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Benign synthesis of carboxamide ligands, H_2Me_2bqb and H_2Me_2bpb . Preparation, characterization and electrochemistry of Ni(II) complexes: The crystal structure of [Ni^{II}(Me_2bqb)]

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Dedicated to Professor Shadpour Mallakpour of Isfahan University of Technology, a pioneer in the synthesis of Step-Growth Polymers such as polyamides in Ionic Liquids, on the occasion of his 57th birthday.

Keywords: Ionic liquid Benign synthesis Bispyridylamide Ni(II) complexes Crystal structure Cyclic voltammetry

1. Introduction

Chemical reactions largely are performed in solutions of volatile organic compounds which are difficult to contain, and are often flammable or peroxidizable and toxic by inhalation. Other harmful compounds, such as pyridine, are also used as solvent in the synthesis of organic compounds such as carboxamides [1–5].

Green chemistry searches for alternative, environmentally friendly reaction media and at the same time strives to increase the reaction rate and efficiency, and lower the reaction temperature. One of the key areas of green chemistry is the replacement of hazardous solvents with environmentally benign ones or the elimination of solvents altogether [6–11].

ABSTRACT

A novel and highly efficient approach for the synthesis of H_2Me_2bqb and H_2Me_2bpb using ionic liquid as an environmentally benign reaction medium has been developed, eliminating the need for the pyridine as a toxic solvent. The Ni(II) complex of the dianionic ligand Me_2bqb^{2-} , $[Me_2bqb^{2-} = 1,2-bis(quinoline-2-carboxamide)-4,5-dimethyl-benzene dianion], has been synthesized and characterized by elemental analyses and spectroscopic methods, and the crystal and molecular structure of <math>[Ni(Me_2bqb)]$ (1), has been determined by X-ray crystallography. The complex exhibits distorted square-planar NiN₄ coordination geometry with two short and two long Ni–N bonds (Ni–N ~1.85 and ~1.96 Å, respectively). The electrochemical behavior of $[Ni(Me_2bqb)]$ (1), has been studied by cyclic voltammetry and compared with the analogous complex, $[Ni(Me_2bpb)]$ (2).

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lonic liquids (ILs) are novel solvents, attracting interest as greener alternatives to conventional hazardous solvents with the aim of facilitating sustainable chemistry [12–17]. However, the high-cost and the potential risk of toxicity associated with common room temperature ILs [18–21] has led to the use of more benign salts in the molten state as practical alternatives. Molten TBAB (tetrabutylammonium bromide), for example, has proved to be an efficient catalyst in a number of useful synthetic transformations [22–27]. These reactions catalyzed by molten TBAB are in general, very fast and clean.

The classical method for the synthesis of carboxamide derivatives, used as ligands, is the reaction of the amines with the appropriate carboxylic acids in pyridine in the presence of an activator such as triphenyl phosphite [1]. Drawbacks of this method include modest yields, and the health hazards resulting from the use of pyridine as the reaction solvent. Using this classical method, a large variety of carboxamido ligands have been synthesized with the goal of investigating their metal-binding properties [2], and providing models from the standpoint of bioinorganic chemistry

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[28]. These ligands have also been used for asymmetric catalysis [29–31], dendrimer synthesis [32], design of molecular receptors [33–35], preparation of metal complexes with antitumor properties [3,36,37], and controlling the molecular architecture [38,39].

Extensive investigation has been devoted to nickel coordination chemistry with amide based ligands, and nickel ion binding to peptides has been recently reviewed [40]. Peptides and proteins are able to form coordination complexes with nickel(II) and copper(II) through ligation of deprotonated amide nitrogens [41,42]. Such coordination helps to stabilize the nickel(III) oxidation state, which may play a key role in the observed DNA strand scission and DNAprotein cross-links [43,44]. Although many nickel complexes have been synthesized and their properties studied, it is only recently that they have found more application in catalysis. Nickel complexes with functionalized bipyridine ligands, potentially tetradentate ligands, have been recently reported to show high catalytic activity toward norbornene polymerization [30,31].

