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Comparative Crystal Field Studies of some Ligands and the Lowest Singlet State of Paramagnetic Nickel(II) Complexes

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The spectra of the ethylenediaminetetraacetates and some other complexes of the first transition group are compared to the spectra of aquo ions. The position of acetylacetonate in the spectrochemical series is found, and the nickel complexes seem to be octahedral. The influence of tetragonal crystal fields in copper(II) complexes is found by comparison with the analogous nickel(II) complexes. The tris-complexes of α,α′-dipyridyl and *o*-phenanthroline with both metals have the absorption spectra predicted by the crystal field theory of a cubic complex. In a series of nickel(II) complexes, the lowest singlet state $^1\Gamma_3(D)$ is shown to intermix strongly with the triplet states, giving rise to double bands in several cases. The energy decrease of this state at increasing crystal field strength must be due to interactions with some states of other electron configurations.

The absorption band of nickel(II) hexaaquo ion in the red is double as pointed out by J. Bjerrum[1], and can be analyzed into two Gaussian curves[2]. But when the crystal field calculations * of Ilse and Hartmann[3] or Santen and Wieringen[4] are applied[5] to $Ni(H_2O)_6^{++}$, one is led to expect the appearance of only one band, corresponding to the transition from the groundstate $^3\Gamma_2(F)$ to $^3\Gamma_4(F)$. Ballhausen[6] explained the splitting as either due to tetragonal effects, which seems highly improbable[7], or to (L,S) coupling effects. If the latter are only connected with the levels[8] in the free ion $^3F_4$, $^3F_3$, $^3F_2$ and $^3P_2$, $^3P_1$, $^3P_0$, it is not easily explained why the third band due to $^3\Gamma_4(P)$ does not show similar splitting, and why only the hexaaquo ion and a few other complexes[9, 10] show the band ~700mμ double. The present author maintains[11] that the singlet level $^1D_2$ is intermixed with the triplet levels due to (L,S) coupling effects. This level splits in the crystal field[3] of an octahedral complex to $^1\Gamma_3$ of lowest energy and $^1\Gamma_5$ of highest. Later[12], some of

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* Recently, Tanabe and Sugano[61] made a very extensive study of the energy levels in octahedral complexes. These authors calculated all the energy matrices of d^n-configurations in crystal fields of cubic symmetry by Racah's methods. The effects of (L,S)-coupling and of interaction with other electron configurations were not investigated.

the experimental results from this paper were used in a demonstration of the change of the relative positions of ${}^3\Gamma_5(F)$ and ${}^3\Gamma_4(F)$ and ${}^1\Gamma_3(D)$ by increasing crystal fields. This behaviour will be discussed below in the theoretical section. For calibration of the crystal field strength scale, it will be useful to compare the absorption spectrum of a given nickel(II) complex with those of other first transition group complexes with the same ligand. In this way, the position of the ligand can be found in the spectrochemical series of hypsochromy, originated by Fajans[13] and extended by Tsuchida[14]. The next three sections involve ethylenediaminetetraacetates and glycinates, aromatic diamines, and acetylacetonates of different transition group ions. In the case of the acetylacetonate comparison with other metals is necessary to demonstrate that the nickel(II) complex is six-coordinated.

ETHYLENEDIAMINETETRAACETATES AND GLYCINATES

The transition group complexes of $[-CH_2N(CH_2COOH)_2]_2$ (here denoted H_4 enta) were first prepared by Brintzinger, Thiele and Müller[15] and later extensively investigated by Schwarzenbach *et al.*[16-19] The latter authors demonstrated the exclusive formation of complexes between one metal ion and one enta^{-4}. In the case of chromium(III), the two nitrogens and three of the four carboxyl groups are coordinated on five places, leaving a water molecule on the sixth. Thus, the free carboxyl group can take up a proton

$$\text{Cr(H}_2\text{O)enta}^- + \text{H}^+ \rightleftharpoons \text{Cr(H}_2\text{O)enta H} \qquad (1)$$

The two forms have the same absorption spectrum, as predicted by crystal field theory where the perturbations from the ligands decreases with about sixth power of the distance. But with $pK = 7$, the complex gives a proton off:

$$\text{Cr(H}_2\text{O)enta}^- \rightleftharpoons \text{Cr(OH)enta}^{--} + \text{H}^+ \qquad (2)$$

and the environment of the chromium(III) ion is changed profoundly with resulting change in spectrum. These spectra have earlier been measured by Hamm[20] and it is seen of Table 1 that the absorption bands have slightly higher wavenumbers than those of the aquo ion. Table 1 gives the band maxima of the ethylenediaminetetraacetate and aquo complexes of the first transition group, except those of nickel and copper, which can be found in Tables 2 and 4. Fig. 1 gives the observed absorption spectra of several of the ethylenediaminetetraacetate complexes.

In the case of cobalt(III), Schwarzenbach found a rather unstable $\text{Co(H}_2\text{O)enta}^-$, which in alcaline solution changes colour, due to formation of Co(OH)enta^{--} (see eq. 2), and a more stable Co enta^-, which does not exhibit such changes. In the latter complex, all six places are used by enta^{-4}. It is seen of Table 1 that the wavenumbers are somewhat larger than in the aquo ion, which according to C. E. Schäffer has maxima at 16 600 and 24 900 cm^{-1}. The nearly identical spectra of, *e.g.* Cr(OH)enta^{--} and Co(OH)enta^{--} do not prove[7] that the first band is due to states with the same quantum number, *viz.* Γ_5, in both cases. In other ethylenediaminetetraacetate complexes the configuration is not exactly known, but one carboxyl group seems to take

