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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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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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Infrared spectra (KBr pellets) were obtained on a FT-IR JASCO 680 plus spectrophotometer. ^{1}H 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)$_2$dien ligand

Bis-(2-hydroxy-1-naphthaldimine)-N-diethylenetriamine, H_2(naph)$_2$dien, 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). ^{1}H 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)$_2$dpt ligand

Bis-(2-hydroxy-1-naphthaldimine)-N-dipropylenetriamine (H_2(naph)$_2$dpt) was prepared by a procedure similar to that of H_2(naph)$_2$dien 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). ^{1}H 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)$_2$dien}(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)$_2$dien ligand (411 mg, 1 mmol) in methanol (25 mL). The pink solution turned brown immediately due to the formation of the [Co^{II}{(naph)$_2$dien}] 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)$_2$dpt}(amine)]BPh_4 were prepared by a procedure similar to that for [Co^{III}{(naph)$_2$dien}(amine)]BPh_4 except that H_2(naph)$_2$dpt ligand (439 mg, 1 mmol) was used instead of H_2(naph)$_2$dien.

*2.2.3.1. [Co{(naph)$_2$dien}(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). ^{1}H 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)$_2$dien}(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). ^{1}H 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)$_2$dien}(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). ^{1}H 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)$_2$dien}(N-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). ^{1}H 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)$_2$dpt}(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). ^{1}H 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)$_2$dpt}(3-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, C═N). UV–Vis: λ_{max} (nm) (ε, L mol^{-1} cm^{-1}) (CH_2Cl_2): 602 (263), 417 (sh, 6600), 400 (7500), 326 (sh, 25 000), 221 (172 000). ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 1.45–5.36 (m, 13H, $H_{a,a',b,b',c,c',NH}$), 1.90 (s, 3H, H_{methyl}), 2.01 (br, 1H, NH), 6.65–7.91 (m, 36H, $H_{naphthyl,3-Mepy,BPh_4^-}$), 8.06, 8.14 (s, 2H, $H_{d,d'}$).

2.3. X-ray crystallography for (**2**) and (**6**)

Dark brown crystals suitable for X-ray crystallography were obtained by slow evaporation of the proper solutions of the complexes at room temperature. Thin-slice ω- and φ-scans (0.5° frames) were collected, at 100 K, on a Bruker Kappa APEX-II CCD diffractometer (Mo Kα radiation, λ = 0.71073 Å) for **2** and **6** [42]. Cell refinement and data reduction were performed with the help of the SAINT program [42]. Empirical absorption corrections, based on redundant intensities, were carried out using SADABS [42]. The structures were solved by direct methods and refined by full matrix least-squares on F^2 data using SHELXL-97 [43]. Anisotropic displacement parameters were assigned to all non-hydrogen atoms. Hydrogen atoms were inserted in calculated positions and treated as riding on their parent atoms. The crystals of **2** contained disordered solvent in isolated voids of 144 Å^3 with ca. 22 electrons per formula unit (four equivalent voids per unit cell). The contribution of this solvent to the structure factors was removed with procedure SQUEEZE of program PLATON [44] prior to the final refinement. Crystal data, together with other relevant information on structure determination, are listed in Table 1.

Table 1
Crystal data and structure refinement for (**2**) and (**6**).