In an attempt towards the development of new methods for the synthesis of carboxamide ligands and following our earlier studies on the synthesis of their complexes, we herein report a new synthetic method for the preparation of H_2Me_2bqb [3] and H_2Me_2bpb [45], replacing the pyridine by TBAB (ionic liquid) as the reaction media. The synthesis, characterization and properties of the new complex [Ni^{II}(Me_2bqb)] (1), are also reported and compared with those of [Ni^{II}(Me_2bpb)] (2), the synthesis of which has already been reported [29]. These results obtained in this work give us an opportunity to elucidate the effect of the fused benzene ring on the spectral and electrochemical properties of these complexes in going from Me_2bpb^{2-} to Me_2bqb^{2-} .

2. Experimental

2.1. Materials and general methods

All solvents and chemicals were from Merck and Aldrich (Grade Pro Analysi). IR spectra were measured with a FT-IR JASCO 680 spectrometer using KBr pellets. Elemental analyses were performed by using a Perkin-Elmer 2400II CHNS-O elemental analyzer. The mass spectra were recorded using a Waters micromass Q-TOF-2 spectrometer in positive ion mode. UV-Vis spectra were obtained on a JASCO V-570 spectrophotometer. Cyclic voltammograms were recorded by using a SAMA 500 Research Analyzer. Three electrodes were utilized in this system, a glassy carbon working electrode, a platinum disk auxiliary electrode and Ag wire as reference electrode. The glassy carbon working electrode (Metrohm 6.1204.110) with 2.0 ± 0.1 mm diameter was manually cleaned with 1 µm alumina polish prior to each scan. Tetrabutylammonium hexafluorophosphate (TBAH) was used as supporting electrolyte. The solutions were deoxygenated by purging with Ar for 5 min. All electrochemical potentials were calibrated versus internal Fc^{+/0} couple under the same conditions [46].

2.2. Synthesis

2.2.1. Synthesis of the ligands

2.2.1.1. H_2Me_2bqb . A mixture of 0.62 g (2 mmol) triphenyl phosphite (TPP), 0.97 g (3 mmol) tetrabutylammonium bromide (TBAB), 0.35 g (2 mmol) quinaldic acid, and 0.14 g (1 mmol) 4,5-dimethyl-1,2-phenylenediamine in a 25 mL round bottom flask was placed in an oil bath. The reaction mixture was heated until a homogeneous solution was formed. The solution was stirred for 1 h at 120 °C. The viscous solution was precipitated by adding 20 mL methanol and the resulting white solid was filtered-off and washed with cold ethanol. The crude product was recrystallized from a mixture of MeOH/CHCl₃ (1:1, V/V). Yield 75%. m.p.

260°C. *Anal.* Calc. for C₂₈H₂₂N₄O₂ (446.50): C, 75.32; H, 4.97; N, 12.55. Found: C, 74.78; H, 4.77; N, 12.33%. ESI-MS: *m*/*z* = 469.16 [M+Na]⁺. FT-IR (KBr, cm⁻¹): *v*_{max}: 3339 (s, N–H), 1688 (s, C=O), 1589 (m, C=C), 1525 (m, C–N). UV–Vis (chloroform): λ_{max} (nm) (ε , L mol⁻¹ cm⁻¹): 330 (15 845), 319 (17 460), 286 (21 440), 241 (90 960). ¹H NMR (CDCl₃, 500 MHz): δ = 2.34 (s, 6H, Me), 7.61 (m, 4H), 7.78 (s, 2H), 7.88 (m, 4H), 8.36 (d, 2H), 8.45 (d, 2H), 10.51 (s, 2H, NH).

