while both lines through our experimental points (assigned intervals, corresponding to $I > 0$) tend to meet at the same point on the y axis (where $I = 0$).

The value of $\log K_s(I = 0)$ for $(UO_2)_3(PO_4)_2{\cdot}8H_2O$ determined in this work (Table II, equilibrium 9) is in very good agreement with the value of $\log K_s(I = 0) = -49.1$ for $(UO_2)_3(PO_4)_2{\cdot}6H_2O$ determined by Chukhlantsev and Alyamovskaya.[18] The value of K_s for $(UO_2)_3(PO_4)_2{\cdot}6H_2O$ at $I = 0.32$ mol dm^{-3} determined by Pekarek, Vesely, and Abbrent[21] was recalculated, and the result is presented in Table II, equilibrium 9.

Baes and Schreyer's data[10-12] on the composition and stability of uranyl phosphato complexes (at $I = 1$ mol dm^{-3}), Vesely, Pekarek, and Abbrent's solubility data (at $I = 0.32$ mol dm^{-3}), and the constants of the homogeneous and heterogeneous equilibria determined in this work (at $I = 0$) give a detailed and complete picture of the uranyl-phosphate system at $1.4 < \text{pH} < 3.2$.

Acknowledgment. The authors wish to thank Dr. Z. Konrad and Dr. Lj. Musani, who performed electrophoretic measurements, and Dr. B. Kojić-Prodić and Lj. Komunjer for the help and suggestions during the final correction of this paper. This work was supported by the Self-Management Council for Scientific Research of S.R. Croatia.

Registry No. UO_2HPO_4, 61156-01-2; $(UO_2)_3(PO_4)_2$, 12037-44-4; U, 7440-61-1; UO_2^{2+}, 16637-16-4.

Contribution from the Department of Chemistry,
University of the Witwatersrand, Johannesburg, South Africa

Mixing of States and the Determination of Ligand Field Parameters for High-Spin Octahedral Complexes of Nickel(II). Electronic Spectrum and Structure of Bis(1,7-diaza-4-thiaheptane)nickel(II) Perchlorate

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The mixing of the ^1E_g and $^3T_{2g}$ excited states in six-coordinate nickel(II) complexes via spin-orbit coupling is discussed. The effect of the mixing of states is that in the above Ni(II) complexes, when the ligand field splitting parameter, $10Dq$, is close to 12 000 cm^{-1}, two bands at approximately 12 500 and 11 500 cm^{-1} are observed, which cannot be assigned to pure $^3A_{2g} \rightarrow {}^3T_{2g}$ or $^3A_{2g} \rightarrow {}^1E_g$ transitions. As $10Dq$ increases from 11 000 to 13 000 cm^{-1}, the positions of these bands remain relatively constant. What does change is their relative intensities. A method is proposed whereby the relative intensities of the two bands in the 12 000-cm^{-1} region can be used to obtain in a simple manner the positions of the two bands corrected for mixing of states. It is shown that these corrections lead to more rational values of $10Dq$ and the Racah parameters. The split bands in the complex $[Ni(daes)_2]^{2+}$ (daes = 1,7-diaza-4-thiaheptane) are assigned to mixing of $^3A_{2g} \rightarrow {}^3T_{2g}$ and $^3A_{2g} \rightarrow {}^1E_g$, rather than trans positioning of the sulfur donors. The crystal structure determination supporting this assignment is reported for $[Ni(daes)_2](ClO_4)_2$. A conventional R factor of 0.08 was achieved. Cis coordination of the sulfurs is found, with a mean Ni-S bond length of 2.459 Å and a mean Ni-N of 2.11 Å.

The electronic spectrum of six-coordinate nickel has been particularly useful in coordination chemistry. The position of the lowest energy band gives a direct measure of $10Dq$, and making such simplifying assumptions as using the rule of average environment, and neglecting distortion to lower than O_h symmetry, gives one some insight into factors influencing bonding to the Ni(II) ion. However, the problem of mixing of spin-allowed with spin-forbidden bands has been discussed only briefly[1,2] in relation to such simple determinations of the ligand field (LF) parameters. This mixing is particularly important for the spin-forbidden $^3A_{2g} \rightarrow {}^1E_g$ and spin-allowed $^3A_2 \rightarrow {}^3T_2$ transitions at values of the LF splitting parameter, $10Dq$, of about 12 000 cm^{-1}. In Figure 1 we have plotted the energies of the $^3A_{2g} \rightarrow {}^1E_g$ and $^3A_{2g} \rightarrow {}^3T_{2g}$ transitions against those of $^3A_{2g} \rightarrow {}^3T_{1g}(F)$, for a variety of Ni(II) complexes containing six nitrogen and/or fluorine donor atoms. For this set there appears to be an inverse relationship between $10Dq$ and B; e.g., these parameters are[1] as follows for the sets of ligands: 6F$^-$, 7300 and 950; 6 H_2O, 8600 and 930; 3 glycine, 10 100 and 926; 6 NH_3, 10 700 and 890; 3 en, 11 500 and 860; 3 bpy, 12 300 and 845 cm^{-1}. If we examine the expressions[3] for the $^3A_{2g}$, $^3T_{2g}$, $^3T_{1g}(F)$, and ^1E_g states, we see that a direct relationship between the energies of $^3A_{2g} \rightarrow {}^3T_{2g}$ and $^3A_{2g} \rightarrow {}^3T_{1g}(F)$, and an inverse relationship between $^3A_{2g} \rightarrow {}^1E_g$ and $^3A_{2g} \rightarrow {}^3T_{1g}(F)$, is expected. (The relationship will break down if ligands with second-row donors such as S or Cl are included, since the relation between $10Dq$ and B is different.) The relationships between $^3A_{2g} \rightarrow {}^3T_{2g}$ and $^3A_{2g} \rightarrow {}^3T_{1g}(F)$ and between $^3A_{2g} \rightarrow {}^1E_g$ and $^3A_{2g} \rightarrow {}^3T_{1g}(F)$ are found to hold very well in Figure 1, except where the transitions to the ^1E_g and $^3T_{2g}$ states approach each other in energy. This is the cause of the difficulty when the energies of these bands are used to calculate the LF parameters in a simple manner for complexes in aqueous solution.

