Allowed and Forbidden d-d Transitions in Poly(3,5-dimethylpyrazolyl)methane Complexes of Nickel(II)†

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ABSTRACT

Absorption spectra of four nickel(II) complexes with poly(pyrazolyl)methane ligands are presented in the NIR-VIS-UV region and the band system corresponding to the lowest-energy spin-allowed and spin-forbidden transitions is analyzed. A quantitative theoretical model involving coupled electronic states provides precise energies for the lowest-energy triplet and singlet excited states and allows comparisons between complexes with a variable number of nitrogen and oxygen ligator atoms. Singlet energies between 12 840 and 13 000 cm⁻¹ are determined for heteroleptic complexes. These energies are in an intermediate range between those for homooleptic complexes with either nitrogen or oxygen ligator atoms with singlet states at approximately 12 000 and 14 000 cm⁻¹, respectively. The new theoretical approach is compared to the traditional ligand-field parameters obtained from the maxima of the broad, spin-allowed absorption bands.

INTRODUCTION

Poly(pyrazolyl)alkane ligands and their metal complexes are used extensively in inorganic and bioinorganic chemistry because of their interesting chemical reactivity and suitability as model compounds. (1–3) Although the electronic structure of these complexes is an important factor determining these properties, only a few investigations of their electronic spectroscopy have been reported. (3–6)

Nickel(II) forms a wide variety of different complexes with poly(pyrazolyl)alkane ligands. The coordination number for these d⁸ complexes is six and distorted octahedral coordination geometries are observed, with the deviations from perfect octahedral structure imposed by the poly(pyrazolyl)alkane ligands, coordinated through their nitrogen ligator atoms. The number and type of poly(pyrazolyl)alkane ligands are easily varied.

We report and analyze the UV-VIS-NIR absorption spectra of four nickel(II) complexes with bis(3,5-dimethylpyrazolyl)methane (bpm*) and tris(3,5-dimethylpyrazolyl)methane (tpm*) ligands. All structures are shown schematically in Chart 1. These ligands offer an opportunity to vary the coordination sphere from three nitrogen and three oxygen atoms in [(tpm*)Ni(η¹-NO3)(η²-NO3)] (1) to four nitrogen and two oxygen atoms in [(bpm*)₂Ni(η¹-NO3)]NO3 (2), to five nitrogen and one oxygen atom in (tpm*)(bpm*)Ni(η¹-NO3)NO3 (3) and finally to six nitrogen atoms in [(tpm*)₂NiI₂ (4). The absorption spectra are analyzed to examine to what extent trends such as the empirical spectrochemical and nephelauxetic series (7,8)—both now correlated and reformulated with advanced electronic structure calculations such as density functional theory (9)—can be used to rationalize the variations observed within complexes 1 to 4. A theoretical model recently developed by Neuhauser et al. (10) is applied and shown to be a useful tool to obtain precise excited-state energies from complete absorption band systems, an intrinsic advantage over traditional models that use only band maxima with often significant uncertainties. This new approach is shown to be successful for variations among closely related compounds, as is the case for the series of complexes 1 to 4.

