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Complexes of Nickel(II) with Ethylenediamine and Perchlorate or Tetraphenylborate

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Complexes of nickel(II) and ethylenediamine with the two weakly co-ordinating anions perchlorate and tetraphenylborate have been prepared and their physical properties are reported. The results indicate that in the solid state the diaquo-ion $[Ni\ en_2(OH_2)_2]^{2+}$ may have the *cis* or the *trans* configuration depending on the anion. Two forms of the anhydrous compound $Ni\ en_2(ClO_4)_2$, have been obtained and the infrared evidence suggests that the orange form contains ionic perchlorate, while the blue form contains bidentate perchlorate.

THIS Paper reports the results of a study of ethylenediamine complexes of nickel(II) with the two anions tetraphenylborate and perchlorate.

EXPERIMENTAL

Tetraphenylborates.—Diaquobis(ethylenediamine)nickel(II) *tetraphenylborate*. The purple diaquo-complex was obtained from hot (80—90°) aqueous solution by the addition of sodium tetraphenylborate to a solution of bis(ethylenediamine)nickel(II) chloride.[1] The *compound*, recrystallised from aqueous ethanol and air-dried, had m. p. 138° (decomp.) (Found: C, 73·15; H, 7·6; N, 6·5. $C_{52}H_{60}B_2N_4NiO_2$ requires C, 73·2; H, 7·1; N, 6·6%).

[1] E. G. Rochow, *Inorg. Synth.*, 1960, **6**, 4, 198.

Bis(ethylenediamine)nickel(II) *tetraphenylborate.* The yellow anhydrous *complex* was prepared by two methods: (*a*) From damp methanol. Bis(ethylenediamine)nickel(II) chloride was dissolved in methanol containing a few drops of water. On the addition of sodium tetraphenylborate the purple methanolo-complex was obtained, even at 0°. This compound, unlike the diaquo-adduct, loses solvent easily at 60° to give yellow $[\text{Ni en}_2](BPh_4)_2$. (*b*) From aqueous solution at 0°. At room temperature, addition of sodium tetraphenylborate to aqueous Ni en_2Cl_2 [1] resulted in precipitation of the purple diaquo-complex from which it was impossible to remove the water by heat or vacuum. However, when the solutions were cooled to 0° before mixing, the yellow anhydrous material was obtained. The yellow solid was filtered off, washed with ice–water, and dried in a cooled vacuum desiccator (m. p. 211°, decomp.) (Found: C, 76·1; H, 7·0; N, 7·0. $C_{52}H_{56}B_2N_4Ni$ requires C, 76·1; H, 6·9; N, 6·8%).

The anhydrous complex rapidly takes up two molecules of water from the atmosphere to give purple $[\text{Ni en}_2(OH_2)_2](BPh_4)_2$ from which it is impossible to remove the water by heating.

Perchlorates.— *Diaquobis(ethylenediamine)nickel*(II) *perchlorate.* Tris(ethylenediamine)nickel(II) perchlorate and hexa-aquonickel(II) perchlorate were mixed in 2 : 1 mole proportions in aqueous solution, giving an aqueous solution of $[\text{Ni en}_2(OH_2)_2(ClO_4)_2$. The mixture was set aside to crystallise, whence the violet product was obtained. Recrystallisation was from hot water (Found: C, 11·8; H, 4·9; N, 13·55. Calc. for $C_4H_{20}Cl_2N_4NiO_{10}$: C, 11·6; H, 4·9; N, 13·5%). This method was found to be preferable to that of Glazer and Pfeiffer.[2]

Orange bis(ethylenediamine)nickel(II) *perchlorate.* The orange anhydrous complex was prepared as follows: Crystals of the diaquoperchlorate were ground to a fine powder and dried in a vacuum oven at 100°. The powder gradually lost water and the anhydrous orange $[\text{Ni en}_2](ClO_4)_2$ was obtained (loss in weight: Found 8·6. Calc. for loss of $2H_2O$: 8·7%). When, however, large crystals of diaquobis(ethylenediamine)nickel(II) perchlorate were heated to 100° in the vacuum oven, the water was expelled to give a brown product, which when allowed to cool below 50° in a dry atmosphere, crumbled rapidly to give the orange $[\text{Ni en}_2](ClO_4)_2$. The colour change, which was not reversible, was accelerated by grinding the brown substance. Cooling the brown product in a damp atmosphere gave a mixture of the purple diaquo and the orange anhydrous forms, which gradually changed completely to the former. The ground diaquo-perchlorate crystals undergo reversibly the purple-orange change as the compound is made to take up and lose water, without the formation of the brown form.