Compound	(**2**)[a]	(**6**)
Empirical formula	$C_{54}H_{52}BCoN_4O_2$	$C_{58}H_{54}BCoN_4O_2$
Formula weight	858.74	908.79
Temperature (K)	100(2)	100(2)
Crystal system	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1/n$
a (Å)	13.6932(7)	14.5268(7)
b (Å)	10.9037(6)	19.3646(9)
c (Å)	31.2252(16)	17.1883(8)
α (°)	90.00	90.00
β (°)	93.472(3)	107.985(2)
γ (°)	90.00	90.00
V (Å^3)	4653.6(4)	4598.9(4)
Z	4	4
D_{calc} (Mg/m^3)	1.226	1.313
μ (mm^{-1})	0.414	0.423
Crystal size (mm)	0.42 × 0.30 × 0.20	0.45 × 0.25 × 0.12
F(0 0 0)	1808	1912
θ Ranges (°)	2.3–30.0	2.2–7.0
Index ranges	$-19 \leqslant h \leqslant 19$, $-15 \leqslant k \leqslant 15$, $-43 \leqslant l \leqslant 43$	$-18 \leqslant h \leqslant 17$, $-24 \leqslant k \leqslant 24$, $-21 \leqslant l \leqslant 21$
Absorption correction	multi-scan	multi-scan
Reflections collected	96 364	64 883
Independent reflections (R_{int})	13 332 (0.059)	10 028 (0.056)
Maximum and minimum transmission	0.92, 0.69	0.95, 0.82
Data/restraints/ parameters	13 332/0/559	10 028/0/596
Goodness-of-fit (GOF) on F^2	1.037	1.046
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0509, wR_2 = 0.1321	R_1 = 0.0534, wR_2 = 0.1224
R indices (all data)	R_1 = 0.0642, wR_2 = 0.1369	R_1 = 0.0785, wR_2 = 0.1381
Largest difference in peak and hole (e Å^{-3})	1.42 and −0.59	1.26 and −1.23

[a] Contains disordered solvent that was *squeezed* with program PLATON [45] and is not contained in chemical formula and quantities derived thereof.

3. Results and discussion

3.1. Synthetic study

H_2(naph)$_2$dien and H_2(naph)$_2$dpt were prepared by the literature method [41] with some modification via the condensation of 2-hydroxy-1-naphthaldehyde with diethylenetriamine (dien) and dipropylenetriamine (dpt), respectively. Methanol was used as the solvent and the bright yellow ligands were precipitated out by adding water to the reaction mixture. The products were characterized by IR, UV–Vis and ^{1}H NMR spectroscopy. The new complexes (**1**–**6**) were prepared through the oxidation of the intermediates [Co^{II}{(naph)$_2$dien}] or [Co^{II}{(naph)$_2$dpt}] in the presence of the appropriate amine (Scheme 1). A vigorous stream of air was passed through a solution of the Co^{II} complexes in methanol to which was gradually added excess amine. The air oxidation was continued for a period of 3 h during which the color changed from brown-red to brown-green. Dark brown crystals of these complexes were obtained after addition of $NaBPh_4$ in good yield (65–75%) for (**1**–**4**) and (60–76%) for (**5**–**6**).

3.2. Description of structures

3.2.1. Crystal structure of [Co^{III}{(naph)$_2$dien}(prldn)]BPh$_4$ (**2**)

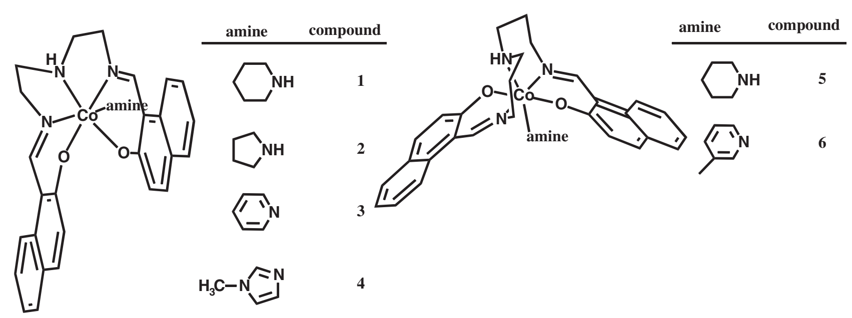
The structure of [Co^{III}{(naph)$_2$dien}(prldn)]BPh$_4$ (**2**) with atom numbering is presented in Fig. 1a. Selected bond angles and distances are listed in Table 2 and are in good agreement with the corresponding data in related complexes [38]. The environment surrounding the Co(III) ion in (**2**) is distorted octahedral in which the three donor N atoms of the Schiff base ligand are arranged in facial positions and the two naphthalate-O atoms are cis. The ancillary pyrrolidine ligand completes the octahedral coordination trans to N1 of the Schiff base. The (naph)$_2$dien ligand adopts a conformation similar to that observed for (Me-sal)$_2$dien in [Co^{III}{(Me-sal)$_2$dien}(pprdn)]BPh$_4$ [38] but different from the arrangement in [Co^{III}{(Me-sal)$_2$dien}(N$_3$)] where the three donor N atoms of (Me-sal)$_2$dien occupy three meridional sites [39].