The explanation for the fact that the two bands appear to repel each other, and never have the same energy, as indicated by the broken lines, is that the Russell-Saunders coupling scheme is breaking down as the separation, δ, between the two excited states becomes smaller, due to coupling between the spin- and orbital-angular momenta. In the simple LF approach such mixing is generally ignored, although, as pointed out by a reviewer, it can be corrected for. One cannot neglect the mixing and assign either of the two band maxima as being the energy of the pure $^3A_{2g} \rightarrow {}^3T_{2g}$ or $^3A_{2g} \rightarrow {}^1E_g$ transition. Doing so has led, for example, to the calculation[4] of anomalously low B values for complexes such as $[Ni(bpy)_3]^{2+}$. The problem of calculating LF parameters arose in our own case with the electronic spectra of the complexes $[Ni(daes)_2]^{2+}$ and [Ni(9-

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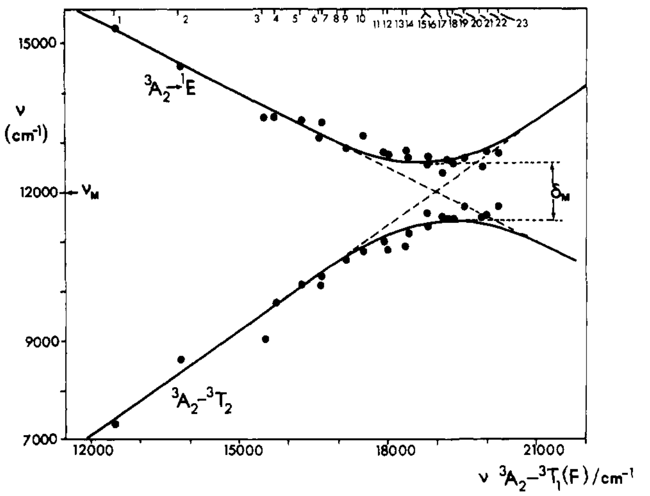

Figure 1. Plot of energy of the two bands in the 12000-cm^{-1} region of spectra of six-coordinate Ni(II) complexes against energy of the $^3A_{2g} \rightarrow {}^3T_{1g}$ transition. The lines have been drawn in so that their extrapolated crossover point is at 12000 cm^{-1}, when $^3A_{2g} \rightarrow {}^3T_{1g}(F)$ has an energy of 19000 cm^{-1}. It is found that complexes with $^3A_{2g} \rightarrow {}^3T_{1g}(F)$ at 19000 cm^{-1} have two bands of equal intensity in the 12000-cm^{-1} region and that the midpoint of these two bands is at 12000 cm^{-1}. The closest approach of the two bands as they are mixed by spin–orbit coupling is indicated as δ_M on the diagram. Key to complexes Ni^{II}L$_x$: L$_x$ = (1) F_6, (2) $(H_2O)_6$, (3) (oxalate)$_3$, (4) (glycine)$(H_2O)_4$, (5) (pn)$(H_2O)_4$, (6) (glycine)$_3$, (7) (en)$(H_2O)_4$, (8) (pyridine-2-carboxylic acid)$_3$, (9) (pn)$_2$ $(H_2O)_2$, (10) $(NH_3)_6$, (11) (HEEN)$_2$, (12) (en)$_2(H_2O)_2$, (13) (en)$_3$ (14) (bpy)$(H_2O)_4$, (15) (AMP)$_3$, (16) (9-aneN$_2$O)$_2$, (17) (Pipi)$_3$, (18) (bpy)$_3$, (19) (*o*-phen)$_3$, (20) (PMI)$_3$, (21) (9-aneN$_3$)$_2$, (22) (bipyrazyl)$_3$, (23) (BdH)$_3$. Abbreviations: pn = 1,3-diaminopropane; otherwise see footnote *b* of Table IV.

aneN$_2$S)$_2$]$^{2+}$ (daes = 1,7-diaza-4-thiaheptane, 9-aneN$_2$S = 1,4-diaza-7-thiacyclononane), where mixing of states occurs. The splitting of the first band in the spectrum of [Ni(daes)$_2$]$^{2+}$, both in the solid state and in solution, has been interpreted[5] as arising from a trans coordination of the sulfur donor atoms. We became convinced that the coordination geometry was cis and that the splitting was in reality due to the close approach of the $^3A_{2g} \rightarrow {}^3T_{2g}$ and $^3A_{2g} \rightarrow {}^1E_g$ transitions, with concomitant increase in intensity of the latter transition. We report here the crystal structure determination of the complex [Ni(daes)$_2$](ClO$_4$)$_2$, plus a discussion of how LF parameters may be corrected in a simple fashion for mixing of states.

Experimental Section

Materials. The synthesis of 9-aneN$_2$S and its bis complex with Ni(II) will be described in a future paper. The ligand daes was obtained from ICN chemicals. The complex [Ni(daes)$_2$](ClO$_4$)$_2$ was synthesized by dissolving a 2/1 mixture of daes plus Ni(ClO$_4$)$_2$·6H$_2$O in water and allowing the water to evaporate. Recrystallization from water gave lilac crystals of a quality suitable for an X-ray structural study. Other Ni(II) complexes whose spectra are discussed in this paper were prepared according to literature methods.

