



Fine electronic state tuning of cobaltadithiolene complexes by substituent groups on the benzene ring



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ABSTRACT

A series of 3,6- and 4,5-dihalogen-substituted 1,2-benzenedithiol (H_2bdt) ligands, (3,6- X^1 -4,5- X^2 -1,2- H_2bdt) ($X^2 = H$, $X^1 = F$ (**1a**), Cl (**1b**), Br (**1c**); $X^1 = H$, $X^2 = Cl$ (**4**)), and their cobalt complexes, $[Cp^*Co(3,6- X^1 -4,5- X^2 -1,2- bdt)]$ ($X^2 = H$, $X^1 = F$ (**2a**), Cl (**2b**), Br (**2c**); $X^1 = H$, $X^2 = Cl$ (**5**)), were synthesized by a modified selective thiolation reaction. The 1,2-diphenyl-substituted cobaltadithiolene complex (**2d**) was also synthesized. The molecular structures of all cobaltadithiolene complexes were determined by single crystal X-ray diffraction analysis. Compounds **2a**, **5** and **12** showed unique packing structures with intermolecular interactions that confirmed them as the first examples of half-sandwich-type metalladithiolene complexes with a Cp^* ligand. The effects of the benzene substituent type and position on the metalladithiolene ring were investigated using UV–vis spectroscopy measurements and cyclic voltammetry. The results indicate that substitution of halogen atoms at the 3 and 6 position of the benzene ring had a larger effect on the dithiolene ring than substitution at the 4 and 5 positions.

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1. Introduction

The electronic state of the central metal ion in metal complexes is one of the main factors determining the nature of the complex. The electronic state is also effected by ligands and ligand substituents. Alteration of the substituents often drastically changes the properties of a complex, such as photophysical [1–8] and catalytic abilities [9–14].

Metalladithiolene complexes have been studied in a wide range of fields because of their unique properties, such as reversible redox activity, magnetic properties and catalytic abilities [15–20]. Many types of dithiolene ligand have been synthesized with different substituents in order to study their effects on the metal center in metalladithiolene rings. In particular, 1,2-benzenedithiolate (bdt^{2-}) is one of the most common ligands in metalladithiolene chemistry. Different substituents on the benzene dithiolate ligand elicit changes in the properties of its complexes, especially catalytic [21–26], magnetic [27] and electrochemical properties [28,29]. Fine control of the electronic state by substitution on the benzene dithiolate ligand is important in order to develop remarkable properties. Systematic halogen exchange on the benzenedithiolate ligand is a conceivable way to exert precise changes on the metal center. Several examples of the synthesis of halogen-substituted benzenedithiolate ligands and their complexes have been reported [21–30]. However, the effect of the substitution position and halogen type have not been investigated in a systematic way because the synthesis of halogen-substituted dithiol ligands is difficult due to the high reactivity of halogens. Therefore, the development of a facile synthetic method for halogen-substituted benzenedithiolate ligands is desirable.

Here, we report the synthesis of 3,6-dihalo and 4,5-dichloro-1,2-benzenedithiols and their incorporation as ligands in cobaltadithiolene complexes. 3,6-Diphenyl-1,2-benzenedithiol and its cobaltadithiolene complex are also synthesized. Their properties are investigated using single crystal X-ray diffraction, UV–vis spectroscopy and electrochemical measurements.

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2. Experimental

2.1. General information

Commercially available reagents were used without further purification. Solvents were purified before use according to reported methods. Reactions were carried out under an argon atmosphere unless stated otherwise. Tetrahydrofuran (THF) was freshly distilled from sodium/benzophenone ketyl under N_2 . Column chromatography was performed using Wakogel® C-200 (Silica Gel, 75–150 μm).

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^1H NMR (300 or 500 MHz) and $^{13}\text{C}\{^1\text{H}\}$ NMR (75 or 126 MHz) spectra were measured using tetramethylsilane as an external standard. ^{19}F NMR (376 MHz) spectra were measured using trifluoroacetic acid as an external standard. All melting points are uncorrected.

For structural determinations, crystal data were collected using a Bruker AXS SMART APEX CCD X-ray diffractometer equipped with a rotating-anode X-ray generator emitting graphite-monochromatic Mo K α radiation (0.7107 Å). Empirical absorption corrections using equivalent reflections and Lorentzian polarization corrections were performed using the SADABS program [31]. All data were collected with SMART and Bruker SAINTPLUS (Version 6.45) software packages. The structures were solved using the SHELXS-97 [32] program and refined against F^2 by using SHELXL-97 [33].

