Polyhedron 30 (2011) 1651-1656

Contents lists available at ScienceDirect

Polyhedron



journal homepage: www.elsevier.com/locate/poly

Synthesis, structure and electrochemistry of Co(III) complexes with an unsymmetrical Schiff base ligand derived from 2-aminobenzylamine and pyrrole-2-carboxaldehyde

Soraia Meghdadi^a, Mehdi Amirnasr^{a,*}, Kurt Mereiter^b, Hajar Molaee^a, Ahmad Amiri^a

^a Department of Chemistry, Isfahan University of Technology, Isfahan 84156-83111, Iran
^b Faculty of Chemistry, Vienna University of Technology, Getreidemarkt 9/164SC, A-1060 Vienna, Austria

ARTICLE INFO

Article history: Received 8 February 2011 Accepted 17 March 2011 Available online 1 April 2011

Keywords: Unsymmetrical N₄ Schiff base Co(III) complexes Crystal structure Electrochemistry

ABSTRACT

A series of cobalt(III) complexes with a new unsymmetrical tetradentate Schiff base ligand *N*,*N*'-bis(pyrrol-2-ylmethylene)-2-aminobenzylamine, H₂pyrabza, formed by the condensation of 2-pyrrole carboxaldehyde and 2-aminobenzylamine, has been synthesized and characterized by elemental analyses, IR, UV–Vis and ¹H NMR spectroscopy. These complexes have the general formula *trans*-[Co^{III}(L)(amine)₂]X {L²⁻ = pyrabza, and amine = N-methylimidazole (N-MeIm) (**1**), 3-methylpyridine (3-Mepy) (**2**), 4-methylpyridine (4-Mepy) (**3**), pyridine (py) (**4**), X = BPh₄⁻}. The structure of compound **1** has been determined by X-ray crystallography. The geometry around the central cobalt ion is distorted octahedral. The electrochemical behavior of these complexes was also investigated. The reduction potential of Co(III), ranging from -0.79 V for **1** to -0.44 V for **4**, shows a relatively good correlation with the σ -donor ability of the axial ligands.

© 2011 Elsevier Ltd. All rights reserved.

1. Introduction

For decades, Schiff bases have played a key role as chelating ligands in main group and transition metal coordination chemistry, due to their ease of synthesis, stability under a variety of oxidative and reductive conditions, and their structural versatility associated with their diverse applications [1–6]. Schiff base complexes of transition metals have been used as drugs and they possess a wide variety of biological activity against bacteria, fungi and certain types of tumors [7-13]. Numerous research groups have devoted their effort to the design, synthesis and characterization of transition metal complexes with unsymmetrical ligands. Most of these unsymmetrical ligands are Schiff bases obtained by stepwise condensation of the appropriate diamine with two different carbonyl compounds [14-17]. These compounds may serve as models of relevance for biologically important species [18-20] or as catalysts for various organic transformations [21-25], and are promising materials for optoelectronic applications [26-29] and the design of biosensors [30].

Recently, the discovery of the role played by some cobalt(III) Schiff-base complexes as potent antitumor agents opened up new avenues for the investigation of Co(III) interactions with proteins and nucleic acids [31]. Cobalt(III) Schiff base complexes with

two amines in axial positions have also been used as antiviral and antibacterial agents [32]. A few reports are sited on the unsymmetrical N4 tetradentate Schiff base complexes of cobalt. In continuation of our work on the synthesis and structural studies of Co(III) complexes containing Schiff base ligands [33–35], we report here the synthesis, spectroscopic characterization and electrochemistry of four *trans*-[Co^{III}(L)(amine)₂]BPh₄ complexes with a new unsymmetrical Schiff base ligand. The crystal structure of complex **1** with amine = N-methylimidazole (N-MeIm) is also reported and discussed.

2. Experimental

2.1. Materials and general methods

All solvents and chemicals were of commercial reagent grade and used as received from Aldrich and Merck. Elemental analyses were performed using a Perkin–Elmer 2400II CHNS-O elemental analyzer. UV–Vis spectra were recorded on a JASCO V-570 spectrophotometer. Infrared spectra (KBr pellets) were obtained on a FT-IR JASCO 680 plus spectrophotometer. The ¹H NMR spectra of the complexes were obtained on a BRUKER AVANCE DR (500 MHz) spectrometer. Proton chemical shifts are reported in parts per million (ppm) relative to an internal standard of Me₄Si. Cyclic voltammograms were recorded using a SAMA 500 Research Analyzer. Three electrodes were utilized in this system, a glassy carbon

^{*} Corresponding author. Tel.: +98 311 391 2351; fax: +98 311 391 2350. *E-mail address:* amirnasr@cc.iut.ac.ir (M. Amirnasr).