Blue bis(ethylenediamine)nickel(II) *perchlorate.* The blue anhydrous complex was prepared as follows: Orange $[\text{Ni en}_2](ClO_4)_2$ was dissolved in acetone containing a few drops of methanol. The blue solution was cooled in a solid carbon dioxide–methanol slush bath and was seeded with a small amount of crystalline bis(ethylenediamine)-nickel(II) chloride. Blue crystals were obtained which were used to seed another mixture. The blue powder which resulted was filtered off and dried in a vacuum desiccator (Found: C, 12·65; H, 4·3; N, 14·75. Calc. for $C_4H_{16}Cl_2N_4NiO_8$: C, 12·7; H, 4·3; N, 14·8%). Subsequently the preparation could not be repeated satisfactorily and it was not possible to prepare enough of this compound for magnetic measurements.

Tris(ethylenediamine)nickel(II) *perchlorate.* The purple tris-complex was prepared as the dihydrate from $[\text{Ni en}_3]Cl_2$ and $NaClO_4$ in aqueous solution (Found: C, 16·9; H, 6·3. Calc. for $C_6H_{28}Cl_2N_6NiO_{10}$: C, 16·9; H, 6·15%).

Solvent Adducts.—These were obtained by the addition of orange anhydrous $[\text{Ni en}_2](ClO_4)_2$ to dry solvents. The mixtures were left until purple solids had formed. These were filtered off and stored in stoppered bottles. All manipulations were carried out in a dry-box.

Infrared Spectra.—These were recorded on a Grubb–Parsons G.S. 2A double-beam spectrophotometer. Spectra were taken of dispersion in Nujol (B.P. Grade) and hexachlorobutadiene (spectroscopic grade), between potassium bromide plates. A polystyrene strip was used for calibration.

Visible Absorption Spectra.—Solid-state spectra were measured on a Unicam SP 500 spectrophotometer fitted with a standard reflectance unit, or were recorded as mulls on filter paper [3] using a Unicam SP 700 recording spectrophotometer. The latter method was found to give better resolution.

Solution spectra were measured on a Unicam SP 700 recording spectrophotometer in stoppered 1 cm. silica cells. The cell compartment was thermostatted at 25°. Solvents were AnalaR or spectroscopic grade except dimethylformamide which was purified by the method described by Bolton *et al.*[4]

Electrolytic Conductances.—These measurements were made at 25° with a Phillips A.C. bridge in a standard cell fitted with bright platinum electrodes. The cell was calibrated with aqueous potassium chloride.

Magnetic Susceptibility Measurements.—These were obtained by the Gouy method. Calibrants were $HgCo(SCN)_4$ [5] and $[\text{Ni en}_3]S_2O_3$.[6] Diamagnetic corrections were calculated from Pascal's constants.[7] The diamagnetic correction for the tetraphenylborate ion was obtained from measurements on sodium tetraphenylborone as $-10^6 \chi_M = 173$ c.g.s. units. The correction used for the perchlorate ion was $-10^6 \chi_M = 32{\cdot}5$ c.g.s. units.[8]

RESULTS AND DISCUSSION

Infrared Spectra.—Perchlorates. The bands assigned to the perchlorate group in the complexes studied are shown in Table 1 and part of the spectra in Figure 1.