2.2.1.2. *H*₂*Me*₂*bpb*. The H₂Mebpb was synthesized by a procedure similar to that used for H₂Me₂bqb except that picolinic acid was used instead of quinaldic acid. The viscous solution precipitated in 10 mL of 1:1 methanol–water mixture. Yield 78%. *Anal.* Calc. for C₂₀H₁₈N₄O₂ (346.38): C, 69.35; H, 5.24; N, 16.17. Found: C, 69.01; H, 5.18; N, 15.84%. ESI-MS: *m*/*z* = 369.13 [M+Na]⁺. FT-IR (KBr, cm⁻¹) *v*_{max}: 3328, 3221 (m, NH), 1677, 1666(s, C=O), 1594 (m, C=C), 1510 (m, C–N). UV–Vis: λ_{max} (nm) (ε , L mol⁻¹ cm⁻¹) (CHCl₃): 290 (12 250), 268 (14 950), 230 (19 550). ¹H NMR (CDCl₃, 500 MHz): δ = 2.29 [s, 6H, Me], 7.44 (m, 2H), 7.62 (s, 2H), 7.88 (m, 2H), 8.30 (d, 2H), 8.55 (d, 2H), 10.16 (s, 2H, NH).

2.2.2. Synthesis of $[Ni(Me_2bqb)]$ (1)

To a solution of nickel(II) acetate tetrahydrate (24.9 mg, 0.1 mmol) in methanol (20 mL) was added slowly a solution of H₂Me₂bqb (44.6 mg, 0.1 mmol) in dichloromethane (20 mL). The resulting dark red solution was stirred for 8 h. Slow evaporation of this solution afforded dark red crystals suitable for X-ray crystallography. The crystals were filtered-off and washed with diethyl ether-dichloromethane-methanol (8:1:1 v/v), and dried in vacuum. Yield 94%. *Anal.* Calc. for C₂₈H₂₀N₄O₂Ni (503.18): C, 66.84; H, 4.01; N, 11.13. Found: C, 66.87; H, 3.85; N, 11.15%. FT-IR (KBr, cm⁻¹): v_{max} : 1626 (s, C=O), 1587 (m, C=C), 1559 (m, C-N). UV-Vis (Chloroform): λ_{max} (nm) (ε , L mol⁻¹ cm⁻¹): 535 (2362) 424 (5838), 352 (19 280), 322 (33 923), 244 (101 675).

2.2.3. Synthesis of [Ni(Me₂bpb)] (2)

The [Ni(Me₂bpb)] complex was synthesized according to the literature procedure [29]. Anal. Calc. for $C_{20}H_{16}N_4O_2Ni$ (403.06): C,

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Crystal data	and	structure	refinement	for	(1

Crystal data and structure refinement for (1))
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Chemical formula	C ₂₈ H ₂₀ N ₄ NiO ₂
Formula weight	503.19
T (K)	100(2)
Crystal system, space group	triclinic, <i>P</i> 1
a (Å)	10.2852(10)
b (Å)	10.4527(10)
c (Å)	11.7761(12)
α (°)	64.578(1)
β (°)	81.846(1)
γ (°)	69.458(1)
$V(Å^3)$	1070.67(18)
Z , D_{calc} (Mg m ⁻³)	2, 1.561
Crystal size (mm)	$0.60\times0.30\times0.12$
$\mu (\mathrm{mm}^{-1})$	0.943
F(0 0 0)	520
θ Range (°)	2.56-30.0
Index ranges	$-14\leqslant h\leqslant 14$, $-14\leqslant k\leqslant 14$,
	$-16 \leqslant l \leqslant 16$
Reflections collected	15 752
Independent reflections (R_{int})	6161(0.018)
Absorption correction	multi-scan
Minimum and maximum transmission	0.75, 0.89
Data/restraints/parameters	6161/0/318
Goodness-of-fit (GOF) on F^2	1.058
Final <i>R</i> indices $[F^2 > 2\sigma(F)]$	$R_1 = 0.028, wR_2 = 0.075$
R indices (all data)	$R_1 = 0.029, wR_2 = 0.076$
Maximum/minimum Δho (e Å $^{-3}$)	0.57 and -0.53

59.60; H, 4.00; N, 13.90. Found: C, 58.96; H, 3.84; N, 14.08%. FT-IR (KBr, cm⁻¹) ν_{max} : 1643 (s, C=O), 1604 (s, C=C), 1564 (m, C–N).

