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Cobalt(II)-Mediated Desulfurization of Thiophenes, Sulfides, and Thiols

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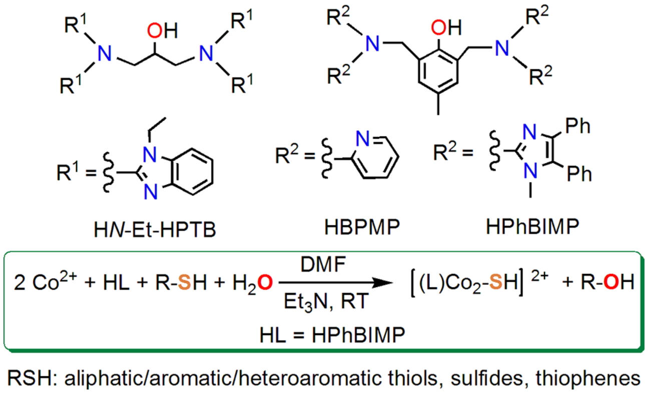
Supporting Information

ABSTRACT: Desulfurization of organosulfur compounds is a highly important reaction because of its relevance to the hydrodesulfurization (HDS) process of fossil fuels. A reaction system involving $Co(BF_4)_2 \cdot 6H_2O$ and the dinucleating ligands HBPMP or HPhBIMP has been developed that could desulfurize a large number of thiophenes, sulfides, and thiols to generate the complexes $[Co_2(BPMP)(\mu_2\text{-}SH)(MeCN)](BF_4)_2$ (**1a**), $[Co_2(BPMP)(SH)_2](BF_4)$ (**1b**), and $[Co_2(PhBIMP)(\mu_2\text{-}SH)(X)](BF_4)_2$ [X = DMF (**2a**), MeCN (**2c**)], while the substrates are mostly converted to the corresponding alcohols/phenols. This convenient desulfurization process has been demonstrated for 25 substrates in 6 different solvents at room temperature.

Cleavage of the C−S bond by transition metals is highly important because of its relevance to the hydrodesulfurization (HDS) process of fossil fuels,[1−5] which is one of the largest-volume industrial catalytic applications of transition metals. The process needs a supported molybdenum sulfide catalyst containing cobalt and operates under high pressure (160−600 psi pressure of H_2) and high temperature (300−450 °C). The HDS process reduces the sulfur content of oils by removing sulfur from thiophenes and thiols as H_2S and thus allows access to more readily processed and more cleanly combusted hydrocarbon products. The level of difficulty in removing sulfur in crude oil by HDS reactions generally increases in the order alkyl mercaptans < aromatic mercaptans < diphenyl sulfide < thiophene, dibenzothiophene.[6,7] Current technology can desulfurize aliphatic and acyclic sulfur compounds quite efficiently but remains relatively less successful in treating aromatic thiols, thiophenes, and its derivatives.[6,7] Consequently, desulfurization reactions of aromatic thiols and thiophenes are being actively pursued.[8−10]

Cleavage of the C−S bonds of various sulfur substrates mediated by transition metals (e.g., Co, Fe, Ni, Cu, W, Rh, Ir, Ru, Os, Pd, and Pt),[11−19] in general, and Co(II), in particular,[11−14,20] has been reported previously. Coordination of low-valent Mo with thiophenes, benzothiophenes, and selenophenes and subsequent C−S bond cleavage are also available in the literature.[8−10,21,22] In most of these reports, only the C−S bonds of coordinated ligands were involved and the products were a result of metal insertion in the C−S bonds instead of complete removal of the −SH functionality from the organosulfur substrates. There are, however, at least two reports regarding the complete removal of S/Se from dibenzothiophene/selenophene using low-valent Mo/W complexes at high temperatures.[10,23] In general, the reaction conditions often involved heating for a long period of time at high temperatures (often ≥100 °C),[9,12,18,19] photolysis using UV light for 1 day,[9] or irradiation with a high-pressure Hg lamp for 12−25 h.[16] On the other hand, Co(II)-mediated C−S bond cleavage of aliphatic thiolates using the *N*,*N*,*N*′,*N*′-tetrakis[2-(1-ethylbenzimidazolyl)]-2-hydroxy-1,3-diaminopropane (H*N*-Et-HPTB) ligand[24,25] (Scheme 1) at ambient conditions has recently been reported by us.[26] To the best of our knowledge, there is currently no convenient method available for complete desulfurization of the HDS substrates. Here we report a Co(II)-mediated complete desulfurization process applicable for almost all of the relevant substrate types of the HDS process at room temperature (RT) in six different solvents.