The free perchlorate ion has symmetry T_d. The vibrations ν_3, the antisymmetric stretch (*ca.* 1100 cm.$^{-1}$) and ν_4, the antisymmetric bend (*ca.* 625 cm.$^{-1}$) are infrared-active. The non-degenerate symmetrical stretch ν_1, which is Raman-active, is usually observed in the infrared spectrum as a weak band at about 930 cm.$^{-1}$.

There is a recent accumulation of evidence supporting

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[2] H. Glazer and P. Pfeiffer, *J. prakt. Chem.*, 1939, **153**, 300.

[3] R. H. Lee, E. Griswold, and J. K. Kleinberg, *Inorg. Chem.*, 1964, **3**, 1279.

[4] R. Bolton, J. Miller, and A. J. Parker, *Chem. and Ind.*, 1962, 426.

[5] B. N. Figgis and R. S. Nyholm, *J. Chem. Soc.*, 1958, 4190.

[6] N. F. Curtis, *J. Chem. Soc.*, 1961, 3147.

[7] ed. J. Lewis and R. Wilkins, "Modern Co-ordination Chemistry," Interscience Publishers, Inc., New York, 1960, p. 403.

[8] C. Stephen and V. C. G. Trew, unpublished results.

co-ordination of the perchlorate ion,[9] most of which is based on the change in symmetry of the perchlorate group on co-ordination, deduced from infrared spectra. Thus the two infrared-active bands, ν_3 and ν_4 in the free ion, are split into two and three bands in the symmetries C_{3v} and C_{2v}, respectively. The symmetrical stretching vibration ν_1 becomes infrared-active in both symmetries.[10]

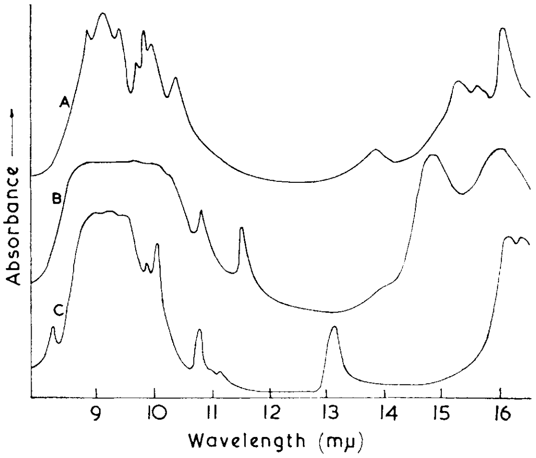

FIGURE 1 Infrared spectra: A, blue Ni $en_2(ClO_4)_2$; B, [Ni $en_2(OH_2)$](ClO$_4$)$_2$; and C, yellow [Ni en_2](ClO$_4$)$_2$

TABLE 1

Bands (cm.$^{-1}$) due to perchlorate group in nickel(II) diamine complexes

[Ni en_3](ClO$_4$)$_2$,2H$_2$O ...	*ca.* 1130—1050vsb; 926m; 621vs
[Ni en_2](ClO$_4$)$_2$ orange	*ca.* 1150—1050vsb; 926m; 621vs; 612vs
[Ni en_2(OH$_2$)$_2$](ClO$_4$)$_2$...	*ca.* 1130—1050vsb; 926m; 621vs
[Ni en_2(MeOH)$_2$](ClO$_4$)$_2$	*ca.* 1125—1080sb; 930wsh; N
[Ni en_2(EtOH$_2$](ClO$_4$)$_2$	*ca.* 1140—1020sb; 933w; N
[Ni en_2(DMF)$_2$](ClO$_4$)$_2$	*ca.* 1125—1075sb; 936m; N
[Ni en_2(ClO$_4$)$_2$] blue ...	1130s, 1093s, 1058s; 962m; 638, 621, 493m

s = Strong, b = broad, v = very, m = medium, sh = shoulder, N = not measured.

In the orange perchlorate, [Ni en_2](ClO$_4$)$_2$, ν_3 is a strong broad absorption which stretches from *ca.* 1150—1050 cm.$^{-1}$, the symmetric stretch, ν_1, is at 926 cm.$^{-1}$. There are three bands in the ν_4 region: 621, 612, and 581 cm.$^{-1}$ (Figure 1). The band at 581 cm.$^{-1}$ disappears on deuteriation and is due to the NH$_2$ group. Thus ν_4 appears to be split.