MATERIALS, CHARACTERIZATION AND METHODS

The syntheses, characterization and crystal structures of complexes 1 to 3 (A. Michaud, F.-G. Fontaine, and D. Zargarian, in press, Inorg. Chim. Acta [2006], doi:10.1016/j.ica.2005.09.046) and 4 (11) are described in the literature. Absorption spectra of complexes 1 to 4 in acetonitrile solution were measured with a Cary 5E spectrometer (Varian Inc., Palo Alto, CA) with the spectral resolution set to 2 nm from 1600 nm to 900 nm, measured for the broad bands in these spectra are typical for the three spin-allowed d-d transitions in six-coordinate, exactly or approximately octahedral complexes of nickel(II), as documented in a detailed compilation. (12) The band maxima for complexes 1 to 4 are summarized in Table 1 and compared to those for selected reference compounds. The bands are easily assigned from the Tanabe-Sugano diagram for octahedral complexes with the d⁸ electron configuration, shown in Fig. 2. The ground state is ³A₂g and three spin-allowed transitions to the ³T₂g,
$^5T_{1g}(3F)$ and $^3T_{2g}(3P)$ excited states are observed. Broad bands are expected for all these transitions, because the excited states arise from electron configurations different from the ground state configuration. Symmetry labels for an idealized octahedral structure are used throughout this analysis. Point-group symmetries of the nickel(II) sites determined by single-crystal X-ray diffraction are $C_1$ for complexes 1 and 2 (A. Michaud, F.-G. Fontaine, and D. Zargarian, accepted for publication), $C_s$ for complex 3 (A. Michaud, F.-G. Fontaine, and D. Zargarian, accepted for publication) and $C_{2h}$ for complex 4 (11). Deviations from octahedral symmetry caused by of the mixed ligand spheres for complexes 1 to 3 do not lead to multiple band maxima for any of the spin-allowed bands in Fig. 1. A formal reason for this is the high holohedrized symmetry of the ligand-field potential (8) in these complexes. The holohedrized symmetry, obtained for orthoaxial complexes by replacing individual ligands along one axis by their average ligand-field strength, is $O_h$ for complex 1 and $D_{4h}$ for complexes 2 and 3, with very similar total ligand field strengths along the three axes, indicating that any splitting of the $^3T_{2g}$ and $^3T_{1g}$ states for octahedral symmetry should be small. All holohedrized symmetries contain a center of inversion, rationalizing the low molar absorptivities as a consequence of the parity selection rule. Complex 4 also has $O_h$ holohedrized symmetry, but shows a particularly broad $^3T_{1g}(3F)$ absorption band with a width at half height of 3340 cm$^{-1}$, significantly larger than the corresponding bands in $[\text{Ni(ethylenediamine)}_3]^{2+}$ and $[\text{Ni(o-phenanthroline)}_3]^{2+}$, complexes with strong trigonal distortions where widths of 1880 and 2030 cm$^{-1}$ are observed. (13,14) Both this large width and the significantly narrower $^3T_{2g}$ band have been rationalized with angular overlap calculations based on single-crystal spectra measured at low temperature (5), which show multiple resolved maxima for this band, as a consequence of the strongly anisotropic nickel(II)-pyrazolyl π bonding in $[\text{Ni(tris(pyrazolyl)methane)}_2]^{2+}$, a complex closely related to 4.

A single band corresponding to a spin-forbidden transition is observed at approximately 13 000 cm$^{-1}$ on the high-energy side of the lowest-energy spin-allowed band for all complexes. Transitions to other singlet states are too weak to be observed in the spectra in Fig. 1. Inspection of the Tanabe-Sugano diagram in Fig. 2 indicates the final state of this transition is $^1E_g$, the lowest-energy singlet state. It arises from the same electron configuration as the ground state and therefore a narrow band is expected.

The band maxima of the spin-allowed transitions are traditionally used to calculate the ligand field parameters 10Dq and B with the following equations: (13,15)

$$10Dq = E(\Delta_{2g} \rightarrow ^3T_{2g})$$
$$15B = E(\Delta_{2g} \rightarrow ^3T_{1g}(3F)) + E(\Delta_{2g} \rightarrow ^3T_{1g}(3P)) - 30Dq$$

All calculated values for 10Dq and B are summarized in Table 1. The 10Dq/B ratios of 11–15 for 1 to 4 are higher than for homoleptic complexes with oxygen ligator atoms, illustrated by [Ni(H$_2$O)$_6$]$^{2+}$ at a 10Dq/B ratio of 9.2 (16) in Fig. 2, and lower than the ratio of 18 for complexes with strong-field ligands such as [Ni(o-phenanthroline)$_3$]$^{2+}$ (13–15), also included on the abscissa of Fig. 2. It has been pointed out for several complexes (4,5,17) that tris(pyrazolyl) ligands appear to be somewhat lower in the spectrochemical series than ligands such as bipyridine or phenanthroline. (18) The maxima of the lowest-energy spin-allowed band for nickel(II) complexes with tris(pyrazolyl)borate ligands (19) have been reported recently. (20) A value of 11 400 cm$^{-1}$ was obtained for [bis(tris(3,5-dimethylpyrazolyl)borate)nickel(II)], lower by only 270 cm$^{-1}$ than for complex 4. In contrast, the homologue [bis(tris(pyrazolyl)borate)nickel(II)] with unsubstituted pyrazolyl groups has a band maximum at 11 900 cm$^{-1}$, higher by 230 cm$^{-1}$ than complex 4. This comparison shows that the energies of spin-allowed
transitions for poly(pyrazolyl)methane and poly(pyrazolyl)borate ligands are very similar and vary by amounts on the same order of magnitude as those for different alkyl substituents on the pyrazolyl groups. The 10Dq/B ratios for complexes 1 to 3 are between 11.7 and 12.3, very similar to the ratio of 12.2 reported for [(bis(3,5-dimethylpyrazol-1-yl)methyl)aminoethane]Ni([N(NO3)])2 (17) as expected from the combination of nitrogen and oxygen ligator atoms, and also to [Ni(NH3)6]2+ and [Ni(pyrazole)6]2+, for which ratios of 12.9 and 12.2 have been determined. (13,16,18) These variations indicate that the 10Dq/B ratio is not a very sensitive quantity for classifying complexes 1 to 4, because similar values are obtained for chemically very different ligands.

