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# Divergent behavior in the chemistry of metal-bis(dithiolene) complexes appended with peripheral aliphatic butyl chains

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**Abstract:** Metal-bis(dithiolene) complexes derived from Ni(II), Co(II), Pd(II), Pt(II) and Au(III), bearing butyl aliphatic chains have been synthesized, and fully characterized by a variety of spectroscopic techniques including NMR, UV-vis, IR, HRMS, CV, and X-ray diffraction studies. This comparative study made possible to establish that the Co(II) species appear to be dimeric in the solid state as well as in solution. On the other hand, the coordination complexes based on Ni(II), Pd(II), Pt(II) and Au(II), feature a monomeric structure in both solution and solid state. These metal-bis(dithiolene) complexes are remarkably stable in solution and, in stark contrast to precedents in the literature, they retain their square planar geometry even in presence of pyridine derivatives reported for their apical binding on metal-bis(dithiolene) complexes.

## Introduction

Square-shaped metal-bis(dithiolene) complexes, combining a metal center and two non-innocent redox ligands, exhibit remarkable optical and electrochemical properties and have been intensively investigated in materials science, especially as precursors from conducting and magnetic crystals,<sup>[1-2]</sup> as NIR dyes for lasers<sup>[3-4]</sup> and as photothermal agents for photothermal therapy<sup>[5-6]</sup> or to develop photoresponsive polymers.<sup>[7-8]</sup>

The electrochemistry associated with square-shaped metal-bis(dithiolene) complexes have been also largely investigated and applied in different fields.<sup>[9]</sup> For instance, nickel-bis(dithiolene) complexes were used in the selective separation of olefins from hydrocarbon mixture through reversible electrochemically controlled olefins binding.<sup>[10]</sup> This work was extended to the study of the reversible electrochemically controlled binding of phosphine on iron and cobalt bis(dithiolene) complexes.<sup>[11]</sup> Metal-bis(dithiolene) complexes were also used as catalysts for the photocatalytic and electrocatalytic reduction of protons. The first experiments on the homogeneous photoreduction of water with  $[\text{Ni}(\text{S}_2\text{C}_2\text{Ph}_2)_2]$  complex as photosensitizer in a THF/water solvent mixture under light irradiation above 290 nm were reported in 1980.<sup>[12]</sup> Since then, a plethora of symmetric, homoleptic metal-(bis)dithiolene complexes were examined for photogeneration of hydrogen under light irradiation.<sup>[13]</sup> However, the energy storage efficiencies remained modest and dithiolene complexes with symmetrical substituents or electron withdrawing groups on the aromatic rings were found unstable. Recently, several monomeric

and dimeric anionic cobalt bis(dithiolene) complexes were found to be stable and highly active photocatalysts for the reduction of protons in aqueous solvents mixtures when combined with  $[\text{Ru}(\text{bpy})_3]^{2+}$  as photosensitizer and electron donors.<sup>[14-16]</sup> The proposed elementary steps in the catalytic process include reduction of the monoanionic catalyst followed by a protonation, either on the cobalt or sulfur atom. The same complexes also act as electrocatalysts for proton reduction in aqueous solvent mixtures in the presence of a weak acid.

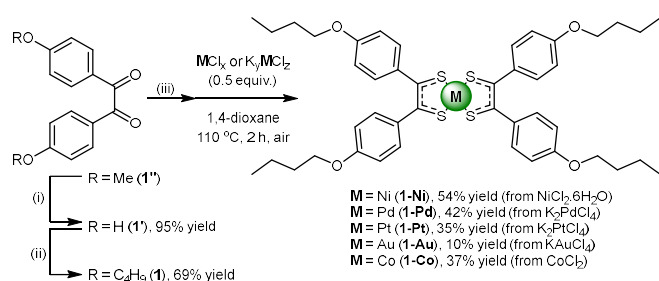
Metal-bis(dithiolene) complexes with a low reductive potential are also good candidate for the electro- or photocatalytic reduction of  $\text{CO}_2$ . Fontecave *et al.* developed several bis(dithiolene) complexes of molybdenum and nickel mimicking molybdopterin, producing mainly formate, with minor amounts of carbon monoxide and hydrogen.<sup>[17-19]</sup> A molybdenum-containing Desulfovibrio desulfuricans formate dehydrogenase (Dd FDH) was also reported to catalyze the reduction of  $\text{CO}_2$  to formate.<sup>[20]</sup> Herein, we report on a complete series of metal-bis(dithiolene) complexes bearing butyl aliphatic chains at the periphery with Ni(II), Co(II), Pd(II), Pt(II) and Au(III) metal centers. The coordination behavior and the electronic properties associated with this series of structurally similar metal-based dithiolene complexes were investigated by various characterization techniques including NMR, UV-vis, IR, HRMS, CV, and X-ray diffraction. Whereas the square planar species derived from Ni(II), Pd(II), Pt(II) and Au(III) are monomeric in nature, the Co(II) ones are prone to form dimeric species. The binding of pyridine derivatives to this class of complexes was also investigated.

## Results and Discussion

The metal-based dithiolene complexes of this study comprise peripheral butyl aliphatic chains as shown in **Scheme 1**. Their synthesis was adapted from a classical and well-established three-step protocol reported in the literature<sup>[21-23]</sup> (see Experimental Section). It begins with the virtually quantitative deprotection (95% yield) of the methoxy groups of 4,4'-dimethoxybenzil **1'** under a concentrated mixture of HBr and acetic acid at 140 °C. The <sup>1</sup>H NMR spectrum of the crude reaction mixture revealed the disappearance of the signal corresponding to the methoxy groups at 3.88 ppm. We noted that when the reaction was conducted at lower temperatures (110 °C), the deprotection was not quantitative and the resulting mixture of

