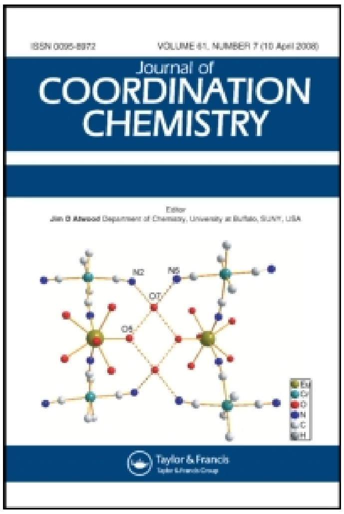

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Facial Coordination Chemistry in Nickel(II) Compounds with Linear Tridentate Ligands: Synthesis, Spectra and Redox Behavior

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FACIAL COORDINATION CHEMISTRY IN NICKEL(II) COMPOUNDS WITH LINEAR TRIDENTATE LIGANDS: SYNTHESIS, SPECTRA AND REDOX BEHAVIOR

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1:1 and 1:2 nickel(II) complexes of bis(benzimidazole-2-ylmethyl)amine (bbma) bis(benzimidazole-2-ylmethyl)sulfide (bbms), bis(benzimidazole-2-ylethyl)sulfide (bbes) and diethylenetriamine (dien) were prepared and their spectroscopic and redox behavior studied. The stereochemistry of nickel(II) complexes with bbma, bbes, bbms and dien have been analyzed, confirming *facial* configuration for $\mathrm{Ni(bbma)_2^{2+}}$ and $\mathrm{Cu(bbma)_2^{2+}}$ and *meridional* geometry for $\mathrm{Ni(dien)_2^{2+}}$ and $\mathrm{Cu(dien)_2^{2+}}$. The factors favoring *facial* or *meridional* coordination of these ligands have been studied. For example, the π-bonding ability of benzimidazole at the termini of the tridentate ligand facilitate the *facial* geometry for the complexes, and the strong σ-donor ability of amine at the termini of the dien ligand favors *meridionally* coordinated complexes. The electronic spectral results indicate that the ligand field strength of the complexes decreases in the following order: $\mathrm{Ni(bbms)^{2+} > Ni(bbes)^{2+} > Ni(bbma)^{2+} > Ni(dien)^{2+}}$, this decreasing order being consistent with the redox potential obtained for these complexes.

Keywords: Nickel complexes; Benzimidazole; Facial; Meridional

INTRODUCTION

The stereochemistry of coordination compounds is of growing interest because of its implication in models for bioinorganic and catalytic systems for enantioselective reactions. The bis-complex of a linear tridentate ligand generally forms two potential geometric isomers *viz*., *meridional* (a) and *facial* (b,c) (Fig. 1). For example, three edge configurations (*u-fac*, *s-fac and mer*) were found for the octahedral $\mathrm{[M(dien)_2]^{2+}}$ complexes [1–10] [M=Cr(II), Co(III), Rh(III), Ir(III), Ni(II), Cu(II) and Zn(II)]; however, the complexes $\mathrm{[Cu(dien)_2](NO_3)_2}$ [11] and $\mathrm{[Cu(dien)_2]Br \cdot H_2O}$ [12] (dien=diethylenetriamine) exhibit only the *mer* isomer, where nitrogen atoms occupy three positions in such a way that two terminal nitrogens are *trans* to each other; thus, half of the meridian of the octahedron is occupied by ligand atoms. In contrast, only an *s-fac* octahedral geometry was obtained for the nickel complex with methyl

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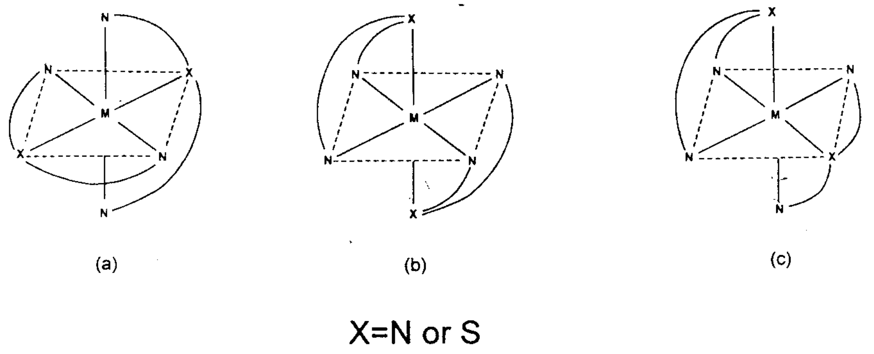

FIGURE 1 Scheme of three geometric isomers (*fac* a, b and *mer* c).

