Spectroscopic investigation of mixed-ligand nickel(II) chelates containing β-ketoenols and 1,2-diamines

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Abstract

The infrared and electronic excitation spectra of a series of new nickel(II) chelates containing N-substituted 1,2-diaminoethane derivatives (enR) and the anion of a 1,3-ketoenol (β-dione) were obtained in the solid state and in solution. The composition and the overall structure of the new chelates depend on ligand concentration, on the substituents within the β-dionato moiety and the counterion present. Whenever the substituents and bulky counteranions fail to stabilise the $[Ni(\beta)enR]^+$ entity, a second diamine molecule confers coordination saturation and the octahedral $[Ni(enR)_2\beta]^+$ species are obtained. The infrared spectra disclose that the 1,2-diamines adopt the *gauche* conformation. The ligand-field excitation spectra and solvatochromic shifts suggest that in the $[Ni(\beta)enR]^+$ entity, the NiN_2O_2 chromophore is square-planar and the diamine nitrogens are coplanar with the resonance stabilised β-dionato ring. Nickel(II) in the $[Ni(\beta)enR]^+$ entity interacts covalently with basic solvents, halides, pseudohalides, and other polyatomic anions. While unidentate ligands preserve the planarity of the NiN_2O_2 chromophore, the spatial requirements and restrictions of bidentate ligands induce rearrangements and octahedral coordination.

Key words: Infrared spectroscopy; Electronic excitation spectroscopy; Nickel complexes; Mixed-ligand complexes; Chelate complexes

Introduction

Nickel(II) has a tendency to achieve coordination numbers exceeding four and this is elegantly demonstrated in the resonance-stabilised bis(β-dionato)nickel(II) compounds and the homoleptic chelates resulting from the coordination of 1,2-diaminoethane and its alkyl derivatives, enR [1–3]. Electronic factors (electronegativity of the ligands, L, nature of the Ni–L bond, ligand field strength, CFSE), steric interactions and meze size effects affect the stereochemistry of the resulting compounds [3]. Therefore, metal–ligand interactions are sensitive to ligand structure and seemingly minor changes may have a profound effect. Groups in the proximity of the coordination site or far away from it induce electronic perturbations and instigate steric interactions. These effects may operate in unison or may oppose each other, thus affecting the coordination geometry of the resulting compounds. The study of the spectral features of a series of similarly structured nickel(II) chelates provides information on metal–ligand interactions, on the influence of electronic effects instigated by substituent groups, and on steric hindrance. Spatial requirements have been invoked [2] to explain the inability of formation of $[Ni(enR)_3]^{2+}$ and even the $[Ni(enR)_2]^{2+}$ species, while electronic effects acting in unison with steric interactions are definitely operative [4] in bis(β-dionato)nickel(II) chelates, $Ni\beta_2$. Steric hindrance can be reduced and may be eliminated altogether by forming mixed-ligand chelates such as those resulting from the concurrent reaction of nickel(II) cations with nitrogenous bases and β-diones [5–11]. The influence of the counteranion becomes quite important whenever the chelating ligands do not bring about coordination saturation, as happens with the $[Ni(enR)\beta]^+$ entity.

In coordinatively unsaturated cationic chelates, anions may interact electrostatically or covalently coordinating in a variety of modes, including linkage isomerism and bridge formation [12]. Since their π-acceptor properties vary and the splitting of the d orbitals is considered sensitive to metal–ligand π bonding, changing the coordinated anion would alter the strength of the ligand field. The anions also influence the bonding mode and

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the conformation of flexible ligands such as the 1,2-diaminoethane derivatives, enR. For instance, upon change of the anion Z^- counterbalancing the charge of the $[Ni(enR)_2]^{2+}$ species in certain nickel(II) chelates, the ligated enR molecules that do not retain their *gauche* conformation act as bridging ligands [13]. Change in the mode of interaction of the anion would have important repercussions on the stereochemistry and the properties of the resulting compounds. A spectroscopic investigation regarding the $[Ni(enR)\beta]^+$ entity would provide more information about the influence of anions on the conformation of the coordinated diamine and the structure of the resulting chelates.

In this work the vibrational and the crystal field spectra of a series of new mixed-ligand cationic nickel(II) chelates of β-ketoenols, 1,2-diamines (mainly N,N-dimethyl-N'-ethyl-1,2-diaminoethane, dmeen) and a variety of anions were obtained and analysed in conjunction with other physicochemical measurements, in order to assess: (i) the parameters affecting bond formation and stoichiometry in the nickel(II) chelates, (ii) the nature of interactions of anions counterbalancing the charge of the chelated nickel(II), (iii) the occurrence of linkage isomers, (iv) the conformation adopted by the 1,2-diamine, (v) the influence of the substituents within the β-dionato moiety on the energy levels, (vi) the consequences of steric interactions and electronic effects on the electron population in the ground state and on group vibrations, (vii) the temperature and solvent effects on the geometry and the energy levels of the chelates. Further it was aimed to seek interrelations between experimentally obtained quantities and parameters describing the interactions induced by the substituents, the counterion and the solvents. The compounds investigated are listed in Table 1.

