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The Spectra of Nickel (II) Complexes

BY

C. J. BALLHAUSEN



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i kommission hos Ejnar Munksgaard

Det Kongelige Danske Videnskabskabernes Selskab

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Various properties of the absorption spectra of the complexes of the first transition group elements have been discussed in the previous papers of this series.<sup>1-4</sup> The basis of these considerations was the crystal-field theory, a theory in which the assumption is made that the main properties of e. g. a complex, are determined by the electrical field originating from the ligands. It was shown that a simple perturbation treatment could account quantitatively for the absorption bands in the copper (II) complexes.

The present paper is intended to give an account of the information that may be obtained about the Ni(II)-complexes when using the crystal field theory. For this purpose the necessary quantitative results for eight equivalent *d*-electrons (or two positrons) will be derived. The derivation will be carried out in the most straightforward manner on the analogy of the method in ref. 2. The formulae derived will be utilized in the numerical calculations of the spectra of the simple para- and diamagnetic Ni(II)-ammines. Further it is shown that a strong hybridization using *3d* orbitals seems out of question in the discussed octahedral Ni(II)-complexes.

### General Theory.

The electronic configuration of the free Ni(II) ion is  $1s^2 2s^2 2p^6 3s^2 3p^6 3d^8$ , the ground state is a  $^3F$  level. The lowest excited states are:  $^1D\ ^3P\ ^1G\ ^1S$ . Unfortunately only the  $^3P$  term value is known with accuracy.<sup>5</sup> It is found at  $17000\text{ cm}^{-1}$ . The "normal" bands with a molar extinction coefficient  $\epsilon \sim 10$  are due to transitions between states with the same multiplicity.<sup>2, 4</sup> Therefore it is the splittings of the  $^3F$  and  $^3P$  terms which determine

the spectra of the paramagnetic complexes, and the splittings of the  ${}^1D$ ,  ${}^1G$  and  ${}^1S$  terms which determine the spectra of the diamagnetic Ni(II) complexes.

We assume that the perturbing field originating from the ligands is so strong that the ( $L-S$ ) coupling can be neglected. The value of  $L$  and the symmetry of the field then determine the number of states into which a given term splits up. We shall use the hole-formalism<sup>2</sup> and treat the eight  $3d$  electrons as equivalent to two  $3d$  positrons. The unperturbed wave functions  $\Psi_{L,M}$  with angular momentum  $L$  and the magnetic quantum number  $M = -L, -L+1 \dots L$  are constructed by combinations of the single particle wave functions  $\psi(1)$  and  $\psi(2)$  of the two  $3d$  positrons.

The wave functions  $\Psi_{3,M}$  for the  ${}^3F$  state can be found by the method of CONDON and SHORTLEY.<sup>6</sup> Leaving out the spin-functions we find:

$$\left. \begin{aligned}
 \Psi_{3,3} &= \sqrt{\frac{1}{2}} (\psi_2(1) \psi_1(2) - \psi_1(1) \psi_2(2)) \\
 \Psi_{3,2} &= \sqrt{\frac{1}{2}} (\psi_2(1) \psi_0(2) - \psi_0(1) \psi_2(2)) \\
 \Psi_{3,1} &= \sqrt{\frac{3}{10}} (\psi_2(1) \psi_{-1}(2) - \psi_{-1}(1) \psi_2(2)) \\
 &\quad + \sqrt{\frac{1}{5}} (\psi_1(1) \psi_0(2) - \psi_0(1) \psi_1(2)) \\
 \Psi_{3,0} &= \sqrt{\frac{1}{10}} (\psi_2(1) \psi_{-2}(2) - \psi_{-2}(1) \psi_2(2)) \\
 &\quad + \sqrt{\frac{2}{5}} (\psi_1(1) \psi_{-1}(2) - \psi_{-1}(1) \psi_1(2)) \\
 \Psi_{3,-1} &= \sqrt{\frac{3}{10}} (\psi_1(1) \psi_{-2}(2) - \psi_{-2}(1) \psi_1(2)) \\
 &\quad + \sqrt{\frac{1}{5}} (\psi_0(1) \psi_{-1}(2) - \psi_{-1}(1) \psi_0(2)) \\
 \Psi_{3,-2} &= \sqrt{\frac{1}{2}} (\psi_0(1) \psi_{-2}(2) - \psi_{-2}(1) \psi_0(2)) \\
 \Psi_{3,-3} &= \sqrt{\frac{1}{2}} (\psi_{-1}(1) \psi_{-2}(2) - \psi_{-2}(1) \psi_0(2))
 \end{aligned} \right\} (1)$$



The indices on the  $3d$  single-particle wave functions refer to the magnetic quantum numbers.

