Spectra of Nickel(II)-Azide Complexes in Organic Solvents

R. Abu-Eittah and S. Elmakabaty
Department of Chemistry, Faculty of Science, Cairo University, Giza, Egypt

(Received September 12, 1972)

The complexing properties of nickel(II) ion with azide ion, in a number of organic solvents, are investigated by spectroscopic methods. The electronic absorption spectra of Ni(II)–N_3^- solutions were studied in the visible-ultraviolet regions using dimethylformamide, absolute methanol and absolute ethanol as solvents. The composition of the possibly obtained complexes was investigated using the continuous variation and the slope ratio methods. The composition of the predominant complex was dependent on the solvent used. Formation as well as dissociation constants of the obtained complexes were computed.

The structure of nickel(II) complexes has been the aim of extensive studies.[1–4] Octahedral, square planar and tetrahedral geometries are known for nickel(II) complexes.[5–7] Piper and Koertge studied the spectra of $[Ni(H_2O)_6]^{2+}$ at low temperature.[8] Conductometric, potentiometric and spectrophotometric studies have shown that the 1 : 1 nickel azide complex predominates in aqueous medium.[9–11] Complexation between azide ion and many transition metals, other than nickel, has been investigated.[12,13]

The complexing power of azide ions with regard to several metal ions in aqueous solutions have been studied using polarographic as well as potentiometric methods.[14]

Experimental

Preparation of standard solutions of nickel perchlorate and of sodium azide was done as explained before.[13] Solvents used were: absolute methanol, absolute ethanol (Apolda grade reagent) and dimethylformamide (Prolabo grade reagent) that were purified by conventional methods found in the literature.[15] Spectra were scanned using a Beckman DK spectrophotometer and a 1.0 cm silica cells.

Results and Discussion

Complexes of Ni(II) and N_3^- in Absolute Methanol. Structure of the Complexes: In water as a solvent, the complex in $[Ni(H_2O)_6]^{2+}$, possessing a simple octahedral geometry, shows two absorption bands at 14, 286 and 25, 641 cm^{-1}. These bands are assigned to the $^3A_{2g}\rightarrow{}^3T_{1g(F)}$ and $^3A_{2g}\rightarrow{}^3T_{1g(P)}$ transitions respectively. In addition to these bands, the ion shows an absorption band in the UV region (~250 nm) which i rather weak. In methanol as a solvent the ion show

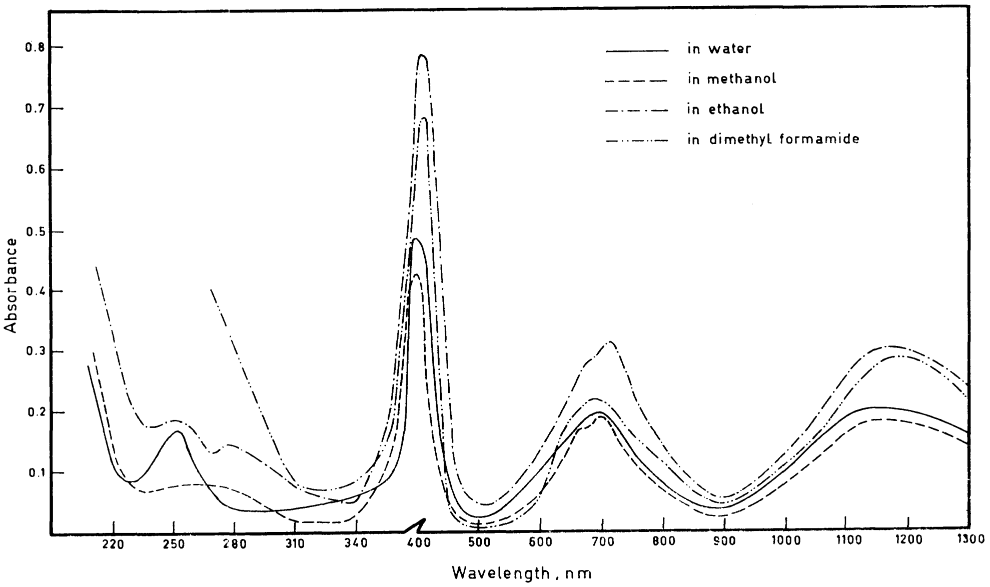

Fig. 1. Absorption spectra of nickel perchlorate in different solvents.

---

[1] E. Uhlemann, G. Hinsche, and H. Braunschweig. *Z. Anorg. Allg. Chem.*, **377**, 321 (1970).

