



Note

Reactions of half-sandwich Co(III) complexes with heterocyclic thione ligands: η^2 -N, S coordination mode and formation of S–S bond

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ABSTRACT

The reactions of $\text{Cp}^*\text{CoI}_2(\text{CO})$ with heterocyclic thione ligands yields a η^2 -N, S coordination family of cobalt complexes for adjacent N, S donor atoms, and dinuclear disulfide cobalt complexes for opposite N, S donor atoms.

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1. Introduction

Heterocyclic thiones have attracted considerable interest as ligands in metal complexes for their structural and reactivity features and their wide range of applications in analytical chemistry, medicine, and biology as biocides [1–9]. There are two or more donor atoms in these types of ligands, which endows them with multifunctional coordination ability. A heterocyclic thionate ligand can coordinate to one metal center as a monodentate or bidentate ligand, and can also act in polynuclear complexes as a bridging ligand between two, three, or even more metal centers [10–14].

Although a lot of complexes of such heterocyclic thione ligand with metal atoms have been synthesized and studied [15–21], the half-sandwich complexes, which have cobalt, rhodium, and iridium centers with these ligands, are still under comprehensive investigation [22–24]. In our previous work, we synthesized complex $\text{Cp}^*\text{CoI}_2(2\text{-PyS})$ in a very high yield, which was used as a starting material to study the reaction with monodentate or bidentate 1,2-dicarba-closo-dodecaborane thiolate, 2-pyridinethiolate, 2-pyridinethione, 4-pyridinethiolate and benzenethiolate ligands and some interesting phenomena were detected, such as C–H activation reaction [25,26]. Herein, we describe the reactions of half-sandwich cobalt(III) diiodide complexes with benzo[d]thiazole-2-thiolate, benzo[d]oxazole-2-thiolate, thiazoline-2-thiolate ligands containing adjacent N, S donor atoms and 4-pyridinethiolate, 4-HS–C₆H₄–N=CH–4'-C₅H₄N (HL) contain-

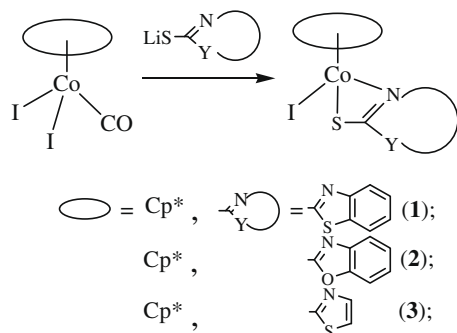
ing opposite N, S donor atoms, respectively. And the unexpected reaction results involving the ligands with opposite N, S donor atoms are also described.

2. Results and discussion

2.1. Reaction with ligands containing adjacent N, S donor atoms

First, we studied the reactions of $\text{Cp}^*\text{CoI}_2(\text{CO})$ with lithium benzo[d]thiazole-2-thiolate, lithium benzo[d]oxazole-2-thiolate or lithium thiazoline-2-thiolate in the THF solvent. And complex $\text{Cp}^*\text{CoI}_2(2\text{-BtaS})$ (**1**), $\text{Cp}^*\text{CoI}_2(2\text{-BoaS})$ (**2**) or $\text{Cp}^*\text{CoI}_2(2\text{-TaS})$ (**3**) was isolated as green crystals in about 80% yield, respectively (Scheme 1). Complexes **1**, **2** and **3** are all a little air sensitive and soluble in common organic solvents, such as CH_2Cl_2 and THF. The ¹H NMR spectra exhibit the resonances for both the heterocyclic thiolate moiety and the cyclopentadienyl ring (see Section 4). Although the S and O atom in the heterocyclic thionate ligands are potential coordinating atoms, the adjacent N atom usually shows stronger coordinating ability to give a η^2 -S, N chelating complex like the complex $\text{Cp}^*\text{CoI}_2(2\text{-PyS})$ [25] that we have reported. And the NMR and Elemental analysis data together with the experimental phenomenon all support the mononuclear result. However, when **1**, **2** or **3** was reacted with the bidentate mercapto ligand $\text{Li}_2\text{S}_2\text{C}_2\text{B}_{10}\text{H}_{10}$ in the same reaction conditions as $\text{Cp}^*\text{CoI}_2(2\text{-PyS})$, respectively, the complex with activation of the ring-methyls in pentamethylcyclopentadienyl was not formed, rather the known dithio-ortho-carboranyl cobalt(III) complex ($\text{Cp}^*\text{CoS}_2\text{C}_2\text{B}_{10}\text{H}_{10}$) was obtained in high yield.