The perturbation term of the Hamiltonian is the same as the one used in ref. 2, equation (3)

$$\mathbf{H}^{(1)} = \mathbf{H}^{(1)}(1) + \mathbf{H}^{(1)}(2)$$

$$\mathbf{H}^{(1)}(1) = -D(m) \frac{1}{\sqrt{2\pi}} \sum_{n=0}^{\infty} \sum_{m=-n}^n \frac{4\pi}{2n+1} \frac{r^n}{r^{n+1}} \bar{Y}_n^m(\theta_1, \varphi_1) \bar{P}_n^m(0)$$

The different terms  $H_{MM'}^{(1)} = \int \Psi_{3M} \mathbf{H}^{(1)} (\Psi_{3M'})^* d\tau$  in the secular equation now have to be evaluated. On the analogy of the argument in ref. 2, it is seen that in the single electron integrals  $n$  must be 4, 2, and 0.  $H_{MM'}^{(1)}$  is then different from zero only for  $m = 4, 2$  and 0, which means that  $M - M'$  must be even.

The secular equation is then:

$$\begin{vmatrix} H_{33}^{(1)} - E^{(1)} & 0 & H_{31}^{(1)} & 0 & H_{3-1}^{(1)} & 0 & H_{3-3}^{(1)} \\ 0 & H_{22}^{(1)} - E^{(1)} & 0 & H_{20}^{(1)} & 0 & H_{2-2}^{(1)} & 0 \\ H_{13}^{(1)} & 0 & H_{11}^{(1)} - E^{(1)} & 0 & H_{1-1}^{(1)} & 0 & H_{1-3}^{(1)} \\ 0 & H_{02}^{(1)} & 0 & H_{00}^{(1)} - E^{(1)} & 0 & H_{0-2}^{(1)} & 0 \\ H_{-13}^{(1)} & 0 & H_{-11}^{(1)} & 0 & H_{-1-1}^{(1)} - E^{(1)} & 0 & H_{-1-3}^{(1)} \\ 0 & H_{-22}^{(1)} & 0 & H_{-20}^{(1)} & 0 & H_{-2-2}^{(1)} - E^{(1)} & 0 \\ H_{-33}^{(1)} & 0 & H_{-31}^{(1)} & 0 & H_{-3-1}^{(1)} & 0 & H_{-3-3}^{(1)} - E^{(1)} \end{vmatrix} = 0 \quad (2)$$

By means of the symmetry conditions of the matrix and by row and column operations we get the four equations:

$$\left. \begin{aligned} E^{(1)} &= H_{22}^{(1)} - H_{-22}^{(1)} \\ (H_{22}^{(1)} + H_{-22}^{(1)} - E^{(1)}) (H_{00}^{(1)} - E^{(1)}) - 2(H_{20}^{(1)})^2 &= 0 \\ (H_{33}^{(1)} \pm H_{-33}^{(1)} - E^{(1)}) (H_{11}^{(1)} \pm H_{-11}^{(1)} - E^{(1)}) - (H_{13}^{(1)} \pm H_{-13}^{(1)})^2 &= 0 \end{aligned} \right\} (3)$$

The different  $H_{MM'}^{(1)}$  are now evaluated. We get e. g. for  $H_{00}^{(1)}$ :

$$H_{00}^{(1)} = \int \Psi_0 \mathbf{H}^{(1)} (\Psi_0)^* d\tau$$

$$H_{00}^{(1)} = \int \left| \sqrt{\frac{1}{10}} (\psi_2^{(1)} \psi_{-2}^{(2)} - \psi_{-2}^{(1)} \psi_2^{(2)}) + \sqrt{\frac{2}{5}} (\psi_1^{(1)} \psi_{-1}^{(2)} - \psi_{-1}^{(1)} \psi_1^{(2)}) \right|^2$$

$$(\mathbf{H}^{(1)}(1) + \mathbf{H}^{(1)}(2)) d\tau_1 d\tau_2 = \frac{2}{5} \int |\psi_2|^2 \mathbf{H}^{(1)}(1) d\tau_1 + \frac{8}{5} \int |\psi_1|^2 \mathbf{H}^{(1)}(1) d\tau_1.$$

The question of obtaining the solutions of a two particle problem has then been reduced to the evaluation of the single-particle integrals. These integrals are tabulated in ref. 2, equation (9). Leaving out the common factor  $\frac{8}{45} \cdot f^2$ , we get:

$$H_{00}^{(1)} = D(0, \mu) \left[ 2 B_0 - \frac{2}{35} B_2 - \frac{3}{28} B_4 \right] + (\mu_5 + \mu_6) \left[ 2 B_0 + \frac{4}{35} B_2 - \frac{2}{7} B_4 \right]$$