## RESEARCH ARTICLE

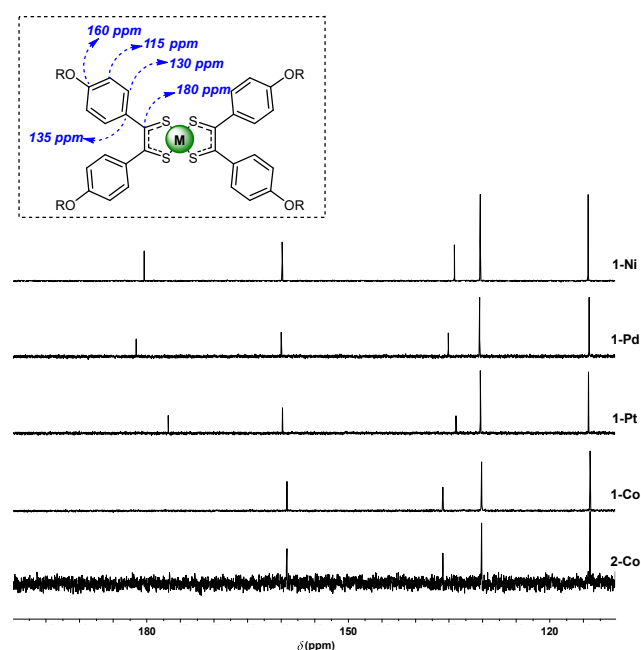
starting material, product and mono-deprotected compound were not trivial to separate by column chromatography. The second step is the *O*-alkylation of 4,4'-dihydroxybenzyl **1'** with 1-bromobutane in the presence of potassium carbonate. The resulting bis-alkylated product **1** was obtained in 69% yield after purification by column chromatography followed by recrystallization. The metal-bis(dithiolene) complexes **1-M** (**M** = Ni, Pd, Pt, Co, Au) were obtained *via* a two-step sequence by an initial treatment of 4,4'-dibutoxybenzyl with  $P_4S_{10}$  that were further reacted with 0.5 equivalents of a metallic chloride salt to yield the corresponding metal-bis(dithiolene) species in yields varying from 10 to 54 % after purification by column chromatography followed by recrystallization. It is relevant to note that the last step was also reported with 1,3-dimethyl-2-imidazolidinone (DMI) as the solvent, typically leading to higher yields, nevertheless, we did not verify this protocol.<sup>[21,22]</sup> Unlike the nickel (**1-Ni**) and (**1-Au**) gold bis-(dithiolene) complexes and that were already reported,<sup>[21-23]</sup> palladium (**1-Pd**), platinum (**1-Pt**) and cobalt (**1-Co**) complexes are reported here for the first time.



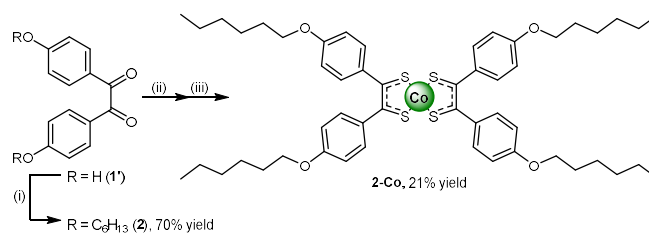
**Scheme 1.** Synthesis of metal-bis(dithiolene) complexes **1-M** containing butyl aliphatic chains at the periphery. Reaction conditions (i) AcOH/HBr, 140 °C, 18 h, air; (ii) bromobutane (2.1 eq),  $K_2CO_3$  (2.1 eq), DMF, 110 °C, 65 h,  $N_2$ ; (iii)  $P_4S_{10}$  (2.1 eq), 1,4-dioxane, 110 °C, 2 h,  $N_2$ .

The spectroscopic characterization of the previously reported **1-Ni** and **1-Au** complexes were identical to those reported in the literature.<sup>[21-23]</sup> The new metal-bis(dithiolene) complexes **1-Pd**, **1-Pt**, and **1-Co** were fully characterized by  $^1H$  and  $^{13}C$  NMR spectroscopy as well as IR, UV-vis and MS (MALDI-TOF). Whereas the **1-Ni**, **1-Pd**, **1-Pt**, and **1-Co**, with a metal ions formally in the +2 oxidation state, are isolated as neutral diamagnetic complexes, the gold complex **1-Au**, with a metal ions formally in the +3 oxidation state, is isolated as a neutral radical complex.<sup>[22-23]</sup> The  $^1H$  NMR fingerprint of these diamagnetic complexes are rather similar. For instance, a classical AX spin system at ca. 7 ppm was observed for the aromatic protons. Those peaks in the free ligand are down-field shifted to ca. 8 ppm. The methoxy  $CH_2$  protons display a signal at ca. 4 ppm as a well-defined triplet. Besides the other aliphatic  $CH_2$  protons, the  $CH_3$  methyl group have a well-defined triplet signal at ca. 1 ppm. The  $^{13}C$  NMR fingerprint of these diamagnetic complexes are rather similar too with the unexpected exception of the cobalt complex **1-Co**. In fact, the  $^{13}C$  NMR of the cobalt complex **1-Co** differs by the absence of a peak corresponding to the quaternary carbon atom linked to the cobalt-coordinating sulfur (**Figure 1**). In the case of **1-Ni**, **1-Pd** and **1-Pt** complexes, the signal associated with this carbon atom displays a  $\delta = 180$  ppm chemical shift. For comparison purposes, a cobalt complex similar to **1-Co**, but comprising a longer aliphatic hexyl chain (**2-Co**) was synthesized (**Scheme 2**) and, like for **1-Co** complex, the same carbon signal is absent in its  $^{13}C$  NMR spectrum (**Figure 1**). This unprecedented quaternary carbon quenching in **1-Co** NMR is probably attributed

to the closer proximity of these carbon atoms to the paramagnetic Co(II) center, although the overall dimeric complex is diamagnetic (*vide infra*). Although cobalt-dithiolene complexes with different functional groups on the peripheral positions have been synthesized and studied in diverse areas of research,<sup>[24-48]</sup> to the best of our knowledge, these observations associated with  $^{13}C$  NMR spectroscopy have not been reported so far. Note that DOSY NMR studies performed on **1-Ni** and **1-Co** displayed almost identical diffusion values ( $D = 1.4 \times 10^{-5} \text{ cm}^2 \cdot \text{s}^{-1}$ ). According to precedents in the literature,<sup>[21-23]</sup> we noted that the IR spectra of all **1-M** complexes displayed similar profiles. Elemental analysis also confirmed the homogeneity of the different metal complexes.