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Scheme 1. Synthesis of complex 1–3.

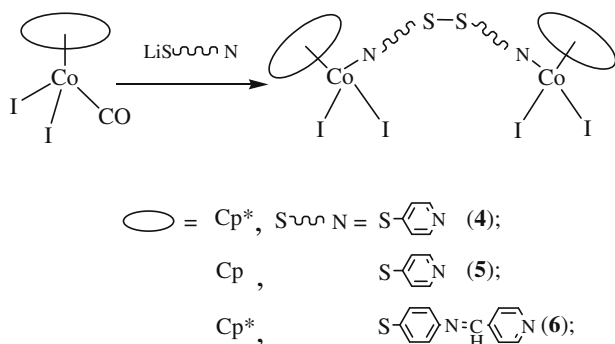
2.2. Reaction with containing opposite N, S donor atoms

Following the successful generation of **1**, **2** and **3**, we focused our interest on ligands with S and N atoms in opposite position (Scheme 2). We chose lithium pyridine-4-thiolate in order to get novel compound, which we expected to be multinuclear or even a metallocycle. During the reaction, the color of mixture changed from purple to yellow, then to green, which was similar to that of reaction process of $\text{Cp}^*\text{Co}_2(\text{CO})$ with adjacent S, N ligand. However, after purification, we got green solids **4** with yield of only 38%. Single Crystals suitable for X-ray diffraction analysis were obtained by slow diffusion of hexane into a saturated solution of complex **4** in dichloromethane. The structure of complex **4** was out of our expectation, in which two pyridine-4-thiolato ligands connect each other by S–S bond, with its two nitrogen atoms coordinating to two half-sandwich cobalt centers, respectively, resulting in a dinuclear disulfide compound (Fig. 1). Here, the S–S bond distance is 2.021(5), and the C–S–S–C torsion angle is 91.33(6). These values are comparable to those in some other reported complexes [27–30].

Except the main product **4**, we also observed some other by-products, which were hard to be separated and identified. Since the whole process were taken under N_2 atmosphere, the starting cobalt(III) complex here may partially play a role of oxidant, however, it is not easy to explain the mechanism of the reaction with-out enough supporting information.

The similar reaction of $\text{CpCo}_2(\text{CO})$ and lithium pyridine-4-thiolate gave complex **5** as green solids in yield of 34%. Complex **6** was synthesized in the same way with $\text{Cp}^*\text{Co}_2(\text{CO})$ and 4-LiS-C₆H₄-N=CH-4'-C₅H₄N in THF. Both of these two green complexes are only slightly soluble in common organic solvents, which make us unable to get their NMR information.

It is known that disulfide bond formation is a relevant transformation in many biological processes, and this type of linkage is of



Scheme 2. Synthesis of complex 4–6.