Spectroscopic Measurements. Spectra were recorded in aqueous solution on a Cary 17 UV–visible spectrophotometer.

X-ray Crystallography. A diffraction-quality crystal was selected by standard oscillation and Weissenberg techniques using Cu Kα radiation. The space group and approximate cell constants were determined at the same time. Intensity data and accurate cell dimensions were obtained with a Philips PW 1100 diffractometer using Mo Kα radiation (λ = 0.71070 mm). The structure was determined by Patterson and Fourier techniques, using the SHELX program.[6] Crystal data: monoclinic, space group *C*2, *a* = 17.5 (1), *b* = 8.91 (1) and *c* = 12.39 (1) Å, β = 112.51 (5)°, *Z* = 4, *V* = 1912.3 Å^3, μr(Mo Kα) = 0.733, *F*(000) = 1024. A scan rate of 0.037°/s was used, with background counts on either side of the peak for 30 s, and a scan width of 1.1°. The nickel complex and one perchlorate were found in general positions, while the other perchlorate was found on a twofold axis, disordered around a noncrystallographic center of symmetry on this axis. The disorder of the perchlorate inhibited refinement. The nickel and the chelate ring atoms were refined with anisotropic temperature factors. Eighteen of the twenty-four hydrogen atoms were found by difference synthesis. The other six hydrogen atoms were placed at coordinates derived from a three-dimensional model. The final coordinates are seen in Table I, and the important bond lengths and angles are given in Tables II and III. The final conventional *R* factor was 0.08. This somewhat high value was caused by the disordered perchlorate.

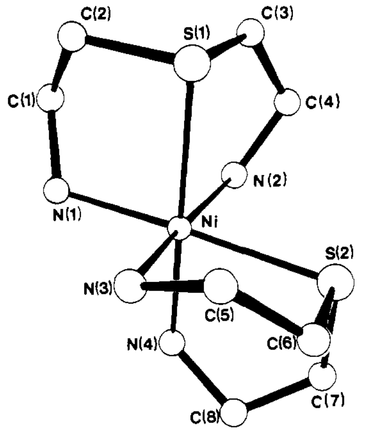

Figure 2. ORTEP[11] drawing of the cation [Ni(daes)$_2$]$^{2+}$ showing the atom-numbering scheme.

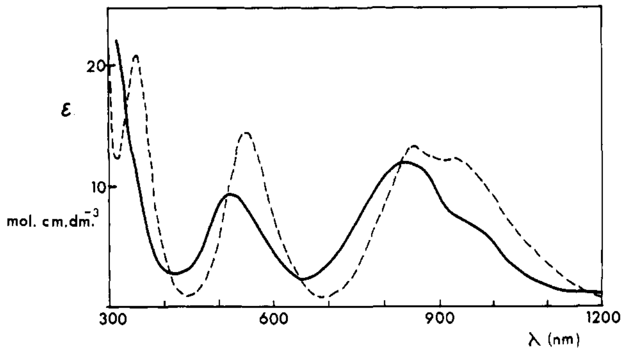

Figure 3. Electronic spectra of [Ni(daes)$_2$]$^{2+}$ (---) and [Ni(9-aneN$_2$S)$_2$]$^{2+}$ (—). Note the fact that the positions of the two bands around 900 nm do not change, but that their relative intensities do, as $^3A_{2g} \rightarrow {}^3T_{1g}(F)$ at about 550 nm moves to higher energy.

Results and Discussion

The unsymmetrical facial coordination found in [Ni(daes)$_2$](ClO$_4$)$_2$ shown in Figure 2 is very similar to that found in the Co(III) and Rh(III) (daes)$_2$ complexes.[7,8] The structure thus confirms that the [Ni(daes)$_2$]$^{2+}$ ion has the sulfurs in the cis positions and supports the contention that the splitting of the first band in the electronic spectrum results from a close approach of the $^3A_{2g} \rightarrow {}^3T_{2g}$ and $^3A_{2g} \rightarrow {}^1E_g$ transitions. The structure is otherwise unremarkable, except that the trans-situated Ni–N(2) and Ni–N(3) bond lengths are 2.05 (2) and 2.17 (2) Å, respectively. Although these average out to the usual Ni–N bond length of 2.11 Å, the statistically significant observed difference is inexplicable.

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Table I

(A) Fractional Atomic Coordinates for Cation[a]

atom	*x*/*a*	*y*/*b*	*z*/*c*
Ni	0.3475 (1)	0.0	0.2392 (1)
S(1)	0.4768 (3)	−0.0634 (6)	0.3370 (3)
S(2)	0.2731 (3)	−0.1130 (7)	0.3704 (4)
N(1)	0.405 (1)	0.124 (2)	0.134 (1)
N(2)	0.356 (1)	−0.199 (2)	0.159 (1)
N(3)	0.345 (1)	0.194 (2)	0.344 (1)
N(4)	0.238 (1)	0.051 (2)	0.149 (1)
C(1)	0.488 (1)	0.078 (2)	0.140 (1)
C(2)	0.527 (1)	0.065 (3)	0.257 (2)
C(3)	0.485 (1)	−0.242 (3)	0.271 (2)
C(4)	0.408 (2)	−0.307 (3)	0.232 (2)
C(5)	0.341 (1)	0.150 (4)	0.459 (2)
C(6)	0.281 (2)	0.041 (4)	0.466 (2)
C(7)	0.178 (1)	−0.077 (3)	0.286 (2)
C(8)	0.176 (1)	0.060 (3)	0.217 (2)

