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Synthesis and Structural Characterization of Cobalt, Nickel and Copper Phosphanylthiolato Complexes

Patricia Fernández,[a] Antonio Sousa-Pedrares,[a] Jaime Romero,[a] María L. Durán,[a] Antonio Sousa,[a] Paulo Pérez-Lourido,[b] and José A. García-Vázquez*[a]

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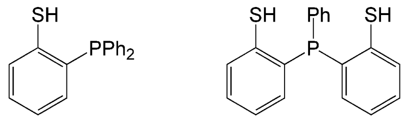
Neutral cobalt, nickel and copper complexes of a series of phosphanylthiol ligands $Ph_nP(C_6H_4SH\text{-}2)_{3-n}$ (n = 1, 2) have been synthesized and characterized by IR and NMR (^{1}H and ^{31}P) spectroscopy, FAB mass spectrometry and X-ray structural analysis. All of the compounds, with the exception of $[Co\{Ph_2PC_6H_4S\text{-}2\}_2]$, were synthesized by electrochemical oxidation of the anodic metal (cobalt, nickel or copper) in an acetonitrile solution of the appropriate ligand and a small amount of tetramethylammonium perchlorate as an electrolytic carrier. The presence of an additional coligand (PPh_3, dppe, dppm or bipy) in the cell led to the synthesis of mixed complexes in one step. The crystal structures of $[Co\{Ph_2P(O)C_6H_4S\text{-}2\}_2]$ (**1**), $[Co_2\{PhP(C_6H_4S\text{-}2)_2\}_2(\mu\text{-}N_2)(bipy)_2]$ (**2**), $[Ni_2\{PhP(C_6H_4S\text{-}2)_2\}_2]$ (**3**), $[Ni_2\{PhP(C_6H_4S\text{-}2)_2\}_2(\mu\text{-dppe})]\cdot CH_2Cl_2$ (**4**), $[Cu_2\{Ph_2PC_6H_4S\text{-}2\}_2(PPh_3)_2]$ (**5**), $[Cu_2\{PhP(C_6H_4S\text{-}2)_2\}(PPh_3)_2(CH_3CN)]$ (**6**), $[Cu_2\{Ph_2PC_6H_4S\text{-}2\}_2(\mu\text{-dppe})]$ (**7**) and $[Cu_2\{Ph_2PC_6H_4S\text{-}2\}_2(\mu\text{-dppm})]$ (**8**) are discussed.

Introduction

There is considerable current interest in the chemistry of metal complexes with heterodonor polydentate ligands that combine tertiary phosphane groups with nitrogen,[1] oxygen[2] or sulfur atoms.[3] Of these, phosphanylthiolato ligands incorporating both thiolato and tertiary phosphane donor atoms form stable complexes with a wide range of metals including lanthanides, transition- and post-transition metals. To date, most studies have focused on bidentate $Ph_2PCH_2CH_2SH$ or $Ph_2PC_6H_4SH\text{-}2$ ligands,[3] while the potentially tridentate ligand $PhP(C_6H_4SH\text{-}2)_2$ has received less attention. In a previous paper, we reported the preparation and crystal structures of Co^{III} and Ni^{II} complexes with the bidentate ligand $Ph_2PC_6H_4SH\text{-}2$ and also with the trimethylsilyl derivative $Ph_2P\{C_6H_4SH\text{-}2(Me_3Si\text{-}3)\}$.[4] More recently, the synthesis, by non-electrochemical methods, of the dimeric compound $[Ni_2\{PhP(C_6H_4S\text{-}2)_2\}]$ was reported, and the crystal structure was examined in order to establish the chemical connectivity – the data were not of sufficient quality for a more detailed analysis.[5] Copper complexes with these ligands have not been previously described.

As a result of our continued interest in the chemistry of metal complexes with phosphanylthiolato ligands,[6] we now report the synthesis and characterization of new cobalt, nickel and copper complexes with the ligands described in Scheme 1. The complexes were obtained by using an electrochemical procedure in which the metal was the anode of a cell containing the ligand in acetonitrile solution. This method is a simple route and avoids the presence of other anionic species that would be competitors for the ligands under investigation. For this reason, the nature of the compounds obtained could occasionally differ from those prepared by more traditional methods. In addition, the method also allowed the preparation of mixed complexes in one step when a second ligand was added to the electrochemical cell.



$Ph_2PC_6H_4SH\text{-}2$ $PhP(C_6H_4SH\text{-}2)_2$

Scheme 1.

Results and Discussion

Cobalt Compounds

The reaction of $CoCl_2$ with the potentially bidentate ligand $Ph_2PC_6H_4SH\text{-}2$ in methanol in the presence of NEt_3 led to the formation of the paramagnetic green compound $[Co\{Ph_2PC_6H_4S\text{-}2\}_2]$. The formation of this Co^{II} species contrasts with that previously observed in the synthesis of cobalt complexes with other bidentate phosphanylthiolato

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[a] Departamento de Química Inorgánica, Universidad de Santiago de Compostela,
15782 Santiago de Compostela, Spain
Fax: +34-981-547102
E-mail: josearturo.garcia@usc.es
[b] Departamento de Química Inorgánica, Universidad de Vigo,
36200 Vigo, Spain

ligands through an electrochemical procedure, in which the formation of diamagnetic octahedral Co^{III} complexes was commonly observed.[4]

Crystals of $[Co\{Ph_2P(O)C_6H_4S\text{-}2\}_2]$ (**1**) suitable for X-ray studies were obtained by slow air concentration of the mother liquor, and structural studies show the presence of a Co^{II} ion with a tetrahedral coordination environment. The oxygen incorporated into the oxophosphanylthiolato moiety could originate from adventitious oxygen during the crystallization process. Such facile oxidation from phosphane to oxophosphane has been observed in other compounds containing this type of ligand.[7]

The electrochemical oxidation of a sacrificial cobalt anode in an electrochemical cell containing an acetonitrile solution of the potentially tridentate ligand $PhP(C_6H_4SH\text{-}2)_2$ gave a brown solid, the analytical data for which are consistent with the formation of the Co^{III} complex $[Co_2\{PhP(C_6H_4S\text{-}2)_2\}_3]$. The electrochemical efficiency (moles of metal dissolved per Faraday of charge) of $0.50\,mol\,F^{-1}$ indicates that the anodic oxidation of the metal leads to the formation of Co^{II}, with subsequent oxidation to Co^{III} in solution as soon as it is formed. The compound is diamagnetic, and the ^1H NMR spectrum confirms the presence of the coordinated ligand. The ^{31}P NMR spectrum shows signals at $\delta = 87$ and 80 ppm and the FAB mass spectrum shows the parent peak at $m/z = 1092$ with the appropriate isotopic distribution, and this is consistent with the proposed formula.

Attempts to obtain crystals suitable for an X-ray study were unsuccessful and, as a result, the proposed structure for this compound should be considered as tentative. However, the structure could be similar to that found for the Fe^{III} compound $[Fe_2\{PhP(C_6H_4S\text{-}2)_2\}_3]$, which has the same ligand, an equivalent empirical formula,[8] and the X-ray structure shows the presence of a dimer in which both metal atoms are in a distorted octahedral geometry and the two octahedra share a common face comprising three thiolato sulfur atoms.

When 2,2′-bipyridine was added to the electrochemical cell as a coligand, the procedure led to the formation of the mixed Co^{II} complex $[Co\{PhP(C_6H_4S\text{-}2)_2\}(bipy)]$. The presence of the coligand allows the stabilization of the metal in the low oxidation state, as observed previously in the synthesis of other mixed cobalt complexes containing similar ligands.[8] The mother liquors from the synthesis processes were concentrated gently by passing a stream of nitrogen through in an attempt to avoid possible oxidation of the metal and/or ligand. This process gave rise to brown crystals that were suitable for X-ray diffraction. The resolved structure (vide infra) shows the presence of the species $[Co_2\{PhP(C_6H_4S\text{-}2)_2\}_2(bipy)_2(\mu_2\text{-}N_2)]$ (**2**), in which two units of the initial compound are joined together by a dinitrogen molecule that acts as a bridging ligand between the two original molecules. Although not common, cobalt complexes that contain dinitrogen as a bridging ligand are known, usually with the metal in a relatively low oxidation state and in the presence of phosphorus donor ligands. Examples of such complexes include (μ_2-dinitrogen)-bis[1,1,1-tris(diphenylphosphanylmethyl)ethane]dicobalt[9] and (μ_2-dinitrogen)-bis{bis[2-(diisopropylphosphanyl)-4-methylphenyl]amido}dicobalt.[10] In both of these cases, the bond length between the nitrogen atoms and the presence of a linear Co–N–N–Co group are consistent with the situation found in the compound reported here.

