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Generation and Reactivity of Polychalcogenide Chains in Binuclear Cobalt(II) Complexes

Kamal Hossain, Angshuman Roy Choudhury, and Amit Majumdar*

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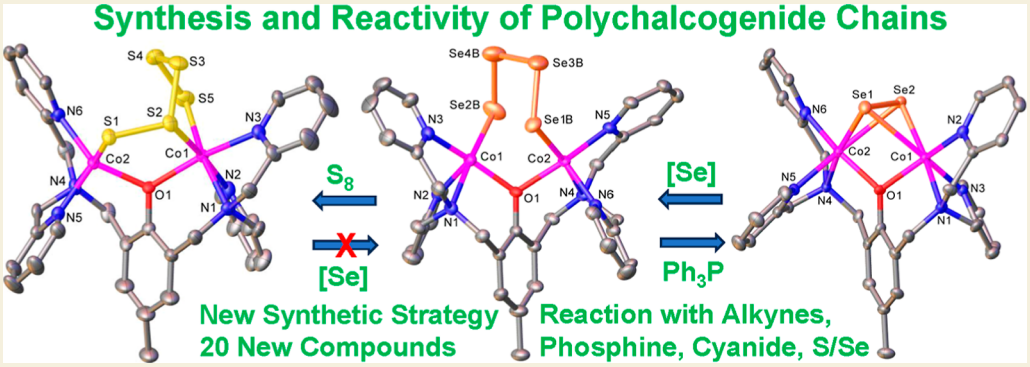

ABSTRACT: A series of six binuclear Co(II)−thiolate complexes, $[Co_2(BPMP)(S{-}C_6H_4\text{-}o\text{-}X)_2]^{1+}$ (X = OMe, **2**; NH_2, **3**), $[Co_2(BPMP)(\mu\text{-}S{-}C_6H_4\text{-}o\text{-}O)]^{1+}$ (**4**), and $[Co_2(BPMP)(\mu\text{-}Y)]^{1+}$ (Y = bdt, **5**; tdt, **6**; mnt, **7**), has been synthesized from $[Co_2(BPMP)(MeOH)_2(Cl)_2]^{1+}$ (**1a**) and $[Co_2(BPMP)(Cl)_2]^{1+}$ (**1b**), where $BPMP^{1-}$ is the anion of 2,6-bis[[bis(2-pyridylmethyl)-amino]methyl]-4-methylphenol. While **2** and **3** could allow the two-electron redox reaction of the two coordinated thiolates with elemental sulfur (S_8) to generate $[Co_2(BPMP)(\mu\text{-}S_5)]^{1+}$ (**8**), the complexes, **4**−**7**, could not undergo a similar reaction. An analogous redox reaction of **2** with elemental selenium ([Se]) produced $[\{Co_2(BPMP)(\mu\text{-}Se_4)\}\{Co_2(BPMP)(\mu\text{-}Se_3)\}]^{2+}$ (**9a**) and $[Co_2(BPMP)(\mu\text{-}Se_4)]^{1+}$ (**9b**). Further reaction of these polychalcogenido complexes, **8** and **9a**/**9b**, with PPh_3 allowed the isolation of $[Co_2(BPMP)(\mu\text{-}S)]^{1+}$ (**10**) and $[Co_2(BPMP)(\mu\text{-}Se_2)]^{1+}$ (**11**), which, in turn, could be converted back to **8** and **9a** upon treatment with S_8 and [Se], respectively. Interestingly, while the redox reaction of the polyselenide chains in **9a** and **11** with S_8 produced **8** and [Se], the treatment of **8** with [Se] gave back only the starting material (**8**), thus demonstrating the different redox behavior of sulfur and selenium. Furthermore, the reaction of **8** and **9a**/**9b** with activated alkynes and cyanide (CN^-) allowed the isolation of the complexes, $[Co_2(BPMP)(\mu\text{-}E_2C_2(CO_2R)_2)]^{1+}$ (E = S: **12a**, R = Me; **12b**, R = Et; E = Se: **13a**, R = Me; **13b**, R = Et) and $[Co_2(BPMP)(\mu\text{-}SH)(NCS)_2]$ (**14**), respectively. The present work, thus, provides an interesting synthetic strategy, interconversions, and detailed comparative reactivity of binuclear Co(II)−polychalcogenido complexes.

KEYWORDS: *polychalcogenide, pentasulfide, tetraselenide, diselenide, diselenolene, cyanide detoxification, selenium, sulfur*

INTRODUCTION

The coordination chemistry of transition metals with hydrosulfide (HS^-), sulfide (S^{2-}), and polysulfides (S_n^{2-}) is very rich and versatile. Sulfur displays intriguing redox chemistry, and the anions derived from sulfur (HS^-, S^{2-}, S_n^{2-}) can bridge multiple metal centers involving different bridging modes to produce both homo and hetero multimetallic compounds. Moreover, transition metal complexes of hydrosulfide and sulfide are often considered as the key to many important aspects of inorganic chemistry such as catalysis, energy, environment, and materials.[1] The important roles of transition metal sulfides are quite evident in the biocatalysis of various small molecules, such as dinitrogen, as well.[2] Metal−sulfur assemblies are found to be the integral parts of the active sites of different enzymes. Some important examples include the active sites of nitrogenases,[3−9] [Fe−Fe]-hydrogenase,[10−13] [NiFe]-hydrogenase,[10,13] sulfite reductase,[14−18] aconitase,[19−21] A and C cluster of [NiFe]-CODH,[22−25] [MoCu]-carbon monoxide dehydrogenase (CODH),[25−28] and bifunctional CODH/acetyl Co-A synthase (ACS).[29,30] The presence of these active sites provide proof for intriguing structures and offer formidable challenges to synthetic inorganic chemists. Combination of all these factors has immensely helped in the

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development of the chemistry of transition metals with hydrosulfides[31−40] and sulfides.[8,9,41,42]

Polysulfide anions (S_n^{2-}) are classic examples of the catenation property of sulfur and are quite well-known in the literature.[1,43−49] The synthesis, structural diversity, and reactivity of an appreciable number of mono-, bi-, and poly nuclear compounds of polysulfide involving transition metals, lanthanides, and main group elements have been reported previously.[50−78] It may, however, be noted that most of these metal−polysulfido compounds are strictly organometallic compounds.[55−57,60−65,67−69,71,72,74,77] While reports on several binuclear transition metal-polysulfido compounds are available in the literature,[50,51,55,79−85] the majority of these compounds are, however, metal sulfides and clusters with only S-donor ligands (HS^-, S^{2-}, and S_n^{2-}). Representative examples of such clusters include $[Cu_2(S_3)(S_4)]^{2-}$, $[Ni_2(\mu\text{-}S_4)]^{2+}$, $[Ni_2(\mu\text{-}S_5)]^{2+}$, $[Co_2(\mu\text{-}S_4)]^{2+}$, $[Co_2(\mu\text{-}S_5)]^{2+}$, $[Fe_2(\mu\text{-}S_5)]^{2+}$, $[Fe_2(\mu\text{-}S_4)]^{2+}$, $[Fe_2(\mu\text{-}S)_2(S_5)_2]^{2-}$, $[S_5Fe(\mu\text{-}S)_2FeS_5]^{2-}$, $[Mn_2(\mu\text{-}S_4)]^{2+}$, and $[Mn_2(\mu\text{-}S_5)]^{2+}$ as well as few higher nuclearity clusters.[86] Moreover, the mono-, bi-, and trinuclear polysulfido complexes of first-row transition metals in N/O-donor ligands[82,83,87−101] are relatively less explored. It may be noted that almost all the reported binuclear first-row transition metal−polysulfido complexes in N/O-donor ligands were synthesized by the redox reaction of low-valent metals in the respective precursor complexes with elemental sulfur. Few exceptions to this general trend include the synthesis of $[Co^{III}(\mu\text{-}S_2)([15]aneN_4)]_2^{2+}$ from the reaction of Co(II) salts with S_2^{2-} or S_4^{2-} in the presence of the macrocyclic ligand[94] and the synthesis of $[Fe(NO)_2(S_5)]^{1-}$ by the reaction of the coordinated thiolates in $[Fe(NO)_2(SR)_2]^{1-}$ (R = $[C_6H_4\text{-}o\text{-}NHC(O)Me]$, $[C_4H_3]$, Ph) with elemental sulfur.[102] Most of the polysulfido (S_n^{2-}) complexes feature the smallest polysulfido unit (S_2^{2-}),[82,90−94,96,97,101] while only a handful of complexes with longer polysulfido chains such as S_3^{2-} or S_4^{2-}[89,95] and polysulfido chain (S_n^{2-}) of $n > 4$[87,88,102] have been reported. Considering the new results in the area of binuclear Co(II)-polychalcogenido complexes in an N, O-donor binucleating ligand described in the present work, it may be noted that most of the previous reports on polysulfido compounds of cobalt, such as $[(\eta^5\text{-}C_5Me_5)_2Co_2S_4]$,[77] $[C_5H_5(PMe_3)CoS_5]$,[103] $[CoS_2(\eta^5\text{-}C_{60}Ar_5)]_2$,[104] $[Co_2(\mu\text{-}S_2)_2(\mu\text{-}S_4)(CNAr^{Mes2})_4]$,[105] and $[CoS_3(\eta^5\text{-}C_{60}Ar_5)]$,[104,106,107] fall strictly in the domain of organometallic chemistry and involved cobalt in +III oxidation state. On the other hand, the only reports involving Co(II) did not include the characterization of the proposed Co(II)−polysulfido complexes (such as the electrochemically generated species, $[Co_2(\mu\text{-}S_4)]^{2+}$ and $[Co_2(\mu\text{-}S_5)]^{2+}$)[79,81,108] by single crystal X-ray structure determinations. Moreover, almost all the "nonorganometallic" polysulfido complexes of cobalt available in the literature involve Co(III),[94,95,109] and there is no report for the synthesis and reactivity of a well-characterized binuclear Co(II)−polysulfido complex.