**Figure 1.**  $^{13}C\{^1H\}$  NMR (101 MHz,  $CDCl_3$ ) spectra of **1-Ni**, **1-Pd**, **1-Pt**, **1-Co** and **2-Co** highlighting the aromatic area with the missing signal at ca. 180 ppm for **1-Co** and **2-Co**.

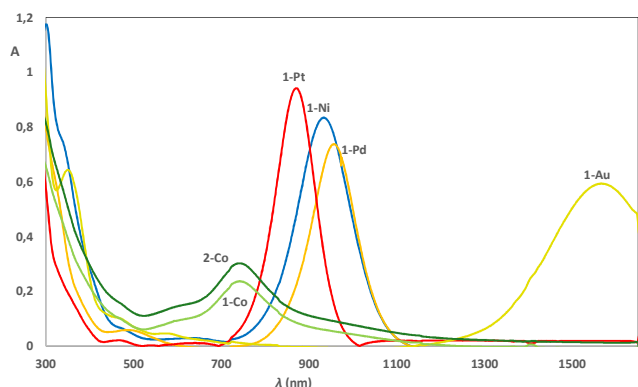


**Scheme 2.** Synthesis of cobalt-bis(dithiolene) complex **2-Co** containing hexyl aliphatic chains in the periphery. Reaction conditions (i) bromohexane (2.1 eq),  $K_2CO_3$  (2.1 eq), DMF, 110 °C, 65 h,  $N_2$ ; (ii)  $P_4S_{10}$  (2.1 eq), 1,4-dioxane, 110 °C, 2 h,  $N_2$ ; (iii)  $CoCl_2$  (0.5 eq), 1,4-dioxane, 110 °C, 2 h, air.

Such divergent behaviour encountered in solution for the cobalt complexes **1-Co** and **2-Co** with respect to the other metal-bis(dithiolene) complexes was also evidenced by UV-vis spectroscopy studies with the maximal absorbance wavelength strongly depending on the metal ion (**Figure 2**). For instance, **1-Ni**, **1-Pd** and **1-Pt** complexes displayed respectively maximum absorbance at 933 ( $\epsilon = 34791 \text{ L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$ ), 956 ( $\epsilon = 46862 \text{ L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$ ) and 871 nm ( $\epsilon = 41497 \text{ L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$ ). The gold complex **1-Au** displayed a maxima ca. 1566 nm ( $\epsilon = 28018 \text{ L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$ ),

## RESEARCH ARTICLE

which was ascribed to the classical relativistic effects this metal displays.<sup>[22]</sup> Unexpectedly, the cobalt complexes **1-Co** and **2-Co** featured a maximum absorbance at a significantly lower wavelengths of 742 nm ( $\epsilon = 9200 \text{ L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$  for **1-Co** and  $\epsilon = 15300 \text{ L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$  for **2-Co**) compared to the other similarly oxidized metals (nickel, palladium, platinum). To complement the characterization studies, we noted that the cobalt complex **1-Co** displayed  $m/z$  peaks corresponding to both monomeric ( $m/z = 832$ ) and dimeric ( $m/z = 1662$ ) species by MS analysis. These features were not observed in the other metal complexes, which only showed peaks corresponding to the monomeric species. The above-described combination of data suggests that the cobalt-dithiolene complexes exist in a dimeric form in solution<sup>[49]</sup> and that the dimer is partially dissociated during the MS analysis.



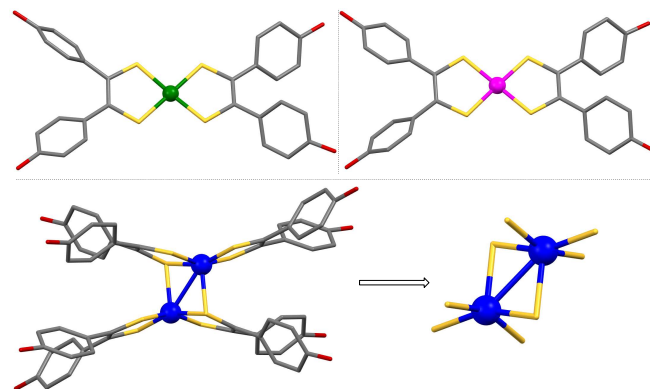
**Figure 2.** UV-visible spectra (in  $\text{CH}_2\text{Cl}_2$ ) of metal-bis(dithiolene) complexes **1-Ni** (blue), **1-Pd** (orange), **1-Pt** (red), **1-Au** (yellow), **1-Co** (light green) and **2-Co** (dark green). Concentration  $\approx 2 \cdot 10^{-5} \text{ mol}\cdot\text{L}^{-1}$ .

Further evidences for the dimeric form of the cobalt-dithiolene complexes in solution was inferred by cyclic voltammetry (CV) studies (Table 1, Figures S19-S22).<sup>[50]</sup> Whereas the **1-Ni**, **1-Pd**, **1-Pt** and **1-Au** displayed characteristic two reversible one electron reduction waves corresponding respectively to  $\text{LM}^{0/-1}$  and  $\text{LM}^{-1/-2}$  redox couples, the cobalt complexes **1-Co** and **2-Co** displayed an additional irreversible reduction wave. As it was reported elsewhere for other dinuclear cobalt complexes.<sup>[4,31]</sup> In this case, due to the dimeric nature of these complexes, the first reversible reduction wave is one electron process corresponding to  $(\text{LM-LM})^{0/-1}$  redox couple. The second one electron reduction process yield  $(\text{LM-LM})^{2-}$  that dissociate immediately in solution to form two monomer as indicated by the irreversibility of the reduction wave. The current intensity of the last reversible wave corresponding to  $\text{LM}^{-1/-2}$  is two times higher than that of the two previous waves because the concentration of the monomer is twice that of the initial dimer, confirming once again the dimeric nature of the cobalt complexes in solution.

**Table 1.** Measured electrochemical data (in V vs. NHE, 0.1 M  $[\text{Bu}_4\text{N}]\text{PF}_6$ ,  $100 \text{ mV s}^{-1}$ ).