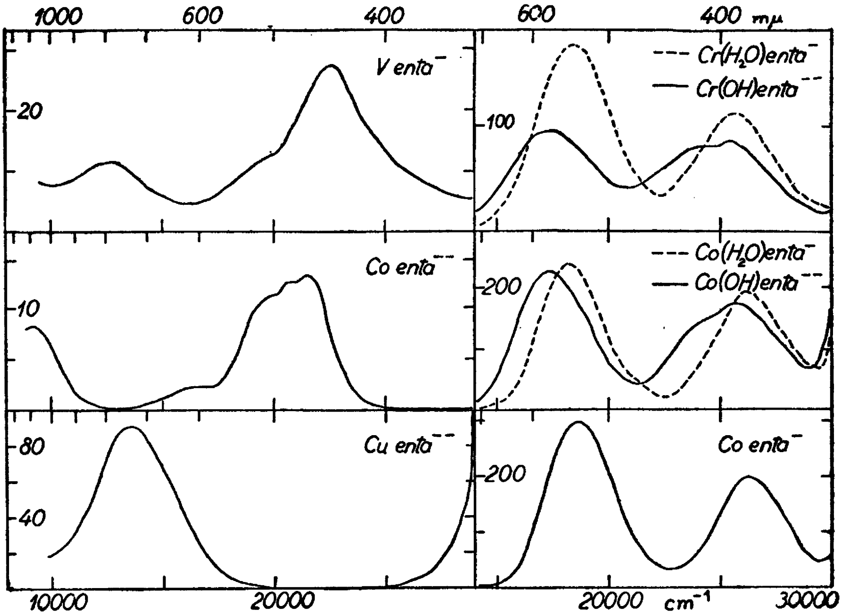

Fig. 1. Absorption spectra of ethylenediaminetetraacetates.

0.08 M V enta$^-$, pH$\sim$8.
0.02 M Cr(H_2O) enta$^-$ (pH$\sim$4) and Cr(OH) enta^{--} (pH$\sim$10).
0.1 M Co enta^{--}, pH$\sim$8.
0.01 M Co(H_2O) enta$^-$ (pH$\sim$2) and Co(OH) enta$^-$ (pH$\sim$10).
0.01 M Cu enta^{--}, pH$\sim$8.
0.01 M Co enta$^-$, pH$\sim$2.

up[19] protons. Thus, M(H_2O)enta is most likely. The crystal field of such an entity would have a cubic part[7] determined by two amino-, three carboxyl and one water positions. Since the carboxyl group is placed before water in the spectrochemical series and the amino group much later than water, a position of enta^{-4} slightly after H_2O might be predicted. But the complexes will show deviations from the cubic crystal field which will result in splitting of the bands[7]. Holleck and Eckardt[21] have used enta^{-4} as ligand for lanthanide ions and removed nearly all the $(2J+1)$-fold degeneracy of a given level, because the crystal field has so low a symmetry. The complex with divalent cobalt shows three bands at the position predicted[22] for $^4\Gamma_4(P)$, where the aquo ion also exhibits fine structure[2]. Here, the mixture of (L,S) coupling effects and deviations from cubic symmetry cannot easily be disentangled. Even with the two nitrogens in *cis*-position, there exist two possible geometrical isomers of M(H_2O)enta with rhombic and tetragonal symmetry[7], respectively. The two forms have the water in *trans*- or in *cis*-position to nitrogen.

As will be shown below, the nickel(II) complex has an absorption spectrum mainly of "cubic" appearance and with no splittings except the small band, due to $^1\Gamma_3$. The nickel(II) complexes of other amino-acids show a similar beha-

Table 1. Absorption band maxima for ethylenediaminetetraacetate and aquo complexes of the first transition group (except of Ni^{++} and Cu^{++}). Wavenumbers in cm^{-1}. Shoulders in parentheses.

Ti $(H_2O)_6^{+++}$	20 300
Ti enta$^-$	18 400
V $(H_2O)_6^{+++}$	17 700; 25 600
V enta$^-$	12 500; (19 400); 22 600
VO^{++}	12 900; (15 400)
VO enta^{--}	12 800; 17 200
Cr $(H_2O)_6^{+++}$	17 400; 24 700
Cr enta H_2O^-	18 400; 25 600
Cr enta OH^{--}	17 300; (23 800); 25 300
Fe $(H_2O)_6^{++}$	10 400
Fe enta^{--}	9 700
Co $(H_2O)_6^{++}$	8 100; (16 000); 19 400; (21 550)
Co enta^{--}	9 100; (16 300); 19 900; 20 600; 21 500
Co $(H_2O)_6^{+++}$	16 600; 24 900
Co enta$^-$	18 650; 26 300
Co enta H_2O^-	18 200; 26 200
Co enta OH^{--}	17 400; (24 100); 25 900
Co enta Br^{--}	17 100; 25 500

viour in absorption spectrum. Thus, a tris(glycinato) complex * can be identified in the solutions with 0.1 M $Ni(NO_3)_2$ and between 0.3 and 0.5 M potassium glycinate, here denoted K gly. As expected from the crystal field theory, Ni enta^{--} and Ni gly$_3^-$ have band maxima at nearly the same places. The intensity of the first band of Ni gly$_3^-$ is not so anomalously high as that of Ni enta^{--} (see Table 3). Similar behaviour is found in chromium(III) glycinates, compared to Cr enta$^-$, where the first band is due to the transition Γ_2—Γ_5 analogous to the first band of paramagnetic nickel(II) complexes.

Copper(II) bis (glycinate) has the band at a much higher wavenumber than Cu enta^{--}. (See Table 2.) As will be discussed in the next section, Cu gly$_2$ must have a crystal field of pronounced tetragonal symmetry [23], while Cu enta^{--} is less tetragonal, and the tris-complexes of aromatic diamines are nearly cubic with correspondingly low wavenumbers of their band maxima.

At the beginning of the first transition group, the absorption spectra of enta-complexes show some peculiarities. The titanium(III) complex, which easily reduces water with evolution of hydrogen, has the maximum at 18 500 cm^{-1}, while that of Ti $(H_2O)_6^{+++}$ is situated [24] at 20 300 cm^{-1}. This smaller crystal field than water is also found in the yellow V enta$^-$ of trivalent vanadium [18]. While the tris-complexes of dicarboxy-acids, according to Bürger [25], have two bands at smaller wavenumbers than those of V $(H_2O)_6^{+++}$, the ethylenediaminetetraacetate has a quite complicated spectrum (Table 1). It might support the chemical evidence ** that amino groups seem to be weaker bound to V^{+++} than to Cr^{+++} and the heavier ions. In a following paper, the spectra of vanadium(IV) complexes will be discussed.

