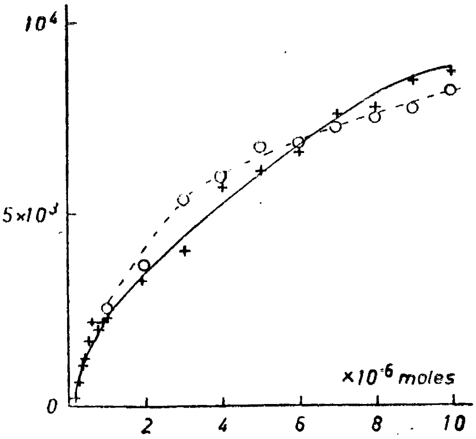

Fig. 2. **Dosage curves for vanillin-blue:**
a. Diluted with 70 % sulphuric acid o ——— o
b. Diluted with 96 % ethanol + ——— +

tion with ethanol, and (28.4 ± 0.9) × 10^8 units/mole, for sulphuric acid dilution. The advantage in diluting with ethanol is the maximal absorption at 600 mμ. The interference with other coloured substances formed, *i. e.*, the red substance in the supernatant liquid will be less in ethanol. On the other hand the alcoholic solutions are less stable. A point to be noted in the practical application of the method is that both an aged vanillin-sulphuric acid solution and a freshly prepared one will give the same dosage curve.

For the use of vanillin-blue as a peroxide reagent, it is unnecessary to know its formula or the reaction mechanism. The amount of vanillin exceeds greatly that of the peroxides (ranging from 1:10 to 1:10^4). It is doubtful whether the vanillin-blue formed and precipitated has a constant composition. However, an analysis was made, giving C 68.2, H 5.46, and O 24.3 (1 % ash).

Campbell and Coppinger [2] added *t*-butyl hydroperoxide to 2,6-di-*t*-butyl-*p*-cresol, and obtained a substance described as 1-methyl - 1 - *t* - butylperoxy - 3,5 - di - *t* - butylcyclohexadienone-4. With this type of peroxide (which have an absorption maximum at 234 mμ) vanillin-blue seems to have little in common. We exclude a compound with the *t*-BuOO-group directly attached to the aromatic ring as such compounds will not be stable. In view of the small amounts of peroxide needed for the formation of colour and the unknown behaviour of less stable peroxides such as the methylhydroperoxide, no formula for vanillin-blue is advanced.

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Received March 19, 1955.

4s-Electrons in the First Transition Group Complexes

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When the crystal field theory is applied [1,2] to the absorption spectra of hexaaquo ions and other simple complexes of the first transition group, small discrepancies (~ 5 %) occur between the calculated and observed wavenumbers of the band maxima. Mainly based on magnetic evidence, Owen [3] has interpreted these effects by ~ 20 % intermixing of σ-electrons from the ligands with the γ_3-electrons (the highest energy state of d-electrons in an octahedral complex while the other is γ_5). In the present note attention will be drawn to the electron configuration $3d^{n-1}$ 4s, which in the free, divalent ion is situated [4] ~ 50 000 cm^{-1} over the groundstate, due to $3d^n$.

Since these two electron configurations have the same parity (the sum of the l-values is even) they can directly intermix. The author [5] even maintains that the crystal field induces an intermixing with $3d^{n-1}4p$ and electron transfer states, explaining the observed transitions which would else be forbidden by Laporte's rule. The former interaction will *inter alia* depress the energy of the levels with the same Γ_n as the lowest level of the excited $3d^{n-1}$ 4s configuration. Thus, in d^3-systems, the levels $^4\Gamma_4$ will be depressed by the groundstate $\gamma_5{}^2\gamma_1$ of $3d^24s$. Now, Mr. C. E. Schäffer has kindly pointed out to me that the observed energy difference, $^4\Gamma_4 - {}^4\Gamma_5$, between the two strong bands of chromium (III) complexes decreases by increasing crystal field strength, while it should [6] be slightly increasing or constant, if no interaction appeared. Also V^{++} shows this effect if $^4\Gamma_5$ is placed at 12 200 cm^{-1}, contrary to Owen [3].