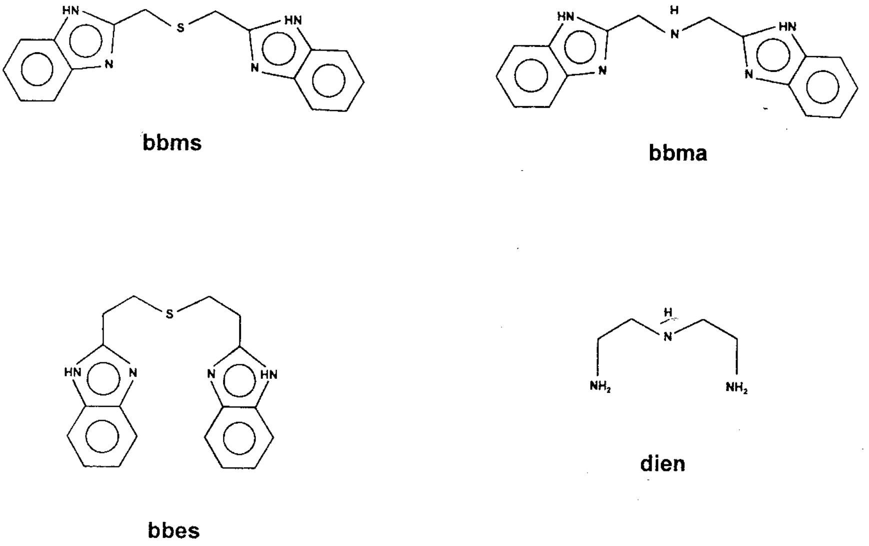

FIGURE 2 Scheme of ligand systems.

substituted dien, [Ni(medien)$_2$](NO$_3$)$_2$ [13], where the nitrogen atoms occupied the corners of the triangular face of the octahedron structure. Bis(2-pyridylmethyl)amine (bpma) formed both *fac* isomers but not the *mer* isomer for the complexes [M(bpma)$_2$]X$_2$ (M=Mn(II), Zn(II), or Cd(II), X=ClO$_4$, or Cl); similarly, *fac*-[Fe(bpma)$_2$](ClO$_4$)$_2$ was isolated [14,15]; however, the structures of the bis-medien (methyl substituted dien) complexes of cadmium are different from those of the dien complexes, showing that the *s-fac* geometry is more common in the former, whereas the latter preferred *mer* geometry. Further, the Cu(IDA) complex (IDA=iminodiacetate) reveals that its *fac* configuration was inverted to *mer* [16] when benzimidazole was added to the Cu(IDA). Although the geometrical isomerism of tridentate ligands with different metal ions has already been studied, the geometrical behaviors of the nickel(II) complexes with different tridentate linear ligands (Fig. 2) is still a topic for research; factors favoring the geometric preference need to be studied. This observation prompted our interest in the coordination chemistry of different tridentate ligands, bis(benzimidazole-2-ylmethyl)amine, bis(benzimidazole-2-ylmethyl)-sulfide, bis(benzimidazole-2-ylethyl)sulfide and diethylentriamine with nickel(II) and their geometrical and spectral behaviors are discussed in this paper.

EXPERIMENTAL

Chemicals

The following reagents were used as received: $Ni(II)Cl_2 \cdot 6H_2O$, $Ni(II)(ClO_4)_2 \cdot 6H_2O$, 1,2-diaminobenzene, 3,3′-thiodipropionic acid, thiodiglycolic acid, diethylenetriamine, iminodiacitic acid (Aldrich). Tetra-*n*-hexylammonium perchlorate (G.F. Smith) was recrystallized twice from aqueous ethanol.

Physical Measurements

Elemental analyses were carried out in the Faculty of Chemistry, UNAM, México. The estimation of nickel was determined by voltammetric techniques [17]. The diffuse reflectance and methanolic absorption spectra were measured on a Hitachi U-3400 double beam UV/VIS/NIR spectrophotometer. All voltammetric experiments were performed in a single-compartment cell with a three-electrode configuration on a EG and G PAR 263 A potentiostat/galvanostat interfaced with a computer along with EG and G M270 software which has employed to carry out the experiments. The reference electrode was $Ag(s)/(AgNO_3)$ in methanol. The solutions were deoxygenated by bubbling them with research-grade nitrogen. Methanol for electrochemistry was distilled over magnesium turnings.

Synthesis of Ligands

Bis(benzimidazole-2-ylmethyl)sulfide (bbms) [18], bis(benzimidazole-2-ylethyl)sulfide (bbes) [19] and bis(benzimidazole-2-ylmethyl)amine (bbma) [20,22] were synthesized, as reported elsewhere. Diethylenetriamine (dien) was purchased from Aldrich.

Preparation of Complexes

The following complexes were prepared according to the procedure reported elsewhere [15,22].