In contrast to the plethora of reports on the chemistry of transition metal−polysulfido complexes in general, the chemistries of polyselenides and polytellurides are comparatively less developed.[43,49,110−115] While an appreciable number of transition metal−polyselenido and relatively a smaller number of transition metal−polytellurido compounds are now available in the literature, most of these examples feature either metal−polyselenido/polytellurido compounds having Se/Te/P-donor ligands[116−124] or only Se/Te-donor ligands (polyselenide/polytelluride)[116,117,120−123] or organometallic compounds,[63,67,125−131] while some other reports include $[Fe(Se_3)L_2]^{1-}$ (L = *N*(Dipp)$SiMe_3$, Dipp = 2,6-diisopropylphenyl),[132] $[Cu_2(Se_2)(Bn_3TACH)_2]^{2+}$[133] and $[Mn(dien)_2]_2[SbSe_4Cu(\mu\text{-}Se_4)]$ (dien = diethylenetriamine).[134] The majority of these metal−polychalcogenido compounds are organometallic compounds. Unlike the reactions described in the present work, the synthetic strategy used for the preparation of these reported organometallic compounds, in general, involved either (i) the redox reaction of low-valent metal salts/compounds with elemental chalcogens (S, Se, and Te)[63,116,118,119,122,125,128,131,133,134] or (ii) the reaction of metal complexes with polychalcogenide salts,[117,118,120,121,123,127,132] often for a long time (2−6 days) at high temperatures (80−145 °C). The majority of these reported complexes feature the smallest polychalcogenide units (Se_2^{2-}/Te_2^{2-}) with the exception of compounds such as $[\{Mn(\mu\text{-}Se_6)(tren)\}_2]$.[135] Moreover, considering the synthesis and detailed reactivity of binuclear Co(II)−polychalcogenido complexes in a N, O-donor ligand described in the present work, it may be noted that all the available reports on polyselenido compounds of cobalt either fall in the domain of organometallic chemistry or involve Co(III),[122−124] except the only known Co(II)−diselenido compound, $[(Co(nacnac))_2(\mu,\eta^2\text{-}Se_2)]$.[136]

Therefore, considering the scarcity of reports on binuclear polychalcogenido complexes of first-row transition metals in association with binucleating N, O-donor ligands in the literature and keeping in mind the scopes for interesting reactivity of such complexes, we have recently started exploring the synthesis and reactivity of such species using different binucleating N, O-donor ligands. In this line, binuclear Zn(II) complexes of polysulfide ligands (S_3^{2-} and S_5^{2-}) in association with two different binucleating N, O-donor ligands have been reported from our laboratory.[140,141] Our results featured a new and distinct structural type for first-row transition metal−polysulfido complexes compared to the types of complexes (metal sulfides and clusters with only S-donor ligands) reported previously in the literature.[50,51,55,79−81] It may be noted that unlike the prevalent reaction strategies (either reaction of low-valent metal and elemental sulfur/selenium or the reaction of metal complexes with polychalcogenide salts, in general) used in the literature reports, we employed the two-electron redox reaction between coordinated thiolates (used as sacrificial reductants) in preformed binuclear complexes of bivalent first-row transition metals and elemental sulfur/selenium at ambient reaction conditions to generate the polysulfide/polyselenide chains. Here, we report, six new dicobalt(II)−thiolate complexes and their two-electron redox reaction with elemental sulfur (S_8) and elemental selenium (gray Se) for the generation of a series of new dicobalt(II) complexes, featuring coordinated polysulfide and polyselenide chains (Chart 1). A detailed comparative reactivity study and interconversion of these unprecedented dicobalt(II)−polychalcogenido complexes are presented which include the reaction of these complexes with triphenylphosphine (PPh_3), elemental chalcogens (S, Se), and activated alkynes and cyanide (CN^-).

■ RESULTS AND DISCUSSION

Synthesis of Binuclear Co(II)-polychalcogenido Complexes

The binuclear Co(II) compounds, $[Co_2(BPMP)(MeOH)_2(Cl)_2](ClO_4)$ [**1a** (ClO_4)] and $[Co_2(BPMP)(Cl)_2](BPh_4)$ [**1b** (BPh_4)] (Figures S1 and S2), were conceived as

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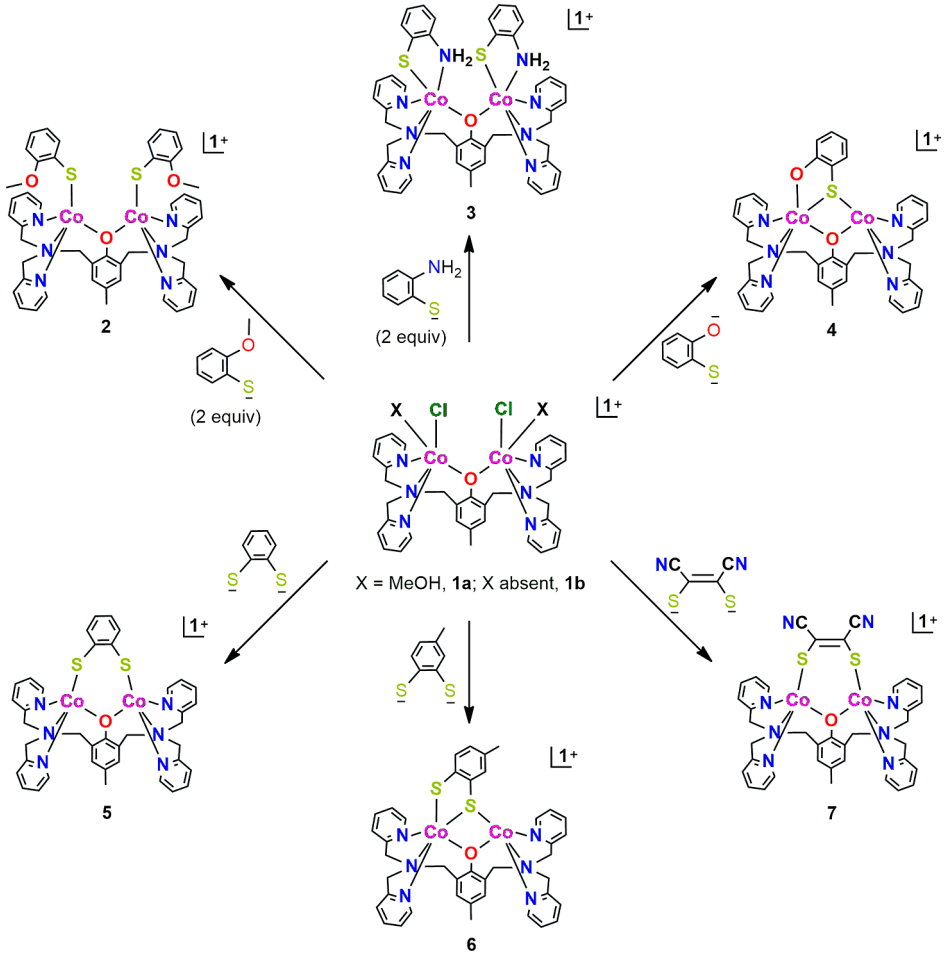
Chart 1. Abbreviations and Designations of the Binuclear Co(II) Complexes and Ligands[a]

$[Co_2(BPMP)(MeOH)_2(Cl)_2]^{1+}$	**1a**
$[Co_2(BPMP)(Cl)_2]^{1+}$	**1b**
$[Co_2(BPMP)(S\text{-}C_6H_4\text{-}o\text{-}X)_2]^{1+}$	X = OMe, **2**; NH_2, **3**
$[Co_2(BPMP)(\mu\text{-}S\text{-}C_6H_4\text{-}o\text{-}O)]^{1+}$	**4**
$[Co_2(BPMP)(\mu\text{-}Y)]^{1+}$	Y = bdt, **5**; tdt, **6**; mnt, **7**
$[Co_2(BPMP)(\mu\text{-}S_5)]^{1+}$	**8**
$[\{Co_2(BPMP)(\mu\text{-}Se_4)\}\{Co_2(BPMP)(\mu\text{-}Se_3)\}]^{2+}$	**9a**
$[Co_2(BPMP)(\mu\text{-}Se_4)]^{1+}$	**9b**
$[Co_2(BPMP)(\mu\text{-}S)]^{1+}$	**10**
$[Co_2(BPMP)(\mu\text{-}Se_2)]^{1+}$	**11**
$[Co_2(BPMP)(\mu\text{-}S_2C_2(CO_2R)_2)]^{1+}$	**12a**, R = Me; **12b**, R =Et
$[Co_2(BPMP)(\mu\text{-}Se_2C_2(CO_2R)_2)]^{1+}$	**13a**, R = Me; **13b**, R =Et
$[Co_2(BPMP)(\mu\text{-}SH)(NCS)_2]$	**14**
$[Co_2(BPMP)(NCS)_3]$	**15**

[a]HBPMP,[137−139] 2,6-bis[[bis(2-pyridylmethyl)amino]methyl]-4-methylphenol; bdt, benzenedithiolate; tdt, toluenedithiolate; mnt, maleonitriledithiolate. Complex **1b** has previously been reported by us as a tetrafluoroborate salt.[35]

prospective starting materials for the synthesis of the desired binuclear Co(II) complexes featuring mono- and bidentate thiolate ligands. While **1a** and **1b** are both binuclear Co(II) complexes featuring two terminal chloride atoms (Scheme 1), **1a** additionally features two coordinated MeOH molecules. The use of $BPMP^{1-}$ as the choice of ligand in the present work relies on our previous results which showed that unlike the formation of transition metal−monothiolate complexes while using some other mixed N, O-donor binucleating ligands,[38,39,140,142] $BPMP^{1-}$ allows the synthesis of bis(thiolate) complexes.[141] It may be noted that bis(thiolate) complexes would be necessary for a stoichiometrically precise two-electron redox reaction with exogenous elemental chalcogens. The reaction of **1a** with 2 equiv of 2-methoxybenzenethiolate and 2-aminobenzenethiolate allowed the isolation of $[Co_2(BPMP)(S{-}C_6H_4\text{-}o\text{-}OMe)_2]^{1+}$ (**2**) and $[Co_2(BPMP)(S{-}C_6H_4\text{-}o\text{-}NH_2)_2]^{1+}$ (**3**), respectively, (Scheme 1 and Figures S3−S5). In the same line, treatment of **1a** with 1 equiv each of 2-mercaptophenolate, 1, 2-benzenedithiolate (bdt^{2-}), toluenedithiolate (tdt^{2-}), and maleonitriledithiolate (mnt^{2-}) allowed the isolation of $[Co_2(BPMP)(S{-}C_6H_4\text{-}o\text{-}O)]^{1+}$ (**4**), $[Co_2(BPMP)(\mu\text{-bdt})]^{1+}$ (**5**), $[Co_2(BPMP)(\mu\text{-tdt})]^{1+}$ (**6**), and $[Co_2(BPMP)(\mu\text{-mnt})]^{1+}$ (**7**), respectively, (Scheme 1 and Figures S6−S11). Molecular structures of the complexes **1a**, **1b**, and **2**−**7** are provided in Figure 1. With the possible exception of **4** (featuring only one thiolate functionality), all these dicobalt(II)−thiolate complexes could, in principle, undergo a stoichiometrically precise two-electron redox reaction with elemental sulfur (S_8) to generate a polysulfide