The Raman spectra of complexes 1 to 4 show multiple distinct peaks in the region of the metal-ligand stretching modes. All vibrational energies between 200 and 600 cm\(^{-1}\) are listed in Table 2, but unambiguous assignments to either metal-ligand stretching modes or low-frequency ligand-centered vibrational modes cannot be made. In contrast, the Raman-active \(v_1\) vibrational mode of the nitrate anion can be used to confirm the coordination of the NO\(_3\) ligands in complexes 1 to 3. Complex 4 does not contain nitrate and can be used to assign Raman peaks to modes of the poly(pyrazolyl)methane ligands. The \(v_1\) frequency of NO\(_3\) is 1390 cm\(^{-1}\) in the uncoordinated anion (21), and a peak is observed at 1395 cm\(^{-1}\) in complexes 2 and 3, assigned to the NO\(_3\) counterions. The degeneracy of this mode is lifted for coordinated nitrate ligands and two bands are observed. In compounds 1 to 3, they are separated by approximately 150 cm\(^{-1}\), as summarized in Table 2. The frequencies for both monodentate and bidentate coordination are within the characteristic ranges established from Raman (22) and IR (23) spectroscopy, and in agreement with the monodentate and bidentate coordination for the nitrate ligands defined by the crystal structures and shown in Chart 1 for complexes 1 to 3.

**DISCUSSION**

**Traditional ligand-field parameters**

Complexes 1 to 4 show spin-allowed band maxima higher in energy than those for homoleptic complexes with oxygen ligator atoms and lower in energy than those observed for complexes with nitrogen ligator atoms. (13,14,23) The values of 10Dq/B in Table 1 illustrate this trend, in particular when compared to the homoleptic complexes included in the Table and on the abscissa of Fig. 2. Within the series of compounds 1 to 4, it is not obvious to establish the expected systematic trends along the spectrochemical and nephelauxetic series (7–9) from the values of 10Dq and B in Table 1. Compound 4 has the highest value of 10Dq, 11 670 cm\(^{-1}\), as expected for its six nitrogen ligator atoms. According to the

<table>
<thead>
<tr>
<th>Complex</th>
<th>(1A_{1g})</th>
<th>(1T_{2g})</th>
<th>(3A_{2g})</th>
<th>(3T_{1g})</th>
<th>10Dq</th>
<th>B†</th>
<th>10Dq/B</th>
</tr>
</thead>
<tbody>
<tr>
<td>[(tpm*)Ni(NO3)2]3</td>
<td>10 300</td>
<td>16 410</td>
<td>27 040</td>
<td>10 300</td>
<td>837</td>
<td>12.3</td>
<td></td>
</tr>
<tr>
<td>[(tpm*)Ni(NO3)3]+ (2)</td>
<td>10 170</td>
<td>16 800</td>
<td>26 750</td>
<td>10 170</td>
<td>869</td>
<td>11.7</td>
<td></td>
</tr>
<tr>
<td>[(tpm*)Ni(NO3)3]+ (3)</td>
<td>10 420</td>
<td>17 264</td>
<td>27 366</td>
<td>10 420</td>
<td>891</td>
<td>11.7</td>
<td></td>
</tr>
<tr>
<td>[(tpm*)Ni(NO3)]3+ (4)</td>
<td>11 670</td>
<td>18 470</td>
<td>28 330</td>
<td>11 670</td>
<td>786</td>
<td>14.8</td>
<td></td>
</tr>
<tr>
<td>[Ni(pyrazole)6]3+</td>
<td></td>
<td>10 650</td>
<td>17 100</td>
<td>27 500</td>
<td>10 650</td>
<td>843</td>
<td>12.6</td>
</tr>
<tr>
<td>[Ni(NH3)6]3+ §</td>
<td></td>
<td>10 730</td>
<td>17 530</td>
<td>28 110</td>
<td>10 730</td>
<td>830</td>
<td>12.9</td>
</tr>
<tr>
<td>[Ni(o-phenanthroline)6]3+</td>
<td></td>
<td>12 690</td>
<td>19 050</td>
<td>n/a</td>
<td>12 690</td>
<td>710</td>
<td>17.9</td>
</tr>
<tr>
<td>[Ni(H2O)6]3+ §</td>
<td></td>
<td>8850</td>
<td>14 300</td>
<td>25 370</td>
<td>8850</td>
<td>929</td>
<td>9.2</td>
</tr>
</tbody>
</table>