Of the three trans angles, one {O1–Co1–N3, 177.06(5)°} is close to ideal and the other two {O2–Co1–N2, 175.02(5)° and N1–Co1–N4, 173.50(6)°} deviate slightly. The two chelate bite angles formed by the two imine-N and the secondary amine-N of the Schiff base {N1–Co1–N2, 84.15(6)°; N2–Co1–N3, 83.88(6)°} are almost identical. However, the six-membered chelate rings formed by the naphthalate-O and the imine-N atoms have different bite angles {O1–Co1–N1, 88.77(6)°; O2–Co1–N3, 93.43(5)°}. This difference is the result of structural demands (intra- and intermolecular) on the (naph)$_2$dien Schiff base ligand, which forced the atoms C11, N1, C12, C13, N2 to be 0.65, 0.61, 1.69, 2.31, and 1.21 Å off from the l.s. plane of napthyl moiety 1 (C1 through C10), whereas their equivalents C16, N3, C15, C14, N2 are only 0.13, 0.20, 0.31, 0.53, and 0.27 Å off from the l.s. plane of naphthyl moiety 2 (C17 through C26). Thus the [Co^{III}{(naph)$_2$dien}(prldn)]$^+$ cation attains a distinctly twisted structure with sterically notably inequivalent arms of the (naph)$_2$dien Schiff base ligand.

The packing diagram of (**2**), (Fig. 2), shows no significant bonding features (π–π stacking or strong hydrogen bonding); however it is apparent that the complex cations are arranged in layers parallel to (0 0 1) and alternate with layers of BPh$_4$ anions. Within one layer the complex cations show many short ranged C–H···C,O interactions.

3.2.2. Crystal structure of [Co^{III}{(naph)$_2$dpt}(3-Mepy)]BPh$_4$ (**6**)

The structure of [Co^{III}{(naph)$_2$dpt}(3-Mepy)]BPh$_4$ (**6**) with atom numbering is presented in Fig. 1b. Selected bond angles and distances are listed in Table 2 and are in good agreement with



Scheme 1. Structural formula of the Co(III) complexes and ligands. BPh_4^- omitted for simplicity.