Description of the Structures

Compounds $[Co\{Ph_2P(O)C_6H_4S\text{-}2\}_2]$ (**1**) and $[Co_2\{PhP(C_6H_4S\text{-}2)_2\}_2(\mu\text{-}N_2)(bipy)_2]$ (**2**) were studied by X-ray diffraction. The molecular structure of **1** is shown in Figure 1 together with the atom labelling scheme adopted. Selected bond lengths and angles (with the estimated standard deviations) are listed in Table 1. The compound consists of discrete molecules in which the metal is coordinated to two monoanionic bidentate ligands bonded to the metal atom through the oxygen and sulfur atoms. The environment around the metal can be described as a slightly distorted tetrahedral $[CoO_2S_2]$, in which the bond angles corresponding to six-membered chelate rings are slightly smaller than those expected for compounds with a regular geometry.

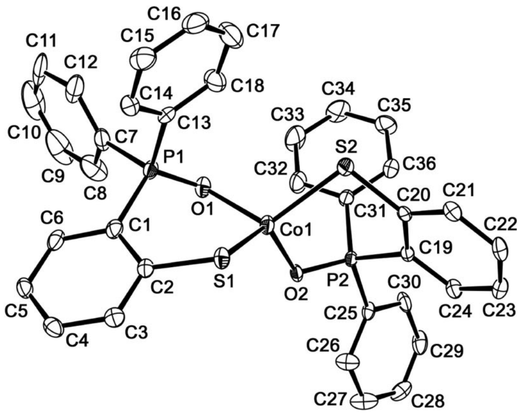

Figure 1. ORTEP diagram of the molecular structure of **1** with 50% thermal ellipsoid probability.

Table 1. Selected bond lengths [Å] and angles for **1**.

Co1–O1	1.996(2)	S2–C20	1.758(4)
Co1–O2	1.989(2)	P1–O1	1.522(3)
Co1–S1	2.2690(11)	P2–O2	1.517(2)
Co1–S2	2.2946(11)	S1–C2	1.765(4)
O2–Co1–O1	102.55(10)	O2–Co1–S2	100.57(7)
O1–Co1–S1	100.47(8)	S1–Co1–S2	113.40(4)
O2–Co1–S1	125.05(8)	O1–Co1–S2	114.98(8)

The Co–S [2.2690(11) and 2.2946(11) Å] and Co–O [1.996(2) and 1.989(2) Å] bond lengths are very close to those reported for Co^{II} complexes with related ligands. Thus, these values are similar to those found in the tetrahedral complex $[Co\{N(OPPh_2)(SPPh_2)\text{-}O,S\}_2]$ [av. Co–S 2.331 Å, av. Co–O 1.980(6) Å],[11] in the anion $[Co(SC_{10}H_{13})_3CH_3CN]^-$ [av. Co–S 2.28 Å],[12] in $[Co\{N(SPPh_2)_2\}_2]$ [av. Co–S 2.335(2) Å][13] or in other monomeric Co^{II} compounds with a tetrahedral geometry.[14]

The bond lengths and angles in the coordinated ligand are similar to those in the free ligand.[15] The average value for the P–O bond, 1.519(3) Å, is slightly longer than that [1.493(3) Å] found in the free ligand, and this can be attributed to the weakening of the P–O bond by coordination to the metal.

A view of the molecular structure of **2** is shown in Figure 2 together with the atom labelling scheme adopted. A selection of bond lengths and angles (with the estimated standard deviations) is listed in Table 2. The compound is dinuclear, and the two cobalt atoms are joined to one another through an –N–N– group that acts as a bridge between the two metal centres, which gives rise to an inversion centre between the two nitrogen atoms. A dianionic phosphanylthiolato ligand is also coordinated to each of the cobalt centres, and each of these is bound to the metal through the two thiolato sulfur atoms and the phosphorus atom. The coordination sphere around each metal is completed with a bipyridine ligand coordinated in a chelate manner through the two nitrogen donor atoms. The environment around each metal is octahedral [CoN_3S_2P] and this is essentially regular, as can be seen from the bond angles for this compound.

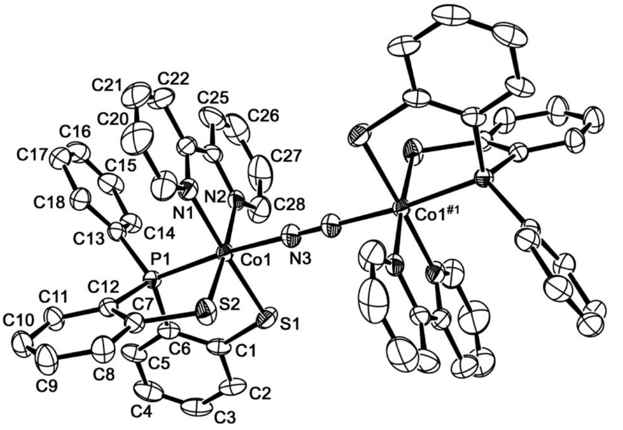

Figure 2. ORTEP diagram of the molecular structure of **2** with 50% thermal ellipsoid probability.

Table 2. Selected bond lengths [Å] and angles [°] for **2**.[a]

Co1–N3	1.910(4)	Co1–S1	2.2397(14)
Co1–N1	1.986(4)	Co1–S2	2.2468(15)
Co1–N2	1.991(4)	N3–N3$^{\#}$	1.156(7)
Co1–P1	2.1759(13)	S1–C1	1.769(5)
N3–Co1–N1	91.31(17)	N1–Co1–S2	95.17(16)
N3–Co1–N2	94.01(17)	N2–Co1–S2	175.69(15)
N3–Co1–P1	173.26(14)	P1–Co1–S2	86.14(5)
N3–Co1–S1	88.25(14)	S1–Co1–S2	88.09(6)
N3–Co1–S2	87.58(14)	N1–Co1–N2	80.77(19)
N2–Co1–P1	92.45(11)	N1–Co1–P1	91.66(12)
N2–Co1–S1	96.02(13)	N1–Co1–S1	176.73(15)
P1–Co1–S1	89.13(5)	N3$^{\#}$–N3–Co1	176.0(6)

[a] Symmetry transformations used to generate equivalent atoms: #: $-x$, $-y$, $-z$ + 1.

It is worth highlighting the presence of a Co–N–N–Co group that is practically linear, with a N3$^{\#}$–N3–Co angle of 176.0(6)°, a situation similar to that found in previously described complexes that contain a dinitrogen molecule as a bridge.[9,10] On the other hand, the bond length between the two nitrogen atoms, 1.156(7) Å, is relatively short and is similar to that in the aforementioned complexes and is also very similar to the value of 1.147(4) Å for the anion (μ_2-dinitrogen)-bis{tris[bis(isopropyl)phosphanylmethyl]-phenylborato}dicobaltate.[16]

The bond lengths Co–S and Co–P are as one would expect and are comparable to those found in related complexes.[4,17] Similarly, the Co–N(bipy) bond lengths are within the range found for these bonds in octahedral Co^{II} complexes with a chelate bipyridine donor ligand.[18] Finally, the shortest bond length corresponds to the Co–N3 bond, 1.910(4) Å, and is slightly greater than those in the above-mentioned tetracoordinate dinitrogen cobalt compounds,[9,10] which have values in the range 1.768–1.806 Å, and this difference can probably be attributed to the change in coordination number from four to six.