[Ni(bbes)]$(ClO_4)_2 \cdot 2H_2O$ A solution of $Ni(ClO_4)_2 \cdot 6H_2O$ (0.36 g, 1.0 mmol) in methanol (5.0 mL) was added under stirring (10 min) to bbes (0.322 g, 1.0 mmol) dissolved in methanol (10.0 mL). The resulting solution was kept at room temperature. The bluish-green crystals obtained were collected, washed with small amounts of methanol and dried over P_4O_{10} in vacuum (yield, 85%).

[Ni(bbes)]$Cl_2 \cdot H_2O$ To ligand ‘bbes’ (0.322 g, 1.0 mmol) dissolved in methanol (10.0 mL) was slowly added under stirring (10 min) to a methanolic solution of $NiCl_2 \cdot 6H_2O$ (0.237 g, 1.0 mmol). The resulting blue solution was kept at room temperature. The light blue crystals formed were collected, washed with small amounts methanol and dried over P_4O_{10} in vacuum (yield, 80%).

TABLE I Elemental analysis of the Ni(II) complexes with calculated values in parenthesis

	Compounds	*%C*	*%H*	*%N*	*%Ni*
1	$[Ni(bbes)](ClO_4)_2 \cdot 2H_2O$	34.96	3.84	9.50	9.90
		(35.14)	(3.60)	(9.11)	(9.54)
2	$[Ni(bbes)]Cl_2 \cdot H_2O$	46.58	4.00	12.13	12.88
		(46.07)	(4.29)	(11.94)	(12.51)
3	$[Ni(bbes)_2](ClO_4)_2$	47.96	3.97	12.25	6.55
		(47.95)	(4.02)	(12.43)	(6.50)
4	$[Ni(bbes)_2]Cl_2$	55.51	4.35	14.02	7.28
		(55.88)	(4.69)	(14.48)	(7.59)
5	$[Ni(bbms)](ClO_4)_2 \cdot 2H_2O$	32.55	2.18	10.00	10.42
		(32.73)	(3.09)	(9.54)	(9.99)
6	$[Ni(bbms)]Cl_2 \cdot H_2O \cdot MeOH$	44.32	4.05	12.01	12.48
		(44.66)	(4.41)	(12.24)	(12.84)
7	$[Ni(bbms)_2](ClO_4)_2$	45.39	3.35	12.97	6.81
		(45.45)	(3.34)	(13.25)	(6.94)
8	$[Ni(bbma)](ClO_4)_2 \cdot MeOH \cdot H_2O$	34.67	3.40	12.00	9.90
		(34.95)	(3.62)	(11.99)	(10.05)
9	$[Ni(bbma)]Cl_2 \cdot 2H_2O$	44.97	4.35	16.23	13.50
		(45.10)	(4.49)	(16.43)	(13.77)
10	$[Ni(bbma)_2](ClO_4)_2 \cdot MeOH$	46.50	4.00	16.22	6.50
		(46.99)	(4.06)	(16.61)	(6.96)
11	$[Ni(dien)](ClO_4)_2 \cdot 2H_2O$	12.30	4.84	10.87	15.35
		(12.57)	(5.01)	(11.00)	(15.36)
12	$[Ni(dien)]Cl_2 \cdot 2H_2O$	22.13	7.06	15.44	22.00
		(22.57)	(7.20)	(15.80)	(22.06)
13	$[Ni(dien)_2](ClO_4)_2$	20.68	5.70	18.18	12.58
		(20.74)	(5.66)	(18.14)	(12.67)
14	$[Ni(dien)_2]Cl_2 \cdot H_2O$	26.96	8.00	23.68	16.33
		(27.21)	(7.99)	(23.80)	(16.62)

$[Ni(bbes)_2](ClO_4)_2$ A methanolic solution of $Ni(ClO_4)_2 \cdot 6H_2O$ (0.36 g, 1.0 mmol) was added to the 'bbes' (0.644 g, 2.0 mmol) dissolved in methanol (20 mL) under stirring for 10 min. The resulting blue solution was kept at room temperature. The bluish-green crystals obtained were collected, washed with small amounts of methanol and dried over P_4O_{10} in vacuum (yield, 80%).

The above procedures were used to prepare the following nickel(II) complexes using bbms, bbma, and dien ligands: $[Ni(bbms)](ClO_4)_2 \cdot 2H_2O$, $[Ni(bbms)]Cl_2 \cdot H_2O \cdot MeOH$, $[Ni(bbms)_2](ClO_4)_2$, $[Ni(bbma)](ClO_4)_2 \cdot MeOH \cdot H_2O$, $[Ni(bbma)]Cl_2 \cdot MeOH$, $[Ni(bbma)_2](ClO_4)_2 \cdot MeOH$, $[Ni(dien)](ClO_4)_2 \cdot 2H_2O$, $[Ni(dien)]Cl_2 \cdot 2H_2O$, $[Ni(dien)_2](ClO_4)_2$ and $[Ni(dien)_2]Cl_2 \cdot H_2O$. Table I contains microanalytical data for these complexes.

