

Comparative Crystal Field Studies II. Nickel(II) and Copper(II) Complexes with Polydentate Ligands and the Behaviour of the Residual Places for Co-Ordination

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The complexes of nickel(II) and copper(II) with ethylenediaminetetraacetate, nitrogentriacetate and β, β', β'' -tris(ethylamino)amine have one or more residual places left for co-ordination. The absorption spectra of such complexes containing either water, ammonia, ethylenediamine, glycinate or cyanide were determined. The wavenumbers of the bands illustrate the regular behaviour of paramagnetic octahedral nickel(II) complexes, whereas the intensities vary. Some copper(II) complexes are much more tetragonally distorted than others. The "chelate" effect in formation constants is not only due to the different dependence on dilution of the degree of formation of polydentate ligands' complexes, but can be estimated from the spectra in some cases to contain actual stabilization energies. The different crystal field strength of six nitrogens in nickel(II) amine complexes is further illustrated, e.g. by 1,3-diaminopropane. The bonding of cyanide in paramagnetic complexes is not very strong and the complexes slowly react to form yellow, diamagnetic nickel(II) and colourless copper(I) cyanides. β, β', β'' -tris(ethylamino)amine does not form a tetrahedral complex with nickel(II), since the water in *cis*-position of the octahedral complex can be exchanged with ammonia, ethylenediamine or glycinate. The last complex has a very hypsochromic spectrum corresponding to a high stabilization energy. The absorption spectra of nickel(II) complexes demonstrate intermediate coupling and decreased values of the Racah parameters of electrostatic interaction between d-electrons, relative to the gaseous ion.

The first paper of this series¹ treated nickel(II) complexes with increasing crystal field strength, corresponding to yellow, green, blue, purple and red colours. The four strongest absorption bands can be interpreted as transitions from the groundstate ${}^3\Gamma_2 (F)$ to ${}^1\Gamma_3 (D)$, ${}^3\Gamma_5 (F)$, ${}^3\Gamma_4 (F)$ and ${}^3\Gamma_4 (P)$ in the notation of Bethe². It was shown that the singlet state ${}^1\Gamma_3 (D)$ is intermixed with ${}^3\Gamma_5 (F)$ and ${}^3\Gamma_4 (F)$ by effects of intermediate coupling. In the present paper, nickel(II) is studied in different environments, supplied partly by polydentate ligands. Further, characteristic properties of copper(II), compared to nickel(II) complexes will be discussed¹.

Empirically, the absorption spectra of mixed complexes have led to the idea of averaged environment. For example, except for very small solvent effects, the six atoms in the first co-ordination sphere of an octahedral complex determine the absorption spectrum. The position of the absorption bands can be predicted mainly from one parameter, expressing the average of the positions of the ligands in the spectrochemical series. Thus, Mead³ studied mixed ethylenediamine- and oxalate complexes of chromium(III) and cobalt(III); Tsuchida⁴ investigated many complexes of the same two metals, e.g. acido-pentammines. Mathieu⁵ investigated the influence of amino-acids on the two residual places in *cis*-bis(ethylenediamine)cobalt(III) ions. Linhard and Weigel studied the halogenopentammines⁶ and the *cis*- and *trans*-tetrammines and pentammines of cobalt(III) with carboxyl groups on the residual places⁷. Copper(II) complexes with ethylenediamine and other ligands have been studied by Jonassen *et al.*⁸, copper(II) bis(acetylacetonate) with different solvents by Belford⁹ and cobalt(III) complexes by Basolo, Ballhausen and Bjerrum¹⁰. In some cases crystal fields of pronounced tetragonal symmetry produce new bands by splitting as in *trans*-Co en₂Cl₂⁺. In the second and third transition group, Delépine's complexes of rhodium(III) and iridium(III) exhibit similar behaviour¹¹. Since water is exchanged without change of the co-ordination number, the consecutive uptake of six ammonia molecules to nickel(II), studied by J. Bjerrum¹², or of three ethylenediamine molecules, measured by Ballhausen¹³, can also be cited as examples of mixed complexes with water as one of the ligands.

Table 1 gives the absorption spectra measured here of nickel(II) complexes and Table 3 of copper(II) complexes. Table 2 collects the band maxima of nickel(II) and gives also the results of the first paper¹.

The following abbreviations will be used for the ligands:

en	= ethylenediamine = 1,2-diaminoethane
tn	= trimethylenediamine = 1,3-diaminopropane
bdn	= 1,3-diaminobutane
ptn	= 1,2,3-triaminopropane
tren	= β, β', β'' -tris(ethylamino)amine
trien	= triethylenetetramine
den	= diethylenetriamine
tetren	= tetraethylenepentamine
temeen	= C,C',C'',C'''-tetramethyl-ethylenediamine
dip	= α, α' -dipyridyl = 2,2'-bipyridine
phen	= <i>o</i> -phenanthroline = 1,10-phenanthroline
gly ⁻	= glycinate = aminoacetate
ata ⁻³	= ammoniatriacetate * = nitrilotriacetate = nitrogentriacetate
enta ⁻⁴	= ethylenediaminetetraacetate.

NICKEL(II) ETHYLENEDIAMINETETRAACETATES

Schwarzenbach¹⁴ studied the colour reactions of Ni en₂ with NH₃, en and CN⁻. He pointed out that the formation constant of Ni en₂ is so large that the other ligands do not decompose this complex. While this has a somewhat limited validity in the case of Ni en₂ + en, as discussed below, the ligands must be assumed to exchange with the water present in the first co-ordination sphere of Ni en₂, H₂O⁻. The latter complex has a free carboxyl group, which can take up protons¹⁵ with pK = 3, forming Ni en₂H, H₂O⁻. In Table 1, two forms are given of nickel(II) ethylenediaminetetraacetate, denoted α and β . The latter form corresponds to the intermediate form which is observed¹ during the slow formation reactions. However, at low pH \sim 3,

* As proposed by Martell and Calvin in *The Chemistry of the Metal Chelate Compounds*, New York 1952. Professor K. A. Jensen has proposed the name "nitrogentriacetate".

Table 1. Absorption bands of nickel (II) complexes. Wavelength λ_n , wavenumber ν_n and molar extinction coefficient ϵ_n of the maxima; $\delta(-)$ and $\delta(+)$ the half-width towards lower and higher wavenumbers, and P the oscillator strength for each band.

	Excited level	λ_n m μ	ν_n cm $^{-1}$	ϵ_n	$\delta(-)$ cm $^{-1}$	$\delta(+)$ cm $^{-1}$	P · 10 $^{-5}$
α -Ni enta $^{2-}$	3G_5 (F)	990	10 100	31.0	1 400	1 300	38
	1G_3 (D)	790	12 700	5.4	—	—	3
	3G_4 (F)	587	17 000	8.4	1 700	1 500	12
	3G_4 (P)	382	26 200	12.6	1 700	2 100	22
β -Ni enta $^{2-}$	3G_5 (F)	1 010	9 900	26	—	1 400	34
	1G_3 (D)	780	13 000	3	—	300	1
	3G_4 (F)	592	16 900	8.2	1 700	1 500	12
	3G_4 (P)	379	26 400	13.8	1 600	1 900	22
Ni entaNH $_3^{2-}$	3G_5 (F)	980	10 200	16.6	—	1 500	23
	1G_3 (D)	785	12 700	3.4	—	—	2
	3G_4 (F)	582	17 200	10.9	2 000	1 900	19
	3G_4 (P)	372	26 900	20.2	1 600	1 700	30
Ni enta en $^{2-}$	3G_5 (F)	995	10 050	25	—	1 400	32
	1G_3 (D)	796	12 550	4.7	—	—	4
	3G_4 (F)	579	17 300	8.1	1 800	1 600	13
	3G_4 (P)	368	27 100	10.8	2 400	~3 000	27
Ni enta CN $^{3-}$	3G_5 (F)	955	10 500	14	—	1 700	22
	1G_3 (D)	800	12 500	5.4	—	—	6
	3G_4 (F)	570	17 500	12	2 100	1 600	20
	3G_5 (F)	1 050	9 500	16.0	—	1 400	21
Ni ata $^{-}$	1G_3 (D)	753	13 300	2.5	—	—	1
	3G_4 (F)	625	16 000	6.6	1 900	1 400	10
	3G_4 (P)	391	25 600	12.8	1 800	2 000	22
	3G_5 (F)	960	10 400	5.4	1 400	1 500	7
Ni ata $_2^{-4}$	1G_3 (D)	770	13 000	1.5	—	—	1
	3G_4 (F)	575	17 400	4.3	2 600	1 400	8
	3G_4 (P)	370	27 000	6.4	2 000	—	15
		350	28 600	6.0	—	—	
Ni ata(NH $_3$) $_2^{-}(\?)$	3G_5 (F)	1 045	9 600	11.0	—	1 600	16
	1G_3 (D)	761	13 100	2.3	—	—	2
	3G_4 (F)	607	16 500	9.3	2 000	1 600	15
	3G_4 (P)	375	26 600	16.2	1 800	2 000	28
Ni ata en $^{-}$	3G_5 (F)	1 060	9 400	11	—	1 700	18
	1G_3 (D)	772	13 100	2.3	—	—	2
	3G_4 (F)	592	16 900	7.7	2 300	1 900	15
	3G_4 (P)	367	27 200	13.2	2 200	2 200	27
Ni ata gly $^{-}$	3G_5 (F)	1 010	9 900	9.8	—	1 800	16
	1G_3 (D)	771	13 000	2.9	—	—	3
	3G_4 (F)	584	17 100	7.0	2 300	1 500	12
	3G_4 (P)	381	26 200	11.1	1 800	2 900	24
Ni ata den $^{-}$	3G_5 (F)	915	10 900	7.4	1 700	1 900	12
	1G_3 (D)	798	12 500	5.1	—	—	—
	3G_4 (F)	568	17 600	6.8	2 200	2 000	13
	3G_4 (P)	348	28 700	8.8	2 200	—	17
Ni tren(H $_2$ O) $_2^{++}$	3G_5 (F)	950	10 500	15.5	1 400	1 800	23
	1G_3 (D)	782	12 800	6.3	—	—	
	3G_4 (F)	561	17 800	9.3	1 800	1 700	15
	3G_4 (P)	360	27 800	12.0	2 200	—	24
Ni $_2$ tren $_3^{+4}$	3G_5 (F)	935	10 700	9.4	1 400	1 800	14
	1G_3 (D)	800	12 500	4.6	—	—	
	3G_4 (F)	548	18 300	7.2	2 000	1 600	12
	3G_4 (P)	348	28 700	9.3	1 700	—	15