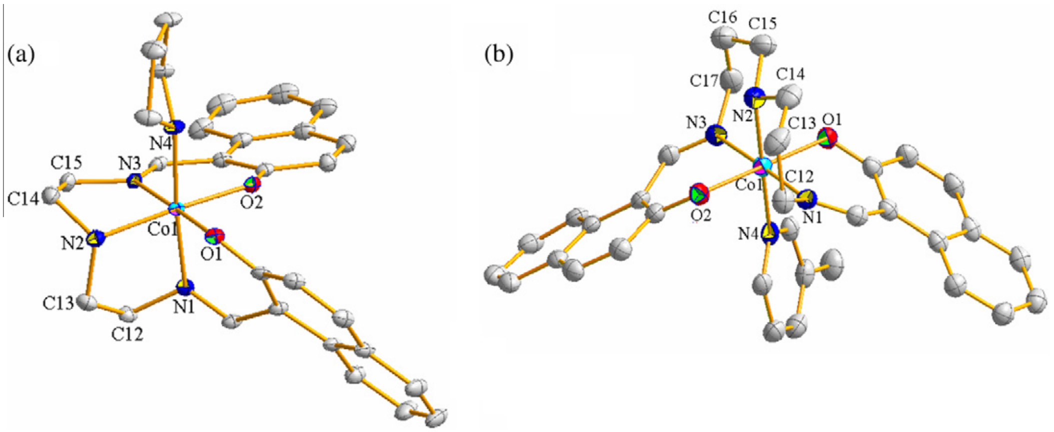


Fig. 1. ORTEP diagram of (a) complex (**2**) cation $[Co^{III}\{(naph)_2dien\}(prldn)]^+$, and (b) complex (**6**) cation $[Co^{III}\{(naph)_2dpt\}(3\text{-}Mepy)]^+$ with the atom labeling scheme. The displacement ellipsoides are drawn at the 50% probability level.

Table 2
Selected bond lengths (Å) and angles (°) for (**2**) and (**6**).

Complex (**2**)		Complex (**6**)	
Bond lengths			
Co(1)–N(1)	1.8797(14)	Co(1)–N(1)	1.929(2)
Co(1)–N(2)	1.9772(14)	Co(1)–N(2)	2.000(3)
Co(1)–N(3)	1.8910(14)	Co(1)–N(3)	1.920(2)
Co(1)–N(4)	2.0097(14)	Co(1)–N(4)	1.967(2)
Co(1)–O(1)	1.8985(12)	Co(1)–O(1)	1.889(2)
Co(1)–O(2)	1.8813(11)	Co(1)–O(2)	1.878(2)
Bond angles			
O(1)–Co(1)–N(1)	88.77(6)	O(1)–Co(1)–N(1)	88.89(9)
N(1)–Co(1)–N(2)	84.15(6)	N(1)–Co(1)–N(2)	89.92(10)
N(2)–Co(1)–N(3)	83.88(6)	N(2)–Co(1)–N(3)	90.42(10)
O(2)–Co(1)–N(3)	93.43(5)	O(2)–Co(1)–N(3)	89.58(9)
O(1)–Co(1)–O(2)	89.17(5)	O(1)–Co(1)–O(2)	177.06(8)
O(1)–Co(1)–N(2)	93.61(5)	O(1)–Co(1)–N(2)	89.75(10)
O(1)–Co(1)–N(4)	85.20(6)	O(1)–Co(1)–N(4)	89.50(9)
O(2)–Co(1)–N(1)	91.80(5)	O(2)–Co(1)–N(1)	88.90(9)
O(2)–Co(1)–N(4)	85.71(5)	O(2)–Co(1)–N(4)	92.46(9)
N(1)–Co(1)–N(3)	92.50(6)	N(1)–Co(1)–N(3)	178.43(10)
N(2)–Co(1)–N(4)	98.62(6)	N(2)–Co(1)–N(4)	179.02(10)
N(3)–Co(1)–N(4)	93.64(6)	N(3)–Co(1)–N(4)	89.00(10)
O(1)–Co(1)–N(3)	177.06(5)	O(1)–Co(1)–N(3)	92.64(9)
O(2)–Co(1)–N(2)	175.02(5)	O(2)–Co(1)–N(2)	88.32(9)
N(1)–Co(1)–N(4)	173.50(6)	N(1)–Co(1)–N(4)	90.69(9)

the corresponding data in related complexes [37]. The overall geometry around Co^{III} center in (**6**) is distorted octahedral in a fashion that the three donor N atoms of the Schiff base ligand are arranged in meridional positions and the two naphthalate-O atoms are trans. This arrangement is similar to that of $[Co^{III}\{(Me\text{-}sal)_2\text{-}dpt\}(py)]PF_6$ [37] and $[Co^{III}\{(Me\text{-}sal)_2dpt\}(N_3)]$ [39].