Scheme 1. Synthesis of the Binuclear Co(II) Complexes 2−7 from 1a/1b



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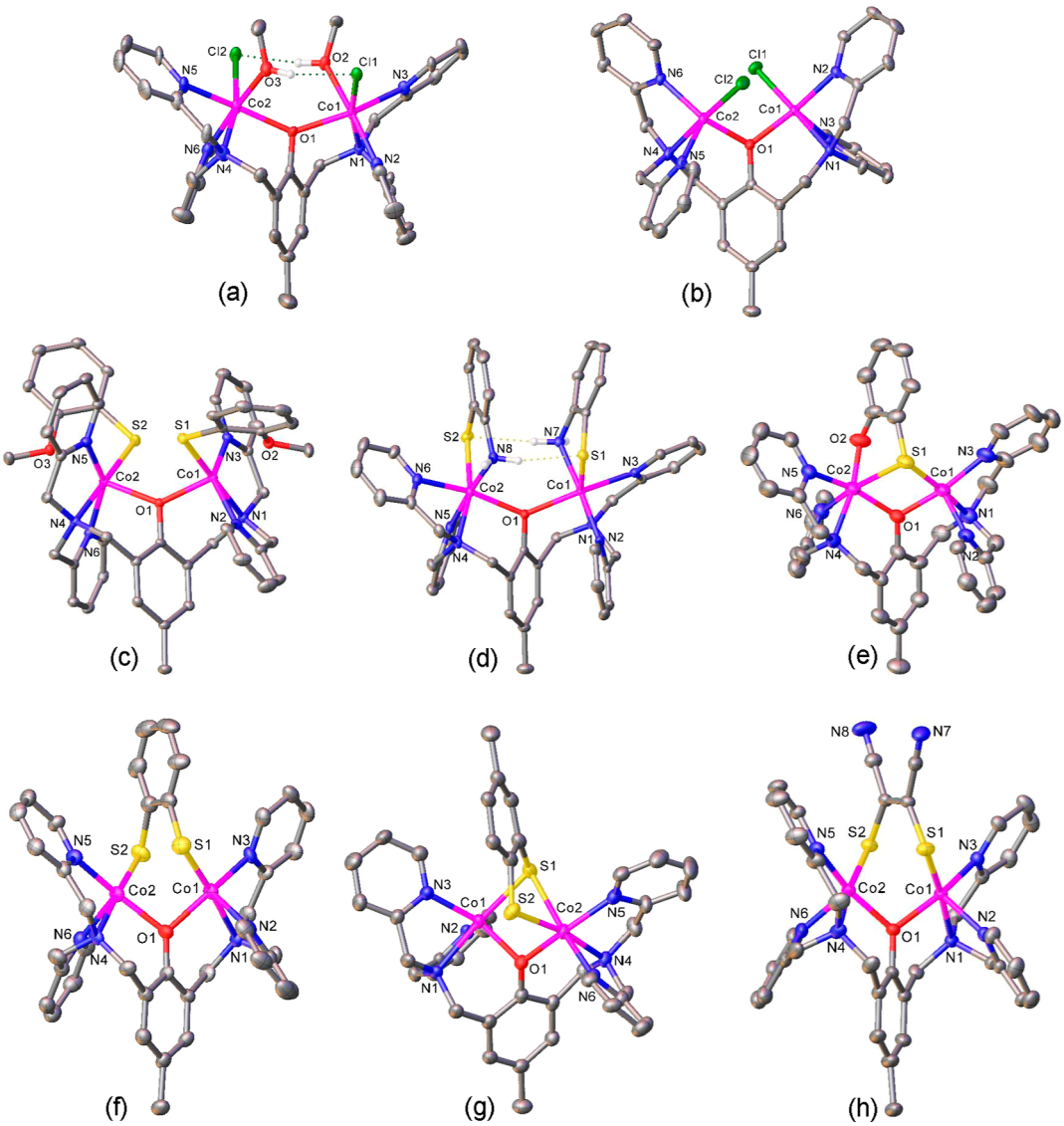

Figure 1. Molecular structures of **1a** (a), **1b** (b), **2** (c), **3** (d), **4** (e), **5** (f), **6** (g), and **7** (h) with 30% probability thermal ellipsoids and partial atom labeling scheme. Hydrogen atoms are omitted for clarity (except for the hydroxy group of the coordinated MeOH in **1a** and amino groups in **3**).

chain (S_n^{2-}) and the disulfide of the corresponding thiolates. Indeed, reaction of **2** and **3** with S_8 allowed the isolation of an unprecedented dicobalt(II) complex, $[Co_2(BPMP)(\mu\text{-}S_5)]^{1+}$ (**8**), featuring a coordinated pentasulfido chain (Figure 2a and Figures S12−S26). Complex **8** features Co−S distances of 2.358(2) Å (Co2−S1) and 2.354(3) Å (Co1−S5), while the Co1 center is additionally coordinated by one sulfur atom (S2) of the S_5^{2-} chain with a long Co−S2 distance of 2.600(3) Å. The S−S distances within the S_5^{2-} chain are 2.016(4)−2.047(4) Å which are similar to those observed in the case of an isostructural Zn(II) complex (1.931−2.054 Å)[141] and in some mononuclear Co(III)−polysulfido complexes [2.016(2)−2.076(1) Å].[103,109]

The oxidation state of the cobalt centers and the presence of the sulfur atoms in **8** were further confirmed by X-ray photoelectron spectroscopy (XPS) of **8** (ClO_4) (Figure 2b,c). The separation of 15.6 eV between the Co $2p_{3/2}$ and Co $2p_{1/2}$ peaks and the presence of the intense satellite peaks (Figure 2b) confirmed[109,143−146] the oxidation state of the cobalt centers in **8** to be +II, while the characteristic signature of S 2p (Figure 2c) confirmed[36,40,109,147] the presence of sulfur atoms in **8**. The XPS of **8** shows three S 2p peaks at 161.3, 162.6, and 163.4 eV (Figure 2c). It may be noted that multiple S 2p peaks are expected for coordinated polysulfido ligands and are dependent on the effective charge on the sulfur atoms.[78,148,149] Examples include the assignment of the three S 2p peaks at 161.9, 162.8, and 163.2 eV (observed for a thin film of $(NH_4)_2[Pt(S_5)_3]\cdot 2H_2O$ on metallic gold) to the sulfur atoms nearest to the metal centers (sulfide like electronic environment, S 2p at 162.0 eV for Na_2S[150]), next-nearest sulfur atoms (electronic environment intermediate between sulfides and elemental sulfur), and the furthest sulfur atoms (elemental sulfur like electronic environment, S 2p at 164.2 eV for S_8[150]), respectively;[149] assignment of the S 2p peaks at 161.4 and 163.0 eV (observed for layers of sulfur electrochemically deposited on gold) to the sulfur atoms nearest to the gold and to the outermost sulfur atoms, respectively;[149] assignment of the corresponding values (161.8 and 163.2 eV) in the case of layers of sulfur deposited electrochemically on platinum;[149] and the assignment of the S 2p peaks at 161.9 and 163.5 eV to the terminal and the central sulfur atom of the polysulfide chain in K_2S_n, respectively.[148] Considering these assignments

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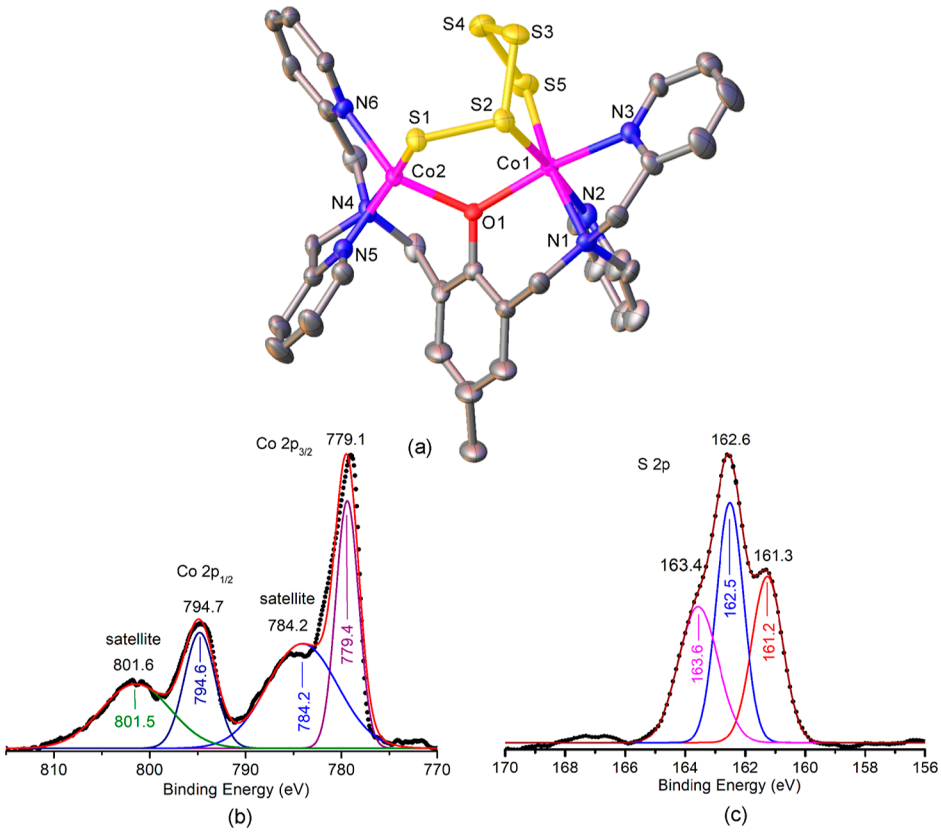

Figure 2. Molecular structures of **8** [for **8** (ClO_4)] with 30% probability thermal ellipsoids and partial atom labeling scheme (hydrogen atoms are omitted for clarity) (a) and XPS of **8** (ClO_4) showing the Co 2p (b) and S 2p (c) regions.

of the multiple S 2p peaks in the previous reports,[78,148,149] the S 2p peak at 161.3 eV may be assigned to S1 and S5 (closest to the Co(II) centers), the peak at 162.6 eV may be assigned to S2 and S4 (sulfur atoms next-nearest to the Co(II) centers), and the peak at 163.4 eV may be assigned to S3 (furthest from the Co(II) centers) in the present work. Generation of the corresponding disulfides, namely, *o*-OMe−C_6H_4−S−S−C_6H_4-*o*-OMe and *o*-NH_2−C_6H_4−S−S−C_6H_4-*o*-NH_2, during these reactions, were identified and quantified by GC−MS (Figures S27 and S28).