Nickel Compounds

The electrochemical oxidation of a nickel anode in a solution of $PhP(C_6H_4SH\text{-}2)_2$ in acetonitrile led to the formation of a crystalline product, the analytical data for which are consistent with the formula [Ni{$PhP(C_6H_4S\text{-}2)_2$}]. The complex is diamagnetic, and the ^{131}P NMR spectrum has a single signal at δ = 73 ppm, which is clearly at a lower field than the corresponding signal in the free ligand (δ = –21 ppm); this indicates that the phosphorus is coordinated to the metal in the complex. Crystals suitable for study by X-ray diffraction were obtained directly from the electrochemical cell. The resolved structure shows the presence of a dimeric species in which the metal atoms are joined by a double thiolato bridge, a situation that is consistent with the spectroscopic data discussed above and with previously reported data.[5]

The presence in the electrochemical cell of additional phosphorus donor coligands enabled mixed complexes to be obtained in a single step. For example, the presence in the cell of PPh_3 led to the formation of [Ni{$PPh(C_6H_4S\text{-}2)_2$}PPh_3], the X-ray structure of which shows it to be structurally equivalent to the complex [Ni{$PPh(C_6H_4S\text{-}2)_2$}(PPh_2Me)], previously synthesized from the precursor [$NiCl_2(PPh_2Me)_2$].[5] As a result, the structure of this compound will not be discussed here.

The incorporation of diphosphane 1,2-bis(diphenylphosphanyl)ethane (dppe) as an additional ligand led to the formation of the mixed complex [Ni_2{$PPh(C_6H_4S)_2$}$_2$(μ-dppe)]. The ^{31}P NMR spectrum contains two signals at δ = 73 and 34 ppm, which result from the presence of two inequivalent phosphorus atoms in the complex. Crystals of [Ni_2{$PhP(C_6H_4S\text{-}2)_2$}$_2$(μ-dppe)]·CH_2Cl_2 (**4**) suitable for X-ray studies were obtained by crystallization of the initial product from dichloromethane/acetone.

Description of the Structures

Compounds [Ni_2{$PhP(C_6H_4S\text{-}2)_2$}$_2$] (**3**) and [Ni_2{$PhP(C_6H_4S\text{-}2)_2$}$_2$(μ-dppe)]·CH_2Cl_2 (**4**) were studied by X-ray diffraction. The molecular structure of **3** is shown in Figure 3, together with the atom labelling scheme adopted. A selection of bond lengths and angles (with the estimated standard deviations) is listed in Table 3. The structural analysis reveals that this compound is dinuclear and consists of two nickel–phosphanylthiolato units joined together by two sulfur atoms, which act as bridges between the two metal centres. The environment around each metal centre is [NiS_3P] square planar, and the Ni1 and Ni2 atoms are located 0.1068 and 0.0814 Å, respectively, from the best plane defined by the four donor atoms. The planes around each of the nickel centres form a dihedral angle of 76.27°.

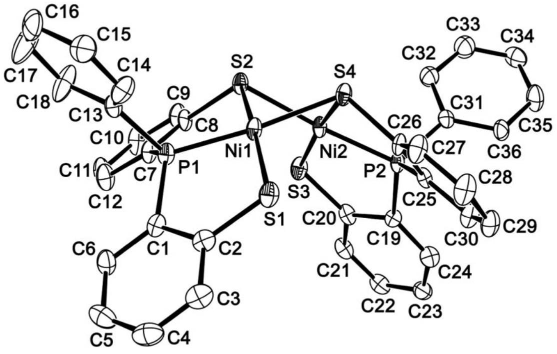

Figure 3. ORTEP diagram of the molecular structure of **3** with 50% thermal ellipsoid probability.

Table 3. Selected bond lengths [Å] and angles [°] for **3**.

Ni1–P1	2.110(2)	Ni2–S4	2.199(2)
Ni1–S1	2.156(2)	Ni2–P2	2.105(2)
Ni1–S2	2.197(2)	Ni2–S2	2.234(2)
Ni1–S4	2.236(2)	Ni2–S3	2.156(2)
P1–Ni1–S1	89.07(9)	S2–Ni1–S4	83.94(8)
P1–Ni1–S2	88.05(9)	P2–Ni2–S3	88.48(9)
S1–Ni1–S2	168.08(10)	P2–Ni2–S4	87.69(9)
P1–Ni1–S4	171.90(10)	S3–Ni2–S4	170.52(10)
S1–Ni1–S4	99.01(9)	P2–Ni2–S2	171.59(9)

The Ni–Ni bond length in small molecules are in the range of 2.914 to 3.555 Å, and the value of 2.7197(14) Å in our compound could indicate the existence of some degree of interaction between the metal centres.[19] The Ni–S(terminal) bond lengths, which involve sulfur atoms from the chelate rings, are slightly shorter [2.156(2)–2.156(2) Å] than those for Ni–S (bridge) distances, in the range 2.197(2)–2.236(2) Å, as in the case in other systems with terminal and bridging sulfur atoms.[20] The Ni–P bond lengths [2.110(2) and 2.105(2) Å], although within the expected range, are at the lower end of the range found in complexes that contain this type of ligand.[4,21]

The molecular structure of **4** is shown in Figure 4, together with the atom labelling scheme adopted. A selection of bond lengths and angles (with the estimated standard deviations) is listed in Table 4. The molecule has an inversion centre located at the mid-point of the C–C bond of the ethylene group of the dppe ligand, and the structural analysis shows that the compound consists of discrete dimers in which two Ni–phosphanylthiolato units are connected to one another through a diphosphane ligand that acts as a bridge between the two nickel atoms; each metal is coordinated through one of the phosphorus atoms. The environment around each of the metals is square planar [NiS_2P_2], although the distortion in this case is more marked than that observed in the other complexes discussed here.

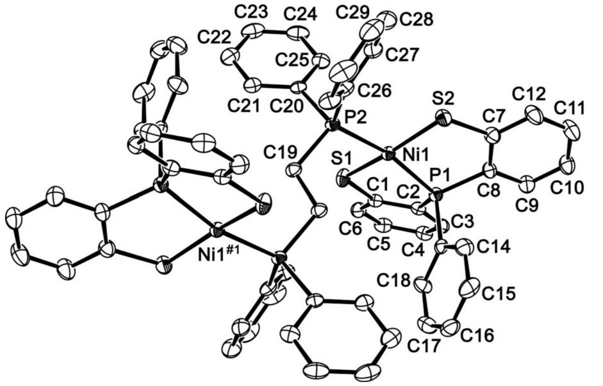

Figure 4. ORTEP diagram of the molecular structure of **4** with 50% thermal ellipsoid probability.

Table 4. Selected bond lengths [Å] and angles in **4**.[a]

Ni1–P1	2.1161(8)	Ni1–P2	2.2214(8)
Ni1–S1	2.1753(8)	S1–C1	1.777(3)
Ni1–S2	2.1647(8)	S2–C7	1.772(3)
P1–Ni1–S1	87.03(3)	P1–Ni1–P2	165.34(3)
P1–Ni1–S2	87.97(3)	S1–Ni1–P2	92.02(3)
S2–Ni1–S1	163.51(4)	S2–Ni1–P2	96.71(3)

[a] Symmetry transformations used to generate equivalent atoms: # $-x$, $-y$, $-z + 1$.

The Ni–S bond lengths, 2.1647(8) and 2.1753(8) Å, are similar and are analogous to those found in [$Ni(Ph_2PC_6H_4S\text{-}2)_2$][21] [2.151(3) Å] and [$Ni\{Ph_2PC_6H_3S\text{-}2\text{-}(Me_3Si\text{-}6)\}_2$][4] [2.180(1) Å]. These values fall within the range 2.149–2.179 Å usually found in square planar nickel complexes with chelating ligands that contain sulfur donor atoms. The Ni–P distances, on the other hand, are different [2.1161(8) Å and 2.214(8) Å] depending on the nature of the ligand bound to the metal and are slightly shorter in the case of the chelating ligand. This situation is consistent with those found in the systems described above, in which the constraints caused by the ligand lead to a shortening of the bond length in question. The species crystallizes with a molecule of dichloromethane, and this is located within the network without establishing significant interactions with the complex itself.

Copper Complexes

Neutral complexes [$Cu\{Ph_2PC_6H_4S\text{-}2\}$] and [$Cu_2\{PhP(C_6H_4S\text{-}2)_2\}$] were obtained by electrochemical oxidation of anodic copper metal in a cell containing the ligand dissolved in acetonitrile. E_f values of 1.0 mol F^{-1} indicate that the anodic oxidation of the metal leads to the formation of Cu^{I}.