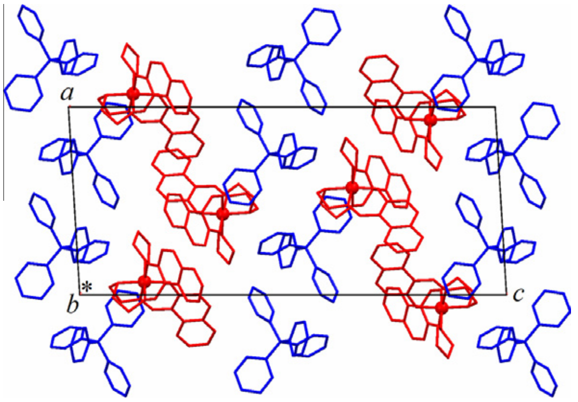


Fig. 2. Packing diagram of (**2**) along the b axis. H-atoms omitted for clarity.

In contrast to (**2**), the three trans angles in (**6**) {O1–Co1–O2, 177.06(8)°; N1–Co1–N3, 178.43(10)° and N2–Co1–N4, 179.02(10)°} are all close to ideal. The four chelate bite angles formed by the two imine-N and the secondary amine-N of the Schiff base {N1–Co1–N2, 89.92(10)°; N2–Co1–N3, 90.42(10)°} and the six-membered chelate rings formed by the naphthalate-O and the imine-N atoms {O1–Co1–N1, 88.89(9)°; O2–Co1–N3, 89.58(9)°} are almost identical. It is evident that the deviation from ideal is less significant in complex (**6**) relative to (**2**). This is presumably due to the presence of the additional $-CH_2-$ group in $(naph)_2dpt$ making it structurally more adaptive than $(naph)_2dien$.

In the adopted conformation of the $(naph)_2dpt$ ligand in (**6**), the naphthaldimine groups are bent away from the axial position occupied by the secondary amine of dpt with different angles (the angle between the normal to equatorial plane [Co1, O1, O2, N1, N3] and the normal to the two naphthalene rings are 30.15°, 36.41°). The two six-membered chelate rings formed by the iminic nitrogens (N1 and N3) and the secondary amine nitrogen (N2) have different conformations, one being boat and the other chair. These rings, linking the naphthaldimine moieties to the secondary amine nitrogen (N2), presumably play the major role in the asymmetrical bending of the two naphthaldimine groups.

No significant bonding features (π–π stacking or strong hydrogen bonding), have been observed in the packing diagram of (**6**) except that two complexes make a dimer in the crystal owing to an edge-to-edge π–π interaction between two 3-Mepy ligands of the adjacent complexes (Fig. 3).

3.3. Spectral characterization

The IR spectrum of H_2(naph)$_2$dien and H_2(naph)$_2$dpt exhibit a broad band characteristic of OH at 3418 and 3433 cm^{-1}, respectively. The absence of these bands in the IR spectra of the complexes indicates that the ligands are coordinated as dianions. The bands at 1633 and 1631 cm^{-1} characteristic of the imine C=N, in the free ligands are shifted to lower frequencies in the IR spectra of the corresponding complexes, due to coordination of the imine nitrogen [39].

The electronic absorption spectrum of H_2(naph)$_2$dien in dichloromethane consists of two intense bands centered at 233 and 308 nm, assigned to $\pi \rightarrow \pi^*$ transitions of the naphthalene rings and the azomethine group, respectively, and two bands at 403 and 419 nm, corresponding to $n \rightarrow \pi^*$ which, upon coordination of the ligand, disappears from the UV–Vis spectrum of its cobalt complexes. The electronic spectra of the complexes show, in addition to bands in the UV region due to internal transitions in the ligand, charge-transfer bands at 423–447 nm and bands in the visible region at 558–589 nm corresponding to d → d transition.

