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An Infrared and Electronic Spectroscopic Study of a Series of Nickel(II) Amine Complexes

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Summary. Qualitative infrared and electronic spectroscopic data for a series of nickel(II) amine complexes suggest structures involving octahedral (transtetragonal) symmetry and associated with varying degrees of cation-anion interaction. N-methyl ligand substituents contribute significantly to ligand conformations, complex symmetry, and cation-anion steric interactions. From the electronic data, the parameters *Dq, B′, C, C/B′*, β_{35}, and Z^* are determined for each complex and a spectrochemical and nephelauxetic series is proposed for the associated amine ligands.

Keywords. Nickel(II) amine complexes; Electronic spectra; Infrared spectra; Cation-anion interactions.

Infrarot- und elektronenspektroskopische Untersuchungen einer Reihe von Nickel(II)-Amin-Komplexen

Zusammenfassung. Die qualitative Auswertung von Daten aus Infrarot- und Elektronenspektroskopie von Nickel(II)-Amin-Komplexen erlaubte die Zuordnung einer oktaedrischen (trans-tetragonalen) Symmetrie mit verschieden abgestuften Kation-Anion-Wechselwirkungen. Substituenten am N-Methyl-Liganden tragen signifikant zur Ligandenkonformation, Komplexsymmetrie und Kation-Anion-Wechselwirkung bei. Aus den elektronenspektroskopischen Daten wurden die Parameter *Dq, B′, C, C/B′*, β_{35} und Z^* für jeden Komplex bestimmt und als Kriterium für eine Reihung der Aminliganden herangezogen.

Introduction

Numerous infrared spectroscopic and other physiochemical studies of nickel(II) amine complexes have been reported [1 – 16], and the most relevant conclusions from these studies are: (i) free perchlorate ions have T_d symmetry, with a ν_3 antisymmetric stretching band at 1100 cm^{-1} and a ν_4 antisymmetric bending at 625 cm^{-1} and ν_1, a weak symmetrical stretching vibration [5, 17] (Raman active only) at 930 cm^{-1}; (ii) coordinated perchlorate ions exhibit split ν_3 and ν_4 vibrational modes. Unidentate perchlorate ions of C_{3v} symmetry exhibit two components for the ν_3 and ν_4 bands. These vibrational modes for bidentate perchlorate (C_{2v} symmetry) split into three components. Bidentate perchlorate typically exhibits three bands near 625 cm^{-1} and 1100 cm^{-1}, respectively, and the Raman active band at 930 cm^{-1} becomes infrared active due to reduced symmetry [18]; (iii) fingerprint bands in the infrared spectrum of a metal(II) amine complex are: NH_2 stretching vibration (3340 – 3188 cm^{-1}); NH_2 degenerate deformation (scissor: 1596 – 1581 cm^{-1}); NH_2 symmetric deformation (wag: 1 332 cm^{-1}) and NH_2 twisting vibration (ca. 1 100 cm^{-1}) [19]; (iv) free tetrafluoroborate anions of T_d symmetry have four normal modes of vibration. The two triply degenerate, infrared active modes exhibit bands at 1 100 cm^{-1} (s) and 520 cm^{-1} (s), respectively [6, 7]; (v) coordinated tetrafluoroborate anions of C_{3v} symmetry (unidentate coordination) are indicated by sharp bands near 1 110 cm^{-1} (s), 1 075 cm^{-1} (s), 1 025 cm^{-1} (s), 965 cm^{-1} (s), 530 cm^{-1} (s), 465 cm^{-1} (s), and 353 cm^{-1} (s) [6, 7]; (vi) ν (Ni – N)) is expected [20] near 360 – 400 cm^{-1} while ν (Ni – N) has been assigned by Rao [8] within the broad range of 300 – 500 cm^{-1}; (vii) Goodgame and Venanzi [21] claim that the perchlorate anion is a relatively non-coordinating anion, while Duff [22] has shown that perchlorate anions act as unidentate ligands in many nickel(II) amine complexes, and (viii) the NH_2 rocking vibration in nickel(II) amine complexes is most sensitive to the effects of coordination and hydrogen bonding [23]. Considering the collective data, and the definitive reports of Rao [8] and Adams [24], the NH_2 rocking vibration may be assigned to the spectral region of 850 – 700 cm^{-1}.