Caution: Although no accident occurred with nickel perchlorate complexes during the experimental work, it should be remembered that perchlorates are potentially explosive.

RESULTS AND DISCUSSION

The stereochemistry of nickel complexes with the tridentate ligands bbma, bbes, and dien were analyzed. In our previous papers [15,22], the crystal structure for $Ni(bbma)_2^{2+}$ in *sym-facial* [22] and for $Cu(bbma)_2^{2+}$ [15] in *unsym-facial* were established, indicating that the complex formed by using bbma with nickel(II) or copper(II) facilitates the *facial* geometry, differing only in the symmetry unit. The octahedral structure of $Ni(bbma)_2^{2+}$, where the equatorial plane was formed by a amine and three benzimidazole nitrogens and the axial positions were occupied by the remaining amine and benzimidazole nitrogens, possessed *unsym-facial* configuration; however, $Cu(bbma)_2^{2+}$ exhibits the *sym-facial* geometry, where four benzimidazol nitrogens lie on the equatorial plane and one benzimidazole and secondary amine nitrogen are located at the axial positions. Also, in the case of the triclinic octahedral structure $Ni(bbes)_2^{2+}$ [23], bbes coordinates with nickel ion *trans*-facially, consequently, the equatorial plane of the complex was formed by four nitrogens from the benzimidazole moiety and two thioether sulfurs occupy the axial positions; thus, *facial* geometry occurs in the complex. Further, it is interesting to note that only *facial* coordination is favored by the metal complexes (M=Cu and Ni) using bbes, bbma and bpma [24] (bpma=bispyridylmethylamine). These observations suggest that steric hindrance caused by benzimidazole or the pyridyl group at the terminus of the tridentate linear ligands (bbes, bbma and bpma) favors a *facial* coordination with the nickel ion. This implies that the *facial* coordination appears to be facilitated when the terminal-donor sites in the tridentate ligand (bbes or bbma) possess partial rigidity, thus reducing the σ-donor as well as enhancing the π-bonding ability of benzimidazole. However, this is contrary to the metal complexes with dien, which exhibit mostly *mer* geometry [25,26]; indicating that the formation of *mer* configuration is certainly due to less steric crowding from dien; consequently, it allowed the formation of the *mer* configuration. For example, the $[Ni(dien)_2]^{2+}$ unit in $[Ni(dien)_2][Ni(CN)_4] \cdot 2H_2O$ is a distorted octahedral environment with the two tridentate dien molecules coordinated meridionally [25]. The complexes $[Cu(dien)_2](NO_3)_2$ and $[Cu(dien)_2]Br \cdot H_2O$ (dien=diethylenetriamine) exhibit only the *mer* isomer [11,12]. On the other hand, the crystal structure for $[Ni(medien)_2](NO_3)_2$ [13] reveals that it possesses an *s-fac* octahedral geometry, meaning that the methyl substitution in the secondary nitrogen of dien causes steric hindrance around the nickel. Thus, the *meridional* cooridination is generally facilitated when primary amine nitrogens with strong σ-donor ability form the termini of the ligand. If the central nitrogen in the 'dien' ligand carried a methyl substituent, as in the case of medien, it seems to favor the *fac* isomer. The M–N bond lengths are plotted (Fig. 3) for the following different metal complexes containing the benzimidazole or amine as the termini of tridentate ligands, showing that the bond distances, $M–N_{bzim}$ for the metal complexes [Co(II), Ni(II), Cu(II) and Zn(II)] steadily decrease; this is contrary to the bond lengths $M–N_{amine}$, observed for the complexes, *i.e.*, the bond distance increases. On the other hand, the $Cu–N_{amine}$ distance is higher than the $Zn–N_{amine}$ which is obviously due to Jahn-Teller effect.

	$Co(bbes)_2^{2+}$ [27]/ $Co(dien)_2^{2+}$ [6]	$Ni(bbma)_2^{2+}$ [22]/ $Ni(dien)_2^{2+}$ [25]	$Cu(bbma)_2^{2+}$ [15]/ $Cu(dien)_2^{2+}$ [12]	$Zn(bbma)_2^{2+}$ [28]/ $Zn(dien)_2^{2+}$ [12]
$M–N_{bzim}$	2.132	2.061	2.018	2.005
$M–N_{amine}$	1.970	2.132	2.265	2.220

Electronic Spectra

The assignments of the electronic spectral bands of all three spin-allowed transitions (Table II) typical of d^8 high-spin complexes of nickel(II) in methanol, are ${}^3A_{2g} \rightarrow {}^3T_{2g}$