(B) Fractional Atomic Coordinates for Hydrogen Atoms[b]

atom	*x*/*a*	*y*/*b*	*z*/*c*
HN11	0.393 (11)	0.228 (8)	0.144 (15)
HN12	0.393 (9)	0.141 (23)	0.056 (4)
HN21	0.380 (9)	−0.197 (22)	0.094 (9)
HN22	0.310 (8)	−0.261 (16)	0.153 (14)
HN31	0.311 (9)	0.280 (11)	0.341 (15)
HN32	0.385 (7)	0.268 (17)	0.361 (15)
HN41	0.222 (9)	−0.020 (16)	0.091 (10)
HN42	0.233 (10)	0.140 (12)	0.103 (13)
HC11	0.484 (10)	−0.019 (11)	0.105 (12)
HC12	0.519 (9)	0.114 (19)	0.086 (11)
HC21	0.578 (5)	0.023 (22)	0.263 (12)
HC22	0.519 (10)	0.148 (14)	0.304 (13)
HC31	0.515 (9)	−0.245 (24)	0.211 (9)
HC32	0.519 (8)	−0.298 (18)	0.326 (12)
HC41	0.417 (11)	−0.397 (12)	0.191 (13)
HC42	0.384 (9)	−0.333 (21)	0.296 (11)
HC51	0.381 (8)	0.090 (18)	0.501 (12)
HC52	0.330 (10)	0.244 (12)	0.492 (14)
HC61	0.238 (6)	0.104 (20)	0.433 (14)
HC62	0.277 (9)	0.031 (23)	0.543 (6)
HC71	0.146 (8)	−0.061 (22)	0.342 (11)
HC72	0.173 (11)	−0.160 (15)	0.236 (12)
HC81	0.192 (10)	0.153 (13)	0.254 (13)
HC82	0.129 (5)	0.058 (21)	0.165 (11)

(C) Fractional Atomic Coordinates, Site Occupancy Factors (sof), and Isotropic Temperature Factors (*U*) for Perchlorates

atom	*x*/*a*	*y*/*b*	*z*/*c*	sof	*U*, Å^2
Cl(1)	0.712 (1)	−0.035 (1)	0.136 (1)	1.0	0.047 (1)
Cl(2)	0.5	0.455 (2)	0.5	0.403 (9)	0.076 (2)
Cl(2′)	0.5	0.427 (7)	0.5	0.097 (9)	0.076 (2)
Cl(3)	0.5	−0.529 (2)	0.0	0.343 (5)	0.076 (2)
Cl(3′)	0.5	−0.375 (3)	0.0	0.157 (5)	0.076 (2)
O(11)	0.641 (1)	−0.109 (2)	0.091 (1)	1.0	0.068 (4)
O(12)	0.722 (1)	−0.041 (2)	0.252 (1)	1.0	0.062 (3)
O(13)	0.273 (1)	−0.607 (2)	0.097 (1)	1.0	0.073 (4)
O(14)	0.706 (1)	0.118 (2)	0.099 (1)	1.0	0.077 (4)
O(21)	0.495 (1)	0.375 (2)	0.397 (1)	0.807 (18)	0.076 (2)
O(22)	0.434 (1)	0.547 (2)	0.488 (2)	0.807 (18)	0.076 (2)
O(21′)	0.420 (3)	0.487 (11)	0.504 (6)	0.193 (18)	0.076 (2)
O(22′)	0.517 (4)	0.583 (7)	0.472 (6)	0.193 (18)	0.076 (2)
O(31)	0.499 (1)	−0.554 (3)	0.123 (2)	0.686 (11)	0.076 (2)
O(32)	0.571 (1)	−0.602 (3)	0.021 (2)	0.686 (11)	0.076 (2)
O(31′)	0.478 (2)	−0.542 (5)	0.010 (3)	0.314 (11)	0.076 (2)
O(32′)	0.440 (2)	−0.359 (5)	0.030 (3)	0.314 (11)	0.076 (2)

[a] Coordinates for non-hydrogen atoms; estimated standard deviations are given in parentheses. Thermal parameters available as supplementary material. [b] All refined with a common isotropic temperature factor of 0.057 Å^2.

Table II. Important Bond Lengths (Å)

Ni-S(1)	2.455 (5)	S(2)-C(7)	1.84 (2)
Ni-S(2)	2.463 (6)	N(1)-C(1)	1.50 (3)
Ni-N(1)	2.09 (2)	N(2)-C(4)	1.53 (3)
Ni-N(2)	2.05 (2)	N(3)-C(5)	1.49 (3)
Ni-N(3)	2.17 (2)	N(4)-C(8)	1.48 (3)
Ni-N(4)	2.11 (1)	C(1)-C(2)	1.50 (2)
S(1)-C(2)	1.83 (2)	C(3)-C(4)	1.47 (3)
S(1)-C(3)	1.81 (3)	C(5)-C(6)	1.45 (4)
S(2)-C(6)	1.80 (3)	C(7)-C(8)	1.50 (3)

Table III. Important Bond Angles (deg)

S(1)-Ni-S(2)	97.3 (2)	N(3)-Ni-N(1)	90.6 (6)
N(1)-Ni-S(1)	85.6 (4)	N(3)-Ni-N(2)	172.4 (6)
N(1)-Ni-S(2)	172.4 (5)	N(4)-Ni-S(1)	177.5 (4)
N(2)-Ni-S(1)	84.5 (5)	N(4)-Ni-S(2)	84.4 (4)
N(2)-Ni-S(2)	93.4 (5)	N(4)-Ni-N(1)	93.0 (6)
N(2)-Ni-N(1)	93.9 (7)	N(4)-Ni-N(2)	93.6 (6)
N(3)-Ni-S(1)	89.8 (4)	N(4)-Ni-N(3)	92.3 (6)
N(3)-Ni-S(2)	82.4 (5)		