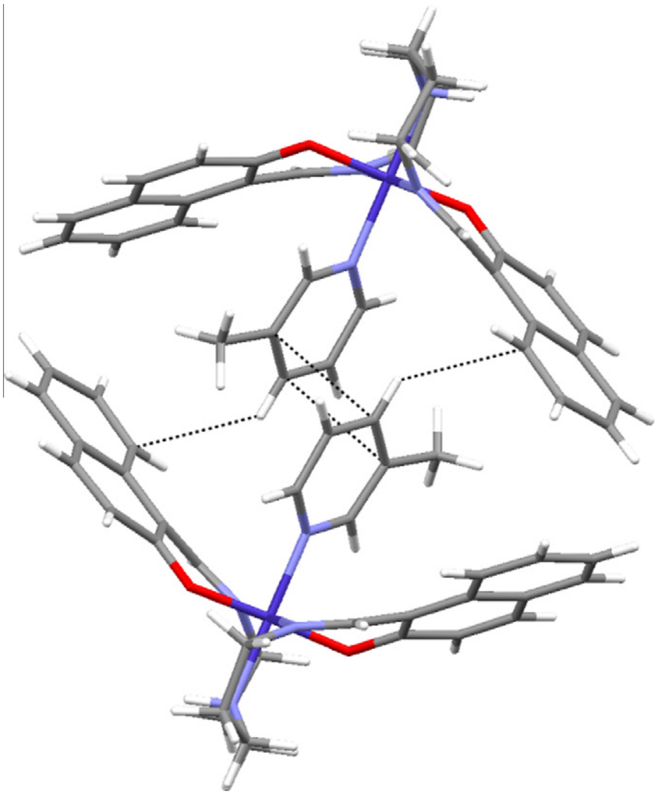


Fig. 3. Edge-to-edge π–π interaction between two 3-Mepy ligands of [Co^{III}{(naph)$_2$dpt}(3-Mepy)]BPh$_4$.

The electronic absorption spectrum of H_2(naph)$_2$dpt in dichloromethane shows features similar to those for H_2(naph)$_2$dien, the two $\pi \rightarrow \pi^*$ transitions at 232 and 306 nm, and the two $n \rightarrow \pi^*$ excitation bands appear at 403 and 421 nm. The $n \rightarrow \pi^*$ band is absent in the spectrum of the cobalt complexes. The first d → d transition appears in 602–626 nm region in the spectra of Co(III) complexes and the charge transfer transitions appear in 400–419 nm region.

The d → d transition for (naph)$_2$dpt complexes appears at longer wavelengths relative to those of (naph)$_2$dien. This significantly lower ligand field strength can be rationalized considering the conformations adopted by (naph)$_2$dpt and (naph)$_2$dien and the mutual steric effects between the two naphthalene rings in these two complexes and the ancillary ligand. Such structural effects are not present in [Co{(Me-sal)$_2$dien}(N_3)] and [Co{(Me-sal)$_2$dpt}(N_3)] complexes containing a small ligand such as N_3^- [39]. The aforementioned steric effects seem to have some influence on the electrochemical properties of this series (vide infra).

The ^{1}H NMR spectral data of the compounds are given in Section 2. The two imine protons of the ligand appear as two singlet peaks in the ^{1}H NMR of the corresponding complexes agreeing with the non-similarity of the environment of the two imine protons. The secondary amine NH is a broad multiplet at 1.81 ppm in H_2(naph)$_2$-dien that is shifted to lower field in spectra of the complexes. Signals due to the aliphatic protons of the ethylene and propylene linkages in the chelate rings are multiplets in the range of 0.84–5.06 ppm, and the aromatic protons of naphthalene rings as complex multiplets appearing between 6.92 and 8.01 ppm.

3.4. Electrochemical studies

The cyclic voltammograms of the complexes were obtained at 25 °C under an argon atmosphere using dichloromethane solution containing 0.1 M TBAH as supporting electrolyte and complex concentrations of 4×10^{-3} M at a glassy carbon working electrode. Ferrocene (Fc) was used as the internal standard, and all redox potentials are referenced to the Fc$^{+/0}$ couple. The electrochemical data are presented in Table 3.

