$_2$ compounds; the differences being within experimental error.

Furthermore, calculations were carried out to explain the obtained D values. We already calculated the crystal-field parameters and Racah parameters from our ligand-field data. For the following section the spectroscopic parameters obtained for the lower temperature were used. The D values are, apart from the spectroscopic parameters also determined by the spin orbit coupling parameters $\zeta_\parallel$ and $\zeta_\perp$. To fit D values with spin-orbit coupling parameters two different methods were followed:

1. Anisotropic spin-orbit interaction. Because it is assumed that the coordination perpendicular to the pseudo-tetragonal axis is equal for all three Ni(mpz)$_4$X$_2$ compounds, $\zeta_\perp$ was fixed and set at $\zeta_\perp = 500$ cm^{-1} introducing a reduction from the free ion value of 20%. The $\zeta_\parallel$ values were now chosen such that they were consistent with the D value.

2. The spin-orbit coupling parameter was assumed to be isotropic and chosen to be consistent with the D value. The spin-orbit coupling parameters that were obtained according to the two methods are shown in Table IV.

From Table IV it can be seen that the ζ values derived according to method 2 vary very much for the various anions. Especially the very low ζ value for Ni(mpz)$_4$I$_2$ seems to be unrealistic. In the past it has been shown that for some pseudo-tetragonal Ni compounds zero field splittings could be explained only by assuming an anisotropy in the spin-orbit coupling parameter [26].

Table IV. Zero field splitting and spin-orbit coupling parameters of Ni(II) compounds (in cm^{-1}).

Compound	D	Method 1		Method 2
		$\zeta_\parallel$	$\zeta_\perp$	ζ
Ni(mpz)$_4$Cl$_2$	7.4	500	460	582
Ni(mpz)$_4$Br$_2$	5.3	500	522	438
Ni(mpz)$_4$I$_2$	2.5	500	620	241
Ni(pz)$_4$Cl$_2$	7.2	500	468	571
Ni(pz)$_4$Br$_2$	5.4	500	540	419

Also in our case the ζ values calculated according to method 1 seem to be more realistic than the ζ values according to method 2. We remark that $\zeta_\parallel$ increases in the sequence Cl$^-$ < Br$^-$ < I$^-$. The larger value of $\zeta_\parallel$ in the halogen direction for Br$^-$ compared to Cl$^-$ was found before [28].

Conclusions

From the results of our investigations the following conclusions may be drawn:

i. Both the ground-state splitting and the excited-state splitting of these pseudo-tetragonal Ni(II) compounds can be fit with a single set of parameters.

ii. The zero-field splittings of the compounds Ni(mpz)$_4$X$_2$ closely resemble those of the corresponding pz compounds.

iii. The interpretation of the zero-field splittings using an anisotropic spin-orbit interaction shows that ζ in the halogen direction has the sequence Cl < Br < I.

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