Experimental

Reagents

The nickel(II) salts were procured from Fluka. The N-substituted ethylenediamines (enR), N,N-dimethyl-N'-ethyl-1,2-diaminoethane (dmeen), N,N-dimethyl-1,2-diaminoethane (me$_2$en) and the symmetric N,N'-dimethyl-1,2-diaminoethane (meenme), as well as the β-diones ($R^1COCH_2COR^2$, βH), 2,4-pentanedione (acetylacetone, acacH), 1-phenyl-1,3-butanedione (benzoylacetone, bzacH), 1,3-diphenyl-1,3-propanedione (dibenzoylmethane, dbmH), 2,2,6,6-tetramethyl-3,5-heptanedione (dipivaloylmethane, dpmH), 1,1,1-trifluoro-2,4-pentanedione (tfacH), 1-phenyl-4,4,4-trifluoro-1,3-butanedione (bztfH), 1-(2-thienyl)-4,4,4-trifluoro-1,3-butanedione (thtfH), 1,1,1,5,5,5-hexafluoro-2,4-pentanedione (hfacH), were purchased from Aldrich.

Preparation of the chelates

The nickel(II) chelates $[Ni(enR)_2]Z_2$ ($Z = Cl^-, NO_3^-, ClO_4^-$) were obtained by dehydrating the nickel(II) 'salts' with 2,2-dimethoxypropane and then dissolving them in dry ethanol. Subsequently a slight excess of the stoichiometric amount of the 1,2-diamine was added dropwise to the ethanolic solution of the appropriate nickel(II) 'salt' while stirring continuously. The bis(β-dionato)nickel(II) chelates were prepared as dihydrates, $[Ni\beta_2(H_2O)_2]$, by standard methods [14]. Prior to their use the compounds were recrystallised and their purity was checked by elemental analysis and analysis of their IR spectra. The ternary chelates $[Ni(enR)\beta]^+$, were prepared by exploiting the lability of nickel(II) compounds. Thus an amount of a nickel(II) β-ketoenolate was mixed with an equimolar quantity of nickel(II) 'salt', $NiZ_2 \cdot xH_2O$, and absolute ethanol was added, sufficient to effect dissolution. The resulting ($Ni\beta Z$) species were reacted with the required amount of 1,2-diamine, enR. While stoichiometric addition of dmeen in the presence of bulky anions usually afforded the ionic $[Ni(enR)\beta]^+$ compounds, use of the other 1,2-diaminoethanes yielded chelates having two diamine molecules bonded to nickel(II), i.e. $[Ni(enR)_2\beta]^+$. In cases in which the $NiZ_2 \cdot xH_2O$ species were unavailable or are unreactive, the preparation of the corresponding nickel(II) chelates entailed exchange reactions. For instance, $Ni(NO_2) \cdot xH_2O$ was prepared metathetically from $Ni(NO_3) \cdot 6H_2O$ and sodium nitrite. Alternatively the anion Z^- was inserted by reacting $[Ni(dmeen)bzac]ClO_4$ with excess of NaZ or NH$_4$Z.

Physical measurements and determinations

Carbon, hydrogen and nitrogen were determined by microanalysis using a Perkin-Elmer 240B elemental analyser. Melting points were determined on a Reichert heated plate apparatus and are uncorrected (Table 1). Molar conductivities were measured on a WTW conductivity bridge employing a calibrated dip type cell. The measurements were performed in a series of solutions of analytical grade nitrobenzene and nitromethane, and concentrations ranging from 10^{-4} to 10^{-2} M were employed in order to examine the likelihood of concentration dependence. Molecular mass determinations were accomplished on a Knauer apparatus. Magnetic susceptibility measurements in powdered samples were performed at 25 °C employing the Faraday method on a home-built balance calibrated against $Hg[Co(SCN)_4]$. Diamagnetic corrections were estimated from Pascal's constants. The effective magnetic moments, μ_{eff}, were calculated using the expression

$$\mu_{eff}(BM) = 48.98(\chi_M^{corr})^{1/2} \ (T = 298 \ K)$$

Electronic spectra in solution were measured on a Shimadzu 160A spectrophotometer using 10 mm teflon

TABLE 1. Elemental analyses and physicochemical data of some nickel(II) compounds, Ni(β)dmeen(Z), and allied chelates