Complex	$E^1$	$E^2$	$E^3$	Solvent
<b>1-Ni</b>	0.202	-0.649	-	THF
<b>1-Pd</b>	1.139	0.181	-0.436	DCM
<b>1-Pt</b>	1.225	-0.110	-0.614	DCM
<b>1-Au</b>	1.616	1.022	0.480	DCM
<b>1-Co</b>	0.183	-0.282	-0.781	DMF
<b>2-Co</b>	0.183	-0.278	-0.776	DMF

In addition, we were able to obtain single crystals suitable for X-ray diffraction studies for complexes **1-Pd**, **1-Pt** and **2-Co** (Figure 3, Table 2 and 3). In the solid state, **1-Pd** and **1-Pt** species are monomeric with an almost perfect square planar geometry around the  $\text{Pd}^{2+}$  and  $\text{Pt}^{2+}$  metal centers (Figure 3, top), thus being isostructural with respect to the known **1-Ni** and **1-Au** species.<sup>[21-23]</sup> On the other hand, **2-Co** crystallized as a well-defined dimeric structure in which the  $\text{Co}^{2+}$  center adopt a slightly distorted square planar geometry around the sulfur coordinating atoms, with an additional apical binding to a  $\text{Co}^{2+}$  center and sulfur atoms from another **2-Co** molecule. The intermetallic  $\text{Co}\dots\text{Co}$  distance was found to be 2.774 Å and the intermolecular  $\text{Co}\dots\text{S}$  distance was 2.364 Å, thereby leading to a dinuclear cluster-like structure (Figure 3, bottom). Additional single crystal information are presented in SI.



**Figure 3.** Single crystal X-ray diffraction studies of **1-Pd** (top, left), **1-Pt** (top, right) and **2-Co** (bottom). Hydrogen atoms and aliphatic chains are not represented for the sake of clarity. Color code: carbon (grey), oxygen (red), sulfur (yellow), palladium (dark green), platinum (pink) and cobalt (dark blue).

## RESEARCH ARTICLE

**Table 2.** Selected crystallographic data.

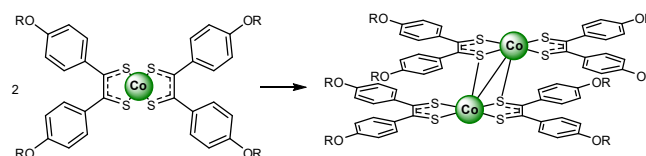
	1-Pd	1-Pt	2-Co	1-Ni(pyr)
system	triclinic	triclinic	triclinic	triclinic
space group	P-1	P-1	P-1	P-1
<i>a</i> (Å)	9.3759(14)	9.3337(9)	9.3034(14)	9.501(2)
<i>b</i> (Å)	13.7748(19)	13.8450(9)	16.496(2)	14.728(3)
<i>c</i> (Å)	18.341(3)	18.3912(12)	18.089(3)	17.058(4)
$\alpha$ (deg)	104.658(3)	104.680(2)	97.962(4)	105.343(5)
$\beta$ (deg)	100.277(4)	100.244(2)	93.160(4)	95.001(5)
$\gamma$ (deg)	107.115(3)	107.270(2)	105.831(4)	93.403(5)
<i>V</i> (Å <sup>3</sup> )	2106.7(3)	2111.4(2)	2632.4(7)	2284.7(9)

The central C-C bond and the C-S bonds on the dithiolene ligands are close (see **Table 3**), indicating that all ligands are in the same oxidation state. These distances, which are intermediate to those observed in the ene-1,2-dithiolate (C-S = 1.75 and C-C = 1.36 Å) and  $\alpha$ -dithione forms (C-S = 1.66 and C-C = 1.44 Å), confirm the presence of monoanionic  $\pi$ -radical ligands on all the complexes.<sup>[51]</sup> The bond analysis confirms that the metal center in the Pd, Pt, Ni and Co complexes are in a +II state. The formation of the diamagnetic dimeric cobalt complex can be viewed as two antiferromagnetically coupled paramagnetic Co(II) complexes each having two monoanionic  $\pi$ -radical ligands. Comparison of the bond distances between **2-Co** and a parent structure with methoxy groups (Table 3, **Co-OMe**, Co-Co: 2.7703(8) Å)<sup>[25]</sup> shows that there is no impact of the chain length on the central metal-containing core. The S deviation from the square planar  $D_{4h}$  symmetry calculated using the Continuous Shape Measures (CSHM's) algorithm implemented in the SHAPE 2.1 software<sup>[52]</sup> for **1-Pd**, **1-Pt** and **1-Ni** are very low (0.112, 0.154 and 0.074, respectively). When the square planar geometry is considered for **2-Co**, the S value significantly increase (S = 0.849) compared to the "true square planar" while a much lower S value of 0.184 is obtained when considering a  $ML_5$  coordination in a  $C_{4v}$  square pyramid geometry.

**Table 3.** Selected crystallographic bond distances.

Compound	<i>d</i> <sub>C-C</sub> (Å)	<i>d</i> <sub>C-S</sub> (Å)	<i>d</i> <sub>M-S</sub> (Å)
<b>1-Pd</b>	C1-C2 1.392(5)	C1-S1 1.722(4)	Pd1-S1 2.2616(11)
	C3-C4 1.391(6)	C2-S2 1.708(4)	Pd1-S2 2.2470(12)
		C3-S3 1.706(4)	Pd1-S3 2.2515(11)
		C4-S4 1.716(4)	Pd1-S4 2.2427(12)
<b>1-Pt</b>	C1-C2 1.396(6)	C1-S1 1.715(4)	Pt1-S1 2.2544(11)
	C3-C4 1.392(6)	C2-S2 1.714(4)	Pt1-S2 2.2430(12)
		C3-S3 1.709(4)	Pt1-S3 2.2464(11)
		C4-S4 1.724(4)	Pt1-S4 2.2475(12)
<b>2-Co</b>	C1-C2 1.406(4)	C1-S1 1.702(3)	Co-S1 2.1501(8)
	C3-C4 1.378(4)	C2-S2 1.706(3)	Co-S2 2.1682(8)
		C3-S3 1.737(3)	Co-S3 2.1707(9)
		C4-S4 1.709(3)	Co-S4 2.1901(8)
<b>1-Ni(pyr)</b>	C1-C2 1.393(7)	C1-S1 1.717(6)	Ni-S1 2.1178(16)
	C3-C4 1.409(7)	C2-S2 1.715(5)	Ni-S2 2.1277(17)
		C3-S3 1.709(6)	Ni-S3 2.1233(17)
		C4-S4 1.704(6)	Ni-S4 2.1280(17)
<b>Co-OMe</b> <sup>[25]</sup>	C1-C2 1.398(4)	C1-S1 1.700(3)	Co-S1 2.1701(9)
	C3-C4 1.371(4)	C2-S2 1.697(3)	Co-S2 2.1498(9)
		C3-S3 1.721(3)	Co-S3 2.1934(8)
		C4-S4 1.745(3)	Co-S4 2.1751(8)