^{0277-5387/\$ -} see front matter @ 2011 Elsevier Ltd. All rights reserved. doi:10.1016/j.poly.2011.03.041

working electrode, a platinum disk auxiliary electrode and Ag wire as a 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 a supporting electrolyte. Acetonitrile was dried over CaH₂. The solutions were deoxygenated by purging with Ar for 5 min. All electrochemical potentials were calibrated vs. an internal Fc^{+/o} (E° = 0.40 V vs. SCE) couple under the same conditions [36].

2.2. Synthesis

2.2.1. Preparation of the asymmetric Schiff base ligand, H₂pyrabza

The asymmetric ligand, H₂pyrabza, was prepared by condensation of pyrrole-2-carbaldehyde with 2-aminobenzylamine according to the following procedure (Scheme 1). To a stirring solution of 2-pyrrolecarboxaldehyde 0.950 g (10 mmol) in 20 mL of ethanol in a round bottom flask was added 0.620 g (5 mmol) of 2-aminobenzylamine. The mixture was refluxed for 3 h to give a yellow solution. The final reaction mixture was filtered off and the filtrate was kept in a refrigerator for 12 h. The resulting yellow crystals were filtered off, washed with cold ethanol and dried under vacuum. Yield: 1.12 g, 81%. Anal. Calc. for C₁₇H₁₆N₄: C, 73.89; H, 5.84; N, 20.27. Found: C, 73.70; H, 5.72; N, 20.19%. FT-IR (KBr, cm⁻¹) v_{max} : 1616, 1636 (s, C=N), 3155 (b, N-H). UV-Vis: λ_{max} (nm) (ϵ , L mol⁻¹ cm⁻¹) (CH₂Cl₂): 330 (28 548), 286 (21 725), 218 (129 150). ¹H NMR (CDCl₃, 500 MHz) δ: 4.84 (s, 2H, CH₂), 6.15-6.69 (6H, H_{pyrrole}), 7-7.32 (4H, ArH), 7.99 (s, 1H_{imine}), 8.09 (s, 1H_{i-} mine), 8.4-11.5 (br, 2H, N-H pyrrole).

2.2.2. Synthesis of trans- $[Co(L)(N-MeIm)_2]BPh_4(1)$

To a stirring solution of Co(CH₃COO)₂·4H₂O, 25 mg (0.1 mmol) in methanol (40 mL) was added an equimolar of H₂pyrabza 28 mg (0.1 mmol) in methanol (40 mL). The pink solution turned brown immediately upon the formation of the cobalt complex. To this solution was added dropwise 25 mmol (2.0 mL) of N-methylimidazole over a period of 45 min and the reaction mixture was stirred at room temperature for an additional 15 min. The final reaction mixture was filtered off and a solution of 34.2 mg (0.1 mmol) of NaBPh₄ in methanol (20 mL) was slowly added to the filtrate. The final solution was left undisturbed at room temperature. Brown crystals of the complex (suitable for X-ray crystallography) were obtained after a few hours. The crystals were filtered, washed with cold methanol and dried under vacuum. Yield 53.6 mg, 66%. Anal. Calc. for C₄₉H₄₆N₈BCo: C, 72.06; H, 5.68; N, 13.72. Found: C, 71.85; H, 5.61; N, 13.58%. FT-IR (KBr, cm⁻¹) v_{max}: 1561, 1582 (s, C=N), 3049-2982 (m, C-H). UV-Vis: λ_{max} (nm) (ε, L mol⁻¹ cm⁻¹) (CH₂Cl₂): 566 (307), 418 (32 075), 341 (24 520), 273 (52 230), 230 (75 620). ¹H NMR (CDCl₃, 500 MHz) δ : 2.55 (s, 6H, CH₃), 4.22 (s, 2H_{benzylic}), 5.85-7.55 (16H_{Ar}, 20 H_{BPh4}), 7.74 (s, 1H_{imine}), 8.04 (s, 1H_{imine}).

2.2.3. Synthesis of trans- $[Co(L)(3-Mepy)_2]BPh_4(2)$

This complex was prepared by the same method as for **1**, except that 3-Mepy was used instead of N-MeIm. The resulting red green solution was left undisturbed at room temperature for few hours to

give red green crystals. The crystals were isolated by filtration, washed with cold methanol and dried under vacuum. Yield 58.4 mg, 70%. *Anal.* Calc. for C₅₃H₄₈N₆BCo: C, 75.90; H, 5.77; N, 10.02. Found: C, 75.63; H, 5.64; N, 10.08%. FT-IR (KBr, cm⁻¹) ν_{max} : 1560, 1586 (s, C=N), 3053–2980 (m, C–H). UV–Vis: λ_{max} (nm) (ε , L mol⁻¹ cm⁻¹) (CH₂Cl₂): 592 (266), 422 (23 280), 357 (11 150), 269 (24 720), 230 (65 600). ¹H NMR (CDCl₃, 500 MHz) δ : 1.55 (s, 6H, CH₃), 1.86 (s, 2H_{benzylic}), 6.4–7.61 (18H_{Ar}, 20H_{BPh4}), 7.76 (s, 1H_{i-mine}), 8.09 (s, 1H_{imine}).