Both compounds were obtained at the bottom of the cell as insoluble solids. The presence of a single ligand that does not coordinatively satisfy the metal leads to a polymerization process in which the thiolato sulfur atoms act as bridges between the metal centres. As a consequence, these compounds are insoluble in the majority of commonly used organic solvents, and attempts to obtain monocrystals suitable for X-ray diffraction proved unsuccessful. The IR spectra of both compounds contain bands associated with the coordinated ligands, and the FAB mass spectra of [Cu{$Ph_2PC_6H_4S$-2}] shows peaks corresponding to species arising from different levels of polymerization (see Experimental Section). The FAB mass spectra of [Cu_2{PhP(C_6H_4S-2)$_2$}] could not be recorded because of the lack of solubility of the compound in the matrix.

The presence in the cell of coligands that can coordinatively saturate the metal must to some extent inhibit the polymerization process, and, as a result, the formation of oligomeric species with lower molecular masses was observed. For example, the addition of PPh_3 to the electrochemical cell enabled the isolation of the molecular species, the analytical and X-ray structural data of which are consistent with compounds with the empirical formulae [Cu_2{$Ph_2PC_6H_4S$-2}$_2$(PPh_3)$_2$] (**5**) and [Cu_2{PhP(C_6H_4S-2)$_2$}(PPh_3)$_2$(CH_3CN)] (**6**). Similarly, the presence in the cell of bidentate phosphorus donor ligands such as dppe or dppm led to the formation of species for which the analytical and structural data are consistent with compounds with the empirical formulae [Cu_2{$Ph_2PC_6H_4S$-2}$_2$(μ-dppe)] (**7**) and [Cu_2{$Ph_2PC_6H_4S$-2}$_2$(μ-dppm)] (**8**).

Description of the Structures

Compounds **5**–**8** were studied by X-ray diffraction. A selection of bond lengths and angles (with the estimated standard deviations) in listed in Tables 5–8.

Table 5. Selected bond lengths [Å] and angles [°] for **5**.[a]

Cu1–P1	2.2797(16)	S1–Cu1$^{\#}$	2.3916(16)
Cu1–P2	2.2581(13)	Cu1–Cu1$^{\#}$	2.9566(12)
Cu1–S1	2.3323(8)	S1–C2	1.799(7)
P1–Cu1–S1	89.85(6)	P1–Cu1–S1$^{\#}$	109.21(6)
P2–Cu1–P1	114.69(3)	P2–Cu1–S1$^{\#}$	112.13(5)
P2–Cu1–S1	125.79(6)	S1–Cu1–S1$^{\#}$	102.52(5)

[a] Symmetry transformations used to generate equivalent atoms: #: $-x + 2$, $-y$, $-z + 1$.

The resolved structure of [Cu_2{$Ph_2PC_6H_4S$-2}$_2$(PPh_3)$_2$] (**5**) (Figure 5) shows that the compound is composed of centrosymmetric dimeric species in which the two thiolato sulfur atoms from the two phosphanylthiolato ligands act as bridges between the two metal atoms, and these are related to one another through a centre of symmetry located at the centre of the Cu2S2 ring. In addition, each copper atom is coordinated to a phosphorus atom of one of the phosphanylthiolato ligands and to the phosphorus atom of the triphenylphosphane. As a result, the ligand acts as a PS chelate system with respect to one of the copper atoms and as a bridge to both metals.

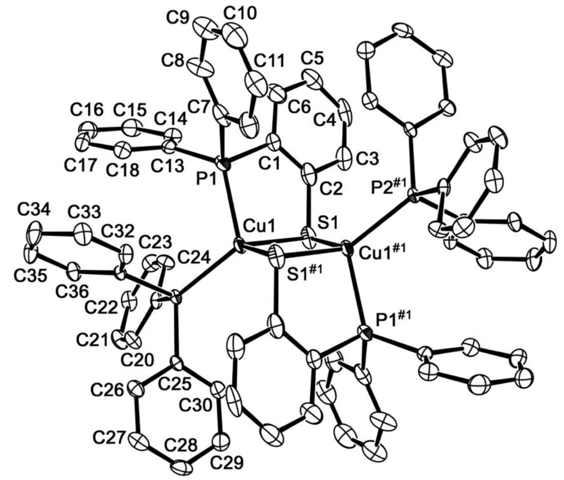

Figure 5. ORTEP diagram of the molecular structure of **5** with 50% thermal ellipsoid probability.

The environment around each copper atom is a slightly distorted tetrahedron [P2S2]. The two copper centres are 2.9566(16) Å from one another, and this distance is greater than the sum of the radii for these two metal atoms (2.56 Å)[22] and is sufficiently high as to preclude the possibility of an interaction between the two metals. Despite the fact that X-ray structural data are not available for other copper complexes with phophinothiol ligands, the values for the Cu–S distances are similar to those found in other dimeric tetrahedral copper complexes that contain thiolato ligands – e.g. in [Cu_2(3-Me_3Sipyt)$_2$(dppe)$_3$] with a Cu–S bond length of 2.320(3) Å.[23] The two Cu–P distances for the two phosphanes [2.2797(16) and 2.2581(13) Å] are similar to one another and are in the range found in the indicated complex, i.e. [Cu_2(3-Me_3Sipyt)$_2$-(dppe)$_3$].

The molecular structure of [Cu_2{PhP(C_6H_4S-2)$_2$}(PPh_3)$_2$-(CH_3CN)] (**6**) is shown in Figure 6, together with the atom labelling scheme adopted. A selection of bond lengths and angles (with the estimated standard deviations) is listed in Table 6. The compound consists of dimeric units in which the two copper atoms are joined by two sulfur atoms of the dianionic ligand, which acts as a bridge between the two metal centres. In this coordination mode the ligand acts as a tripodal system – it chelates in a PS fashion to one of the copper centres and doubly bridges the two metal centres.

The coordination spheres around the copper centres are different. Cu1 is bonded to two bridging sulfur atoms, and the coordination sphere is completed by a phosphorus atom from the same phosphothiolato ligand and another phosphorus atom from a triphenylphosphane molecule. In contrast, the second copper centre, Cu2, is bonded to the phosphorus atom of a triphenylphosphane molecule and the nitrogen atom of an acetonitrile molecule (which originates from the solvent used in the synthetic process), in addition

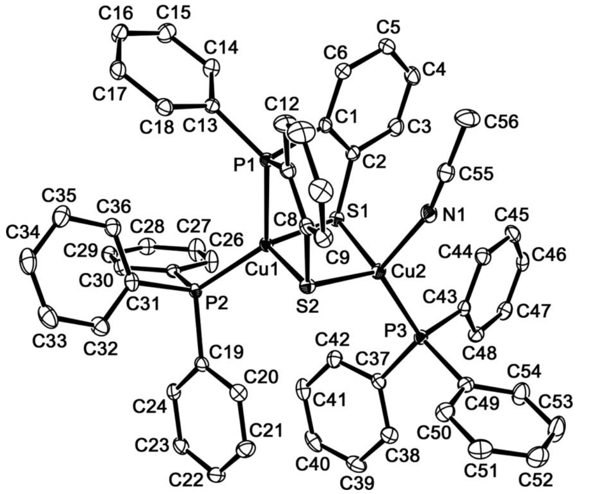

Figure 6. ORTEP diagram of the molecular structure of **6** with 50% thermal ellipsoid probability.

Table 6. Selected bond lengths [Å] and angles [°] for **6**.

Cu1–P1	2.2395(4)	Cu2–N1	2.0299(13)
Cu1–P2	2.2178(4)	Cu2–P3	2.2260(4)
Cu1–S1	2.3351(4)	Cu2–S2	2.3519(4)
Cu1–S2	2.3772(4)	Cu2–S1	2.4055(4)
Cu1–Cu2	2.8045(2)	N1–C55	1.136(2)
P1–Cu1–S1	90.636(14)	N1–Cu2–P3	116.21(4)
P1–Cu1–S2	90.168(14)	P3–Cu2–S2	124.646(14)
P2–Cu1–P1	127.744(15)	N1–Cu2–S2	101.20(4)
P2–Cu1–S1	122.718(15)	S2–Cu2–S1	105.957(13)
P2–Cu1–S2	112.256(14)	N1–Cu2–S1	101.97(4)
S1–Cu1–S2	107.429(14)	P3–Cu2–S1	104.390(14)

to the two bridging sulfur atoms. In both cases the copper environment can be considered to be tetrahedral, in which the two sulfur atoms form the common edge of the two tetrahedra. A significant angular distortion is evident in the Cu1 environment, and this is due to the chelating nature of the phosphinothiolato ligand.