Deuteriation of the diaquo-perchlorate, [Ni en_2(OH$_2$)$_2$](ClO$_4$)$_2$, showed that of the bands between 600 and 700 cm.$^{-1}$, only that at 621 cm.$^{-1}$ is due to perchlorate. Again ν_3 is a broad strong absorption and ν_1 is at 921 cm.$^{-1}$. This compound and the other solvated complexes contain ionic perchlorate.

By comparison with the spectrum of [Ni$_2$en$_4$Cl$_2$]Cl$_2$, the bands at 1031, 1015, and 1000 cm.$^{-1}$ in the blue anhydrous perchlorate are due to amine vibrations, while three strong bands at 1130, 1093, and 1058 cm.$^{-1}$ are due to the perchlorate group. The band at 962 cm.$^{-1}$ can be assigned to the symmetric stretch of perchlorate. In the 500—700 cm.$^{-1}$ region there are bands at 654, 638m, 621, and 493 cm.$^{-1}$. By comparison with [Ni en_3]Cl$_2$ and [Ni$_2$en$_4$Cl$_2$]Cl$_2$, where the bands due to the NH$_2$ rocking modes are at 661 and 678 cm.$^{-1}$, respectively, the band at 654 cm.$^{-1}$ is assigned to the NH$_2$ group, leaving the remaining three as perchlorate bands. The spectrum is very very similar to that of the complex Ni(*NNN'*-trimeen)$_2$(ClO$_4$)$_2$ reported by Pavkovic and Meek [9] and assigned by them to bidentate perchlorate (C_{2v}). It appears from the infrared evidence that the blue anhydrous compound contains bidentate co-ordinated perchlorate.

Magnetic Measurements.—The magnetic moments of some of the paramagnetic complexes are shown in Table 2.

TABLE 2

Magnetic moments of some nickel(II) diamine complexes

Compound	Temp. (°K)	μ_{eff} (B.M.)
[Ni en_2(OH$_2$)$_2$](BPh$_4$)$_2$	293	3·37
[Ni en_2(OH$_2$)$_2$](ClO$_4$)$_2$	297	3·24
[Ni en_3](ClO$_4$)$_2$,2H$_2$O	293	3·21
[Ni en_2](BPh$_4$)$_2$	290	Diamagnetic
[Ni en_2](ClO$_4$)$_2$ orange	290	Diamagnetic

TABLE 3

Conductance (ohm^{-1} mole^{-1} cm.^{2}) in dimethylformamide solution at 25°

Compound	0·01M	0·001M
[Ni en_2](BPh$_4$)$_2$	85	110
[Ni en_2(OH$_2$)$_2$](BPh$_4$)$_2$ [a]	87	118
[Ni en_3](BPh$_4$)$_2$	80	119
[Ni pn_2](BPh$_4$)$_2$	70	113
[Ni pn_2(OH$_2$)$_2$](BPh$_4$)$_2$ [b]	78	114
[Ni en_2 (OH$_2$)$_2$](ClO$_4$)$_2$ [c]	116	198
NaBPh$_4$	23	60
cis-[Co en_2NO$_2$Cl]SCN	—	84
[Ni en_3](SCN)$_2$	—	150

[a] Methanol soln. (10^{-3}M), 87 ohm^{-1}. [b] Methanol soln. (10^{-3}M), 79 ohm^{-1}. [c] Water soln. (10^{-3}M), 270 ohm^{-1}.

Conductance Measurements.—The conductances of some of the complexes in *NN'*-dimethylformamide solution are reported in Table 3. The conductances of sodium tetraphenylborate, and of known 1 : 1 and 2 : 1 electrolytes, are also included in Table 3. The results for the last two compounds agree well with those of Quagliano *et al.*[11]

The conductances of all the tetraphenylborate salts are low. This seems likely to be due to the low mobility of the large tetraphenylborate ion in dimethylformamide solution. Similar results have been obtained for tetraphenylborate salts in methanol.[12]

Visible Absorption Spectra.—The visible absorption spectra of the complexes are shown in Tables 4—6.