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* Flood and Lorås [50] have determined the three consecutive formation constants in the nickel(II) glycinate system, $\log K_1 = 5.77$, $\log K_2 = 4.80$, and $\log K_3 = 3.61$. In the corresponding copper(II) system, $\log K_1 = 8.22$, and $\log K_2 = 6.97$, while $\log K_3$ is very small. From the spectra, the latter constant can be estimated: $\log K_3 \sim 0.36$ by Keefer.[58]

** if the configuration of the complex is not so different from the octahedral that a diamagnetic groundstate is stabilized (*cf.* $Mo(CN)_8^{-4}$ investigated by Griffiths, Owen and Ward [53]).

a,a'-DIPYRIDYL- AND *o*-PHENANTHROLINE COMPLEXES

Roberts and Fields [9] and Basolo, Hayes and Neumann [26] have measured the spectrum of Ni $phen_3^{++}$ which exhibits bands at slightly higher wavenumbers than Ni en_3^{++}, corresponding to a larger value of the crystal field strength (E_1—E_2). The interesting fine structure of the first band will be discussed below. In the present section, the copper(II) complexes will be compared to those of nickel(II). The maximum coordination number [1] 6 of copper(II) is easily obtained with three molecules of *a,a'*-dipyridyl and *o*-phenanthroline, in contrast to the behaviour of the ligands ammonia and ethylenediamine. While the absorption spectra in the latter cases show "pentammine effects" [23], *i.e.* the band maxima are displaced towards lower wavenumbers by the uptake of the fifth NH_3 or third en, the spectra of the complexes of aromatic diamines with divalent copper have a regular cubic appearance. Thus, Cu dip_2^{++} and Cu $phen_2^{++}$ have their broad maxima at a lower wavenumber than the tris-complexes. Fig. 2 shows the spectra of the two systems with 2, 2.5, 3 and 4 molecules of diamine added per copper ion. The high intensity of the bis-complex, which can be extrapolated from the figure, supports the idea that is has mainly the *cis*-configuration. The *trans*-configuration would have a less intense band at a higher wavenumber than the tris-complex in analogy to Cu en_2^{++}. The weak bands found below 9 000 cm^{-1} in Cu $phen_3^{++}$ and Cu dip_3^{++} are not easily explained from the crystal field theory.*

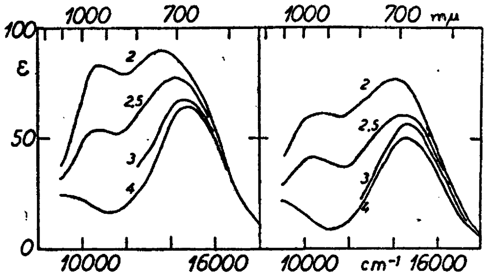

Fig. 2. Absorption spectra of copper (II) complexes of aromatic diamines. Left-hand side a,a'-dipyridyl, right-hand side o-phenanthroline. Moles of diamine per Cu++ given as numbers of curves (2, 2.5, 3, 4). Curve 4 represents the pure tris-complex. The solutions contain about 50 % ethanol and 0.02 M Cu.

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* Hartmann [39], Owen [44], and Orgel [45] have elaborated the old suggestion by Van Vleck [52] that the intermixing of molecular γ_3-orbitals would produce the same effect as the electrostatic crystal field separation of γ_3 and γ_5 of 3d-electrons, i.e. an increase of (E_1—E_2). In tetragonal complexes with four 3d-levels, the molecular orbital intermixing may produce much more individual behaviour of the levels than suggested by the calculations on pure $3d^n$-configurations [7, 46]. Much evidence can be found (also from diamagnetic, planar nickel (II) complexes) that γt_2 has unusually high energy. Thus, the band $^2\Gamma t_2 \rightarrow {}^2\Gamma t_1$ may be situated ~ 8 000 cm^{-1} in nearly cubic copper (II) complexes and ~ 10 000 cm^{-1} in the more tetragonal hexaaquo ion [23], while it is masked by the principal band in the most tetragonal complex Cu en_2^{++}.

Table 2. The first absorption band of several nickel(II) and copper(II) complexes. Double bands are given in parentheses. The ratio between the wavenumbers is given to show tetragonality effects.

Complex	ν_{Ni}	ν_{Cu}	ν_{Cu}/ν_{Ni}
$(H_2O)_6$	8 500	12 600	1.48
$(NH_3)_4\ (H_2O)_2$	~10 000	16 900	1.7
$(NH_3)_6$	10 750	15 600	1.45
$en_2(H_2O)_2$	(10 000; 11 100)[6]	18 200	1.72
en_3	11 200	16 400	1.46
$gly_2(H_2O)_2$	9 800	15 800	1.60
gly_3	10 100	~15 100	1.50
enta H_2O	10 100	13 700	1.36
$dip_2(H_2O)_2$	—	(10 500; 13 900)	1.1
dip_3	(11 500; 12 650)	14 700	1.21
$phen_2(H_2O)_2$	10 900[26]	(10 200; 13 300)	1.15
$phen_3$	(11 550; 12 700)	14 700	1.21

Table 2 gives the wavenumbers of the first band maximum of a series of nickel(II) and copper(II) complexes. If the complexes were cubic, the wavenumbers would in both cases[27] be equal to $(E_1—E_2)$. This quantity would be expected[5] to be of the same magnitude in divalent nickel and copper. The ratio between the observed wavenumbers ν_{Cu}/ν_{Ni} gives a relative measure for the tetragonality of the copper complex, because the nickel(II) spectra are nearly not affected by tetragonality. It is seen of Table 2 that ν_{Cu}/ν_{Ni} varies from 1.1 in cases where the copper complexes approximates cubic symmetry to 1.7 in the cases of strong tetragonality, as *e.g.* the bis(ethylenediamine) complex.

Table 3. The absorption bands of acetylacetonates and other oxo complexes of the first transition group. Wavenumbers in cm^{-1}. Shoulders in parentheses.