No.	Compound	Colour	Yield (%)	M.p. (°C)	C (%)	H (%)	N (%)	Λ_M (S cm^2 mol^{-1})	μ_{eff} (BM)
1	[Ni(me$_2$en)$_2$bzac]B(Ph)$_4$	light green	98	189–192	70.0 (69.56)	6.24 (6.31)	8.32 (8.55)	57	2.96
2	[Ni(meenme)$_2$bzac]B(Ph)$_4$	light green	97	88–91	69.2 (69.56)	6.38 (6.31)	8.71 (8.55)	64	3.05
3	[Ni(meenme)bzac(NO$_3$)]	light green	56	90–92	45.1 (45.44)	5.66 (5.72)	11.2 (11.36)	20	2.97
4	[Ni(meenme)$_2$bzac](NO$_3$)	grey green	73	155–158	47.5 (47.18)	7.41 (7.26)	11.3 (11.29)	62	3.17
5	[Ni(dmeen)bzac]PF$_6$	green	53	174–172	40.1 (39.95)	5.32 (5.24)	5.79 (5.82)	65	3.34
6	[Ni(dmeen)bzac]BF$_4$	green	41	63–66	46.0 (45.44)	5.96 (5.96)	2.53 (2.56)	42	2.32
7	[Ni(dmeen)bzac]ClO$_4$	red	92	73–76	73.6 (73.31)	7.01 (6.92)	4.33 (4.27)	88	1.23
8	[Ni(dmeen)bzac(O$_2$NO)]	green	75	80–83	48.9 (48.27)	6.55 (6.33)	10.2 (10.55)	20	3.09
9	[Ni(dmeen)bzac(O$_2$N)]	green	95	70–72	49.9 (50.29)	6.44 (6.60)	10.8 (11.00)	22	3.16
10	[Ni(dmeen)bzac(H$_2$O)N$_3$]	light green	93	203–205	49.0 (48.51)	6.72 (6.87)	18.1 (17.68)	13	3.36
11	[Ni(dmeen)bzac(H$_2$O)NCS]	grey green	80	97–100	49.2 (49.54)	6.51 (6.60)	9.95 (10.19)	18	3.32
12	[Ni(dmeen)bzac(H$_2$O)NCO]	bright green	88	184–187	51.8 (51.54)	6.73 (6.87)	11.1 (10.61)	14	3.14
13	[Ni(dmeen)bzac(H$_2$O)Cl]	turquoise	80	206–208	48.8 (49.33)	6.67 (6.99)	7.34 (7.19)	18	3.34
14	[Ni(dmeen)bzac(H$_2$O)Br]	green	86	75–78	43.7 (44.28)	6.01 (6.27)	6.62 (6.45)	27	3.01
15	[Ni(dmeen)bzac(H$_2$O)I]	olive green	90	64–67	40.4 (39.95)	5.33 (5.66)	5.94 (5.82)	51	2.98
16	[Ni(dmeen)dpm]B(Ph)$_4$	red	84	68–70	73.2 (72.69)	8.24 (8.18)	3.98 (4.13)	62	1.15
17	[Ni(dmeen)acac]B(Ph)$_4$	reddish	93	50–54	71.1 (70.86)	7.54 (7.31)	4.75 (4.72)	68	1.74
18	[Ni(dmeen)bzac]B(Ph)$_4$	red	92	80–84	71.4 (73.31)	7.34 (6.92)	4.37 (4.27)	59	1.20
19	[Ni(dmeen)dbm]B(Ph)$_4$	red	93	101–104	78.8 (79.34)	6.48 (6.60)	3.77 (3.90)	64	1.38
20	[Ni(dmeen)tfac(H$_2$O)$_2$]B(Ph)$_4$	green	92	67–71	65.2 (64.95)	6.15 (6.23)	4.42 (4.33)	53	3.02
21	[N(dmeen)bztf(H$_2$O)$_2$]B(Ph)$_4$	green	71	79–82	67.5 (67.73)	6.03 (5.97)	4.01 (3.95)	51	3.24
22	[Ni(dmeen)thtf(H$_2$O)$_2$]B(Ph)$_4$	green	89	84–88	64.1 (63.81)	5.57 (5.64)	3.78 (3.92)	50	2.61
23	[Ni(bzac)$_2$dmeen]	green	89	47–50	63.1 (62.80)	7.01 (6.89)	5.74 (5.63)	–	3.22
24	Ni(dmeen)$_2$Cl$_2$	bluish green	42	222–225	39.5 (39.81)	8.88 (8.91)	15.4 (15.48)	36	3.19

stoppered quartz cells. The solid state electronic spectra were obtained from nujol mulls. IR spectra were obtained by the KBr disc technique and were recorded on a Perkin-Elmer 1430 spectrophotometer with a range 4000–200 cm^{-1} calibrated against polystyrene. FT-IR spectra were measured on a Bomem, Michelson series, spectrophotometer.
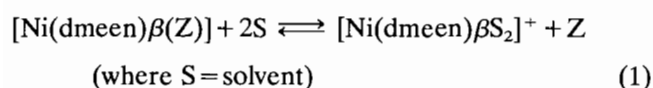
The new mixed-ligand nickel(II) chelates {Ni(enR)$_x\beta$(Z)} ($x=1$ or 2; Z=I$^-$, Cl$^-$, Br$^-$, N$_3^-$, OCN$^-$, SCN$^-$, ONO$^-$, NO$_3^-$, ClO$_4^-$, BF$_4^-$, PF$_6^-$, BPh$_4^-$) are deeply coloured crystals or crystalline powders and, with the exception of compounds containing polyfluorinated β-diones, are stable in the air, both in the solid state and in organic solvents. The chelates prepared, their elemental analyses and some physicochemical quantities and parameters are listed in Table 1. The structure of the red species, for thermodynamic reasons [3] and according to the evidence accumulated, is believed to be square planar. Employment of nonsymmetrically substituted 1,2-diamines insinuates the occurrence of isomers when the substituent groups attached to the carbonyl carbon atoms of the β-dione, R^{1}COCHXCOCR^2, differ (X=H; R$^1 \neq$ R^2). However, no separation was attempted. It should be noted that in dmeen the nitrogen atom bearing the ethyl group upon coordination completes its tetrahedral stereochemistry and becomes chiral. Evidence, presented later on, suggests that the N-substituted ethylenediamines

(enR) attain the *gauche* conformation that implies an increase in isomers.