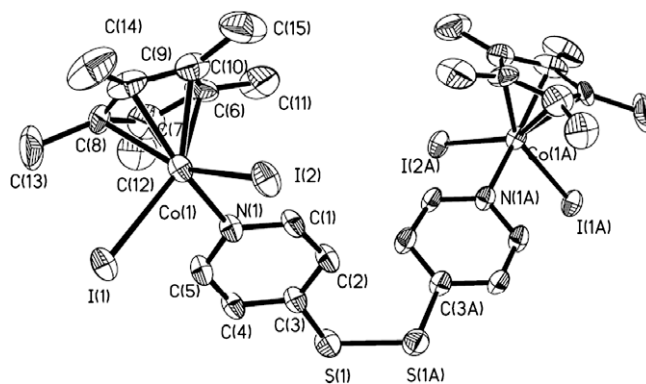


Fig. 1. Molecular structure of **4**, ellipsoids at the 30% probability level. H atoms and solvent molecules are omitted for clarity. Selected bond lengths (Å) and angles (°): Co(1)–I(1) 2.6059(11), Co(1)–N(1) 2.001(6), C(3)–S(1) 1.760(8), S(1)–S(1A) 2.021(5), N(1)–Co(1)–I(1) 93.33(17), N(1)–Co(1)–I(2) 92.71(6), I(1)–Co(1)–I(2) 91.30(7).

high practical value in industry such as useful polymers, rubber, or for the design of rechargeable lithium batteries [31,32]. Although lots of investigations involving thiol-disulfide interconversion by direct oxidation of molecular oxygen or metal-containing oxidants and catalytic oxidation in the presence of metal catalyst have been reported [33–38], disulfide bond formation at room temperature in the present of $\text{Cp}^*\text{Co}(\text{CO})\text{I}_2$ have not been mentioned or discussed. So our findings should be very interesting and valuable to be further investigated.

3. Conclusion

We have studied the reactions of half-sandwich Co(III) complexes with heterocyclic thione ligands. Three half-sandwich cobalt complexes with η^2 -N, S coordination mode were synthesized from the reaction between $\text{Cp}^*\text{Co}_2(\text{CO})$ with benzo[d]thiazole-2-thiolate (**1**), benzo[d]oxazole-2-thiolate (**2**), thiazoline-2-thiolate (**3**) ligands. In contrast, the reaction between half-sandwich Co(III) complexes with heterocyclic thione containing opposite N, S donor atoms resulted in S–S bond formation and three dinuclear complexes (Cp^*Co_2)₂(4-PDS) (**4**), (CpCo_2)₂(4-PDS) (**5**) and (CpCo_2)₂(L-L) (**6**). These interesting results are valuable to be further investigated.

4. Experimental

4.1. General procedures

All reactions and manipulations were carried out under nitrogen atmosphere using standard Schlenk techniques. Solvents were dried and deoxygenated by M. Braun Solvent Purification System (4464) and collected just before use. $\text{Cp}^*\text{Co}(\text{CO})\text{I}_2$ [39], $\text{CpCo}(\text{CO})\text{I}_2$ [39] and 4-HS-C₆H₄-N=CH-4'-C₅H₄N(HL) [40] were prepared according to the procedures described in the literature. 4-Mercaptopyridine, 2-mercaptobenzothiazole, 2-mercaptobenzoxazole and 2-mercaptothiazoline were used as purchased without further purifications.

4.2. Synthesis of $\text{Cp}^*\text{Co}(\text{CO})\text{I}_2$ (**1**)

A solution of *n*-BuLi (1.6 M, 0.27 ml, 0.42 mmol) in hexane was added dropwise to a solution of 2-mercaptobenzothiazole (70 mg, 0.42 mmol) in 8 ml THF at 0 °C. The suspension was stirred for another 1 h at room temperature. Then the solution was slowly added to a solution of $\text{Cp}^*\text{Co}(\text{CO})\text{I}_2$ (200 mg, 0.42 mmol) in THF (15 mL) at –78 °C. After it had been stirred at room temperature