2.2.4. Synthesis of trans- $[Co(L)(4-Mepy)_2]BPh_4$ (3)

This complex was prepared by the same method as for **1**, except that 4-Mepy was used instead of N-MeIm. The resulting deep green solution was left undisturbed at room temperature for few hours to give dark green crystals. The crystals were isolated by filtration, washed with cold methanol and dried under vacuum. Yield 54.4 mg, 65%. *Anal.* Calc. for C₅₃H₄₈N₆BCo: C, 75.90; H, 5.77; N, 10.02. Found: C, 75.58; H, 5.63; N, 10.03%. FT-IR (KBr, cm⁻¹) ν_{max} : 1562, 1583 (s, C=N), 3049–2984 (m, C=C). UV–Vis: λ_{max} (nm) (ε , L mol⁻¹ cm⁻¹) (CH₂Cl₂): 593 (281), 420 (22 350), 351 (16 690), 260 (21 440), 231 (66 900). ¹H NMR (CDCl₃, 500 MHz) δ : 2.16 (s, 6H, CH₃), 3.77 (s, 2H_{benzylic}), 6.43–7.52 (18H_{Ar}, 20H_{BPh4}), 7.79 (s, 1H_{imine}).

2.2.5. Synthesis of trans- $[Co(L)(py)_2]BPh_4$ (4)

This complex was prepared by the same method as for **1** except that py was used instead of N-MeIm. The resulting deep green solution was left undisturbed at room temperature for a few hours to give dark green crystals. The crystals were isolated by filtration, washed with cold methanol and dried under vacuum. Yield 49 mg, 60%. *Anal.* Calc. for C₅₁H₄₄N₆BCo: C, 75.56; H, 5.43; N, 10.37. Found: C, 75.43; H, 5.34; N, 10.40%. FT-IR (KBr, cm⁻¹) ν_{max} : 1560, 1585 (s, C=N), 3053–2982 (m, C–H). UV–Vis: λ_{max} (nm) (ε , L mol⁻¹ cm⁻¹) (CH₂Cl₂): 598 (277), 421 (24 810), 354 (18 035), 292 (28 045), 231 (75 220). ¹H NMR (CDCl₃, 500 MHz): δ : 3.81 (s, 2H_{benzylic}), 6.44–7.55 (20H_{Ar}, 20H_{BPh4}), 7.80 (s, 1H_{imine}), 8.09 (s, 1H_{imine}).

2.3. X-ray crystallography

Brown crystals of **1** suitable for X-ray crystallography were obtained from methanol. X-ray data of **1** were collected at T = 100 K on a Bruker Kappa APEX-2 CCD diffractometer with graphite monochromated Mo K α ($\lambda = 0.71073$ Å) radiation and $0.5^{\circ} \omega$ - and φ -scan frames. Cell refinement and data reduction were performed with the help of the program SAINT [37]. Correction for absorption was carried out with the multi-scan method and the program SAD-ABS [37]. The structure was solved with direct methods using the program SHELXS97 and structure refinement on F^2 was carried out with the program SHELXL97 [38].

All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were inserted in calculated positions and treated as riding on their parent atoms. Crystal data, together with other relevant information on the structure determination, are listed in Table 1.



Scheme 1. Synthesis of the asymmetric H₂pyrabza ligand.



Fig. 1. ORTEP drawing of complex 1 with the atom numbering scheme.

Table	1
-------	---

Crystal data and structure refinement for 1.

Chemical formula	C ₂₅ H ₂₆ CoN ₈ C ₂₄ H ₂₀ B
Formula weight	816.68
Temperature (K)	100(2)
Crystal system, space group	monoclinic, $P2(1)/n$
Unit cell dimensions	
a (Å)	10.4816(11)
b (Å)	22.534(2)
c (Å)	17.3479(19)
β(°)	98.770(2)
V (Å ³)	4049.5(8)
Z, $D_{calc}y$ (g/cm ³)	4, 1.340
Crystal size (mm)	$0.60\times0.18\times0.12$
μ (mm ⁻¹)	0.47
F(0 0 0)	1712
θ Range (°)	2.3-30.0
Index ranges	$-14 \leqslant h \leqslant 14$, $-31 \leqslant k \leqslant 31$,
	$-24 \leqslant l \leqslant 24$
Reflections collected	59 873
Absorption correction	multi-scan
Minimum and maximum	0.84, 0.95
transmission	
Independent reflections (R_{int})	11 743(0.0333)
Data/restraints/parameters	11 743/0/534
Goodness-of-fit on F^2	1.024
Final R indices $[I > 2\sigma(I)]$	$R_1 = 0.0334$, $wR_2 = 0.0785$
R indices (all data)	$R_1 = 0.0462, wR_2 = 0.0855$
Maximum/minimum Δho (e Å $^{-3}$)	0.37 and -0.65