2.3. X-ray crystallography

The diffraction data for compound (1) were collected on a Bruker Kappa APEX-2 CCD diffractometer employing graphite-monochromated Mo K α (λ = 0.71073 Å) radiation at *T* = 100 K. Cell refinement and data reduction were performed with the help of program SAINT [47]. Correction for absorption was carried out with the multi-scan method and program SADABS [47]. The structure was solved with direct methods and refined on *F*² using SHELXTL [47]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were inserted in idealized positions and were refined riding with the atoms to which they were bonded. The crystallographic and refinement data are summarized in Table 1.

3. Results and discussion

3.1. Synthesis and characterization

3.1.1. Synthesis of the ligands

Since the recognition of ILs as new reaction media and catalysts. these compounds have been used for replacing hazardous solvents. reducing reaction time, and increasing yields of products compared to conventional methods [6-11]. We have used an efficient and benign procedure for the preparation of the two carboxamide ligands, H₂Me₂bqb and H₂Me₂bpb by eliminating the toxic pyridine and using TBAB as the reaction media. The significant advantages of using TBAB are to avoid the use of toxic pyridine, drastic reduction of the reaction time, and a considerable increase in the yields of products. The optimization of the reaction condition by varying the reaction temperature, period of heating, and amount of TBAB were examined to obtain the products in high yield. Interestingly, in the preparation of H₂Me₂bqb carried out by this method, the reaction time reduced from 5 to 1 h and the yield increased from 57% to 75% as compared to the conventional method reported in the literature [3]. The reaction time for the synthesis of H₂Me₂bpb by this method reduced from 4 to 1 h and the yield increased from 47% [45] to 78%.

3.1.2. Synthesis of complexes

The new Ni(II) complex of the dianionic ligand, Me_2bqb^{2-} , was prepared by the reaction of equimolar quantities of the ligand and nickel acetate in methanol–chloroform solution. Dark needle like crystals of Ni(Me_2bqb) (1), suitable for X-ray structure analysis were obtained by slow evaporation of the solvent over a period of one week at room temperature. Ni(Me_2bpb) (2), was prepared according to the published procedure [29].

3.2. Description of structure of [Ni(Me₂bqb)] (1)

Table 1 summarizes the crystal data, together with other relevant information on structure determination, for complex (1). Table 2 gives significant bond lengths and angles. A perspective view of (1), with atom labelling scheme, is shown in Fig. 1. Fig. 2a and b is the packing illustrations. The nickel complex (1) has a square-planar structure distorted towards a tetrahedron as evidenced by the N2–Ni1–N3 and N1–Ni1–N4 bond angles of 165.66(4)° and 165.18(4)°. The average N(amide)–Ni bond length of 1.848(1) Å in (1) and 1.920(2) Å in (2) [29] agrees with those reported (1.82–2.02 Å) for other deprotonated N(amide)–Ni bonds [4] and is significantly shorter than the N(quinoline/pyridine)–Ni bond length of 1.961(1) Å in (1) and 2.02(2) in (2) [29]. This is in accord with the fact that the deprotonated amide nitrogen is a very

Table 2

Selected bond lengths (Å) and angles (°) for (1).

Bond lengths	
Ni1-N2	1.8468(10)
Ni1-N4	1.8488(10)
Ni1-N1	1.9595(10)
Ni1-N3	1.9623(10)
01-C1	1.2372(14)
02-C11	1.2375(14)
N2-C1	1.3426(14)
N2-C21	1.4055(14)
N4-C11	1.3372(15)
N4-C26	1.4048(14)
Bond angles	
N1-Ni1-N2	83,47(4)
N3-Ni1-N4	83.04(4)
N2-Ni1-N4	84.09(4)
N1-Ni1-N3	110.12(4)
N1-Ni1-N4	165.18(4)
N2-Ni1-N3	165.66(4)
C1-N2-C21	125.88(10)
C1-N2-Ni1	117.31(8)
C21-N2-Ni1	115.57(8)
C11-N4-C26	126.29(10)
C11-N4-Ni1	117.30(8)
C26-N4-Ni1	115.53(8)
N2-C21-C26	112.34(10)
N4-C26-C21	112.34(10)
01-C1-N2	128.71(11)
01-C1-C2	121.50(10)
N2-C1-C2	109.73(10)
N4-C11-O2	129.23(11)
C12-C11-O2	121.33(10)
N4-C11-C12	109.39(9)