for 1 day, the solvent was removed under reduced pressure, and the residue was extracted with CH_2Cl_2 . The filtrate was concentrated to about 5 mL and hexane was added, to give **1** as green solids. Recrystallization of product from CH_2Cl_2 /hexane afforded green crystals of **1**. Yield: 167 mg, 83%. Anal. Calc. for $\text{C}_{17}\text{H}_{19}\text{NCoS}_2$: C, 41.90; H, 3.93; N, 2.88. Found: C, 41.85; H, 3.98; N, 2.84%. ^1H NMR (500 MHz, CDCl_3 , ppm): δ 7.60(d, 1H, mbtz), 7.57(d, 1H, 2-mbtz), 7.39(t, 1H, 2-mbtz), 7.20(t, 1H, 2-mbtz), 1.79(s, 15H, Cp^*). ^{13}C NMR (125 MHz, CDCl_3 , ppm): δ 174.52, 148.01, 139.10, 125.90, 123.30, 122.05, 116.72(2-mbtz), 90.46, 11.35 (Cp^*). IR (KBr): 2983, 2950, 2909, 1454, 1394, 1368, 1255, 1085, 1039, 1015, 765, 689 cm^{-1} .

4.3. Synthesis of $\text{Cp}^*\text{Co}(2\text{-BoaS})$ (**2**)

Using *n*-BuLi (1.6 M, 0.27 ml, 0.42 mmol), 2-mercaptobenzoxazole (63 mg, 0.42 mmol) and $\text{Cp}^*\text{Co}(\text{CO})_2$ (200 mg, 0.42 mmol) to give **2** as green solids. Yield: 161 mg, 81%. Anal. Calc. for $\text{C}_{17}\text{H}_{19}\text{NCoSO}$: C, 43.32; H, 4.07; N, 2.97. Found: C, 43.30; H, 4.11; N, 2.93%. ^1H NMR (500 MHz, CDCl_3 , ppm): δ 7.70(d, 1H, 2-mboz), 7.46(d, 1H, 2-mboz), 7.40(t, 1H, 2-mboz), 7.13(t, 1H, 2-mboz), 1.82(s, 15H, Cp^*). ^{13}C NMR (125 MHz, CDCl_3 , ppm): δ 170.52, 152.26, 144.75, 136.47, 132.75, 125.88 (2-mboz), 90.52, 11.35 (Cp^*). IR (KBr): 2954, 2909, 2851, 1463, 1444, 1414, 1372, 1337, 1283, 1240, 1132, 1093, 1009, 893, 802, 745 cm^{-1} .

4.4. Synthesis of $\text{Cp}^*\text{Co}(2\text{-TaS})$ (**3**)

Using *n*-BuLi (1.6 M, 0.27 ml, 0.42 mmol), 2-mercaptothiazoline (50 mg, 0.42 mmol) and $\text{Cp}^*\text{Co}(\text{CO})_2$ (200 mg, 0.42 mmol) to give **3** as green solids. Yield: 145 mg, 79%. Anal. Calc. for $\text{C}_{13}\text{H}_{19}\text{NCoS}_2$: C, 35.54; H, 4.36; N, 3.19. Found: C, 35.51; H, 4.39; N, 3.17%. ^1H NMR (500 MHz, CDCl_3 , ppm): δ 3.54(t, 2H, 2-mtz); 3.37(t, 2H, 2-mtz), 1.71(s, 15H, Cp^*). ^{13}C NMR (125 MHz, CDCl_3 , ppm): δ 153.25, 56.90, 32.46 (2-mtz), 89.72, 10.79 (Cp^*). IR (KBr disk): ν = 2962, 2918, 2851, 1655, 1509, 1468, 1374, 1261, 1097, 1048, 802, 705 cm^{-1} .