Electrochemical data were recorded with an ALS 650E electrochemical analyzer. Bu_4NClO_4 used as a supporting electrolyte, which was recrystallized from EtOH, and dried under vacuum for 24 h. A series of measurements were carried out under an argon atmosphere in a three-electrode cell (BAS Inc.), using 3 mm-diameter glassy carbon as a working electrode (BAS Inc.), a platinum wire as a counter electrode and Ag/AgClO_4 as a reference electrode (0.01 M AgClO_4 in 0.1 M Bu_4NClO_4 /acetonitrile, BAS Inc.). After each measurement, ferrocene was added as an internal standard. Caution; Bu_4NClO_4 is a potentially explosive chemical.

Elemental analyses were performed using a PerkinElmer 2400II CHNS analyzer. Satisfactory elemental analyses for compounds **1a–1c**, **2a**, **2c**, **2d**, **4**, **5** and **7** could not be obtained, but high resolution mass spectra for **1a–1c**, **2a**, **2c**, **2d**, **4**, **5** and **7** are in accord with the formulations.

1,2,3,4-Tetrabromobenzene (**3c**) [34] and 1,2-difluoro-3,6-diiodobenzene (**11**) [35] were prepared according to the methods described in the literature.

2.2. General procedure for the synthesis of 3,6-dihalo-1,2-benzenedithiol

1,2,3,4-Tetrahalobenzene (10 mmol), iron powder (0.89 equiv.), sulfur (0.66 equiv.) and $\text{NaSH}\cdot n\text{H}_2\text{O}$ (4.0 equiv.) were added to dry *N,N*-dimethylformamide (32 equiv.). The mixture was heated to 140 °C for 16 h. The reaction mixture was cooled to room temperature and added to water (50 mL). The mixture was filtered and air-dried to afford a black solid. The black solid was then added to a solution of methanol (20 mL), ZnO (1.2 equiv.), NaOH (6.5 equiv.) and water (20 mL), and allowed to reflux for 2 h. After cooling to room temperature, the mixture was filtered with Celite. The filtrate was added to 2 M H_2SO_4 and then extracted with dichloromethane. The organic phase was washed with brine and dried with MgSO_4 . After filtration, evaporation and drying, the corresponding 3,6-dihalo-1,2-benzenedithiol was afforded as a solid.

2.3. Synthesis of 3,6-difluoro-1,2-benzenedithiol (**1a**)

The general procedure was performed using 1,2,3,4-tetrafluorobenzene **3a** (1.5 g, 10 mmol) and $\text{NaSH}\cdot n\text{H}_2\text{O}$ (1.9 g, 22 mmol, 2.2 equiv.). The reaction mixture was stirred for 24 h at 140 °C in a sealed tube to obtain **1a** as a dark green solid (0.37 g, 21%).

^1H NMR (500 MHz, CDCl_3) δ , ppm: 6.87 (2H, t, $J = 6.5$ Hz, Ar–H), 3.93 (2H, s, SH); $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3) δ , ppm: 155.0 (dd, $J = 242$, 3.8 Hz), 120.2 (dd, $J = 16$, 9.6 Hz), 112.4 (dd, $J = 21$, 13 Hz); ^{19}F NMR (470 MHz, CDCl_3) δ , ppm: –110.95 (t, $J = 5.9$ Hz); HR-MS (HR-ESI-TOF) m/z calc. for $\text{C}_6\text{H}_3\text{F}_2\text{S}_2$: 176.96497 $[\text{M}–\text{H}]^-$, found: 176.96448.

2.4. Synthesis of 3,6-dichloro-1,2-benzenedithiol (**1b**)

The general procedure was performed using 1,2,3,4-tetrachlorobenzene **3b** (0.43 g, 2 mmol) to obtain **1b** as a dark green solid (0.13 g, 13%).

^1H NMR (300 MHz, CDCl_3) δ , ppm: 7.17 (2H, s, Ar–H), 4.62 (2H, s, SH); IR (KBr, ν/cm^{-1}): 3057 (CH), 2563 (SH).

2.5. Synthesis of 3,6-dibromo-1,2-benzenedithiol (**1c**)

The general procedure was performed using 1,2,3,4-tetrabromobenzene **3c** (9.4 g, 24 mmol) to obtain **1c** as a brown viscous solid (0.69 g, 23%).