In d^5-systems as Mn^{++}, Orgel[2] discussed a systematical depression of ^4G and other excited terms in the hexaaquo ion, compared with the free ion[4]. This might also be explained by interactions especially with the low $^4\Gamma_3$ and $^4\Gamma_4$ of $3d^44s$. With the Cary spectrophotometer a very broad band ($\delta \sim 1\,500$ cm^{-1}) is observed of 2 M $MnSO_4$ in H_2O at 32 600 cm^{-1}. This is undoubtedly due to $^4\Gamma_4$, and the band[1] at 29 700 cm^{-1} to $^4\Gamma_3$, as pointed out by Orgel[2]. At 38 500 and at 40 600 cm^{-1}, two bands are observed, probably due to $^4\Gamma_4$ and $^4\Gamma_5$ of the term ^4F, which should be displaced upwards by perturbations[2]. $^4\Gamma_2$ can be assigned to one of the two shoulders observed at 35 900 and 37 000 cm^{-1}. The three latter levels show definitely the decrease in energy of ^4F, due to interactions with states of other electron configurations, *e. g.* $3d^44s$. All the quartet levels of $3d^5$ in Mn^{++} seem now detected.

In d^8-systems as Ni^{++}, the lowest levels of $3d^74s(\gamma_5{}^4\gamma_3\gamma_1)$ are $^3\Gamma_3$ and $^1\Gamma_3$. The latter level will depress the lowest singlet level[7] of nickel(II) complexes. Without this interaction the transition $^3\Gamma_2 - {}^1\Gamma_3$ would correspond to the weak band[2,7] at 18 350 cm^{-1} of $Ni(H_2O)_6{}^{++}$. But the "extra" band at 15 400 cm^{-1} has been assigned[5] to this transition. In a paper to be published the energy of $^1\Gamma_3$ in a wide range of nickel(II) complexes will be studied. Table 1 shows the observed maxima in cm^{-1} of complexes, which are not all of cubic symmetry (*e. g.* the ethylenediaminetetraacetate or the solutions in concentrated acids). The parentheses indicate cases of very strong intermixing, where the distinction between $^1\Gamma_3$ and the triplet state has no physical significance[8]. This results in nearly equal intensities and halfwidths, while $^1\Gamma_3$ ordinarily is weak and narrow.

While the band[7] should be quite constant $\sim 18\,000$ cm^{-1} as an intermixing of ^1D and ^1G found by Shenstone[9], the observed values decrease considerably with increased crystal field strength. In tetragonal complexes the interaction will be even more pronounced. Thus, the energy difference, necessary to make a planar complex diamagnetic, will be rather 11 000 than 18 000 cm^{-1} (*cf.* eq. 29 of Ref. 7). This agrees better with the observed tendency of changing groundstate.

The ethanol solvate of nickel(II)bis-(acetylacetonate), which probably is octahedral[10], has a shoulder at 13 000 cm^{-1} besides the stronger triplet bands at 9 100 and 15 550 cm^{-1}. If nickel nitrate in 60 % glycerol is cooled by liquid air, a sharp band in the far red can be distinguished in a spectroscope, corresponding to a later place in the Table. The non-diagonal elements[8] in the matrices between ^1D and ^3F, due to (L, S) coupling, are half the smallest distances between the two bands, when the levels are crossing, ~ 800 cm^{-1} in the table. If the non-diagonal elements between $3d^n$ and $3d^{n-1}4s$ are of the order of magnitude of 10 000 cm^{-1}, then the intermixing in squares of the wavefunctions will be about 4 %, and the energy decreases of the lowest levels $\sim 2\,000$ cm^{-1}, agreeing well with the observed effects.

Table 1.

	$^1\Gamma_3(D)$	$^3\Gamma_5(F)$	$^3\Gamma_4(F)$	$^3\Gamma_4(P)$
free	14 000	0	0	16 900
H_2SO_4	14 800	—	12 200	23 350
H_3PO_4	14 900	—	13 150	24 500
$(H_2O)_6$	(13 500)	8 500	(15 400)	25 300
enta	12 700	10 100	17 000	26 200
glycine$_3$	13 100	10 100	16 600	27 600
$(NH_3)_6$	13 150	10 750	17 500	28 200
en$_3$	12 400	11 200	18 350	29 000
$\alpha\alpha'$-dip$_3$	(11 500)	(12 650)	19 200	—
o-phen$_3$	(11 550)	(12 700)	19 300	—

