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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.

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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 $[Ni(Me_2bqb)]$ (**1**), has been determined by X-ray crystallography. The complex exhibits distorted square-planar NiN_4 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**).

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].

Ionic 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 DNA–protein 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/$CHCl_3$ (1:1, V/V). Yield 75%. m.p. 260°C. *Anal.* Calc. for $C_{28}H_{22}N_4O_2$ (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}): ν_{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 ($CDCl_3$, 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_2Me_2bpb. The H_2Mebpb was synthesized by a procedure similar to that used for H_2Me_2bqb 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 $C_{20}H_{18}N_4O_2$ (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}) ν_{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}) ($CHCl_3$): 290 (12 250), 268 (14 950), 230 (19 550). ^1H NMR ($CDCl_3$, 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 H_2Me_2bqb (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 $C_{28}H_{20}N_4O_2Ni$ (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}): ν_{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(Me_2bpb)] (**2**)

The [Ni(Me_2bpb)] complex was synthesized according to the literature procedure [29]. *Anal.* Calc. for $C_{20}H_{16}N_4O_2Ni$ (403.06): C,

Table 1
Crystal data and structure refinement for (**1**).

Chemical formula	$C_{28}H_{20}N_4NiO_2$
Formula weight	503.19
T (K)	100(2)
Crystal system, space group	triclinic, $P\bar{1}$
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 × 0.30 × 0.12
μ (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 R 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 $\Delta\rho$ (e Å^{-3})	0.57 and −0.53