Results and discussion

The reaction of nickel(II) with N-substituted 1,2-diamines, enR, and the anion of a β-ketoenol (β^-), affords the reactive entity [Ni(enR)β]$^+$. The formation of this entity and the isolation of the corresponding chelates (Table 1) indicate that the mixed-ligand chelates are in most cases more stable than the binary compounds. The stoichiometry of the chelates and the electrical properties of their solutions in non-coordinating solvents indicate that the stability of the [Ni(enR)β]$^+$ entity depends on several factors including the nature of the anion that confers electrical neutrality. Steric interactions rather than mere size effects seem to be of particular importance. While [Ni(dmeen)-bzac]ClO$_4$ is readily obtained and employment of 1,2-dianilinoethane, ΦenΦ, affords [10] [Ni(ΦenΦ)-bzac]ClO$_4$ as well as [Ni(ΦenΦ)$_2$bzac]ClO$_4$, use of either the symmetric N,N'-dimethyl-1,2-diaminoethane, meenme, or the geminal N,N-dimethyl-1,2-diaminoethane, me$_2$en, fails to produce the [Ni(enR)bzac]-ClO$_4$ compounds. Instead, the octahedral [Ni(enR)$_2$bzac]ClO$_4$ chelates are isolated, their formation apparently instigated by the tendency of

nickel(II) to achieve coordination numbers exceeding four and the limited ability of the perchlorate group to form covalent bonds. Counteranions known to participate in covalent bond formation, e.g. NO_3^-, also have a stabilising effect and, in addition to the ionic $[Ni(enR)_2\beta]NO_3$ compounds, the neutral $[Ni(enR)$-$bzac(O_2NO)]$ chelates are also obtained [8]. Coordination of anions is revealed by the absorptions in specific regions of the electromagnetic spectrum, by the shifts in certain bands in the IR region (discussed later on), by the change in the electrical properties and the enhancement of paramagnetism (Table 1). On the basis of the conductometric results the nickel(II) chelates may be divided into two main classes: (i) chelates the molar conductances of which are indicative of 1:1 electrolytes regardless of solvent, such as the $[Ni(dmeen)\beta]BPh_4$ and the $[Ni(enR)_2\beta]BPh_4$ compounds $(\Lambda_M \geqslant 65 \ S \ cm^2 \ M^{-1}$ in nitromethane); (ii) compounds with labile metal–anion bonds, i.e. the $[Ni(enR)\beta(O_2NO)]$ chelates, the electrolytic conductance of which depends on the solvent. Solution in solvents that are sufficiently polar to act as ionising media and possess coordinating ability, e.g. $(CH_3)_2SO$, exhibit molar conductances indicative of 1:1 electrolytes. Apparently, in these solutions the solvent molecules tend to replace the coordinated anions and exhibit equilibria of the type:

$$[Ni(dmeen)\beta(Z)] + 2S \rightleftharpoons [Ni(dmeen)\beta S_2]^+ + Z$$

$$(where \ S = solvent) \qquad (1)$$

$$[Ni(dmeen)\beta]^+ + 2S \rightleftharpoons [Ni(dmeen)\beta S_2]^+ \qquad (2)$$

A third class encompassing chelates that have very low molar conductances and may be classified as non-electrolytes, results when the charge of the $[Ni(enR)\beta]^+$ entity is neutralised by an additional anion of the β-dione, i.e. the adducts $[Ni(dmeen)\beta_2]$.

Dissolution of the $[Ni(dmeen)\beta]^+$ entity in basic solvents is accompanied by change in colour, indicative of solute–solvent interactions (reaction (2)). The observed solvatochromism is not dependent on temperature (above ambient) and is distinctly different from the one exhibited by the corresponding copper(II) compounds [15]. While the ligand field excitation bands of the copper(II) chelates are gradually shifted to lower energies upon increase of the 'donor number' of the solvent, the change in the nickel(II) chelates is abrupt. The solvatochromic shifts and the change in the intensity suggest that the geometry of the $[Ni(dmeen)\beta]^+$ entity is rather square-coplanar resulting from bidentate coordination of both β^- and the diamine, the latter participating in a five-membered chelate ring. The $[Ni(dmeen)bzac]^+$ compounds thus constitute an isostructural series in which the Lewis acidity is controlled by the substituents within the β-dionato moiety. Geo-

metrical isomers are envisaged whenever the substituent groups within the β-dionato moiety differ $(R^1 \neq R^2)$ since either group may be opposite the chiral nitrogen atom. Isostructural, albeit with different stereochemistry, is the series in which the size and the polarisability of the coordinated anion vary gradually from NCO^- to Cl^-, Br^- and I^-. The absence of large solvatochromic shifts suggests that the green $[Ni(dmeen)\beta]PF_6$ and $[Ni(dmeen)\beta]BF_4$ compounds may not be completely devoid of axial water molecules.