Transitions between the configurations $3d^n$ and $3d^{n-1}4s$ can next be sought for in the absorption spectra. Orgel[2] pointed out that copper(I) complexes do not show such bands in the wavenumber range 21 900 − 26 300 cm^{-1}, where levels of ^3D and ^1D of $3d^9$ 4s are distributed in the free ion[4]. Solutions of $Cu(NH_3)_2{}^+$ in 0.2 M NH_4ClO_4 and 1 M NH_3 show on the Cary absorption above 35 000 cm^{-1}. If this is identified as these transitions, giving not much higher intensities than the usual crystal field spectra, it is seen that the 4s-electron has considerably higher energy in the crystal field than in the free ion. This is formally connected with the different values[11] of the crystal field parameter B_0 in different configurations. Orgel[12] has reviewed the "electron transfer" spectra and agrees with Dainton that some bands with $\varepsilon \sim 100$ of divalent ions in the ultraviolet are due to transfer of electrons from the central ion to the ligands, the opposite way of the ordinary bands (with $\varepsilon \sim 5\,000$) found in oxidizing metal ions such as Fe^{+3}, Cu^{+2}, Ir^{+4}, Pu^{+4}, *etc.* The former type of band, observed in V^{++} at 33 000 cm^{-1} and in Cr^{++} at 40 000 cm^{-1} may be ascribed to the $3d^{n-1}4s$ states. Since ^4F and ^5F of these configurations are situated at 44 000 and 49 000 cm^{-1} in the free ions [4], the crystal field splittings of the excited terms must here be considerable in order to explain the low wavenumbers observed. It might be argued that ^7S of $3d^64s$ in Fe^{++} at 30 000 cm^{-1} should give even lower wavenumbers. But for more than five d-electrons, the highest multiplicity of $3d^{n-1}4s$ gives spin-forbidden bands, and first ^6S at 41 000 and ^6G at 63 000 cm^{-1} will give ordinary intensities in Fe^{++}, where a band [12] is observed $\sim$40 000 cm^{-1}.

Orgel [2] and Owen [3] investigate the possibility of covalent bonding, *i. e.* molecular orbitals being occupied by electrons from both central ion and ligands. This is undoubtedly the case of ligands with considerable electron affinity, as CO, CN^-, NO^+, aromatic amines, PCl_3, trialkylphosphines, but it is not easily decided in the case of ordinary ligands (H_2O, NH_3, *etc.*) where the most conspicuous effect [2, 3] on the absorption spectra is only an increased energy difference ($E_1 - E_2$) between γ_3- and γ_5-electrons, analogous to the crystal field influence. It is interesting that ($E_1 - E_2$) is nearly constant $\sim$20 000 cm^{-1} in trivalent hexaaquo ions, while it is $\sim$10 000 cm^{-1} in divalent ions, and here decreasing [1] with the atomic number as implied from the theory [13]. This can only be explained by considerably smaller distances to the effective negative charges of the ligands of the trivalent ions than in the divalent ions, if the covalent hypothesis is not accepted. It must be remarked that the parameters in the crystal field model of Ilse and Hartmann [13] have no quantitative physical significance. *E. g.*, the hydrogen-like 3d wavefunction with the effective charge $Z = 4$ has its maximum at a distance 1.18 Å from the nucleus, while the radius of Ti^{+3} is assumed to be 0.8 Å. Some problems related to effective quantum numbers will be discussed elsewhere [14]. The transitions between different configurations, $5f^n \rightarrow 5f^{n-1}6d$ in the actinide ions, are also known from absorption spectra [15].

A valuable implication from the theory of molecular orbitals [2,3] is that the strong electron transfer bands are due to transitions from the odd γ_4-states. Hartmann [16] pointed out that the series of energy of the molecular orbitals in an octahedral complex should be:

$$\gamma_1, \gamma_4, \gamma_3, \gamma_5(d), \gamma_3(d), \gamma_1(s), \gamma_4(p) \ldots$$

If the lowest γ_3 had a much higher energy than the lowest γ_4, weak bands would be found in the electron transfer spectra at lower wavenumbers than the strong bands.

Acknowledgments. I am much indebted to Professor Jannik Bjerrum for interesting discussions. Further, I thank Dr. L. E. Orgel for the opportunity to see the manuscripts of several new papers.

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Received March 24, 1955.

Dihydro-thionaphthene-2- and -3-carboxylic Acids

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The acids have been prepared in connection with current work on optically active plant growth substances. They are easily obtained by hydrogenation of the corresponding thionaphthene-carboxylic acids using sodium amalgam.