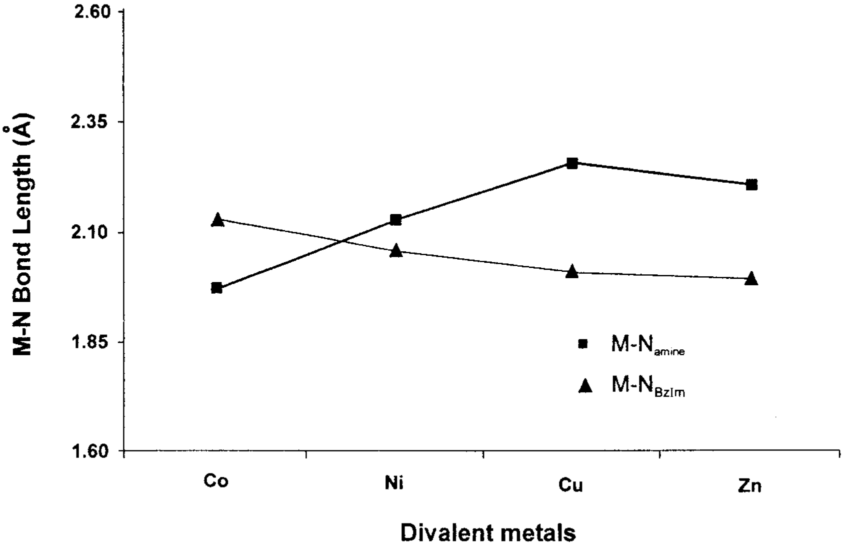

FIGURE 3 Plot of M–N bond length *vs.* divalent metals.

(1030–847 nm), $^3A_{2g}\rightarrow{}^3T_{1g}(F)$ (782–550 nm). The higher energy band observed around 400 nm [$^3A_{2g}\rightarrow{}^3T_{1g}(P)$] is obscured by a charge-transfer band [29–32]. For all 1 : 2 complexes the three main bands are obtained. However, an additional shoulder (apart from the main bands), was detected for 1 : 1 complexes, meaning that $^3A_{2g}\rightarrow{}^3T_{1g}(F)$ transition is split into two components as a consequence of the spin-orbit coupling of ^1E (D) and T_{1g}. This indicates that 1 : 1 complexes possess tetragonal geometry, which is consistent with the ligand field parameter Dq for 1 : 1 complexes being much lower than for 1 : 2 compounds. Further, the 1 : 2 complexes where six coordinating atoms in an octahedron, show higher ε values than 1 : 1 compounds because of the less distorted geometries of the former as found for x-ray structure of Ni(bbes)$_2^{2+}$ [23] and Ni(bbma)$_2^{2+}$ [22].

The spectral parameter of the 1 : 2 complexes reveal their ligand field strength in increasing order: Ni(bbms)$_2^{2+}$ (1019 cm^{-1}) < Ni(bbes)$_2^{2+}$ (1029 cm^{-1}) < Ni(bbma)$_2^{2+}$ (1067 cm^{-1}) < Ni(dien)$_2^{2+}$ (1154 cm^{-1}). For the Ni(bbms)$_2^{2+}$ complex, adjacent five-membered chelating ring (555 and 555 for each ligand) around the nickel ion cause more strain towards the metal ion, leading to comparatively lower ligand field energy ($B = 1019\ \text{cm}^{-1}$) than in the case of the remaining 1 : 2 nickel(II) complexes. On the contrary, a more effective in-plan σ-interaction with nickel is expected for Ni(dien)$_2^{2+}$, thereby raising the ligand field energy (Fig. 4). The degree of distortion in the geometry depends upon the strain caused by the number of five-membered chelate rings and as well as the number of sterically hindered bulky groups around the metal ion. For bbes complexes, six-membered (666 and 666 each ligand) chelating rings were formed, causing less strain than bbms but more strain than dien towards the metal ion. Although a similar trend in ligand field strength has also been observed for 1 : 1 complexes: Ni(bbms)$^{2+}$ (941 cm^{-1}) < Ni(bbes)$^{2+}$ (988 cm^{-1}) < Ni(bbma)$^{2+}$ (1054 cm^{-1}) < Ni(dien)$^{2+}$ (1154 cm^{-1}), the ligand field energy obtained for 1 : 2 complexes was much higher than the 1 : 1 compounds, which is expected since higher ligand field strength is produced by N_6 or N_4S_2 chromophores. This is consistent with ε

TABLE II Electronic absorption spectral data in nm with $\varepsilon(\mathrm{m}^{-1}\,\mathrm{cm}^{-1})$ in parentheses