Fig. 1. ORTEP diagram of complex (1) with the atom labelling scheme.

strong σ donor. The cis angles in the two complexes span a wide range, 83.04(4)°-110.12(4)° in (1), and 82.75(7)°-111.72(10)° in (2), which is usual for complexes of H₂bpb and H₂bqb ligands [4,5,29,48].

The dihedral angle between the Ni/Nam/Nam' and Ni/Npy/Npy' planes at the nickel atom is $8.88(8)^{\circ}$ for (1) and 4.24° for (2) [29]. Two pyridyl rings are tilted a lot with the dihedral angle of $25.80(5)^{\circ}$ for (1) and 9.42° for (2) [29]. The steric hindrance due to the quinoline rings in (1) (side-on contact between C9 and C19 of only 2.914 Å) leads, as expected, to a larger tetrahedral distortion of the nickel atom than the modest hindrance from the pyridines in (2) (contact distance between ortho-H atoms 2.2 Å). These differences show some influence on the electronic spectra and the redox potentials of the two complexes (vide infra).

The geometrical properties of the two complexes in the solid state are comparable to the parent complexes [Ni(bpb)] [48,49], [Ni(bqb)] [4], [Ni(Mebpb)], [Ni(Mebqb)] [50] and their relatives [Co(bpb)] [51], [Cu(bpb)] [52], and [Cu(Mebpb)] [38].



Fig. 2. Packing diagrams of (a) [Ni(Me₂bqb)] (1) viewed down the *b*-axis of the triclinic primitive unit cell (black parallelogram), and (b) [Ni(bqb)] [4] viewed along the *c*-axis of the monoclinic *C*-centered unit cell. In diagram (a) the orange parallelogram outlines the triclinic C-centered unit cell (see text) and the pink lines on the left symbolize the two different kinds of π - π -stacking interactions between the quinoline moieties. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

The architecture of the crystal structure of $[Ni(Me_2bqb)]$ (1) shows interesting relationships with its homologues [Ni(bqb)] [4] and [Ni(Mebqb)] [50]. The parent compound [Ni(bqb)] crystallizes in a monoclinic C-centered lattice of space group C2/c, a = 17.425 Å, b = 12.968 Å, c = 9.726 Å, $\beta = 115.28^{\circ}$, V = 1987.4 Å³, Z = 4 [4]. The [Ni(bqb)] complexes adopt a crystallographic C_2 symmetry and are aligned with their longest extension parallel to the b-axis. The structure is dominated by one-sided π - π -stacking interactions between the quinoline moieties of neighbouring [Ni(bqb)] complexes forming thereby columns parallel to [101]. On transition to [Ni(Mebqb)], i.e. by addition of a methyl group, the previous packing is largely retained and apart from modest changes in unit cell dimensions, essentially only the symmetry of the complex as well as that of the lattice is lowered by the loss of C_2 symmetry whereas the *c*-glide planes are retained. Thus, the unit cell data of [Ni(Mebgb)] are perceptibly similar to the parent compound: space group *Cc*, *a* = 17.092 Å, *b* = 13.791 Å, *c* = 9.692 Å, $\hat{\beta} = 115.18^{\circ}$, $\hat{V} = 2067.5 \text{ Å}^3$, Z = 4 [50]. The addition of two methyl groups to [Ni(bqb)] under formation of [Ni(Me₂bqb)] (1) leads to a more significant change in the crystal lattice. As shown in Table 1, a triclinic lattice with space group $P\overline{1}$ is the result. None the less, the structure of [Ni(Me₂bqb)] retains a remarkable close relationship to the parent lattice of [Ni(bqb)], which becomes evident by using a unit cell with following new base vectors: $\mathbf{a}_{new} = \mathbf{a} + \mathbf{c}$, $\mathbf{b}_{\text{new}} = \mathbf{c} - \mathbf{a}$, $\mathbf{c}_{\text{new}} = -\mathbf{b}$ (cf. Fig. 2). This new unit cell has space group symmetry $C\overline{1}$ and cell dimensions a' = 16.698 Å, b' = 14.495 Å, c' = 10.453 Å, $\alpha' = 95.73^{\circ}$, $\beta' = 121.26^{\circ}$, $\gamma' = 82.19^{\circ}$, $V = 2135.3 \text{ Å}^3$, Z = 4. While the basic alignment and spatial arrangement of the Ni complexes in [Ni(bqb)] is retained in [Ni(Me₂bqb)], their interactions are different. For example, the quinoline moiety 1 (N1, C2 to C10) shows a π - π -stacking interaction over its full length of two rings with a centrosymmetric equivalent, but the quinoline moiety 2 (N3, C12 to C20) shows such an interaction only for its terminal benzene ring (C15 to C20) but not for its pyridine part (Fig. 2a). As a result the distortion of the complex [Ni(Me₂bqb)] in solid state is notably asymmetric and the quinoline moiety 2 is more bent from the plane of the o-phenvlene diamine part than the quinoline moiety 1 (e.g. C9 and C19 deviate by 0.84 and -1.67 Å from this plane).