† B is 1082 cm\(^{-1}\) for the free Ni(II) ion.
§ (16).
|| (14).

Within the series of compounds 1 to 4, it is not obvious to establish the expected systematic trends along the spectrochemical and nephelauxetic series (7–9) from the values of 10Dq and B in Table 1. Compound 4 has the highest value of 10Dq, 11 670 cm\(^{-1}\), as expected for its six nitrogen ligator atoms. According to the
spectrochemical series. Values for 10Dq should decrease if nitrogen ligator atoms are replaced by oxygen atoms. Compound 1, with the largest number of oxygen ligator atoms among the four complexes studied here, has a 10Dq value of 10 300 cm⁻¹, significantly lower than 4. In contrast, the intermediate complexes 2 and 3, with two and one oxygen ligator atoms, respectively, do not show a continuous increase of 10Dq.

These irregular trends can be rationalized qualitatively by considering nickel(II)-N(pyrazolyl) bond lengths in tpm*, bpm*, and one oxygen ligator atoms, respectively, do not show lengths are slightly longer, on the order of 2.07 to 2.09 Å for complexes with a mixed ligand sphere. In view of the large number of angular-overlap parameters, the Racah parameter B was determined from the broad absorption maxima in solution spectra. We apply a theoretical model to calculate the absorption spectrum of a forbidden spin-flip transition close in energy to an allowed interconfigurational band. This model successfully reproduces the spectra of many high-symmetry homo-leptic complexes of nickel(II) and chromium(III) where coupled excited states, including their significant interaction through spin-orbit coupling, which is quantitatively included in the model.

**Table 2. Selected Raman frequencies in cm⁻¹**

<table>
<thead>
<tr>
<th>Compound</th>
<th>Ni-ligand stretching region</th>
<th>NO₃⁻, νₒ(E) counterion†</th>
<th>NO₃⁻, νₛ monodentate‡</th>
<th>NO₃⁻, νₛ chelate§</th>
</tr>
</thead>
<tbody>
<tr>
<td>(bpm*)Ni(NO₃)₂</td>
<td>222, 258, 327, 349, 406, 423, 442, 577</td>
<td>n/a</td>
<td>1309, 1460</td>
<td>1325, 1482</td>
</tr>
<tr>
<td>(bpm*)₂Ni(NO₃)</td>
<td>225, 250, 285, 367, 435</td>
<td>1395</td>
<td>n/a</td>
<td>1305, 1480</td>
</tr>
<tr>
<td>(bpm*)₃(tpm*)Ni(NO₃)⁺</td>
<td>216, 347, 383, 416, 480, 491</td>
<td>1396</td>
<td>1275, 1459</td>
<td>n/a</td>
</tr>
<tr>
<td>(tpm*)₂Ni⁺</td>
<td>225, 242, 342, 383, 404, 423, 488</td>
<td>n/a</td>
<td>n/a</td>
<td>n/a</td>
</tr>
</tbody>
</table>

† 1390 cm⁻¹ (21).
‡ 1253–1290 cm⁻¹, 1481–1531 cm⁻¹ (22).
§ 1230–1350 cm⁻¹, 1480–1650 cm⁻¹ (22).