The ligands are electro-inactive from +0.8 to −2.0 V. The redox properties of the Co(III) complexes exhibit grossly similar features consisting of an electrochemically irreversible Co^{III}/Co^{II} reduction in the range −0.614 to −0.747 V, due to:

$$[\mathrm{Co^{III}(naph)_2dien(amine)}]^+ + e^- \rightarrow [\mathrm{Co^{II}(naph)_2dien}] + \mathrm{amine}$$

Or

$$[\mathrm{Co^{III}(naph)_2dpt(amine)}]^+ + e^- \rightarrow [\mathrm{Co^{II}(naph)_2dpt}] + \mathrm{amine}$$

The reduction process of Co(III) is accompanied by the loss of the ancillary amine ligand, due to the fact that one electron is added to the antibonding d_{z^2} orbital [13]. The reduction potential of these complexes is summarized in Table 3. The Co^{III}/Co^{II} reduc-

Table 3
Redox potentials of cobalt complexes in dichloromethane.[a]

Complex	E_{pc} (V)	E_{p_a} (V)	ΔE (V)	pK_a (amine)
[Co{(naph)$_2$dien}(pprdn)] BPh$_4$	−0.718	0.045	0.763	11.12
[Co{(naph)$_2$dien}(prldn)] BPh$_4$	−0.747	0.006	0.753	11.31
[Co{(naph)$_2$dien}(py)] BPh$_4$	−0.614	−0.015	0.599	5.21
[Co{(naph)$_2$dien}(N-MeIm)] BPh$_4$	−0.692	−0.248	0.444	7.4
[Co{(naph)$_2$dpt}(pprdn)] BPh$_4$	−0.614	0.12	0.734	11.12
[Co{(naph)$_2$dpt}(3-Mepy)] BPh$_4$	−0.679	0.058	0.737	6.0

[a] Potentials are vs. Fc$^{+/0}$ in 0.1 M TBAH, T = 298 K. Scan rate, 100 mV/s. Approximate concentrations: 4×10^{-3} M.

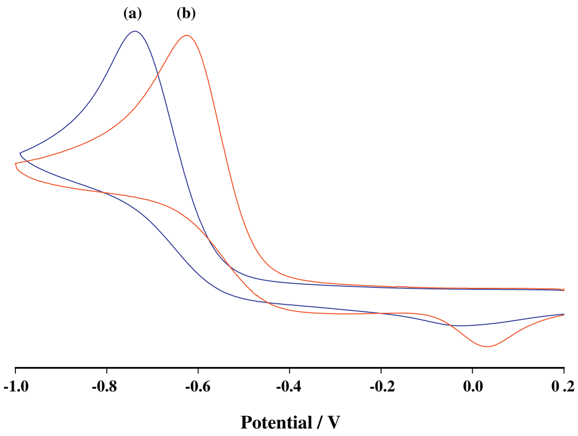


Fig. 4. Cyclic voltammogram corresponding to Co(III) → Co(II) for (a) [Co{(naph)$_2$dien}(pprdn)] BPh$_4$ (**1**) and (b) [Co{(naph)$_2$dpt}(pprdn)] BPh$_4$ (**5**) in dichloromethane at 298 K. Scan rate, 100 mV/s. Approximate concentrations: 4 × 10^{-3}.

tion potential in [Co^{III}{(naph)$_2$dien}(amine)]$^+$ complexes is relatively sensitive to the nature of the ancillary amine ligand. From the E_{pc} values (Table 3), it is evident that, stronger amine ligands shift the reduction potentials to more negative values. A similar electrochemical behavior has been observed for [Co^{III}{(naph)$_2$dpt}(amine)]$^+$ complexes.

The mutual steric hindrance between pentadentate Schiff base and the bulky ancillary ligands is another factor affecting the Co^{III}/Co^{II} reduction potential. Fig. 4 shows the cyclic voltammograms of [Co^{III}{(naph)$_2$dien}(pprdn)]$^+$, (**1**), and [Co^{III}{(naph)$_2$dpt}(pprdn)]$^+$, (**5**), complexes. The Co^{III}/Co^{II} reduction potential of [Co^{III}{(naph)$_2$dpt}(pprdn)]$^+$ complex is shifted to more positive values relative to that of the corresponding [Co^{III}{(naph)$_2$dien}(pprdn)]$^+$ complex. This is presumably due to the fact that the electron density transferred to the central Co(III) in (**5**) is less than that of (**1**) and is in agreement with the spectroscopic data. Interestingly, the first transition in the UV–Vis spectrum of [Co^{III}{(naph)$_2$dpt}(pprdn)]$^+$ complex appears at a longer wavelength (λ_{max} = 627 nm) relative to that of [Co^{III}{(naph)$_2$dien}(pprdn)]$^+$ (λ_{max} = 589 nm).