3. Results and discussion

3.1. Synthesis of complexes

All the cobalt(III) complexes have been prepared by the direct reaction of the corresponding ligand, H_2 pyrabza, and Co(CH₃₋COO)₂·4H₂O in the presence of the appropriate amine at room temperature. In the preparation of complexes **1–4**, the final reaction

T able 2 Selected bond lengths (Å) and angles (°) for 1 .
Bond lengths	
$C_0(1) = N(1)$	1 9282(

bonu icngins	
Co(1)-N(1)	1.9282(11)
Co(1)-N(2)	1.9607(10)
Co(1)-N(3)	1.9125(10)
Co(1)-N(4)	1.9217(11)
Co(1)-N(5)	1.9617(11)
Co(1)-N(7)	1.9384(11)
Bond angles	
N(1)-Co(1)-N(2)	83.87(5)
N(1)-Co(1)-N(3)	172.83(5)
N(1)-Co(1)-N(4)	100.54(5)
N(1)-Co(1)-N(5)	87.38(4)
N(1)-Co(1)-N(7)	93.00(4)
N(2)-Co(1)-N(3)	92.40(4)
N(2)-Co(1)-N(4)	174.66(4)
N(2)-Co(1)-N(5)	93.16(4)
N(2)-Co(1)-N(7)	89.13(4)
N(3)-Co(1)-N(4)	83.54(5)
N(3)-Co(1)-N(5)	86.72(4)
N(3)-Co(1)-N(7)	93.06(4)
N(4)-Co(1)-N(5)	90.07(4)
N(4)-Co(1)-N(7)	87.64(4)
N(5)-Co(1)-N(7)	177.71(4)

mixture was stirred for an additional 15 min while in contact with air. Suitable crystals of these complexes were obtained in good yield (about 70%).

3.2. Description of the structure of 1

The molecular structure and atom numbering scheme of **1** is presented in Fig. 1. The crystallographic data and structure analysis for complex **1** is summarized in Table 1. Selected bond distances, and bond angles are given in Table 2.

As expected, the ligand (pyrabza²⁻) in compound **1** binds to the trivalent metal ion (Co^{III}) *via* two pyrrole N atoms and two imine N atoms in the equatorial plane of the octahedron. Two N-methylimidazole molecules occupy the axial positions. The pyrabza ligand is not flat but shows a characteristic saddle-like deformation, which is attributable mainly to the benzylic CH₂ group.

The angles around the Co center deviate significantly from 90°. The N2–Co–N3 and N1–Co–N4 angles have opened up to 92.40(4)° and 100.53(5)° respectively, and the N1–Co–N2 and N3–Co–N4 angles have reduced to 83.87(5)° and 83.54(5)°, indicating distortion from a regular octahedron.

The Co-N_{imine} bond distances, Co-N2 = 1.9607(10) Å and Co-N3 = 1.9125(10) Å, show a difference of *ca*. 0.05 Å, which reflects the chemical inequivalence of the two imine nitrogen atoms (aryl and benzyl bonded nitrogen). On average, these distances may be compared with those reported for [Co{(pyrrol)₂dien}(4-Me-Co-N2 = 1.9128(9) Å and (Co-N_{imine}: Co-N4 = py)]BPh₄ 1.9020(8) Å) [39], and $[Co{(BA)_2pn}(py)_2]ClO_4$, ${(BA)_2pn = N,N'-}$ bis(benzoylacetone)-1,3-propylenediimine dianion} (1.939(4) and 1.962(3) Å) [35]. The somewhat shorter Co-N_{axial} (Co-N5 = 1.9617(11) Å and Co–N7 = 1.9384(11) Å) bond lengths of **1** relative to those reported for the [Co{(pyrrol)₂dien}(4-Mepy)]BPh₄ complex (1.9765(8) Å) reflect the higher basicity of the N-MeIm ligand (pK_a = 7.06) vs. 4-Mepy (pK_a = 5.25) [40]. The trans N5–Co–N7 unit, with a bond angle of $177.71(4)^{\circ}$, is almost linear and the planes of the two N-MeIm rings form a dihedral angle of 74.71° with each other.

The Co atom is displaced slightly out of the mean plane of the four N atoms of the planar Schiff base ligand by 0.023 Å toward the N5 atom. The dihedral angle between the Co/N2/N3 and Co/N1/N4 planes is $6.55(1)^{\circ}$ at the cobalt atom. The angles between the two pyrrole rings and the N1/N2/N3/N4 plane are 8.76(1)

and $6.72(1)^\circ$. The dihedral angle between the two pyrrole portions is 15.44° .

3.3. Spectral characterization

The newly prepared metal complexes are all air-stable solids and have good elemental analyses. The octahedral geometry of complex **1** is evident from the X-ray structure analysis (Fig. 1). An octahedral trans-structure for other complexes (**2**, **3** and **4**) can be inferred based on the similarity of the spectral data of these complexes with those of complex **1**.