Similarly we obtain:

$$\left. \begin{aligned} H_{11}^{(1)} &= D(0, \mu) \left[ 2 B_0 - \frac{3}{70} B_2 - \frac{1}{56} B_4 \right] + (\mu_5 + \mu_6) \left[ 2 B_0 + \frac{3}{35} B_2 - \frac{1}{21} B_4 \right] \\ H_{22}^{(1)} &= D(0, \mu) \left[ 2 B_0 + \frac{1}{8} B_4 \right] + (\mu_5 + \mu_6) \left[ 2 B_0 + \frac{1}{3} B_4 \right] \\ H_{33}^{(1)} &= D(0, \mu) \left[ 2 B_0 + \frac{1}{14} B_2 - \frac{3}{56} B_4 \right] + (\mu_5 + \mu_6) \left[ 2 B_0 - \frac{1}{7} B_2 - \frac{3}{21} B_4 \right] \\ H_{-22}^{(1)} &= D(4, \mu) \left[ -\frac{5}{24} B_4 \right] \\ H_{20}^{(1)} &= D(2, \mu) \left[ -\frac{5}{28} \sqrt{\frac{1}{30}} B_2 - \frac{3}{7} \sqrt{\frac{1}{30}} B_4 \right] \\ H_{-33}^{(1)} &= 0 \\ H_{-11}^{(1)} &= D(2, \mu) \left[ -\frac{5}{42} B_4 - \frac{3}{35} B_2 \right] \\ H_{13}^{(1)} &= D(2, \mu) \left[ \frac{15}{28} \sqrt{\frac{1}{15}} B_4 - \frac{3}{14} \sqrt{\frac{1}{15}} B_2 \right] \\ H_{13}^{(1)} &= D(4, \mu) \cdot \left( -\frac{5}{8 \sqrt{15}} B_4 \right). \end{aligned} \right\} (4)$$

The first order perturbation energies of the Ni(II) complex are obtained by inserting (4) into (3) and solving the equations



with respect to  $E^{(1)}$ . Because of the complexity of the final formulae for the general case, these will not be written out. Calculations for some definite cases are given below.

From the  ${}^3P$  term we get analogously:

$$\left. \begin{aligned} \Psi_{11} &= \sqrt{\frac{2}{10}} \psi_{-1}^{(1)} \psi_2^{(2)} - \sqrt{\frac{3}{10}} \psi_0^{(1)} \psi_1^{(2)} + \sqrt{\frac{3}{10}} \psi_1^{(1)} \psi_0^{(2)} - \sqrt{\frac{2}{10}} \psi_2^{(1)} \psi_{-1}^{(2)} \\ \Psi_{1,0} &= \sqrt{\frac{4}{10}} \psi_{-2}^{(1)} \psi_2^{(2)} - \sqrt{\frac{1}{10}} \psi_{-1}^{(1)} \psi_1^{(2)} + \sqrt{\frac{1}{10}} \psi_1^{(1)} \psi_{-1}^{(2)} - \sqrt{\frac{4}{10}} \psi_2^{(1)} \psi_{-2}^{(2)} \\ \Psi_{1,-1} &= \sqrt{\frac{2}{10}} \psi_{-2}^{(1)} \psi_1^{(2)} - \sqrt{\frac{3}{10}} \psi_{-1}^{(1)} \psi_0^{(2)} + \sqrt{\frac{3}{10}} \psi_0^{(1)} \psi_{-1}^{(2)} - \sqrt{\frac{2}{10}} \psi_1^{(1)} \psi_{-2}^{(2)} \end{aligned} \right\} (5)$$

The secular equation is

$$\begin{vmatrix} H_{-1-1}^{(1)} - E^{(1)} & 0 & H_{1-1}^{(1)} \\ 0 & H_{00}^{(1)} - E^{(1)} & 0 \\ H_{-11}^{(1)} & 0 & H_{11}^{(1)} - E^{(1)} \end{vmatrix} = 0,$$

i. e.

$$\left. \begin{aligned} E^{(1)} &= H_{00}^{(1)} \\ E^{(1)} &= H_{11}^{(1)} \pm H_{1-1}^{(1)}, \end{aligned} \right\} (6)$$

where

$$H_{00}^{(1)} = D(0_1\mu) \left[ 2B_0 + \frac{1}{5}B_2 \right] + (\mu_5 + \mu_6) \left[ 2B_0 - \frac{2}{5}B_2 \right]$$

$$H_{11}^{(1)} = D(0_1\mu) \left[ 2B_0 - \frac{1}{10}B_2 \right] + (\mu_5 + \mu_6) \left[ 2B_0 + \frac{1}{5}B_2 \right]$$

$$H_{1-1}^{(1)} = 0.$$

### The Hexa-Coordinated Ni(II)-Complexes.

The energy levels of Ni(II) complexes, with six equal point dipoles placed in a regular octahedron around the cation, are obtained from (3) and (6):

The  ${}^3F$  state splits up into three levels:

$${}^3F \left\{ \begin{array}{ll} \frac{8}{45} f^2 \mu [12 B_0 - B_4] & \Gamma_4 \\ \frac{8}{45} f^2 \mu \left[ 12 B_0 + \frac{1}{3} B_4 \right] & \Gamma_5 \\ \frac{8}{45} f^2 \mu [12 B_0 + 2 B_4] & \Gamma_2 \end{array} \right\} \quad (7)$$