Cr $(H_2O)_6^{+++}$	17 400; 24 700
Cr ox_3^{---}	17 400; 24 000
Cr aca_3	17 900; (22 800; 24 400); 25 800; 26 500
Co $(H_2O)_6^{+++}$	16 600; 24 900
Co ox_3^{---}	16 500; 23 800
Co $(CO_3)_3^{---}$	15 700; 22 800
Co aca_3	16 900, —
Ni $(H_2O)_6^{++}$	8 500; 13 500; (15 400); 25 300
Ni aca_2	8 800; (12 900); 15 250, —
Ni $aca_2(C_2H_5OH)_2$	9 100; (13 000); 15 550, —

ACETYLACETONATES

2,4-Pentanedione (here denoted H aca) forms complexes with metals, which usually are neutral molecules, *i.e.* inner-salts. The place of aca^- in the spectrochemical series can be found from the chromium(III) and diamagnetic cobalt(III) complexes, which certainly are cubic[11]. It is seen of Table 3 that in both cases the wavenumbers are slightly larger than for the hexaaquo ions. In the ultraviolet a strong electron transfer spectrum appears, which masks the second band of the green Co aca_3. Other green cobalt(III) complexes have

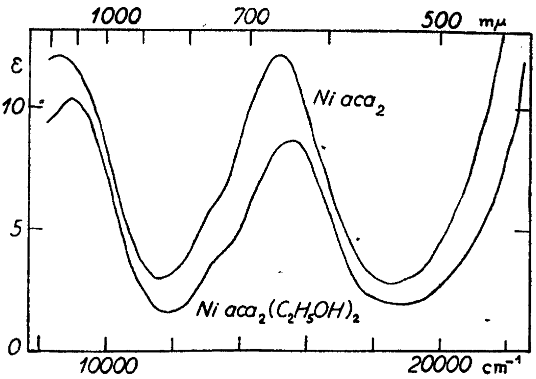

Fig. 3. Absorption spectra of 0.05 M anhydrous nickel (II) bis (acetylacetonate) in benzene and of the same solution with 2 volume % ethanol added.

smaller (E_1—E_2) than H_2O, such as the tris(carbonato) complex given in Table 3.* The spectra of tris(oxalato) complexes were measured by Mead [28].

These examples show that the concept of the Orgel diagram [5, 29] has only an approximative character, when very fine details are considered. This diagram gives the energy levels as function of only one cubic crystal field strength (E_1—E_2). Thus there should exist a treshold value of (E_1—E_2) of diamagnetism in cobalt(III) complexes, which is not reached in the hexafluoro complex, while it is exceeded in the tris(carbonato) complex. This seems to contradict the usual order of CO_3^{--} and F^- in the spectrochemical series. The tris(oxalato) complexes of trivalent chromium and cobalt have a smaller spacing between the two strong bands than have the aquo ions. This departure from the regular evolution of levels in the Orgel diagram might be ascribed to interactions with other electron configurations [12]. In this special case, the intermixing is presumably due to electron transfer states, which seem to have a great influence on the intensities of the absorption bands of oxalato and thiocyanato complexes [11].

The anhydrous form of Ni aca$_2$ is soluble with dark green colour in benzene or carbon tetrachloride. If water is added, the dihydrate precipitates out. The latter complex has undoubtedly octahedral configuration, as found by Kanekar [30, p. 404]. If ethanol is added in small quantities (not much more than 2 moles per nickel atom) to the dark green solutions, they turn bright bluish green with a displacement of their bands towards higher wavenumbers. The latter form is presumably the octahedral Ni (aca)$_2$ (C_2H_5OH)$_2$. Besides the steep absorption in the blue, due to the electron transfer band, the two

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* Shimura, Ito and Tsuchida [54] have studied several oxo complexes, *e.g.* the heteropolymolybdates with six oxygen atoms around the metal ion, as also studied by Baker *et al.* [55]. The absorption bands are situated [54] at 18 400 and 25 000 cm^{-1} of Cr^{+3} and at 16 500 and 24 300 cm^{-1} of Co^{+3} with lower ε than the aquo ions. For Mn^{+4}, a broad band is observed [54] at 21 400 cm^{-1}, while the narrow spin-forbidden d^3-band $^4\Gamma_2$—$^2\Gamma_3$ is found at 14 300 cm^{-1}. In the ruby, the present author has measured the spin-allowed bands at 18 500 and 24 400 cm^{-1}.

forms each show two bands and shoulder on the second band, as given in Table 3 and shown in Fig. 3.

In Ni $(aca)_2(C_2H_5OH)_2$, these two bands correspond undoubtedly to the transitions from $^3\Gamma_2(F)$ to $^3\Gamma_5(F)$ and $^3\Gamma_4(F)$, because the crystal field is of similar strength to that of the aquo ion. This is further supported by the sky-blue colour of the ammonia addition compound Ni $(aca)_2(NH_3)_2$, where the cubic contribution [7] is larger.

The anhydrous Ni aca_2 seems now also to be mainly octahedral, perhaps with solvate molecules perpendicular to the plane of the two acetylacetonate ligands. The relatively low intensity of the crystal field bands does not either support the tetrahedral configuration.*

NICKEL(II) COMPLEXES

In Table 4, the observed bands of a series of nickel(II) complexes are given with their parameters [2]: wavelength λ_n, wavenumber ν_n and molar extinction coefficient ε_n, all in the band maximum, and the half-widths δ (—) and δ (+) towards smaller and larger wavenumbers. In the case of $Ni(H_2O)_6^{++}$, a Gaussian analysis was performed [2], while the other entries in the table refer to directly observed maxima. Further, the approximate value of the oscillator strength P is given by [2]:

$$P = 4.60 \times 10^{-9}\varepsilon_n[\delta\,(—) + \delta\,(+)] \qquad (3)$$

In relation to Ballhausens's paper on intensities [31] the ratio PR/ν_n is also given, which in some cases is assumed to be approximately constant [31]. R is the Rydberg constant 109 740 cm^{-1}. Fig. 4 gives the observed spectra in the wavenumber range 8—17 000 cm^{-1}, where the $^1\Gamma_3$ phenomenae discussed below take place. The following complexes are arranged according to increasing value of $(E_1—E_2)$:

Sulphuric acid solutions. The yellow solution of nickel(II) carbonate in concentrated sulphuric acid presents the lowest $(E_1—E_2)$ observed. The stoichiometric composition of the complexes is not known, but the solution is rather unchanged by addition of even 20 % of water.

Phosphoric acid solutions. The yellowish-green solutions of nickel(II) carbonate in 85 % phosphoric acid are very sensitive to temperature. The smaller $(E_1—E_2)$ developed in the warm, yellow solutions can partly be ascribed to bathochromic effects, common to all complexes [22] and partly to formation of complexes with polyphosphate ligands.