Scheme 1. General Reaction Scheme for the Desulfurization Reactions[a]



[a]Also shown are the ligands.

We initiated our investigation of C−S bond cleavage by using 2,6-bis[[bis(2-pyridylmethyl)amino]methyl]-4-methylphenol (HBPMP) ligand[27−29] (Scheme 1) and $Co(BF_4)_2 \cdot 6H_2O$. The addition of 2 equiv of $Co(BF_4)_2 \cdot 6H_2O$ into a mixture of NaS^tBu, HBPMP, and Et_3N (1:1:4) in *N*,*N*-dimethylformamide (DMF) at RT initially resulted in a green solution, which changed to a brown solution upon stirring for 2 days and subsequently yielded a mixture of pink and green crystals. Molecular structure

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determinations for the pink and green crystals confirmed their identity as $[Co_2(BPMP)(\mu_2\text{-}SH)(MeCN)](BF_4)_2$ (**1a**; CCDC 1845105) and $[Co_2(BPMP)(\mu_2\text{-}OH)](BF_4)_2$ (**1c**; CCDC 1845102), respectively (Figure S1). The use of 2 equiv of NaS^{t}Bu in the above reaction yielded $[Co_2(BPMP)(SH)_2](BF_4)$ (**1b**; CCDC 1845103; Figure 1) along with **1c**, thus confirming C−S bond cleavage of NaS^{t}Bu. Moreover, the initial green solution changed to pink within a day when the reaction was performed using 1 equiv of NaS^{t}Bu in the absence of Et_3N, which subsequently yielded **1a**. Also, the use of less Et_3N (∼1.5 equiv) diminished the formation of **1c** during the synthesis of **1b**. We may therefore conclude that $Co(BF_4)_2{\cdot}6H_2O$ mediates the C−S bond cleavage of thiolates in the presence or absence of a base (here Et_3N). However, in the presence of a base, generation of the OH^- ion in the solution may be promoted, thus generating a $Co^{II}(\mu_2\text{-}OH)Co^{II}$ species (**1c**) along with **1a**/**1b**. Furthermore, **1c** could also be converted to **1a** in 46% yield upon treatment with ^{t}BuSH. However, it was soon realized that **1a** and **1b** were somewhat difficult to isolate as analytically pure crystalline solids. On the basis of the results obtained using HBPMP (this work) and H*N*-Et-HPTB (earlier work),[26] we therefore moved our attention to 2,6-bis[bis[(*N*-1-methyl-4,5-diphenylimidazoylmethyl)amino]methyl]-4-methylphenol (HPhBIMP),[30] which bears some structural similarities to both HBPMP and H*N*-Et-HPTB (Scheme 1).

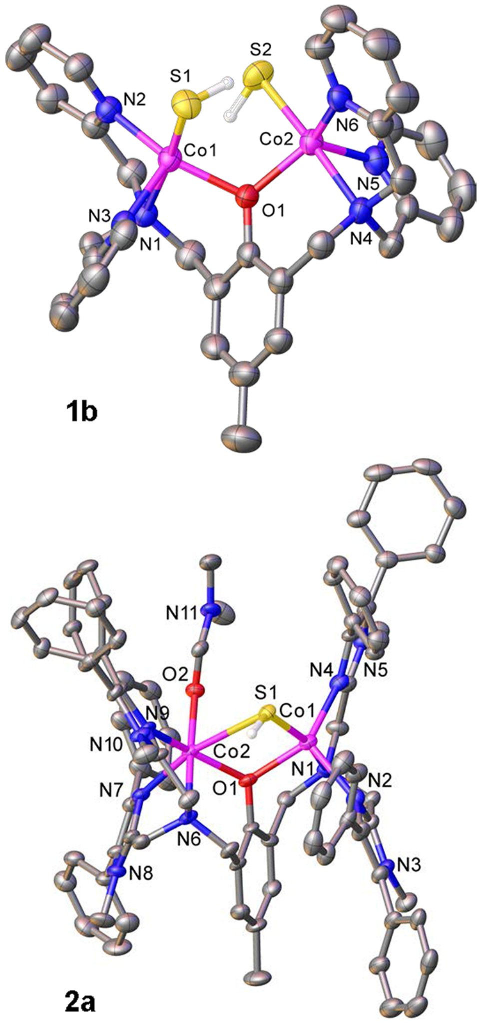


Figure 1. Molecular structures (50% probability thermal ellipsoids) for the cationic parts of **1b** and **2a**.