The  $\Gamma$  notation is the nomenclature of BETHE.<sup>7</sup>

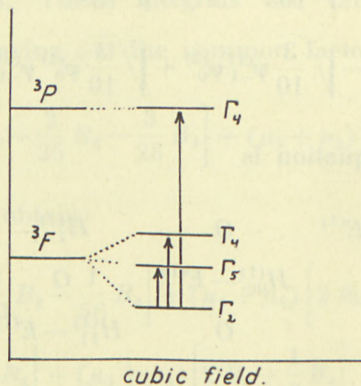


Fig. 1.

The term scheme of the paramagnetic octahedral Ni(II) complexes with cubic symmetry.

For the  ${}^3P$  state, which does not split up in a cubic crystal-field, we get:

$${}^3P: \frac{8}{45} f^2 \mu \cdot 12 B_0 \quad \Gamma_4.$$

The energy levels for one  $d$ -positron is<sup>2</sup>:

$$\left. \begin{array}{l} E_1 = \frac{8}{45} f^2 \mu [6 B_0 + B_4] \\ E_2 = \frac{8}{45} f^2 \mu \left[ 6 B_0 - \frac{2}{3} B_4 \right]. \end{array} \right\} \quad (8)$$

A combination of (8) and (7) in the notation of HARTMANN and ILSE<sup>8</sup> gives



$${}^3F: \left\{ \begin{array}{ll} \frac{1}{5} E_1 + \frac{9}{5} E_2 & \Gamma_4 \\ E_1 + E_2 & \Gamma_5 \\ 2 E_1 & \Gamma_2 \end{array} \right\} \quad (9)$$

$${}^3P: \frac{4}{5} E_1 + \frac{6}{5} E_2 \quad \Gamma_4 \quad (10)$$

Between these four levels three transitions from the ground state  ${}^3F\Gamma_2$  are possible. (See Fig. 1). The frequencies of the three absorption bands are:

$$\left. \begin{array}{l} \nu_1 = (E_2 - E_1) \text{ cm}^{-1} \\ \nu_2 = \frac{9}{5} (E_2 - E_1) \text{ cm}^{-1} \\ \nu_3 = 17000 + \frac{6}{5} (E_2 - E_1) \text{ cm}^{-1}. \end{array} \right\} \quad (11)$$

From these is obtained the simple rule that  $\nu_2/\nu_1 = 1.8$ .

The spectra of  $\text{Ni aq}_6^{++}$  and  $\text{Ni en}_3^{++}$  are given in Fig. 2. As abscissa the wave number  $\nu$  is taken and as ordinate the molar extinction coefficient  $\epsilon$ . Inserting  $(E_2 - E_1)_{aq} = 7600 \text{ cm}^{-1}$  and  $(E_2 - E_1)_{en} = 10500 \text{ cm}^{-1}$  into (11), we find the absorption maxima given in Table 1.

TABLE 1.

*Comparison of experimental and calculated absorption maxima.  
Wave numbers in  $\text{cm}^{-1}$ .*

	$\text{Ni (H}_2\text{O)}_6^{++}$		$\text{Ni en}_3^{++}$	
	obs.	calc.	obs.	calc.
$\nu_3$ .....	25300	26000	29000	29500
$\nu_2$ .....	14000	13700	18350	18900
$\nu_1$ .....	8000	7600	11200	10500
$\nu_2/\nu_1$ .....	1.75	1.80	1.64	1.80

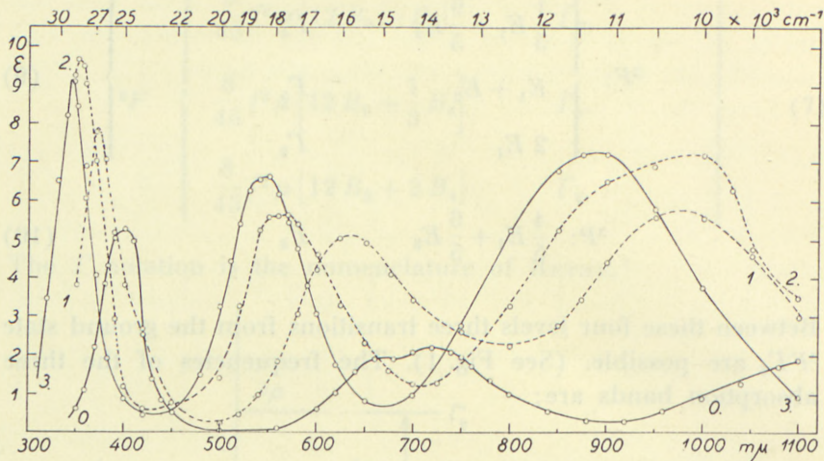


Fig. 2.

