Copper, Cobalt and Platinum Complexes with Dithiothiophene-Based Ligands

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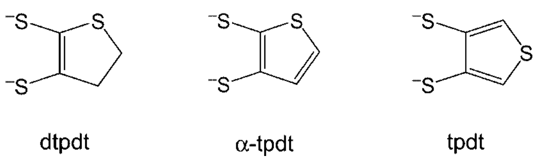
The preparation and characterisation of new thiophenedithiolate complexes of Cu, Co and Pt with the ligands α-tpdt and tpdt (α-tpdt = 2,3-thiophenedithiolate, tpdt = 3,4-thiophenedithiolate) is reported. The Co and Pt complexes present regular square-planar coordination geometry and low oxidation potentials when compared with complexes with simpler ligands, but their monoanionic state is found to be rather unstable. The Co(tpdt)$_2$ complex can be isolated both in the monoanionic and dianionic states as a stable compound but the Co(α-tpdt)$_2$ and the Pt complexes can be obtained only in the dianionic state, while their monoanionic state is unstable. The Co and Pt complexes can, however, be easily oxidised to the neutral state, giving a fine-powdered microcrystalline material without high electrical conductivity. With Cu only a less frequent geometry based on a tetrametallic Cu^I cluster and three ligands is observed as $[Cu_4(\alpha\text{-tpdt})_3]^{2-}$ and $[Cu_4(tpdt)_3]^{2-}$.

Introduction

Transition metal dithiolene complexes, $M(S_2X)_2$, because of a rich variety of coordination geometry and a vivid redox behaviour, have attracted continuing interest during the last 30 years.[1] Depending on the metal, M, coordination geometry and oxidation state, these complexes can be diamagnetic or carry different magnetic moments and therefore have been choice building blocks for the design of functional molecular materials.[2] Square-planar coordination geometries are favoured, with metals of Ni and Cu group in the anionic form $[M(S_2X)_2]^-$, and such complexes have been widely used as counterions in charge transfer solids with a variety of donors, often giving rise to new molecular materials displaying unconventional electrical and magnetic properties, including ferromagnetism,[3] metallic[4] and even superconducting properties.[5]

Another common coordination geometry in bisdithiolene complexes is the square pyramidal, 4+1, in dimerised arrangements, $[M(S_2X)_2]_2^{2-}$, favoured for M = Fe, Co and to a smaller extent occurring also for Ni.[6,7] Other geometries are known in metal bisdithiolene complexes and, for example, for Co, trimerised, $[Co(S_2X)_2]_3^{2-}$,[8] and even polymeric, $[Co(S_2X)_2]_n^{n-}$,[9] arrangements of square planar units also have been described.

The accessibility to different oxidation states in these complexes is greatly dependent on the type of ligand because their contribution to the HOMO and LUMO is often dominant. Extended π ligands favour both a lower oxidation potential and larger solid state interactions between neighbouring units in stacked structures of square-planar complexes. Sulfur-rich ligands with additional sulfur atoms in the periphery of the complex are expected to provide intermolecular S···S contacts that may enhance the magnitude and the dimensionality of the solid state intermolecular interactions.



In this context we recently focused our efforts on exploring complexes based on thiophenedithiolate ligands (α-tpdt = 2,3-thiophenedithiolate, dtpdt = 2,3-dihydro-5,6-thiophenedithiolate and tpdt = 3,4-thiophenedithiolate, Scheme 1). Previously we described the properties of the first Au[10] and Ni[11] complexes with thiophenedithiolate