In contrast to the formation of **8** from the reaction of **2** and **3** with S_8, treatment of **4**−**7** with S_8 gave back only the starting complexes (Figures S29−S32) and thus indicated the reluctance of the coordinated chelating thiolates in **4**−**7** to take place in the redox reaction. These results indicated that the coordinated thiolates might need to be released in solution during the redox reaction with S_8. The apparent reluctance of the coordinated thiolates as compared to free thiolates in solution to undergo a redox reaction with S_8 may be due to the transfer of electron density from the sulfur centers in thiolates to the Co(II) centers upon coordination, which might make the oxidation of the coordinated thiolates relatively less facile. A direct proof for this proposed prerequisite for the redox reaction described in the present work, however, would require the use of a dicobalt(II)−bis(thiolate) complex featuring two different thiolates (say R^1S^- and R^2S^-) in the reaction with S_8, where the generation of all three possible disulfides (R^1S−SR^2, R^1S−SR^1, and R^2S−SR^2) would confirm the proposal presented here, while the generation of only the mixed disulfide (R^1S−SR^2) would confirm that the redox reaction may take place between S_8 and the coordinated thiolates. Such a dicobalt(II) complex bearing two different monodentate terminal thiolates, however, could not be synthesized by us. Moreover, there is no report for any such binuclear transition metal complex in the literature which could be tested to validate this proposal. Nevertheless, based on the observations in the present work, the apparent reluctance of **5**−**7** (**4** features only one thiolate functionality) to undergo the two-electron redox reaction with S_8 may possibly be attributed to the dianionic bidentate chelating nature of the coordinated thiolates, the release of which from the Co(II) centers in **5**−**7** would be comparatively less facile than the monoanionic bidentate thiolate (^-S−C_6H_4-*o*-NH_2) in **3** and the monodentate thiolate (^-S−C_6H_4-*o*-OMe) in **2**. However, it may be noted that the thermodynamically unfavorable formation of a disulfide involving a strained 4-member ring in the case of bdt^{2-}, tdt^{2-}, and mnt^{2-} may also be an important reason behind the observed chemical inertness of **5**−**7** in the reaction with elemental sulfur.

In the same line, treatment of **2** (ClO_4) with gray selenium ([Se]) allowed the isolation of a dicobalt(II)−polyselenido complex, $[\{Co_2(BPMP)(\mu\text{-}Se_4)\}\{Co_2(BPMP)(\mu\text{-}Se_3)\}](ClO_4)_2$ (**9a** $(ClO_4)_2$) (Figures S33−S37), while the generation of the disulfide, *o*-OMe−C_6H_4−S−S−C_6H_4-*o*-OMe, was identified and quantified by GC−MS (Figure S38). Molecular structure determination of **9a** showed two distinct molecules in the asymmetric unit, namely, a binuclear Co(II) complex featuring a coordinated Se_4^{2-} chain (not shown) and a binuclear Co(II) complex featuring a coordinated Se_3^{2-} chain (shown in Figure 3a) of which the molecular unit with the coordinated Se_4^{2-} chain revealed an occupancy disorder between Se_4^{2-} and Se_3^{2-}. The presence of

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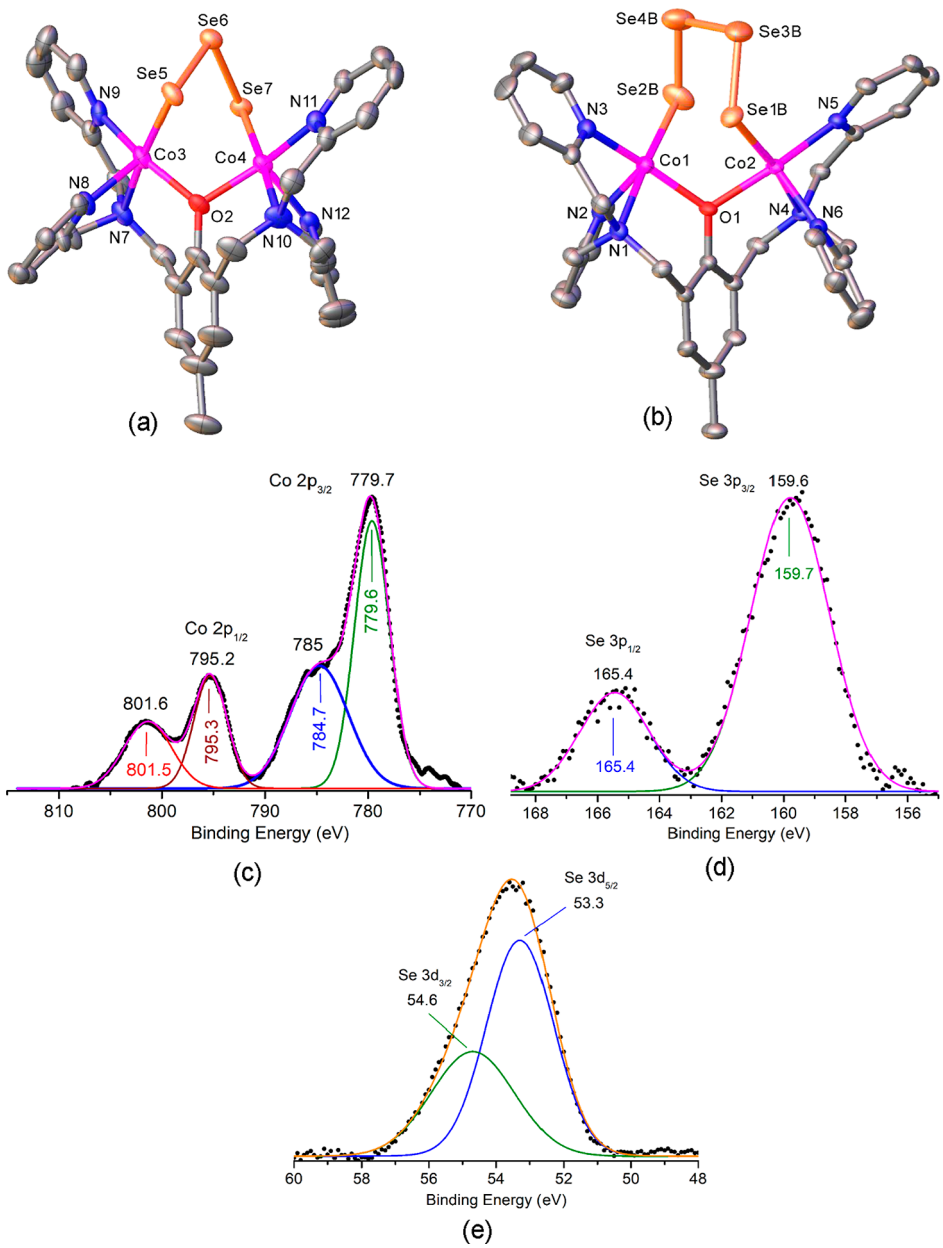

Figure 3. Molecular structures of **9a** (a) and **9b** (b) with 30% probability thermal ellipsoids and partial atom labeling scheme (hydrogen atoms are omitted for clarity) and XPS of **9b** (BPh_4) showing the Co 2p (c), Se 3p (d), and Se 3d (e) regions. Note that only the Co_2Se_3 unit of $[\{Co_2(BPMP)(\mu\text{-}Se_4)\}\{Co_2(BPMP)(\mu\text{-}Se_3)\}](ClO_4)_2$ [**9a** $(ClO_4)_2$] is shown (a).

these two distinct molecules in the asymmetric unit of **9a** $(ClO_4)_2$ was found to be reproducible by single crystal X-ray structure determination from multiple batches of **9a** $(ClO_4)_2$. Reaction of **2** (BPh_4) with [Se], on the other hand, allowed the isolation of $[Co_2(BPMP)(\mu\text{-}Se_4)](BPh_4)$ (**9b** (BPh_4)) (Figures S39−S43), the molecular structure of which showed a binuclear Co(II) complex featuring a coordinated Se_4^{2-} chain (Figure 3b). It may be noted that the coordinated Se_4^{2-} chain in **9b** revealed an occupancy disorder between Se_4^{2-} and Se_3^{2-}, and this situation was again reproduced by single crystal X-ray structure determination from multiple batches of **9b** (BPh_4). The generation of the disulfide, *o*-OMe−C_6H_4−S−S−C_6H_4-*o*-OMe, was identified and quantified by GC−MS (Figure S44). Complex **9a** shows Co−Se distances of 2.5144(12)−2.5345(12) Å, while the Se−Se distance ranges from 2.208(2) to 2.584(4) Å. Complex **9b** features Co−Se distances of 2.5171(13) and 2.5203(11) Å, while the Se−Se distance ranges from 2.2001(18) to 2.473(3) Å. The occupancy disorder present in the molecular structure of both **9a** $(ClO_4)_2$ and **9b** (BPh_4) and the consistent results showing the presence of two separate units featuring Se_4^{2-} and Se_3^{2-} chains in the asymmetric unit of **9a** $(ClO_4)_2$ may be attributed to the generation of polyselenide chains of different chain lengths (Se_n^{2-}, n = 3, 4) in solution during the reactions of **2** (ClO_4) and **2** (BPh_4) with [Se]. Polychalcogenide units of specific chain lengths might then be trapped by the binuclear Co(II) units, where the counteranions (either ClO_4^- or BPh_4^-) might play a crucial role in the crystallization of the products (either **9a** or **9b**). The oxidation states of the cobalt centers and the presence of the selenium atoms in **9b** were further confirmed by XPS of **9b** (BPh_4) (Figure 3c−e). The separation of 15.5 eV between the Co $2p_{3/2}$ and Co $2p_{1/2}$ peaks