A prominent feature of the absorption spectra in Fig. 1 is the shoulder near the lowest-energy spin-allowed 3A₂g → 3T₂g band, assigned as the spin-forbidden 3A₂g → 3Eg transition. The close proximity of these two excited states leads to strong mixing through spin-orbit coupling, an effect that has been analyzed in detail for a number of homoleptic complexes of nickel(II). The mixing causes an increase of the intensity and bandwidth of the spin-forbidden transition, leading to a band that is easy to detect in the spectra in Fig. 1, in contrast to all other transitions to singlet excited states, which are not observed in Fig. 1. An important consequence of the coupled excited states is the change of band shapes, which also influences the energies of the band maxima. In order to analyze these effects, a quantitative model has to be used, and calculated spectra have to be fitted to experimental data. We apply a theoretical model to calculate the absorption spectrum of a forbidden spin-flip transition close in energy to an allowed interconfigurational band. This model successfully reproduces the spectra of many high-symmetry homo-leptic complexes of nickel(II) and chromium(III) where coupled electronic states of different multiplicity occur. In the following, we apply it for the first time to lower-symmetry, heteroleptic complexes. Figure 3 illustrates the model and all parameters used for the analysis.

The potential energy curves for the 3A₂g ground state as well as the 1Eg and 3T₂g excited states are given by the solid curves in Fig. 3, calculated from ground state vibrational frequencies ω₀ obtained experimentally from the Raman spectra summarized in Table 2 and using the harmonic approximation. Identical frequencies were used for all electronic states in Fig. 3. We use the symbols for all relevant quantities defined in the original publication of this model (10). The energy minimum of the ground-state curve corresponds to the equilibrium geometry. Because no metal-ligand bonding changes occur in the singlet state, its minimum is placed at the same position as the ground state along the normal coordinate in...
Fig. 3. The minimum for the triplet excited state is offset by \( x_A \). The Franck-Condon maximum for the triplet band is given by the parameter \( \Delta \), and the energy differences between the ground and excited state potential energy minima are \( \epsilon_F \) and \( \epsilon_A \) for the singlet and triplet excited states, respectively. The two excited states are coupled by the constant \( \gamma \), expected to be similar in magnitude to the spin-orbit coupling constant for first-row transition metal ions and leading to the adiabatic potential energy surfaces shown as dotted lines in Fig. 3, different from the harmonic diabatic curves. Both sets of curves are necessary to calculate the absorption band system arising from transitions to these coupled excited states. The Hamiltonian for the two excited states described by the coupled potential energy surfaces is given by:

\[
H = \frac{p^2}{2M} + \left[ \begin{array}{cc} 1 & 0 \\ 0 & 1 \\ \end{array} \right] + \left[ \begin{array}{cc} \frac{1}{2} M \alpha^2 \gamma^2 + \epsilon_F \\ \gamma \\ \frac{1}{2} M \alpha^2 (x - x_A)^2 + \epsilon_A \\ \end{array} \right]
\]

(3)

Analytical and numerical solutions for the absorption spectrum resulting from transitions to these two coupled excited states have been published and discussed (10,25). The calculated spectrum involving the coupled states is given by:

\[
\sigma(\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} \langle \psi_0 | e^{-i(\omega_0 x - i\omega t)} | \psi_0 \rangle dt
= \frac{1}{\pi} \text{Im} \langle \psi_0 | H - \omega - i\Gamma^{-1} | \psi_0 \rangle
\]

(4)

The absorption spectra in Fig. 1 do not allow an experimental determination of all triplet excited levels arising from \( ^3T_{2g} \) split by deviations from octahedral symmetry and spin-orbit coupling. We describe the bandshape for the allowed transition to the triplet excited state in the absence of coupling to the singlet excited state by a Lorentz profile with a width of \( \sqrt{\alpha_0 \lambda} \). (10) With this simplification, which also makes it unnecessary to specify individual normal coordinates and offsets \( x_A \), an analytical equation for the absorption spectrum is obtained:

\[
\sigma(\omega) = -\frac{1}{\pi} \text{Im} \left( \frac{\beta}{1 - i\gamma^2 \beta} \right)
\]

(5)

where \( \alpha \) and \( \beta \) are defined as:

\[
\alpha = \frac{1}{\omega - \epsilon_F + i\Gamma}
\]

\[
\beta = \frac{1}{\omega - \Delta + i\sqrt{\alpha_0 \lambda}}
\]

(6)