[2] R. Eisenberg, R. Curran, and J. A. Cunningham, *Inorg. Chem.*, **9**, 2749 (1970).

[3] D. Goodgame, M. Goodgame, and G. W. Rayner-Canham, *Inorg. Chim. Acta.*, **3**, 406 (1969).

[4] T. Tarantelli, P. Riccieri, and C. Furlani, *J. Inorg. Nucl. Chem.*, **31**, 3585 (1969).

[5] C. K. Jørgenesen, *Acta. Chem. Scand.*, **9**, 1362 (1955).

[6] C. K. Jørgenesen, *ibid.*, **10**, 887 (1956).

[7] L. M. Venanzi, *J. Chem. Soc.*, **1958**, 719.

[8] T. S. Piper and N. Koertge, *J. Chem. Phys.*, **32**, 559 (1960).

[9] C. Heinrich Egghart, *J. Inorg. Nucl. Chem.*, **31**, 1538 (1969).

[10] V. Gutmann and H. Bardy, *Z. Anorg. Allg. Chem.*, **361**, 213 (1968).

[11] P. Senise, O. E. S. Godinho, *J. Inorg. Nucl. Chem.*, **32**, 3641 (1970).

[12] H. I. Feinstein, *Anal. Chim. Acta*, **15**, 288 (1956).

[13] R. Abu-Eittah and G. Arafa, *J. Inorg. Nucl. Chem.*, **32**, 3337 (1970).

[14] P. Senise, N. Almeida, and F. Eduard, *An. Acad. Brasil. Cienc.*, **41**, 333 (1969).

[15] R. I. Vogel, "Practical Organic Chemistry," 3rd., Ed. Longmans, London, (1956).

(Fig. 1) the same absorption bands that were slightly red-shifted. On adding azide ion to the Ni(II) solution, the formed azidoaquo nickel(II) complex is also assumed to possess octahedral structure. Mixing of ligands will cause but a slight distortion from the simple cubic symmetry. Displacement of water molecules by azide ions can be represented as:

$$[\mathrm{Ni(H_2O)_6}]^{2+} + X\mathrm{N_3}^- \rightleftharpoons$$

$$[\mathrm{Ni(H_2O)}_{6-x}(\mathrm{N_3})_x]^{+2-x} + X\mathrm{H_2O}$$

The number of azide ions ligated to the Ni(II) ion will be dependent on the solvent used. In water, as a solvent, it has been proved that only one azide ion is ligated to the Ni(II) ion.[10,16] If we use an organic solvent, miscible with water, we expect that the number of N_3^- ions ligated to Ni(II) ion will increase.

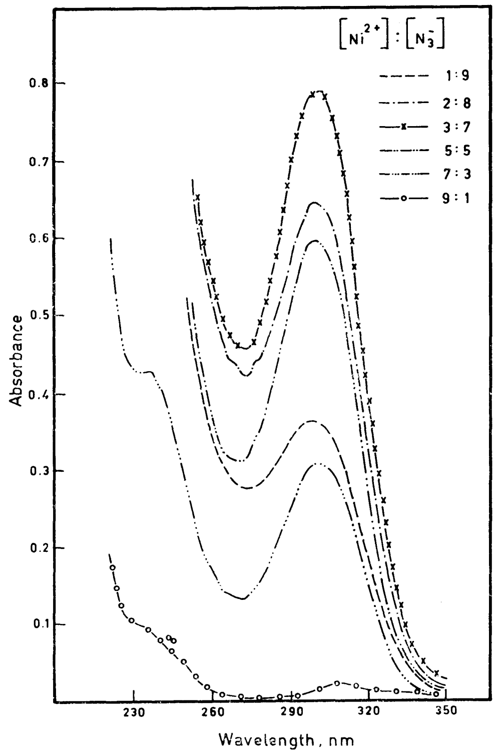

Fig. 2. Absorption spectra of nickel azide solutions in methanol.

Figure 2 shows the absorption spectra of solutions, in absolute methanol, made by mixing nickel perchlorate and sodium azide with total concentration of 2×10^{-3} M. The formed nickel azide complex has an absorption band of its own with $\lambda_{\max}$ at 300 nm. Absorbance of free Ni(II) or azide ions is negligible at this wavelength. It is interesting to remember that the monoazidoaquonickel(II) complex[16] has an absorption band of its own at ~290 nm. This suggests that the nature of the Ni(II)–N_3^- complex, when water is the solvent, differs from its nature when absolute methanol is the solvent. Job's[17] method of continuous variation was applied to results of Fig. 2. In Fig. 3 one plots the absorbance *versus* the mole fraction of azide ion. A well-defined maximum appears at 0.7 mol fraction of azide ion which suggests that the predominant nickel azide complex may be the 1:2 or the 1:3 complex. Data needed to plot Fig. 3 are given in Table 1.