Thiocyanate solutions. Mr. K. G. Poulsen has kindly informed me that in strong thiocyanate solutions, the intensity ratio between the two parts of the band in the red is reversed, compared to the aquo ion. It has been meas-

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* Recently, Hartmann and Fischer-Wasels [56] published extensive calculations on the energy levels of tetrahedral and tetragonal nickel (II) complexes. Since the tris (diamine) complexes presumably are octahedral, and since *e.g.* the aquo ion exhibits smooth changes in spectrum by uptake of six ammonia molecules [1], these simple nickel (II) complexes are not tetrahedral, and it is still in doubt, if any exists. As will be discussed in another paper, it is also improbable that the manganese (II) aquo ion is tetrahedral, as maintained by Schläfer [57]. The only evidence for tetrahedral configuration of divalent $3d^n$-metal ions in solution is the zinc tetrammine ion [1] and the cobalt halide complexes [22, 45].

Table 4. Absorption Bands of Nickel(II) Complexes in Solution.

Complex and identifications of the excited states:	λ_n mμ	ν_n cm^{-1}	ε_n	$\delta(-)$ cm^{-1}	$\delta(+)$ cm^{-1}	P $\times 10^{-5}$	PR/ν_n $\times 10^{-5}$
Sulphuric acid ((E_1-E_2) = 7 000 cm^{-1}):							
$^3\Gamma_4(F)$	820	12 200	2.6	~1 200	~1 000	2.6	23
$^1\Gamma_3(D)$	680	14 700	0.5	—	400	0.2	2
$^3\Gamma_4(P)$	428	23 350	8.3	1 400	1 400	10.7	50
Phosphoric acid (7 900):							
$^3\Gamma_4(F)$	760	13 150	3.2	1 400	1 500	5.3	40
$^1\Gamma_3(D)$	672	14 900	1.8	—	500		
$^3\Gamma_4(P)$	408	24 500	8.5	1 600	1 400	11.8	53
Hexaaquo ion (8 500):							
$^3\Gamma_5(F)$	1 180[35]	8 500	2.0	1 200	1 200	2.2	28
$^3\Gamma_4(F)$	740 [2]	13 500	1.8	1 100	1 100	3.5	27
$^1\Gamma_3(D)$	650 [2]	15 400	1.5	1 200	1 200		
$^3\Gamma_4(P)$	395 [2]	25 300	5.2	1 500	1 500	7.2	31
Thiocyanates (8 600):							
$^1\Gamma_3(D)$	725	13 800	5	~1 000	—	12	80
$^3\Gamma_4(F)$	655	15 300	7	—	~1 300		
$^3\Gamma_4(P)$	393	25 500	16	1 600	1 600	23	100
Ethylenediaminetetraacetate (10 000):*							
$^3\Gamma_5(F)$	990	10 100	31	1 400	1 300	38	420
$^1\Gamma_3(D)$	790	12 650	5	—	500	2.3	20
$^3\Gamma_4(F)$	587	17 000	8.3	1 700	1 550	12.4	80
$^3\Gamma_4(P)$	382	26 200	12.2	1 750	2 300	22.7	95
Tris(glycinate) (10 100):							
$^3\Gamma_5(F)$	990	10 100	9.9	—	1 500	13.6	145
$^1\Gamma_3(D)$	763	13 100	2.0	—	300	0.6	5
$^3\Gamma_4(F)$	602	16 600	8.2	1 800	1 800	13.6	90
$^3\Gamma_4(P)$	362	27 600	14.4	1 700	1 800	23.2	92
Hexa(ammonia) (10 800):							
$^3\Gamma_5(F)$	930	10 750	4.0	1 500	1 400	5.3	54
$^1\Gamma_3(D)$	760	13 150	0.5	—	~500	0.2	2
$^3\Gamma_4(F)$	571	17 500	4.8	1 550	1 600	7.0	44
$^3\Gamma_4(P)$	355	28 200	6.3	1 600	1 800	9.8	38
Tris(ethylenediamine) (11 600):							
$^3\Gamma_5(F)$	890 [2]	11 200	7.3	1 250	—	10.3	98
$^1\Gamma_3(D)$	805	12 400	5	—	—		
$^3\Gamma_4(F)$	545 [2]	18 350	6.7	1 650	1 650	10 2	61
$^3\Gamma_4(P)$	345 [2]	29 000	8.6	1 700	1 900	14.3	54
Tris(a,a'-dipyridyl) (12 100):							
$^1\Gamma_3(D)$	868	11 500	5.7	850	—	9.6	86
$^3\Gamma_5(F)$	790	12 650	7.1	—	1 250		
$^3\Gamma_4(F)$	521	19 200	11.6	1 700	2 100	20	~110
Tris(*o*-phenanthroline) (12 200):							
$^1\Gamma_3(D)$	865	11 550	5.5	1 000	—	9.4	84
$^3\Gamma_5(F)$	788	12 700	6.8	—	1 350		
$^3\Gamma_4(F)$	519	19 300	11.9	1 650	1 700	19	~110

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* Hamm[20] observed an intermediate form of $Cr(H_2O)$ enta$^-$, perhaps another geometrical isomer. There is some evidence that Ni enta^{--} for some minutes can exist with the absorption maxima at 9 900, 12 900, 16 900, and 26 400 cm^{-1} with ε_n = 25, 2, 8 and 14, respectively.