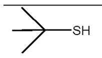
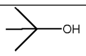
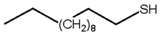
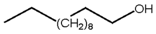
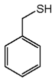
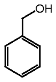
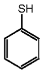
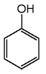
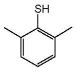
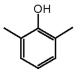
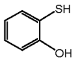
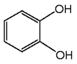
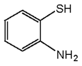
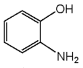
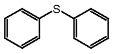
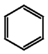
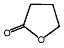
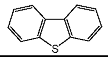
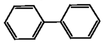
The use of HPhBIMP allowed C−S bond cleavage of NaS^{t}Bu in the presence of Et_3N and $Co(BF_4)_2{\cdot}6H_2O$ in DMF (1:1:2:2) at RT, and complex $[Co_2(PhBIMP)(\mu_2\text{-}SH)(DMF)](BF_4)_2$ (**2a**; CCDC 1845108; Figure 1) was isolated as purple crystals in 68% yield. Unlike the formation of **1b**, the use of excess NaS^{t}Bu in the above reaction did not change the identity or yield of the product. Interestingly enough, the use of NaSPh in the above reaction also yielded **2a** in comparable yield (61%). The formation of ^{t}BuOH (47%) and PhOH (57%) during the reactions involving NaS^{t}Bu and NaSPh, respectively, was identified by gas chromatography (GC) analysis (Figure S4), which further substantiated the desulfurization process.

In the next stage, the range of solvents suitable for the desulfurization reactions was explored. MeCN is known to undergo base-catalyzed partial hydrolysis to generate acetamide, which, in turn, may coordinate to the dicobalt(II) unit.[26] In the absence of both Et_3N and thiol, the reaction in MeCN yielded a solvent-coordinated complex, $[Co_2(PhBIMP)(MeCN)_2](BF_4)_3$ (**2b**; CCDC 1845107; Figure S2), thus indicating that a dinuclear Co(II) species may readily form in the reaction system. The reaction of $Co(BF_4)_2{\cdot}6H_2O$, HPhBIMP, and NaS^{t}Bu/NaSPh in MeCN, finally, allowed C−S bond cleavage, and the complex isolated was characterized as $[Co_2(PhBIMP)(\mu_2\text{-}SH)(MeCN)](BF_4)_2$ (**2c**; CCDC 1845104; Figure S2). The desulfurization process in the presence of Et_3N was further confirmed to be operative in tetrahydrofuran, methanol, ethanol, and ethyl acetate (Table S3). Complex **2a** was isolated in each case, with yields ranging from 35 to 50% compared with 42% and 68% in MeCN (**2c**) and DMF (**2a**), respectively. Therefore, the desulfurization reaction could be carried out in six different solvents, of which DMF comes out to be the best choice.

In the molecular structures of both **1a** and **2a**, the −SH group forms an unsymmetrical bridge between the two Co(II) atoms with short and long Co−S distances of 2.358(1) and 2.717(1) Å (for **1a**) and 2.358(1) and 2.644(1) Å (for **2a**), while the Co−Co distances are 3.313 and 3.322 Å, respectively. The molecular structure of **2c** is almost identical with that of **2a** with Co−S distances of 2.339(2) and 2.730(2) Å. The terminal hydrosulfides in **1b** showed relatively smaller Co−S distances [2.330(1) and 2.316(1) Å], while the Co−Co distance is comparatively longer (3.344 Å) than that in **1a** or **2a**. The presence of coordinated −SH groups in **1a**, **1b**, **2a**, and **2c** was further confirmed by IR spectroscopy [ν_{SH} = 2493 cm^{-1} (**1a**), 2489 cm^{-1} (**1b**), 2491 cm^{-1} (**2a**), 2514 cm^{-1} (**2c**)] and ^{1}H NMR spectroscopy [δ_{S-H} = 44.09 ppm (**1a**), 44.13 ppm (**1b**); 36.17 ppm (**2a**), 36.09 ppm (**2c**)], which are comparable with the data for previously reported metal hydrosulfide complexes.[31−34] Analogous chloro complexes $[Co_2(BPMP)(Cl)_2](BF_4)$ (**1d**; CCDC 1857215) and $[Co_2(PhBIMP)(\mu_2\text{-}Cl)(DMF)](CoCl_4)$ (**2e**; CCDC 1857216; Figures S1 and S3) were also synthesized for their use as control compounds for the assignments of ^{1}H NMR signals and IR stretching frequencies of the coordinated SH groups of **1a**, **1b**, and **2a** and **2c**, respectively.