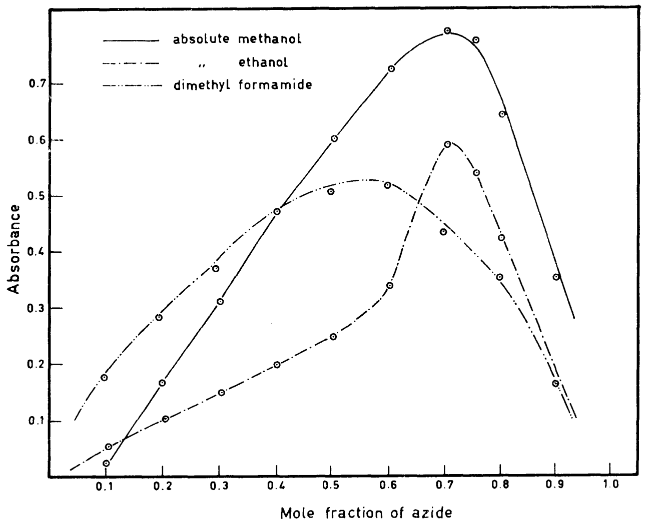

Fig. 3. Structure of nickel azide complexes, in different solvents, using the continuous variation method.

TABLE 1. VARIATION OF ABSORBANCE OF NICKEL-AZIDE SOLUTIONS WITH AZIDE ION CONCENTRATION, IN DIFFERENT SOLVENTS (ABSOLUTE ALCOHOLS AND DIMETHYLFORMAMIDE)

$[Ni^{2+}]:[N_3^-]$	Absorbance		
	Methanol (300 nm)	Ethanol (302 nm)	Dimethylformamide (305 nm)
1:9	0.36	0.165	0.165
2:8	0.645	0.425	0.35
2.5:7.5	—	0.540	—
3:7	0.795	0.590	0.43
4:6	0.725	0.34	0.52
5:5	0.600	0.25	0.51
6:4	0.470	0.20	0.475
7:3	0.310	0.15	0.37
8:2	0.165	0.10	0.285
9:1	0.02	0.055	0.18

To confirm the above results, the slope ratio method was applied.[18] Spectra of solutions made by mixing constant excess $[Ni^{2+}]$, 4×10^{-3} M with variable $[N_3^-]$, from 0.6×10^{-3}—1.0×10^{-3} M, were scanned. Also, spectra of solutions made by mixing constant excess $[N_3^-]$, 1.6×10^{-3} M with variable $[Ni^{2+}]$ from 0.1×10^{-3} to 0.5×10^{-3} M were scanned. In Fig. 4 we plot the absorbance (at 300 nm) *versus* the concentration of the variable components. Straight lines are obtained, ratio between their slopes gives the ratio of the two components of the complex. Results of Fig. 4 give a ratio of 1:2.79 of the $[Ni^{2+}]$: $[N_3^-]$ in the obtained nickel azide complex. This suggests that in methanol, the

---

[16] R. Abu-Eittah and S. Elmakabaty, *J. Inorg. Nucl. Chem.*, to be published.

[17] P. Job and C.R. Held, *Séanc. Acad. Sci. Paris*, **180**, 228 (1925).

[18] A. E. Harvey and D. L. Manning, *J. Amer. Chem. Soc.*, **72**, 4488 (1950).

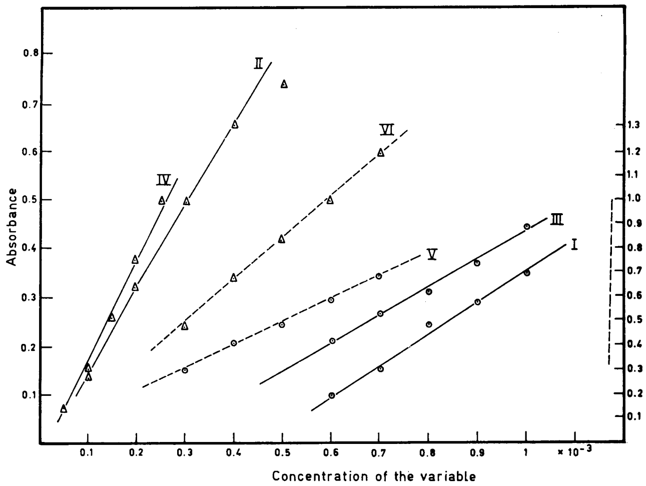

Fig. 4. Application of the slope ratio method to the structure of nickel azide.