Compounds	*Medium*	*Ligand field*[a]	*Dq-values* cm^{-1}	β[b] *values*	*Charge-transfer*[a]
$[\mathrm{Ni(bbes)}](\mathrm{ClO_4})_2 \cdot 2\mathrm{H_2O}$	Methanol	964 (12) 718 (10) 636 (13)	1037	0.32 0.58	391 (23)
$[\mathrm{Ni(bbes)}]\mathrm{Cl_2} \cdot \mathrm{H_2O}$	Methanol	1012 (14) 730 (13) 640 (15)	988	0.36 0.58	380 (27)
$[\mathrm{Ni(bbes)_2}](\mathrm{ClO_4})_2$	Methanol	972 (24) 632 (18)	1029	0.63	382 (28)
$[\mathrm{Ni(bbes)_2}]\mathrm{Cl_2}$	Methanol	996 (27) 640 (20)	1004	0.65	380 (31)
$[\mathrm{Ni(bbms)}](\mathrm{ClO_4})_2 \cdot 2\mathrm{H_2O}$	Methanol	1063 (9) 918 (4) 718 (7) 654 (8)	941	0.47 0.82	400 (15)
$[\mathrm{Ni(bbms)}]\mathrm{Cl_2} \cdot \mathrm{H_2O} \cdot \mathrm{MeOH}$	Methanol	1064 (10) 918 (5) 718 (7) 654 (8)	940	0.27 0.42	400 (17)
$[\mathrm{Ni(bbms)_2}](\mathrm{ClO_4})_2$	Methanol	964 (18) 645 (15)	1019	0.54	390 (28)
$[\mathrm{Ni(bbma)}](\mathrm{ClO_4})_2 \cdot \mathrm{MeOH} \cdot \mathrm{H_2O}$	Methanol	948 (22) 715 (14) 656 (13)	1054	0.31 0.47	393 (30)
$[\mathrm{Ni(bbma)}](\mathrm{ClO_4})_2 \cdot \mathrm{H_2O}$	Methanol	955 (26) 718 (15) 659 (15)	1047	0.32 0.47	399 (36)
$[\mathrm{Ni(bbma)_2}](\mathrm{ClO_4})_2 \cdot \mathrm{MeOH}$	Methanol	937 (32) 609 (18)	1067	0.65	396 (25)
$[\mathrm{Ni(dien)}](\mathrm{ClO_4})_2 \cdot 2\mathrm{H_2O}$	Methanol/DMSO	882 (33) 550 (24) 400 (20)	1134	0.89	355 (35)
$[\mathrm{Ni(dien)}]\mathrm{Cl_2} \cdot \mathrm{H_2O} \cdot \mathrm{MeOH}$	Methanol/DMSO	890 (39) 558 (30)	1124	0.85	363 (28)
$[\mathrm{Ni(dien)_2}](\mathrm{ClO_4})_2$	Methanol/DMSO	866 (42) 536 (30)	1154	0.95	350 (52)
$[\mathrm{Ni(dien)_2}]\mathrm{Cl_2} \cdot \mathrm{H_2O}$	Methanol/DMSO	869 (35) 534 (30)	1151	1.00	367 (63)

[a]Concentration 5×10^{-2}; [b]Calculated from $B = 2\nu_1^2 + \nu_2^2 - 3\nu_1\nu_2/(15\nu_2 - 27\nu_1)$; in the free ion $B = 1038$, $\beta = B_{\mathrm{complex}}/B_{\mathrm{free\ ion}}$ and ${}^3\mathrm{A_{2g}}$–${}^3\mathrm{T_{2g}}$ (ν_1) and ${}^3\mathrm{A_{2g}}$–${}^3\mathrm{T_{1g}}$ (ν_2).

values observed for 1 : 1 compounds which are comparatively lower than the 1 : 2 complexes.

The nephelauxetic ratio calculation (β) [32,33] obtained for 1 : 1 nickel complexes is lower than 1 : 2 compounds, indicating that delocalization of the nickel t_{2g} electron cloud toward coordinated ligand atoms is greater for the former complexes than for the latter. The significantly lower value of β (covalency parameter) for the nickel complex with sulfur containing ligands (bbms and bbes), where the metal electron clouds expand towards the thioether sulfur is much higher than with the nitrogen atom; hence the thioethers manifest a much greater nephelauxetic effect [34,35]. Further, the Dq is slightly lower for $\mathrm{Ni(bbma)_2^{2+}}$ with respect to $\mathrm{Ni(bpma)_2^{2+}}$ [24]; this is undoubtedly due to the importance of the strongly π-bonding pyridine donors in pyridyl containing complexes over the strongly σ-donating but sterically demanding nitrogen from benzimidazole in bezimidazole containing ligands.