Ni tren(NH ₃) ₂ ++	³ Γ ₅ (F)	910	11 000	12.5	1 600	1 800	} 19
	¹ Γ ₃ (D)	784	12 750	7.0	—	—	
	³ Γ ₄ (F)	549	18 200	10.1	1 700	1 600	
Ni tren en ++	³ Γ ₄ (P)	354	28 200	13.0	2 200	2 200	26
	³ Γ ₅ (F)	910	11 000	11.0	1 400	—	16
	¹ Γ ₃ (D)	800	12 500	8.1	—	—	—
Ni tren gly+	³ Γ ₄ (F)	534	18 700	8.8	2 400	2 400	19
	³ Γ ₄ (P)	345	29 000	14.2	3 000	—	38
	³ Γ ₅ (F)	890	11 200	14.0	1 300	—	} 19
¹ Γ ₃ (D)	794	12 600	9.8	—	—		
³ Γ ₄ (F)	532	18 800	11.0	1 800	1 600	17	
Ni en gly ₂	³ Γ ₄ (P)	354	28 200	11.0	2 400	—	24
	³ Γ ₅ (F)	955	10 500	8.7	1 700	1 700	14
	¹ Γ ₃ (D)	770	13 000	2.6	—	—	3
Ni en ₂ gly+	³ Γ ₄ (F)	577	17 300	8.0	1 800	1 700	13
	³ Γ ₄ (P)	356	28 100	12.7	1 800	2 200	23
	³ Γ ₅ (F)	922	10 800	9.2	1 400	1 800	} 14
¹ Γ ₃ (D)	790	12 650	4.2	—	—		
³ Γ ₄ (F)	560	17 900	8.7	1 700	1 700	14	
Ni py ₂ ++(?)	³ Γ ₄ (P)	350	28 600	12.0	1 800	—	20
	³ Γ ₅ (F)	985	10 150	3.7	—	1 900	6
	¹ Γ ₃ (D)	743	13 500	1.2	—	—	1
Ni tn ₂ ++	³ Γ ₄ (F)	607	16 500	5.4	1 700	1 600	8
	³ Γ ₄ (P)	371	27 000	9.9	1 600	1 700	15
	³ Γ ₅ (F)	920	10 900	5.9	1 600	1 600	} 9
¹ Γ ₃ (D)	798	12 500	2.7	—	—		
³ Γ ₄ (F)	563	17 800	7.7	1 600	1 500	11	
Ni bdn ₂ ++	³ Γ ₄ (P)	354	28 200	10.8	2 500	2 800	26
	³ Γ ₅ (F)	915	10 950	6.5	1 400	—	8
	¹ Γ ₃ (D)	790	12 700	3.0	—	—	—
Ni ptn ₂ ++	³ Γ ₄ (F)	556	18 000	7.0	1 600	1 500	10
	³ Γ ₄ (P)	350	28 600	10.0	1 800	—	17
	³ Γ ₅ (F)	890	11 200	4.7	1 600	—	} 8
¹ Γ ₃ (D)	800	12 500	3.8	—	—		
³ Γ ₄ (F)	526	19 000	4.5	1 800	1 700	7	
Ni den ₂ ++	³ Γ ₄ (P)	337	29 700	4.6	1 900	—	8
	³ Γ ₅ (F)	872	11 500	12.9	1 500	1 800	20
	³ Γ ₄ (F)	535	18 700	7.7	1 900	1 400	12
Ni tetren ++	³ Γ ₄ (P)	344	29 100	10.8	1 900	—	19
	³ Γ ₅ (F)	920	10 900	12.3	1 700	1 900	21
	¹ Γ ₃ (D)	792	12 600	7.7	—	—	—
Ni tetren NH ₂ ++	³ Γ ₄ (F)	543	18 400	6.8	2 200	1 700	12
	³ Γ ₄ (P)	351	28 500	9.8	2 100	—	19
	³ Γ ₅ (F)	902	11 100	13	1 500	—	18
Ni tetren NH ₃ ++	¹ Γ ₃ (D)	800	12 500	9	—	—	—
	³ Γ ₄ (F)	536	18 700	8.3	1 900	1 500	13
	³ Γ ₄ (P)	350	28 600	11	2 200	—	22

the β -form is stable and can be formed by addition of acids to the α -form. This cannot be due to a partly decomposition to hexaaquo ions, since the fourth band of the β -form is higher and shifted towards higher wavenumbers than of the α -form, while the other three bands show a different behaviour*. Since two isomers are possible¹ for the complex Ni enta (H₂O), with water in *cis*- or *trans*-position to one of the nitrogen atoms, α - and β -may represent two

* Plumb, Martell and Bersworth⁵⁸ measured the spectra of some enta⁻⁴-complexes. The height of the first band indicate the β -structure of their Ni enta⁻⁴.

different equilibrium mixtures, where the equilibrium is changed by the formation of Ni enta H , H_2O^- . But the change might also be due to a variable number of water molecules in the environment. An anhydrous complex analogous to Co enta^- , would be promoted by high pH and might thus participate in the α -form.

It is seen from Table 1 that the enormously high intensity of the first band of $\alpha\text{-Ni enta}^{--}$ decreases for the addition compounds of NH_3 , en and CN^- , while the other bands show mainly increasing intensities. The fourth band of Ni enta en^{--} is not high, but rather broad. This may be ascribed to tetragonal splitting¹⁶ or to the presence of more isomers. Although enta^{-4} probably occupies only four co-ordination positions in this complex, the question might be raised as to whether one or two NH_3 are bound in the ammonia complex. If ammonia is added to 0.1 M Ni enta^{--} the ϵ values of the fourth band are, respectively:

$\alpha\text{-Ni enta}^{--}$	12.6
$\beta\text{-Ni enta}^{--}$	13.8
1 NH_3 : 1 Ni	16.0
2 NH_3 : 1 Ni	18.1
3 NH_3 : 1 Ni	19.5
10 NH_3 : 1 Ni	20.2

This suggests a formation constant for Ni enta NH_3^{--} of about 20, leaving 0.05 M free NH_3 at its 50 % formation. The small band-width (Table 1) does not suggest the presence of more complexes, but this can of course not be excluded. The intensity demonstrates that the decomposition to enta -free ammonia complexes cannot be advanced. $\log K = 1.3$ resembles much the average value¹² in the nickel(II)-ammonia system, *viz.* $\log K_{\text{av}} = 1.43$, whilst $\log K_6 = 0.01$.

If 1 M potassium cyanide is gradually added to 0.1 M Ni enta^- , a more intense blue-violet colour is observed. The colour becomes distinctly more lilac at the ratio 3 CN^- : 1 Ni. These solutions do not change for several weeks at room temperature. They are, however, slightly decomposed due to local excess concentrations during the preparation as shown by the high absorption in the ultraviolet due to $\sim 1\%$ $\text{Ni}(\text{CN})_4^{--}$. Therefore, the fourth absorption band can only be observed as a shoulder. Solutions in the ratio 5 CN^- : 1 Ni decompose in a few seconds to the yellow colour of diamagnetic nickel(II). The formation constants of the paramagnetic, violet forms are not exceedingly large, as shown by the slow variation of the spectrum with the ratio $x \text{CN}^-$: 1 Ni. A similar behaviour was found by Schwarzenbach¹⁴ for Co enta SCN^{-3} which has the formation constant $K = 0.7$.

NICKEL(II) NITROGENTRIACETATES

Schwarzenbach and Biedermann¹⁷ found two nitrogentriacetate complexes of several metal ions, *e. g.* Ni ata^- and Ni ata_2^{-4} with $\log K_1 = 11.26$ (as later determined by Schwarzenbach and Freitag⁵⁹) and $\log K_2 = 4.7$. As seen in Table 1, the first band of blue-green Ni ata^- is not as high as that of Ni enta^{--} and the band intensities of the violet-blue Ni ata_2^{-4} are low, suggesting the presence of a centre of inversion^{10,18}. It is not known whether ata^{-3} functions

as a tri- or tetradentate ligand, but this will not be of great importance to the spectra, since H_2O and $RCOO^-$ are nearly adjacent in the spectrochemical series. In the $Ni\ ata_2^{-4}$, one would for symmetry reasons expect bonding of one nitrogen and two carboxyl groups from each ligand. The two nitrogen atoms may be in *cis*- or *trans*-configuration. The *cis*-form does not seem very likely, since the intensity relations are different from $Ni\ enta^{-2}$ with two *cis*-nitrogens. The fourth band of $Ni\ ata_2^{-4}$ has a shoulder on the side of high wavenumbers, and the second band a less pronounced shoulder towards the lower wavenumbers. This may be ascribed to tetragonal effects (of the rare "compressed" type^{11,16} in the *trans*-complex) or to the presence of different isomers.

The uptake of ammonia and ethylenediamine in $Ni\ ata^-$ does not lead to very high displacements towards higher wavenumbers (Table 1) whereas glycinate in $Ni\ ata\ gly^-$ has a stronger effect. The first absorption band is particularly difficult to move, and the direction of change is even opposite to that expected for $Ni\ ata\ en^-$. $Ni\ ata^-$ decomposes very rapidly upon addition of CN^- probably due to more positions for "attack" than in $Ni\ enta^-$. $Ni\ ata\ den^-$ has broad bands with relatively very high wavenumbers.

NICKEL(II) tren-COMPLEXES

Cox and Webster¹⁹ investigated the crystal structure of $Ni\ tren(SCN)_2$, which could either be a *cis*-octahedral or a tetrahedral complex. Mr. C. J. Ballhausen and the present author have a year ago measured the spectrum of $Ni\ tren^{++}$ which is similar to that of $Ni\ en_2^{++}$, strongly supporting the *cis*-diaquo configuration. Mr. S. E. Rasmussen has kindly presented me with a sample of anhydrous $Ni\ tren(SCN)_2$ which in 0.03 M aqueous solution has an identical spectrum. In solution, the thiocyanate ions are thus exchanged with water.

Data in Table 1 show that $Ni\ tren^{++}$ reacts with dilute NH_3 and one mole of *en* with a slight displacement of the bands towards lower wavenumbers, as expected for the exchange of H_2O by NH_3 and *en* in an octahedral complex. Most surprising is the behaviour of the purplish red $Ni\ tren\ gly^+$, which is much more hypsochromic than either $Ni\ tren^{++}$, $Ni\ gly_3^-$ or $Ni_2\ tren_3^{+4}$. This deviation from the rule of average environment can be ascribed to an actual chelate effect, or to the electrostatic effect of binding one glycinate and thus decreasing the external charge. On the other hand $Ni\ en_2\ gly^+$ is not so strongly hypsochromic.