3.3. Spectral studies

The FT-IR spectral data of the complexes are listed in Section 2. The amidic NH exhibits a band at 3321-3339 cm⁻¹ in the IR spec-

tra of H₂Me₂bqb and the H₂Me₂bpb ligands. The lack of N-H stretching bands in the IR spectra of these two complexes confirms that the ligands are coordinated in their deprotonated form [48]. A further indication of the formation of deprotonated complexes is the rather large decrease in the carbonyl stretching frequency exhibited by the ligands upon complex formation. The two sharp C=O stretching vibration bands at 1688 cm^{-1} for H₂Me₂bqb and 1677 and 1666 cm⁻¹ for H₂Me₂bpb are shifted to lower frequencies, which is in accordance with the data reported for the related complexes [4,5]. The observation of a sizable increase in the frequency of C-N stretching vibration of medium intensity for the coordinated Me_2bqb^{2-} (1587 cm⁻¹) and Me_2bpb^{2-} (1564 cm⁻¹) relative to the free ligands (1525 and 1510 cm⁻¹, respectively) gives additional support to the coordination of these amides in their deprotonated form. This is presumably due to the resonance enhancement in the deprotonated amide which in turn leads to the strengthening of C–N bond [48].

The absorption spectral data are reported in Section 2. The H_2Me_2bqb ligand exhibits a shoulder at 330 nm ($\varepsilon = 15845 L mol^{-1} cm^{-1}$), two overlapping bands at 319 nm ($\varepsilon = 17460 L mol^{-1} cm^{-1}$) and 286 nm ($\varepsilon = 21440 L mol^{-1} cm^{-1}$), and a distinct absorption band at 241 nm ($\varepsilon = 90960 L mol^{-1} cm^{-1}$). The peak positions of the ligand undergo a red shift of 33–94 nm when complex (1) is formed. [Ni(Me₂bqb)] exhibits two broad bands at 424 nm ($\varepsilon = 5838 L mol^{-1} cm^{-1}$) and 535 nm ($\varepsilon = 2362 L mol^{-1} cm^{-1}$) which are assigned to the ligand field transitions with CT admixture.

The UV–Vis spectra of H₂Me₂bpb ligand displays a shoulder at 290 nm ($\varepsilon = 12\ 250\ L\ mol^{-1}\ cm^{-1}$) and two bands at 268 nm ($\varepsilon = 14\ 950\ L\ mol^{-1}\ cm^{-1}$) and 230 nm ($\varepsilon = 19\ 550\ L\ mol^{-1}\ cm^{-1}$). A red shift of 1–34 nm is observed in the spectrum of the coordinated ligand in Ni(Me₂bpb). An additional new shoulder at 427 nm appears in the spectrum of Ni(Me₂bpb) complex which is assigned to the ligand field transitions with CT admixture, and is consistent with the square-planar structure of the complex having slight tetrahedral distortion (vide supra) [53]. It is reasonable to assume that there is a larger tetrahedral distortion in (1) relative to (2) leading to the splitting of the electronic states and appearance of additional absorption bands.