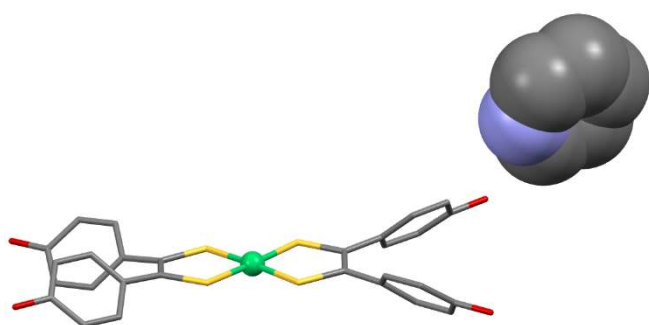
The overall combination of data supports that the metal dithiolene complexes **1-Co** and **2-Co** species exist in a dimeric form (**Scheme 3**). Alternatively, the other metal dithiolene complexes derived from nickel, palladium, platinum and gold are monomers in both solution and solid state.

**Scheme 3.** Self-assembly formation of a dimeric structure involving the cobalt dithiolene complexes **1-Co** and **2-Co**. R = butyl or hexyl.

Next, we explored the potential cleavage of the dimeric structure **1-Co** using different Lewis base adducts derived from pyridine in solution.<sup>[50]</sup> However, no changes were observed in the <sup>1</sup>HNMR spectrum of **1-Co** upon the addition of equimolar amounts of the pyridine derivatives. UV-vis studies also showed no evidence for an interaction between the pyridine and the metal-dithiolene complexes. This was further supported by X-ray diffraction studies performed on single crystals derived from **1-Ni** grown in the presence of an excess of pyridine (**Figure 4** and **Table 2**). In the solid state, the nickel center from **1-Ni** adopts an almost perfect square planar geometry around the dithiolene ligands with the pyridine molecule located in the unit cell far away from the nickel center ( $d_{Ni...N} = 10.080$  Å). This observation strikingly contrasts with other nickel-dithiolene complexes that do exhibit coordination with pyridine derivatives leading to octahedral nickel complexes comprising two-fold pyridine binding in *trans,trans*- or *cis,cis*-configuration.<sup>[53-54]</sup> Attempts of growing crystals suitable for X-ray diffraction studies of **1-Ni** in the presence of an even stronger coordinating ligand such as 4-dimethylaminopyridine were also unsuccessful. 2,3,5,6-tetrafluoropyridine was also evaluated as a potential ligand to

## RESEARCH ARTICLE

coordinate **1-Ni** in solution as both  $^1\text{H}$  and  $^{19}\text{F}$  could be used as a probe for NMR spectroscopy studies. We did only observe a limited chemical shifts associated with the proton atom and both fluorine atoms upon titration of **1-Ni** with increasing quantities of 2,3,5,6-tetrafluoropyridine (Figure S27-S32).<sup>[50]</sup> Although the titration suggest a 1:1 assembly, the curve fitting failed to establish a reliable association constant due to the very minor variation of the chemical shifts, thereby suggesting a negligible interaction taking place in this system. In solution, triphenylphosphine ligand did not coordinate to the **1-Ni** complex according to  $^1\text{H}$  and  $^{31}\text{P}$  NMR spectroscopy studies neither.<sup>[28]</sup> Therefore, it can be concluded that this class of metal-bis(dithiolene) complexes with phenyl substituents is too electron-rich to accept the lone pair of the pyridine and triphenylphosphine ligand on the metal center.



**Figure 4.** Single crystal X-ray diffraction studies of **1-Ni** with pyridine. Hydrogen atoms and aliphatic chains are not represented for the sake of clarity, and the pyridine is represented in spacefill style. Color code: carbon (grey), oxygen (red), sulfur (yellow), nitrogen (blue) and nickel (light green).

Finally, very preliminary experiments seems to indicate that the dinuclear cobalt complexes **1-Co** and **2-Co** display some electrocatalytic activity for  $\text{CO}_2$  reduction in DMF (see Figure S22 in the Supporting Information).

## Conclusion

In summary, we have disclosed the difference of coordination behavior between monomeric and dimeric structures in a series of structurally related metal-bis(dithiolene) complexes comprising peripheral butyl aliphatic chains. In contrast to the nickel, palladium, platinum and gold derivatives, cobalt complexes have a strong preference for rearranging as dimeric species according to MS,  $^{13}\text{C}$  NMR and CV spectroscopy as well as X-ray diffraction studies, in particular. It is remarkable that such long and bulky aliphatic substituents do not forbid dimeric formation for the case of **1-Co** and **2-Co**. All the reported metal complexes are chemically robust and do not bind ligands such as pyridine and triphenylphosphine neither in solution nor in the solid state. Overall, the present contribution highlights that even well-known and exploited metal-bis(dithiolene) complexes can still lead to interesting finding as regards of the coordination chemistry and electrochemistry herein discussed.