The problem of correct band assignment in six-coordinate high-spin Ni(II) complexes with 10*Dq* values of about 12 000 cm^{-1} is illustrated in Figure 3, where we have shown the electronic spectra of $[Ni(daes)_2]^{2+}$ and $[Ni(9\text{-aneN}_2S)_2]^{2+}$. Following usual procedures, we would assign the most intense bands as the $^3A_{2g} \rightarrow {}^3T_{2g}$ transitions. These occur at 11 700 cm^{-1} in $[Ni(daes)_2]^{2+}$ and 11 770 cm^{-1} in $[Ni(9\text{-aneN}_2S)_2]^{2+}$, so that one would then suppose that there was very little difference in ligand field strength between the two ligands. If correct, this would be a most interesting result, since the difference in 10*Dq* between the macrocycles of the type 9-aneX_3 (X_3 = N_3, N_2O) and their linear analogues with Ni(II) is large,[9] being up to 1000 cm^{-1}.

One can show that the above apparent lack of difference in 10*Dq* is probably not correct by comparing the spectra of $[Ni(daes)(H_2O)_3]^{2+}$ and $[Ni(9\text{-aneN}_2S)(H_2O)_3]^{2+}$, which we have recorded in aqueous solution. In these two complexes, the transition $^3A_{2g} \rightarrow {}^3T_{2g}$ occurs well away from the very weak $^3A_{2g} \rightarrow {}^1E_g$, and we now see that $^3A_{2g} \rightarrow {}^3T_{2g}$ occurs at 10 100 cm^{-1} in the 9-aneN_2S complex and 9800 cm^{-1} in its daes analogue. From the rule of average environment we would expect double this difference in 10*Dq* in the bis complexes, a difference of roughly 600 cm^{-1}. At the same time, we would expect from 10*Dq* = 8600 cm^{-1} in the Ni(II) aquo ion that $^3A_{2g} \rightarrow {}^3T_{2g}$ would occur at 11 600 cm^{-1} in the $(9\text{-aneN}_3)_2$ complex and at 11 000 cm^{-1} in the $(daes)_2$ complex.

The lines in Figure 1 have been drawn so as to cross at 12 000 cm^{-1}, which is where the band intensities of the $^3A_{2g} \rightarrow {}^3T_{2g}$ and $^3A_{2g} \rightarrow {}^1E_g$ transitions are equal. This then satisfies the theoretical condition that the band intensities of the two transitions are equal when they would have the same energy in the absence of spin–orbit coupling effects. We should thus be able to read 10*Dq* off the extrapolated (broken) line for the relationship between the energies of $^3A_{2g} \rightarrow {}^3T_{2g}$ and $^3A_{2g} \rightarrow {}^3T_{1g}(F)$ and thereby correct for spin–orbit coupling. This then comes down to determining 10*Dq* from the energy of the $^3A_{2g} \rightarrow {}^3T_{1g}(F)$ transition. This might be a little risky as a procedure in the absence of evidence that it is correct and certainly cannot be used for other donors such as S or Cl where the relationship between *Dq* and *B* is different from that found for N and O donors.

The most important factor that indicates to us the extent of mixing of the two states, and thereby the position of the $^3A_{2g} \rightarrow {}^3T_{2g}$ transition in the absence of mixing of states, is the relative intensity of the two bands in the 12 000-cm^{-1} region. According to first-order perturbation theory,[10] the ratio of intensities of the two bands, ϵ_1/ϵ_2 (ϵ is the extinction coefficient at the band maximum), is directly proportional to ζ/Δ, where Δ is the energy difference between the two bands in the ground state, i.e., before any mixing of states occurs.

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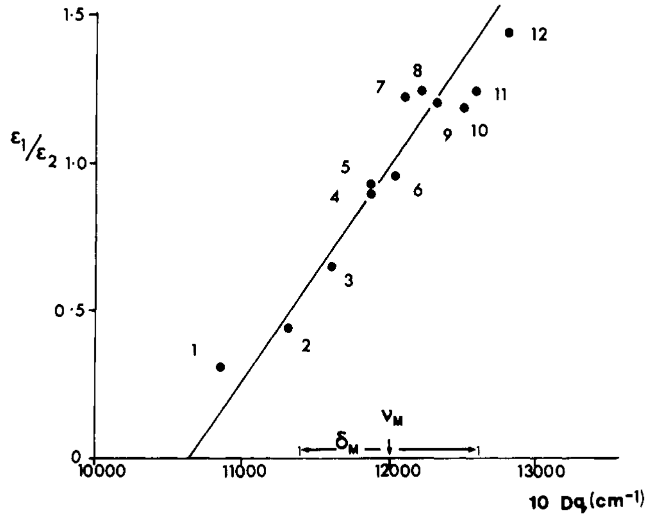

Figure 4. Plot of the ratio of the extinction coefficients, ϵ_1/ϵ_2, of the higher energy to the lower energy band in the 12 000-cm^{-1} region against 10*Dq* estimated, as described in the text, from Figure 1. The crossover point, ν_M, of the two bands is at 12 000 cm^{-1} and corresponds to an ϵ_1/ϵ_2 ratio of 1. The minimum separation of the two bands is indicated as δ_M. Key to ligands: (1) (ODEN)$_2$, (2) (HEEN)$_2$, (3) (en)$_3$, (4) (AMP)$_3$, (5) (9-aneN$_2$O)$_2$, (6) (PiPi)$_3$, (7) (bpy)$_3$, (8) (*o*-phen)$_3$, (9) (PMI)$_3$ (10) (PMH)$_3$, (11) (9-aneN$_3$)$_2$, (12) (BdH)$_3$. Abbreviations are explained in footnote *b* of Table IV.