[9] (*a*) C. M. Harris and E. D. McKenzie, *J. Inorg. Nuclear Chem.*, 1962, **19**, 372; (*b*) B. J. Hathaway, D. G. Holah, and M. Hudson, *J. Chem. Soc.*, 1963, 4586; (*c*) L. E. More, R. B. Gayhard, and W. E. Bull, *J. Inorg. Nuclear Chem.*, 1964, **26**, 289; (*d*) W. R. McWhinnie, *J. Inorg. Nuclear Chem.* 1964, **26**, 21; (*e*) E. A. Wickenden and R. A. Krause, *Inorg. Chem.*, 1965, **4**, 404; (*f*) S. F. Pavkovic and D. W. Meek, *Inorg. Chem.*, 1965, **4**, 1091.

[10] B. J. Hathaway and A. E. Underhill, *J. Chem. Soc.*, 1961, 3091.

[11] J. V. Quagliano, J. Fujita, G. Franz, D. J. Phillips, J. A. Walmsley, and S. Y. Tyree, *J. Amer. Chem. Soc.*, 1961, **83**, 3770.

[12] M. A. Coplan and R. M. Fuoss, *J. Phys. Chem.*, 1964, **68**, 1177.

TABLE 4

Visible absorption spectra of nickel(II) diamine tetraphenylborates

Cation	State	Absorption maximum in cm.$^{-1}$ × 10^{-3} (ε molar for solution)				
		I	IV	V	II	III
Ni $en_2(OH_2)^{2+}$	R	11·0	—	—	18·0	—
	DMF (0·025M)	11·0 (8·7)	—	—	17·5 (8·5)	28·3 (15·4) [a]
Ni en_2^{2+}	R	—	—	22·4, 11·4	—	—
	CH_2Cl_2 [b]		—	22·6	—	—
	DMF (0·025M)	10·8 (8·5)	—	—	17·7 (8·4)	28·3 (19·9) [a]
Ni en_3^{2+}	M	11·3	12·5	—	18·8	29·0

[a] Intensity varies with time. [b] Slightly soluble, saturated solution. R = solid state, reflectance. M = solid state, Nujol mull.

The spectra of the tetraphenylborate salts have been measured in the solid state and in solution in dichloromethane and in dimethylformamide. In the solid state the yellow complex shows a band in the region of 22,500 cm.$^{-1}$ and a weak band near 11,400 cm.$^{-1}$ (Band V in Table 4). The band at 22,500 cm.$^{-1}$ is also shown by solutions in dichloromethane. This band may be assigned[13] to the lowest-energy transition $^1A_{1g} \longrightarrow {}^1A_{2g}$. In solution in the co-ordinating solvent dimethylformamide, three bands characteristic of octahedral paramagnetic nickel(II) were observed. These correspond to the transitions[14] $^3A_{2g} \longrightarrow {}^3T_{2g}$, Band I; $^3A_{2g} \longrightarrow {}^3T_{1g}(F)$, Band II; and $^3A_{2g} \longrightarrow {}^3T_{1g}(P)$, Band III.

TABLE 5

Solid-state visible absorption spectra of some nickel(II) ethylenediamine perchlorates (band maximum in cm.$^{-1}$ × 10^{-3})

Compound	I	V	IV	II	III
$[Ni\,en_3](ClO_4)_2,2H_2O$ [a] ...	11·3	—	12·5	18·5	29·0
$[Ni\,en_2(OH_2)_2](ClO_4)_2$ [a]...	13·7,9·8	—	12·6	18·4	29·0
$[Ni\,en_2](ClO_4)_2$ (orange) [b]	—	22·4, 14·0	—	—	—
$Ni\,en_2(ClO_4)_2$ (blue) [b] ...	11·2	(22·4)	—	16·8	27·0
$[Ni\,en_2(MeOH)_2](ClO_4)_2$ [b]	11·25	—	—	18·2	—
$[Ni\,en_2(EtOH)_2](ClO_4)_2$ [b]	10·9	—	—	17·4	—
$[Ni\,en_2(DMF)_2](ClO_4)_2$ [b]	10·9	—	—	17·5	—

[a] Nujol mull. [b] Reflectance.