The interaction of the new chelates with magnetic fields is dependent, again, on the bidentate ligands and the anion. Octahedral and tetragonal nickel(II) chelates have magnetic moments falling within or near the 3.0–3.3 BM range, while the square-coplanar compounds are in most cases diamagnetic. The narrow range of the magnetic moments of the $[Ni(dmeen)\beta_2]$, the $[Ni(dmeen)_2\beta]^+$ and the aquo compounds (Table 1) is indicative of octahedral coordination. The spectral features of the $[Ni(dmeen)\beta]BPh_4$ compounds, discussed later on, are not reconcilable with tetragonal or tetrahedral arrangement and the observed low magnetic moments require some explanation. Paramagnetism is not uncommon in square-planar nickel(II) compounds and it has been argued that the chelates may have a thermally accessible spin triplet state, ^3L, of slightly higher energy than the spin singlet ground state, $^1L(^1A_{1g})$. The existence of these two spin states in equilibrium may render the compounds paramagnetic and implies temperature-dependent magnetic moments. In order to test this hypothesis a single magnetic moment determination was made on $[Ni(dmeen)bzac]ClO_4$ at about 70 °C, since a thermostated magnetic balance was not available for temperature dependency studies. The small increase in the value of the magnetic moment from the 1.23 BM value at 25 °C could not explain convincingly the room-temperature magnetic behaviour of the $[Ni(dmeen)\beta]^+$ entity, in which no fluorine atoms are present. Fluorination of the β-diones enhances the tendency of nickel(II) for coordination saturation and the magnetic behaviour as well as the elemental analysis indicate the presence of water molecules and octahedral coordination.

The octahedral coordination does not imply that the relative positions of the β-dionato moiety and the diamine are unaffected by the other ligands. The planar arrangement of the NiN_2O_2 chromophore in the $[Ni(enR)\beta]^+$ entity is destroyed upon addition of a second bidentate ligand since structural considerations preclude occupation of the axial positions. For instance, in the $[Ni(enR)_2\beta]^+$ species the basal plane comprises the NiO_2NN' part of the $NiO_2N_2N'_2$ chromophore with the remaining nitrogen atoms, one of each diamine molecule, perpendicular to the plane [16]. The distortions are greater when the newly created chelate

ring has only four members, i.e. when the nitrito and nitrato groups coordinate. Such restrictions are not operative whenever solvent molecules or unidentate ligands confer coordination saturation and impose tetragonal geometry. The imperceptible differences in the magnetic moments suggest that the out-of-plane crystal field strength produced by the axial ligands may be of no great importance in these chelates.

Infrared spectra

In the IR spectra of the newly obtained chelates appears a plethora of discrete bands. The bands may be classified in those originating from the β-dione, in those emanating from the diamine, in those emerging from polyatomic anions and in those due to bonds formed between nickel(II) and the donor atom. Disregarding minor shifts, comparison with the spectra of model compounds facilitates the deduction of the origin of the bands. For example, since polyatomic anions absorb in specific regions of the spectrum, the intense absorptions of the [Ni(dmeen)bzac]Z chelates that are not present in the spectra of the adduct [Ni(bzac)$_2$dmeen] should be associated with the anion Z$^-$.

Spectra of the bidentate ligands

The anions of β-ketoenols usually coordinate as bidentate ligands [17]. Bonding through the carbonyl oxygens and formation of a six-membered chelate ring comprising the nickel(II) and the anion of the β-dione, β^-, are disclosed by the intense absorptions in the region 1650–1500 cm^{-1} originating from the bands attributed to perturbed C$\dddot{}$O and conjugated C$\dddot{}$C bonds and the other changes in the frequencies of the vibrational modes of the free ligands [18]. As one transverses the [Ni(dmeen)β]BPh$_4$ series, frequency shifts are observed attributed to the well documented receptiveness of the conjugated π framework to mass and electronic effects [19].

Many of the bands that are evident in the IR spectra of the free nitrogenous bases (enR) upon coordination lose intensity, become shifted or even disappear while few bands remain virtually unchanged. The absence of absorptions at frequencies above 3330 cm^{-1}, other than those attributable to hydrogen bonding, and the emergence of bands in the region 550–400 cm^{-1} are indicative of bidentate coordination and chelate ring formation [20]. The 1,2-diamines are capable of attaining various configurations while the chelated 1,2-diamines usually adopt the *gauche* conformation rather than the *cis* [20]. Corey and Bailar [21] pointed out that since nitrogen upon coordination completes its tetrahedral arrangement (with the prochiral nitrogen atoms becoming chiral), the puckering requirements of the chelate ring favour the *gauche* conformation as has actually been

observed [11]. Under the circumstances the orientations of substituents on the nitrogen atoms may be described as 'axial' or 'equatorial' and these positions are interconvertible by internal rotation. Corey and Bailar indicated that the 'axial' positions are thermodynamically unfavourable, the implication being that in a symmetrically N,N'-disubstituted 1,2-diamine the preferred disposition will be 'equatorial'. Investigations by Gollogly and Hawkins [22] led them to suggest that small changes in the metal–nitrogen bond lengths may render other configurations more favourable. In the compounds investigated the pattern exhibited by the bands attributable to the chelated dmeen resembles that of analogous copper(II) chelates for which X-ray structure elucidation revealed *gauche* conformation of the 1,2-diamine and 'equatorial' disposition of the ethyl group. Attainment of the *gauche* conformation of the dianilinoethane molecule, ΦenΦ, and 'equatorial' disposition of the phenyl groups have also been observed [16] in the compound [Ni(hfac)$_2\Phi$enΦ].