Spectra calculated with equation (5) are shown in the inset to Fig. 3. The spectra calculated with a value of zero for the coupling constant \( \gamma \) are shown as Lorentz profiles denoted by dotted traces for two different values of \( \epsilon_A \). The traces therefore differ only in the position of the band maximum along the wavenumber axis. The corresponding spectra calculated with a nonzero coupling constant are shown as solid traces in the inset, indicating the important influence of the energy difference between \( \epsilon_A \) and \( \epsilon_F \). For a small difference, a characteristic band shape with two maxima separated by a minimum, denoted as the interference dip (10,25,26), is calculated, as illustrated by the spectrum peaking at higher energy. The difference between this spectrum and the Lorentz profile is given as a dotted trace at zero absorbance, and it shows the maximum–minimum–maximum characteristic typical for coupled excited states in molecular spectra (10), in marked contrast to atomic spectra. (27) The band shape is less obvious for the larger separation between \( \epsilon_A \) and \( \epsilon_F \), where a spectrum with a maximum and a shoulder is observed, also given in the inset of Fig. 2. The difference trace for this situation is given as a solid line starting at zero absorbance, and it again clearly shows the maximum–minimum–maximum profile, but with a weaker low-energy maximum and a broader minimum denoting the interference dip than for the dotted difference trace. This comparison shows quantitatively that absorption spectra involving coupled excited states retain a characteristic band shape with an interference dip, even if no clearcut minimum can be distinguished in the experimental spectrum. A model using the full set of coupled potential energy curves shown in Fig. 3 has to be applied for a precise analysis of these spectra, as described in the following for complexes 1 to 4.

In order to analyze experimental spectra with this model, as many parameters as possible are set to experimental quantities. Vibrational frequencies 0 were held constant at values observed...
in the Raman spectra and initial values for $\Delta$ and $\varepsilon_F$ were estimated from the spectra. The coupling constant $\gamma$ was limited to values below 1000 cm$^{-1}$, corresponding to the order of magnitude of the spin-orbit coupling constant for nickel(II). Only \( \lambda \), a factor contributing to the width of the spin-allowed absorption band, and \( \Gamma \), a phenomenological parameter defining the shape of the spectrum in the region of the formally spin-forbidden band, were treated as adjustable parameters without numerical constraints. The most important parameter values obtained from the fits are band maxima $\Delta$ for the allowed transition and energies $\varepsilon_F$ for the lowest-energy singlet excited state of complexes 1 to 4.

Figure 4 shows a comparison of experimental and calculated spectra. The agreement is excellent, and the numerical values of all parameters used for the calculations are summarized in Table 3. We carried out calculations with several different experimental vibrational frequencies, because multiple totally-symmetric metal-ligand stretching modes are expected for complexes with a mixed ligand sphere, such as complexes 1 to 3, or for complexes with lower than O$_h$ point group symmetry, such as complex 4. Numerical results for two different frequencies $\omega_0$ from Table 2 are given in Table 3 for compounds 1 and 4. The calculated spectra obtained with different vibrational frequencies cannot be distinguished on the scale of Fig. 4. It is important to note that the energies of the singlet state $\varepsilon_F$ obtained from fits to the absorption spectra using different values for the vibrational frequencies $\omega_0$ vary by less than 50 cm$^{-1}$, illustrating that the model is reliable for the low-symmetry complexes with nonuniform ligand spheres studied here. We have shown and discussed before that this approach avoids the pitfalls of $^1E_g$ energies obtained from phenomenological procedures, such as fitting a sum of Gaussian profiles to the observed absorption bands (14).

**Table 3.** Parameter values from fits of Eq. 5 to the absorption spectra in Fig. 4. All values are in cm$^{-1}$ units. Values obtained using two different frequencies $\omega_0$ are given for compounds 1 and 4

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\omega_0$</th>
<th>$\lambda$</th>
<th>$\Gamma$</th>
<th>$\gamma$</th>
<th>$\varepsilon_F$</th>
<th>$\Delta$</th>
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<td>[{tpm*}Ni(NO$_3$)$_2$] (1)</td>
<td>577</td>
<td>3760</td>
<td>274</td>
<td>436</td>
<td>12873</td>
<td>10389</td>
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<tr>
<td>[{tpm*}Ni(NO$_3$)$_2$] (1)</td>
<td>222</td>
<td>9760</td>
<td>274</td>
<td>397</td>
<td>12854</td>
<td>10370</td>
</tr>
<tr>
<td>[{tpm*}Ni(NO$_3$)$_2$] (2)</td>
<td>285</td>
<td>11728</td>
<td>500</td>
<td>500</td>
<td>12838</td>
<td>10305</td>
</tr>
<tr>
<td>[{tpm*}Ni(NO$_3$)$_2$] (3)</td>
<td>416</td>
<td>7454</td>
<td>188</td>
<td>228</td>
<td>12994</td>
<td>10465</td>
</tr>
<tr>
<td>[{tpm*}Ni(NO$_3$)$_2$] (4)</td>
<td>423</td>
<td>7463</td>
<td>500</td>
<td>450</td>
<td>12923</td>
<td>11765</td>
</tr>
<tr>
<td>[{tpm*}Ni(NO$_3$)$_2$] (4)</td>
<td>242</td>
<td>14358</td>
<td>313</td>
<td>243</td>
<td>12862</td>
<td>11765</td>
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</tbody>
</table>