The absorption spectra of nickel-ethylenediamine complexes in aqueous solutions at 25° C. Curve (0):  $\text{Ni}(\text{aq})_6^{++}$  Curve (1)  $\text{Ni}(\text{en})_2\text{aq}_2^{++}$  Curve (2)  $\text{Ni}(\text{en})_2\text{aq}_2^{++}$  Curve (3)  $\text{Ni}(\text{en})_3^{++}$  Solutions of the composition:  $C_{\text{Ni}(\text{NO}_3)_2} = 0.05M$ ,  $C_{\text{KCl}} = 0.15M$ ,  $C_{\text{HNO}_3} = 0.05M$  with varying concentrations of ethylenediamine were measured on a Beckman D. U. Curve (0) is obtained from solutions with  $C_{\text{en}} \lesssim 0.05$ . Curve (3) from solutions with  $C_{\text{en}} \lesssim 0.30$ . For solutions with intermediate ethylenediamine concentrations curves (1) and (2) are computed by means of the method of BJERRUM.<sup>13</sup> The consecutive constants were determined to be:  $\log K_1 = 7.17$ ,  $\log K_2 = 6.07$  and  $\log K_3 = 4.27$ .

In Fig. 2 it is seen that the second band  $\nu_2$  in the spectrum of  $\text{Ni}(\text{aq})_6^{++}$  is not symmetrical. A closer analysis<sup>3</sup> shows that it is actually composed of two adjacent bands with a  $\Delta\nu \sim 2000\text{ cm}^{-1}$ . A slightly tetragonal field may produce such an effect. However, a tetragonal field would also turn  $\nu_3$  into a double band, which has not been observed. The second band in the spectrum of  $\text{Ni}(\text{en})_3^{++}$  is seen to be Gaussian-shaped. Therefore, a possible explanation of the double band in the spectrum of  $\text{Ni}(\text{aq})_6^{++}$  may rather be that the splitting due to the ( $L-S$ ) coupling in the  $^3F$  state<sup>5</sup> ( $\sim 2200\text{ cm}^{-1}$ ) is not totally quenched by the weak water ligand field. This is possibly the case for the stronger field produced by the ethylenediamine.

The formulae (9) and (10) can also be applied to the spectrum of  $\text{V}(\text{aq})_6^{+++}$ . The energy levels of the  $^3F$  state are here placed in the opposite order of that in the hexaquo  $\text{Ni}(\text{II})$  complex,



and the  ${}^3P$  state is situated at  $13200\text{ cm}^{-1}$ . Experiments<sup>9</sup> show that this complex has two bands placed in the visible region of the spectrum, the first at  $17200\text{ cm}^{-1}$ , the second at  $25000\text{ cm}^{-1}$ , so that  $\nu_2/\nu_1 = 1.46$ . It seems improbable that the bands can be due to transitions between the  ${}^3F$  levels only, since the ratio  $\nu_2/\nu_1$  in this case would be  $2.25^{1,8}$  (cf. (11)). On the other hand, if we assume that the term scheme is that given by ORGEL,<sup>10</sup> the bands are due to:  ${}^3F\Gamma_4 \rightarrow {}^3F\Gamma_5$  and  ${}^3F\Gamma_4 \rightarrow {}^3P\Gamma_4$ , i. e.  $\nu_2/\nu_1 = 1.56$ . This predicts a third band in  $\text{Vaq}_6^{+++}$  placed at  $37000\text{ cm}^{-1} \sim 270\text{ m}\mu$  and due to  ${}^3F\Gamma_4 \rightarrow {}^3F\Gamma_2$ .

### Mixed Ni(II) Complexes.

The complexes  $\text{Nienaq}_4^{++}$  and  $\text{cis-Nien}_2\text{aq}_2^{++}$  have both the same formal configuration, i. e. two dipoles  $\mu_2$  placed in a cis-position to each other. Assuming all distances to be equal, the energy levels for the  ${}^3F$  state (leaving out the factor  $\frac{8}{45}f^2$ ) is:

$$\left. \begin{aligned}
 E(\Gamma_{2(t3)}) &= \mu_1 \left[ 8 B_0 + \frac{4}{3} B_4 \right] + \mu_2 \left[ 4 B_0 + \frac{2}{3} B_4 \right] \quad (\text{ground level}) \\
 E(\Gamma_{5(t4)}) &= \mu_1 \left[ 8 B_0 + \frac{1}{2} B_4 \right] + \mu_2 \left[ 4 B_0 - \frac{1}{6} B_4 \right] \\
 E(\Gamma_{5(t5)}) &= \mu_1 \left[ 8 B_0 - \frac{1}{35} B_2 - \frac{11}{42} B_4 \right] + \mu_2 \left[ 4 B_0 + \frac{1}{35} B_2 - \frac{1}{14} B_4 \right] \\
 &+ \frac{1}{2} \sqrt{\left[ \mu_1 \left( -\frac{8}{35} B_2 - \frac{11}{42} B_4 \right) + \mu_2 \left( \frac{8}{35} B_2 - \frac{1}{14} B_4 \right) \right]^2 + (\mu_1 + \mu_2)^2 \cdot \frac{5}{12} (B_4)^2} \\
 E(\Gamma_{4(t2)}) &= \mu_1 \left[ 8 B_0 + \frac{4}{35} B_2 - \frac{11}{14} B_4 \right] + \mu_2 \left[ 4 B_0 - \frac{4}{35} B_2 - \frac{3}{14} B_4 \right] \\
 E(\Gamma_{4(t5)}) &= \mu_1 \left[ 8 B_0 - \frac{1}{35} B_2 - \frac{11}{42} B_4 \right] + \mu_2 \left[ 4 B_0 + \frac{1}{35} B_2 - \frac{1}{14} B_4 \right] \\
 &- \frac{1}{2} \sqrt{\left[ \mu_1 \left( -\frac{8}{35} B_2 - \frac{11}{42} B_4 \right) + \mu_2 \left( \frac{8}{35} B_2 - \frac{1}{14} B_4 \right) \right]^2 + (\mu_1 + \mu_2)^2 \cdot \frac{5}{12} (B_4)^2}
 \end{aligned} \right\} \quad (12)$$

and for the  ${}^3P$  term:

$$\left. \begin{aligned} E(\Gamma_{4(t2)}) &= \mu_1 \left[ 8 B_0 - \frac{2}{5} B_2 \right] + \mu_2 \left[ 4 B_0 + \frac{2}{5} B_2 \right] \\ E(\Gamma_{4(t5)}) &= \mu_1 \left[ 8 B_0 + \frac{1}{5} B_2 \right] + \mu_2 \left[ 4 B_0 - \frac{1}{5} B_2 \right]. \end{aligned} \right\} (13)$$

The formulae for the levels of the trans-Nien<sub>2</sub>aq<sub>2</sub><sup>++</sup> complex, in which the two water dipoles  $\mu_2$  are placed in trans-position to each other, is for the <sup>3F</sup> state:

$$\left. \begin{aligned} E(\Gamma_{2(t3)}) &= \mu_1 \left[ 8 B_0 + \frac{4}{3} B_4 \right] + \mu_2 \left[ 4 B_0 + \frac{2}{3} B_4 \right] \quad (\text{ground level}) \\ E(\Gamma_{5(t4)}) &= \mu_1 \left[ 8 B_0 - \frac{1}{3} B_4 \right] + \mu_2 \left[ 4 B_0 + \frac{2}{3} B_4 \right] \\ E(\Gamma_{5(t5)}) &= \mu_1 \left[ 8 B_0 + \frac{2}{35} B_2 - \frac{1}{7} B_4 \right] + \mu_2 \left[ 4 B_0 - \frac{2}{35} B_2 - \frac{4}{21} B_4 \right] \\ &+ \frac{1}{2} \sqrt{\left[ \mu_1 \left( -\frac{16}{35} B_2 + \frac{1}{7} B_4 \right) + \mu_2 \left( \frac{16}{35} B_2 + \frac{4}{21} B_4 \right) \right]^2 + \frac{5}{3} \mu_1^2 (B_4)^2} \\ E(\Gamma_{4(t2)}) &= \mu_1 \left[ 8 B_0 - \frac{8}{35} B_2 - \frac{3}{7} B_4 \right] + \mu_2 \left[ 4 B_0 + \frac{8}{35} B_2 - \frac{4}{7} B_4 \right] \\ E(\Gamma_{4(t5)}) &= \mu_1 \left[ 8 B_0 + \frac{2}{35} B_2 - \frac{1}{7} B_4 \right] + \mu_2 \left[ 4 B_0 - \frac{2}{35} B_2 - \frac{4}{21} B_4 \right] \\ &- \frac{1}{2} \sqrt{\left[ \mu_1 \left( -\frac{16}{35} B_2 + \frac{1}{7} B_4 \right) + \mu_2 \left( \frac{16}{35} B_2 + \frac{4}{21} B_4 \right) \right]^2 + \frac{5}{3} \mu_1^2 (B_4)^2} \end{aligned} \right\} (14)$$

and for the <sup>3P</sup> state:

$$\begin{aligned} E(\Gamma_{4(t5)}) &= \mu_1 \left[ 8 B_0 - \frac{2}{5} B_2 \right] + \mu_2 \left[ 4 B_0 + \frac{2}{5} B_2 \right] \\ E(\Gamma_{4(t2)}) &= \mu_1 \left[ 8 B_0 + \frac{4}{5} B_2 \right] + \mu_2 \left[ 4 B_0 - \frac{4}{5} B_2 \right]. \end{aligned}$$