Counterion spectra

The presence of BPh$_4^-$ in the corresponding compounds is disclosed by the split band with peaks at 735 and 708 cm^{-1} attributable to the in-plane and out-of-plane vibrations of the hydrogens of the phenyl groups. A strong broad band at 835 cm^{-1} reveals the presence of the PF$_6^-$ group. The absence of splittings in this band is indicative of the existence of this group in the solid state as the anion [23]. The occurrence of the BF$_4^-$ ion is revealed by the broad band at *c.* 1060 cm^{-1}, attributed to the ν_3 vibrational mode [24]. The inability to observe either the ν_2 or the ν_1 modes, which when activated by coordination are expected to be present at *c.* 355 and 765 cm^{-1}, respectively, and the absence of splittings in the band at 518 cm^{-1} (ν_4 mode) indicate ionic existence. The broad intense band with a poorly defined maximum at about 1090 cm^{-1} that appears in the spectra of [Ni(enR)$_2$bzac]ClO$_4$, notwithstanding other groups that also absorb in the same region (Table 2), indicates that the tetrahedral ClO$_4^-$ group may not be considered to be even semi-coordinated [25]. Lack of covalent interactions is also inferred by the shape of this band in the spectrum of [Ni(dmeen)bzac]ClO$_4$. The concentration of 1,2-diamine dictates the mode of interaction of NO$_3^-$. Ionic existence of the NO$_3^-$ group is envisaged in the [Ni(enR)$_2\beta$]NO$_3$ compounds and this is corroborated by the frequencies of the characteristic bands [26] even though they are coincident with the richer parts of the spectrum of the β-dionato moiety. For instance the band at 1380 cm^{-1} (ν_3 mode, doubly generate stretch) is indicative of the ionic existence of this group. In [Ni(bzac)dmeen(O$_2$NO)] the band at ~1470 cm^{-1} is intensified, band splittings and shifts occur suggesting

TABLE 2. Ligand field excitation energies of some nickel(II) compounds, Ni(β)dmeen(Z), and allied chelates in CH_2Cl_2

No.	Compound	${}^3T_{2g} \leftarrow {}^3A_{2g}$ $\bar{\nu}$ (μm^{-1})	${}^1E_g \leftarrow {}^3A_{2g}$ $\bar{\nu}$ (μm^{-1})	${}^3T_{1g} \leftarrow {}^3A_{2g}$ $\bar{\nu}$ (μm^{-1})	ν_2/ν_1
1	[Ni(me$_2$en)$_2$bzac]B(Ph)$_4$	0.983 (10)[a]	~1.28(sh)	1.718 (8)[a]	1.75
2	[Ni(meenme)$_2$bzac]B(Ph)$_4$	1.059 (10)	~1.27(sh)	1.742 (9)	1.64
3	[Ni(meenme)bzac(NO$_3$)]	0.991 (10)	~1.29(sh)	1.686 (13)	1.70
		1.007 (10)[b]	~1.28(sh)	1.695 (10)	1.68
		1.001 (9)[c]	1.29(sh)	1.661 (8)	1.66
4	[Ni(meenme)$_2$bzac](NO$_3$)	1.060 (12)	~1.27(sh)	1.748 (10)	1.65
		1.062 (11)[b]	~1.26(sh)	1.741 (10)	1.64
		1.058 (13)[c]	~1.29(sh)	1.733 (11)	1.64
5	[Ni(dmeen)bzac]PF$_6$	0.935 (9)		1.582 (14)	1.70
6	[Ni(dmeen)bzac]BF$_4$	0.971 (7)	~1.29(sh)	1.634 (7)	1.68
7	[Ni(dmeen)bzac]ClO$_4$	1.031 (9)[b]	~1.28(sh)	1.709 (11)	1.66
		0.965 (7)[c]	~1.31(sh)	1.591 (7)	1.65
8	[Ni(dmeen)bzac(O$_2$NO)]	0.973 (11)	~1.25(sh)	1.656 (19)	1.70
9	[Ni(dmeen)bzac(O$_2$N)]	0.994 (8)		1.658 (21)	1.67
10	[Ni(dmeen)bzac(H$_2$O)N$_3$]	0.985 (14)	~1.24(sh)	1.605 (10)	1.62
11	[Ni(dmeen)bzac(H$_2$O)NCS]	0.985 (10)	~1.26(sh)	1.608 (22)	1.63
		0.986 (11)[b]	~1.29(sh)	1.653 (13)	1.68
		0.956 (10)[c]	~1.30(sh)	1.587 (9)	1.66
12	[Ni(dmeen)bzac(H$_2$O)NCO]	0.958 (11)	~1.27(sh)	1.587 (9)	1.66
13	[Ni(dmeen)bzac(H$_2$O)Cl]	0.952 (8)		1.531 (22)	1.60
14	[Ni(dmeen)bzac(H$_2$O)Br]	0.946 (8)		1.527 (21)	1.61
15	[Ni(dmeen)bzac(H$_2$O)I]	0.934 (9)		1.623 (30)	1.63
16	[Ni(dmeen)dpm]B(Ph)$_4$	1.020 (9)[b]	~1.27(sh)	1.670 (10)	1.64
		0.967 (8)[c]	~1.29(sh)	1.571 (8)	1.62
17	[Ni(dmeen)acac]B(Ph)$_4$	0.989 (9)[b]	~1.27(sh)	1.660 (12)	1.68
		0.957 (10)[c]	1.32(sh)	1.600 (9)	1.67
18	[Ni(dmeen)bzac]B(Ph)$_4$	1.012 (11)[b]	~1.27(sh)	1.692 (13)	1.67
		0.962 (9)[c]	~1.29(sh)	1.610 (8)	1.67
19	[Ni(dmeen)dbm]B(Ph)$_4$	1.020 (10)[b]	~1.27(sh)	1.710 (15)	1.68
		0.969 (9)[c]	1.30(sh)	1.611 (10)	1.66
20	[Ni(dmeen)tfac(H$_2$O)$_2$]B(Ph)$_4$	0.985 (10)	~1.29(sh)	1.623 (24)	1.65
21	[Ni(dmeen)bztf(H$_2$O)$_2$]B(Ph)$_4$	1.025 (17)		1.686 (23)	1.64
22	[Ni(dmeen)thtf(H$_2$O)$_2$]B(Ph)$_4$	0.971 (13)		1.629 (25)	1.68
23	[Ni(bzac)$_2$dmeen]	0.971 (14)	~1.29(sh)	1.629 (12)	1.68