The FT-IR data of the complexes are listed in Section 2. All the complexes show similar IR spectral features. The IR spectrum of the free ligand exhibits the characteristic bands of two different imine C=N, which appear at 1636 and 1616 cm⁻¹ [34]. Similar features are observed in the IR spectra of the cobalt complexes, with the C=N stretching vibrations appearing in the 1560–1583 cm⁻¹ region. The v(CN) band is generally shifted to lower frequencies relative to the free ligand, indicating a decrease in the C=N bond order due to the coordination of the imine nitrogen to the metal and back bonding from the Co(III) metal to the π^* orbital of the azomethine group [41]. Moreover, the absence of a broad band at 3155 cm⁻¹, characteristic of the N–H_{pyrrole} group, in the IR spectra of the complexes is indicative of the fact that the equatorial ligand is coordinated in its deprotonated form.

The UV-Vis data of H₂pyrabza and complexes 1-4 in CH₂Cl₂ are presented in the Experimental Section. The electronic absorption spectrum of pyrabza in dichloromethane consists of two relatively intense bands centered at 218 and 288 nm, assigned to the π - π * transitions of the aromatic rings and the azomethine group, and a third band at 330 nm, corresponding to a $n-\pi^*$ transition [34,42]. All the four cobalt complexes show 4 bands at λ_{max} 213– 423 nm, assigned to intraligand π - π * transitions within the aromatic rings and a CT transition with some ligand field admixture. The first d-d transition appears as a shoulder in the range 566-598 nm (ε = 266–307) and is in agreement with a similar transition in related complexes [43]. Since the equatorial positions in all four complexes are occupied by the tetradentate ligand pyrabza^{2–}, the energy of the ligand field transitions is directly related to the pK_a of the axial ligands. It is therefore expected to see a difference in the color of these complexes, notably for the N-MeIm complex with $pK_a = 7.4$ (brown) and the py complex with $pK_a = 5.21$ (dark green). In addition, the size and types of crystals that are obtained for these compounds may lead to some difference in their appear-







Fig. 3. Cyclic voltammogram of *trans*-[Co(pyrabza)(N-Melm)₂]BPh₄ (1) in acetonitrile at 298 K, $c = 2.1 \times 10^{-4}$ M, scan rate = 100 mV s⁻¹.

ance and color. As in related low spin d⁶-metal complexes, the expected ${}^{1}A_{1g} \rightarrow {}^{1}T_{2g}$ band is apparently masked by intense charge-transfer bands [44].

The ¹H NMR spectral measurements were performed in CDCl₃ solution to throw light on the solution structure of these complexes. The chemical formula of **1–4** are presented in Scheme 2. The main parameters of ¹H NMR spectroscopic data of the Schiff base ligand pyrabza and the four cobalt complexes **1–4** are given in Section 2. The absence of the pyrrole N–H signal at 11.5–8.4 ppm in the spectrum of these complexes clearly demonstrates the coordination of the Schiff base ligand in its deprotonated form [35,45]. The signal appearing as a singlet at 4.2 ppm for **1**, 1.98 ppm for **2**, 3.77 ppm for **3** and 3.81 ppm for **4** in the ¹H NMR spectra of these complexes is assigned to the benzylic CH₂ group of pyrabza. The two signals appearing as singlets at 8.1–7.7 ppm are assigned to the two different = CH_{imine} groups. These



Scheme 2. Chemical formula of the cobalt complexes.

features, that are common between the ¹H NMR spectra of complexes **1**, **2**, **3**, and **4**, indicate that, as in **1**, the equatorial coordination sites in complexes **2**, **3** and **4** are occupied by the pyrabza ligand. The aromatic protons of the coordinated Schiff base and the axial amine ligands, and those of the BPh₄ counter-ion, appear in the appropriate region (5.8–7.9 ppm) [34,43]. The signals due to the aliphatic protons of the methyl substituent on the axial ligands appear in the range 1.55–2.55 ppm.

3.4. Electrochemistry

The electrochemical behavior of the H₂pyrabza ligand and the corresponding complexes **1–4** was studied at 25 °C using acetonitrile solutions with 0.1 M TBAH as the supporting electrolyte at a glassy carbon working electrode under an argon atmosphere. Ferrocene (Fc) was used as the internal standard and all redox potentials are referenced to the Fc^{+/0} couple. The approximate concentrations of the compounds were 10^{-3} to 10^{-5} M.

It is evident from the cyclic voltammogram of H₂pyrabza, displayed in Fig. 2, that the ligand is electroactive over a range from -1.5 to -2.3 V in acetonitrile solvent. Two ligand-centered reductions observed at -1.9 and -2.21 V are attributed to the pyrrole rings.

