Inorganica Chimica Acta 371 (2011) 6–12

Contents lists available at ScienceDirect

Inorganica Chimica Acta

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

Synthesis, and characterization of cobalt(III) complexes with Schiff bases derived from 2-hydroxynaphthaldehyde, $(naph)_2dien$ and $(naph)_2dpt$, and monodentate amine ligands: Crystal structure, spectral and redox properties

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ARTICLE INFO

Article history:
Received 24 November 2010
Received in revised form 8 February 2011
Accepted 11 February 2011
Available online 24 February 2011

Keywords:
Cobalt(III) complexes
Pentadentate Schiff base ligand
Cyclic voltammetry
X-ray crystal structure

ABSTRACT

Two series of complexes of the type $[Co^{III}\{(naph)_2dien\}(amine)]BPh_4$ $\{(naph)_2dien$ = bis-(2-hydroxy-1-naphthaldimine)-N-diethylenetriamine dianion, and amine = piperidine (pprdn) (**1**), pyrrolidine (prldn) (**2**), pyridine (py) (**3**), N-methylimidazole (N-MeIm) (**4**)}, and $[Co^{III}\{(naph)_2dpt\}(amine)]BPh_4$ $\{(naph)_2dpt$ = bis-(2-hydroxy-1-naphthaldimine)-N-dipropylenetriamine dianion, and amine = piperidine (pprdn) (**5**), 3-methylpyridine (3-Mepy) (**6**)} have been synthesized and characterized by elemental analyses, IR, UV–Vis, and ^1H NMR spectroscopy. The crystal structures of (**2**) and (**6**) have been determined by X-ray diffraction. The redox potentials of the central cobalt ion show a relatively good correlation with the σ-donor ability of the axial ligands. The spectroscopic and electrochemical properties of these complexes are also influenced by the mutual steric hindrance between the pentadentate Schiff base and the ancillary ligands.

1. Introduction

Schiff bases, characterized by the azomethine group (–RC=N–), form a significant class of compounds in medicinal and pharmaceutical chemistry and are known to have biological applications due to their antibacterial [1–6], antifungal [3–6], and antitumor [7,8] activity. The incorporation of transition metals into these compounds leads to the enhancement of their biological activities and decrease in the cytotoxicity of both metal ion and Schiff base ligand [9–11].

The structural diversity of transition metal complexes of Schiff base ligands and the structure–function relationships of the resulting complexes have been the focus of extensive research in recent years [12–18]. A great deal of effort has been directed toward the design and synthesis of functional material with a variety of applications such as production of redox-active sensors [19], ionic ferroelectrics [20], highly efficient catalysts in various fields of synthesis and other useful reactions [21–25], and biologically active compounds [9–11,26,27].

Extensive investigation of the reactivity and structural aspects of metal complexes with pentadentate N_3O_2 ligands has been carried out and it has been found that, apart from the structural demands of the pentadentate ligand, many other factors play their roles in the realized structures of these compounds [28,29]. Among the most widely studied compounds, cobalt complexes with pentadentate Schiff base ligands have been investigated for their many applications such as molecular magnets, antifungal and antimicrobial agents [30–34].

In continuation of our work on the synthesis and structural studies of transition metal complexes of pentadentate Schiff base ligands [35–39], herein we report the synthesis of two pentadentate Schiff base ligands by improving the literature method [40] and their relevant cobalt(III) complexes. These compounds have been characterized by elemental analyses, IR, UV–Vis, and ^1H NMR spectroscopy, and the X-ray crystal structures of (**2**) and (**6**) have been determined. The electrochemical behavior of these complexes, with the goal of evaluating the effect of axial and equatorial ligation and the mutual steric hindrance between the pentadentate Schiff base and the ancillary ligands on their spectral and redox properties, is also reported and discussed.