The bridging sulfur atoms are equidistant from the two copper centres, i.e. the thiolato bridge is symmetrical, with bond lengths in the range 2.3351(4)–2.4055(4) Å, values very similar to those found in the compound described above. The Cu–P bond lengths associated with the triphenylphosphane ligand, 2.2178(4) and 2.2260(4) Å, are practically identical whereas that corresponding to the thiolato ligand is slightly longer, 2.2395(4) Å. However, these values are as one would expect and are analogous to those found in $[Cu\{Ph_2PC_6H_4S\text{-}2\}PPh_3]_2$ and in other Cu^I complexes with phosphane ligands.[23]

The complex contains a coordinated acetonitrile molecule that originates from the solvent used in the electrochemical synthesis. This molecule completes the coordination sphere of Cu2 by coordination through the nitrogen atom. The Cu–N bond length, 2.0299(13) Å, and the C55–N1–Cu2 bond angle, 163.29(13)°, are as one would expect, with the former value analogous to the value 1.944(7) Å found in the dimeric complex $[Cu_2(C_6H_7N_3S_2)_2(CH_3CN)_2](BF_4)_2$, which also contains thiolato bridges and a coordinated acetonitrile molecule.[24] The acetonitrile molecule is essentially linear [N1–C55–C56 bond angle of 178.80(18)°], and the N1–C55 bond length [1.136(2) Å] is indicative of a triple bond between the carbon and nitrogen atoms.[25] The compound crystallizes with three acetonitrile molecules that are located within the network but do not interact significantly with the complex.

The molecular structure of $[Cu_2\{Ph_2PC_6H_4S\text{-}2\}(\mu\text{-dppe})]$ (**7**) and $[Cu_2\{Ph_2PC_6H_4S\text{-}2\}(\mu\text{-dppm})]$ (**8**) are shown in Figure 7, together with the atom labelling scheme adopted. A selection of bond lengths and angles (with the estimated standard deviations) is listed in Tables 7 and 8. The structures of both compounds are similar and consist of dimeric species in which the copper atoms are joined by a double thiolato bridge with sulfur atoms from two different ligands and a phosphorus atom of the diphosphane ligand, which also acts as a bridge. In this way, the environment around each of the copper atoms is a slightly distorted tetrahedral [P2S2]. This situation is reflected by the bond angles in the

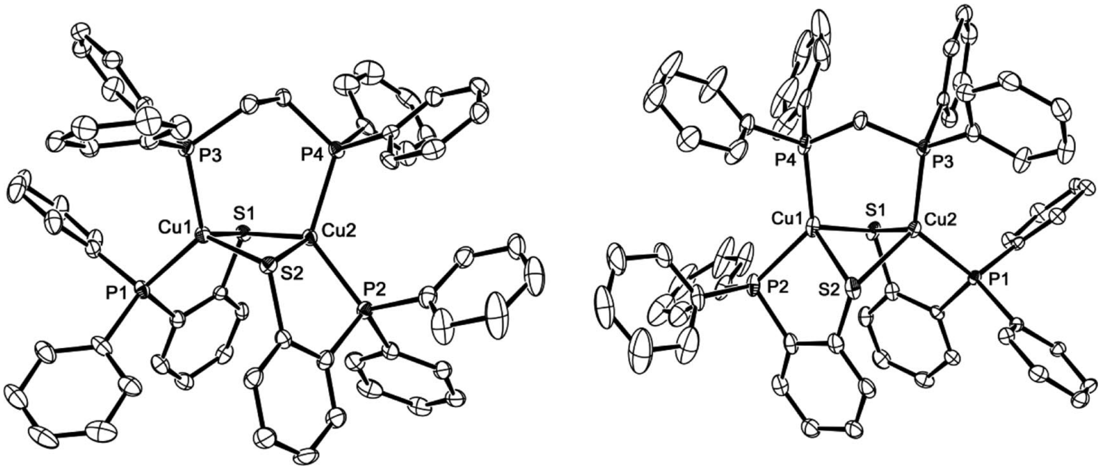

Figure 7. ORTEP diagrams of the molecular structures of **7** and **8** with 50% thermal ellipsoid probability.

metal environment, which cover a wide range of values; the lowest angle corresponds to the five-membered chelate ring.

Table 7. Selected bond lengths [Å] and angles [°] for **7**.

Cu1–P1	2.2457(11)	Cu1–P3	2.2636(11)
Cu1–S2	2.3455(10)	Cu1–S1	2.4472(10)
Cu2–P2	2.2510(11)	Cu2–P4	2.2576(10)
Cu2–S1	2.3707(10)	Cu2–S2	2.4297(10)
Cu1–Cu2	2.6751(6)	S1–C2	1.781(4)
P1–Cu1–P3	126.26(4)	P1–Cu1–S2	123.27(4)
P3–Cu1–S2	98.16(4)	P1–Cu1–S1	84.99(4)
P3–Cu1–S1	112.99(4)	S2–Cu1–S1	110.48(4)
P2–Cu2–P4	125.28(4)	P2–Cu2–S1	123.27(4)
P4–Cu2–S1	100.42(4)	P1–Cu2–S2	85.51(4)
P4–Cu2–S2	110.70(4)	S1–Cu2–S2	109.92(4)

Table 8. Selected bond lengths [Å] and angles [°] for **8**.

Cu1–P4	2.1998(13)	Cu1–P2	2.2293(13)
Cu1–S2	2.3516(11)	Cu1–S1	2.4748(11)
Cu2–P3	2.2269(12)	Cu2–P1	2.2402(10)
Cu2–S1	2.3946(11)	Cu2–S2	2.4599(11)
Cu1–Cu2	2.6223(7)	S1–C2	1.782(4)
P4–Cu1–P2	130.14(5)	P4–Cu1–S2	118.92(5)
P2–Cu1–S2	88.80(4)	P4–Cu1–S1	109.01(4)
P2–Cu1–S1	105.71(4)	S2–Cu1–S1	99.20(4)
P3–Cu2–P1	126.89(4)	P3–Cu2–S1	113.22(4)
P1–Cu2–S1	86.59(4)	P3–Cu2–S2	116.02(4)
P1–Cu2–S2	108.23(4)	S1–Cu2–S2	98.44(4)

The thiolato bridge can be considered to be symmetrical, as the bond lengths are only slightly different. The values of the Cu–P and Cu–S bond lengths for these compounds are similar to those reported for **5** and **6** and do not warrant further discussion.

Compound **8** crystallizes with half a molecule of dichloromethane that is located within the network but does not interact significantly with the complex.

Conclusions

A number of Co^{II}, Ni^{II} and Cu^{I} complexes with a series of phosphanylthiol ligands $Ph_nP(C_6H_4SH\text{-}2)_{3-n}$ (n = 1, 2) have been prepared and characterized. With the exception of $[Co\{Ph_2P(O)C_6H_4S\text{-}2\}_2]$ (**1**), the complexes have been synthesized by electrochemical oxidation of a metal anode (cobalt, nickel or copper) in a cell containing the appropriate phosphanylthiol ligand or this ligand and a coligand such as PPh_3, dppe, dppm or bipy. With the ligand $Ph_2P(C_6H_4SH\text{-}2)$, the complexes **5**, **7** and **8** are dinuclear, and the ligand acts as a bridging P(μ-S) ligand between both metallic centres. However, **1** is mononuclear, and the ligand oxophosphanylthiolato coordinated as bidentate chelate (PS) ligand is the result of oxidation of the phosphanylthiolato ligand. In the dinuclear compounds **2**, **3**, **4** and **6**, the ligand $PhP(C_6H_4SH\text{-}2)_2$ acts as a tridentate ligand in all cases, but displays a different coordination behaviour. Thus, in **2** and **4**, the ligand acts as a chelating PS_2 ligand and is coordinated to each metal atom. In **3**, the ligand behaves as a PS(μ-S) system, in which the phosphorous and one of the sulphur atoms are coordinated to one metal, while the other sulfur atom acts as a bridge. In compound **6**, the ligand behaves as a $P(\mu\text{-}S)_2$ donor; the P atom is coordinated to one of the copper atoms, and the sulfur atoms act as a bridge between the two metal centres.