With respect to previous electronic spectral studies of nickel(II) amine complexes, it has been widely reported [25, 26] that octahedral, paramagnetic nickel(II) complexes exhibit characteristic bands for the transitions:

$^3A_{2g} \rightarrow {}^3T_{2g}$ [971 – 926 nm],

$^3A_{2g} \rightarrow {}^3T_{1g}(F)$ [588 – 572 nm],

and

$^3A_{2g} \rightarrow {}^3T_{1g}(P)$ [377 – 353 nm],

which are assigned as bands I, II, and III, respectively. A shoulder at 806 nm attributed to the $^3A_{2g} \rightarrow {}^1E_g$ (D) transition for a trans-tetragonal structure, may also be evident. For example, the trans-tetragonal structure for $[Ni(\mathit{en})_2(H_2O)_2](ClO_4)_2$ [17] is indicated by a triplet-singlet transition band at 794 nm, while bands at 1 020 nm and 730 nm are due to splitting of the $^3A_{2g} \rightarrow {}^3T_{2g}$ transition. For effective D_{4h} symmetry (distortion along the Z axis) however, the bands I – III split into the $^3B_{1g} \rightarrow {}^3A_{2g}$; $^3B_{1g} \rightarrow {}^3E_g$; $^3B_{1g} \rightarrow {}^3B_{2g}$ and $^3B_{1g} \rightarrow {}^3A_{2g}$ transitions [17, 27] since the chelate ring reduces the symmetry to a group lower than octahedral, even when the six donor atoms are identical. Further, tetragonal distortions can arise as a result of lattice requirements or Jahn-Teller effects. The absence of splitting of the $^3A_{2g} \rightarrow {}^3T_{1g}(F)$ transition band in the $[Ni(\mathit{en})_3]^{2+}$ species indicates the absence of spin-orbit coupling between the $^3T_{1g}(F)$ and ^1E_g states [28] which is indicative of a strong ligand field produced by three ethylenediamine ligands. In aqueous solution however, a weak band at 445 nm attributed to a $^1A_{1g} \rightarrow {}^1A_{2g}$ transition is also evident which is expected for absorption by square planar species [17, 27]; the presence of this band reflects the enhanced stability of the square planar species relative to the tris-species in aqueous solution.

The present paper reports a comprehensive infrared and electronic spectroscopic study of a series of Ni(II) amine complexes. The aim is to investigate the existence of cation-anion interactions, the effect of ligand C-substitution and the effect of chelate ring size on the central Ni(II) electronic environment in these complexes. Of particular interest is the bonding nature of the counterion to the complex cation, either by direct axial bonding to the central metal ion or via hydrogen bonding to the ligand amine functional groups.

Experimental

The nickel(II) amine complexes were prepared according to the following general procedure [20]:

A mixure of $\mathrm{Ni(II)}X_2$ salt ($X = \mathrm{BF_4^-}$, $\mathrm{ClO_4^-}$, $\mathrm{Cl^-}$ or $\mathrm{NO_3^-}$) and amine, in a 1 : 2 or 1 : 3 molar ratio, in anhydrous methanol (200 $\mathrm{cm^3}$) was maintained at 40°C for 1 h with continuous stirring. The resulting precipitate was collected by filtration (Buchner), washed with cold anhydrous methanol and dried over anhydrous $\mathrm{P_4O_{10}}$ in vacuo for 48 h. The complexes prepared by this general procedure were:

1	$\mathrm{Ni}\,(\mathit{phen})_3\,(\mathrm{BF_4})_2$,	**2**	$\mathrm{Ni}\,(\mathit{phen})_3\,(\mathrm{ClO_4})_2$,
3	$\mathrm{Ni}\,(\mathit{dien})_2\,(\mathrm{NO_3})_2$,	**4**	$\mathrm{Ni}\,(\mathit{en})_3\,\mathrm{Cl_2}\cdot 2\mathrm{H_2O}$,
5	$\mathrm{Ni}\,(\mathit{o\text{-}ph})_2\,(\mathrm{ClO_4})_2$,	**6**	$\mathrm{Ni}\,(1{,}4\text{-}\mathit{DAB})_3\,(\mathrm{ClO_4})_2$,
7	$\mathrm{Ni}\,(\mathit{en})_3\,(\mathrm{ClO_4})_2$,	**8**	$\mathrm{Ni}\,(1{,}3\mathit{DAP})_3\,(\mathrm{ClO_4})_2$,
9	$\mathrm{Ni}\,(\mathit{en})_3\,(\mathrm{NO_3})_2$,	**10**	$\mathrm{Ni}\,(\mathit{en})_2\,\mathrm{Cl_2}\cdot 2\mathrm{H_2O}$,
11	$\mathrm{Ni}\,(1{,}2\text{-}\mathit{DMP})_2\,(\mathrm{BF_4})_2$,	**12**	$\mathrm{Ni}\,(\mathit{pn})_2\,(\mathrm{BF_4})_2$,

The ligands are abbreviated as: 1,10-phenanthroline (*phen*); diethylenetriamine (*dien*); ethylenediamine (*en*); *o*-phenylenediamine (*o-ph*), 1,4-diaminobutane (1,4-*DAB*); 1,3-diaminopropane (1,3-*DAP*); 1,2-diamino-2-methylpropane (1,2-*DMP*); 1,2-diaminopropane (*pn*); N, N, N′-trimethylethylenediamine (*N, N, N′-Me₃en*).