2. Experimental

2.1. Materials and physical measurements

All solvents and chemicals were purchased from commercial sources and used as received. Elemental analyses were performed by using a Perkin–Elmer 2400II CHNS–O elemental analyzer. UV–Vis spectra were recorded on a JASCO V-570 spectrophotometer.

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0020-1693/$ - see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.ica.2011.02.027

Infrared spectra (KBr pellets) were obtained on a FT-IR JASCO 680 plus spectrophotometer. ^1H NMR spectra were measured with a Bruker AVANCE DR X500 spectrometer (500 MHz). Proton chemical shifts are reported in ppm relative to Me_4Si as internal standard. The redox properties of the complexes were studied by cyclic voltammetry. 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 a silver 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. Cyclic voltammetric measurements were performed in dichloromethane. The solutions were deoxygenated by purging with Ar for 5 min. All electrochemical potentials were calibrated versus internal $Fc^{+/0}$ ($E^0 = 0.46$ V versus SCE) couple under the same conditions [41].

2.2. Synthesis

2.2.1. Synthesis of $H_2(naph)_2dien$ ligand

Bis-(2-hydroxy-1-naphthaldimine)-N-diethylenetriamine, $H_2(naph)_2dien$, was synthesized by the literature method [40] with some modification leading to a higher yield. A solution of diethylenetriamine (dien) (103 mg, 1 mmol) in methanol (25 mL) was added to a solution of 2-hydroxy-1-naphthaldehyde (344 mg, 2 mmol) in methanol (25 mL) at room temperature and the reaction mixture was stirred for 1 h. The product was precipitated as a yellow powder by adding water. The precipitate was then filtered off, washed with diethyl ether and dried under vacuum. Yield 95%. *Anal.* Calc. for $C_{26}H_{25}N_3O_2$: C, 75.89; H, 6.12; N, 10.21. Found: C, 75.55; H, 6.04; N, 10.25%. FT-IR (KBr, cm^{-1}) ν_{max}: 3282 (m, N–H), 1633 (s, C=N). UV–Vis: λ_{max} (nm) (ε, L mol^{-1} cm^{-1}) (CH_2Cl_2): 419 (22 000), 403 (24 000), 308 (52 000), 233 (160 000). ^1H NMR ($CDCl_3$, 500 MHz): $\delta = 1.81$ (br, 1H, NH), 3.03 (t, 4H, H_a), 3.71 (t, 4H, H_b), 6.90 (d, 2H, H_i), 7.21 (dd, 2H, H_f), 7.38 (dd, 2H, H_e), 7.58 (d, 2H, H_g), 7.65 (d, 2H, H_h), 7.84 (d, 2H, H_d), 8.79 (s, 2H, H_c), 14.44 (s, 2H, OH).

2.2.2. Synthesis of $H_2(naph)_2dpt$ ligand

Bis-(2-hydroxy-1-naphthaldimine)-N-dipropylenetriamine ($H_2(naph)_2dpt$) was prepared by a procedure similar to that of $H_2(naph)_2dien$ except that dipropylenetriamine (dpt) (131 mg, 1 mmol) was used instead of diethylenetriamine (dien). Yield 90%. *Anal.* Calc. for $C_{28}H_{29}N_3O_2 \cdot H_2O$: C, 73.50; H, 6.83; N, 9.18. Found: C, 73.81; H, 6.80; N, 9.23%. FT-IR (KBr, cm^{-1}) ν_{max}: 3274 (m, N–H), 1631 (s, C=N). UV–Vis: λ_{max} (nm) (ε, L mol^{-1} cm^{-1}) (CH_2Cl_2): 421 (17 000), 403 (16 000), 306 (24 000), 232 (93 000). ^1H NMR ($CDCl_3$, 500 MHz): $\delta = 1.91$ (m, 4H, H_b), 2.77 (t, 4H, H_a), 3.71 (t, 4H, H_c), 6.90 (d, 2H, H_j), 7.20 (dd, 2H, H_g), 7.38 (dd, 2H, H_f), 7.58 (d, 2H, H_h), 7.66 (d, 2H, H_i), 7.82 (d, 2H, H_e), 8.71 (s, 2H, H_d).