3.4. Electrochemistry

Table 3

The electrochemical behavior of the two ligands H₂Me₂bqb and H₂Me₂bpb and their corresponding Ni(II) complexes, in dichloromethane solutions with 0.1 M [N(*n*-Bu)₄]PF₆ as the supporting electrolyte, was studied at a glassy carbon working electrode. The approximate concentrations of the compounds were 10^{-3} to 10^{-4} M. The electrochemical data obtained in this study are summarized in Table 3.

As reported in our previous studies, the carboxamide ligands are electroactive in the potential range of 1.5 to -2 V in different solvents [50,5]. Fig. 3 shows the cyclic voltammogram of H₂Me₂bqb ligand. The electrochemically irreversible anodic peak at +1.56 V, is due to the oxidation of 1,2-diaminobenzene ring [50,5]. Using spectroelectrochemistry and EPR spectroscopy, Wieghardt et al., established that the π system in the 1,2-diaminoben-

Redox potentials of H2Me2bqb and H2Me2bpb ligands and corresponding complexes.^a

Compound	$E_{\rm pc}1$	$E_{\rm pa}1$	$E_{\rm pc}2$	$E_{\rm pa}2$	$E_{\rm pc} \ {\rm Ni}^{\rm III/II}$	E _{pa} Ni ^{II/III}
H ₂ Me ₂ bqb	0.21	1.56	-1.81	0.02	-	_
[Ni ^{II} (Me ₂ bqb)]	-0.41 1.24	1.34	-2.05 -1.32	-0.14 -0.44	0.75	0.81
[Ni ^{II} (Me ₂ bpb)]	1.28	1.41	-1.57		0.77	0.86

^a Potentials are vs. Fc^{+/0} in 0.1 M TBAH, T = 298 K. Scan rate 100 mV s⁻¹. Approximate concentrations: 10⁻³ to 10⁻⁴ M. In the text $E_{1/2} = (E_{pc} + E_{pa})/2$.



Fig. 3. Cyclic voltammogram of H_2Me_2bqb , $c = 7.8 \times 10^{-4}$ M in CH_2Cl_2 at 298 K. Scan rate, 100 mV s⁻¹.

zene ring is the expected site of oxidation, generating a cation radical [54]. The irreversible reduction peak at -1.81 V (Fig. 3) is attributed to the first step reduction of quinoline rings and is shifted to the more positive values in the corresponding complexes (Table 3).

Similar behavior is observed for H_2Me_2bpb ligand. In general the redox couples of this ligand are shifted to more cathodic potentials relative to those of H_2Me_2bqb . The presence of a quinolic ring makes the reduction potential more positive for H_2Me_2bqb relative to H_2Me_2bpb ligand.

The cyclic voltammogram of the $[Ni^{II}(Me_2bqb)]$ (1) was measured in dichloromethane solvent and the representative voltammogram is shown in Fig. 4. The first quasi-reversible oxidation process at $E_{1/2} = 1.31$ V (Fig. 4 and Table 3), is mainly ligand centered. The oxidized form of the deprotonated ligand is stabilized by coordination to Ni(II). This is presumably due to the increased delocalization of electrons in the more planer conformation, acquired by the coordinated ligand. The observation of a similar redox process in our previous investigations [50,5] gives further support to this assignment. The second reversible oxidation process at $E_{1/2} = 0.78$ V (Fig. 4 and Table 3), is due to the Ni^{II/III} redox process, which is in agreement with similar reports on carboxamido Ni(II) complexes [50,55]. The final electrochemically irreversible



Fig. 4. Cyclic voltammogram of [Ni^{II}(Me₂bqb)], $c = 2.7 \times 10^{-3}$ M in CH₂Cl₂ at 298 K. Scan rate, 100 mV s⁻¹.