Complexes **1** and **2** were obtained as fine pink powders (yield 95%), complexes **3**, **5**, **7**, **8**, and **10** as purple crystals (yield 80%), and complexes **4**, **6**, **9**, **11**, and **12** as blue crystals (yield 75%).

Preparation of Bis(ethylenediamine)nickel(II)perchlorate

The reaction procedure of Farago et al. [17] was adopted. The resulting precipitate was collected by filtration (Buchner), washed with cold anhydrous methanol and dried over anhydrous $\mathrm{P_4O_{10}}$ in a vacuum desiccator for 2 days. $\mathrm{Ni}(\mathit{en})_2(\mathrm{ClO_4})_2$ was obtained as a fine blue powder (yield 75%).

Preparation of Bis(N, N, N′-trimethylethylenediamine)nickel(II)perchlorate

The reaction procedure of Pavkovic and Meek [18] was adopted. The resulting precipitate was collected by filtration (Buchner), washed with anhydrous methanol and dried in vacuo at 110°C for 60 h. $\mathrm{Ni}(N,N,N'-Me_3en)_2(\mathrm{ClO_4})_2$ was obtained as a green powder (yield 95%).

The infrared spectra were recorded on a Perkin-Elmer 457 Grating Infrared Spectrophotometer in the range 4 000 − 250 $\mathrm{cm^{-1}}$. Solid samples were analysed using the KBr pellet technique. UV-visible spectra were recorded on a Shimadzu UV-240 Recording Spectrophotometer with a Shimadzu PR-1 graphic printer attachment, using 1 cm path length matched quartz cells and purified solvents. Spectra were recorded in the range 190 − 900 nm. The perchlorate and tetrafluoroborate complexes were analysed in acetonitrile, while the remaining complexes were analysed in water.

Results and Discussion

The main infrared bands for the twelve nickel(II) amine complexes studied are recorded in Table 1. The band assignments are in accordance with the definitive data of Powell and Sheppard [25], and are characteristic of nickel(II) amine complexes. The broad band in the range 3 380 − 3 600 $\mathrm{cm^{-1}}$ is assigned to the O − H stretching vibration associated with hydration water. The main ligand bands are characteristic of metal(II) amine complexes. Also, it is apparent that the $\delta\,(\mathrm{NH_2})$ rocking vibrational mode and $\delta\,(\mathrm{NH_2})$ twisting vibrational mode are sensitive to subtle changes in ligand and anion environments. The infrared data (Table 1) for $\mathrm{Ni}(\mathit{o\text{-}ph})_2(\mathrm{ClO_4})_2$, $\mathrm{Ni}(\mathit{phen})_3(\mathrm{ClO_4})_2$, $\mathrm{Ni}(1{,}4\text{-}\mathit{DAB})_3(\mathrm{ClO_4})_2$, $\mathrm{Ni}(\mathit{en})_3(\mathrm{ClO_4})_2$,

Table 1. Infrared data for some nickel(II) amine complexes (cm^{-1}). All complexes have skeletal bands in the range 1 305–1 000 cm^{-1}. Ni(*dien*)$_2$(NO$_3$)$_2$ and Ni(*en*)$_3$(NO$_3$)$_2$ indicate $\nu(\mathrm{N-O})$ of $\mathrm{NO_3^-}$ at 830 s (cm^{-1}). Extra bands in Ni(o−*ph*)$_2$(ClO$_4$)$_2$ are: 745 s, 738 s (cm^{-1}) [δ(CH) out of plane, Φ]