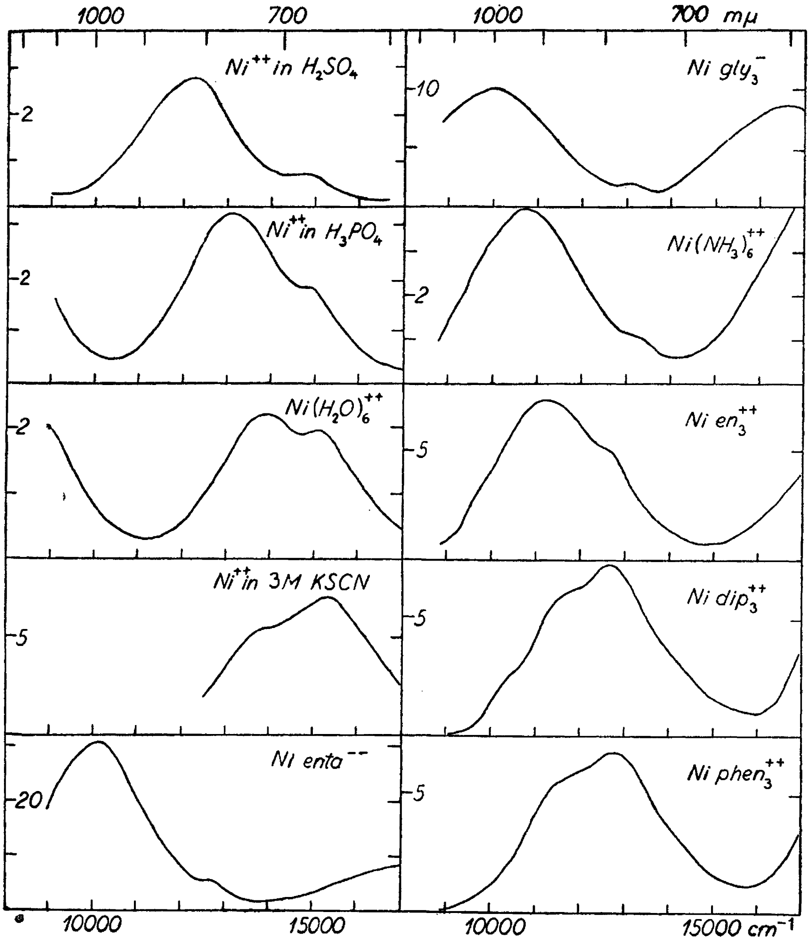

Fig. 4. Absorption spectra of nickel(II) complexes in the range 8 000—17 000 cm^{-1}.

0.02 M Ni in 98 % H_2SO_4 — 0.1 M $Nigly_3^-$ (from 0.4 M Kgly).
0.1 M Ni in 85 % H_3PO_4 — 0.2 M Ni $(NH_3)_6^{++}$ in 10 M NH_3.
0.5 M Ni $(NO_3)_2$ in H_2O — 0.2 M Ni en_3^{++} in 1 M en
0.1 M Ni in 3M KSCN — 0.02 M Ni dip_3^{++} (from 0.08 M dip, 80 % ethanol)
0.05 M Ni $enta^{--}$, pH~8. — 0.02M Ni $phen_3^{++}$ (from 0.08M phen, 80 % ethanol)

ured by Fronæus[32] and is seen in Fig. 4 for a solution, 3 M in KSCN, which probably[32] contains complexes with at least 3 thiocyanates per Ni. Since $^3\Gamma_4(P)$ has nearly the same position as in the aquo ion, the crystal field strength is not much larger.

Hexa(ammonia) and tris(ethylenediamine) complexes. Their absorption spectra are quite similar with about 7 % difference in $(E_1—E_2)$ The shoulder at 12 400 cm^{-1} in Ni en_3^{++} caused the large value of δ (+), found by the author[2].

Tris(α,α'dipyridyl) and tris(o-phenanthroline) complexes. The crystal field bands of Ni dip$_3^{++}$ correspond to (E_1-E_2) being only 0.5 % smaller than in Ni phen$_3^{++}$. In the ultraviolet, very strong absorption is observed in both cases, but the α,α'-dipyridyl complex seems to have a smooth increase below 32 000 cm^{-1}, while the *o*-phenanthroline complex exhibits very characteristic, narrow bands[9]. The band $^3\Gamma_2(F)-^3\Gamma_4(P)$ predicted ~30 000 cm^{-1} is totally hidden by these high bands common to all complexes of aromatic diamines[33]. The crystal field bands ~19 300 cm^{-1} might be suspected to be partially due to impurities of iron(II) complexes, which here have[33] ε ~10 000. But attempts to oxidize any trace of iron to the trivalent state before addition of the diamine did not change the spectrum of the nickel(II) complex, and the present author agrees with Roberts and Field[9] in the values of ε_n.

In Table 4, the values of P are calculated from the hypothesis of equal half-widths, if only one is known. In the case of shoulders, only the total sum of P is calculated as rationalized in the theoretical discussion. The first band of Ni(H$_2$O)$_6^{++}$ is measured by Dreisch and Trommer[34]. The value of (E_1-E_2) given after the name of each complex is taken as the energy difference between the centre of gravity of $^3\Gamma_5(F)$ and the groundstate $^3\Gamma_2(F)$, rather than the values earlier given[5], which were fitted to all three strong bands. The new values are used for the Orgel diagram in Fig. 5.

THEORETICAL

The preceding absorption spectra of nickel(II) complexes give the possibility of drawing the Orgel diagram with exceptionally small differences between the individual (E_1-E_2) of the complexes, and thus to investigate the concept of lines in the Orgel diagram determined as eigenvalues of matrices[7,29] similar to those for intermediate coupling[35]. After the recent investigation by Shenstone[36], the levels of the free ions Ni^{++} are:

[A] 3d^8:	$^3F_4$	0 cm^{-1}
	$^3F_3$	1 361
	$^3F_2$	2 270
	$^1D_2$	14 032
	$^3P_2$	16 662
	$^3P_1$	16 978
	$^3P_0$	17 231
	$^1G_4$	23 109
[A] 3d^7 4s:	^5F	53 704, 54 658, . . .
	^3F	61 339, . . .
	^5P	71 067, . . .
	^3G	75 123, . . .
[A] 3d^7 4p:	^5F	110 212, . . .
	^5D, ^5G, ^3G, ^3F, . . .	~112 000

It is seen that the multiplet splitting is rather large, corresponding to a departure from pure Russell-Sounders coupling. In the first transition group, only Cu^{++} with the energy difference 2 072 cm^{-1} between the groundstate