With excess *tren*, $Ni\ tren^{++}$ forms the complexes $Ni_2\ tren_3^{+4}$ or $Ni\ tren_2^{++}$ with a crystal field strength similar to that of $Ni\ en_3^{++}$. Similar behaviour was found by Jonassen and Douglas²⁰ for nickel(II) complexes of triethylenetetramine = *trien*. The spectra found for $Ni\ trien^{++}$ and $Ni_2\ trien_3^{+4}$ have the absorption bands at almost the same wavenumbers as do $Ni\ en_2^{++}$ and $Ni\ en_3^{++}$, respectively. Jonassen and Douglas²⁰ have measured the double band, corresponding to the intermixing¹ of $^1Y_3\ (D)$ and $^3F_5\ (F)$, but did not draw the curves through the points. In the case of $Hg\ tren^{++}$, Prue and Schwarzenbach⁴² demonstrated the existence of mixed complexes with chloride and bromide ions on the residual places. Cf. also the observations by Mann⁶⁶ of hexaco-ordinated $Pt\ trenI_2$ and $Pt\ ptn_2^{++}$.

NICKEL(II) COMPLEXES OF ETHYLENEDIAMINE AND GLYCINATES

Ballhausen¹³ determined the spectra of $\text{Ni en}(\text{H}_2\text{O})_4^{++}$ and $\text{Ni en}_2(\text{H}_2\text{O})_2^{++}$ from the observed spectra of Ni^{++} -en-mixtures treated by the method of J. Bjerrum¹². However, Ballhausen did not observe the weak singlet transition¹ to ${}^1G_3(D)$. In mixtures of 1 Ni : 1 en, a narrow band can be distinguished at 734 $\mu\mu$ with an effective $\epsilon = 2.1$. Since the mixed spectrum of $\text{Ni}^{++} + \text{Ni en}_2^{++}$ is approximately a horizontal line in this wavelength range¹³, the measured band occurs at the same place for pure Ni en^{++} as it does for the mixture (18 % each of Ni^{++} and Ni en_2^{++} and 64 % Ni en^{++} at $\bar{n} = 1$).

$\text{Ni en}_2 \text{ gly}^+$ was measured (Table 1) for comparison with Ni tren gly^+ . The spectrum of $\text{Ni en}_2 \text{ gly}^+$ is not changed noticeably with excess of gly^- . However, the formation constants with en are so large¹² relative to glycinate²¹ that no appreciable disproportionation occurs.

Further the spectrum of Ni en gly_2 was determined in solution (Table 1), which for similar reasons does not deviate much from that of the pure complex. The spectra agree well with the interpolation between Ni en_3^{++} and Ni gly_3^- .

NICKEL(II) COMPLEXES OF VARIOUS AMINES

In the first paper¹, several nickel(II) complexes were studied with six nitrogen atoms surrounding the central ion, *viz.* $\text{Ni}(\text{NH}_3)_6^{++}$, Ni en_3^{++} , Ni dip_3^{++} and Ni phen_3^{++} . The crystal field strength ($E_1 - E_2$) varies from 10 800 to 12 200 cm^{-1} in this series. Since the groundstate is stabilized 1.2 ($E_1 - E_2$) by the $\gamma_5^6 \gamma_3^2$ -configuration²², this represents a considerable range of energy differences, relative to ($E_1 - E_2$) = 8 500 cm^{-1} in $\text{Ni}(\text{H}_2\text{O})_6^{++}$. J. Bjerrum and the present author pointed out²³ that these stabilizations actually can be found in the values of ΔG for formation of nickel(II) complexes, compared with the similar values of Ca^{++} , Mn^{++} and Zn^{++} without crystal field stabilization. There has been much discussion²⁴ as to whether the large formation constants for complexes with chelates are only due to effects of entropy, leaving ΔH nearly constant, or if a real "chelate effect" exists also in the bond strength. Since the absorption spectra demonstrate stronger stabilization of ethylenediamine than of ammonia complexes, the chelate effect according to I. Poulsen and J. Bjerrum²⁵ must be partly real in the complexes with unfilled d-shells, while it may be due to entropy alone in complexes with closed shells. I. Poulsen and J. Bjerrum²⁵ also investigated ΔG and ΔH of nickel(II) and copper(II) complexes with tn. Trimethylenediamine was found to be distinctly weaker bound to these metal ions than ethylenediamine. As seen from Tables 1 and 2 the place of tn in the spectrochemical series is between NH_3 and en, and rather near to NH_3 . Except for the first absorption band of Ni tn_3^{++} , the bands are higher than that of Ni en_3^{++} , as often found by increasing size of the organic ligand¹⁸.

Similar behaviour is found in Ni bdn_3^{++} , as by C-methylsubstituted ethylenediamine complexes studied by F. Basolo. The position of bdn in the spectrochemical series is between tn (of which it is the methyl substitute) and en.

Table 2. The four strong absorption bands in nickel (II) complexes, classified according to the number of nitrogen atoms in the first co-ordination sphere. Wavenumbers of maxima in cm^{-1} .

	${}^3\Gamma_4 (F)$	${}^1\Gamma_2 (D)$	${}^3\Gamma_4 (F)$	${}^3\Gamma_4 (P)$
0 nitrogen:				
Ni(H ₂ O) ₆ ++	8 500	(13 500)	(15 400)	25 300
1 nitrogen:				
Ni ata(H ₂ O) ₅ -	9 500	13 300	16 000	25 600
2 nitrogens:				
Ni en(H ₂ O) ₄ ++	9 800	13 600	15 800	26 800
α -Ni enta(H ₂ O) ₄ --	10 100	12 700	17 000	26 200
β -Ni enta(H ₂ O) ₄ --	9 900	12 800	16 900	26 400
Ni ata gly--	9 900	13 000	17 100	26 200
Ni ata ₁ ⁺	10 400	13 000	17 400	27 000
3 nitrogens:				
Ni ata(NH ₃) ₃ - (?)	9 600	13 100	16 500	26 600
Ni ata en-	9 400	13 100	16 900	27 200
Ni enta(NH ₃) ₂ -	10 200	12 700	17 200	26 900
Ni gly ₂ -	10 100	13 100	16 600	27 600
Ni enta(CN) ₂ -	10 500	12 500	17 500	—
4 nitrogens:				
Ni(NH ₃) ₄ (H ₂ O) ₂ ++	—	—	16 700	—
Ni enta en--	10 050	12 550	17 300	27 100
Ni en gly ₂	10 500	13 000	17 300	28 100
Ni tren(H ₂ O) ₃ ++	10 500	12 800	17 800	27 800
Ni en ₂ (H ₂ O) ₃ ++	10 500	—	17 900	28 100
Ni ata den-	10 900	12 500	17 600	28 700
5 nitrogens:				
Ni(NH ₃) ₅ (H ₂ O)++	—	—	17 250	—
Ni en ₂ gly+	10 800	12 650	17 900	28 600
Ni tetren++	10 900	12 600	18 400	28 500
Ni tren gly+	11 200	12 600	18 800	28 200
6 nitrogens:				
Ni py ₂ ++ (?)	10 150	13 500	16 500	27 000
Ni(NH ₃) ₆ ++	10 750	13 150	17 500	28 200
Ni tn ₂ ++	10 900	12 500	17 800	28 200
Ni bdn ₂ ++	10 950	12 700	18 000	28 600
Ni en ₃ ++	11 200	12 400	18 350	29 000
Ni tren(NH ₃) ₃ ++	11 000	12 750	18 200	28 200
Ni ₂ tren ₂ + ⁺	10 700	12 500	18 300	28 700
Ni tren en++	11 000	12 500	18 700	29 000
Ni tetren NH ₃ ++	11 100	12 500	18 700	28 600
Ni den ₂ ++	11 500	—	18 700	29 100
Ni ptn ₂ ++	11 200	12 500	19 000	29 700
Ni dip ₂ ++	(11 500)	(12 650)	19 200	—
Ni phen ₂ ++	(11 550)	(12 700)	19 300	—

Prue and Schwarzenbach²⁶ have studied the complex formation with 1,2,3-triaminopropane. It is found here that at least two complexes are formed in solutions with up to three moles ptn per nickel ion. The purple complex finally formed (presumably Ni ptn₂⁺⁺) has about 1 % higher value of ($E_1 - E_2$) than Ni en₃⁺⁺, but has lower band maxima. The upper limit of ($E_1 - E_2$) for aliphatic amines does not seem to be more than 1 % higher than that of en, as exemplified by tren, trien and ptn, while larger alkyl radicals and larger chelate rings, as in tn and to a lesser degree in bdn have an decreasing influence on bonding strength.

Another aliphatic amine with a high crystal field strength is C,C',C',C'-tetramethyl-ethylenediamine of which Basolo, Chen and Murmann report²⁷ diamagnetic, planar yellow ions Ni temeem_2^{++} (with only one absorption maximum²⁷ at $23\,000\text{ cm}^{-1}$, while the reflection spectrum of the salmon-pink¹⁶ solid $[\text{Ni en}_2][\text{AgBrI}]_2$ shows a band at $20\,800\text{ cm}^{-1}$). Basolo and the present author observed that solid $[\text{Ni temeem}_2]\text{Cl}_2$ reacts with concentrated aqueous ammonia to a violet solution*. It was obvious to suppose the existence of a paramagnetic ion $\text{Ni temeem}_2(\text{NH}_3)_2^{++}$. However, the solution shows bands at nearly the same place as $\text{Ni}(\text{NH}_3)_6^{++}$, and a solution, 0.05 M Ni^{++} , 6 M NH_3 , 0.12 M temeem , which contains less than 2 % of the yellow form, is decomposed by addition of 50 volume % 0.4 M temeem to a mixture of about 60 % Ni temeem_2^{++} and 40 % of the violet form. It is not a reasonable behaviour for a mixed ammonia complex, but is rather caused by the sudden break-down of the chelate complex at increasing ammonia concentration, as discussed below. Basolo, Chen and Murmann²⁷ found that Ni temeem_3^{++} cannot be formed, due to steric hindrance; and $\text{Ni temeem}_2\text{Cl}_2$ has the same absorption spectrum in water and absolute ethanol, showing no tendency of solvation or association of chloride ions in the first co-ordination sphere. Neither has it been possible to identify a purple *cis*- $\text{Ni temeem}_2\text{en}^{++}$ in mixed solutions.