Figure 5. Energies of the lowest-energy singlet (squares, $^1E_g$ in O$_h$ symmetry) and triplet (circles, $^3T_{2g}$ in O$_h$ symmetry) excited states as a function of the number of nitrogen ligator atoms. Solid symbols denote energies obtained from the spectra calculated with (Eq. 5) and shown in Fig. 4. Open symbols denote values obtained from the ligand field parameters in Table 1 with Eqs. 1 and 6.

Comparison of model parameters

The model illustrated in Fig. 3 and leading to the calculated spectra in Fig. 4 provides numerical values for the lowest-energy spin-allowed and spin-forbidden transitions, summarized in Table 3 as $\Delta$ and $\varepsilon_F$, respectively. They are illustrated for compounds 1 to 4 in Fig. 5 and compared to corresponding values from the traditional ligand-field analysis, where the maximum of the lowest-energy spin-allowed band corresponds to 10D$q$, as obtained by Eq. 1 and summarized in Table 1. The comparison of 10D$q$ with $\Delta$ shows very similar values and an almost identical variation with the number of nitrogen ligator atoms. The 10D$q$ values are systematically lower by approximately 100 cm$^{-1}$ than those obtained for $\Delta$, a consequence of the omission of spin-orbit coupling in the determination of 10D$q$. The magnitude of this difference is on the order expected for spin-orbit coupling effects for complexes of the first-row transition metal ions. Coupling between the singlet and triplet excited states leads to the lower-energy adiabatic potential energy curve, shown as a dotted line in Fig. 3 below the corresponding diabatic curve denoted by a solid line. This diabatic curve defines $\Delta$, and the higher values summarized in Table 3 clearly are a consequence of coupling between the two excited states. The comparison of the maxima for the lowest-energy spin-forbidden transition to the $^1E_g$ state is less obvious. The values for B and 10D$q$ from Table 1 can be used to calculate the energy of the
\( {1E_g} \) excited state. Assuming a constant ratio of the Racah parameters \( C/B = 4 \), its energy is given by (13):

\[
E(1E_g) = 16B - 6B^2/10Dq
\]  

(7)

Energies of the \( 1E_g \) state calculated with Eq. 7 are compared to the \( \varepsilon_F \) values from Table 3 as the top two traces in Fig. 5. The values for \( B \) in Table 1 lead to a large variation of 700 cm\(^{-1}\) for the energy of the \( 1E_g \) excited state, in contrast to the energies \( \varepsilon_F \) obtained from the calculated spectra in Fig. 4, where a variation of less than 160 cm\(^{-1}\) as a function of the number of nitrogen ligator atoms is observed. The parameters from the calculations in Table 3 can be used to obtain alternative values of the ratio 10Dq/B. The model parameter \( \Delta \) corresponds to 10Dq, and Eq. 7 can be used with \( \varepsilon_F \) denoting the energy of the \( 1E_g \) state to calculate an alternative \( B \) value. The ratio \( \Delta/B \) obtained in this manner is 12.5 for complexes 1 to 3 and 14.2 for complex 4. This set of ratios is closer to the expectations from the spectrochemical and nephelauxetic series than the traditional approach based on the maxima of the spin-allowed transitions and reflects the constant \( 1E_g \) energies observed in the absorption spectra of all complexes studied here.

CONCLUSION

The analysis of readily obtained spectroscopic data such as the solution absorption and solid-state Raman spectra presented here reveals detailed information on fundamental aspects of the electronic structure of complexes with poly(pyrazolyl)methane ligands, an important ligand system forming a variety of low-symmetry transition metal compounds. This new approach leads to a straightforward characterization of the electronic structure and is easily applied to other classes of complexes. Of particular interest could be spectra with several spin-forbidden transitions, providing an opportunity to explore trends obtained from multiple band systems in order to gain more detailed insight into this classic problem in the absorption spectroscopy of transition metal compounds.

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