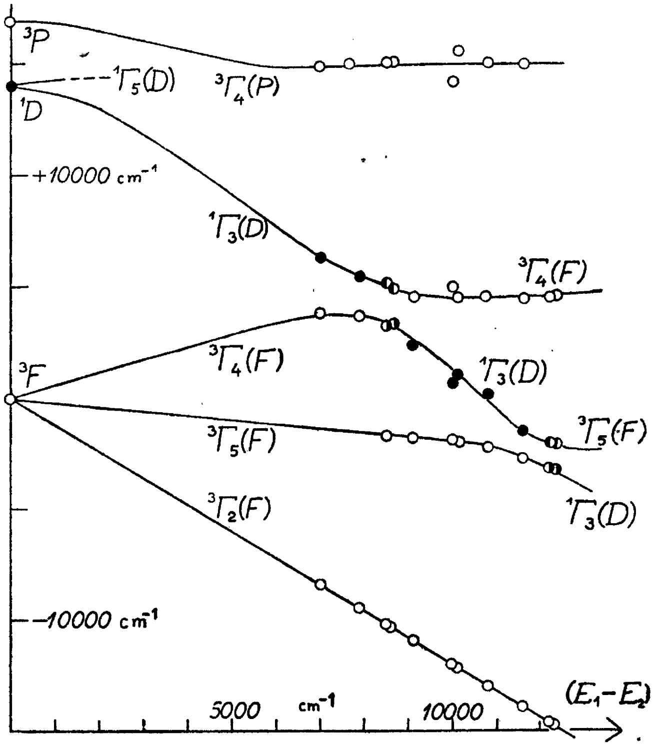

Fig. 5. Orgel diagram of octahedral nickel(II) complexes.
The three triplet levels and the lowest singlet level ($^1\Gamma_3$) *as function of the crystal field strength* (E_1-E_2). *Intermixing effects between the singlet level and the two triplet levels* $^3\Gamma_4(F)$ *and* $^3\Gamma_5(F)$ *are shown by the filled circles, which denote singlet character. The values of* (E_1-E_2) *and positions of the band maxima from Table 4. The groundstates are fixed*[27] *on the line* $-\frac{6}{5}(E_1-E_2)$.

$^2D_{5/2}$ and $^2D_{3/2}$ has a larger dependance on J (the vector sum of L and S, which is given as index for the levels in the free ion). In the theory of intermediate coupling[35], the states with the same J interact as a function of the Landé multiplet splitting factor ζ_{nl} (*cf.* as a concrete example the lanthanide and actinide ions[37]), the pure Russell-Saunders coupling being the limiting case $\zeta_{nl}=0$. In Ni^{++}, ζ_{3d} is calculated to be $\cong$ 600 cm^{-1} from the observed levels in the free ion. As seen Ref.[35, p. 269], the interaction between the states with $J=2$ in Ni^{++} is particularly strong, since the non-diagonal elements are

$$(^3F_2 \quad ^1D_2) = -2\sqrt{3/5}\zeta_{3d} \qquad (4)$$
$$(^3P_2 \quad ^1D_2) = \sqrt{21/10}\zeta_{3d}$$

which in both cases have the numerical value ~1 000 cm^{-1}. The usual approximation in crystal field theory, when applied to the transition group ions[38] that the coupling between L and S is negligible compared to the crystal field strength $(E_1—E_2)$, is thus slightly weakened in the case of nickel(II) complexes, where $(E_1—E_2)$ is $\sim$10 000 cm^{-1}.

The Orgel diagram of nickel(II) complexes, as seen in Fig. 5, seems really to show the interaction between $^1\Gamma_3(D)$ when passing over firstly $^3\Gamma_4(F)$ at $(E_1—E_2) = 8\,000$ cm^{-1} and secondly over $^3\Gamma_5(F)$ at $(E_1—E_2) = 12\,000$ cm^{-1}. These values correspond to the water-thiocyanate and the ethylenediamine —α,α'-dipyridyl range of increasing crystal field strength. If no interaction occurred between $^1\Gamma_3(D)$ and the triplet states, the lines would simply cross in the Orgel diagram without anomalies such as bent curves near the cross-point. But if an interaction occurs with the nondiagonal element [7] of energy = K, the two states will have the minimum distance $2K$ and do not cross each other. Of Fig. 5 can be seen that K is = 800 cm^{-1} between $^1\Gamma_3$ and $^3\Gamma_4(F)$ and = 500 cm^{-1} between $^1\Gamma_3$ and $^3\Gamma_5(F)$, a remarkably large part of the interaction between the pure levels with $J = 2$ which of course cannot be represented by the triplet states in crystal fields.

Contrary to the case of simple crossing (when $K = 0$), the interesting phenomenon of intermixing occurs between the two interacting states. When the distance $E_a—E_b$ between the states decreases, the wavefunctions will be intermixed with coefficients $\simeq \left(\frac{K}{E_a—E_b}\right)^2$ in the squares (being 1 %, when $K = 0.1\ (E_a—E_b)$ *etc.*). The energy of the lowest state will be decreased by the amount $\frac{K^2}{E_a—E_b}$, while the energy of the highest state will be increased by the same amount (this is often called "resonance energy" in chemical textbooks [39]). In the minimum distance, the energy decrease is = K and the intermixing 50 %. After this point, the intermixing as function of the free variable (in the Orgel diagram the crystal field strength) will be reversed; the energy repulsions decrease rapidly and the highest level now assume the wave function, which before the point of minimum distance was characteristic for the lowest level. Actually, at large distance from the point of near crossing, the levels behave as straight lines in the Orgel diagram, and especially as if they *had* crossed. Only near the cross-point of the asymptotes, the intermixing is so large that it has no physical significance to label one of the levels as having just the quantum numbers, characteristic for one of the two asymptotic straight lines.

One of the properties which clearly is intermixed in our case, is the total spin number S. As pointed out by Hellwege [40], the transitions between states with different S is only possible in so far as S is not strictly defined, "is not a good quantum number". This is caused by intermediate coupling effects. The usually cited intensity ratio [5] 0.01 between bands, where S changes 1, and where S is constant, corresponds to an intermixing of 1 % of the other S-value. In the case of nickel(II) complexes, the intermixing of triplet character ($S=1$) in $^1\Gamma_3(D)$ can assume much higher values*, as seen of Table 4,

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* The triplet character ($S = 1$) of the weak band is calculated to 0.1 for Ni^{++} in H_2SO_4, 0.1 for Ni^{--} enta, 0.03 for Ni gly_3^- and 0.05 for $Ni(NH_3)_6^{++}$ with the two values of K given above, if the influence of the two triplets is additive. This is in outstanding agreement with the relative values of P, given in Table 4.