Although the heterocyclic diamines as α,α' -dipyridyl and *o*-phenanthroline have even larger crystal field strengths¹ than ethylenediamine, the heterocyclic monamine pyridine has a smaller crystal field strength than ammonia. It is not easy to identify the hypothetical Ni py_6^{++} in solution. The solutions of nickel(II) nitrate in pyridine with a small water content may still contain nitrate complexes²⁸, which perhaps also were important in the system *n*-butylamine-water-copper(II) nitrate, studied by Bjerrum and Lamm²³. Robust complexes of cobalt(III) and rhodium(III) are only known with at most four molecules of pyridine. Nevertheless, the results in Table 1 and 2 demonstrate a low crystal field strength of pyridine, compared to other amines agreeing well with the observed weak tendency to complex formation⁵¹.

Table 1 gives also the spectra of Ni den_2^{++} , Ni tetren^{++} , and $\text{Ni tetren NH}_3^{++}$, demonstrating the regular behaviour of nickel(II), compared to copper(II), of which Table 3 gives Cu den^{++} , Cu den NH_3^{++} , Cu den_2^{++} , and Cu tetren^{++} . The latter series of complexes resembles much the spectra of $\text{Cu}(\text{NH}_3)_n(\text{H}_2\text{O})_{6-n}^{++}$ with $n = 3, 4, 6,$ and 5 , respectively, exhibiting pentammine effect in the two last cases³². Haendler⁶⁷ measured the absorption spectra of Cu^{++} and Ni^{++} with 1 and 2 moles of den. While K_1/K_2 is so large in the first case that Cu den^{++} disproportionates only to the extent $10^{-5.4}$, 5 % each of Ni^{++} and Ni den_2^{++} occur for $n = 1$. The complex formation with the "guirlande" chain amines den, trien, tetren with H_2O and NH_3 on the residual places will be discussed later.

* However, Basolo isolated a violet solid from the action of liquid ammonia. Since this solid returns to the original yellow complex upon standing in the air, Basolo assumes the solid to be the mixed complex $[\text{Ni temeem}_2(\text{NH}_3)_2]\text{Cl}_2$. (Private communication).

Table 3. Absorption bands of copper(II) complexes. Notation as in Table 1.

	λ_n m μ	ν_n cm ⁻¹	ϵ_n	$\delta(-)$ cm ⁻¹	$\delta(+)$ cm ⁻¹	$P \cdot 10^{-5}$
Cu enta ⁻	734	13 600	91	2 000	2 200	185
Cu enta NH ₃ ⁻	722	13 800	38	—	2 200	75
Cu ata ⁻	880	11 400	60	2 400	—	} 170
	775	12 900	54	—	2 600	
Cu ata ₂ ⁻⁴	658	15 200	37	2 700	2 400	90
Cu tren ⁺⁺	860	11 600	117	2 600	3 300	320
Cu tren(NH ₃) ₂ ⁺⁺	785	12 700	134	2 500	3 300	360
Cu den ⁺⁺	611	16 300	74	2 300	2 600	170
Cu den NH ₃ ⁺⁺	576	17 400	84	2 600	2 600	200
Cu den ₂ ⁺⁺	~850	11 800	~70	1 800	—	} 310
	630	15 900	106	—	2 600	
Cu tetren ⁺⁺	~840	11 900	~100	1 700	—	} 520
	643	15 600	165	—	2 400	
Cu tn ₂ ⁺⁺	568	17 600	111	2 700	2 300	250
Cu bdn ₂ ⁺⁺	566	17 700	125	2 500	2 300	280
Cu ptn ₂ ⁺⁺	559	17 900	66	2 300	2 200	140
Cu en ₂ ⁺⁺	549	18 200	63	2 400	2 400	140
Cu teme ₂ ⁺⁺	547	18 300	120	2 700	2 500	290

COPPER(II) ETHYLENEDIAMINETETRAACETATES

It was shown above that the absorption spectra of paramagnetic nickel(II) complexes can be described roughly by only one parameter, which may be identified with the energy difference ($E_1 - E_2$) between γ_3 - and γ_5 -electrons in a regularly octahedral complex^{13,16,30,31}. In copper(II) complexes, one further parameter is necessary to describe the relative tetragonality² varying from a regular octahedron to square planar complexes with decreasingly weaker ligands on the perpendicular axis. Empirically, the ratio ν_{Cu}/ν_{Ni} between the principal band of the copper(II) complex and the first band of the corresponding nickel(II) complex is proposed¹. This ratio is roughly 1 in copper(II) complexes with cubic symmetry, increasing to about 1.8 in the most extremely tetragonal cases.

J. Bjerrum, Ballhausen and the author³² discussed previously the ligands ammonia and ethylenediamine, which form the distinctly tetragonal planar complexes Cu(NH₃)₄⁺⁺ and Cu en₂⁺⁺ with two weakly bound water molecules, resulting in $\nu_{Cu}/\nu_{Ni} = 1.7$. If stronger bound ligands such as ammonia, replace water on the z-axis, a pentammine effect is observed to decrease the value of this ratio. Recently Linford⁹ studied the solvates of copper(II) bis(acetylacetonate) and similar planar complexes with chloroform, acetone, dioxan, alcohols, pyridine and piperidine solvates, arranged according to increasing z-axis contribution. Most of the results obtained are readily explained except for the absorption band of Cu en₂⁺⁺ which is shifted 800 cm⁻¹ in the wrong direction by solvation with ethanol³³. This effect is much larger than the solvation effects of the second co-ordination sphere, studied by J. Bjerrum, Adamson, and Bostrup³⁴.

A series of copper(II) complexes with much lower values of ν_{Cu}/ν_{Ni} have been investigated¹. The behaviour of amines as ligands is rather capricious,

some form "cubic" and some "tetragonal" complexes without conspicuous regularities. The polydentate amino-acids, however, form only weakly tetragonal copper(II) complexes whenever, of steric reasons, the carboxyl groups cannot be bound in the plane of four strongly bound atoms. In the case¹ of Cu enta(H₂O)⁻ we have $\nu_{\text{Cu}}/\nu_{\text{Ni}} = 1.36$.

Bonnett and Schmidt³⁵ found that the less coloured Cu enta(OH)⁻³ is formed with $pK = 11.35$ in 1 M Na₂SO₄ and with higher pK at lower ionic strength. Schwarzenbach and Heller³⁶ found $pK = 7.39$ for the acidity of Cr enta(H₂O)⁻ and 7.49 for the first proton of Fe enta(H₂O)⁻. It is known from pK of Cu(H₂O)₆⁺⁺ and from the formation³² of Cu(NH₃)₃OH⁺ that copper(II) complexes generally are more acidic than those of nickel(II) and zinc(II). Even though the external charge and the oxidizing power (the intermixing of electron transfer states stabilizes perhaps the groundstate of the hydroxo complexes) make an important contribution to the acidity, there is, *inter alia*, an evident effect of deviation from cubic symmetry for metal ions with unfilled d-shells²². This is especially evident for the tetragonal d⁴- and d⁹-systems.

Data in Table 3 show that the band of Cu entaNH₃⁻ has much lower intensity than that of Cu entaH₂O⁻. This cannot be ascribed to the formation of Cu enta OH⁻ in aqueous ammonia, since addition of a large amount of NH₄NO₃ has no effect on the spectrum. The maximum in Cu entaNH₃⁻ is only shifted 2 % towards higher wavenumbers, relative to Cu entaH₂O⁻. Thus, the ammonia molecule must be placed on the axis, perpendicular to the plane containing the two *cis*-nitrogen atoms of enta⁻⁴.

Upon addition of KCN to 0.02 M Cu enta⁻³, the maximum at 734 $m\mu$ is displaced to 719 $m\mu$ with 1 CN⁻ : 1 Cu and to 706 $m\mu$ with 3 CN⁻ : 1 Cu. The corresponding violet colours can be changed even further towards brownish purple. Such solutions are very unstable (the lowest maximum measured is 695 $m\mu$) and change in a minute to colourless copper(I) cyanide complexes. It is interesting to note that a high electron transfer spectrum in the violet is present in the intermediate copper(II) complex. Representative values of the effective ϵ are 16 at 400 $m\mu$, 75 at 375 $m\mu$ and 280 at 350 $m\mu$, while the decomposed solution has only $\epsilon = 9$ at 350 $m\mu$ and $\epsilon = 20$ at 325 $m\mu$. Also Cu enta⁻ has an electron transfer spectrum¹ with $\epsilon = 46$ at 350 $m\mu$, and similar values are found for Cu enta NH₃⁻.

Thus, the intrinsic tendency of a redox process in Cu enta(CN)⁻³ is depicted by the electron transfer spectrum, as is also the case of CuCl₄⁻ and CuBr₄⁻. Duke and Courtney³⁷ demonstrated the strong colour produced in copper(II) solutions in ammonia water by CN⁻, which contained rather stable complexes of the type Cu(NH₃)₃CN⁺. Analogously, Cu en⁺⁺ forms purple and reddish intermediate complexes with CN⁻, probably corresponding to high values of the tetragonality. The position of CN⁻ is at the extreme end of the spectrochemical series. For example the first band of tris(ethylenediamine) complexes of cobalt(III), rhodium(III) and iridium(III)³⁸ has 1.30 times as large a wavenumber as in the corresponding hexaquo ions. The similar ratio is 1.96 for Co(CN)₆⁻⁻⁻.