Complex	ν(OH)	ν(NH$_2$)	ν(CH$_2$)	δ(NH$_2$) scissor	δ(CH$_2$) scissor	δ(CH$_2$) wag	δ(NH$_2$) wag	δ(CH$_2$) twist
Ni(*phen*)$_3$(BF$_4$)$_2$	3 380 mb		3 040 m		1 340 s			
			2 980 m ν(CH)		δ(CH)			
Ni(*phen*)$_3$(ClO$_4$)$_2$	3 500 mb		3 060 m ν(CH)		1 340 s δ(CH)			
Ni(*dien*)$_2$(NO$_3$)$_2$	3 450 sb	3 330 sb 3 250 s 3 160 s	2 940 s 2 880 s	1 590 s		1 370 sb	1 140 s	
Ni(*en*)$_3$Cl$_2$		3 300 sb	2 950 s 2 900 s	1 650 sb 1 590 sb	1 465 s	1 375 s 1 400 s	1 335 s	1 285 s
Ni(*o-ph*)$_2$(ClO$_4$)$_2$	3 530 m	3 310 s 3 290 s 3 250 s 3 170 s	3110 s 3 035 s ν(CH)					
Ni(1,4−*DAB*)$_3$(ClO$_4$)$_2$		3 310 s 3 270 s	2 950 s 2 895 s 2 880 s 2 850 s	1 600 s 1 590 s	1 459 s	1 385 s 1 400 s	1 334 m 1 325 m	
Ni(*en*)$_3$(ClO$_4$)$_2$	3 450 s	3 310 s 3 260 s 3 220 s 3 140 s	2 920 s 2 862 s	1 590 s 1 575 s	1 450 s		1 320 s	

Table 1 (continued)

Complex	$\nu(\mathrm{C=N})$	$\nu(\mathrm{C=C})$	$\delta(\mathrm{NH_2})$ twist	$\delta(\mathrm{NH_2})$ rock	$\nu(\mathrm{Cl-O})$ or $\nu(\mathrm{B-F})$	$\delta(\mathrm{CH_2})$ rock	$\nu(\mathrm{Ni-N})$
$\mathrm{Ni}(\mathit{phen})_3(\mathrm{BF_4})_2$	1 622 s	1 600 s 1 580 s 1 515 s 1 495 s 1 430 s			1 105 sb 1 035 s 1 060 s 650 s	873 s 860 s 856 s 775 s 735 s	432 s
$\mathrm{Ni}(\mathit{phen})_3(\mathrm{ClO_4})_2$	1 620 s	1 600 s 1 580 s 1 510 s 1 490 s 1 425 s			1 085 sb 625 s	870 s 845 s 770 s 730 s	430 s
$\mathrm{Ni}(\mathit{dien})_2(\mathrm{NO_3})_2$			1 095 s 980 s 930 s	718 s		895 s 915 s 790 s	
$\mathrm{Ni}(\mathit{en})_3\mathrm{Cl_2 2\,H_2O}$			1 110 m 985 s, 975 s	730 s		885 s 872 s	
$\mathrm{Ni}(\mathit{o\text{-}ph})_2(\mathrm{ClO_4})_2$		1 600 s 1 550 s 1 490 s 1 450 s		755 s	1 070 sb 625 s	845 s	450 s 418 s
$\mathrm{Ni}(1{,}4-\mathit{DAB})_3(\mathrm{ClO_4})_2$			1 000 s 920 s	760 s	1 060 sb 620 s		462 w
$\mathrm{Ni}(\mathit{en})_3(\mathrm{ClO_4})_2$			972 s 932 s	775 m	1 100 sb 620 s	870 m 855 m	490 s

Table 1 (continued)

Complex	ν(OH)	ν(NH_2)	ν(CH_2)	δ(NH_2) scissor	δ(CH_2) scissor	δ(CH_2) wag	δ(NH_2) wag	δ(CH_2) twist
Ni(1,3 − *DAP*)$_3$(ClO_4)$_2$		3 320 s 3 235 sb 3 140 s	2 920 s 2 875 s	1 590 s	1 470 m 1 445 m	1 405 m 1 390 m	1 330 m	1 280 s 1 260 m
Ni(*en*)$_3$(NO_3)$_2$		3 300 s 3 260 s 3 160 s	2 920 s 2 880 s	1 590 s 1 580 s	1 455 s	1 400 s	1 320 s 1 350 s 1 140 m	1 275 s
Ni(*en*)$_2$$Cl_2$2$H_2O$	3 460 s	3 305 s 3 280 s 3 230 s 3 150 s	2 940 s 2 880 s	1 645 s 1 600 s 1 583 s	1 455 s	1 380 m 1 365 m	1 325 s 1 152 s	1 275 s
Ni(1,2 − *DMP*)$_2$(BF_4)$_2$	3 420 sb	3 320 m 3 142 s 3 110 s 3 040 s	2 940 m	1 580 s	1 465 w 1 455 w	1 405 m 1 392 m 1 370 m	1 332 w	1 295 m 1 288 m 1 268 m
Ni(*pn*)$_2$(BF_4)$_2$		3 320 s 3 260 s	2 950 s 2 920 s 2 860 s	1 580 s 1 540 m 1 525 m	1 440 m			
Ni(*en*)$_2$(ClO_4)$_2$		3 320 s 3 260 s 3 140 s	2 920 s 2 860 s	1 590 s 1 580 s	1 455 s	1 400 s	1 335 n 1 152 s	1 275 s
Ni(*N*, *N*, *N′* − *Me*$_3$*en*)$_2$(ClO_4)$_2$	3 622 sb	3 290 mb	2 900 mb 2 880 mb 2 700 m	1 620 sb	1 470 mb	1 390 m 1 355 m		1 295 m