2.2.3. Synthesis of the cobalt complexes

Complexes of the type $[Co^{III}\{(naph)_2dien\}(amine)]BPh_4$ were prepared by the following general method. To a stirring solution of $Co(CH_3COO)_2 \cdot 4H_2O$ (249 mg, 1 mmol) in methanol (25 mL) was added an equimolar amount of the $H_2(naph)_2dien$ ligand (411 mg, 1 mmol) in methanol (25 mL). The pink solution turned brown immediately due to the formation of the $[Co^{II}\{(naph)_2dien\}]$ complex. To this solution was then added the appropriate amine (4 mmol) and air was bubbled through the reaction mixture for about 3 h. To the final green-brown solution was added $NaBPh_4$ (342 mg, 1 mmol). Dark green crystals were obtained from the filtrate by the slow evaporation of the solvent. The crystals were filtered off, washed with cold methanol and dried under vacuum.

Complexes of the type $[Co^{III}\{(naph)_2dpt\}(amine)]BPh_4$ were prepared by a procedure similar to that for $[Co^{III}\{(naph)_2dien\}(amine)]BPh_4$ except that $H_2(naph)_2dpt$ ligand (439 mg, 1 mmol) was used instead of $H_2(naph)_2dien$.

*2.2.3.1. $[Co\{(naph)_2dien\}(pprdn)]BPh_4$ (**1**).* Dark brown crystals of (**1**) were obtained after 72 h in methanol. The crystals were filtered off, washed with cold methanol and dried under vacuum. Yield 65%. *Anal.* Calc. for $C_{55}H_{54}BCoN_4O_2$: C, 75.69; H, 6.24; N, 6.42. Found: C, 75.29; H, 6.31; N, 6.45%. FT-IR (KBr, cm^{-1}) ν_{max}: 3254 (m, N–H), 1618 (s, C=N). UV–Vis: λ_{max} (nm) (ε, L mol^{-1} cm^{-1}) (CH_2Cl_2): 589 (350), 445 (4700), 423 (5060), 322 (sh, 19 000), 220 (190 000). ^1H NMR ($CDCl_3$, 500 MHz): $\delta = 1.1–3.8$ (m, 20H, $H_{a,a',b,b',NH,pprdn}$), 6.93–7.78 (m, 32H, $H_{naphthyl,BPh_4^-}$), 8.21 (s, 2H, $H_{c,c'}$).

*2.2.3.2. $[Co\{(naph)_2dien\}(prldn)]BPh_4$ (**2**).* Dark brown crystals of (**2**) suitable for X-ray analysis were obtained after 72 h in methanol. The crystals were filtered off, washed with cold methanol and dried under vacuum. Yield 66%. *Anal.* Calc. for $C_{54}H_{52}BCoN_4O_2$: C, 75.52; H, 6.10; N, 6.52. Found: C, 75.57; H, 6.01; N, 6.59%. FT-IR (KBr, cm^{-1}) ν_{max}: 3254, 3223 (m, N–H), 1617 (s, C=N). UV–Vis: λ_{max} (nm) (ε, L mol^{-1} cm^{-1}) (CH_2Cl_2): 582 (330), 445 (5500), 423 (6600), 322 (21 000), 221 (170 000). ^1H NMR ($CDCl_3$, 500 MHz): $\delta = 1.26–3.47$ (m, 18H, $H_{a,a',b,b',NH,prldn}$), 6.93–7.78 (m, 32H, $H_{naphthyl,BPh_4^-}$), 8.26 (s, 2H, H $_{c,c'}$).