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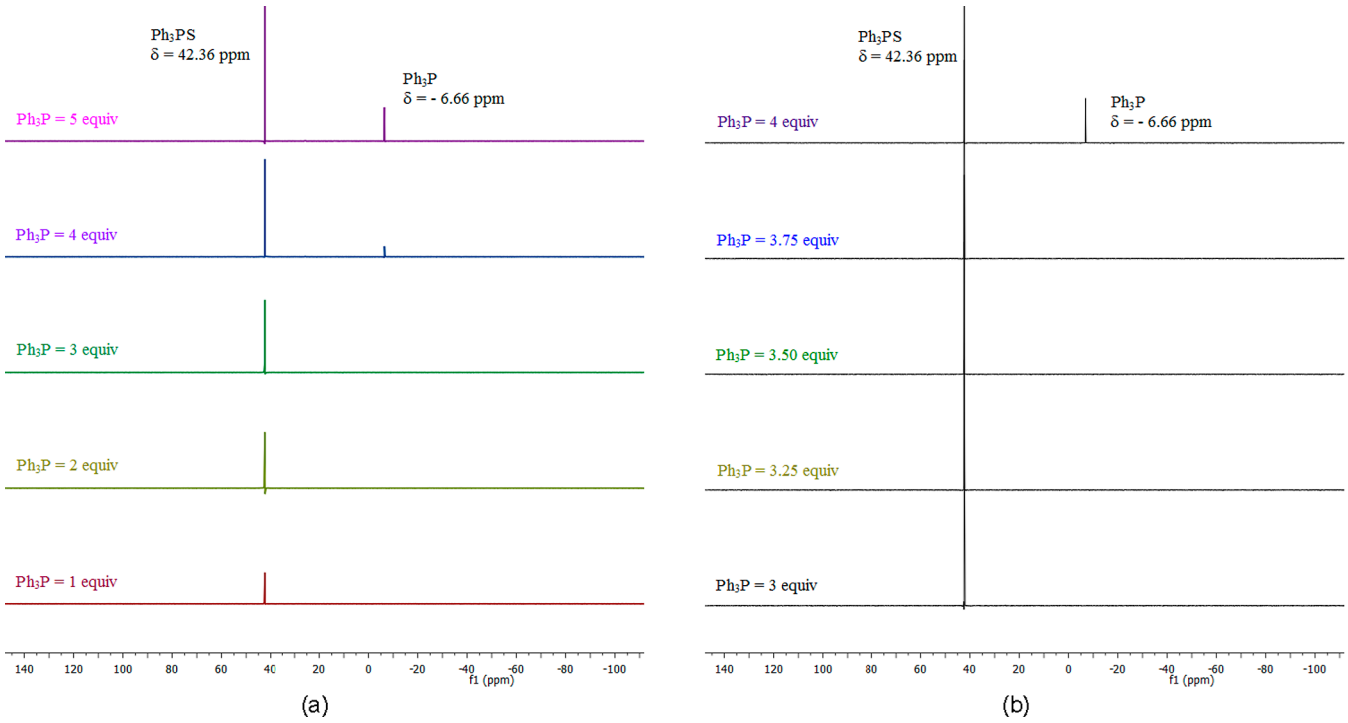

Figure 4. ^{31}P NMR (^{1}H decoupled, DMSO-d_6, 600 MHz) spectroscopic monitoring for the reaction of **8** (ClO_4) with varying equivalents of PPh_3. Ratio of **8** (ClO_4)/PPh_3 = 1:n, where n = 1, 2, 3, 4, 5 (a); n = 3, 3.25, 3.50, 3.75, 4 (b).

and the presence of the intense satellite peaks (Figure 3c) confirmed[109,143−146] the oxidation state of the cobalt centers in **9b** to be +II, while the presence of the characteristic Se 3p and Se 3d peaks (Figure 3d−e) confirmed[151−160] the presence of selenium atoms in **9b**.

Reaction of the Coordinated Polychalcogenide Chains with Elemental Chalcogens and PPh_3

Upon successful synthesis and characterization of the desired binuclear Co(II) complexes featuring coordinated polysulfide and polyselenide chains, the reactivity of these complexes (**8**, **9a** and **9b**) toward elemental chalcogen (S/Se) and PPh_3 was explored in order to study their comparative reactivity and also to explore the possibility for the isolation of new binuclear Co(II)−chalcogenide complexes. Interestingly, the treatment of either **9a** or **9b** with S_8 allowed the isolation of **8** (Table S3 and Figures S45−S49 for the reaction of **9a** and S_8) along with the precipitation of a gray solid. Reaction of the isolated gray solid with PPh_3 indicated the generation of Ph_3PSe by ^{31}P NMR spectroscopy (Figure S50) and thus confirmed the gray solid to be elemental selenium which was generated during the conversion of **9a** and **9b** to **8**. This result might be attributed to the reduction of S_8 by the coordinated Se_n^{2-} chains (n = 3, 4) in **9a** and **9b** to generate S_n^{2-}, while the Se_n^{2-} chains are oxidized to generate elemental selenium. The reverse reaction involving **8** and [Se], however, gave back only **8** (Table S3). These results thus nicely demonstrated that while S_8 can oxidize the coordinated Se_n^{2-} chains to generate [Se] and S_n^{2-}, the reverse reaction (oxidation of S_n^{2-} by [Se]) might not be feasible.

Coordinated polychalcogenide chains have previously been shown by us and others to react with PPh_3 for the generation of Ph_3PE (E = S, Se) and coordinated polychalcogenide chains of shortened chain lengths.[109,141,161] The reaction of **8** with PPh_3 was therefore monitored by ^{31}P NMR spectroscopy (Figure 4). The ^{31}P NMR spectroscopic titration experiment with **8** and PPh_3 showed that the characteristic peak for unreacted PPh_3 showed up upon addition of 4 equiv of PPh_3 (Figure 4a) and thus apparently suggested that **8** might consume a maximum of 3 equiv of PPh_3. However, further experiment involving the addition of PPh_3 in varying amounts in a narrower range of 3−4 equiv showed that **8** could consume a maximum of 3.75 equiv (i.e. ∼4 equiv) of PPh_3 (Figure 4b). Accordingly, the reaction of **8** with 4 equiv of PPh_3 allowed the isolation of a new binuclear Co(II) complex, $[Co_2(BPMP)(\mu\text{-}S)]^{1+}$ (**10**), along with the generation of Ph_3PS (Figure S51). Complex **10** featured a bridging sulfido (S^{2-}) group and was identified by a single crystal X-ray structure determination (Figure 5a). Complex **10** features two five-coordinate Co centers with Co−Co separation of 2.9548(9) Å and <Co1−S1−Co2 angle of 80.58(4)°. The Co−S distances of 2.2899(12) and 2.2793(12) Å in **10** are similar to that observed (av. Co−S = 2.223 Å) for a reported complex featuring two bridging sulfido ligands.[162] However,

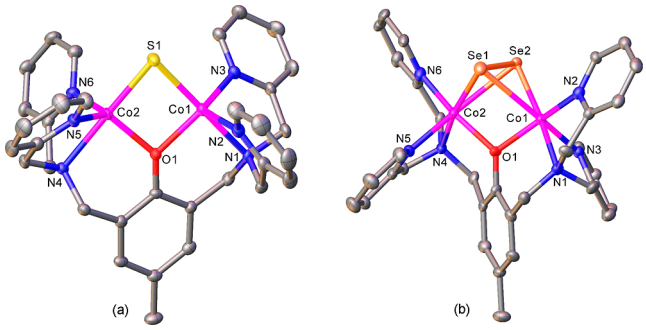

Figure 5. Molecular structure of **10** (a) and **11** (b) with 30% probability thermal ellipsoids and partial atom labeling scheme. Hydrogen atoms are omitted for clarity.

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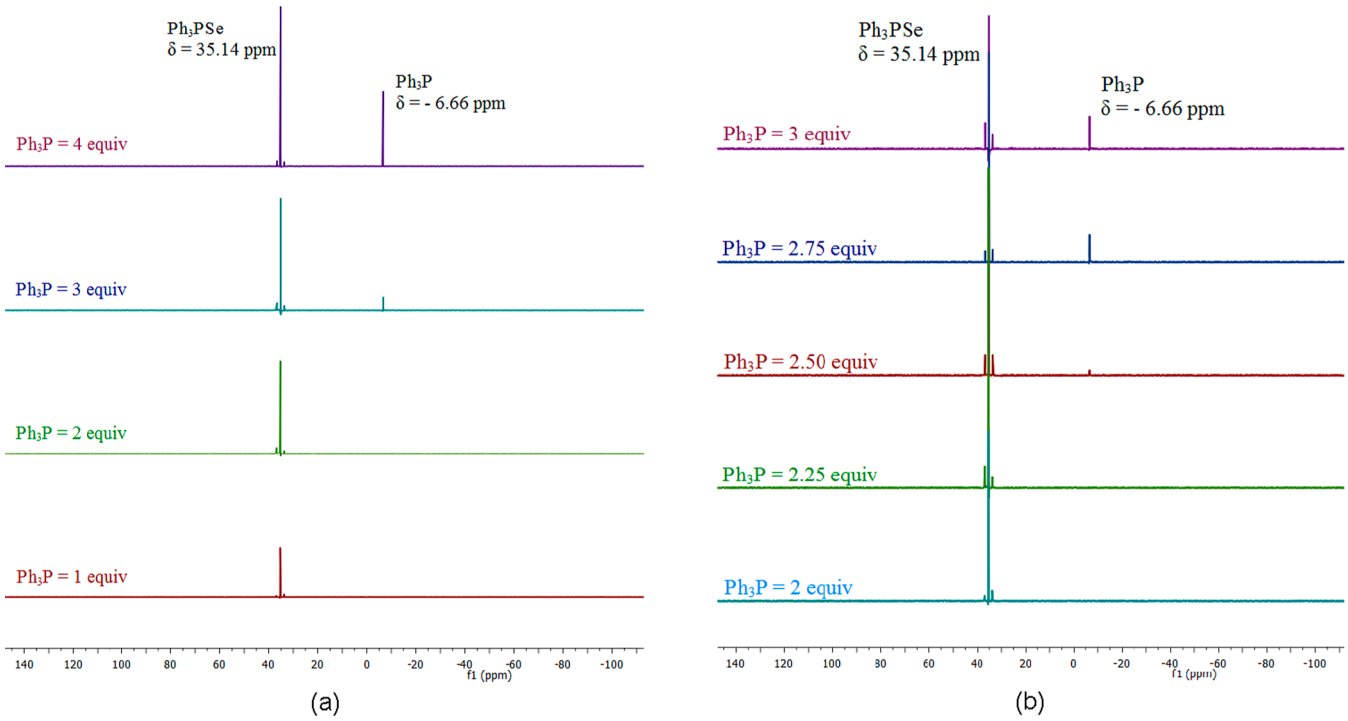

Figure 6. ^{31}P NMR (^{1}H decoupled, DMSO-d_6, 600 MHz) spectroscopic monitoring for the reaction of **9b** (BPh_4) with varying equivalents of PPh_3: (a) ratio of **9b** (BPh_4)/PPh_3 = 1:n, where n = 1, 2, 3, 4 and (b) ratio of **9b** (BPh_4)/PPh_3 = 1:n, where n = 2, 2.25, 2.50, 2.75, 3.