## Experimental Section

**General Methods.** Solvents were purified with an MB SPS-800 purification system. Toluene was dried with  $\text{CaH}_2$  and distilled prior to use.  $\text{CDCl}_3$  was

filtered through alumina and stored under argon over molecular sieves. All employed chemicals were purchased from commercial sources and used as received. Unless otherwise specified, reactions were carried out under nitrogen atmosphere by employing standard Schlenk and vacuum-line techniques.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded with a Bruker (400 MHz and 300 MHz) spectrometer.  $^1\text{H}$  NMR spectra were referenced to residual protonated solvent ( $\delta = 7.26$  ppm for  $\text{CDCl}_3$  and  $\delta = 2.17$  ppm for acetone- $d_6$ ).  $^{13}\text{C}$  NMR spectra were referenced to  $\text{CDCl}_3$   $\delta = 77.16$  ppm). Abbreviations for signal couplings are: br, broad; s, singlet; d, doublet; t, triplet; q, quadruplet; p, quintuplet; hept, heptuplet; m, multiplet; dd, doublet of doublets; dt, triplet of doublets; td, doublet of triplets; tt, triplet of triplets; tdd, doublet of doublet of triplets. Coupling constants,  $J$ , were reported in hertz unit (Hz). UV/Vis absorption spectra were recorded with a Shimadzu 3600 plus 205 UV/Vis/NIR spectrophotometer and quartz cuvettes of 1 cm path length. Mass spectroscopy were recorded with a MALDI-TOF (less resolution). FT-IR spectra were recorded using a Bruker VERTEX 70 spectrometer equipped with an ATR apparatus. All electrochemical experiments were performed on a Metrohm Autolab 302N potentiostat. Homogeneous cyclic voltammograms were obtained in a three-electrode electrochemical cell, with a glassy carbon (3 mm diameter) working electrode (GCE), saturated calomel reference electrode (SCE), and a platinum wire counter electrode.  $[\text{Bu}_4\text{N}]\text{PF}_6$  in DMF was used as the electrolyte. When the electrolyte was saturated with  $\text{CO}_2$ , mQ  $\text{H}_2\text{O}$  was added as the proton source for possible  $\text{CO}_2$  electro-reduction. Potentials were converted to the normal hydrogen electrode (NHE) as reference scale in homogeneous electrochemical study by the following formula:

$$E \text{ (V vs NHE)} = \text{Applied potential (V vs SCE)} + 0.244 \text{ V.}$$

**Synthesis and characterization of 4,4'-dihydroxybenzil (1').** 4,4'-dimethoxybenzil **1''** (2.37 g, 8.8 mmol) was added in a mixture of glacial acetic acid (63 mL) and hydrobromic acid 38 % wt (63 mL). This mixture was stirred for 18 h at  $140^\circ\text{C}$ . After the reaction, water (300 mL) was added to the mixture and the compound was extracted with ethyl acetate (3 x 250 mL). The organic phase was neutralized with sodium hydroxide to pH = 7 and washed with water (3 x 250 mL). The organic phase was dried over  $\text{MgSO}_4$  and the ethyl acetate was removed. The product **1'** was isolated as an orange powder (2.03 g, 95% yield).  $^1\text{H}$  NMR (400 MHz, acetone- $d_6$ ):  $\delta = 9.75$  (s, 2H), 7.87 (dt,  $J = 8.7, 1.8$ , 4H), 7.04 (dt,  $J = 8.8, 2.0$ , 4H) ppm. The analytical match those previously reported.<sup>[55]</sup>

**Synthesis and characterization of 4,4'-dibutyloxybenzil (1):** A mixture of 4,4'-dihydroxybenzil **1'** (0.43 g, 1.8 mmol), bromobutane (0.50 g, 3.6 mmol) and potassium carbonate (0.51 g, 3.7 mmol) was stirred in DMF (50 mL) under  $\text{N}_2$  pressure for 48 h at  $110^\circ\text{C}$ . The DMF was evaporated under a vacuum. The residual was extracted with  $\text{CH}_2\text{Cl}_2$  (3 x 40 mL). The organic phases were washed with water (3 x 40 mL), dried over  $\text{MgSO}_4$  and the solvent was evaporated to dryness. The product was purified with chromatography on silica gel, eluting with dichloromethane/petroleum ether (7:3). Needle yellow crystal was obtained by slow diffusion of methanol on a solution of the product in dichloromethane (0.41 g, 65%). The product **1** was isolated as an orange powder (2.03 g, 95% yield).  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta = 7.94$  (dt,  $J = 9.1, 2.1$ , 4H), 7.14 (dt,  $J = 8.8, 2.0$ , 4H), 4.18 (t,  $J = 6.5$ , 4H), 1.88–1.77 (m, 4H), 1.61–1.47 (m, 4H), 1.01 (t,  $J = 7.3$ , 6H) ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta = 195.25, 166.30, 133.64$  (CH), 127.75, 116.60 (CH), 69.76 (OCH<sub>2</sub>), 32.57 (CH<sub>2</sub>), 20.55 (CH<sub>2</sub>), 14.78 (CH<sub>2</sub>) ppm. The analytical match those previously reported.<sup>[55]</sup>

**Synthesis and characterization of nickel-dithiolene complex 1-Ni:** A mixture of 4,4'-dibutyloxy-benzil **1** (0.39 g, 1.1 mmol) and phosphorous pentasulfide (0.99 g, 2.2 mmol) was stirred in 1,4-dioxane (5 mL) under  $\text{N}_2$  pressure for 2 h at  $110^\circ\text{C}$ . The mixture was cooled, the precipitated was filtered and washed with 1,4-dioxane. A solution of nickel chloride hexahydrate (II) (0.13 g, 0.6 mmol) in water (1 mL) was introduced at filtrate. The mixture was stirred for 2 h at  $110^\circ\text{C}$ . Methanol was added to the mixture and the precipitate was filtered, and washed with methanol. The purification of the product was carried out by chromatography on silica gel, eluting with petroleum ether/dichloromethane (1:1). The resulting

product **1-Ni** was isolated as black crystalline powder (0.25 g, 54% yield).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.32 (dt,  $J$  = 8.9, 2.0, 8H), 6.79 (dt,  $J$  = 8.8, 1.7, 8H), 3.97 (t,  $J$  = 6.5, 8H), 1.82–1.73 (m, 8H), 1.55–1.45 (m, 8H), 0.99 (t,  $J$  = 7.4, 12H) ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 180.74, 160.21, 134.57, 130.71 (CH), 114.67 (CH), 68.13 (OCH<sub>2</sub>), 31.62 (CH<sub>2</sub>), 19.59 (CH<sub>2</sub>), 14.20 (CH<sub>3</sub>) ppm. MS (Maldi-TOF):  $m/z$  calcd. for  $\text{Ni}_4\text{O}_4\text{C}_{44}\text{H}_{52}$  [ $\text{M}$ ]<sup>+</sup>: 831.83, found: 832.0. Elemental analysis (%) calcd. for  $\text{Ni}_4\text{O}_4\text{C}_{44}\text{H}_{52}$ : C 63.53, H 6.30, N 0.00, S 15.42; found: C 63.58, H 6.23, N 0.00, S 15.36.