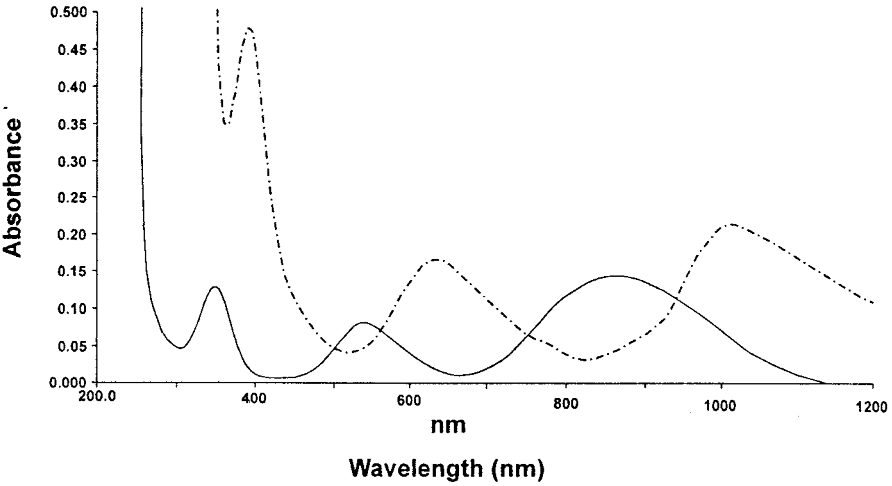

FIGURE 4 Electronic absorption spectra of $Ni(bbes)_2^{2+}$(— · — · —) and $Ni(dien)_2^{2+}$(—).

NMR Studies

The ^1H NMR spectroscopy was performed in order to show that the solid state structure of $Ni(bbma)_2^{2+}$, $Ni(bbes)_2^{2+}$ and $Ni(dien)_2^{2+}$ is preserved in solution. The chemical shifts (in ppm) for the complexes are collected (below) along with our proposed assignments. The dipolar broadened, isotropical contact-shifted resonance was observed for the complexes in the range 6.5–28.2 ppm, which is typical of high spin nickel(II) [36,37]. The contact-shifted broaden signal (74.1 ppm for bbma and 66.8 ppm for bbes) has been assigned to C(4)–H (the proton from bzim ring) which lies closest to Ni(II). The sharp peaks in the range 6.5–8.1 ppm for $Ni(bbma)_2^{2+}$ and 7.7–7.5 for $Ni(bbes)_2^{2+}$, correspond to other bzim-ring protons which lie farther from the Ni(II). The broad peaks at 16.3 and 29.7 ppm are assigned to the N–H protons from the benzimidazole and the secondary amino groups, respectively. It is interesting to observe that the broad signal at 16.3 (N–H of Bzim) for $Ni(bbma)_2^{2+}$ is moved down to 14.1 ppm for $Ni(bbes)_2^{2+}$, suggesting that the benzimidazole coordination is more effective towards the nickel ion, *i.e.* the Ni^{2+} is closer to bbma than bbes; this is consistent with the observed bond length, $Ni–N_{bzim}$ for bbma, which is shorter than that of bbes (Fig. 3). For $Ni(dien)_2^{2+}$, which is insoluble in methanol, the solvent mixture (DMSO-d_6 and CD_3OD) was used to record the NMR spectra, in which only two signals were obtained. The first is at 4.04 ppm, corresponding to $-CH_2-$ and the other is around 24.3 ppm (broad), which corresponds to the amino group of the dien;

$Ni(bbma)_2^{2+}$	*Assignments*	$Ni(bbes)_2^{2+}$	*Assignments*	$Ni(dien)_2^{2+}$	*Assignments*
6.5–8.1	C–H (bzim)	6.7–7.5	C–H (bzim)	4.40	$-CH_2-$
16.3	N–H (bzim)	14.1	N–H (bzim)	–	–
28.4	$-CH_2$	28.2	$-CH_2$	–	–
29.7	N–H	–	–	24.3	N–H
74.1	C(4)–H (bzim)	66.8	C(4)–H (bzim)	–	–

Bzim=benzimidazole.

the unexpected contact shift value observed for the amino group is certainly due to the solvent effect from the mixture of DMSO-$d_6 + CD_3OD$. The value was expected to appear less than the value of N–H of bzim (14.1 ppm), because the Ni–N_{amine} bond length [25] reported in earlier crystal structural data, is much less than that of Ni–N_{bzim} [22]; thus the non-preservability of solid state structure of $Ni(dien)_2^{2+}$ in solution is established.

Electrochemical Properties

The redox behavior of the Ni(II) complexes was studied by using cyclic voltammetry (CV) on a stationary platinum electrode. Electrochemical experiments were carried out in methanol, and tetra-*n*-hexylammonium perchorate was used as a supporting electrolyte. Since all the nickel complexes exhibit an irreversible Ni(I)/Ni(II) redox process, except $Ni(bbma)_2^{2+}$, which reveals a quasi-reversible redox behavior, the Differential Pulse Voltammetry (DPV) technique was employed to measure $E_{1/2}$ for the complexes. Electrochemical data collected for the complexes are presented in Table III. The non-Nernstian behavior may be ascribed to heterogeneous electron-transfer kinetics. This is evident from the cathodic shift of the reduction peak and the anodic shift of the oxidation wave that increases with the scan rate [38]. As expected, the nickel complexes with thioether ligands (bbes or bbms) exhibit a more positive potential than complexes of bbma and dien (Fig. 5), because of the thioether sulfur, which is both a weak σ-donor and a weak π-acceptor in contrast to the purely σ-donor amine nitrogens; this is consistent with the ligand field values obtained in the electronic spectral studies for the complexes. The order of the redox potentials [Ni(II)/Ni(I)] of perchlorates (Table III) is $[Ni((dien)_2)^{2+} < [Ni(bbma)_2)^{2+} < [Ni(bbes)_2)^{2+} \approx [Ni(bbes)_2]^{2+}$; this order demonstrates that stabilization of Ni(II) is greater with the σ-donor nitrogen than the both weak σ-donor and weak π-acceptor.