Pfeiffer and Schmitz³⁹ maintain the existence of enta-complexes with two metal ions in the solid compound Ca Cu enta, 3.5 H₂O. Although such complexes would be very

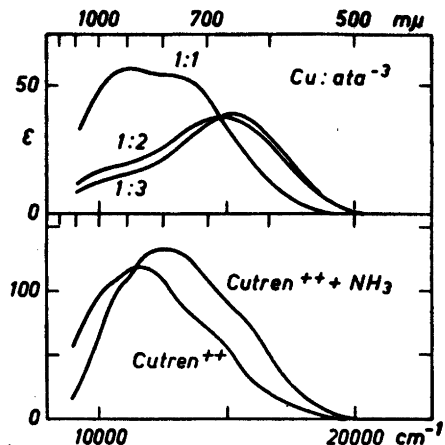


Figure 1. Upper part: Absorption spectra, demonstrating the consecutive formation of Cu ata^- and Cu ata_2^{-4} . The solutions measured were:

0.04 M Cu^{++} , 0.04 M ata^{-3}
 0.04 M Cu^{++} , 0.08 M ata^{-3}
 0.04 M Cu^{++} , 0.12 M ata^{-3}

Lower part: Absorption spectra of the two complexes $\text{Cutren}(\text{H}_2\text{O})_2^{++}$ and $\text{Cutren}(\text{NH}_3)_2^{++}$ (or perhaps $\text{Cu tren}(\text{NH}_3)(\text{H}_2\text{O})^{++}$) from solutions:

0.01 M Cu^{++} , 0.01 M tren
 0.01 M Cu^{++} , 0.01 M tren , 1 M NH_3

interesting it would not appear that there is any good evidence for their existence. Pfeiffer and Schmitz³⁹ found that $\text{Cu}(\text{OH})_2$ is precipitated with NaOH from CaCu enta , while $\text{Na}_2\text{Cu enta}$ is not decomposed. But this may be a consequence of the presence of calcium ions, removing enta^{-4} from the equilibria by formation of Ca enta^{--} with $\log K = 10.59$, while Cu enta^{--} has $\log K = 18.4$. Mixtures of Ni enta^{--} and Ni^{++} do not react, according to the spectra, and in alkaline solution, $\text{Ni}(\text{OH})_2$ is precipitated. The second formation constant of Ca enta_2^{-6} is⁴¹ less than 20, but the investigation is rendered difficult by the relatively low value of $\text{p}K = 11.39$ for formation of $\text{Ca}(\text{OH})\text{enta}^{-3}$. The intention of Pfeiffer and Schmitz³⁹ to prepare isomeric enta -salts, differing only in the free metal ion, is more apt to occur with robust species, e.g. $[\text{Cr}(\text{H}_2\text{O})_6]_2$, $[\text{Ni enta}]_2$ and $[\text{Ni}(\text{H}_2\text{O})_6][\text{Cr enta}]_2$.

COPPER(II) NITROGENTRIACETATES

The robin-egg's blue Cu^+ata^- reacts with an excess of ata^- to form darker blue complexes. It is seen from Fig. 1 that the formation of Cu ata_2^{-4} is not totally complete at the ratio $2 \text{ ata}^{-3} : 1 \text{ Cu}^{+2}$ but the spectrum is a linear combination of that of Cu ata^- with the new complex.

The intensity of Cu ata_2^{-4} is much lower than of Cu ata^- , analogous to the nickel(II) complexes. Since $\nu_{\text{Cu}}/\nu_{\text{Ni}}$ goes from 1.25 for Cu ata^- to 1.45 for Cu ata_2^{-4} , the two nitrogens in the latter complex determine the tetragonal plan. The development has the opposite direction¹ in Cu gly_2 with $\nu_{\text{Cu}}/\nu_{\text{Ni}} = 1.60$, which decreases in Cu gly_3^- . The complex formation necessitates in the latter case relatively large free concentrations of the ligand.

Cu ata^- has two absorption bands (Table 3) with a distance of $1\,500\text{ cm}^{-1}$ between the maxima, while Cu ata_2^{-4} has only an extreme large half-width towards the infra-red. The former phenomenon resembles $\text{Cuphen}_2(\text{H}_2\text{O})_2^{++}$ and $\text{Cudip}_2(\text{H}_2\text{O})_2^{++}$, both of which are presumed to have *cis*-configuration¹. R. Linn and Geneva Belford⁹ assume that the broad bands of copper (II) complexes can be resolved into three Gaussian curves⁴⁰ with three different half-widths, but with $\delta(-) = \delta(+)$ for each band⁴⁰. While the existence of three bands may be theoretically justified⁹, the determination of their positions is certainly near to the limits of experimental uncertainty. However, at least two bands are constituents of most of the spectra of copper(II) complexes^{1,32}, and three are observed in Fig. 1 of Cu tren^{++} .

COPPER(II) tren -COMPLEXES

Cu tren^{++} is sea-blue with the same tint as the hexaquo ion and the high band is displaced to $860\text{ m}\mu$, compared to Cu $(\text{H}_2\text{O})_6^{++}$ at $790\text{ m}\mu$. Hence the crystal field is strong in Ni $\text{tren}(\text{H}_2\text{O})_2^{++}$, $\nu_{\text{Cu}}/\nu_{\text{Ni}}$ is only $= 1.08$, the lowest value found in any copper(II) complex. Thus, a *cis*-diaquo configuration for Cu $\text{tren}(\text{H}_2\text{O})_2^{++}$ can be proposed. In aqueous ammonia a flat maximum is obtained at $785\text{ m}\mu$. This increases the ratio $\nu_{\text{Cu}}/\nu_{\text{Ni}}$ only slightly to 1.11.

Thus, the tendency of forming cubic copper(II) complexes is not restricted to heterocyclic diamines, but can also be found in aliphatic amines with steric resistance against formation of planar complexes. However, in the discussion of copper(II) complexes of polydentate ligands a special precaution must be taken: Contrary to most calculational assumptions^{9,16}, the six atoms in an octahedral complex are not bound to the axes of a Cartesian co-ordinate system, but instead may have a triclinic symmetry. Geometrically a *cis*-complex MA_4B_2 with loosely bound B can smoothly transform to a tetrahedral complex MA_4 , first of non-regular and later of regular symmetry. During this process, the cubic contribution¹⁶ will change in sign, and the energies of the five d-orbitals, if calculated from the electrostatic model⁴¹ will cross in a very complicated way. The most stable configuration is obtained when the average energy of the d-electrons is relatively low and the interaction energies of the ligands low, while the highest d-orbital has a relatively high energy. The latter orbital contains only one electron in Cu^{++} . A further complication arises, because the regularly tetrahedral symmetry of copper(II) is unstable, due to the Jahn-Teller effect²². Actually, bonding of tren to Cu^{++} is rather strong: Prue and Schwarzenbach⁴² determined $\log K = 14.65$ for Zn tren^{++} , 18.8 for Cu tren^{++} and 14.8 for Ni tren^{++} . Contrary to this behaviour, the heterocyclic diamines have their formation constants in the order²³ $\text{Ni} > \text{Cu} > \text{Zn}$. However, the profound analogy (Fig. 1) between the spectra with two shoulders at nearly the same place strongly supports the *cis*-configuration of mainly octahedral Cu $\text{tren}(\text{H}_2\text{O})_2^{++}$ and Cu $\text{tren}(\text{NH}_3)_2^{++}$ (or Cu $\text{tren}(\text{NH}_3)(\text{H}_2\text{O})^{++}$).

COPPER(II) COMPLEXES WITH ALIPHATIC DIAMINES

I. Poulsen and J. Bjerrum²⁵ found the formation heats for copper(II) amine complexes for the four first co-ordination places the series $\text{NH}_3 < \text{tn} < \text{en}$. As seen from Table 3, ν_n of Cu tn_2^{++} occurs between that of $\text{Cu (NH}_3)_4^{++}$ and Cu en_2^{++} and $\nu_{\text{Cu}}/\nu_{\text{Ni}}$ is therefore ~ 1.7 . The stabilization energy is probably also roughly proportional to the wavenumber of the principal band in tetragonal complexes.

The highest wavenumber observed yet in a copper(II) complex occurs in Cu temeenn_2^{++} (Table 3), 1/2 % larger than that of Cu en_2^{++} . The diamagnetism of Ni temeenn_2^{++} corresponds to an even higher tendency of tetragonality²⁷ with the highly destabilized orbital γ_{13} which is empty¹⁶.

The tridentate ptn does not utilize the possibility of forming a nearly cubic, hexa-coordinated copper(II) complex such as dip and phen . On the other hand Cu ptn_2^{++} is dark violet with $\nu_{\text{Cu}}/\nu_{\text{Ni}} = 1.6$ and must be assumed to bind only four nitrogen atoms, as already proposed by Mann and Pope⁶⁵. It would be interesting to know, if the residual amine group has affinity to silver ions, forming perhaps the bi-nuclear complex $\text{Cu ptn}_2 \text{Ag}^{+3}$ with linear environment of the silver^{12,60}.

While the tridentate amines ptn and den (of which the latter has one secondary amine group) form similar nickel(II) complexes, is Cu den_2^{++} distinctly hexa-(or penta-)co-ordinated, and has high intensity of the double band, as also Cu tetren^{++} has.

The band intensity of Cu ptn_2^{++} is of the same magnitude as for Cu en_2^{++} , while Cu temeenn_2^{++} , Cu tn_2^{++} , and Cu bdn_2^{++} are much stronger coloured. In the bis(diamine) complexes, the absorption band vanishes in the infra-red. the values of ϵ being:

	800 $m\mu$	900 $m\mu$	1 000 $m\mu$
Cu en_2^{++}	2.7	0.7	0.3
Cu tn_2^{++}	13.0	4.1	1.4
Cu ptn_2^{++}	7.2	3.4	1.5
Cu temeenn_2^{++}	9.6	4.0	2.4
Cu bdn_2^{++}	19.6	6.0	2.0
Cu den^{++}	11.5	3.4	1.0

CHELATE STABILIZATION EFFECTS

In Table 2, the wavenumbers of the four strong absorption bands of paramagnetic nickel(II) complexes are classified, according to the number of nitrogen atoms in the first co-ordination sphere. The formulae of Ni py_6^{++} , $\text{Ni ata(NH}_3)_2^-$, $\text{Ni enta(NH}_3)^-$ and Ni enta CN^{-3} are tentative.

The last complex is classified as a system with three N.

It is a rather good approximation except for the highly polarizable anions as SCN^- , NO_2^- , and CN^- to write the spectrochemical series according to the elements alone as:



In the amino-acid complexes, the active atoms in the first co-ordination sphere are O from carboxyl groups and water and N from the amine groups. The oxygen atoms are not very different. The oxalate ion is nearly coincident

with water in the spectrochemical series ⁴, but has a similar position among carboxyl groups as ethylenediamine has among the amines. The other carboxyl groups are slightly bathochromic, as found by Linhard and Weigel ⁷ and for nickel(II) propionates etc. by Pestemer and Alslev-Klinker ⁴⁴. The results reported in this paper show the following spreading of the amines in the spectrochemical series:



Already Russell, Cooper and Vosburgh ⁵⁷ found empirically that the formation constants of nickel(II) amine complexes increase with the hypsochromic effect of the ligand.