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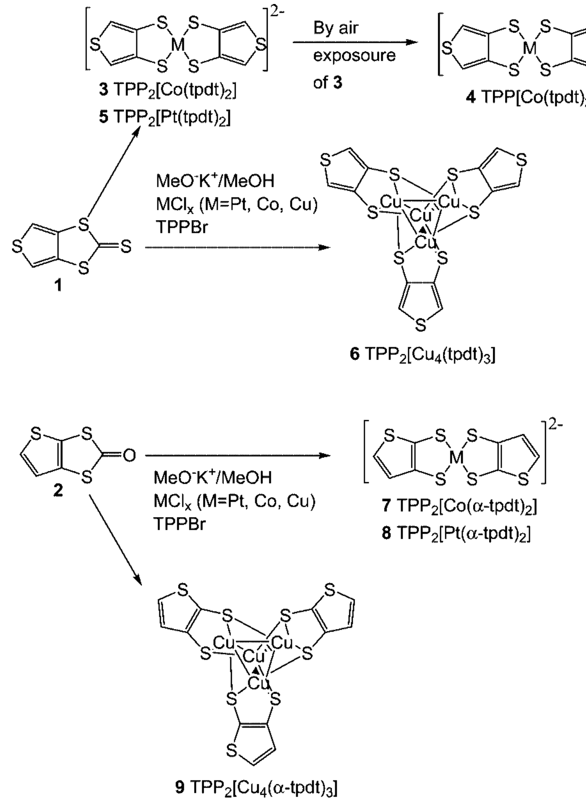
ligands, which are generally characterised by rather low oxidation potentials. Many of these complexes can be obtained as a neutral species such as Au(α-tpdt)$_2$, one of the rare electrically conducting compounds based on a neutral molecule, and the first one showing metallic transport properties in spite of being characterised only as a polycrystalline sample.[10] The paramagnetic Ni^{III} complex was the key component of an interesting charge transfer salt displaying a metamagnetic transition.[11] More recently, other neutral Ni complexes based on more extended bisdithiolene ligands have been obtained as single crystals and were characterised as unimolecular metallic systems.[12]



Scheme 1. Preparation of the transition metal complexes **4**–**9**.

These results led us to prepare similar bisthiophenedithiolate complexes with different transition metals and to explore their possible use as building blocks for the preparation of magnetic or electrically conducting materials. In this paper we report on the preparation and properties of new thiophenedithiolate complexes of Cu, Co and Pt with the ligands α-tpdt and tpdt having diverse oxidation states and geometries.

Results and Discussion

The synthesis of TPP$_y$M(xtpdt)$_z$ followed a procedure (Scheme 1) similar to the one previously described for other transition metal complexes with dithiolatethiophene ligands, with minor modifications. The previous preparation of Au[10] and Ni[11] complexes with thiophenedithiolate ligands was made as tetrabutylammonium (TBA) salts. However, difficulties in crystallising the salts of these complexes with such cations led us to work with larger cations such as tetraphenylphosphonium (TPP), which favours the crystallisation process. The ligands were obtained in methanol solution from 5,6-thieno[2,3-*d*]-1,3-dithiol-2-one (**1**) for [M(α-tpdt)$_2$]$^{x-}$ salts, and from thieno[3,4-*d*]-1,3-dithiol-2-thione (**2**) in the case of [M(tpdt)$_2$]$^{x-}$ complexes, by cleavage with potassium methoxide. These ligands, without intermediate isolation, were immediately treated with the appropriate metal chloride to give the Co^{II}, Pt^{II} and Cu^{I} complexes, which precipitated as red (**5**), green (**3**), orange (**8**), dark brown (**7**) and golden brown (**6**, **9**) TPP salt, by treatment with TPPBr. These reactions were carried out in strictly anaerobic conditions inside a glovebox. The TPP[Co(tpdt)$_2$] complex (**4**) was obtained as a dark blue precipitate, just by stirring an acetonitrile solution of **3** under air. After recrystallisation, all compounds give air-stable crystals with yields ranging from 50 to 80%. The Pt complex **8** in acetonitrile solution, when exposed to air, changes colour to green, indicating that an oxidation process takes place, in agreement with the low oxidation potential observed in the cyclic voltammetry data (see below). However, possibly because of decomposition and instability of the Pt^{III} complexes, it was not possible to isolate the monoanionic species. Although with only a slightly larger oxidation potential the Pt(tpdt)$_2$$^{2-}$ complex **5** does not undergo any oxidation upon air exposure.