3.4.1. Electrochemistry of the complexes

The cyclic voltammogram of the *trans*-[Co(pyrabza)(N-Melm)₂]BPh₄ complex is shown in Fig. 3 as a representative example for the cobalt complexes. Three main features are observed in these cyclic voltammograms. (i) The counter ion oxidation process. For all the complexes **1–4**, the first electrochemically irreversible oxidation wave in the potential range 0.80–0.89 V is attributed to the oxidation of the benzene rings of BPh₄ [46]

 $\text{BPh}_4^- \rightarrow \text{BPh}_4 \bullet + e^-$

(ii) The metal centered redox processes. An irreversible wave in the range -0.44 to -0.79 V is observed, due to the electrochemically irreversible Co^{III}/Co^{II} reductive response. As an example, an electrochemically irreversible Co^{III}/Co^{II} reduction process ($\Delta E_{p=}$ 725 mV) with an E_{pc} value of -0.79 V appears in the cyclic voltammograms of **1** (Fig. 3). This is presumably due to the occurrence of a structural change during the reduction process. Accordingly we assume that the lack of reversibility observed is most likely due to the loss of axial ligands from the cobalt(II) centre, because the electron is added to the antibonding dz^2 orbital of the metal ion [34,47–50].

trans-
$$[Co^{III}(pyrabza)(N-MeIm)_2]^+ + e^-$$

 \rightarrow [Co^{II}(pyrabza)] + 2N-MeIm

The $E_{\rm pc}$ value of this reduction process is greatly influenced by the nature of the axial ligands, indicating that this process is presumably metal centered. From the $E_{\rm pc}$ values (Table 3) it is evident that stronger axial ligands shift the potential to more negative values.

The next reduction process observed at -1.53 to -1.59 V is due to the reduction of the Co^{II}/Co^I center. The low sensitivity of the

Table 3
Redox potentials of complexes 1-4 in acetonitrile. ^a



Fig. 4. Cyclic voltammograms of *trans*- $[Co^{III}(Pyrabza)(N-MeIm)_2]BPh_4$ (1) at different N-MeIm concentrations ratios (0, — blue), (20, — green), (60, red), (100, — black) in acetonitrile at 298 K. Scan rate 100 mV s⁻¹, $c = 5.3 \times 10^{-4}$ M.

 Co^{II}/Co^{I} reduction potential to the change in the axial ligands suggests that the species being reduced at this stage have almost the same structure for all of complexes **1–4**, namely [Co^{II}(pyrabza)(MeCN)], which results from the solvolysis of the Co^{III}/Co^{II} reduction product [47–50].

The nature of the Co^{II/I} reduction process in CH₃CN is dependent on the used scanning potential window and is irreversible when the measurements is carried out in the potential range 1.5 to -2.2 V. However, when the scanning potential window is narrowed to 0.6 to -1.6 V, this process becomes quasireversible ($\Delta E = 118$ mV, $i_{pa}/i_{pc} = 0.77$) (Fig. 3). The irreversibility of Co^{II/I} is apparently due to the instability of the reduced product in the more negative potentials. These observations are in accord with the results obtained for the related Co(I) complexes of tetradentate Schiff base ligands with steric strain on the structural framework [34].

(iii) The ligand centered redox processes. The final electrochemically irreversible reduction process observed in the voltammograms is mostly ligand centered and is due to the reduction of the pyrrole rings. The corresponding reduction potential remains close to that of the free ligand. This is in accord with expectation, since the pyrrole moieties are now coordinated in their deprotonated form to Co(II).

3.4.2. Electrochemistry of the complexes in the presence of amines

In many *trans*- $[Co^{III}(N_4)(L)_2]^+$ Schiff base and carboxamide complexes, the first irreversible reduction process (Co^{III}/Co^{II}) can become quasi-reversible under controlled concentrations of axial amine ligands [47–50]. In an attempt to investigate the possibility of reversible electrochemical behavior in cobalt pyrabza complexes, the electrochemistry of $[Co^{III}(pyrabza)(N-MeIm)_2]BPh_4$ was studied in the presence of excess N-MeIm. Fig. 4 shows the cyclic voltammograms of *trans*- $[Co^{III}(pyrabza)(N-MeIm)_2]BPh_4$ (1), at different concentrations of N-MeIm. As already pointed out, the first reduction process of (Co^{III}/Co^{II}) is electrochemically

No.	Compound	Epa1	Epc2	Epa2	Epc3	Epa3	Epc4	Epa4
1	[Co(pyrabza)(N-MeIm)2]BPh4	0.86	-0.79	-0.07	-1.59	-1.48	-2.23	-2.05
2	[Co(pyrabza)(3-MePy) ₂]BPh ₄	0.89	-0.50	-0.02	-1.55	-1.43	-2.25	-2.05
3	[Co(pyrabza)(4-MePy) ₂]BPh ₄	0.80	-0.45	-0.08	-1.50	-1.41	-2.19	-2.04
4	[Co(pyrabza)(Py) ₂]BPh ₄	0.84	-0.44	-0.05	-1.53	-1.42	-2.22	-2.03

1655

^a Potentials are vs. Fc^{+/0} in 0.1 M TBAH, T = 298 K. Scan rate 100 mV/s. Approximate concentrations: 1×10^{-3} - 10^{-5} -M.

irreversible (ΔE = 725 mV) in the absence of additional amine. Upon addition of excess amine, the oxidation wave of Co(II) is shifted towards more negative potentials (Fig. 4) (ΔE = 502 mV), indicating increased formation of the six-coordinated adduct; i.e. the electrode process is preceded by a reversible chemical reaction:

$$\begin{split} & [\text{Co}^{\text{II}}(\text{pyrabza})] \overset{\text{Excess amine}}{\rightleftharpoons} [\text{Co}^{\text{II}}(\text{pyrabza})(\text{amine})_2] \\ & \rightarrow [\text{Co}^{\text{III}}(\text{pyrabza})(\text{amine})_2]^+ + e^- \end{split}$$

The redox potential of the Co(II/I) couple is not changed significantly by the addition of excess amine and can be regarded as approximately independent.