Inspired by such facile desulfurization of both aliphatic and aromatic thiols, we carried out a systematic exploration for desulfurization of a diverse series of 25 substrates in DMF. Complex **2a** was isolated in varying yields and was characterized by unit cell determination of the single crystals in each case (Table S4). A list of 10 different substrates arranged according to the generally increasing difficulty level of desulfurization in the HDS process[6,35−37] are provided in Scheme 2. The corresponding organic products (mostly alcohols/phenols) were identified by gas chromatography−mass spectrometry (GC-MS; Figures S4 and S5). Yields for the organic products were also measured (Figures S6−S11) using GC and were found to be comparable with the respective yields of **2a** (Table S4). The formation of **2a** was further confirmed by ^{1}H NMR, IR, electronic absorption spectroscopy, and electrospray MS (ESI-MS) of the purple crystalline solids obtained after desulfurization of 10 representative substrates (Figures S27−S36). Isolation of **2a** in the case of sulfides and thiophene derivatives (Scheme 2) confirmed the complete desulfurization of these substrates. In addition to one thiol group, the substrates 2-mercaptophenol, 2-aminothiophenol, 4-mercaptopyridine, and 2-thiobarbituric acid feature additional N/O-donor functional groups, which might potentially bind to the Co(II) centers and thus might hinder the reaction. Successful desulfurization of even those substrates in 22−62% yield therefore suggests appreciable functional group tolerance.

Scheme 2. Yields of 2a and Organic Products Obtained by Desulfurization of 10 Representative Substrates

Organosulfur substrates	Products	Yields of products (%)	Yields of 2a (%)
		47	68
		61	68
		84	60
		57	61
		44	35
		40	36
		19	32
		20	32
		18	40
		2	15

Careful investigations revealed that the addition of 2 equiv of Co(BF$_4$)$_2$·6H$_2$O into a reaction mixture of HPhBIMP, NaS^{t}Bu/NaSPh, and Et$_3$N (1:1:2) in DMF initially resulted in the formation of a green solution, presumably because of the formation of a Co$^{II}_2$(OH$^-$) species. In the case of NaS^{t}Bu, the green color changed to purple within 1 min, while for NaSPh, it took ∼2 days for the visual color change to start taking place. While multiple attempts were made to isolate the green compound, only **2a** was isolated after ∼5−6 days in 68% and 61% yield, respectively. The facile conversion of the green solution to the purple solution (Figure S14) justified the problem encountered in isolation of the green species. The mass spectrometric study of the green solution within 30 min of its generation also indicated the presence of both [Co$_2$(PhBIMP)(SH)]$^{2+}$ and [Co$_2$(PhBIMP)(OH)]$^{2+}$ at m/z 649.96 and 642.45, respectively (Figure S17). Finally, in the absence of Et$_3$N, the reaction mixtures containing either NaS^{t}Bu or NaSPh immediately form a purple/pink solution (instead of green), which, upon standard workup, yielded **2a** in 54% and 52% yield, respectively. These results indicate that the formation of a Co$^{II}_2$(OH$^-$) species (green) may be promoted by the addition of Et$_3$N. Interestingly, while using thiophene as the substrate in the absence of Et$_3$N, a few block-shaped pink crystals were obtained along with the characteristic needle-shaped purple crystals of **2a**, and the pink compound was identified as [Co$_2$(PhBIMP)(H$_2$O)$_2$(DMF)$_2$](BF$_4$)$_3$ (**2d**; CCDC 1845106; Figure S3). The same reaction with thiophene in the presence of Et$_3$N, however, yielded only **2a** in 40% yield. A combination of the results for both aliphatic and aromatic thiols, in general, strongly suggests that a dicobalt(II) unit containing terminal OH$^-$ and H$_2$O (in the presence and absence of Et$_3$N, respectively)[26] may indeed be generated. Such a dicobalt(II) complex may subsequently accommodate a terminal or bridging thiolate group, followed by the attack of a nearby OH$^-$/H$_2$O at the carbon center bearing the thiol group to yield **2a** and the corresponding phenol/alcohol.

In summary, a unique, Co(II) mediated, complete desulfurization process of industrially relevant thiols, sulfides and thiophene derivatives has been developed. Unlike all of the high-temperature desulfurization reactions reported in the literature so far, the current method may be operated at RT in six different solvents. Additionally, this innovative synthetic strategy may initiate further investigations involving other transition metals such as Fe(II) for the synthesis of a new class of diiron−hydrosulfide complexes and subsequent exploration of their reactivity in future.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorgchem.8b01588.

Experimental details, molecular structures and spectroscopic data (PDF)

Accession Codes

CCDC 1845102−1845108 and 1857215−1857216 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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