With the exception of the copper salts **6** and **9**, the abovementioned synthetic procedure leads to the dianionic species M^{II} with M = Co and Pt in a square-planar coordination geometry. Cu complexes are always obtained with a different stoichiometry, of four metals to three ligands. This stoichiometry, although unexpected, is not entirely new as it has been previously reported for a few [Cu$_4$(S$_2$X)$_3$]$^{2-}$ complexes.[13] However in most of these previous examples the stoichiometry of the complexes obtained is controlled by the metal–ligand proportion, the ligand excess favouring the formation of the square-planar Cu^{II} complex. In the present case we were not able to obtain the square-planar Cu coordination, even with a large excess of the ligands.

The crystal structures of complexes **4**–**9** were solved by single-crystal X-ray diffraction and their crystal and structure refining data are listed in Table 1 and Table 2. The Co and Pt complexes present identical, essentially planar, geometry (Figure 1 and Figure 2), with small nonplanar deviations observed only in the thiophenic sulfur atoms of complex **5**, which are displaced towards opposite directions giving rise to a very small chair-type distortion.

By contrast, this usual square-planar coordination geometry, found also in the previously described Au and Ni complexes with these ligands,[10,11] was not observed in the Cu complexes **6** and **9**, which present a different stoichiometry and structure: [Cu$_4$(xtpdt)$_3$]$^{2-}$. In these complexes the dianion is composed by four Cu^{I} atoms, each one coordinated to the other three Cu atoms. The Cu2, Cu3 and Cu4 atoms are chelated to two sulfurs from one dithiothiophene ligand and to another sulfur atom from a neighbouring ligand. Although Cu1 is also coordinated to three sulfur atoms,

Table 1. Crystal data and structure refinement of compounds **4**, **5**, **7** and **8**.

	TPP$_2$[Co(α-tpdt)$_2$] (**7**)	TPP[Co(tpdt)$_2$] (**4**)	TPP$_2$[Pt(tpdt)$_2$] (**5**)	TPP$_2$[Pt(α-tpdt)$_2$] (**8**)
Empirical formula	$C_{56}H_{44}CoP_2S_6$	$C_{32}H_{24}CoPS_6$	$C_{56}H_{44}P_2PtS_6$	$C_{56}H_{44}P_2PtS_6$
Formula mass	1030.14	690.77	1166.30	1166.30
Temperature [K]	293(2)	293(2)	120(2)	293(2)
Crystal system, space group	monoclinic, $P2_1/n$	triclinic, $P\bar{1}$	monoclinic, $P2_1/n$	monoclinic, $P2_1/n$
a [Å]	11.4352(18)	9.6591(11)	11.5361(2)	11.396(2)
b [Å]	14.649(3)	10.0699(9)	14.4982(2)	14.6302(18)
c [Å]	14.5746(15)	16.6435(15)	14.4816(3)	14.632(2)
α [°]	90.0	93.428(7)	90.0	90.0
β [°]	94.209(5)	106.465(8)	93.3204(5)	93.856(9)
γ [°]	90.0	92.886(8)	90.0	90.0
Volume [Å^3]	2434.9(6)	1545.9(3)	2418.02(7)	2433.9(7)
Z, D_{calcd} [Mg/m^3]	2, 1.405	2, 1.484	2, 1.602	2, 1.591
μ [mm^{-1}]	0.714	1.034	3.266	3.244
F(000)	1066	708	1168	1168
Crystal size [mm]	0.6 × 0.4 × 0.2	0.5 × 0.3 × 0.12	0.36 × 0.108 × 0.02	0.5 × 0.3 × 0.2
θ range [°]	1.97–26.01	2.03–26.04	2.91–27.48	1.97–25.98
Index range (h,k,l)	–0/14, 0/18, –17/+17	0/11,–12/12, –20/19	–14/14, –18/16, –18/18	0/14, –17/0, –18/17
Reflections collected/unique	4974/4733 [R_{int} = 0.0187]	6369/5992 [R_{int} = 0.0236]	25490/5440 [R_{int} = 0.0520]	4969/4728 [R_{int} = 0.037]
Absorption correction	Psi-scan	Psi-scan	SORTAV	Psi-scan
T_{max} and T_{min}	0.9994 and 0.9262	0.9995 and 0.8675	0.39761 and 0.36873	0.9991 and 0.7707
Data/parameters	4733/323	5992/364	5440/295	4728/323
Goodness-of-fit on F^2	1.106	1.044	1.021	0.938
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0421, wR_2 = 0.0851	R_1 = 0.0508, wR_2 = 0.0862	R_1 = 0.0264, wR_2 = 0.0599	R_1 = 0.0456, wR_2 = 0.0688
$\Delta\rho_{max./min.}$ [e/A^3]	0.341/–0.276	0.348/–0.343	0.911/–1.206	0.904/–0.515