For the numerical evaluation we insert all the distances  $R$  equal to 2.0 Å (see ref. 1, 11 and 14) and  $Z = 7.20$  according to SLATER,<sup>12</sup> i. e.  $x = \frac{7.20}{3} \cdot 3.78 = 9.1$ . From Table 3 in ref. 2



$B_2/B_4 = 2.26$ . Further, we assume that the values of the dipole moments are the same both in the "mixed" and in the "unmixed" complexes. Then

$$\left. \begin{aligned} (E_2 - E_1)_{\text{lig.}} &= \left( \frac{8}{45} f^2 \mu B_4 \right) \cdot \frac{5}{3} = \left( \frac{8}{45} f^2 \mu B_2 \right) \cdot \frac{5}{3} \cdot \frac{1}{2.26} \text{ i. e.} \\ \frac{8}{45} f^2 \mu B_4 &= 0,60 (E_2 - E_1)_{\text{lig.}} \\ \frac{8}{45} f^2 \mu B_2 &= 1,35 (E_2 - E_1)_{\text{lig.}} \end{aligned} \right\} \quad (15)$$

The results of the calculation are shown in Table 2. The observed absorption spectra of  $\text{Nienaq}_4^{++}$  and  $\text{Nien}_2\text{aq}_2^{++}$  are shown in Fig. 2; the maxima of the bands are tabulated in Table 3.

TABLE 2.

*Calculated absorption maxima. Wave lengths in  $m\mu$ .*

$\text{Nienaq}_4^{++}$	cis- $\text{Nien}_2\text{aq}_2^{++}$	trans $\text{Nien}_2\text{aq}_2^{++}$
1230	1150	1140
1100	1100	950
650	590	580
640	580	570
360	360	380
350	330	330

TABLE 3.

*Experimentally found absorption maxima. Wave lengths in  $m\mu$ .*

$\text{Nienaq}_4^{++}$	$\text{Nien}_2\text{aq}_2^{++}$
980	900, 1000
640	550, 570
370	340

The calculated absorption maxima are nearly identical with those found by experiments. However, it is only in a few cases that the adjacent bands can be distinguished from one another

on the measured absorption curves. It is seen that the spectra of the cis- and trans-Nien<sub>2</sub>aq<sub>2</sub><sup>++</sup> complexes are nearly equal.

The spectra of the [Ni(NH<sub>3</sub>)<sub>n</sub>(H<sub>2</sub>O)<sub>6-n</sub>]<sup>++</sup> complexes can be treated analogously. Taking  $(E_2 - E_1)_{NH_3} = 10100 \text{ cm}^{-1}$ , e. g. the band of Nickel monoquo pentammine, which BJERRUM<sup>12</sup> found to have a maximum at  $17200 \text{ cm}^{-1}$ , is placed at  $17300 \text{ cm}^{-1}$ . It is instructive to compare the absorption curves in Fig. 13, ref. 13, of the nickel ammines with the absorption curves in Fig. 2 of the nickel ethylenediamine complexes. It is observed that the spectra of the [Ni(NH<sub>3</sub>)<sub>2</sub>(H<sub>2</sub>O)<sub>4</sub>]<sup>++</sup> and [Ni(NH<sub>3</sub>)<sub>4</sub>(H<sub>2</sub>O)<sub>2</sub>]<sup>++</sup> complexes show a slight displacement towards the red as compared with the corresponding ethylenediamine complexes. This is also to be expected, as  $(E_2 - E_1)_{NH_3} = 10100 \text{ cm}^{-1}$  is slightly lower than  $(E_2 - E_1)_{en} = 10500 \text{ cm}^{-1}$ .

The dipole moments for the distance  $2.0 \text{ \AA}$  and for  $Z = 7.20$  are calculated to be:

$$\begin{aligned}\mu_{H_2O} &= 3.45 \text{ Debye} \\ \mu_{NH_3} &= 4.55 \text{ —} \\ \mu_{en} &= 4.74 \text{ —}\end{aligned}$$

Thus both the chemical evidence, as shown by BJERRUM,<sup>13</sup> and the model developed here seem to verify that the hexacoordinated Ni(II) complexes are built very nearly as regular octahedrons.

### The Four-Coordinated Ni (II) Complexes.

It has been shown by X-ray examinations that the diamagnetic four-coordinated Ni(II) complexes have a square-planar configuration. (For a review, see ref. 14). According to the magnetic evidence the ground level must be a singlet.