[a]Extinction coefficients in M^{-1} cm^{-1}.   [b]In acetonitrile solution.   [c]In DMSO solution.

that the degeneracy of the ν_3 mode is lifted and a clearly discernible band at ~1280 cm^{-1} implicates bidentate coordination. Upon coordination and chelate ring formation the symmetry of the NO_3^- group is reduced to C_{2v}, as a recent X-ray structure elucidation of the similar nickel(II) chelate [Ni(acac)ΦenΦ(O$_2$NO)] has divulged [16]. The bands in the IR spectra of [Ni(bzac)dmeen(O$_2$N)] at 1286 and 1209 cm^{-1} that reveal the presence of the NO_2^- group, are assigned to the asymmetric and symmetric N–O stretch, respectively. The shifts, relative to the free ion values, preclude coordination through nitrogen and indicate [27] chelate formation (O,O nitrito). The NO_2^- group, capable of interacting in a variety of modes [27], apparently coordinates in a manner similar to that of the NO_3^- group.

The electrical conductivity of the compounds in which halides and pseudohalides are present also indicates covalent interactions. The pseudohalides coordinate in

a variety of modes and since linkage isomerism is a possibility, several alterations in the method of preparation were tried and different solvents were employed in recrystallisation. The IR spectra of the chelates under consideration were found to be the same, regardless of the method of preparation and recrystallisation, and provided evidence on the mode of coordination of the anions. In the spectrum of [Ni(dmeen)bzac(H$_2$O)NCO] the strong band observed at 2167 cm^{-1}, a frequency associated with the cyano group, precludes coordination through carbon and so does the band at 610 cm^{-1} attributed to the deformation of the group, δ(NCO). More informative is the intense absorption at 1335 cm^{-1} that rather suggests coordination through nitrogen since this absorption in cyanates occurs at lower frequencies [28]. In the spectra of [Ni(bzac)dmeen(NCS)] the band due to ν(CN) appears at 2089 cm^{-1} and precludes coordination of (NCS$^-$) as a bridging ligand. In the same spectra the absorption associated with the

C–S stretch is not observed, while the medium intensity band at 445 cm^{-1} is very likely due to the NCS$^-$ bend. The shape, intensity and frequency of these bands have been suggested as criteria for the determination, with a reasonable degree of certainty, of the mode of bonding of the NCS$^-$ group [29]. The frequencies of the C–N stretch and the δ(NCS) vibration both suggest an N-bonded group since in thiocyanato compounds the latter vibration occurs [29] at frequencies lower than 440 cm^{-1}. The splitting of ν(CN) in the aforementioned compounds could imply two distinct crystallographic sites for the (NCS$^-$) and the (NCO$^-$) groups (Table 2). The N$_3^-$ group exhibits an intense narrow split band peaking at 2046 cm^{-1}, a discrete band at 1274 cm^{-1} and a sharp band at 589 cm^{-1}.

The IR absorption bands of the nickel–halide bond provide little information as to whether the halides act as bridging ligands or not. The chloride compound absorbs at 386 cm^{-1}, the bromide exhibits a band at 262 cm^{-1}, while the frequency of the nickel–iodide stretch is observed at 228 cm^{-1}.