Table 2. Crystal data and structure refinement of compounds **6** and **9**.

	TPP$_2$[Cu$_4$(α-tpdt)$_3$] (**9**)	TPP$_2$[Cu$_4$(tpdt)$_3$] (**6**)
Empirical formula	$C_{60}H_{46}Cu_4P_2S_9$	$C_{60}H_{46}Cu_4P_2S_9$
Formula mass	1371.61	1371.61
Temperature [K]	293(2)	293(2)
Wavelength [Å]	0.71073	0.71069
Crystal system, space group	monoclinic, $P2_1/c$	hexagonal, $P61$
a []	12.1360(19)	13.5743(14)
b [Å]	21.0210(17)	13.5743(14)
c [Å]	23.3280(19)	53.931(8)
α [°]	90.000(5)	90.000(5)
β [°]	100.808(9)	90.000(5)
γ [°]	90.000(5)	120.000(5)
Volume [Å^3]	5845.7(11)	8606.1(18)
Z, $D_{calcd.}$ [Mg/m^3]	4, 1.558	6, 1.588
μ [mm^{-1}]	1.851	1.886
F(000)	2784	4176
Crystal size [mm]	0.5 × 0.2 × 0.1	
θ range [°]	1.71–25.98	1.73–25.03
Index range (h,k,l)	0/14, 0/25, –28/28	–16/13, 0/16, –64/0
Reflections collected/unique	11986/11428 [R_{int} = 0.1083]	15903/5090 [R_{int} = 0.2518]
Absorption correction	Psi-scan	
T_{max} and T_{min}	0.9998 and 0.9702	
Refinement method	full-matrix least-squares on F^2	full-matrix least-squares on F^2
Data/restraints/parameters	11428/78/676	5090/1/676
Goodness-of-fit on F^2	0.881	1.012
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.1023, wR_2 = 0.1739	R_1 = 0.0835, wR_2 = 0.0833
$\Delta\rho_{max./min.}$ [e/A^3]	0.809 and –0.489	0.488 and –0.434

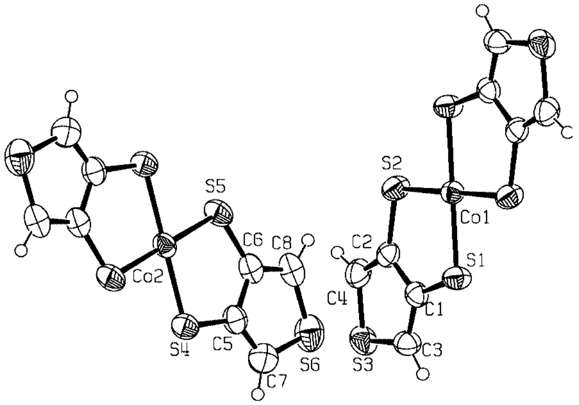


Figure 1. ORTEP views and atomic numbering scheme of [Co(tpdt)$_2$]$^-$ with thermal ellipsoids at 40% probability level. The atomic numbering scheme is the same in the case of [Pt(tpdt)]$^{2-}$.