Since the energies of $^3A_{2g} \rightarrow {}^3T_{2g}$ and $^3A_{2g} \rightarrow {}^1E_g$ are, from Figure 1, inversely related to each other, we would expect a linear relation between the energy of either band and the ratio ϵ_1/ϵ_2. In Figure 4 is plotted the ratio ϵ_1/ϵ_2 vs. the energy of the transition $^3A_{2g} \rightarrow {}^3T_{2g}$. This is not the observed value but that read off the interpolation line in Figure 1 for $^3A_{2g} \rightarrow {}^3T_{2g}$. The linearity of the relation is thus in good agreement with the predictions of theory. For simplicity, no resolution of the two bands has been attempted, since it is not even certain what shape these bands should have[2] in the region of mixing. Thus, ϵ_1 is the extinction coefficient at the observed frequency of the $^3A_{2g} \rightarrow {}^1E_g$ transition, while ϵ_2 is the extinction coefficient at the observed frequency of the $^3A_{2g} \rightarrow {}^3T_{2g}$ transition. A complex with 10*Dq* of 12 000 cm^{-1} thus has two bands of equal intensity, separated by an energy δ_M, which is the closest approach of the two bands, having a value of about 1200 cm^{-1} for Ni(II) with only nitrogen and oxygen donors on the ligands. The complexes $[Ni(PiPi)_3]^{2+}$ and $[Ni(9\text{-}aneN_2O)_2]^{2+}$ have 10*Dq* values very close to the crossover point and thus have two bands of very nearly equal intensity in the 12 000-cm^{-1} region.

The linearity of the relation in Figure 4 in agreement with theory supports the idea that the values of $^3A_{2g} \rightarrow {}^3T_{2g}$ read off the interpolation line in Figure 1 are the appropriate values to use in calculating 10*Dq*. Having established a relation between the ratio ϵ_1/ϵ_2 and 10*Dq*, we can make further small adjustments to the estimated value of the latter for complexes such as $[Ni(bpy)_3]^{2+}$ where the ratio ϵ_1/ϵ_2 is a little high for the value of 10*Dq* estimated from Figure 1 and the position of the $^3A_{2g} \rightarrow {}^3T_{1g}(F)$ transition. The estimate of 10*Dq* for this complex is thus raised slightly from 12 100 to 12 300 cm^{-1} to allow the point for this complex in Figure 4 to fall on the line. The ratio ϵ_1/ϵ_2 is thus the final arbiter of the value of 10*Dq*. Equation 1 is the empirical relationship between 10*Dq*

$$10Dq = 10630 + 1370\epsilon_1/\epsilon_2 \tag{1}$$

and ϵ_1/ϵ_2 derived from Figure 4. It can be used to correct the $^3A_{2g} \rightarrow {}^3T_{2g}$ band position for Ni(II) complexes with a set of N_xO_{6-x} donor atoms, by using the measured value of ϵ_1/ϵ_2.

Table IV contains revised values of 10*Dq* and *B*, together with the uncorrected values for comparison. The largest change in 10*Dq* is only some 500 cm^{-1}, which may not seem very important. However, from the chemical insights that one obtains, these changes are extremely important. The changes remove the odd quantum leap in 10*Dq* from about 11 500 to 12 500 cm^{-1}, which must be made when ϵ_1/ϵ_2 changes from just below 1 to just above it, if we follow the usual practice of assigning the more intense band as $^3A_{2g} \rightarrow {}^3T_{2g}$. We now see that 10*Dq* for $[NiL_3]^{2+}$, where L = AMP, is 11 850 cm^{-1}, intermediate in value between that for L = en at 11 500 cm^{-1} and that for L = bpy at 12 300 cm^{-1}. That this intermediate value of 10*Dq*, expected for the AMP complex from the rule of average environment, is correct can be seen from the 10*Dq* values[2] for the Co(II) tris complexes of 11 800 (en), 12 200 (AMP), and 12 650 cm^{-1} (bpy). Without the corrections we have 10*Dq* for the Ni(II) tris complexes of 11 200 (en), 11 300 (AMP), and 12 650 cm^{-1} (bpy).

Table IV. Values of 10*Dq* and *B* for Ni^{II} Complexes, Corrected for Mixing of States As Described in the Text and Calculated by Using a Conventional Approach[a]

		cor		uncor	
complex[b]	ϵ_1/ϵ_2[c]	10*Dq*[d]	*B*, cm^{-1}	10*Dq*[e]	*B*, cm^{-1}
$[Ni(BdH)_3]^{2+}$[f]	1.45	12 600	(995)[g]	12 800	(955)
$[Ni(9\text{-}aneN_3)_2]^{2+}$	1.26	12 350	(966)	12 500	(990)
$[Ni(bpy)_3]^{2+}$	1.24	12 300	845	12 650	750
$[Ni(PMI)_3]^{2+}$[f]	1.22	12 275	(940)	12 670	(810)
$[Ni(PMH)_3]^{2+}$[f]	1.19	12 250		12 690	
$[Ni(PBI)_3]^{2+}$[f]	1.02	12 030		12 500	
$[Ni(PiPi)_3]^{2+}$[f]	0.96	11 950	(975)	11 490[h]	(1240)
$[Ni(9\text{-}aneN_2O)_2]^{2+}$	0.94	11 900	855	11 600	915
$[Ni(AMP)_3]^{2+}$	0.90	11 850	865	11 300	1010
$[Ni(en)_3]^{2+}$	0.65	11 500	866	11 200	880
$[Ni(HEEN)_2]^{2+}$	0.45	11 250	860	11 100	850
$[Ni(PdMH)_3]^{2+}$[f]	0.72[i]	10 900		10 440	
$[Ni(9\text{-}aneN_2S)_2]^{2+}$	1.34[i]	11 560		11 770	
$[Ni(daes)_2]^{2+}$	1.06[i]	11 180		11 700	