where braces in the identification column denote cases, where no distinction can be made between the singlet and the nearest triplet level. Therefore, only the total sum of P is calculated in such cases, because the intensity is distributed proportional to the triplet character of the levels. The question arises as to whether the groundstate $^3\Gamma_2(F)$ of paramagnetic nickel(II) complexes would be intermixed with the singlet state when these are crossing, *i.e.* when the magnetism is changed by increasing crystal field strength. If so, this would make this transition point indefinite. But it can be argued that the internal vector group product [7] of Γ_4 (corresponding to $S = 1$) with the other states has the following values:

$$\begin{aligned} \Gamma_2 \times \Gamma_4 &= \Gamma_5 \\ \Gamma_4 \times \Gamma_4 &= \Gamma_1 + \Gamma_3 + \Gamma_4 + \Gamma_5 \\ \Gamma_5 \times \Gamma_4 &= \Gamma_2 + \Gamma_3 + \Gamma_4 + \Gamma_5 \end{aligned} \qquad (5)$$

These sums consist of the quantum numbers of levels with different J[38] from ^3F. Only $^3\Gamma_5$ and $^3\Gamma_4$ contain representations of Γ_3, which can intermix with $^1\Gamma_3(D)$.

Ballhausen [31] has suggested that the deviations from Hellwege's selection rules for octahedral complexes [11, 40] are due to intermixing of the quantum numbers $^{2S+1}\Gamma_n$. If this is valid, a similar mechanism must act on $^3\Gamma_5(F)$ and distribute it on $^3\Gamma_4(F)$ and $^3\Gamma_4(P)$ in Ni^{++}, because only the transition Γ_2—Γ_5 is allowed, sofar symmetry reasons are considered [40]. Mr. C. E. Schäffer has pointed out to me by an analogous argument that $^4\Gamma_4(F)$, but not $^4\Gamma_4(P)$, must be highly intermixed with $^4\Gamma_5(F)$ in Cr^{+++}. Another explanation may be found in the coupling with vibrations [39] which produce group products containing several different Γ_n.

Polder [41] discussed the crystal field splittings of ^2D in Cu^{++} in tetragonal and rhombic crystal fields and pointed out that (L,S) coupling effects can separate the highest level in tetragonal complexes, *viz.* $^2\Gamma_{t5}$, into two with the distance ~800 cm^{-1}. Abragam and Pryce [42] investigated the magnetic properties of copper(II) salts along these lines, and Ballhausen [43] later interpreted the absorption spectra on basis of the crystal field model of Ilse and Hartmann [3]. It is interesting that even in a cubic complex of Cu^{++}, the state $^2\Gamma_5$ would split due to (L,S) coupling effects in a similar way as in tetragonal fields [43].

Evidently, (L,S) coupling effects have some importance for the absorption spectra of the last elements in the first transition group, *viz.* Co^{++}, Ni^{++} and Cu^{++}. As a further example may be cited the three bands of Co enta^{--} (see Table 1) and fine structure of $Co(H_2O)_6^{++}$, discussed by Abragam and Pryce [44]. For a complete analysis of these spectra it is further necessary to consider the interactions with other electron configurations (see the list of levels of Ni^{++} above) which are not very distant in the divalent ions. Besides this, the electron transfer states seem very important in many cases. Especially, Orgel [45] has pointed out that a class of diamagnetic nickel(II) complexes with ligands showing tendency of π-bonding have very peculiar spectra. But also the ordinary complexes, which are only σ-bonding in the theory of Owen [46], have interaction effects. In the present paper is shown that $^1\Gamma_3$ is systematically decreased by increasing ($E_1—E_2$) in paramagnetic nickel(II) complexes, compared to ${}^3\Gamma_2$ (see Fig. 5). These two states should, if no electron configuration interaction is assumed, have the asymptotical distance [7]

$$\tfrac{4}{7}\,({}^1D) + \tfrac{3}{7}\,({}^1G) - ({}^3F) = 18\,000 \text{ cm}^{-1} \qquad (6)$$

which is actually found to be 13 000 cm^{-1} or less (see Table 4).

It is seen of Table 4 that ${}^1\Gamma_3(D)$ generally is situated about 0.45 ($E_1—E_2$) below the predicted place. Thus, it might be concluded by extrapolation that a purely cubic nickel(II) complex would be diamagnetic, if $(E_1—E_2) > 40\,000$ cm^{-1}. But due to the Jahn-Teller effect the state would spontaneously change to a tetragonal configuration [7], and at much lower values of ($E_1—E_2$), the lowest of the diamagnetic tetragonal levels, ${}^1\Gamma_{t1}$, will be the groundstate. This is observed in the penta- (and presumably also the hexa-) cyanide complex of nickel(II), which is red-orange with the band of the yellow Ni $(CN)_4^{--}$ displaced towards lower wavenumbers, analogous to [47] $PdCl_6^{-4}$ compared to $PdCl_4^{--}$.

EXPERIMENTAL

Materials. The ethylenediaminetetraacetates in solutions were prepared from stock solutions of chromium(III) nitrate, cobalt(II) sulphate, nickel(II) nitrate and copper(II) sulphate of AnalaR grade and 1 M Na_4enta from analytical pure H_4enta and two moles of Na_2CO_3. At room temperature the complete formation of Ni enta^{--} takes several hours. Co enta^{--} in NaOH was oxidized by H_2O_2 according to Schwarzenbach [17]. Vanadium(III) was prepared from ammonium metavanadate with hydrochloric acid and zinc or from $NH_4V(SO_4)_2$, 12 H_2O after Palmer [48]. Solutions of glycinates were made from 1 M potassium glycinate and the metallic salts. Acetylacetonates were prepared from acetylacetone and stoichiometric amounts of Na_2CO_3 and metallic salts. Ni $aca_2(H_2O)_2$ was made anhydrous by azeotropic distillation with toluene. Co aca_3 was prepared from $Co(OH)_3$ according to Urbain and Debierne [49]. 0.1 M solutions of *a,a'*-dipyridyl and o-phenanthroline (Merck's p.a.) in ethanol were added to nickel and copper salts.

Measurements. In the wavelength range below 800 *mμ*, the spectra were measured on a Cary spectrophotometer and recorded at least twice with rather high dispersion. Above 700 *mμ* several measurements were performed on the Beckman DU spectrophotometer, and the bands in the infra-red determined with an interval of 10 *mμ*. In both cases 1 cm, 2 cm, and 5 cm cells were used.

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