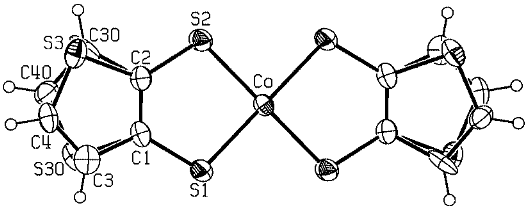


Figure 2. ORTEP views and atomic numbering scheme of [Co(α-tpdt)$_2$]$^{2-}$ with thermal ellipsoids at 40% probability level. The atomic numbering scheme is the same in the case of [Pt(α-tpdt)$_2$]$^{2-}$.

each one belongs to different dithiothiophene ligands (Figure 3 and Figure 4). The Cu–Cu distances range from 2.740 to 2.640 Å and 2.729 to 2.655 Å, for complexes **6** and **9**, respectively, values which are comparable to the few similar complexes with other dithiolate ligands.[13] The Cu–S distances can be divided into two different ranges: one, Cu–S$_L$, involving sulfur atoms in the same ligand that range from 2.264 to 2.320 Å in salt **6** and 2.252 to 2.336 Å in salt **9**, and the other with slightly shorter bond lengths between the sulfur atom in the neighbouring ligand, Cu–S$_N$, that range from 2.216 to 2.231 and 2.212 to 2.240 for complexes **6** and **9**, respectively.

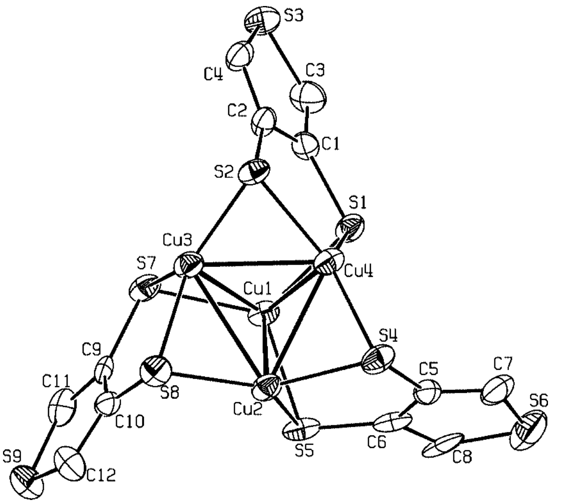


Figure 3. ORTEP views and atomic numbering scheme of [Cu$_4$(tpdt)$_3$]$^{2-}$ with thermal ellipsoids at 40% probability level.

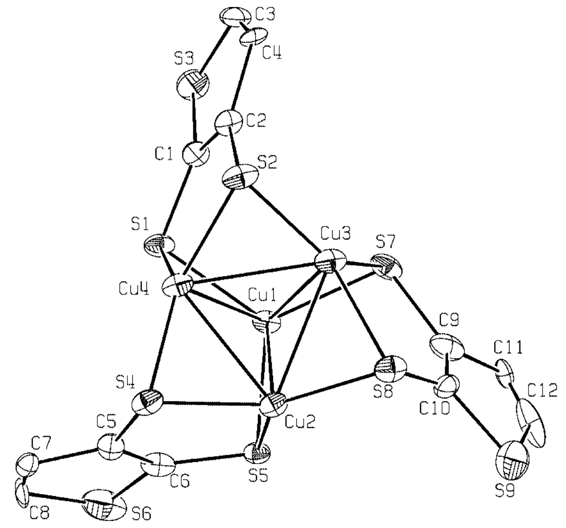


Figure 4. ORTEP views and atomic numbering scheme of [Cu$_4$(α-tpdt)$_3$]$^{2-}$ with thermal ellipsoids at 40% probability level.

The angles between the average planes of each ligand are close to 70° (Figure 3 and Figure 4). In all cases, within the ligand, the bond lengths in the thiophenic ring are very close to those found in the corresponding Ni and Au analogues (Table 3 and Table 4).[10,11] The α-tpdt complexes of Co (**7**) and Pt (**8**) present a disorder in the orientation of the thiophenic sulfur of the ligands (Figure 2), making it impossible to distinguish between a *cis* or *trans* conformation of the complex, as both configurations with orientation disorder in the crystal could give the observed results. As the Ni(α-tpdt)$_2$[11] and Au(dtpdt)$_2$[10] complexes previously studied were found to crystallise in the *trans* configuration, the observed disorder is most likely the result of orientational disorder of the complex in the *trans* configuration. In this respect it should be mentioned that in those cases one specific orientation of the complexes is favoured by several hydrogen bonds and strong S···S contacts involving the thiophenic ring, and therefore preventing possible orientational disorder of the complex in those structures. This is at variance with the structure of **7** and **8** where there are no strong thiophenic S···S contacts and the existing hydrogen bonds do not present any specific orientation.