I—II in absolute methanol ⊙ $[Ni^{2+}]$ constant
III—IV in absolute ethanol △ $[N_3^-]$ constant
V—IV in dimethyl formamide

Table 2. Absorbances of nickel(II)-azide solutions containing constant excess $[Ni^{2+}]$, with variable $[N_3^-]$ and others containing constant excess $[N_3^-]$ with variable $[Ni^{2+}]$ in absolute methanol at 300 nm

Constant $[Ni^2]^+$: 4×10^{-3}		Constant $[N_3^-]$: 1.6×10^{-3}	
$[N_3^-]$	Absorbance	$[Ni^{2+}]$	Absorbance
0.6×10^{-3}	0.1	0.1×10^{-3}	0.145
0.7×10^{-3}	0.155	0.2×10^{-3}	0.32
0.8×10^{-3}	0.245	0.3×10^{-3}	0.5
0.9×10^{-3}	0.28	0.4×10^{-3}	0.66
1×10^{-3}	0.35	0.5×10^{-3}	0.74

1: 3 nickel azide complex is obtained. Data needed to plot Fig. 4 are given in Table 2.

Stability Constants: The predominant complexes were found to be the 1: 2 and the 1: 3 complexes. Dissociation constant K' was computed following the Harvey-Manning method.[18] Dissociation of the nickel azide complex can be represented by:

$$\begin{array}{llll} [Ni(N_3)_n]^{+2-n} \rightleftarrows & Ni^{2+} + & nN_3^- & \\ C & 0 & 0 & \text{initial concentration} \\ C(1-\alpha) & \alpha C & n\alpha C & \text{equilibrium concentration} \end{array}$$

The dissociation constant K' is given by.

$$K' = (\alpha C)(n\alpha C)^n/C(1-\alpha)$$

where, "α" represent the degree of dissociation and is given by $(A_m - A_S)/A_m$. The value of (A_m) represents the absorbance when all the nickel present is complexed, that of (A_S) is the absorbance at the stoichiometric molar ratio of N_3^- to Ni^{2+} in the complex. The value of "n" will be the number of azide ions per ion of nickel and "C" will be taken as the concentration of nickel used.

The spectra of a series of nickel-azide solutions, with the ratio $[Ni^{2+}]$: $[N_3^-]$ varying from 1: 1 to 1: 20 were scanned. The absorbance at 300 nm is plotted against the number of moles azide per mole nickel in Fig. 5. The values of (α) were found to be 0.584 and 0.471, from Fig. 5, at "n" equals to 2 and 3. Data needed to plot Fig. 5 is given in Table 3.

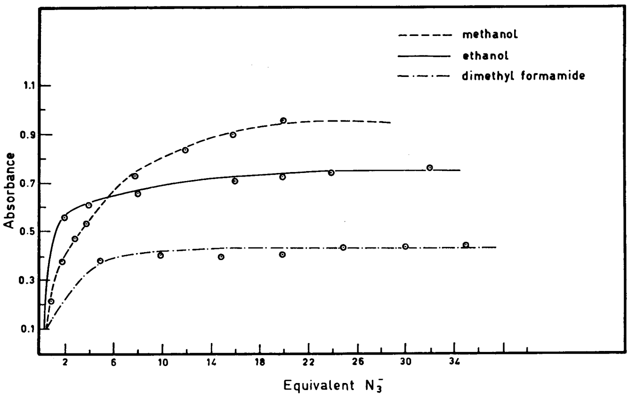

Fig. 5. Variation of absorbance of nickel azide solution with azide concentration.