*2.2.3.3. $[Co\{(naph)_2dien\}(py)]BPh_4$ (**3**).* Dark brown crystals of (**3**) were obtained after 48 h in methanol. The crystals were filtered off, washed with cold methanol and dried under vacuum. Yield 75%. *Anal.* Calc. for $C_{55}H_{48}BCoN_4O_2$: C, 76.22; H, 5.58; N, 6.46. Found: C, 75.06; H, 5.52; N, 6.37%. FT-IR (KBr, cm^{-1}) ν_{max}: 3234 (m, N–H), 1616 (s, C=N). UV–Vis: λ_{max} (nm) (ε, L mol^{-1} cm^{-1}) (CH_2Cl_2): 582 (514), 445 (sh, 5700), 423 (6200), 316 (18 500), 229 (71 900). ^1H NMR ($CDCl_3$, 500 MHz): $\delta = 2.00$ (br, 1H, NH), 3.17–3.33 (m, 4H, $H_{a,a'}$), 3.43–3.58 (m, 4H, $H_{b,b'}$), 6.92–8.01 (m, 37H, $H_{naphthyl,py,BPh_4^-}$), 8.36, 8.37 (s, 2H, $H_{c,c'}$).

*2.2.3.4. $[Co\{(naph)_2dien\}(N\text{-}MeIm)]BPh_4$ (**4**).* Dark brown crystals were obtained after 48 h in methanol. The crystals were filtered off, washed with cold methanol and dried under vacuum. Yield 70%. *Anal.* Calc. for $C_{54}H_{49}BCoN_5O_2$: C, 74.57; H, 5.68; N, 8.05. Found: C, 74.54; H, 5.61; N, 8.13%. FT-IR (KBr, cm^{-1}) ν_{max}: 3261 (m, N–H), 1617 (s, C=N). UV–Vis: λ_{max} (nm) (ε, L mol^{-1} cm^{-1}) (CH_2Cl_2): 558 (402), 447 (5400), 424 (5200), 321 (18 000), 221 (120 000). ^1H NMR ($CDCl_3$, 500 MHz): $\delta = 1.74–3.62$ (m, 9H, $H_{a,a',b,b',NH}$), 3.68 (s, 3H, H_{methyl}), 6.92–7.83 (m, 35H, $H_{naphthyl,N-MeIm,BPh_4^-}$).

*2.2.3.5. $[Co\{(naph)_2dpt\}(pprdn)]BPh_4$ (**5**).* Dark brown crystals of (**5**) were obtained after 72 h in methanol. The crystals were filtered off, washed with cold methanol and dried under vacuum. Yield 60%. *Anal.* Calc. for $C_{57}H_{58}BCoN_4O_2$: C, 76.00; H, 6.49; N, 6.22. Found: C, 74.02; H, 6.48; N, 6.29%. FT-IR (KBr, cm^{-1}) ν_{max}: 3205 (m, N–H), 1617 (s, C=N). UV–Vis: λ_{max} (nm) (ε, L mol^{-1} cm^{-1}) (CH_2Cl_2): 626.5 (237), 419 (6700), 403 (7500), 326 (17 800), 266 (65 000). ^1H NMR ($CDCl_3$, 500 MHz): $\delta = 0.84–5.06$ (m, 24H, $H_{a,a',b,b',c,c',NH,pprdn}$), 6.79–7.76 (m, 32H, $H_{naphthyl,BPh_4^-}$), 8.24, 8.30 (s, 2H, $H_{d,d'}$).

*2.2.3.6. $[Co\{(naph)_2dpt\}(3\text{-}Mepy)]BPh_4$ (**6**).* Dark brown crystals of (**6**) were obtained after 72 h in methanol. Recrystallization from dichloromethane:ethanol:1-propanol (2:1:1 v/v) gave dark brown crystals suitable for X-ray analysis that were filtered off, washed with cold methanol and dried under vacuum. Yield 76%. *Anal.* Calc. for $C_{58}H_{54}BCoN_4O_2$: C, 76.65; H, 5.99; N, 6.16. Found: C, 76.59; H, 6.90; N, 6.22%. FT-IR (KBr, cm^{-1}) ν_{max}: 3220 (m, N–H), 1618 (s,