Two different types of crystal packing were found on the studied salts. The first one consists of isolated anions, surrounded by the TPP cations and this type of crystal packing is shared for complexes **5**, **6**, **7**, **8** and **9** (Figure 5 and Figure 6). Although they are not isostructural, they present the same crystal packing pattern. The interactions between the anions and the cations are established through several hydrogen bonds. The interactions found are of the C–H···S type, involving both the thiophenic and the coordination sulfur atoms (Table 5). The effect on the crystal structure

Table 3. Selected bond lengths [Å] for $[M(L)_2]^{x-}$ in complexes **4**, **5**, **7** and **8**.

	$[Co(\alpha\text{-tpdt})]^{2-}$	$[Co(tpdt)]^{-}$	$[Pt(tpdt)]^{2-}$	$[Pt(\alpha\text{-tpdt})]^{2-}$
M–S1	2.2139(7)	2.177(1)	2.3109(6)	2.306(2)
M–S2	2.2215(8)	2.182(1)	2.3113(6)	2.314(2)
M–S4	–	2.178(1)	–	–
M–S5	–	2.167(1)	–	–
S1–C1	1.743(3)	1.749(4)	1.759(3)	1.740(8)
S2–C2	1.736(3)	1.760(4)	1.754(3)	1.731(7)
S4–C5	–	1.753(4)	–	–
S5–C6	–	1.746(4)	–	–
S3–C2	1.713(4)	--	–	1.736(16)
S3–C4	1.689(10)	1.709(4)	1.715(3)	1.690(40)
S3–C3	–	1.710(4)	1.721(3)	–
S30–C1	1.717(14)	–	–	1.718(13)
S30–C40	1.72(2)	–	–	1.710(30)
S6–C7	–	1.702(4)	–	–
S6–C8	–	1.708(5)	–	–
C1–C2	1.355(4)	1.420(5)	1.437(3)	1.351(10)
C5–C6	–	1.417(5)	–	–
C1–C3	1.47(2)	1.359(5)	1.362(4)	1.530(40)
C3–C4	1.39(2)	–	–	1.470(60)
C2–C4	–	1.345(5)	1.370(3)	–
C2–C30	1.55(3)	–	–	1.410(50)
C5–C7	–	1.361(5)	–	–
C6–C8	–	1.368(5)	–	–
C30–C40	1.45(3)	–	–	1.420(80)

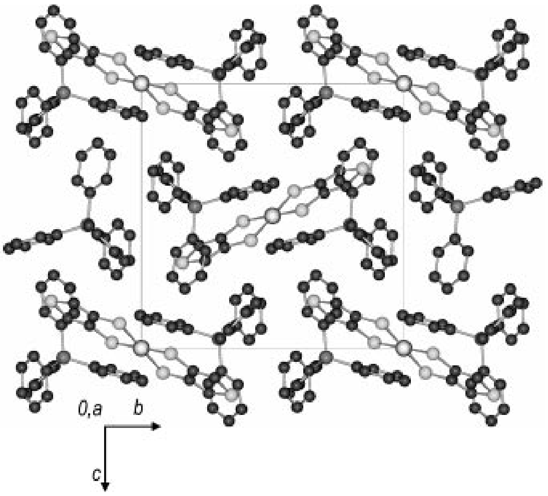


Figure 5. View of the crystal structure of **7** along *a*. The crystal packing for complexes **5** and **8** is very similar.