Table 3. Absorbance of nickel-azide solutions in different solvents

$[Ni^{2+}]$: $[N_3^-]$	Absorbance		
	Methanol (300 nm)	Ethanol (302 nm)	Dimethyl-formamide (305 nm)
1:1	—	0.205	—
1:2	0.37	0.555	—
1:3	0.47	—	—
1:4	0.53	0.600	—
1:5	—	—	0.365
1:8	0.71	0.64	—
1:10	—	—	0.39
1:12	0.83	—	—
1:15	—	—	0.385
1:16	0.89	0.695	—
1:20	0.95	0.71	0.4
1:24	—	0.73	—
1:25	—	—	0.435
1:30	—	—	0.435
1:32	—	0.75	—
1:35	—	—	0.450

Substituting by these values in the equation for K' one gets 0.208×10^{-6} and 0.9×10^{-10} for the dissociation constants of the 1: 2 and 1: 3 nickel azide complexes. Formation constants of these complexes are 4.8×10^6 and 1.99×10^{10} respectively. These values reflect the quite stability of the obtained nickel azide complex.

Nickel(II)-azide Complexes in Absolute Ethanol. To see the effect of solvent on the composition of Ni(II)-azide complexes, the spectra of mixtures of nickel perchlorate and sodium azide were studied using absolute ethanol as a solvent. Mixtures were prepared so as the total concentration was 1.0×10^{-3} M. Job's method of continuous variation was applied to the results of the spectra (Fig. 3). In absolute ethanol, as a solvent, formation of more than one complex was evident. Figure 3 shows a break at azide mole fraction of 0.6, peak at azide mole fraction of 0.72 and a break at azide mole fraction of 0.8. This means that the complexes: $[Ni(N_3)_2(H_2O)_4]^0$; $[Ni(N_3)_3(H_2O)_3]^-$ and $[Ni(N_3)_4(H_2O)_2]^{2-}$ are obtained on mixing nickel perchlorate and sodium azide solutions in absolute ethanol as a solvent. Formation of more than one complex, at the same time, is expected not to give a well-defined spectrum. This can be seen from Fig. 6 where the spectra of Ni(II)–N_3^- solutions, in the studied solvents, are given. In absolute ethanol, bands were not well defined as they were in other solvents which indicates the formation of more than one complex.

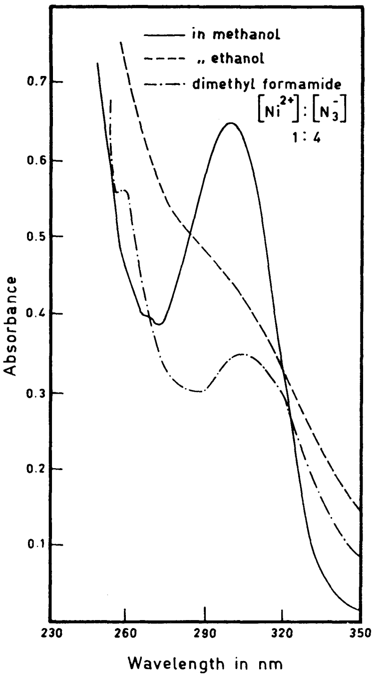

Fig. 6. Absorption spectra of nickel(II)-azide solutions in different solvents.

The slope ratio method was used to confirm the composition of nickel azide complex when absolute ethanol is the solvent. In Fig. 4 the relation between absorbance (at 302 nm) and concentration of the variable component is plotted. Data needed to plot this curve is given in Table 4.

Table 4. Absorbances of nickel-azide solutions with excess constant $[Ni^{2+}]$ and with excess constant $[N_3^-]$ in absolute ethanol as a solvent

$[Ni^{2+}]=4\times10^{-3}$		$[N_3^-]=0.8\times10^{-3}$	
$[N_3^-]$	Absorbance (302 nm)	$[Ni^{2+}]$	Absorbance (302 nm)
0.6×10^{-3}	0.215	0.05×10^{-3}	0.075
0.7×10^{-3}	0.27	0.1×10^{-3}	0.155
0.8×10^{-3}	0.315	0.15×10^{-3}	0.26
0.9×10^{-3}	0.37	0.2×10^{-3}	0.38
1×10^{-3}	0.445	0.25×10^{-3}	0.5

The slope ratio method indicated that with the used concentrations of Ni^{2+} and N_3^- a 1:4 nickel azide complex is probably obtained.

The instability constant of the 1:4 nickel azide complex was computed as before. In Fig. 5 we plot the absorbance (at 302 nm) *versus* the moles of azide per mole of nickel. From that figure values of (α), (A_m), and (A_S) were computed. The value of "*n*" was used as 4 and K' was computed to be 26.214×10^{-16}. Hence the formation constant of the 1:4 nickel azide complex is found to be 3.81×10^{14}.