4. Conclusion

In this investigation, we have reported the synthesis and characterization of four Co(III) complexes with an asymmetrical N4 type Schiff base ligand. The coordination geometry around the Co(III) center in these complexes is a distorted CoN_6 octahedron. Electrochemical studies revealed that the first reduction process, Co(III/II), is irreversible and strongly influenced by the nature of the axial amines. The position of Co(III/II) cathodic peak changes from -0.79 to -0.44 V by changing the axial ligands from **1** to **4**. The Co(II/I) reduction process in CH₃CN is irreversible when the measurements is carried out in the potential range 1.5 to -2.2 V. However, by narrowing the scanning potential window down to 0.6 to -1.6 V, this process becomes quasireversible.

5. Supplementary data

CCDC 796474 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.

Acknowledgment

Partial support of this work by the Isfahan University of Technology Research Council is gratefully acknowledged.

References

- [1] R. Ziessel, Coord. Chem. Rev. 216-217 (2001) 195.
- [2] P.G. Cozzi, Chem. Soc. Rev. 33 (2004) 410.
- [3] K.C. Gupta, A.K. Sutar, Coord. Chem. Rev. 252 (2008) 1420.
- [4] J.P. Costes, S. Shova, W. Wernsdorfer, J. Chem. Soc., Dalton Trans. (2008) 1843-1849.
- [5] X.G. Ran, L.Y. Wang, Y.C. Lin, J. Hao, D.R. Cao, Appl. Organometal. Chem. 24 (2010) 741.
- [6] M. Orio, O. Jarjayes, H. Kanso, C. Philouze, F. Neese, F. Thomas, Angew. Chem., Int. Ed. 49 (2010) 4989.
- [7] J. Balsells, L. Mejorado, M. Phillips, F. Ortega, G. Aguirre, R. Somanathan, P.J. Walsh, Tetrahedron Asymmetry 9 (1998) 4135.
- [8] A. Datta, N.K. Karan, S. Mitra, G. Rosair, Z. Naturforsch. 57b (2002) 999-1002.
- [9] R.C. Maurya, S. Rajput, J. Mol. Struct. 794 (2006) 24.