Table 1 (continued)

Complex	$\delta(NH_2)$ twist	$\delta(NH_2)$ rock	$\nu(Cl-O)$	$\nu(B-F)$	$\delta(CH_2)$	$\nu(Ni-N)$
$\mathrm{Ni}(1{,}3-\mathit{DAP})_3(\mathrm{ClO_4})_2$	940 s 900 s	777 s	1 100 sb 625 s		875 s	480 s
$\mathrm{Ni}(\mathit{en})_3(\mathrm{NO_3})_2$	975 s	710 s			825 s 870 m	490 s
$\mathrm{Ni}(\mathit{en})_2\mathrm{Cl_2 2H_2O}$	1 095 m	720 m			875 w 865 w	
$\mathrm{Ni}(1{,}2-\mathit{DMP})_2(\mathrm{BF_4})_2$	965 m	750 m		1 110 s 1 075 s 1 025 s 530 s	810 m	
$\mathrm{Ni}(\mathit{pn})_2(\mathrm{BF_4})_2$	935 m	770 m		1 100 s 1 075 s 1 025 s 530 s		440 m
$\mathrm{Ni}(\mathit{en})_2(\mathrm{ClO_4})_2$	1 090 m	720 m	1 060 sb 620 s 1 110 s 1 075 s		870 m	
$\mathrm{Ni}(\mathit{N,N,N'}-\mathit{Me_3en})_2(\mathrm{ClO_4})_2$	930 m		1 100 sb 620 sb		855 m	

Ni($N, N, N' - Me_3en$)$_2$(ClO_4)$_2$, and Ni(1,3-DAP)$_3$(ClO_4)$_2$ are consistent with "free" perchlorate ions; while the infrared data for Ni($phen$)$_3$(BF_4)$_2$ support the assignment of "free" tetrafluoroborate ions. Unidentate (coordinated) tetrafluoroborate and perchlorate ions are indicated in the infrared spectra of Ni(1,2-DMP)$_2$(BF_4)$_2$ and Ni(en)$_2$(ClO_4)$_2$, respectively. The assignment of coordinated perchlorate ions in Ni(o-ph)$_2$(ClO_4)$_2$ is not confirmed, in contrast to the conclusion of Duff [22], however, extreme elongation (tetragonal distortion) of the $Ni-ClO_4$ bonds may not be evident in the infrared spectrum. The spectrum of Ni(en)$_2$Cl$_2$ suggests axially bound chloride ions. The spectra of Ni(en)$_3$Cl$_2$, Ni($dien$)$_2$(NO_3)$_2$, and Ni(en)$_2$(NO_3)$_2$ suggest "free" un-coordinated anions. The ν(NH) bands in Ni(en)$_3$Cl$_2$, Ni(1,3-DAP)$_3$(ClO_4)$_2$, and Ni($N, N, N' - Me_3en$)$_2$(ClO_4)$_2$ are indicative of hydrogen bonding, suggesting that the anionic groups are forming hydrogen-bonds to the amine hydrogen atoms.

The ν(Ni$-$N) vibrational band(s) are tentatively assigned within the range $430-490\,cm^{-1}$. The unassigned bands (Table 1) in the range 280–$380\,cm^{-1}$ may be attributed to various δ(NMN) skeletal vibrations, duly recognising that vibrational bands in this range of the far infrared region are most likely to be highly coupled to other molecular vibrations.

The electronic spectral data for the nickel(II) amine complexes studied compare favourably with other literature data for structurally similar nickel(II) amine complexes (Table 2). These data, together with their solid state coloration [28, 30, 31] suggest octahedral site-symmetry of Ni^{2+} in these nickel(II) amine complexes. A single band at ~787 nm, attributed to the $^3A_{2g} \rightarrow {}^1E_g(D)$ transition, indicates a trans tetragonal structure for these nickel(II) amine complexes.