Experimental Section

General Considerations: All manipulations were carried under an inert atmosphere of dry nitrogen. Cobalt, nickel and copper (Aldrich Chemie) were used as plates (ca. 2 × 2 cm). All other reagents were used as supplied. The synthesis of the ligands was carried out by using slight modifications of the standard literature procedure.[26] Elemental analyses were performed by using a Carlo–Erba EA microanalyzer. IR spectra were recorded as KBr discs with a Bruker IFA-66 spectrophotometer. ^1H and ^{31}P spectra were recorded on a Bruker AMX 300 MHz instrument with $CDCl_3$ as solvent. ^1H NMR chemical shifts were determined against tms as internal standard and those of ^{31}P against 85% H_3PO_4. The mass spectra (FAB) were recorded on a Micromass Autospec spectrometer by using 3-nitrobenzyl alcohol as the matrix material.

Synthesis of the Complexes

$[Co\{Ph_2PC_6H_4S\text{-}2\}_2]$: This compound was prepared by reaction of anhydrous $CoCl_2$ and the ammonium salt of the ligand. A solution of the ligand (0.200 g, 0.680 mmol) in methanol (50 mL) was treated with tetramethylammonium hydroxide (0.285 mL, 0.680 mmol) in the same solvent. The solution was evaporated to dryness, the resulting solid was dissolved in acetonitrile, and a solution of anhydrous $CoCl_2$ (0.044 g, 0.340 mmol) in acetonitrile was added. The colour of the solution changed to dark green, and the resulting solid was recovered, washed with acetonitrile and ether, and dried under vacuum. $C_{36}H_{28}CoP_2S_2$ (645.6): calcd. C 66.9, H 4.3, S 9.9; found C 66.6, H 4.5, S 9.6. IR (KBr): $\tilde{\nu}$ = 1571 (m), 1482 (s), 1442 (s), 1243 (m), 1091 (s), 1001 (m) 738(s), 694 (s), 524 (s) cm^{-1}. FAB MS: m/z = 645 $[M]^+$. Crystals of $[Co\{Ph_2P(O)C_6H_4S\text{-}2\}_2]$ (**1**) suitable for X-ray studies were obtained by slow air concentration of the mother liquor.

Electrochemical Synthesis: The rest of the metal complexes were obtained by using an electrochemical procedure.[27] The cell consisted of an anode suspended from a platinum wire, and the cathode was also a platinum wire. The ligand was dissolved in acetonitrile, and a small amount of tetramethylammonium perchlorate was added to the solution as a supporting electrolyte (**Caution**: *perchlorate compounds are potentially explosive and should be handled in small quantities and with great care*). For the synthesis of the mixed complexes, the additional coligand was also added to the solution. Applied voltages of 5–10 V allowed sufficient current flow for smooth dissolution of the metal. Under these conditions, the electrochemical cell can be summarized as:

$Pt_{(-)}/CH_3CN + Ph_nP(C_6H_4SH\text{-}2)_{3-n}/M_{(+)}$

$Pt_{(-)}/CH_3CN + Ph_nP(C_6H_4SH\text{-}2)_{3-n} + L'/M_{(+)}$

n = 1, 2; M = Co, Ni, Cu; L′ = PPh_3, dppe, dppm, bipy.

$[Co_2\{PhP(C_6H_4S\text{-}2)_2\}_3]$: A solution of the ligand (0.225 g, 0.690 mmol) in acetonitrile (50 mL) was electrolyzed at 10 mA over 2.5 h, and 27.0 mg of the metal was dissolved from the anode (E_f = 0.50 mol F^{-1}). The colour of the solution changed to deep red, and by the end of the electrolysis a red product had been deposited in the cell. The solid was washed with acetonitrile and ether and dried under vacuum. $C_{54}H_{39}Co_2P_3S_6$ (1091.1): calcd. C 59.5, H 3.6, S 17.6; found C 59.9, H 3.8, S 17.8. IR (KBr): ṽ = 1570 (m), 1442 (s), 1425 (s), 1250 (m), 1103 (s), 1047 (w), 740 (s), 696 (m), 532 (s) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 8.0–6.6 (m, 13 H) ppm. ^{31}P NMR (300 MHz, $CDCl_3$, 25 °C): δ = 87, 80 ppm. FAB MS: *m*/*z* = 1092 $[M]^+$, 767 $[M - PhP(C_6H_4S\text{-}2)_2]^+$.

$[Co\{PhP(C_6H_4S\text{-}2)_2\}(bipy)]$: A solution of the ligand (0.124 g, 0.380 mmol) and 2,2′-bipyridine (0.060 g, 0.380 mmol) in acetonitrile (50 mL) was electrolyzed at 10 mA over 2 h, and 22.1 mg of the metal was dissolved from the anode (E_f = 0.50 mol F^{-1}). The solid formed was recovered, washed with acetonitrile and ether, and characterized as $[Co\{PhP(C_6H_4S\text{-}2)_2\}(bipy)]$. $C_{28}H_{21}CoN_2PS_2$ (539.5): calcd. C 62.3, H 3.9, N 5.2, S 11.9; found C 61.9, H 3.9, N 5.6, S 12.0. IR (KBr): ṽ = 1569 (m), 1439 (s), 1427 (s), 1028 (w), 767 (s), 742 (s), 735 (s), 698 (m) 530(s) cm^{-1}. FAB MS: *m*/*z* = 540 $[M]^+$, 384 $[M\text{–}bipy]^+$. Brown crystals of $[Co_2\{PhP(C_6H_4S\text{-}2)_2\}_2(\mu_2\text{-}N_2)(bipy)_2]$ (**2**) suitable for X-ray studies were obtained upon slow concentration of the mother liquor by bubbling N_2 gas through the solution.

$[Ni\{PhP(C_6H_4S\text{-}2)_2\}]$: In a similar experiment with nickel as the anode, a solution of the ligand (0.124 g, 0.380 mmol) in acetonitrile (50 mL) was electrolyzed at 10 mA over 2 h, and 22.0 mg of the metal was dissolved from the anode (E_f = 0.50 mol F^{-1}). $C_{18}H_{13}NiPS_2$ (383.1): calcd. C 56.4, H 3.4, S 16.7; found C 56.0, H 3.4, S 16.5. IR (KBr): ṽ = 1571 (s), 1430 (s), 12157 (m), 1099 (m), 999 (m), 736 (s), 524 (s) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.8–6.6 (m, 13 H) ppm. ^{31}P NMR (300 MHz, $CDCl_3$, 25 °C): δ = 73 ppm. FAB MS: *m*/*z* = 765 $[M_2]^+$, 383 $[M]^+$. Crystals of $[Ni_2\{PhP(C_6H_4S\text{-}2)_2\}_2]$ (**3**) suitable for X-ray studies were obtained directly from the cell.

$[Ni_2\{PhP(C_6H_4S\text{-}2)_2\}_2(PPh_3)]$: A solution of the ligand (0.124 g, 0.380 mmol) and PPh_3 (0.098 g, 0.380 mmol) in acetonitrile (50 mL) was electrolyzed at 10 mA over 2 h, and 23.5 mg of the metal was dissolved from the anode (E_f = 0.53 mol F^{-1}). $C_{36}H_{28}NiP_2S_2$ (645.35): calcd. C 67.0, H 4.3, S 9.9; found C 66.7, H 4.3, S 9.8. IR (KBr): ṽ = 1569 (s), 1480 (m), 1178 (m), 742 (m), 530 (s) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.8–6.8 (m, 29 H) ppm. ^{31}P NMR (300 MHz, $CDCl_3$, 25 °C): δ = 35.6, 28.1 ppm. FAB MS: *m*/*z* = 382 $[M - Ph_3P]^+$.