Fig. 5. Cyclic voltammogram of $[Ni^{II}(Me_2bpb)]$, $c = 4.8 \times 10^{-4}$ M in CH₂Cl₂ at 298 K. Scan rate, 100 mV s⁻¹.

reduction process observed at $E_{\rm pc}$ of -1.32 V, is attributed to the one step reduction of the quinoline rings. The second step reduction of the quinoline rings is obscured due to the potential scanning limitations of dichloromethane solvent.

The cyclic voltammogram of [Ni^{II}(Me₂bpb)] (2) in dichloromethane solution (Fig. 5) shows features similar to those observed for [Ni^{II}(Me₂bqb)] (1). It is interesting to note that, the first ligand centered and second Ni^{II/III} oxidation processes at $E_{1/2}$ = 1.345 and 0.815 V are shifted to more positive values relative to those observed for [Ni^{II}(Me₂bqb)] (**1**) (1.305 and 0.78 V), demonstrating the weaker electron-donating character of Me₂bpb²⁻ ligand in (2) relative to Me_2bqb^{2-} in (1). This behavior conforms to the structural data obtained from X-ray structure analysis (Table 2). The average bond lengths of Ni-Nam (1.848 Å) and Ni-Ngu (1.960 Å) in $[\text{Ni}^{II}(\text{Me}_2\text{bqb})]$ (1) are shorter than Ni–N_{am} (1.920 Å) and Ni–N_{pv} (2.02 Å) in [Ni^{II}(Me₂bpb)] (2) complex. For complex 1, the occurrence of the first quasi-reversible oxidation process at lower potential (1.305 V) relative to complex 2 (1.345 V) is most likely due to the higher π -electron delocalization in the coordinated Me₂bqb relative to Me₂bpb.

A comparison between the electrochemical results obtained in this study for $[Ni^{II}(Me_2bqb)]$ (1) and $[Ni^{II}(Me_2bpb)]$ (2) complexes with those of the corresponding monomethyl complexes, $[Ni^{II}(Mebpb)]$ and $[Ni^{II}(Mebqb)]$ [50], reveals that the presence of an additional methyl group on the ligands in (1) and (2) leads to a cathodic shift in the redox potentials of these two complexes relative to those of the corresponding monomethyl complexes.

4. Conclusion

This work demonstrates the synthesis of two carboxamide ligands, H_2Me_2bqb and H_2Me_2bpb , by a new methodology using a green reaction media, and full characterization of two Ni(II) complexes of these two ligands. Part of our characterization includes the single-crystal X-ray structural analysis of [Ni^{II}(Me_2bqb)]. The important findings of this study are:

(1) To the best of our knowledge, for the first time an ionic liquid has been used as the reaction media for the synthesis of aforementioned ligands. The toxic pyridine used in the classical method, has been replaced by TBAB, the yield has increased and the reaction time reduced to a considerable extent. Further application of TBAB in the green and efficient synthesis of other carboxamide ligands is underway in our laboratory.

- (2) The coordination geometry around Ni(II) center in complex (1) is distorted square-planar. In solid state the nickel complex is stabilized by inter-ligand π -stacking interactions causing the complex to deviate significantly from C₂ symmetry of the free complex. The overall solid state structure of (1) is related to that of [Ni^{II}(bqb)] and [Ni^{II}(Mebqb)], but has a triclinic instead of the monoclinic symmetry of the latter.
- (3) In dichloromethane solutions, the Ni(II) complexes are capable of undergoing three 1e⁻ redox processes, one metal-and two-ligand centered. The redox potentials of the coordinated ligands and the metal center are influenced by the inductive effect from the methyl substituents, structural distortions, and charge delocalization by the fused phenyl rings in Me₂bqb.

5. Supplementary data

CCDC 759583 contains the supplementary crystallographic data for **1**. These data can be obtained free of charge via http:// www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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