Table 2. Electronic spectral data for some Ni(II) amine complexes

Complex	Band I (nm)	II (nm)	III (nm)
Ni($phen$)$_3$(BF_4)$_2$	851.0	525.0	342.0
Ni($phen$)$_3$(ClO_4)$_2$	850.0	524.0	341.0
Ni(o-ph)$_2$(ClO_4)$_2$	912.0	532.0	349.0
Ni(en)$_3$(ClO_4)$_2$	888.0	545.0 590.0	344.0
Ni(1,3-DAP)$_3$(ClO_4)$_2$	915.0	556.0	351.0
Ni(en)$_3$(NO_3)$_2$	886.0	545.0	344.0 302.0
Ni(en)$_2$Cl$_2$2 H$_2$O	885.0	544.0	344.0
Ni(1,2-DMP)$_2$(BF_4)$_2$	960.0	575.0	362.0
Ni(pn)$_2$(BF_4)$_2$	947.0	554.0	354.0 360.0
Ni(en)$_3$Cl$_2$2 H$_2$O	889.0	545.0 590.0	344.0
[Ni(en)$_3$]$^{2+}$ [a]	900.0	545.0	345.0
[Ni(o-ph)$_2$(ClO_4)$_2$][b]	961.0	595.0	377.0

[a] From Ref. [20]

[b] From Ref. [16]

Table 3. Electronic parameters for some Ni(II) amine complexes

Complex	*Dq*	*B′*	*C*	*C*/*B′*	β_{35}	*Z**
Ni(*phen*)$_3$(BF$_4$)$_2$	1 175.0	869.2	3 052.9	3.51	0.84	1.17
Ni(*phen*)$_3$(ClO$_4$)$_2$	1 175.6	873.7	3 054.3	3.49	0.85	1.19
Ni(*o-ph*)$_2$(ClO$_4$)$_2$	1 096.1	968.4	2 722.1	2.81	0.94	1.63
Ni(*en*)$_3$(ClO$_4$)$_2$	1 126.6	908.0	2 913.8	3.21	0.88	1.34
Ni(1,3-*DAP*)$_3$(ClO$_4$)$_2$	1 092.3	913.8	2 940.3	3.22	0.89	1.37
Ni(*en*)$_3$(NO$_3$)$_2$	1 128.8	904.8	2 953.4	3.26	0.88	1.33
Ni(*en*)$_2$Cl$_2$2 H$_2$O	1 130.3	903.3	2 944.5	3.26	0.88	1.32
Ni(1,2-*DMP*)$_2$(BF$_4$)$_2$	1 041.7	917.6	–	–	0.89	1.38
Ni(*pn*)$_2$(BF$_4$)$_2$	1 055.6	938.8	–	–	0.91	1.48
Ni(*en*)$_3$Cl$_2$2 H$_2$O	1 124.6	911.4	2 898.6	3.18	0.88	1.36
[Ni(*en*)$_3$]$^{2+}$ [a]	1 123.6	908.4	–	–	0.88	–
[Ni(*o-ph*)$_2$(ClO$_4$)$_2$][b]	1 040.0	806.7	3 051.0	3.78	0.78	–

[a] From Ref. [20]

[b] From Ref. [16]

The value of *Dq* for the [Ni(*en*)$_3$]$^{2+}$ species studied (Table 3) is in the range 1 124 – 1 128 cm^{-1}, which is consistent with the *Dq* reported for the [Ni(*en*)$_3$]$^{2+}$ species (1 123.6 cm^{-1}) by Jorgensen [26], and effectively characterizes these complexes. Splitting of the excited states is not apparent for most nickel(II) complexes, consistent with the conclusion by Karn [32] that such a feature is prevalent for tetragonal nickel(II) complexes.