In order to investigate which state could possibly be the ground state we shall first consider the splittings of the levels in a distorted octahedron. The lowest level of the <sup>1</sup>G term in a distorted octahedron (<sup>1</sup>G *F*<sub>4(t2)</sub> in the nomenclature of BETHE<sup>7</sup>) is:

$$E^{(1)} = \frac{8}{45} f^2 \mu_1 [8 B_0 + \frac{8}{7} B_2 + \frac{1}{7} B_4] + \frac{8}{45} f^2 \mu_2 [4 B_0 - \frac{8}{7} B_2 + \frac{4}{21} B_4].$$



This is the level which splits up the most in a tetragonal field, and as none of the other states has this symmetry, the level can cross these. Taking  $B_2/B_4 = 2.26$  and  $\mu_2 = 0$ , we get for the square-planar complex

$$E^{(1)} = \frac{8}{45} f^2 \mu_1 [8 B_0 + 2.72 B_4].$$

For relatively strong ligand fields this level can be the ground state, and the complex thus diamagnetic. However, paramagnetic

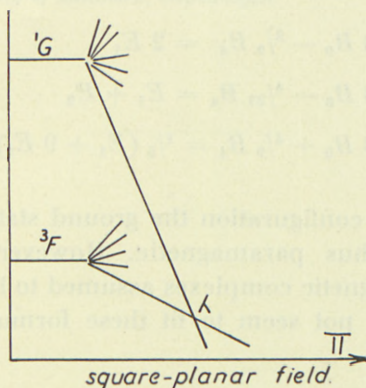


Fig.3.

Fig. 3. The term splittings in the square-planar configuration. The ground level is changed from a triplet to a singlet at the point  $\lambda$ .

complexes with square-planar configuration seem also to be possible (Fig. 3).

The  ${}^1G$  state is estimated by CONDON and SHORTLEY<sup>6</sup> to be placed at  $\sim 22000 \text{ cm}^{-1}$ , and a reasonable value of the splitting of the  ${}^3F$  level in a square-planar field is  $\sim 12000 \text{ cm}^{-1}$ . If  ${}^1G ({}^1G_{4(12)})$  is the ground state,  $\frac{8}{45} f^2 \mu \cdot 2.72 B_4 > 34000 \text{ cm}^{-1}$ , i. e.  $\frac{8}{45} f^2 \mu B_4 > 12500 \text{ cm}^{-1}$ , which in fact corresponds to a rather strong crystal-field.

Even if our calculations are only valid for small ligand-fields, we can e. g. try to calculate the first absorption band of Nistien<sub>2</sub><sup>++</sup>. (stien = C, C-di(phenyl)ethylenediamine). If we use  $\frac{8}{45} f^2 \mu B_4 = 13000 \text{ cm}^{-1}$ , this band  ${}^1G ({}^1G_{4(12)}) \rightarrow {}^1D ({}^1D_{3(11)})$  is placed at  $550 m\mu$ . Experiments show only one band situated

at  $450 m\mu$ . Another possibility is that second order effects have already depressed the  ${}^1D$  ( $\Gamma_{3(t1)}$ ) level beneath the  ${}^1G$  ( $\Gamma_{4(t2)}$ ) level. It is known that in strong crystal fields this level is placed below the former.

The splittings in a regular tetrahedron are similar, but the inverse of the splittings in a regular octahedron.<sup>17</sup> It turns out that the coefficients to  $B_4$  obtained in the octahedral case are to be multiplied by the factor  $-4/9$ , e. g. for the  ${}^3F$  state: (the factor  $\frac{8}{45}f^2\mu$  is omitted)

$${}^3F \left\{ \begin{array}{ll} 8 B_0 - \frac{8}{9} B_4 = 2 E_1 & \Gamma_2 \\ 8 B_0 - \frac{4}{27} B_4 = E_1 + E_2 & \Gamma_5 \\ 8 B_0 + \frac{4}{9} B_4 = \frac{1}{5} (E_1 + 9 E_2). & \Gamma_4 \end{array} \right.$$

In the tetrahedral configuration the ground state is a triplet and the complex is thus paramagnetic. However, the absorption spectra of paramagnetic complexes assumed to have a tetrahedral configuration<sup>14</sup> do not seem to fit these formulae.

### General Remarks.

As demonstrated in the above sections the simple crystal-field theory is able to account for most of the experimental material. Thus it seems unlikely that the overlap-integrals between the ligands and the metal-ion can be of much importance. This seems to be in accordance with recent calculations by CRAIG, MACCOLL, NYHOLM, ORGEL and SUTTON.<sup>15</sup> The hybridization  $3d^2 4s 4p^3$  would produce two  $4d$  electrons, predicting a level order inversed to the one found and with a ratio  $\nu_2/\nu_1 = 2.25$  (cf. formula (9)). However, the actual ratio  $\nu_2/\nu_1 = 1.64$  of the  $\text{Ni}_{3^{++}}$  bands is, as we have seen, in fair agreement with the picture of an unchanged electronic configuration of the metal ion.

VAN VLECK<sup>16</sup> pointed out that complexes are held together more by polarization forces than by true valence forces. This seems to be true for the  $\text{Ni(II)}$  complexes discussed here.



In later publications the theory will be extended to the simpler cobalt and chromium complexes and to their poly-nuclear compounds.

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*Chemistry Department A,  
Technical University of Denmark, Copenhagen.*

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