4.5. Synthesis of $(\text{Cp}^*\text{Co}_2)_2(4\text{-PDS})$ (**4**)

Using *n*-BuLi (1.6 M, 0.13 ml, 0.2 mmol), 4-mercaptopyridine (22 mg, 0.2 mmol) and $\text{Cp}^*\text{Co}(\text{CO})_2$ (95 mg, 0.2 mmol) to give **4** as green solids. Yield: 42 mg, 38%. Anal. Calc. for $\text{C}_{30}\text{H}_{38}\text{N}_2\text{Co}_2\text{I}_4\text{S}_2$: C, 32.27; H, 3.43; N, 2.51. Found: C, 32.28; H, 3.46; N, 2.50%. ^1H NMR (500 MHz, CDCl_3 , ppm): δ 7.84(d, 4H, 4-PDS); 7.31(d, 4H, 4-PDS) 1.68(s, 30H, Cp^*). ^{13}C NMR (125 MHz, CDCl_3 , ppm): δ 172.75, 150.36, 129.05 (4-PDS), 91.74, 11.81 (Cp^*). IR (KBr disk): ν = 3058, 2962, 2917, 2849, 1589, 1478, 1410, 1374, 1261, 1215, 1102, 1058, 1019, 803, 714 cm^{-1} .

4.6. Synthesis of $(\text{CpCo}_2)_2(4\text{-PDS})$ (**5**)

Using *n*-BuLi (1.6 M, 0.13 ml, 0.2 mmol), 4-mercaptopyridine (22 mg, 0.2 mmol) and $\text{CpCo}(\text{CO})_2$ (95 mg, 0.2 mmol) to give **5** as green solids. Yield: 33 mg, 34%. Anal. Calc. for $\text{C}_{20}\text{H}_{18}\text{N}_2\text{Co}_2\text{I}_4\text{S}_2$: C, 24.60; H, 1.86; N, 2.87. Found: C, 24.55; H, 1.93; N, 2.83%. IR (KBr disk): ν = 3087, 1588, 1466, 1419, 1241, 1110, 1056, 1015, 813, 728 cm^{-1} .

4.7. Synthesis of $(\text{CpCo}_2)_2(\text{L-L})$ (**6**)

Using *n*-BuLi (1.6 M, 0.13 ml, 0.2 mmol), HL (43 mg, 0.2 mmol) and $\text{Cp}^*\text{Co}(\text{CO})_2$ (95 mg, 0.2 mmol) to give **6** as green solids. Yield: 40 mg, 30%. Anal. Calc. for $\text{C}_{44}\text{H}_{48}\text{N}_4\text{Co}_2\text{I}_4\text{S}_2$: C, 39.94; H, 3.66; N, 4.24. Found: C, 39.97; H, 3.70; N, 4.23; S, 4.92%. IR (KBr disk):

ν = 2958, 2905, 2843, 1613, 1592, 1477, 1425, 1375, 1321, 1209, 1170, 1107, 1058, 1012, 837, 691 cm^{-1} .

4.8. Crystal structure determinations

Selected crystallographic data for **4**: CH_2Cl_2 : $\text{C}_{32}\text{H}_{42}\text{Cl}_4\text{Co}_2\text{I}_4\text{N}_2\text{S}_2$, $M = 1286.06$, Monoclinic, $\text{C}2/c$, $a = 24.771(6)$ Å, $b = 11.618(3)$ Å, $c = 16.011(4)$ Å, $\alpha = 90^\circ$, $\beta = 101.544(4)^\circ$, $\gamma = 90^\circ$, $V = 4515(2)$ Å³, $Z = 4$, $D_c = 1.892$ g cm^{-3} , $\mu(\text{Mo K}\alpha) = 3.823$ mm⁻¹; GOF on F^2 , 1.013; R indices ($I > 2I$): $R_1 = 0.0544$, $wR_2 = 0.1400$; R indices (all data): $R_1 = 0.0881$, $wR_2 = 0.1600$.

Diffraction data of **4**: CH_2Cl_2 were collected on a Bruker Smart APEX CCD diffractometer (Mo $\text{K}\alpha$ radiation). The structures were solved by direct methods and subsequently refined on F^2 by using full-matrix least-squares techniques (SHELXL-97), all non-hydrogen atoms were refined anisotropically, and hydrogen atoms were located at calculated positions.

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Appendix A. Supplementary material

CCDC 708835 contains the supplementary crystallographic data for **4**: CH_2Cl_2 . These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via http://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.jorganchem.2009.01.040](https://doi.org/10.1016/j.jorganchem.2009.01.040).

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