TABLE 6

Visible absorption spectra of orange $[Ni\,en_2](ClO_4)_2$ in various solvents [band maximum in cm.$^{-1}$ × 10^{-3} and ($\varepsilon_{max.}$)]

Solvent	I	II	III
H_2O [a]	10·6 (7·1)	17·4 (5·7)	28·1 (8·8)
MeOH [a]	10·55 (10·6)	17·4 (6·7)	28·0 (7·5)
EtOH [b, c]	10·5	17·35	27·5
D.M.F.[a]	10·5 (10·9)	17·3 (7·9)	27·8 (13·9)
D.M.S.O.[a]	10·4 (10·2)	17·2 (6·3)	27·7 (8·5)
Pr^iOH [b]	10·35	17·1	27·7
Pr^nOH [b]	10·3	17·0	26·5

[a] 0·1M Solution (D.M.F. = dimethylformamide; D.M.S.O. = dimethyl sulphoxide). [b] Saturated solution. [c] Spectrum also show weak band at 22·6 cm.$^{-1}$ × 10^{-3}.

The spectrum of the diaquo-perchlorate $[Ni\,en_2(OH_2)_2](ClO_4)_2$, is different from that of the tetraphenylborate (Table 5 and Figure 2). There are five bands in the former at 9800, 13,700, 12,600, 18,400, and 29,000 cm.$^{-1}$. The band at 12,600 cm.$^{-1}$ may be assigned to the triplet–singlet transition, and those at 9800 and 13,700 cm.$^{-1}$ to a splitting of Band I indicative of a *trans* tetragonal structure. For effective D_{4h} symmetry (distortion along the z axis) the bands may be assigned: I, $^3B_{1g} \longrightarrow {}^3A_{2g}$, $^3B_{1g} \longrightarrow {}^3E_g$; II, $^3B_{1g} \longrightarrow {}^3B_{2g}$; and III, $^3B_{1g} \longrightarrow {}^3A_{2g}$.

The spectrum of the solid perchlorate salt $[Ni\,en_2(OH_2)_2](ClO_4)_2$ is very similar to that of $[Ni\,en_2\,(OH_2)_2](NO_3)_2$ and that of $[Ni\,en_2(ONO_2)_2]$, recently reported by Curtis and Curtis.[15] These authors suggested that both these complexes have *trans* tetragonal structures with four nitrogens in-plane and two oxygens axially co-ordinated. Similarly the cation in the solid perchlorate salt has been assigned the *trans* tetragonal structure. In solution, however, it reverts to the more stable *cis* form.

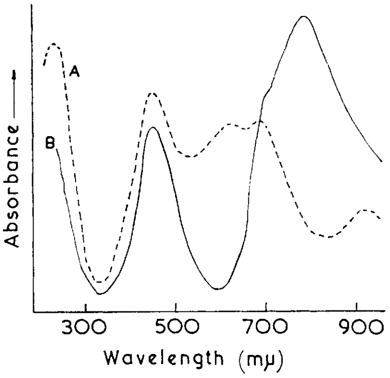

FIGURE 2 Visible absorption spectra of solids: A, $[Ni\,en_2(OH_2)_2](ClO_4)_2$; B, $[Ni\,en_2(OH_2)_2](BPh_4)_2$

The cation of the latter diaquo-compound, $[Ni\,en_2(OH)_2](BPh_4)_2$, can be assigned the *cis* configuration. The spectrum of the solid compound is very like that of the $[Ni\,en_2(OH_2)_2]^{2+}$ cation in solution. This cation has been assigned[16] the *cis* configuration on the basis that its spectrum is in turn similar to that of $[Ni\,tren(OH_2)_2]^{2+}$ which, like $[Ni\,tren(NCS)_2]$, must have a *cis* structure.[17] The spectra of these complexes show

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[13] H. B. Gray and C. J. Ballhausen, *J. Amer. Chem. Soc.*, 1963, **85**, 260; D. M. L. Goodgame and L. M. Venanzi, *J. Chem. Soc.*, 1963, 616, 5909.