$[Ni_2\{PhP(C_6H_4S\text{-}2)_2\}_2(\mu\text{-}dppe)]$: A solution of the ligand (0.124 g, 0.380 mmol) and dppe (0.150 g, 0.380 mmol) in acetonitrile (50 mL) was electrolyzed at 10 mA over 2 h, and 21.9 mg of the metal was dissolved from the anode (E_f = 0.50 mol F^{-1}). $C_{62}H_{50}Ni_2P_4S_4$ (1164.6): calcd. C 63.9, H 4.3, S 11.0; found C 63.8, H 4.3, S 10.9. IR (KBr): ṽ = 1568 (s), 1178 (m), 1000 (m), 718 (m) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 8.0–7.0 (m, 33 H), 2.0 (m, 4 H) ppm. ^{31}P NMR (300 MHz, $CDCl_3$, 25 °C): δ = 73, 34 ppm. FAB MS: *m*/*z* = 1165 $[M]^+$, 780 $[M - PhP(C_6H_4S\text{-}2)_2]^+$. Crystals of $[Ni_2\{PhP(C_6H_4S\text{-}2)_2\}_2(\mu\text{-}dppe)]\cdot 2CH_2Cl_2$ (**4**) suitable for X-ray studies were obtained by crystallization of the initial product from dichloromethane/acetone.

$[Cu\{Ph_2PC_6H_4S\text{-}2\}]$: A solution of the ligand $Ph_2PC_6H_4SH\text{-}2$ (0.230 g, 0.784 mmol) in acetonitrile (50 mL) was electrolyzed at 10 mA over 2 h, and 48 mg of the metal was dissolved from the anode (E_f = 1.0 mol F^{-1}). Within a few minutes an insoluble solid appeared at the bottom of the cell. This solid was recovered, washed with acetonitrile and ether, and dried under vacuum. $C_{18}H_{14}CuPS$ (356.0): calcd. C 60.6, H 3.9, S 8.9; found C 60.1, H 4.1, S 8.7.IR (KBr): ṽ = 1571 (s), 1436 (s), 1421 (s), 1095 (s), 999 (w), 740 (s), 694 (s), 524 (m) cm^{-1}. NMR: insoluble compound. FAB MS: *m*/*z* = 1071 $[M_3]^+$, 714 $[M_2]^+$, 357 $[M]^+$; 293 $[L^+]$.

$[Cu_2\{PhP(C_6H_4S\text{-}2)_2\}]$: $Ph(PC_6H_4SH\text{-}2)_2$ (0.160 g, 0.495 mmol), 2.5 h, 60 mg of metal dissolved (E_f = 1.0). The insoluble solid that precipitated in the cell was filtered off, washed with acetonitrile and ether, and dried under vacuum. $C_{18}H_{13}Cu_2PS_2$ (451.5): calcd. C 47.9, H 2.9, S 14.2; found C 47.8, H 3.0, S 13.9. IR (KBr): ṽ = 1573 (m), 143 (s), 1118 (s), 1035 (m), 748 (s), 696 (m), 551 (s) cm^{-1}. NMR: insoluble compound. FAB MS: insoluble compound.

$[Cu\{Ph_2PC_6H_4S\text{-}2\}(PPh_3)]$: Electrochemical oxidation of a copper anode in a cell containing a solution of $Ph_2PC_6H_4SH\text{-}2$ (0.120 g, 0.410 mmol) and PPh_3 (0.110 g, 0.410 mmol) in acetonitrile (50 mL) at 14 V, 10 mA for 1 h led to the dissolution of 24.8 mg of copper (E_f = 1.1 mol F^{-1}). During electrolysis, hydrogen was evolved at the cathode, and at the end of the reaction, a crystalline solid appeared at the bottom of the vessel. The solid was filtered off, washed with acetonitrile and ether, and dried under vacuum. $C_{36}H_{29}CuP_2S$ (619.1): calcd. C 69.8, H 4.7, S 5.1; found C 69.4, H 4.8, S 4.9. IR: ṽ = 1569 (m), 1479 (m), 1436 (s), 1417 (s), 1097 (s), 997 (w), 745 (s), 695 (s), 508 (m) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 8.0–7.0 (m, 29 H) ppm. ^{31}P NMR (300 MHz, $CDCl_3$, 25 °C): δ = 32.7, 27.8 ppm. FAB MS: *m*/*z* = 1239 $[M_2]^+$, 619 $[M^+]$, 356 $[M^+ - PPh_3]$. Crystals of $[Cu_2\{Ph_2PC_6H_4S\text{-}2\}_2(PPh_3)_2]$ (**5**) suitable for X-ray analysis were obtained by crystallization of the solid from dichloromethane/methanol.

$[Cu_2\{PhP(C_6H_4S\text{-}2)_2\}(PPh_3)_2(CH_3CN)]$: The same procedure was used for the synthesis of this compound. $Ph(PC_6H_4SH\text{-}2)_2$ (0.061 g, 0.190 mmol) and PPh_3 (0.100 g, 0.380 mmol) in acetonitrile (50 mL), 12 V, 10 mA, 1 h, 24.4 mg of metal dissolved (E_f = 1.0 mol F^{-1}). At the end of the electrolysis, the solid deposited in the cell was recovered, washed with diethyl ether, and dried under vacuum. $C_{56}H_{46}Cu_2NP_3S_2$ (1017.1): calcd. C 66.1, H 4.6, N 1.4, S 6.3; found C 65.8, H 4.5, N 1.5, S 6.6. IR (KBr): ṽ = 1569 (m), 1434 (s), 997 (w), 742 (m) cm^{-1}. ^1H NMR (300 MHz, CD_3Cl, 25 °C): δ = 7.8–6.8 (m, 43 H) ppm. ^{31}P NMR (300 MHz, $CDCl_3$, 25 °C): δ = 27.8, 25.3 ppm. FAB MS: *m*/*z* = 1017 $[M^+]$, 977 $[M - CH_3CN]^+$. Crystals of $[Cu_2\{PhP(C_6H_4S\text{-}2)_2\}(PPh_3)_2(CH_3CN)]\cdot 3CH_3CN$ (**6**) suitable for X-ray studies were obtained by slow concentration of the mother liquor.

$[Cu_2\{Ph_2PC_6H_4S\text{-}2\}_2(dppe)]$: A solution of the ligand (0.230 g, 0.780 mmol) and dppe (0.620 g, 1.560 mmol) in acetonitrile was electrolyzed for 1.5 h at 10 mA, and 37.0 mg of the metal was dissolved (E_f = 1.0 mol F^{-1}). At the end of the electrolysis, the yellow solution was filtered to remove any impurities and concentrated by bubbling through N_2 gas. Crystals of $[Cu_2\{Ph_2PC_6H_4S\text{-}2\}_2(dppe)]$ (**7**) were obtained that were suitable for X-ray studies. $C_{62}H_{52}Cu_2P_4S_2$ (1112.2): calcd. C 67.0, H 4.7, S 5.8; found C 66.8, H 4.9, S 5.5. IR (KBr): ṽ = 1545 (m), 1433 (s), 1026 (m), 999 (w), 740 (m), 720 (m) cm^{-1}. ^1H NMR (300 MHz, CD_3Cl, 25 °C): δ = 8.0–6.8 (m, 48 H), 2.2 (br. s, 4 H) ppm. ^{31}P NMR (300 MHz, $CDCl_3$, 25 °C): δ = 33.6, 31.9 ppm. FAB MS: *m*/*z* = 1112 $[M]^+$, 754 $[M - Ph_2PC_6H_4S\text{-}2]^+$.