It is easily seen from Table 2 that the polydentate amino-acids generally are further removed in the spectrochemical series than interpolated directly from the rule of average environment. Thus, one N in Ni ata⁻ and two N in Ni enta⁻² function as 2.5 NH₃ and 4.5 NH₃, respectively, if the visible band is compared to the spectra of Ni (NH₃)_n (H₂O)_{6-n}⁺⁺ found by J. Bjerrum ¹². Since the crystal field strength is roughly proportional ^{9,41,45,46} to R^{-5} , where R is the distance to the negative charge of the ligand, this observation can easily be explained by a slightly tighter bonding. It is interesting ¹ that even the anhydrous Co enta⁻ is 2.5 % hypsochromic in the first band, compared to Co enta H₂O⁻. As seen from the method of preparation ¹⁴, the latter complex must be highly thermodynamically unstable in aqueous solution.

Even if ΔG and ΔH cannot be calculated from the spectrochemical series, ignoring the many unknown factors in the case of closed-shells as Zn⁺⁺, considerable correlation can be found between the relative values for ΔG and ΔH . For example, the differences between negative and neutral ligands are particularly large. The exchange with water of chloride ions has formation constants slightly below 1, whereas the relative crystal field strength ³⁸ of Cl⁻ and H₂O is 0.76 and the corresponding ratio for amines and H₂O is ~ 1.3 . Thus, the high formation constants for enta⁻⁴-complexes are partly due to electrostatic effects.

J. Bjerrum and the author ²³ discussed the ethylenediaminetetraacetates of the divalent ions of the first transition group, log K varies ¹⁵ from 10.96 for Ca⁺⁺ over 14.04 for Mn⁺⁺ to 16.50 for Zn⁺⁺. If Ni⁺⁺ had a closed d-shell, log K would extrapolate 15.5 instead of the observed value 18.62. The stabilization of 2.8 in log K corresponds to 3.8 kcal/mole = 1 300 cm⁻¹. Analogously, the formation constants for lanthanide-enta complexes vary smoothly from log K = 15.50 for La enta⁻ over 17.37 for Gd enta⁻ to 19.83 for Lu enta⁻. These half- and closed shell structures represent the standard state of electrostatic behaviour while all the other complexes are stabilized between 0.2 and 0.3 units in log K , due to the smaller influence of the crystal field on f- than on d-electrons.

In Table 4, a series of stabilization energies are compiled for Fe⁺⁺, Co⁺⁺, Ni⁺⁺ and Cu⁺⁺, when the non-stabilized values of log K_n are assumed to vary linearly with the number of d-electrons between Mn⁺⁺ and Zn⁺⁺. Most examples are taken from the article of Schwarzenbach ²⁴ on the chelate effect,

Table 4. Crystal field stabilization of complexes of the second half of the first transition group. Most formation constants refer to 20° C and the ionic strength ~ 0.1 . ρ is the stabilization parameter²² valid for regularly octahedral complexes, viz. energy decrease = $0.2\rho(E_1 - E_2)$. Ref. 63 considers *N*-substituted iminodiacetates $RN(CH_2COO^-)_2$, here denoted Rada. The consecutive formation constants are considered in cases, where the formulae indicate the binding of the second or the third ligand.

Ref. No.	Ligands beside water	log K_n		Stabilization found from the hypothesis of linear variation of log K_n with the number of d-electrons from 5 to 10			
		Mn ⁺⁺	Zn ⁺⁺	Fe ⁺⁺	Co ⁺⁺	Ni ⁺⁺	Cu ⁺⁺
62	py	0.14	0.95	0.41	0.68	1.15	1.62
24	en	2.8	6.0	1.0	1.9	3.2	5.4
24	en ₂	2.1	3.3	1.0	2.4	3.8	6.3
24	en ₃	0.9	2.0	0.9	1.9	3.1	-1.7
24	tren	5.8	14.6	1.2	3.5	3.7	6.0
24	trien	4.9	12.1	1.5	3.2	4.8	9.7
24	penten	9.4	16.2	0.4	3.7	5.8	7.6
59	ata	7.44	10.45	0.8	2.0	2.0	2.8
17	ata ₂	3.7	3.0	—	0.5	1.6	—
15	enta	14.04	16.50	~ 0	1.3	3.1	2.8
63	CH ₃ ada	5.40	7.66	0.80	1.32	1.97	3.88
63	(CH ₃ ada) ₂	4.16	6.43	0.76	1.24	1.70	0.85
63	C ₂ H ₅ ada	1.58	3.22	0.10	0.66	0.97	3.68
63	HOC ₂ H ₄ ada	5.55	8.33	0.67	1.23	2.07	4.09
63	(HOC ₂ H ₄ ada) ₂	3.76	3.69	-0.53	0.46	1.25	1.31
63	NH ₂ C ₂ H ₄ ada	7.71	11.93	1.25	2.37	3.50	4.82
	$\rho =$	0	0	2	~ 4	6	3

and from the recent measurements by Schwarzenbach, Anderegg, Schneider and Senn⁶³ on substituted iminodiacetates $R(CH_2COO^-)_2 \equiv R\text{ ada}$. It is seen that the stabilization for iron(II), cobalt(II), and nickel(II) complexes are roughly proportional to the stabilization parameter²² ρ , viz. 2, 4 and 6. In some cases, e. g. the third en or the second HOC₂H₄ada the steric conditions for bonding are better in Mn⁺⁺ than in Zn⁺⁺, but here also the evolution of stabilization energies is rather regular. On the other hand, the strong tendency of tetragonal distortion in copper(II) complexes produces an enormous stabilization of ligands on the four planar places, e. g. in en₂ and trien. The effective value of ρ for Cu⁺⁺ in Table 4 can exceed the value 10, whereas values $\sim 3\nu_{\text{Cu}}/\nu_{\text{Ni}} \sim 5$ might have been expected.

In nickel(II) complexes the crystal field stabilization can be compared to the theoretical value 1.2 ($E_1 - E_2$). However, as seen from Table 2, the value of ($E_1 - E_2$) cannot be found accurately from the absorption spectra, since the relative positions of the bands vary some hundred cm⁻¹ in an irregular way. If the energies of the two lowest levels are defined:

$$\begin{aligned} {}^3\Gamma_2(F) &= -1.20(E_1 - E_2) \\ {}^3\Gamma_5(F) &= -0.20(E_1 - E_2) \end{aligned}$$

then the Orgel diagram of nickel(II) complexes¹ can be approximately described by the three other lines in the range of our interest:

$$\begin{aligned} {}^3\Gamma_4(F) &= 2800\text{ cm}^{-1} + 0.155(E_1 - E_2) \\ {}^3\Gamma_4(P) &= 15100\text{ cm}^{-1} \end{aligned}$$

and after correction for the intermixing of triplet character:

$${}^1G_3(D) = 16\,500 \text{ cm}^{-1} - 1.55 (E_1 - E_2)$$

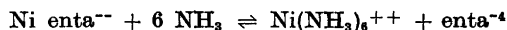
These equations demonstrate that either are the term distances to 3P , 1D , and 1G decreased from the values, found from the gaseous ion, or other electron configurations are intermixed in the states of the complexes. The former alternative explanation is discussed below in the last section.

If $(E_1 - E_2)$ is assumed to be the wavenumber of the first band $10\,100 \text{ cm}^{-1}$ in $\alpha\text{-Ni en}_3^{++}$ and $8\,500 \text{ cm}^{-1}$ in $\text{Ni}(\text{H}_2\text{O})_6^{++}$ the predicted stabilization is $1\,900 \text{ cm}^{-1}$. The similar numbers are:

Ni ata ⁻	1 200 cm ⁻¹ =	3.4 kcal/mole =	2.5 units in log <i>K</i>
Ni gly ₃ ⁻	1 900	5.4	4.0
Ni(NH ₃) ₆ ⁺⁺	2 700	7.7	5.7
Ni tn ₃ ⁺⁺	3 300	9.3	6.9
Ni tren ⁺⁺	2 900	8.2	6.1
Ni en ⁺⁺	3 700	10.5	7.8
Ni phen ₃ ⁺⁺	4 400	12.5	9.3
Ni en ₂ gly ⁺	3 100	8.8	6.5
Ni tren gly ⁺	3 800	10.8	8.0

It must be remembered that these quantities are found from the spectra by subtraction of the even larger stabilization of the hexaquo ion, relative to the free Ni⁺⁺ *in vacuo*. This quantity is $10\,200 \text{ cm}^{-1} = 29 \text{ kcal/mole} = (\log K = 22)$. Orgel⁴⁷ pointed out that this stabilization can actually be observed as a part ($\sim 5\%$) of the absolute heat of hydration of metal ions. I. Poulsen and J. Bjerrum²⁵ found $\Delta H = 21.0 \text{ kcal/mole}$ for $\text{Ni}(\text{NH}_3)_6^{++}$, 21.3 kcal/mole for Ni tn_3^{++} and 27.9 kcal/mole for Ni en_3^{++} . If these values are corrected for the stabilization mentioned above, the residual "closed shell" case gives 13.3, 12.0 and 17.4 kcal/mole, respectively, for $\text{Ni}(\text{NH}_3)_6^{++}$, Ni tn_3^{++} and Ni en_3^{++} . Besides the d-orbital stabilization, the σ -bonding of even γ_1 and odd γ_4 -electrons⁴⁸⁻⁵⁰ may be stronger in the ethylenediamine complexes where the ligands have comparatively smaller distances due to the γ_3 -bonding.

The entropy effects in chelate complexes are rather peculiar, inducing the irregular behaviour of ΔG , compared to ΔH . The discussion that follows is concerned only with the importance of chelating number *L* in reactions of a complex with a polydentate, *viz.* of the type



It is seen from the mass action law that this process is half complete when

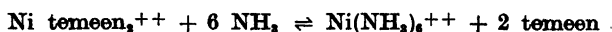
$$\frac{[\text{NH}_3]^6}{[\text{en}_3]} = \frac{K_{\text{Ni en}_3}}{K_{\text{Ni}(\text{NH}_3)_6}}$$

Thus, if a buffer concentration of free $[\text{en}_3] = 0.01 \text{ M}$ is maintained, the free $[\text{NH}_3]$ will be 20 M. If a similar experiment is performed with $[\text{en}_3] = 0.01 \text{ M}$ and the nickel complex is destroyed with tn or en, respectively, $[\text{tn}] = 28 \text{ M}$ and $[\text{en}] = 0.24 \text{ M}$ are necessary for 50 % decomposition to Ni tn_3^{++} or Ni en_3^{++} . Any formation of mixed complexes, as $\text{Ni en}_3 \text{NH}_3^{--}$ and $\text{Ni en}_2 \text{en}^{--}$ studied above, will of course delay the actual destruction of the bonding between Ni⁺⁺ and en_3^{--} .