Electronic excitation spectra

The electronic absorption spectra of the chelates were studied in the visible and the near-IR region, in solution and in the solid state by reflectance. Attempts were made to obtain transmission spectra of nujol mulls but the intensities of the absorption bands were generally too low for reliable determinations of band positions. Inert solvents such as dichloromethane were used whenever possible in order to minimise the likelihood of solvation. Small differences in band positions between the spectra of the solid compounds and the dichloromethane solutions were observed. Two types of spectra were distinguished, that due to the [Ni(dmeen)β]$^+$ entity in the solid state and that when solvent molecules or other ligands increased the coordination number of nickel(II).

In the electronic excitation spectra of the [Ni(enR)β]$^+$ compounds, the composite band observed at about 2.050 μm^{-1} ($\epsilon \approx 120$ M^{-1} cm^{-1}) is indicative of a square-planar structure [30] and its maximum depends on β^- (ν_{max}: dpm = 2.039, acac = 2.045, bzac = 2.049, dbm = 2.070 μm^{-1}). As mentioned before, dissolution in polar solvents induces spectral shifts and the appearance of bands at the same frequencies as those of the [Ni(β)$_2\Phi$enΦ)] and [Ni(ΦenΦ)$_2\beta$]$^+$ chelates. Structural studies revealed that in the [Ni(β)$_2\Phi$enΦ)] and [Ni(ΦenΦ)$_2\beta$]$^+$ species, nickel(II) is virtually at the centre of a distorted octahedron [16]. The ligand-field spectra of the [Ni(enR)$_2\beta$]$^+$ compounds and of those characterised by magnetic moments $\mu_{eff} \approx 3$ BM are all of the same general form and consist of three principal bands in the visible region. Band I appears at about 0.97 μm^{-1}, band II is observed at ~ 1.65 μm^{-1} and

band III occurs at ~ 2.66 μm^{-1}. In the spectra of the solid [Ni(dmeen)$_2$bzac] a weak band is clearly observed on the low energy side of band II, while the solid state spectra of [Ni(dmeen)bzac(O$_2$NO)] and [Ni(meenme)bzac(O$_2$NO)] each contain a shoulder between bands II and III. In some cases the highest energy band is only poorly resolved because of overlap by the more intense charge-transfer and ligand bands. The stoichiometry, magnetic moments, and the energies of the ligand field excitations are consistent with a mononuclear octahedral structure with a triplet ground state. Data from the dichloromethane solution spectra were preferably employed for consistency (Table 2) and because the band maxima could be located more accurately than in the reflectance spectra. The absence of splittings infers that distortions arising from the different ligands, dmeen and the β-ketoenolato and nitrato(O,O') anions, are rather small. This assumption is supported by the similarities with the spectra of the compounds [Ni(ΦenΦ)$_2$Cl$_2$] and [Ni(acac)$_2$(H$_2$O)$_2$] that have been analysed in the theoretical work of Maki [31]. These suggest that notation appropriate to an octahedron (O_h) may be employed although the actual symmetry is much lower. Accordingly, the three principal bands have been assigned to transitions from the ^{3}A$_{2g}$(F) ground state to the excited states ^{3}T$_{2g}$(F) (ν_1), ^{3}T$_{1g}$(F) (ν_2) and ^{3}T$_{1g}$(P) (ν_3), and the weak absorptions to the spin-forbidden transitions to the singlet states ^{1}E$_g$(D) and ^{1}A$_{1g}$(G). The ligand field parameter 10Dq was taken equal to the energy of the first spin-allowed transition (Table 2). For the d^8 chelates with symmetry approaching O_h, increase in the ligand field strength enhances configuration interaction (CI) between the high-spin ^{3}T$_{1g}$(F) and ^{3}T$_{1g}$(P) excited states. The CI gradually lowers the ratio $E(^3$T$_{1g}$(F) $\leftarrow ^3$A$_{2g}$(F)): $E(^3$T$_{2g}$(F) $\leftarrow ^3$A$_{2g}$(F)) from the theoretical value of 1.8 to about 1.5–1.7. The values obtained justify the proposed assignments (Table 2).

In this work it is shown that the concurrent reaction of nickel(II) with β-diones and 1,2-diamines leads to a variety of products. It is demonstrated that stereoelectronic effects engendered by substituents attached to the bidentate ligands induce ligand–ligand interactions, lead to ligand selectivity, afford the omnipresent [Ni(enR)β]$^+$ entity and may prevent nickel(II) from attaining coordination saturation. The IR spectra disclose that in the [Ni(enR)β]$^+$ entity the anions of β-diones form six-membered chelate rings while the 1,2-diamines attain the *gauche* conformation and form five-membered chelate rings with nickel(II) as common vertex. While bulky counteranions stabilise the [Ni(enR)β]$^+$ entity by electrostatic interactions, halides and pseudohalides coordinate. Solvatochromic shifts reveal covalent interactions of the [Ni(enR)β]$^+$ entity with polar solvents. The electronic excitation spectra suggest, in conjunction with other physicochemical prop-

erties, that the reactive $[Ni(enR)\beta]^+$ entity is planar and that the planarity is destroyed when the number of bidentate ligands increases. Consideration of the excitation energies indicates octahedral structures in the six-coordinated nickel(II) compounds.

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