**Synthesis and characterization of palladium-dithiolene complex 1-Pd:** A mixture of 4,4'-dibutyloxy-benzil **1** (0.20 g, 0.6 mmol) and phosphorous pentasulfide (0.51 g, 1.1 mmol) was stirred in 1,4-dioxane (7 mL) under  $\text{N}_2$  pressure for 2 h at 110 °C. The mixture was cooled, the precipitate was filtered and washed with 1,4-dioxane. A solution of potassium tetrachloropalladate (II) (0.084 g, 0.25 mmol) in water (1 mL) was introduced at filtrate. The mixture was stirred for 2 h at 110 °C. Methanol was added to the mixture and the precipitate was filtered, and washed with methanol. The purification of the product was carried out by chromatography on silica gel, eluting with petroleum ether/dichloromethane (1:1). The resulting product **1-Pd** was isolated as black crystalline needles (0.096 g, 42% yield).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.24 (dt,  $J$  = 8.8, 2.2, 8H), 6.78 (dt,  $J$  = 8.8, 2.1, 8H), 3.96 (t,  $J$  = 6.5, 8H), 1.82–1.71 (m, 8H), 1.53–1.43 (m, 8H), 0.98 (t,  $J$  = 7.5, 12H) ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 181.94, 160.37, 135.48, 130.82 (CH), 114.51 (CH), 68.14 (OCH<sub>2</sub>), 31.62 (CH<sub>2</sub>), 19.59 (CH<sub>2</sub>), 14.20 (CH<sub>3</sub>) ppm. MS (Maldi-TOF):  $m/z$  calcd. for  $\text{PdS}_4\text{O}_4\text{C}_{44}\text{H}_{52}$  [ $\text{M}$ ]<sup>+</sup>: 879.56, found: 878.0. Elemental analysis (%) calcd. for  $\text{PdS}_4\text{O}_4\text{C}_{44}\text{H}_{52}$ : C 60.08, H 5.96, N 0.00, S 14.58; found: C 59.11, H 5.98, N 0.00, S 13.87.

**Synthesis and characterization of platinum-dithiolene complex 1-Pt:** A mixture of 4,4'-dibutyloxy-benzil **1** (0.19 g, 0.53 mmol) and phosphorous pentasulfide (0.51 g, 1.1 mmol) was stirred in 1,4-dioxane (6 mL) under  $\text{N}_2$  pressure for 2 h at 110 °C. The mixture was cooled, the precipitate was filtered and washed with 1,4-dioxane. A solution of potassium tetrachloroplatinate (II) (0.113 g, 0.3 mmol) in water (1 mL) was introduced at filtrate. The mixture was stirred for 2 h at 110 °C. Methanol was added to the mixture and the precipitate was filtered, and washed with methanol. The purification of the product was carried out by chromatography on silica gel, eluting with petroleum ether/dichloromethane (1:1). The resulting product **1-Pt** was isolated as black crystalline needles (0.094 g, 35% yield).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.24 (dt,  $J$  = 8.9, 1.7, 8H), 6.80 (dt,  $J$  = 8.7, 2.2, 8H), 3.97 (t,  $J$  = 6.5, 8H), 1.83–1.71 (m, 8H), 1.56–1.44 (m, 8H), 0.98 (t,  $J$  = 7.4, 12H) ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 177.17, 160.16, 134.33, 130.70 (CH), 114.59 (CH), 68.12 (OCH<sub>2</sub>), 31.63 (CH<sub>2</sub>), 19.59 (CH<sub>2</sub>), 14.21 (CH<sub>3</sub>) ppm. MS (Maldi-TOF):  $m/z$  calcd. for  $\text{PtS}_4\text{O}_4\text{C}_{44}\text{H}_{52}$  [ $\text{M}$ ]<sup>+</sup>: 968.22, found: 968.0. Elemental analysis (%) calcd. for  $\text{PtS}_4\text{O}_4\text{C}_{44}\text{H}_{52}$ : C 54.58, H 5.41, N 0.00, S 13.25; found: C 54.41, H 5.52, N 0.00, S 13.24.

**Synthesis and characterization of gold-dithiolene complex 1-Au:** A mixture of 4,4'-dibutyloxy-benzil **1** (0.19 g, 0.53 mmol) and phosphorous pentasulfide (0.51 g, 1.1 mmol) was stirred in 1,4-dioxane (6 mL) under  $\text{N}_2$  pressure for 2 h at 110 °C. The mixture was cooled, the precipitate was filtered and washed with 1,4-dioxane. A solution of potassium tetrachloroaurate (III) (0.113 g, 0.3 mmol) in water (1 mL) was introduced at filtrate. The mixture was stirred for 2 h at 110 °C. Methanol was added to the mixture and the precipitate was filtered, and washed with methanol. The purification of the product was carried out by chromatography on silica gel, eluting with petroleum ether/dichloromethane (1:1). The resulting product **1-Au** was isolated as black crystalline needles (0.027 g, 10% yield). MS (Maldi-TOF):  $m/z$  calcd. for  $\text{AuS}_4\text{O}_4\text{C}_{44}\text{H}_{52}$  [ $\text{M}$ ]<sup>+</sup>: 969.24, found: 968.9. Elemental analysis (%) calcd. for  $\text{AuS}_4\text{O}_4\text{C}_{44}\text{H}_{52}$ : C 54.48, H 5.40, N 0.00, S 13.22; found: C 54.95, H 5.44, N 0.00, S 13.14.