Cation-anion interaction is apparent in many complexes. Ni(*phen*)$_3$(BF$_4$)$_2$ and Ni(*phen*)$_3$(ClO$_4$)$_2$ exhibit comparably excited state energies, with exception of the phen ligand $\pi \rightarrow \pi^*$ transitions; this exceptional feature is attributed to different cation-anion interactions. The phenanthroline bands at approximately 227 nm and 270 nm are comparable to the first weak bands of benzene [33], however, Jorgensen [30] has shown that the phenanthroline bands (227, 264, 289, 309, 324 nm) shift to (227, 269, 294, 312, 327 nm) under the influence of the nickel(II) ion in the Ni(*phen*)$^{2+}_3$ species. The $\pi \rightarrow \pi^*$ transition near 312 nm is not apparent in the spectra of Ni(*phen*)$_3$(BF$_4$)$_2$ and Ni(*phen*)$_3$(ClO$_4$)$_2$ (Table 2) while the remaining bands for the $\pi \rightarrow \pi^*$ transitions of Ni(*phen*)$_3$(BF$_4$)$_2$ and Ni(*phen*)$_3$(ClO$_4$)$_2$ are shifted to (226, 269, 293, 326 nm) and (226, 268, 282 nm), respectively. This feature of non-systematic shifts in $\pi \rightarrow \pi^*$ bands also suggests varying degrees of cation-anion interaction in the Ni(*phen*)$^{2+}_3$ species. The energies for all transitions for the [Ni(*en*)$_3$]$^{2+}$ species (Table 2) are comparably equivalent, suggesting negligible cation-anion interaction in these species. Splitting of the $^3T_{1g}$(F) state for Ni(*en*)$_3$(ClO$_4$)$_2$ and Ni(*en*)$_3$Cl$_2$2 H$_2$O, and splitting of the $^3T_{1g}$(P) state for Ni(*en*)$_3$(NO$_3$)$_2$ is evidence for tetragonal distortion in these complexes. The aqueous solutions of Ni(*en*)$_3$(NO$_3$)$_2$ and Ni(*en*)$_2$Cl$_2$2 H$_2$O do not exhibit a band near 440 nm ($^1A_{1g} \rightarrow {}^1A_{2g}$), which is normally attributed to square planar species. This feature, or lack of it, infers that ethylenediamine and chloride ligands are strongly bound in the axial plane, supporting the previous assignment of a strong ligand field associated with ethylenediamine ligands.

The subtle changes in symmetry for Ni(*en*)$_2$Cl$_2$, Ni(*o-ph*)$_2$(ClO$_4$)$_2$, Ni(1,2-*DMP*)$_2$(BF$_4$)$_2$, and Ni(*pn*)$_2$(BF$_4$)$_2$, which contain different chelate ring sizes, different number of ring substituents and different axial ligands are evident by the different state energies. The marked differences in energies for the $^3T_{2g}$(F), $^3T_{1g}$(F), and $^3T_{1g}$(P) states for Ni(*pn*)$_2$(BF$_4$)$_2$ and Ni(1,2-*DMP*)$_2$(BF$_4$)$_2$ and splitting of the $^3T_{1g}$(P) state for Ni(*pn*)$_2$(BF$_4$)$_2$ are indicative of different degrees of tetragonal distortion associated with these complexes, and possibly to different degrees of steric hindrance between methyl substituents and coordinated tetrafluoroborate groups.

The magnitude of the ligand fields associated with these diamine ligands studied are reflected in the proposed spectrochemical series:

$$1{,}2\text{-}DMP < pn < 1{,}3\text{-}DAP < o\text{-}ph < en < phen.$$

This sequence reflects the symmetry and effect of the ligands on the magnitude of $10\,Dq$ (splitting of the t_{2g} and e_g states) for the nickel(II) complexes (Table 3). The larger Dq for *phen* (relative to *en*) shows the ligand π-orbitals to be higher in energy than the metal t_{2g} orbitals: this factor allows these π and t_{2g} orbitals to overlap, and the t_{2g} orbitals are stabilized.

The Racah parameters, B' and C, are in the ranges of $817-970\,\text{cm}^{-1}$ and $2\,722-3\,054\,\text{cm}^{-1}$, respectively, for the nickel(II) amine complexes studied (Table 3); while the ratio C/B' ranges from 2.8 to 3.5, and the nephelauxetic ratio (β_{35}) is within the range $0.84-0.94$. The lower B' and β_{35} values for the [Ni(*phen*)$_3$]$^{2+}$ species reflect the extensive delocalization ((cloud-expansion) of the metal electrons over the molecular orbitals encompassing the metal and phenanthroline ligands. It is apparent that the [Ni(*en*)$_3$]$^{2+}$ species and the [Ni(*en*)$_2$Cl$_2$] complexes indicate a β_{35} value of 0.88, consistent with that reported by Jorgensen [26]. All nickel(II) diamine complexes (Table 3) exhibit a reduced B' and C, consistent with coordination of the nickel(II) ions. The increased β_{35} value for Ni(*o-ph*)$_2$(ClO$_4$)$_2$ of 0.94 relative to β_{35} for the same complex previously reported [22] (0.78) supports the previous suggestion of bound perchlorate groups in this complex.