[a] In cm^{-1}. [b] Abbreviations: BdH, biacetyl dihydrazone; 9-aneN$_3$, 1 4,7-triazacyclononane; bpy, 2,2′-bipyridyl; PMI, 2-pyridinecarboxaldehyde methylimine; PMH, 2-pyridinecarboxaldehyde methylhydrazone; PBI, 2-pyridinecarboxaldehyde benzylimine; PiPi, 2-pyridinecarboxaldehyde isopropylimine; 9-andN$_2$O, 1,4-diaza-7-oxacyclononane; AMP, 2-aminomethylpyridine; en, ethylenediamine; HEEN, *N*-(hydroxyethyl)ethylenediamine; PdMH, 2-pyridinecarboxaldehyde dimethylhydrazone; 9-aneN$_2$S, 1,4-diaza-7-thiacyclononane; daes, 1,7-diaza-4-thiaheptane. [c] Ratio of extinction coefficients of uncorrected $^3A_{2g} \rightarrow {}^3T_{2g}$ and $^3A_{2g} \rightarrow {}^1E_g$ transitions. [d] Value of 10*Dq* calculated by assuming it to be equal to the energy of $^3A_{2g} \rightarrow {}^3T_{2g}$ calculated with use of the ratio ϵ_1/ϵ_2 and eq 5 in the text. *B* is calculated as a best fit to the remaining bands by using the calculated value of 10*Dq*. Where no *B* is reported, $^3A_{2g} \rightarrow {}^3T_{1g}$ (F) was either not observed or else very intense and therefore clearly strongly mixed with the charge-transfer bands. [e] The value of 10*Dq* is taken as the energy of the point of maximum ϵ in the 12 000-cm^{-1} region. [f] Robinson, M. A.; Curry, J. D.; Busch, D. H. *Inorg. Chem.* **1963**, *2*, 1178–1181. [g] Parentheses indicate that these values of *B* are considered to be far too high. From the position of the $^3A_{2g} \rightarrow {}^1E_g$ band (see text), *B* of about 840 cm^{-1} would seem to be more realistic for these complexes. [h] Taken as 12 380 cm^{-1} in original paper, although this is slightly less intense than the band at 11 490 cm^{-1}. The 12 380-cm^{-1} band leads to a *B* value of 800 cm^{-1}. [i] The ratio ϵ_1/ϵ_2 appears to be out of sequence for these complexes because the parameters ν_M and δ_M in eq 1 are different from those of the first set of complexes.

The calculation of *B* for these complexes is problematic. For those with 10*Dq* much less than 12 000 cm^{-1}, it is found empirically that *B* and *C* can be related to 10*Dq* by eq 2 and 3.

$$B = 1120 - 0.022(10Dq) \tag{2}$$

$$C = 15B - 9975 \tag{3}$$

The *B* and *C* values so generated can be used to reproduce the energies of the three observable spin-allowed and two spin-forbidden bands very satisfactorily. That for $10Dq = 0$ the values of B and C reduce to close to the values for gaseous Ni^{2+} is most interesting. For complexes with $10Dq$ only just below 12 000 cm^{-1}, as seen in Table IV, application of the correction for mixing of the $^3T_{2g}$ and ^1E_g states now gives B values that are in accord with their values of $10Dq$ and eq 2. However, apart from the value of B for the $(bpy)_3$ complex, above $10Dq = 12\,000$ cm^{-1} we calculate B values that are higher even than those for the nickel(II) fluoride. For example, for $[Ni(9\text{-}aneN_3)_2]^{2+}$ we calculate a value of B of 966 cm^{-1}, compared to the 953 cm^{-1} found for $KNiF_3$. If we accept that a lower B value reflects greater covalence in the metal–ligand bond, this seems absurd. Further, reproduction of the corrected energy of the spin-forbidden $^3A_{2g} \rightarrow {}^1E_g$ transition requires the extremely low C value of 2040 cm^{-1} (uncorrected for mixing of states; $C = 1940$ cm^{-1}). Since the nephelauxetic series derived from B and C values tend to parallel each other,[1] this very high B and low C seems unlikely. One might argue that the high B values we calculate for these complexes arise because we are applying a model for octahedral coordination to tetragonally or trigonally distorted systems. This seems unlikely to be the cause since the octahedral model fits the spectra of complexes such as $[Ni(en)_3]^{2+}$ or $[Ni(oxalate)_3]^{2+}$ extremely well, where distortion is considerable. On the other hand, in Ni^{II} complexes with $10Dq$ above 12 000 cm^{-1}, we find that $^3A_{2g} \rightarrow {}^3T_{1g}(F)$ comes very close to the charge-transfer bands and $^3A_{2g} \rightarrow {}^3T_{1g}(P)$ is totally obscured by them. At this stage, we would suggest that the latter two bands are strongly mixed with the Laporte-allowed bands when $10Dq$ is above 12 000 cm^{-1} and require correction in much the same way as is required for the mixing of the $^3T_{2g}$ and ^1E_g states. There is at this point insufficient information on the charge-transfer bands to attempt this.