**Synthesis and characterization of cobalt-dithiolene complex 1-Co:** A mixture of 4,4'-dibutyloxy-benzil **1** (0.20 g, 0.6 mmol) and phosphorous pentasulfide (0.50 g, 1.1 mmol) was stirred in 1,4-dioxane (5 mL) under  $\text{N}_2$  pressure for 2 h at 110 °C. The mixture was cooled, the precipitate was

filtered and washed with 1,4-dioxane. A solution of cobalt chloride (II) (0.037 g, 0.3 mmol) in water (1 mL) was introduced at filtrate. The mixture was stirred for 2 h at 110 °C. Methanol was added to the mixture and the formed precipitate was filtered, and washed with methanol. The purification of the product was carried out by chromatography on silica gel, eluting with petroleum ether/dichloromethane (1:1). The resulting product **1-Co** was isolated as black crystalline needles (0.10 g, 37% yield).  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.16 (d, 8H), 6.66 (d, 8H), 3.93 (t,  $J$  = 6.5, 8H), 1.85–1.69 (m, 8H), 1.57–1.42 (m, 8H), 0.99 (t,  $J$  = 7.5, 12H) ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 159.50, 136.29, 130.52 (CH), 114.37 (CH), 68.07(OCH<sub>2</sub>), 31.69 (CH<sub>2</sub>), 19.62 (CH<sub>2</sub>), 14.21 (CH<sub>2</sub>) ppm. MS (Maldi-TOF):  $m/z$  calcd. for  $\text{CoS}_4\text{O}_4\text{C}_{44}\text{H}_{52}$  [ $\text{M}$ ]<sup>+</sup>: 832.07, found: 832.1. Elemental analysis (%) calcd. for  $\text{CoS}_4\text{O}_4\text{C}_{44}\text{H}_{52}$ : C 63.51, H 6.30, N 0.00, S 15.41; found: C 63.89, H 6.41, N 0.00, S 14.52.

**Synthesis and characterization of 4,4'-dihexyloxybenzil (2):** A mixture of 4,4'-dihydroxybenzil **1'** (1.00 g, 4.1 mmol), bromohexane (1.36 g, 8.3 mmol) and potassium carbonate (1.16 g, 8.4 mmol) was stirred in DMF (25 mL) under  $\text{N}_2$  pressure for 65 h at 110 °C. The DMF was evaporated under a vacuum. The residual was extracted with  $\text{CH}_2\text{Cl}_2$  (3 x 30 mL). The organic phases were washed with water (3 x 30 mL), dried with  $\text{MgSO}_4$  and the solvent was evaporated to dryness. The product **2** was purified with chromatography on silica gel, eluting with dichloromethane/petroleum ether (7:3). Needle yellow crystal was obtained by slow diffusion of methanol on a solution of the product in dichloromethane (1.03 g, 70% yield).  $^1\text{H}$  NMR (400 MHz, acetone- $d_6$ ):  $\delta$  = 7.94 (dt,  $J$  = 9.0, 2.0, 4H), 7.15 (dt,  $J$  = 9.0, 2.2, 4H), 4.18 (t,  $J$  = 6.5, 4H), 1.89–1.81 (m, 4H), 1.57–1.48 (m, 4H), 1.43–1.33 (m, 8H), 0.93 (t,  $J$  = 6.9, 6H) ppm. The analytical match those previously reported.<sup>[55]</sup>

**Synthesis and characterization of cobalt-dithiolene complex 2-Co:** A mixture of 4,4'-dihexyloxybenzil **2** (0.21 g, 0.5 mmol) and phosphorous pentasulfide (0.45 g, 1.0 mmol) was stirred in 1,4-dioxane (5 mL) under  $\text{N}_2$  pressure for 2 h at 110 °C. The mixture was cooled, the precipitate was filtered, and washed with 1,4-dioxane. A solution of cobalt chloride (II) (0.033 g, 0.25 mmol) in water (1 mL) was introduced at filtrate. The mixture was stirred for 2 h at 110 °C. Methanol was added to the mixture and the precipitate was filtered, washed with methanol. The purification of the product was carried out by chromatography on silica gel, eluting with petroleum ether/dichloromethane (1:1). The resulting product **2-Co** was isolated as black crystalline needles (0.094 g, 35% yield).  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.15 (dt,  $J$  = 8.7, 2.2, 8H), 6.66 (dt,  $J$  = 8.9, 2.0, 8H), 3.92 (t,  $J$  = 6.5, 8H), 1.85–1.68 (m, 8H), 1.51–1.43 (m, 10H), 1.43–1.27 (m, 16H), 0.92 (t, 12H) ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 159.50, 136.29, 130.53 (CH), 114.38 (CH), 68.41 (OCH<sub>2</sub>), 31.97 (CH<sub>2</sub>), 29.61 (CH<sub>2</sub>), 26.10 (CH<sub>2</sub>), 22.96 (CH<sub>2</sub>), 14.37 (CH<sub>3</sub>) ppm. MS (Maldi-TOF):  $m/z$  calcd. for  $\text{CoS}_4\text{O}_4\text{C}_{52}\text{H}_{68}$  [ $\text{M}$ ]<sup>+</sup>: 944.29, found: 944.0. Elemental analysis (%) calcd. for  $\text{CoS}_4\text{O}_4\text{C}_{52}\text{H}_{68}$ : C 66.14, H 7.26, N 0.00, S 13.58; found: C 65.80, H 7.12, N 0.00, S 13.29.

Additional spectroscopic and characterization including NMR charts and crystallographic details are provided in the Supporting Information.

Deposition Numbers 2204736 (**1-Pd**), 2204737 (**1-Pt**), 2164848 (**2-Co**) and 2204738 (**1-Ni.pyr**), contain the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service [www.ccdc.cam.ac.uk/structures](http://www.ccdc.cam.ac.uk/structures).

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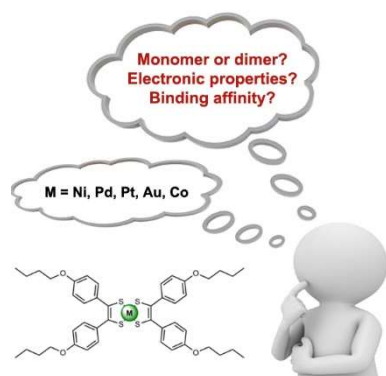
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## Entry for the Table of Contents



Electronic and structural properties as well as ligand binding of a complete series of metal-bis(dithiolene) complexes bearing four butyl and hexyl aliphatic chains at the periphery with Ni(II), Co(II), Pd(II), Pt(II) and Au(III) have been investigated by a variety of characterization techniques including NMR, UV-vis, IR, MS, CV, and X-ray diffraction studies.

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