the mass spectrometry for the bulk sample of **10** (Figures S52 and S53) showed the presence of a total of three species $[Co_2(BPMP)(S)_n]^{1+}$ (n = 1−3) and thus indicated that the reaction of **8** with PPh_3 generated a mixture of complexes of which only **10** could be characterized by a single crystal X-ray structure determination. These results indicated that **8** might first react with 3 equiv of PPh_3 to generate a complex with the apparent formulation, $[Co_2(BPMP)(S_2)]^{1+}$. The bridging S_2^{2-} in such a complex might then generate $[Co_2(BPMP)(S)]^{1+}$ (**10**) and "S^0" ($S_2^{2-} \rightarrow S^{2-} + S^0$), of which the latter might then react with additional equivalents of PPh_3. Such a situation might lead to a mixture of compounds featuring polysulfide chains of varying chain lengths (as observed by the mass spectrometric analysis of **10**, Figures S52 and S53). Nevertheless, the isolation and molecular structure determination of **10** were indeed complementary to the ^{31}P NMR spectroscopic monitoring involving **8** and PPh_3 and clearly demonstrated the reaction of the coordinated S_5^{2-} chain in **8** with PPh_3. Interestingly, the reaction of **10** with S_8 regenerated **8** and was confirmed by a single crystal X-ray structure determination (Table S3) and mass spectrometry (Figures S54−S58). It may be noted that the reaction of a previously reported mononuclear Co(III)−pentasulfido complex, [(Hpy2ald)Co-(S_5)] (where Hpy2ald is 3-{[bis(2-pyridinylmethyl)amino]-methyl}-2-hydroxybenzaldehyde), with PPh_3 produced a dimeric Co(II) complex, $[(Hpy2ald)Co]_2^{2+}$, and no Co(II) or Co(III) complex featuring a polysulfido chain of shorter chain length could be identified.[109]

^{31}P NMR spectroscopic monitoring for the reaction of **9b** with PPh_3 revealed that the characteristic peak for unreacted PPh_3 showed up only upon addition of 3 equiv of PPh_3, thus indicating that **9b** might consume a maximum of 2 equiv of PPh_3 (Figure 6a). A closure inspection of the titration within the range of 2−3 equiv of PPh_3 (Figure 6b) further confirmed that indeed a maximum of 2.25 (i.e ∼2) equiv of PPh_3 might be consumed by **9b**. Considering the possible generation of a complex with apparent formulation, $[Co_2(BPMP)(\mu\text{-}Se_2)]^{1+}$, the maximum equivalents of PPh_3 were consistent with the molecular structures of **9b** (2 equiv PPh_3, total number of neutral selenium = 2). Indeed, the reaction of **9b** with 2 equiv of PPh_3 allowed the isolation of the complex, $[Co_2(BPMP)(\mu\text{-}Se_2)]^{1+}$ (**11**) as **11** (BPh_4) (Figures S59−S61), along with Ph_3PSe (Figure S62). In the same line, the reaction of **9a** (the numbers of neutral selenium are 2 and 1 in the Co_2Se_4 and Co_2Se_3 units, respectively) with 3 equiv of PPh_3 again allowed the isolation of **11** as **11** (ClO_4) (along with Ph_3PSe, Figure S66) and was confirmed by a single crystal X-ray structure determination and mass spectrometry (Figures S63−S65). The molecular structure of **11** is shown in Figure 5b. The two Co centers in **11** are bridged by a Se_2^{2-} chain having a Se−Se distance of 2.4132(14) Å, which is well within the range of 2.2944(9)−2.56 Å reported for Se−Se distances.[124,136,163] Complex **11** features one shorter and one longer Co−Se distance for each of the two Co centers [Co1: 2.4880(14), 2.7910(15) Å; Co2: 2.5098(14), 2.7456(14) Å]. The reaction of **11** (ClO_4) with [Se] regenerated **9a** $(ClO_4)_2$ and was confirmed by a single crystal X-ray structure determination (Table S4). Interestingly, the reaction of **11** (ClO_4) and **11** (BPh_4) with S_8 allowed the isolation of **8** (Figures S67−S77 and Table S3) along with the precipitation of a gray solid. Reaction of the isolated gray solid with PPh_3 indicated the generation of Ph_3PSe by ^{31}P NMR spectroscopy (Figure S78) and thus confirmed the generation of elemental selenium during the conversion of **11** to **8**. These results are in line with the results obtained from the reactions of **9a** and **9b** with S_8, which generated **8** and [Se]. Interestingly, the treatment of **10** (featuring a bridging sulfido) with [Se] allowed the isolation of a reddish brown solid which, when examined by mass spectrometry, indicated the presence of the mixed sulfur−selenium species, $[Co_2(BPMP)(\mu\text{-}Se_2)]^{1+}$, $[Co_2(BPMP)(\mu\text{-}$

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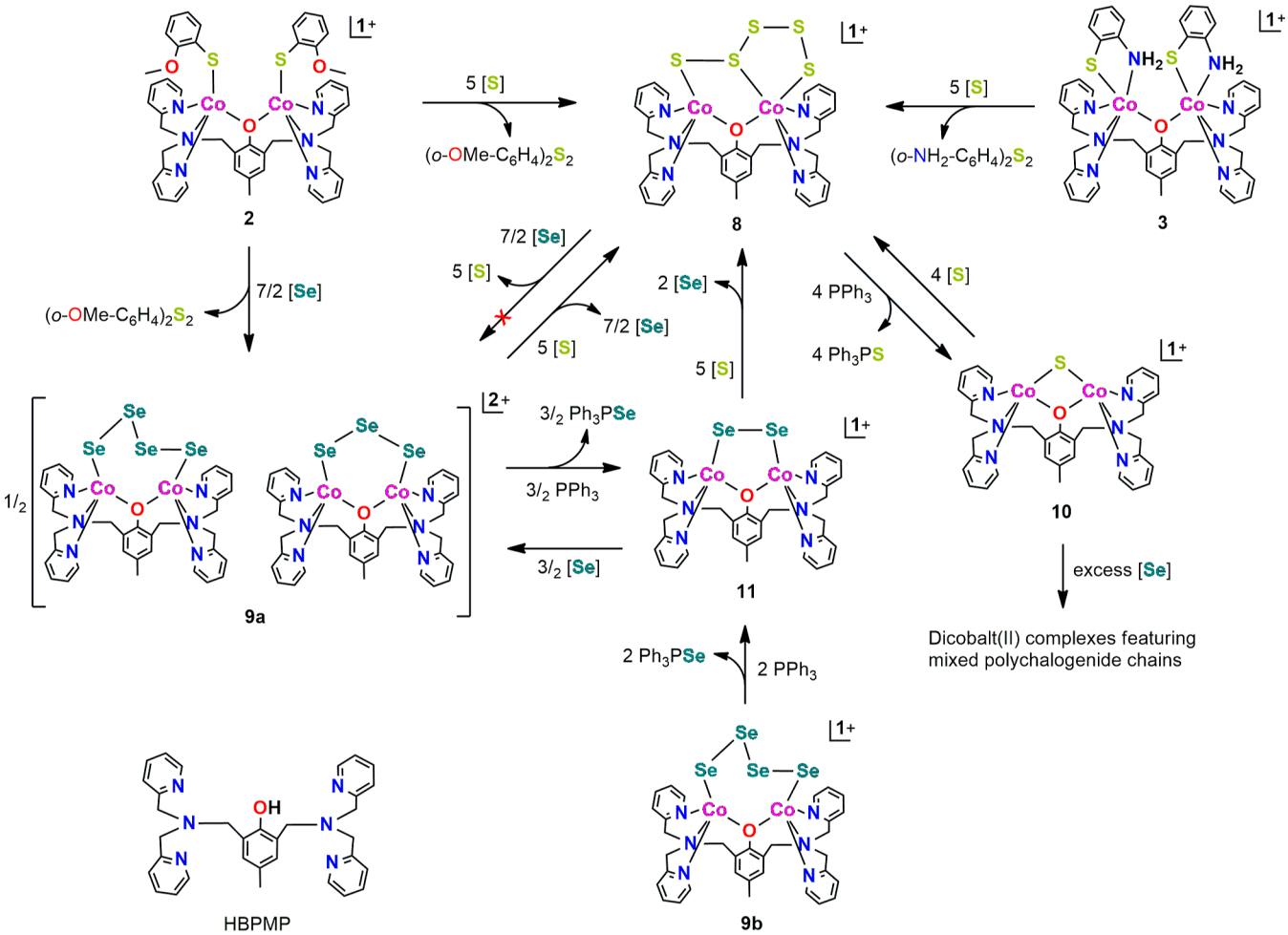
Scheme 2. Schematic Presentation for the Synthesis of Binuclear Cobalt(II)−Polychalcogenido Complexes and Their Interconversion and Reactivity with Phosphines



SSe)]$^{1+}$, and [Co_2(BPMP)(μ-S_2Se)]$^{1+}$ along with the presence of unreacted **10** (Figures S79−S84). This result indicated the insertion of [Se] into a bridging sulfido ligand and showed the difference in the reactivity of binuclear Co(II) complexes featuring polysulfide ligand (**8**) and sulfide ligand (**10**) toward [Se], of which the former reaction gave back only **8**. Moreover, while the reaction of **10** with S_8 allowed the isolation of **8**, further treatment of **8** with S_8 gave back only **8** (Table S3). The observed reluctance of the coordinated polysulfide chain in **8** to allow the insertion of selenium, thus, may not be solely due to a possible less reactive nature of elemental selenium. The optimal chain size of the stable complex **8** might also be a contributing factor which might not allow the insertion of chalcogens in the S_5^{2-} chain any further in the present work. Indeed, a chain size greater than 5 sulfur atoms were never observed during our previous work with Co(III)[109] or with Zn(II).[140,141] The synthesis, interconversion, and the reactivity of the binuclear Co(II)−polychalcogenido complexes with PPh_3 and elemental chalcogens are summarized in Scheme 2.

It may be noted that while the reaction of the dicobalt(II)−pentasulfido complex (**8**) with PPh_3 generated a dicobalt(II)−sulfido complex (**10**), an analogous reaction involving the dicobalt(II)−tetraselenido complex (**9b**) and PPh_3 allowed the isolation of a dicobalt(II)−diselenido complex (**11**). Therefore, in order to check the possible generation of the dicobalt(II)−selenido complex (analogous to **10**), further reaction of **11** with PPh_3 was monitored using ^{31}P NMR spectroscopy (Figure S85), which revealed that **11** could consume a maximum of 1 equiv of PPh_3. In line with this, mass spectrometry of a reaction solution containing **11** and PPh_3 showed the presence of the species, [Co_2(BPMP)(μ-Se)]$^{1+}$ (Figure S86). It therefore appeared that [Co_2(BPMP)(μ-Se_2)]$^{1+}$ (**11**) might generate [Co_2(BPMP)(Se)]$^{1+}$ and "Se^0" ($Se_2^{2-} \rightarrow Se^{2-} + Se^0$) in solution, of which the latter might then react with 1 equiv of PPh_3 to generate [Co_2(BPMP)(μ-Se)]$^{1+}$ and Ph_3PSe. However, the sluggishness of the former reaction might be responsible for the results of the ^{31}P NMR spectroscopic monitoring, as shown in Figure 6. Despite multiple attempts, the species, [Co_2(BPMP)(μ-Se)]$^{1+}$, however, could not be characterized by a single crystal X-ray structure determination.