$[Cu_2\{Ph_2PC_6H_4S\text{-}2\}_2(dppm)]$: Ligand (0.115 g, 0.390 mmol), dppm (0.150 g, 0390 mmol) in acetonitrile, 1 h at 10 mA and 9 V, 24.9 mg of metal dissolved from the anode (E_f = 1.0 mol F^{-1}). At the end of the electrolysis, yellow needles were deposited in the cell. The solid was filtered off, washed with acetonitrile and ether, and dried under vacuum. $C_{61}H_{50}Cu_2P_4S_2$ (1098.2): calcd. C 66.7, H 4.6, S 5.8; found C 66.3, H 4.5, S 5.8. IR (KBr): ṽ = 1572 (m), 1478 (m), 1165 (m), 1089 (s), 779 (m), 744 (m) cm^{-1}. ^1H NMR (300 MHz, CD_3Cl, 25 °C): δ = 7.9–6.9 (m, 48 H), 2.2 (s, 2 H) ppm. ^{31}P NMR (300 MHz, $CDCl_3$, 25 °C): δ = 29.5, 23.4 ppm. FAB MS: *m*/*z* = 1098 $[M]^+$, 805 $[M - Ph_2PC_6H_4S\text{-}2]^+$; 712 $[M - dppm]^+$. Crystals of $[Cu_2\{Ph_2PC_6H_4S\text{-}2\}_2(dppm)]\cdot 1/2(CH_2Cl_2)$ (**8**) suitable for X-ray analysis were obtained by crystallization of the solid from dichloromethane/methanol.

X-ray Crystallography Studies: Intensity data sets for compounds **5**–**8** were collected with a Bruker X8 Kappa APEXII diffractometer (Mo-K_α radiation, $\lambda = 0.71073$ Å) equipped with a graphite monochromator. The ω- and ϕ-scan technique was employed to measure intensities in these crystals. Intensity data for compounds, **1**–**4** were collected by using a Smart-CCD-1000 Bruker diffractometer (Mo-K_α radiation, $\lambda = 0.71073$ Å) equipped with a graphite monochromator. The ω-scan technique was employed in these cases. Compounds **1**, **5**, **6**, **7** and **8** were measured at 100 K, and **2**, **3** and **4** at 293 K. Decomposition of the crystals did not occur during data collection. The intensities of all data sets were corrected for Lorentz and polarization effects. Absorption effects in all compounds were corrected by using the program SADABS.[28] The crystal structures of all compounds were solved by direct methods. Crystallographic programs used for structure solution and refinement were those of SHELX97.[29] Scattering factors were those provided with the SHELX program system. Missing atoms were located in the difference Fourier map and included in subsequent refinement cycles. The structures were refined by full-matrix least-squares refinement on F^2. Hydrogen atoms were placed geometrically and refined by using a riding model with U_{iso} constrained at 1.2 times U_{eq} of the carrier C atom. For all structures, non-hydrogen atoms were anisotropically refined, with the exception of the half disordered molecule of dichloromethane in compound **8** (occupancies 50:50). Disorder was typically handled by introducing split positions for the affected groups into the refinement of the respective occupancies.

Table 9. Summary of crystal data and structure refinement for the cobalt and nickel compounds.

Compound	**1**	**2**	**3**	**4**
Empirical formula	$C_{36}H_{28}O_2P_2S_2Co$	$C_{56}H_{42}Co_2N_6P_2S_4$	$C_{36}H_{26}Ni_2P_2S_4$	$C_{64}H_{54}Cl_4Ni_2P_4S_4$
Formula weight	677.57	1107.00	766.17	1334.41
Crystal size [mm]	0.28 × 0.18 × 0.06	0.22 × 0.10 × 0.07	0.32 × 0.26 × 0.04	0.14 × 0.09 × 0.02
Temperature [K]	100(2)	293(2)	293(2)	293(2)
Wavelength [Å]	0.71073	0.71073	0.71073	0.71073
Crystal system	triclinic	monoclinic	monoclinic	monoclinic
Space group	$P\bar{1}$	$P2(1)/c$	$P2(1)/c$	$P2(1)/n$
a [Å]	11.5896(19)	9.2411(16)	14.1076(17)	9.55620(10)
b [Å]	11.6771(19)	14.873(3)	11.0368(14)	13.8105(2)
c [Å]	12.699(2)	19.511(3)	20.698(3)	22.8897(4)
α [°]	77.243(3)	90	90	90
β [°]	74.252(3)	96.698(4)	96.678	99.4062(6)
γ [°]	77.113	90	90	90
Volume [Å^3]	1588.8(2)	2663.3(8)	3200.8(7)	2980.27(7)
Z	2	2	4	4
μ [mm^{-1}]	0.804	0.883	1.564	1.100
No. reflections collected	20164	20216	18590	12085
No. of independent reflections	6953[R(int) = 0.0604]	4537[R(int) = 0.0771]	3921 [R(int) = 0.0906]	6787 [R(int) = 0.0385]
Data/restraints/parameters	6953/0/388	4536/0/316	3921/0/397	6787/0/352
Goodness-of-fit	1.032	1.062	1.063	1.025
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0516$[a] $wR_2 = 0.1251$[b]	$R_1 = 0.0499$ $wR_2 = 0.1179$	$R_1 = 0.0515$ $wR_2 = 0.1180$	$R_1 = 0.0472$ $wR_2 = 0.0958$

[a] $R_1 = \Sigma[|F_o| - |F_c|/\Sigma F_o]$. [b] $wR_2 = [\Sigma(F_o^2 – F_c^2)/\Sigma(F_o^2)]^{1/2}$.

Table 10. Summary of crystal data and structure refinement for the copper complexes.

Compound	**5**	**6**	**7**	**8**
Empirical formula	$C_{72}H_{58}Cu_2P_4S_2$	$C_{62}H_{55}Cu_2N_4P_3S_2$	$C_{62}H_{52}Cu_2P_4S_2$	$C_{61.5}H_{51}ClCu_2P_4S_2$
Formula weight	1238.26	1140.21	1112.12	1140.55
Crystal size [mm]	0.14 × 0.09 × 0.08	0.44 × 0.30 × 0.16	0.33 × 0.16 × 0.16	0.26 × 0.21 × 0.20
Temperature [K]	100(2)	100(2)	100(2)	100(2)
Wavelength [Å]	0.71073	0.71073	0.71073	0.71073
Crystal system	monoclinic	triclinic	orthorombic	monoclinic
Space group	$P2(1)/c$	$P\bar{1}$	$Pca2(1)$	$P2(1)/c$
a [Å]	13.6052(4)	12. 7255(2)	22.3790(17)	10.3654(8)
b [Å]	13.2026(4)	13.2615(3)	10.8781(9)	13.6462(12)
c [Å]	17. b1891(5)	18.6953(4)	20.8997(17)	38.692(3)
α [°]	90	74.7970(10)	90	90
β [°]	109.8820(10)	87.0630(10)	90	93.606(2)
γ [°]	90	64.2400(10)	90	90
Volume [Å^3]	2913.14(15)	2734(10)	5087.8(7)	5462.1(8)
Z	2	2	4	4
μ [mm^{-1}]	0.956	0.986	1.086	1.060
No. reflections collected	30411	38949	44379	48313
No. of independent reflections	7441 [R(int) = 0.064]	12784 [R(int) = 0.0206]	10351 [R(int) = 0.0504]	11130 [R(int) = 0.0427]
Data/restraints/parameters	7411/0/361	12784/0/662	10351/1/631	11130/84/673
Goodness-of-fit	1.066	1.062	1.016	1.067
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0740$[a] $wR_2 = 0.1832$[b]	$R_1 = 0.0270$ $wR_2 = 0.0707$	$R_1 = 0.0387$ $wR_2 = 0.0824$	$R_1 = 0.0584$ $wR_2 = 0.1263$

[a] $R_1 = \Sigma[|F_o| - |F_c|/\Sigma F_o]$. [b] $wR_2 = [\Sigma(F_o^2 – F_c^2)/\Sigma(F_o^2)]^{1/2}$.

In compound **8**, one of the phenyl rings was also found to be disordered over two positions with occupancies 65:35. Compound **2** presents a severely disordered molecule of dichloromethane in a void of the crystal lattice. This solvent was removed with the Squeeze program[30] implemented in Platon.[31] In the last cycles of refinement of all structures, a weighting scheme was used, with weights calculated by using the following formula $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, where $P = (F_o^2 + 2F_c^2)/3$. Pertinent details of the data collections and structure refinements are collected in Tables 9 and 10. ORTEP3 was used for the drawings of the structures of the compounds.[32] CCDC-716511 (**1**), -716512 (**2**), -716513 (**3**), -716514 (**4**), -716515 (**5**), -716516 (**6**), -716517 (**7**) and -716518 (**8**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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