Even though $\log K_{1-3} = 12.0$ for Ni tn_3^{++} , and $\log K_{1-6} = 8.6$ for $\text{Ni}(\text{NH}_3)_6^{++}$, it is seen that tn and NH_3 in high concentrations are nearly equally effective for decomposing Ni en_3^{--} . This is a result of the occurrence of a sixth power term in the mass action law for NH_3 , but only a third power term for tn. Roughly speaking, a dilute solution of a polydentate amine resembles "coarsegrained" aqueous ammonia. The prob-

ability of finding a high number of amine groups (L groups per molecule) within reach of a certain metal ion is very high, and it is proportional to C^{-1} , whereas, in a monodentate amine like NH_3 , the corresponding probability is proportional to $C \cdot L$.

Inversely, a polydentate complex is affected very little by dilution of the free ligand. Although 0.01 M free enta^{-4} encountered 20 M free NH_3 , above, 10^{-5} M free $[\text{enta}]$ will still afford 6 M free NH_3 for half decomposition of $\text{Ni} \text{enta}^{--}$, and $10^{-9.8}$ M enta^{-4} is sufficient against 1 M NH_3 . Now, it is easily understood why the yellow diamagnetic $\text{Ni} \text{temeen}_2^{++}$ suddenly breaks down at a rather high ammonia concentration:



with the constants $\log K_{1-3} = 14.68$ for $\text{Ni} \text{temeen}_2^{++}$ and $\log K_{1-3} = 8.6$ for $\text{Ni}(\text{NH}_3)_6^{++}$, 50 % decomposition is predicted at $[\text{NH}_3] = 4.8$ M when $[\text{temeen}] = 0.1$ M. At slightly higher ammonia concentration, the decomposition is practically complete, owing to the sixth power dependence.

Reversely, the presence of a mixed complex $\text{Cu} \text{tren} \text{en}^{++}$ can definitely be proven by the absorption spectrum of a solution, 0.001 M Cu , 0.001 M tren , 0.8 M en , which shows the presence of only ~ 50 % of the copper as $\text{Cu} \text{en}_2^{++}$. From the formation constants of $\text{Cu} \text{en}_2^{++}$ and $\text{Cu} \text{tren}^{++}$, the constant for the reaction $\text{en} + \text{Cu} \text{tren}^{++} \rightarrow \text{Cu} \text{tren} \text{en}^{++}$ can be estimated to $\sim 4 \cdot 10^4$.

By comparison of ligands with different chelating number L , it might be reasonable to choose a scale of apparent activity, proportional to C^L . Since the standard state of chemical compounds is often chosen as the pure compounds, the formation constants referring to 1 M solutions are from this point of view exaggerated for polydentate ligands. For instance, tren is less affected by dilution than is NH_3 . J. Bjerrum⁵¹ pointed out for monodentate ligands that the exchange with water might be treated by defining $[\text{H}_2\text{O}] = 55$ M in the dilute solutions. Adamson⁴³ later demonstrated that most of the ΔS by chelate formation²⁴ vanishes, if a new $\Delta G'$ is defined

$$\Delta G' = \Delta G + \Delta \mu RT \ln 55$$

when $\Delta \mu$ is the number of produced moles minus reacted moles, except of the solvent. Actually, the activities of different ligands in dilute solution, compared to the pure compounds, ought to be determined by partial vapour pressures. Adamson's proposal⁴³ is equivalent to the assumption of activities, proportional to the mole fraction. An alternative proposal will be the molar concentration of the ligand in solution divided with the molar concentration of the pure ligand. In ideal gas mixtures, the two concepts based on number and partial volumes, are identical, and in dilute solutions the two concepts are only different by a proportionality constant, characteristic for the solvent and the ligand. In stronger solutions, the two proposals may differ somewhat. The molar concentration of the anhydrous, liquid amines at 25° C are 38 M NH_3 , 15 M en and 12 M tn . Thus the formation constants of nickel(II) complexes can be corrected by the factors 38⁶, 15⁶, and 12⁶, respectively, resulting in $\log K'_{1-3} = 18.1$ for $\text{Ni}(\text{NH}_3)_6^{++}$, $\log K'_{1-3} = 21.8$ for $\text{Ni} \text{en}_2^{++}$ and $\log K'_{1-3} = 15.3$ for $\text{Ni} \text{tn}_2^{++}$. By this method, there appear small residual entropy effects²⁵, and the crystal field stabilization in ΔH will of course still subsist in the values of $\Delta G'$, corresponding, e.g., to the predicted difference 2.1 between $\log K_{1-3}$ for $\text{Ni}(\text{NH}_3)_6^{++}$ and $\log K_{1-3}$ for $\text{Ni} \text{en}_2^{++}$.

THE INTERMIXING OF SINGLET AND TRIPLET LEVELS BY INTERMEDIATE COUPLING

The validity of sharply defined total spin S and total angular momentum L in the free atoms and ions, corresponding² to S and Γ_n in crystal fields, is weakened by increasing values⁵² of Landé's multiplet factor ζ_{nl} . In systems in crystal fields, states with the same Γ_f (found from the internal vector product¹⁶ of $C(S)$ and $C(\Gamma_n)$) are intermixed with nondiagonal elements of energy

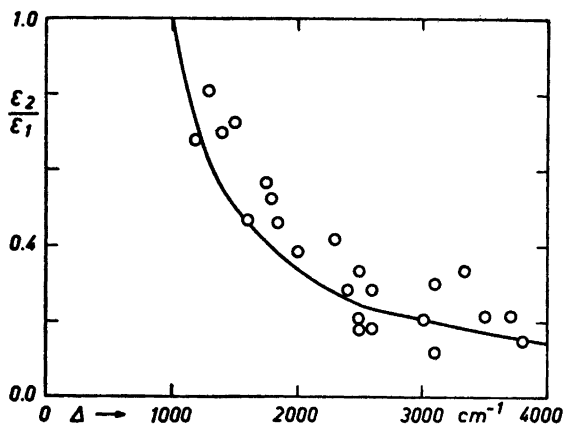


Figure 2. The ratio $\varepsilon_2/\varepsilon_1$ between the directly observed heights of the two first absorption bands of nickel(II) complexes as function of the difference Δ between the wavenumbers of the two maxima. The curve represents the function $\frac{\alpha}{1-\alpha}$ with $\alpha = \frac{500 \text{ cm}^{-1}}{\Delta}$ discussed in the text.

$= k \zeta_n$, where the constants k are not very different from 1. Thus, the usual description of levels in d^n -systems as having definite S and Γ_n breaks down, when $k \zeta_{nl}$ is sufficiently large¹ and the distance Δ between the interacting levels small. The intermixing in the squares of the wavefunctions is approximately $\left(\frac{k \zeta_{nl}}{\Delta}\right)^2$.

The most conspicuous case¹ of intermixing of S in the nickel(II) complexes occurs between the lowest singlet level ${}^1\Gamma_3(D)$ and the two lowest excited triplet levels ${}^3\Gamma_5(F)$ and ${}^3\Gamma_4(F)$ with the values of $k \zeta_{nl} = 500 \text{ cm}^{-1}$ and 800 cm^{-1} , respectively. The numerical results of Tables 1 and 2 are used in Fig. 2 to estimate the former intermixing. The oscillator strength P is divided between the two interacting levels proportional to their triplet character ($S = 1$) since the groundstate for the transition has $S = 1$ to a high degree of precision. But the ratio between the values of P for the two components is not easily accessible from the measurements. Rather, it is assumed that the observed maximum ε_n is proportional to the numerical value of intermixing α , viz.

$$\frac{\varepsilon_2}{\varepsilon_1} = \frac{\alpha}{1-\alpha} \text{ with } \alpha = \frac{k\zeta_{nl}}{\Delta}$$

This is equivalent to assume the half-widths of the bands to be also proportional to ε_n . This is a good approximation, since the pure singlet bands ${}^1\Gamma_3(D)$ are very narrow.

Fig. 2 gives the ratio $\varepsilon_2/\varepsilon_1$ as function of the distance Δ between the two maxima. Further the curve for the function $\frac{\alpha}{1-\alpha}$ with $k \zeta_{nl} = 500 \text{ cm}^{-1}$ is given. It is seen to represent the somewhat scattered points reasonably well.

The influence of the second triplet level ${}^3T_4(F)$ is important for large values of Δ (over 2 000 cm^{-1}) raising the degree of intermixing. On the other side, the non-vanishing half width for $\alpha \rightarrow 0$ should decrease the position of the right-hand side points.

The statistical distribution of the points of mixed complexes demonstrates that no particular deviation from cubic symmetry is necessary for making $k\zeta_{nl}$ large. Fig. 2 demonstrates also the lower limit of $\Delta = 2k\zeta_{nl}$. The two bands are actually repulsed from each other by this impenetrable barrier. Mr. C. E. Schäffer⁵³ has found a similar variation of relative intensities of quartets and doublets with Δ in chromium(III) complexes. Also iridium(III) complexes³⁸ prove that $k\zeta_{nl}$ is rather invariant ($= 2\,000\text{ cm}^{-1}$) in so different ions as IrBr_6^- , IrCl_6^- , $\text{Ir}(\text{NH}_3)_5\text{Cl}^{++}$, Ir en_3^{+++} but here Δ is nearly constant ($= 7\,000\text{ cm}^{-1}$) as function of the crystal field strength, because the singlet and triplet level belong to the same electron configuration³¹ of γ_n .

The other singlet levels of nickel(II) give much lower intensities to the bands. Therefore, it is necessary to measure strong solutions of pure complexes, and the detection is often impossible in the ranges of the triplet bands. Besides ${}^1G_3(D)$, the two levels ${}^1G_5(D)$ and ${}^1G_1(G)$ should be the next excited singlets, as discussed by Tanabe and Sugano⁵⁴, Ballhausen and Klíxbüll Jørgensen¹⁶, and Orgel⁴⁹. ${}^1G_3(D)$ and ${}^1G_1(G)$ have the configuration $\gamma_5^6\gamma_3^2$ common³¹ with the groundstate ${}^3T_2(F)$ and thus should produce narrow bands^{54,55}, while ${}^1G_5(D)$ analogous to ${}^1G_4(G)$, ${}^3T_5(F)$ and ${}^3T_4(F)$ in strong crystal fields are $\gamma_5^5\gamma_3^3$ with broader transitions from the groundstate. The concept of a single distribution of electrons in molecular orbitals seems nevertheless to be rather inadequate⁵⁰ for the description of a given level (S, Γ_n).