Reactivity of the Binuclear Co(II)−Polychalcogenido Complexes with Activated Alkynes and Cyanide

Reaction of polysulfides and polyselenides with activated alkynes to generate the corresponding dithiolenes and diselenolenes has been reported previously,[87,164−166] although mostly for organometallic complexes.[164−166] The reaction was proposed to be initiated by the nucleophilic attack of a sulfur atom of the coordinated polysulfide chain at the alkyne carbon followed by the attack of the newly generated carbanion on another part of the polysulfide chain.[166] Considering these

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reports, we went forward to test the reaction of two activated alkynes, $RO_2C{-}C{\equiv}C{-}CO_2R$ (R = Me, Et), with the coordinated polysulfide and polyselenide chains in **8**, **9a**, and **9b**. Treatment of **8** with $RO_2C{-}C{\equiv}C{-}CO_2R$ (R = Me, Et) confirmed the generation of the desired complexes, $[Co_2(BPMP)(\mu\text{-}S_2C_2(CO_2R)_2)]^{1+}$ (R = Me, **12a**; Et, **12b**), by mass spectrometry (Figures S87 and S88) and elemental analysis. Despite multiple attempts, diffraction quality single crystals for **12a** and **12b**, however, could not be obtained. Nevertheless, an analogous reaction of **9b** with $MeO_2C{-}C{\equiv}C{-}CO_2Me$ allowed the isolation of the desired dicobalt(II)−diselenolene complex, $[Co_2(BPMP)(\mu\text{-}Se_2C_2(CO_2Me)_2)]^{1+}$ (**13a**), and the identity of **13a** was confirmed by a single crystal X-ray structure determination (Figure 7a), elemental

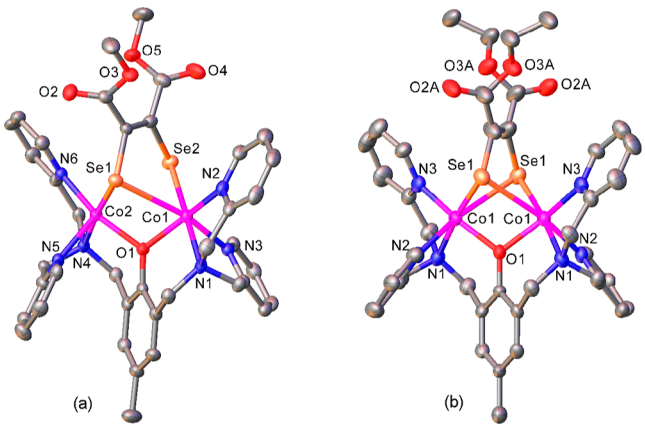

Figure 7. Molecular structures of **13a** (a) and **13b** (b) with 30% probability thermal ellipsoids and partial atom labeling scheme. Hydrogen atoms are omitted for clarity.

analysis, and mass spectrometry (Figure S89). In the same line, treatment of **9a** with $EtO_2C{-}C{\equiv}C{-}CO_2Et$ allowed the isolation of the dicobalt(II)−diselenolene complex, $[Co_2(BPMP)(\mu\text{-}Se_2C_2(CO_2Et)_2)]^{1+}$ (**13b**), and the identity of **13b** was again confirmed by a single crystal X-ray structure determination (Figure 7b), elemental analysis, and mass spectrometry (Figure S90). Interestingly, further treatment of **13a** and **13b** with S_8 indicated the generation of mixed sulfur−selenium species of the type $[Co_2(BPMP)((CO_2R)\mathbf{SeCCS}(CO_2R))]^{1+}$ (R = Me, Et) along with **12a**/**12b** (Figures S91−S98). While the partial or complete substitution of the selenium atoms by sulfur atoms in the coordinated diselenolenes is not unprecedented in the literature, the previous reports include strictly the organometallic complexes of cobalt for such reactions.[167−169] Although the exact mechanism for such reactions could not be established, it was proposed[168,170] that the integrity of the C−Se bond in the metal−diselenolene complexes might be lost in the presence of elemental sulfur. This situation might lead to the generation of free alkyne and elemental selenium in the reaction solution, which, in the presence of elemental sulfur, might generate the dithiolene or mixed selenolatothiolato species.[168,170]

Reaction of cyanide (CN^-) with elemental (neutral) sulfur to generate thiocyanate (SCN^-) has implications in biology in the context of cyanide detoxification.[171−173] Reactions of elemental sulfur and polysulfide,[174] organopolychalcogenides,[175] and transition metal−polysulfido complexes[176,177] with CN^- have also been reported in the literature. The mechanism for the reaction of elemental sulfur and polysulfide with CN^- has been studied very recently which suggested intramolecular cyclization to be the most favorable decomposition pathway for long chain polysulfides, while a mixture of unimolecular decomposition, nucleophilic attack, and scrambling pathways was proposed to be operative in the case of short chain polysulfides.[174] The reaction of **9b** and **8** with $(Bu_4N)(CN)$ was therefore examined using IR spectroscopy (Figures 8 and S100). IR spectroscopic investigation of the

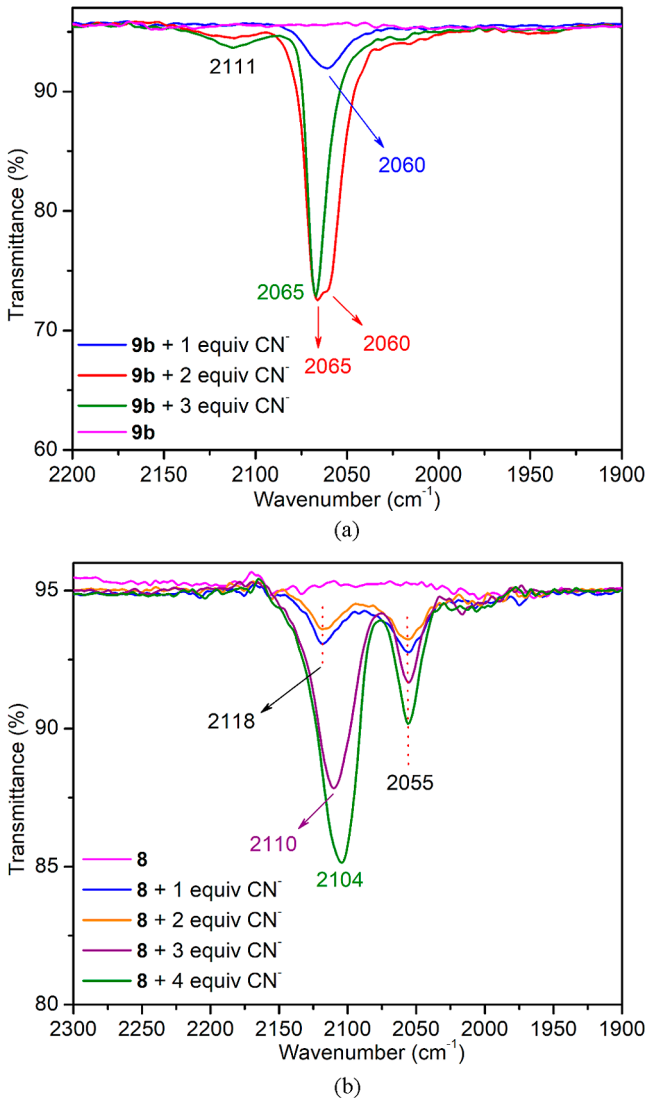

Figure 8. IR spectra (ATR) for the solid products obtained from the reaction of varying equivalents of $(Bu_4N)(CN)$ with **9b** (a) and **8** (b).

solid products obtained from the reaction of **9b** and 1−3 equiv of CN^- (compared with the IR spectrum of **9b**) revealed the generation of new peaks at 2060 cm^{-1} (**9b**/CN^- = 1:1); 2060, 2065, and 2111 cm^{-1} (**9b**/CN^- = 1:2); and 2065, 2111 cm^{-1} (**9b**/CN^- = 1:3). Considering the recent report of ν_{CN} = 2062 cm^{-1} for free $SeCN^-$ generated from the reaction of [K(18-crown-6)][BnSeSe] and [K(18-crown-6)][BnSSe] with $(Bu_4N)(CN)$,[175] the single peak at ν_{CN} = 2060 cm^{-1} (**9b**/CN^- = 1:1) may be attributed to the generation of free $SeCN^-$ upon reaction of the coordinated Se_4^{2-} in **9b** with CN^-. The two peaks at ν_{CN} = 2060 and 2065 cm^{-1} (**9b**/CN^- = 1:2) might then be assigned to free and coordinated $SeCN^-$, respectively, as more $SeCN^-$ would be generated in the second

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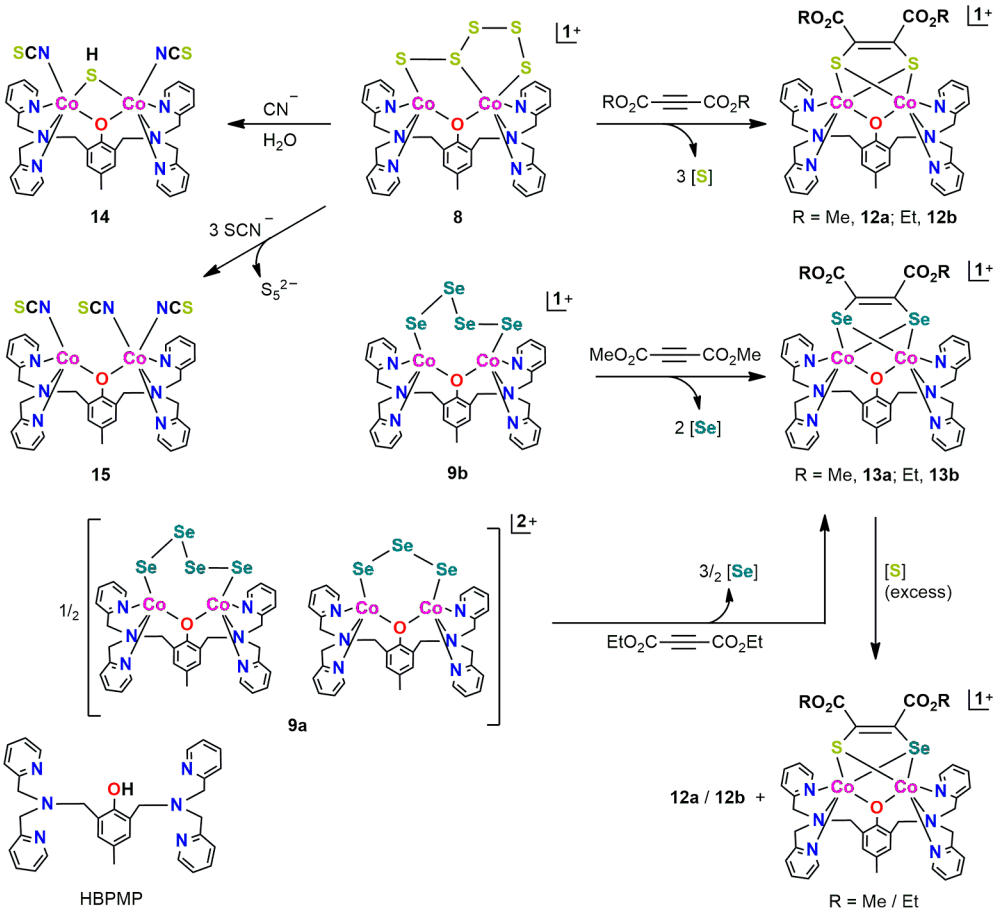
Scheme 3. Schematic Presentation for the Reactivity of Binuclear Cobalt(II)−Polychalcogenido Complexes, 8, 9a, and 9b