A more reliable guide to the value of B is given by the spin-forbidden $^3A_{2g} \rightarrow {}^1E_g$ transitions. If we take $10Dq$ as 11 350 cm^{-1} for $[Ni(9\text{-}aneN_3)_2]^{2+}$ and use eq 2 and 3 to calculate B and C, we find that we predict a value very close to that of $^3A_{2g} \rightarrow {}^1E_g$ ($B = 848$, $C = 2750$ cm^{-1} predicts $^3A_{2g} \rightarrow {}^1E_g$ at 11 940, whereas the observed value corrected for mixing is at 11 700 cm^{-1}). The same approach suggests that B has a value of about 840 cm^{-1} for those complexes indicated in Table IV as having B values in excess of 900 cm^{-1}. The equation to use for correcting the energies in the region of mixing of states is eq 4.

$$\nu({}^3A_2 \rightarrow {}^1E) = 13\,100 - 1100\epsilon_1/\epsilon_2 \qquad (4)$$

For complexes of ligands such as daes and $9\text{-}aneN_2S$ where the relation between B and $10Dq$ is very different from that for the nitrogen/oxygen donor set given by eq 2, the crossing point of the $^3T_{2g}$ and ^1E_g levels will no longer be at 12 000 cm^{-1} above $^3A_{2g}$. Inspection of the spectra of these complexes suggests that it is at 11 100 cm^{-1}. Theoretically, both the slope of a relation such as that in Figure 4 and the value of δ_M should be proportional to ζ. δ_M in the bis complexes of Ni^{II} with $9\text{-}aneN_2S$ and daes has a mean value of 1100 cm^{-1}. We can thus construct the more general equation

$$\nu_1 = \nu_M + 1.142\delta_M(\epsilon_1/\epsilon_2 - 1) \qquad (5)$$

where ν_1 is the energy in cm^{-1} of the transition $^3A_{2g} \rightarrow {}^3T_{2g}$, corrected for mixing with $^3A_{2g} \rightarrow {}^1E_g$, and ν_M is the energy of the crossover point, at 12 000 cm^{-1} for a nitrogen/oxygen donor set and at 11 100 cm^{-1} for daes-type ligands. The factor of 1.142 is derived from the factor of 1370 cm^{-1} in eq 1 divided by $\delta_M = 1200$ cm^{-1} for nitrogen/oxygen donor ligands. We can now apply eq 5 to the problem of $10Dq$ for the daes and $9\text{-}aneN_2S$ complexes. ϵ_1/ϵ_2 is 1.34 for $[Ni(9\text{-}aneN_2S)_2]^{2+}$ and 1.06 for $[Ni(daes)_2]^{2+}$, so that with ν_M at 11 100 cm^{-1} and δ_M of 1100 cm^{-1}, we would calculate ν_1, and hence $10Dq$, of 11 560 and 11 180 cm^{-1} for the two complexes. This difference in $10Dq$ is now much more realistic than if we were to take the peak position at approximately 11 700 cm^{-1} in both of them as $10Dq$. Some all-nitrogen donor ligands such as PdMH clearly also have a value of ν_M rather different from those of the usual ligands such as en or bpy, since the two bands in the 12 000-cm^{-1} region are at 10 440 and 12 180 cm^{-1}, suggesting ν_M equals 11 300 cm^{-1}. From the ϵ_1/ϵ_2 ratio of 0.72 we would calculate that ν_1 is at 10 900 cm^{-1}.

When the separation between the two bands in the 12 000-cm^{-1} region becomes sufficiently large that ϵ_1/ϵ_2 falls below 0.5, the $^3A_{2g} \rightarrow {}^1E_g$ is starting to mix with the $^3A_{2g} \rightarrow {}^3T_{1g}(F)$. In practice, therefore, ϵ_1/ϵ_2 does not fall below 0.25, and begins to rise again, as in the aquo ion, as $10Dq$ is lowered. For ϵ_1/ϵ_2 ratios much below 0.4, one would probably introduce more error by making corrections because of mixing in of the $^3T_1(F)$ exicted state. For more accurate calculations, exactly the same procedure described here for correcting of mixing of the ^1E_g with the $^3T_{2g}$ excited state can be applied to correcting for mixing of the ^1E_g and $^3T_{1g}(F)$ states.

It seems possible that much of the "approximate" nature of the spectrochemical series might be traced to mixing of states in other metal ions. More careful determination of $10Dq$, B, and C values might reveal a greater regularity than is at present considered to exist and at the same time allow evaluation of the role of other effects, specifically steric effects, in determining the values of the ligand field parameters.

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Registry No. $[Ni(daes)_2](ClO_4)_2$, 84579-68-0; $[Ni(BdH)_3]^{2+}$, 84416-86-4; $[Ni(9\text{-}aneN_3)_2]^{2+}$, 59034-11-6; $[Ni(bpy)_3]^{2+}$, 21595-29-9; $[Ni(PMI)_3]^{2+}$, 21676-44-8; $[Ni(PMH)_3]^{2+}$, 84416-87-5; $[Ni(PBI)_3]^{2+}$, 47862-24-8; $[Ni(PBI)_3]^{2+}$, 21676-45-9; $[Ni(9\text{-}aneN_2O)_2]^{2+}$, 84416-88-6; $[Ni(AMP)_3]^{2+}$, 18347-74-5; $[Ni(en)_3]^{2+}$, 15390-99-5; $[Ni(HEEN)_2]^{2+}$, 48145-52-4; $[Ni(PdMH)_3]^{2+}$, 84416-89-7; $[Ni(9\text{-}aneN_2S)_2]^{2+}$, 84416-90-0; $[Ni(daes)_2]^{2+}$, 84518-17-2.

Supplementary Material Available: A listing of anisotropic temperature factors (1 page). Ordering information is given on any current masthead page.