- [10] S. Adsule, V. Barve, D. Chen, F. Ahmed, Q.P. Dou, S. Padhye, F.H. Sarkar, J. Med. Chem. 49 (2006) 7242.
- [11] P.K. Sasmal, R. Majumdar, R.R. Digheb, A.R. Chakravarty, J. Chem. Soc., Dalton Trans. 39 (2010) 7104.
- [12] B.S. Creaven, E. Czeglédi, M. Devereux, É.A. Enyedy, A. Foltyn-Arfa Kia, D. Karcz, A. Kellett, S. McClean, N.V. Nagy, A. Noble, A. Rockenbauer, T. Szabó-Plánka, M. Walsh, J. Chem. Soc., Dalton Trans. 39 (2010) 10854.
- [13] S.-Y. Lee, A. Hille, C. Frias, B. Kater, B. Bonitzki, S. Wölfl, H. Scheffler, A. Prokop, R. Gust, J. Med. Chem. 53 (2010) 6064.
- [14] R. Atkins, G. Brewer, E. Kokot, G.M. Mockler, E. Sinn, Inorg. Chem. 24 (1985) 127.
- [15] E.M. Opozda, W. Łasocha, B. Włodarczyk-Gajda, Z. Anorg. Allg. Chem. 630 (2004) 597.
- [16] P. Mukherjee, M.G.B. Drew, A. Ghosh, Eur. J. Inorg. Chem. (2008) 3372-3381.
- [17] A. Biswas, M.G.B. Drew, A. Ghosh, Polyhedron 29 (2010) 1029.
- [18] T.W. Lane, F.M.M. Morel, Proc. Natl. Acad. Sci. USA 97 (2000) 4627.
- [19] A. Roth, E.T. Spielberg, W. Plass, Inorg. Chem. 46 (2007) 4362.
- [20] R.N. Patel, V.L.N. Gundla, D.K. Patel, Polyhedron 27 (2008) 1054.
- [21] G.-J. Kim, J.-H. Shin, Catal. Lett. 63 (1999) 83.
- [22] D. Chatterjeea, A. Mitra, B.C. Roy, J. Mol. Catal. A: Chem. 161 (2000) 17.
- [23] C. Jayabalakrishnan, R. Karvembu, K. Natarajan, Transition Met. Chem. 27 (2002) 790.
- [24] O. Pouralimardan, A.-C. Chamayou, C. Janiak, H. Hosseini-Monfared, Inorg. Chim. Acta 360 (2007) 1599.
- [25] Z.-J. Xu, R. Fang, C. Zhao, J.-S. Huang, G.-Y. Li, N. Zhu, C.-M. Che, J. Am. Chem. Soc. 131 (2009) 4405.
- [26] C.-C. Kwok, S.-C. Yu, I.H.T. Sham, C.-M. Che, Chem. Commun. (2004) 2758– 2759.
- [27] K.-H. Chang, C.-C. Huang, Y.-H. Liu, Y.-H. Hu, P.-T. Chou, Y.-C. Lin, J. Chem. Soc., Dalton Trans. (2004) 1731–1738.
- [28] C.-M. Che, S.-C. Chan, H.-F. Xiang, M.C.W. Chan, Y. Liub, Y. Wang, Chem. Commun. (2004) 1484–1485.
- [29] J. Gradinaru, A. Forni, V. Druta, F. Tessore, S. Zecchin, S. Quici, N. Garbalau, Inorg. Chem. 46 (2007) 884.
- [30] L. Wang, W. Qin, X. Tang, W. Dou, W. Liu, Q. Teng, X. Yao, Org. Biomol. Chem. 8 (2010) 3751.
- [31] S. Osinsky, I. Leviyin, L. Bubnoskaya, A. Sigan, I. Ganusevich, A. Kovelskaya, N. Valkovskaya, L. Campanella, P. Vardman, Exp. Oncol. 26 (2004) 140.
- [32] E.L. Chang, C. Simmers, D.A. Knight, Pharmaceuticals 3 (2010) 1711.
- [33] M. Amirnasr, K.J. Schenk, A. Gorji, R. Vafazadeh, Polyhedron 20 (2001) 695.
- [34] K.J. Schenk, S. Meghdadi, M. Amirnasr, M.H. Habibi, A. Amiri, M. Salehi, A. Kashi, Polyhedron 26 (2007) 5448.
- [35] S. Meghdadi, M. Amirnasr, M.H. Habibi, A. Amiri, F. Ahmadi, K. Kihara, T. Suzuki, H.R. Bijanzadeh, Transition Met. Chem. 33 (2008) 879.
- [36] N.G. Connelly, W.E. Geiger, Chem. Rev. 96 (1996) 877.
- [37] Bruker computer programs: APEX2, version 2008; SAINT, version 7.68A; SADABS, version 2008/1; SHELXTL, version 2008/4. Bruker AXS Inc., Madison, WI, 2008.
- [38] G.M. Sheldrick, Acta Crystallogr., Sect. A 64 (2008) 112.
 [39] S. Meghdadi, M. Amirnasr, K. Mereiter, M. Karimi Abdolmaleki, Acta
- Crystallogr., Sect. E 66 (2010) m332.
- [40] S. Mukerjee, K. Skogerson, S. DeGala, J.P. Caradonna, Inorg. Chim. Acta 297 (2000) 313.
- [41] P.E. Aranha, J.M. Souza, S. Romera, L.A. Ramos, M.P. dos Santos, E.R. Dockal, E.T.G. Cavalheiro, Thermochim. Acta 453 (2007) 9–13.
- [42] S. Zolezzi, A. Decinti, E. Spodine, Polyhedron 18 (1999) 897.
- [43] M. Ray, R. Mukherjee, J.F. Richardson, R.M. Buchanan, J. Chem. Soc., Dalton Trans. (1993) 2451–2457.
- [44] M. Ray, R.N. Mukherjee, Polyhedron 11 (1992) 2929.
- [45] A. Bacchi, M. Carcelli, L. Gabba, S. Ianelli, P. Pelagatti, G. Pelizzi, D. Rogolino, Inorg. Chim. Acta 342 (2003) 229.
- [46] P.K. Pal, S. Chowdhury, M.G.B. Drew, D. Datta, New J. Chem. 26 (2002) 367.
- [47] A. Böttcher, T. Takeuchi, K.I. Hardcastle, T.J. Meade, H.B. Gray, D. Cwikel, M. Kapon, Z. Dori, Inorg. Chem. 36 (1997) 2498.
- [48] M. Amirnasr, R. Vafazadeh, A. Mahmoudkhani, Can. J. Chem. 80 (2002) 1196.
 [49] S. Meghdadi, M. Amirnasr, M.H. Habibi, A. Amiri, V. Ghodsi, A. Rohani, R.W.
- Harrington, W. Clegg, Polyhedron 27 (2008) 2771.
- [50] S. Meghdadi, M. Amirnasr, K. Mereiter, A. Amiri, V. Ghodsi, Inorg. Chim. Acta 363 (2010) 1587.