[14] (*a*) C. J. Ballhausen, " Introduction to Ligand Field Theory," McGraw-Hill, New York, 1962, and references therein; (*b*) C. K. Jorgensen, " Absorption Spectra and Chemical Bonding in Complexes," Pergamon Press, Oxford, 1962, and references therein; (*c*) C. Furlani and G. Sartori, *J. Inorg. Nuclear Chem.*, 1958, **8**, 126.

[15] N. F. Curtis and Y. M. Curtis, *Inorg. Chem.*, 1965, **4**, 804.

[16] C. K. Jorgensen, *Acta Chem. Scand.*, 1956, **10**, 887.

[17] S. A. Rasmussen, *Acta Chem. Scand.*, 1959, **13**, 2009.

no splitting of Band I and are very similar to the spectrum of octahedral [Ni en_3]$^{2+}$ (see Table 7).

TABLE 7

Bands (cm.$^{-1}$ × 10^{-3}) in the visible spectra of some some nickel(II) complexes

Complex	State	I	IV	II	III
[Ni $en_2(OH_2)_2$]$(ClO_4)_2$	Solid	9·8, 13·7	12·6	18·4	29·0
[Ni $en_2(OH_2)_2$]$(ClO_4)_2$	H_2O soln.	10·6	—	17·4	28·1
[Ni $en_2(OH_2)_2$]$(BPh_4)_2$	Solid	10·0	12·8	18·0	—
[Ni $en_2(OH_2)_2$]$(NO_3)_2$ [a]	Solid	8·8, 14·6	—	18·1	27·4
[Ni $en_2(ONO_2)_2$] [a]	Solid	8·7, 14·1	—	18·4	27·8
[Ni tren$(OH_2)_2$]$^{2+}$ [b] ...	H_2O soln.	10·5	12·8	17·8	27·8
[Ni en_3]$(ClO_4)_2$	Solid	11·3	12·5	18·4	29·0

[a] Data from ref. 15. [b] Data from ref. 16.

In order to stabilise the *trans* diaquo-complex in the solid state some form of interaction in the crystal between water and the oxy-anion is needed, for example, hydrogen bonding between the co-ordinated water and the anion. The tetraphenylborate group cannot participate in such bonding, but in the solid [Ni $en_2(OH_2)_2$]$(BPh_4)_2$ hydrogen bonding could take place between the two *cis*-co-ordinated water molecules. This explains why it is difficult to remove water from [Ni $en_2(OH_2)_2$]$(BPh_4)_2$, the intramolecular hydrogen bonding giving the complex extra stability. (We are indebted to Dr. S. J. Lippard for this suggestion.)

It has been shown by Curtis and Curtis [15] that removal of water from *trans*-[Ni $en_2(OH_2)_2$]$(NO_3)_2$ gives the tetragonal paramagnetic *trans*-[Ni $en_2(ONO_2)_2$]. However, removal of water from *trans*-[Ni $en_2(OH_2)_2$]$(ClO_4)_2$ produces the orange diamagnetic [Ni en_2]$(ClO_4)_2$. As the infrared spectrum of the latter compound indicates that the symmetry of the perchlorate group is lowered from T_d, some interaction in the axial positions between the perchlorate group and the cation exists; the axial field thus produced, however, is not strong enough to produce the triplet state. The complexes of ethylenediamine nickel with nitrate and with perchlorate may be regarded as classical Lifschitz-type [18] complexes, where the planar co-ordination of the diamines is retained and the axial field may be varied.

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[18] I. Lifschitz, J. G. Bos, and K. M. Dijkema, *Z. anorg. Chem.*, 1939, **242**, 97; I. Lifschitz and J. G. Bos, *Rec. Trav. chim.*, 1940, **59**, 407.