The proposed nephelauxetic series for the ligands associated with the nickel(II) amine complexes of this study in accordance with decreasing β_{35} is:

$$o\text{-}ph > pn > 1{,}3\text{-}DAP \simeq 1{,}2\text{-}DMP \simeq en > phen.$$

This sequence represents extensive delocalization between metal ion and *phen* ligands, with the least degree of delocalization in the [Ni(*o-ph*)$_2$]$^{2+}$ species. Misalignment of bonding orbitals in [Ni(*o-ph*)$_2$](ClO$_4$)$_2$ is possibly due to chelate ring strain imposed by the (*o-ph*) "bite" [30] and conflicting stabilization features from the Jahn-Teller effect (tetragonal distortion) account for the decreased π-electron delocalization over the nickel(II) ion. The approximate equivalence of β_{35} for the ligands, 1,3-*DAP*, 1,2-*DMP*, and *en*, as indicated in the proposed nephelauxetic series, suggests a similar degree of Ni−N covalent bonding within the nickel(II) complexes incorporating these ligands. The proposed nephelauxetic series is largely attributed to the reduction of the effective charge on the metal by covalent bond formation and the mixing of metal and ligand orbitals. The calculated effective charges of the Ni(II) ions (Z^*) in the nickel(II) complexes of the present study

(Table 3) indicate a marked decrease in the Ni(*phen*)$_3^{2+}$ species (Z^* ca. 1.18) with the highest charge for Ni(*o-ph*)$_2$(ClO$_4$)$_2$ (Z^*: 1.63), consistent with the proposed nephelauxetic series. The decreased Z^* for Ni(II) of the phenanthroline species reflects extensive π-electron delocalization over the metal ion. The larger charge on Ni(II) for Ni(*o-ph*)$_2$(ClO$_4$)$_2$ ($Z^* = 1.63$) possibly reflects the inductive effect of the coordinated perchlorate. The mean effective charge for Ni(II) in Ni(*en*)$_3^{2+}$ species is 1.34, while the C-substituted complexes, Ni(1,2-*DMP*)$_2$(BF$_4$)$_2$ and Ni(*pn*)$_2$(BF$_4$)$_2$ exhibit a charge of 1.38 and 1.48 respectively. This feature of increased charge [relative to Ni(*en*)$_3^{2+}$] reflects the electron withdrawing nature of the bound tetrafluoroborate anion and reduced site symmetry due to the methyl substituents. The charge on Ni(II) in Ni(1,3-*DAP*)$_3$(ClO$_4$)$_2$ [1.37] reflects a decreased donor ability of the 1,3-diaminopropane ligands.

Conclusion

The infrared data indicate octahedral (trans tetragonal) symmetry for all nickel(II) amine complexes studied, while the variation of δ (NH$_2$) rocking, δ (NH$_2$) twisting, and ν (Ni – N) vibrational modes suggest varying degrees and types of cation-anion interaction, these being coordination or hydrogen bonding interactions. It is suggested that the significant variation of δ (NH$_2$) deformation modes associated with Ni(*pn*)$_2$(BF$_4$)$_2$, compared to the same vibrational modes for the structural analogue, Ni(1,2-*DMP*)$_2$(BF$_4$)$_2$, reflects the influence of methyl substituents on the ligand conformations, with possible concomitant steric interaction between methyl groups and coordinated tetrafluoroborate groups. The lower ν (Ni – N) frequency in the infrared spectra for the nickel(II) amine complexes of Ni(*phen*)$_3X_2$ (X: ClO$_4^-$, BF$_4^-$: $\sim$ 431 cm^{-1}), relative to the ν (Ni – N) for the remaining nickel(II) amine complexes (440 – 490 cm^{-1}), reflects lower Ni – N bond strengths in the former. This feature in the Ni(*phen*)$_3^{2+}$ species possibly reflects significant chelate ring strain, causing misalignment of bonding orbitals between nitrogen atoms and the nickel(II) ion, and a limited degree of π-electron delocalization into the Ni – N bonds. The electronic data indicate octahedral (trans tetragonal) symmetry for all nickel(II) amine complexes studied (in solution), while varying electronic band energies suggest varying degrees and types of cation-anion interaction, these being coordination or hydrogen bonding interactions. The differences in state energies for Ni(*pn*)$_2$(BF$_4$)$_2$, and Ni(1,2-*DMP*)$_2$(BF$_4$)$_2$ support this suggestion on the basis of their respective infrared δ (NH$_2$) deformation modes.

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