case and a fraction of which might coordinate to the Co(II) centers. The third new peak at ν_{CN} = 2111 cm^{-1} (**9b**/CN$^-$ = 1:2) might be due to either free or coordinated CN$^-$ (considering ν_{CN} = 2054 cm^{-1} assigned for free CN$^-$ of $(Et_4N)(CN)$ in DMF;[178] ν_{CN} = 2112−2133 cm^{-1} for $K_3[M(CN)_6]$, where M = Cr, Mn, Fe, Co, Rh, and Ir, while ν_{CN} = 2044 cm^{-1} for $K_4[Fe(CN)_6]$[179]). It may be noted that in the third case (**9b**/CN$^-$ = 1:3), the peak at ν_{CN} = 2060 cm^{-1} (assigned for free SeCN$^-$) completely vanishes, while the peaks at ν_{CN} = 2065 and 2111 cm^{-1} are present and thus fit well with the proposed assignment, namely, coordinated SeCN$^-$ and free/coordinated CN$^-$. However, despite multiple attempts, diffraction quality single crystals could not be obtained from these three reaction systems involving **9b** and 1−3 equiv of CN$^-$.

The reaction of **8** with 1−4 equiv of CN$^-$ was also investigated by IR spectroscopy which again showed the generation of multiple peaks with the addition of varying equivalents of CN$^-$ (Figures 8b and S100b). Considering the report of ν_{CN} = 2050 cm^{-1},[180] and 2060−2075 cm^{-1}[181] for N-bound SCN$^-$, and the general assignment of N-bound SCN$^-$ (≤2100 cm^{-1}) and S-bound SCN$^-$ (>2100 cm^{-1}),[182] the persistent peak at ν_{CN} = 2055 cm^{-1} for 1−4 equiv of CN$^-$ (Figure 8b) might be assigned to the coordinated SCN$^-$ (N-bound), while the peak at ν_{CN} = 2118 cm^{-1} (generated along with the peak at ν_{CN} = 2055 cm^{-1} upon treatment of **8** with of 1 and 2 equiv of CN$^-$) might then be assigned to coordinated SCN$^-$ (S-bound). The peak at ν_{CN} = 2118 cm^{-1} possibly gets masked due to the development of the peak at ν_{CN} = 2110 cm^{-1} obtained upon treatment of **8** with 3 equiv of CN$^-$ which further shifted to ν_{CN} = 2104 cm^{-1} upon treatment of **8** with 4 equiv of CN$^-$. The peaks at ν_{CN} = 2104−2110 cm^{-1} might be assigned to free/coordinated CN$^-$[178,179] which also matches well with the IR spectroscopic investigation of the reaction of **9b** with 1−3 equiv of CN$^-$. Fortunately enough, multiple attempts to isolate the products of the reaction between **8** and CN$^-$ finally allowed the characterization of an unprecedented compound, $[Co_2(BPMP)(\mu\text{-}SH)(NCS)_2]$ (**14**) (Scheme 3), from the reaction of **8** and 1 equiv of CN$^-$. In contrast to the reaction of **8** with CN$^-$, treatment of **10** with CN$^-$ gave back only the starting material (**10**), thus indicating no reaction of **10** with CN$^-$. This result might be attributed to the presence of S^{2-} (and hence no neutral sulfur atom) instead of the presence of neutral sulfur atoms in the S_5^{2-} chain of **8**. On the other hand, a control reaction involving **8** and $(NH_4)(SCN)$ allowed the isolation of $[Co_2(BPMP)(NCS)_3]$ (**15**) (ν_{CN} for the N-bound SCN$^-$ at 2045 cm^{-1}, Figure S101), which indicated that the bridging HS$^-$ has indeed been generated by the reaction of the coordinated S_5^{2-} chain and CN$^-$. Identities of both **14** and **15** were confirmed by single crystal X-ray structure determinations (Figure 9). It may be noted that despite multiple attempts, analytically pure sample of **14** could not be obtained. This is, however, not unexpected since the IR spectroscopic investigation of the products obtained from the reaction of **8** with 1−4 equiv of CN$^-$ (Figures 8b and S100b) indicated the generation of multiple species. The reactions of **8**, **9a**, and **9b** are summarized in Scheme 3.

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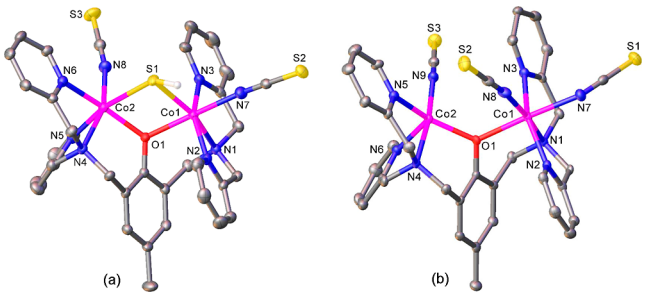

Figure 9. Molecular structures of **14** (a) and **15** (b) with 30% probability thermal ellipsoids and partial atom labeling scheme. Hydrogen atoms are omitted for clarity.

CONCLUSIONS

Binuclear Co(II)−polysulfido and -polyselenido complexes have been synthesized by exploiting the two-electron redox reaction between elemental sulfur/selenium and the coordinated thiolates of new binuclear Co(II)−bis(thiolate) complexes. Reactivity of these unprecedented binuclear Co(II)−polychalcogenido complexes with PPh_3 has been investigated in detail which allowed the isolation of new binuclear Co(II) complexes featuring a bridging sulfido and a bridging diselenido ligand. Interestingly, the binuclear Co(II)−sulfido and Co(II)−diselenido complexes could again be converted back to the binuclear Co(II)−pentasulfido and Co(II)−tetraselenido complexes upon treatment with elemental sulfur and selenium, respectively. The reaction of the binuclear Co(II)−polychalcogenido complexes with activated alkynes allowed the synthesis of a series of binuclear Co(II) complexes featuring bridging dithiolene and diselenolene ligands. Finally, the reactivity of the coordinated polychalcogenide chain with cyanide has been demonstrated by IR spectroscopic investigation and molecular structure determination of an unprecedented binuclear Co(II) complex featuring coordinated hydrosulfide and thiocyanate. In summary, the present work, for the first time, describes the synthesis, characterization, interconversion, and comparative reactivity of a series of new binuclear Co(II) complexes featuring polysulfide and polyselenide ligands of different chain lengths.

METHODS

All reactions and workup procedures were performed under nitrogen atmosphere using either standard Schlenk techniques or a glovebox. Sodium salts of the thiolates were prepared by the reaction of sodium hydride with the corresponding thiols. The yields of the recrystallized compounds are averages of the individual yields obtained from multiple batches. Anhydrous $CoCl_2$ (Sigma-Aldrich, 98%), $NaClO_4$ (Sigma-Aldrich, 98%), $NaBF_4$ (Sigma-Aldrich, 98%), $NaBPh_4$ (Loba Chemie Pvt. Ltd., 99.5%), elemental sulfur (Sigma-Aldrich, 99.5%), gray Se (Aldrich, 99.5%), dimethyl acetylenedicarboxylate (Sigma-Aldrich, 95%), diethyl acetylenedicarboxylate (Sigma-Aldrich, 95%), tetrabutylammonium cyanide (Merck, 95%), PPh_3 (Spectrochem Pvt. Ltd., 98%), ammonium thiocyanate (Merck, 98%), 2-methoxythiophenol (Sigma-Aldrich, 97%), 2-aminothiophenol (TCI, 97%), 2-mercaptophenol (Sigma-Aldrich, 95%), toluene-3,4-dithiol (Sigma-Aldrich, 90%), benzene-1,2-dithiol (Sigma-Aldrich, 96%), dimercaptomaleonitrile disodium salt (Sigma-Aldrich, ≥95.0%), DMSO-d_6 (CIL, 99.9%), CD_3CN (CIL, 99.8%), Mesitylene (Merck, 98%), and sodium hydride (Spectrochem Pvt. Ltd., 58%) were procured from commercial sources.

Caution! Perchlorate salts, in general, are explosive in nature and should be used with care. In the present work, the sodium perchlorate salt was handled in small quantities (<20 mg) with the necessary precautions inside an inert atmosphere glovebox, and no problems were encountered.

Elemental analysis (PerkinElmer 2400 series II CHNS analyzer), ^1H and ^{31}P NMR spectroscopy (either a Bruker Avance DPX 400 MHz spectrometer or a Bruker Avance Neo Ascend 600 MHz spectrometer), IR spectra (PerkinElmer UATR Spectrum Two FT-IR spectrometer), unit cell determinations of single crystals (Bruker D8 VENTURE Microfocus diffractometer), high-resolution mass spectra (Q-Tof-micro-MS system using electron spray ionization techniques), XPS measurement (Omicron Nano Technology 0571), and gas chromatography−mass spectrometry (GC−MS) measurements (Thermo Scientific Trace 1310 gas chromatograph coupled with an ISQ QD mass spectrometer with a maximum temperature of 300 °C using a TG-5MS: 30 m × 0.25 mm × 0.25 μm column) were performed following the procedure described in one of our previous reports.[109]

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/jacsau.3c00790.

Experimental details, X-ray crystallographic tables, tables of unit cell parameters, ^{31}P and ^1H NMR spectra, IR spectra, mass spectra, powder X-ray diffraction data, and gas chromatographic data (PDF)

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AUTHOR INFORMATION

Corresponding Author

Amit Majumdar − *School of Chemical Sciences, Indian Association for the Cultivation of Science, Kolkata, West Bengal 700032, India;* orcid.org/0000-0003-0522-8533; Email: icam@iacs.res.in

Authors

Kamal Hossain − *School of Chemical Sciences, Indian Association for the Cultivation of Science, Kolkata, West Bengal 700032, India*

Angshuman Roy Choudhury − *Department of Chemical Sciences, Indian Institute of Science Education and Research, Mohali, S. A. S. Nagar, Punjab 140306, India;* orcid.org/0000-0002-4018-0451

Complete contact information is available at: https://pubs.acs.org/10.1021/jacsau.3c00790

Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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