Already Gielessen⁵⁶ found a great number of small bands in solid salts of $\text{Ni}(\text{H}_2\text{O})_6^{++}$. In solutions, small bands are found⁴⁹ at 18 400 cm^{-1} and 22 000 cm^{-1} . In Ni en_3^{++} , a weak band can be distinguished at 24 000 cm^{-1} in Ref. 40, Fig. 5. It is not easily decided from the half-widths, which band is the "narrow" ${}^1G_1(G)$, but there is some evidence that it is the band at 18 400 cm^{-1} in the hexaquo ion, contrary to primitive electrostatic calculations¹⁶. It can interact¹ by intermediate coupling with 3T_4 , but not with 3T_5 . While most of the absorption bands in Table 1 are very regular, and do not exhibit signs of tetragonal splitting except the fourth band of Ni ata_2^{-4} , there is a tendency of the third band to have a shoulder towards lower wavenumbers (see the half-widths in Ni en gly_2 , Ni enta NH_3^- , $\alpha\text{-Ni enta}^-$, Ni ata gly^- and Ni ata^-). While this may very well depend on tetragonal splitting and in a few cases be due to presence of more isomers, it is quite suspicious that the phenomenon prevails in a narrow range of the Orgel diagram near $(E_1 - E_2) = 10\,000\text{ cm}^{-1}$. It cannot be excluded that ${}^1G_1(G)$ is going down in the Orgel diagram along a line of the type $23\,000\text{ cm}^{-1} - 1.7(E_1 - E_2)$.

THE DECREASE OF THE PARAMETERS OF ELECTROSTATIC INTERACTION BETWEEN d-ELECTRONS IN COMPLEXES

For a complex with regularly octahedral configuration, the energy levels can be given in the Orgel diagram as function of the crystal field strength $(E_1 - E_2)$. Tanabe and Sugano⁵⁴ and Owen⁴⁸ emphasized that term differen-

Table 5. Crystal field strength ($E_1 - E_2$) and effective term distances for various nickel (II) complexes. The value of ($E_1 - E_2$) is derived from ν_3 and the energies (3P) and $\frac{4}{7}({}^1D) + \frac{3}{7}({}^1G)$ from $\nu_3 + \nu_4$ and ν_2 , respectively. In all cases, the values of ν_n from Table 2 are corrected for effects of intermediate coupling (important for ν_1 and ν_2) and for asymmetry of the bands (usually significant for ν_3). Finally are given the calculated and observed values of the perturbation energy ΔE between ${}^3\Gamma_4$ (F) and ${}^3\Gamma_4$ (P), as defined p. 908. All the energies are given in the unit cm^{-1} .

Complex	$(E_1 - E_2)$	$({}^3P) = 15B$	$\frac{4}{7}({}^1D) + \frac{3}{7}({}^1G)$ $= 8B + 2C$	ΔE , calc.	ΔE , obs.
Free Ni ⁺⁺	0	16 900	17 900	—	—
Ni(H ₂ O) ₆ ⁺⁺	8 500	14 100	14 800	1 080	1 000
Niata ⁻	9 500	12 800	13 300	1 690	1 400
α -Nienta ⁻⁻	10 100	13 000	12 700	1 980	1 300
Ni gly ₃ ⁻	10 100	13 900	13 100	1 730	1 600
Ni py ₆ ⁺⁺ (?)	10 200	13 000	13 500	1 910	1 900
Ni enta NH ₃ ⁻⁻	10 200	13 500	12 700	1 950	1 200
Ni ata ₂ ⁻⁴	10 400	13 400	13 000	1 900	1 900
Ni en gly ₂	10 700	13 500	12 800	2 060	1 750
Ni(NH ₃) ₆ ⁺⁺	10 800	13 400	13 100	2 380	1 950
Ni en ₂ gly ⁺	11 300	12 600	12 200	2 460	2 450
Ni tren(H ₂ O) ₂ ⁺⁺	11 300	11 700	12 000	2 720	2 550
Ni tn ₃ ⁺⁺	11 400	11 900	12 000	2 640	2 650
Ni en ₃ ⁺⁺	11 600	12 600	12 000	2 590	2 550
Ni ptn ₂ ⁺⁺	11 700	12 800	12 000	2 700	2 400
Ni tren(NH ₃) ₂ ⁺⁺	11 700	11 300	12 000	3 030	2 900
Ni tren en ⁺⁺	11 700	12 600	11 800	2 720	2 400
Ni tren gly ⁺	11 800	11 500	11 900	2 500	2 500

ces might also change in complexes from the values for the gaseous ion. Thus, it might be necessary to apply more than one parameter in the Orgel diagram. Actually, the agreement with observed absorption bands can be highly improved by the assumption of decreased term distances in the complexes. Especially, the decrease is larger for many anion complexes than for complexes with neutral ligands.

The energy differences between multiplet terms of a given d^n -configuration can be expressed as multipla of the Slater-Condon-Shortley⁵² parameters F_2 and F_4 . Racah⁶⁴ applies the linear combinations $B = F_2 - 5F_4$ and $C = 35F_4$. In nickel(II) complexes, the distance from the ground term 3F to the other triplet term 3P is $15B$. Table 5 gives this distance inferred from the diagonal sum rule:

$$\nu_3 + \nu_4 = 3(E_1 - E_2) + ({}^3P)$$

The wavenumbers ν_3 and ν_4 of the third and fourth absorption band are corrected for asymmetry by taking the average of $\nu_n - \delta(-)$ and $\nu_n + \delta(+)$ from Table 1. It is seen from Table 5 that B actually decreases to $\sim 70\%$ of the original value, but not as a monotoneous function of $(E_1 - E_2)$. Since three excited triplet levels occur in paramagnetic nickel(II) complexes, it is of interest to see whether the two parameters $(E_1 - E_2)$ and B are sufficient for their description. The two ${}^3\Gamma_4$ levels have energies, which are the roots E_a and E_b of the secular determinant⁴⁹:

$$\begin{vmatrix} E_{33}-E & E_{34} \\ E_{34} & E_{44}-E \end{vmatrix} = 0$$

with $E_{33} = 0.6 (E_1 - E_2)$; $E_{44} = ({}^3P)$; and $E_{34} = 0.4 (E_1 - E_2)$.

We define the perturbation energy ΔE by $E_a = E_{33} - \Delta E$ and $E_b = E_{44} + \Delta E$. The observed and calculated values of ΔE are seen to agree except for the ethylenediaminetetraacetate complexes.

Finally, Table 5 gives the values of $\frac{1}{4}({}^1D) + \frac{3}{4}({}^1G) = 8B + 2C$, which is the asymptotical^{16,54} energy of ${}^1G_3 (D)$ above ${}^3G_2 (F)$. The wavenumber ν_2 is corrected for the influence of intermediate coupling. It is seen that C decreases slightly more than B in the complexes. This can be interpreted as an expansion of the 3d-wavefunction into a larger volume. For isomorphous wavefunctions, both F_2 and F_4 are inversely proportional to the average radius; whereas in the case of spreading from, *e. g.*, the concentration on a spherical surface, F_2/F_4 increases with resulting decrease of the ratio C/B . Owen⁴⁸ assumes that the decrease of B in complexes is caused by covalent bonding. However, it is not easily decided if this is the only possible explanation. It is interesting to compare nickel(II) with other metal ions. Thus, Schäffer⁵³ investigates many chromium(III) complexes, where the distance $\sim 12B$ between ${}^4T_5 (F)$ and ${}^4A_1 (P)$ implies values of B in the range 500–750 cm^{-1} while $B = 950 \text{ cm}^{-1}$ in Cr^{+++} . The distance $\sim 16B$ between 1G_4 and 1G_5 of cobalt(III) complexes⁵⁴ gives slightly smaller values of B . Diamagnetic d^6 -systems of the two next transition groups³⁸ have even smaller values of B : RhCl_6^{-3} has 310 cm^{-1} , $\text{Rh}(\text{NH}_3)_6^{+++}$ and Rhen_3^{+++} both 400 cm^{-1} , and IrCl_6^{-3} has $B = 250 \text{ cm}^{-1}$. On the other hand, manganese(II) complexes have values of B and C , which are not much less than the values for Mn^{++} . Thus, only 7 % decrease is observed⁵⁵ in $\text{Mn}(\text{H}_2\text{O})_6^{++}$ and 11 % in Mn enta^{-} , as will be discussed in the third paper of this series. While it might seem somewhat unsatisfactory to describe four absorption bands of nickel(II) complexes by three parameters, $(E_1 - E_2)$, B , and C , ten bands of manganese(II) can also be described by the three parameters. The crystal field theory can be applied to all d^n -systems, giving a much more unified picture than earlier sharp distinctions between "ionic" and "covalent" complexes.

EXPERIMENTAL

The absorption spectra were measured in the range 800–325 $m\mu$ with a Cary recording spectrophotometer at room temperature, 20° C, and in the range 800–1 080 $m\mu$ with a Beckman DU spectrophotometer. 1 cm absorption cells were always used, and the measurements in the infra-red performed with a maximum interval of 20 $m\mu$.

1.07 M $\text{Ni}(\text{NO}_3)_2$ (AnalaR) and 0.050 M CuSO_4 were transferred to measuring flasks with a Krogh's 1.00 ml syringe pipette. The ligands were added in solutions from micro-burettes, and finally diluted with water. In cases of rarer ligands, 10 ml measuring flasks were shown to be sufficiently precise for the measurement of the spectra.

H_4enta (complexon II) and H_5ata (Prof. Schwarzenbach's sample and complexon I) were dissolved in water with 2 and 1.5 moles of Merck's Na_2CO_3 per mole amino-acid, respectively, and diluted.

$\text{tren H}_2\text{Cl}_2$, $\text{ptn H}_2\text{Cl}_2$ and $\text{tmeen}_2\text{H}_2\text{Cl}_2$ were weighed off and dissolved in stoichiometric amounts of NaOH solution.

H gly was dissolved with 1 equiv. of KOH in water.

Dilute solutions of ammonia and ethylenediamine (Merck's No. 946) were titrated. Ni^{2+} and Co^{2+} were supplied by Shapley Co. Ni^{2+} was purified from the commercial product by fractional distillation and tetren by standing two weeks of the 1 M solution with norite coal, removing the yellow colour. Cu^{2+} and Ni^{2+} were measured in 0.4 M NH_3 and Ni tetren NH_3^{++} in 1 M and 2 M NH_3 .

Redistilled pyridine was kindly furnished by Mr. F. Woldbye.

The concentration of nickel(II) was usually 0.107 M, but more dilute solutions (0.02 M) were made of Ni^{2+} and addition compounds for measurement of the high first band.

The concentration of copper(II) solutions varied between 0.04 M and 0.01 M.

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