^1H NMR (300 MHz, CDCl_3) δ , ppm: 7.25 (2H, s, Ar–H), 4.85 (2H, s, SH); $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, CDCl_3) δ , ppm: 131.9 (s), 134.1 (s), 122.5 (s); HR-MS (HR-FAB) m/z calc. for $\text{C}_6\text{H}_3^{79}\text{Br}^{81}\text{BrS}_2$: 298.8022 $[\text{M}–\text{H}]^-$, found: 298.8055; IR (KBr, ν/cm^{-1}) 2920 (CH), 2543 (SH).

2.6. Synthesis of $\text{Cp}^*\text{CoF}_2\text{bdt}$ (**2a**)

A solution of 3,6-difluoro-1,2-benzenedithiol **1a** (0.18 g, 1.0 mmol) and $\text{Cp}^*\text{Co}_2(\text{CO})$ (0.48 g, 1.0 mmol, 1 equiv.) in THF (5 mL) was stirred for 2 h at room temperature. The reaction mixture was then evaporated, and the crude product was purified by column chromatography on silica gel using dichloromethane/hexane (2:8) as the eluent. The purple first fraction was collected and evaporated to yield **2a** as a dark purple solid (0.23 g, 59%).

^1H NMR (500 MHz, CDCl_3) δ , ppm: 6.77 (2H, t, $J = 6.3$ Hz, Ar–H), 1.97 (15H, s, CH_3); $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3) δ , ppm: 155.8 (dd, $J = 243$, 4.4 Hz), 143.8 (dd, $J = 15$, 9.6 Hz), 107.9 (dd, $J = 20$, 13 Hz), 92.7 (s), 11.0 (s); ^{19}F NMR (470 MHz, CDCl_3) δ , ppm: –117.62 (s); HR-MS (HR-ESI-TOF) m/z calc. for $\text{C}_{16}\text{H}_{18}\text{F}_2\text{CoS}_2\text{Na}$: 392.99694 $[\text{M}+\text{Na}]^+$, found: 392.99682.

2.7. Synthesis of $\text{Cp}^*\text{CoCl}_2\text{bdt}$ (**2b**)

The method described above for the preparation of **2a** was performed using **1b** (0.21 g, 1.0 mmol). The reaction mixture was refluxed for 2 h to obtain **2b** as a dark purple solid (0.59 g, 92%).

^1H NMR (300 MHz, CDCl_3) δ , ppm: 7.32 (2H, s, Ar–H), 1.91 (15H, s, CH_3); $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, CDCl_3) δ , ppm: 154.5 (s), 126.9 (s), 122.5 (s), 93.4 (s), 11.0 (s); Anal. Calc. for $\text{C}_{16}\text{H}_{17}\text{S}_2\text{CoCl}_2$: C, 47.22; H, 4.14. Found: C, 47.54; H, 4.49%.

2.8. Synthesis of $\text{Cp}^*\text{CoBr}_2\text{bdt}$ (**2c**)

The method described above for the preparation of **2a** was performed using **3c** (0.096 mg, 0.32 mmol) to obtain **2c** as a black-purple solid (110 mg, 73%).

^1H NMR (500 MHz, CD_2Cl_2) δ , ppm: 7.27 (2H, s, Ar–H), 1.95 (15H, s, CH_3); $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CD_2Cl_2) δ , ppm: 154.5 (s), 122.5 (s), 93.4 (s), 11.0 (s); HR-MS (HR-APCI-TOF) m/z calc. for $\text{C}_{16}\text{H}_{18}^{79}\text{Br}^{81}\text{BrCoS}_2$: 490.85487 $[\text{M}+\text{H}]^+$, found: 490.85411; IR (KBr, ν/cm^{-1}) 2984 (CH), 2912 (CH).

2.9. Synthesis of 1,2-dichloro-4,5-diiodobenzene (**6**)

A slightly modified reported literature method was used to synthesize **6** in 80% yield, using 1,2-dichlorobenzene instead of 1,2-dibromobenzene [36]. Spectral data for the product was in agreement with the previous report [37].

2.10. Synthesis of 4,5-dichloro-1,2-benzenedithiol (**4**)

The general procedure was performed using **1a** (4.0 g, 10 mmol) to obtain **4** as a gray-green solid (0.9 g, 43%).

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