Complexes of Ni(II) and N_3^- Ions in Dimethylformamide. The extent of displacement of the water molecules, in the inner coordination sphere of Ni(II), by azide ions was investigated when dimethylformamide was the solvent. The absorption spectra of mixtures of sodium azide and nickel perchlorate, using dimethylformamide as a solvent, were investigated. To begin with spectra of solutions of constant total concentration (1.0×10^{-3} M) were scanned. In Fig. 6 the spectrum of one of these mixtures is given. The nickel azide complex, obtained when dimethylformamide is the solvent, has a well-defined and discrete absorption band of its own at 305 nm. In Fig. 3, absorbance is plotted *versus* the mole fraction of azide, a well-defined and discrete maximum appears at an azide mole fraction of 0.6 which suggests that the 1:2 nickel azide complex predominates. Data needed to draw Fig. 3 are given in Table 1.

The slope ratio method was used to confirm the composition of nickel azide complex when dimethylformamide is the solvent. A series of solutions was prepared containing constant excess sodium azide 0.2×10^{-2} M and variable concentrations of nickel perchlorate 0.7×10^{-3} to 0.3×10^{-3} M. Another series of solutions was prepared containing constant excess nickel perchlorate 0.2×10^{-2} M and variable concentration of sodium azide 0.7×10^{-3} to 0.3×10^{-3} M. Absorbance was plotted *versus* the concentration of variable in Fig. 4. Data needed to plot Fig. 4 are given in Table 5. Results of Fig. 4 confirmed that a 1:2 nickel azide complex is obtained when dimethylformamide is the solvent.

Table 5. Absorbances of nickel azide solutions containing excess $[Ni^{2+}]$ and others containing excess $[N_3^-]$ in dimethylformamide

$[Ni^{2+}]=0.2\times10^{-2}$		$[N_3^-]=0.2\times10^{-2}$	
$[N_3^-]\times10^3$	Absorbance	$[Ni^{2+}]\times10^3$	Absorbance
0.70	0.690	0.70	1.20
0.60	0.590	0.60	1.03
0.50	0.493	0.50	0.84
0.40	0.415	0.40	0.680
0.30	0.305	0.30	0.490

The stability constant of the 1:2 nickel azide complex, in dimethylformamide, was obtained using the procedure adopted before. Absorption spectra of Ni(II)–N_3^- solutions with $[Ni^{2+}]$:$[N_3^-]$ ratio varying from 1:5 to 1:35 were scanned. In Fig. 4 absorbance is plotted *versus* the number of moles azide per mole nickel. Data need to plot Fig. 5 is given in Table 3 proceeding as before and using "*n*" equal to "2" the dissociation constant K' of the 1:2 nickel azide complex, in dimethylformamide, is found to be 0.21×10^{-6} or the formation constant is of the order of 5×10^6.

In Fig. 6, we present the spectra of Ni(II)–N_3^- solutions of the same concentration but in different solvents. The figure shows that λ_{max} for the obtained nickel azide complex is dependent on the solvent used. This indicates that the structure of the nickel azide complex is dependent on the solvent used. In absolute ethanol the spectrum is not well defined which indicates that more than one complex are obtained at the same time. In Table 6 we present the stability constants of the nickel azide complexes possibly obtained in different solvents.

TABLE 6. STABILITY CONSTANTS (K) OF THE NICKEL AZIDE COMPLEXES IN DIFFERENT SOLVENTS

Solvent	Complex $[Ni^{2+}]:[N_3^-]$	K
Absolute methanol	1:2	4.8×10^6
	1:3	1.99×10^{16}
Absolute ethanol	1:4	3.81×10^{14}
Dimethylformamide	1:2	5×10^6

Conclusion: When $Ni(ClO_4)_2 \cdot 6H_2O$ is dissolved in water, the nickel ion exists in the simple octahedral geometry with the structure $[Ni(H_2O)_6]^{2+}$. When the solute is dissolved in organic solvents as absolute methanol, ethanol, or dimethylformamide, the octahedral geometry of the Ni(II) complex ion persists though the six ligands may not be entirely water molecules. When the hydrated salt is dissolved in some nonaqueous solvent, depending on the coordination power of the solvent the water molecules are fully or partially substituted by the solvent molecules. This is indicated from Fig. 1, where λ_{max}, intensity of the band and even splitting of some bands is solvent dependent. On adding azide ion to the solution, it has been found that the extent of H_2O (or other solvent molecules) displacement by N_3^- is dependent on the solvent used. When water is the solvent only one H_2O molecule is displaced. With organic solvents, two, three and four molecules were displaced by two, three and four azide ions. The specific complex has it own spectrum.