CONCLUSION

The stereochemistry of nickel complexes with the tridentate ligands shows that *facial* coordination is facilitated when the terminal donor sites of the tridentate ligand are

TABLE III Electrochemical data[a] of Ni(II) complexes at 25°C

Compounds	$E^{b}_{1/2}(V)$	$E^{c}_{pc}(V)$
$[Ni(bbes)](ClO_4)_2 \cdot 2H_2O$	−0.708	−0.810 0.120
$[Ni(bbes)_2](ClO_4)_2$	−0.715	−0.783
$[Ni(bbms)_2](ClO_4)_2 \cdot 2H_2O$	−0.705	−0.812
$[Ni(dien)](ClO_4)_2 \cdot 2H_2O$	−1.182	0.162 −1.056
$[Ni(dien)_2](ClO_4)_2$	−1.212	−1.154
$[Ni(bbma)](ClO_4)_2 \cdot MeOH \cdot H_2O$	−0.982	−0.799
$[Ni(bbma)_2](ClO_4)_2 \cdot MeOH$	−1.106	−0.806

[a] Measured *vs.* non-aqueous silver reference electrode; add 544 mV to convert into normal hydrogen electrode (NHE); scan rate 50 mV s^{-1}, supporting electrolyte tetra-n-hexylammonium perchlorate (0.1 M); complex concentration 1.0 mM.
[b] Difference Pulse Voltammetry, scan rate 1.0 mV s^{-1}, pulse height 50 mV.
[c] Cathodic potential.

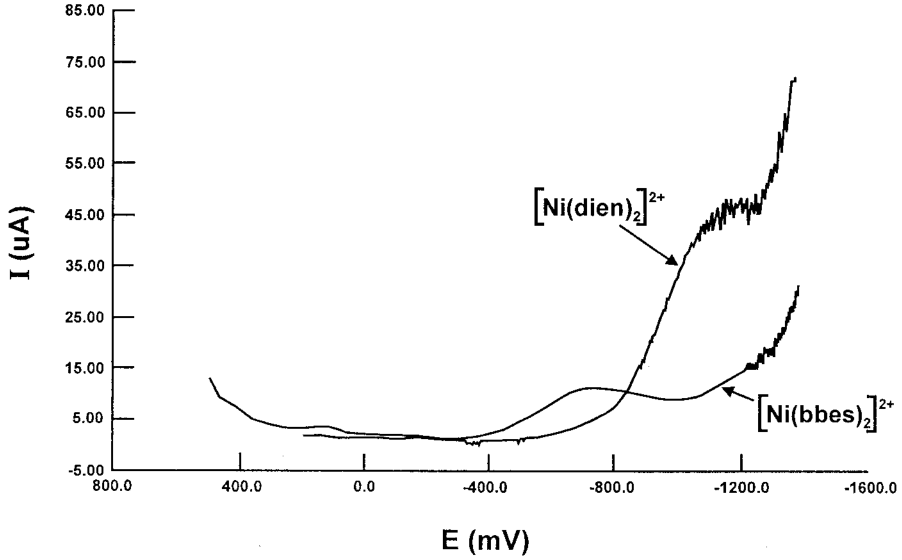

FIGURE 5 Differential pulse voltammograms of 1 mM Ni(bbes)$_2^{2+}$ and Ni(dien)$_2^{2+}$ in methanol at 25°C. Supporting electrolyte: 0.1 M $(NC_6H_{13})_4ClO_4$. Scan rate 1.0 m V s^{-1}.

occupied by the benzimidazole, which implies that the termini possess partially rigid donors that reduce the σ-bonding as well as enhance the π-bonding ability, thus, favoring the *facial* structure. On the other hand, when primary amine nitrogens with strong σ-donor ability are at the termini of the ligand, only *meridional* coordination is facilitated. Although, it is very difficult to predict *facial* or *meridional* geometry by electronic spectral results, the strong σ-donor termini tridentate ligand bis-diethylenetriamine considerably shifts the ligand field band to higher energy than the pyridine (strong π-bond donors) or strong σ-donating with sterically demanding benzimidazole ligands. This observation is supported by the lower redox potential obtained for Ni(dien)$_2^{2+}$ than Ni(bbma)$_2^{2+}$ and Ni(bbes)$_2^{2+}$.

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