These results are in contrast to those reported for Co^{III}{(Me-sal)$_2$dien}(N$_3$)] and [Co^{III}{(Me-sal)$_2$dpt}(N$_3$)] complexes where no significant hindrance is expected from the small N$_3$$^-$ ancillary ligand [39]. As a matter of fact, a better overlap between the donor orbitals of (Me-sal)$_2$dpt ligand and the appropriate d-orbitals of cobalt(III) center relative to (Me-sal)$_2$dien, leads to a more negative reduction potential in [Co^{III}{(Me-sal)$_2$dpt}(N$_3$)] complex as compared to that of [Co^{III}{(Me-sal)$_2$dien}(N$_3$)] [39].

The effect of the fused phenyl rings of the ligands on the redox potential of cobalt center is evident from the comparison between the electrochemical data of these complexes with those obtained for related complexes. These data show that Co$^{III/II}$ reduction of [Co^{III}{(naph)$_2$dien}(amine)]$^+$ and [Co^{III}{(naph)$_2$dpt}(amine)]$^+$ complexes occur at more positive potentials relative to [Co^{III}{(Me-sal)$_2$dien}(amine)]$^+$ and [Co^{III}{(Me-sal)$_2$dpt}(amine)]$^+$ complexes. For example the reduction potentials of [Co^{III}{(naph)$_2$dien}(prldn)]$^+$ and [Co^{III}{(Me-sal)$_2$dien}(prldn)]$^+$ are −0.74 and −0.944 V (ΔE = 197 mV). This can be attributed to the electron withdrawing effect by the fused phenyl rings in (naph)$_2$dien.

The electrochemically irreversible Co^{III}/Co^{II} reduction process can become quasi-reversible in the presence of excess amine. However, contrary to the tetradentate Schiff base cobalt(III) complexes such as *trans*-[Co{(BA)$_2$pn}(4-Mepy)$_2$]ClO$_4$, [45], this process remained irreversible for (naph)$_2$dien complexes. This is presumably due to fact that the steric effects from (naph)$_2$dien leads to drastic structural changes in the reduced Co(II) intermediate.

4. Conclusion

The structures, spectroscopic and electrochemical properties of [Co^{III}{(naph)$_2$dien}(amine)]BPh$_4$ and [Co^{III}{(naph)$_2$dpt}(amine)]BPh$_4$ complexes have been investigated. The structural features of these complexes are similar to the analogous complexes, [Co^{III}{(Me-sal)$_2$dien}(N$_3$)] and [Co^{III}{(Me-sal)$_2$dpt}(N$_3$)]. However, the spectral and electrochemical properties of these complexes are somewhat different from the azido analogs. The Co^{III}/Co^{II} reduction potential of [Co^{III}{(naph)$_2$dpt}(amine)]$^+$ is shifted to more positive values relative to that of the corresponding [Co^{III}{(naph)$_2$dien}(amine)]$^+$ complexes, a trend opposite to that observed for [Co^{III}{(Me-sal)$_2$dien}(N$_3$)] and [Co^{III}{(Me-sal)$_2$dpt}(N$_3$)]. The electron withdrawing effect of the fused phenyl rings in (naph)$_2$dien and (naph)$_2$dpt ligands render the cobalt center to be more easily reducible and the corresponding reduction processes occur at less negative potentials relative to their Me-sal analogs.

Acknowledgment

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Appendix A. Supplementary material

CCDC 796823 and 796824 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2011.02.027.

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