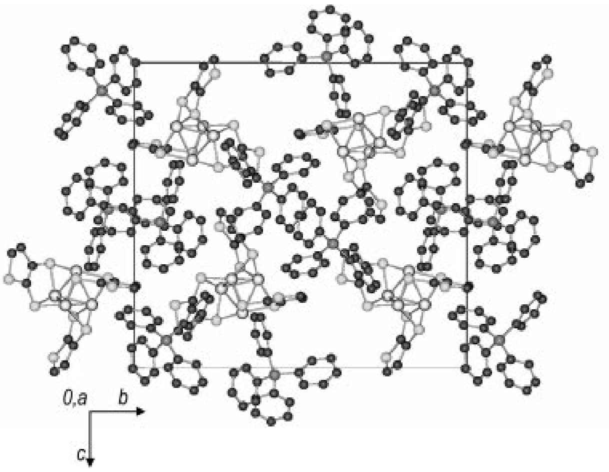


Figure 6. View of the crystal structure of **9** along *a*.

of the sulfur atom position in the thiophenic ring (tpdt or α-tpdt) is negligible.

The crystal structure of **4** is composed by layers of dithiolate anions parallel to the *bc* plane, with TPP cations sitting in holes in these layers. The anionic layers are due to a network of short contacts. Anions of one type are connected between the terminal sulfur atoms by short S(3)···S(3)* [3.492(2) Å] contacts making regular chains along *b*. These chains are interconnected by another dithiolate anion, placed almost perpendicularly to the first ones, through short S6···C1 contacts [3.436(2) Å] (Figure 7). This last contact may denote a weak interaction between this S atom and the carbon π system. The TPP cations are sitting over the spaces left in this anionic layer.

Cyclic voltammetry of all $TPP_yM(xtpdt)_z$ was performed in acetonitrile versus Ag/AgCl and the redox potential values of the different processes observed are listed in Table 6. As in the case of the Au and Ni compounds previously described, these new transition metal complexes with dithiolatethiophene ligands present lower oxidation potentials than complexes with more simple bisdithiolene ligands such as maleonitrile dithiolate (mnt) or even benzodithiolate (bdt). With the exception of the copper complexes, which present a different stoichiometry and coordination environment, when going from tpdt to α-tpdt ligands the redox potentials decrease, showing an increasing facility of these complexes to be oxidised. The complexes with M = Co, Pt present at negative values a reversible process ascribed to

Table 4. Selected bond lengths [Å] for $[Cu_4(L)_3]^{2-}$ in complexes **6** and **9**.

	tpdt	α-tpdt
Cu1–Cu2	2.696(2)	2.727(2)
Cu1–Cu3	2.675(2)	2.688(2)
Cu1–Cu4	2.690(2)	2.690(2)
Cu2–Cu3	2.740(2)	2.670(2)
Cu2–Cu4	2.641(2)	2.652(2)
Cu3–Cu4	2.640(2)	2.681(3)
Cu1–S1	2.284(4)	2.280(4)
Cu1–S5	2.286(4)	2.290(3)
Cu1–S7	2.303(4)	2.294(3)
Cu2–S8	2.216(4)	2.233(4)
Cu2–S4	2.276(4)	2.256(5)
Cu2–S5	2.314(5)	2.308(4)
Cu3–S2	2.231(4)	2.211(4)
Cu3–S8	2.280(4)	2.288(4)
Cu3–S7	2.320(4)	2.312(5)
Cu4–S4	2.220(4)	2.235(4)
Cu4–S2	2.264(4)	2.274(4)
Cu4–S1	2.316(4)	2.333(4)
S1–C1	1.765(15)	1.703(13)
S2–C2	1.757(14)	1.768(12)
S3–C3	1.723(16)	1.733(16)
S3–C4	1.732(15)	–
S3–C1	–	1.706(12)
S4–C5	1.803(16)	1.734(16)
S5–C6	1.733(17)	1.714(15)
S6–C8	1.701(18)	1.860(20)
S6–C7	1.710(19)	–
S6–C6	–	1.711(12)
S7–C9	1.758(13)	1.675(15)
S8–C10	1.755(15)	1.788(19)
S9–C11	1.692(15)	–
S9–C12	1.706(14)	1.742(12)
S9–C10	–	1.733(14)
C2–C1	1.466(17)	1.397(15)
C5–C6	1.424(19)	1.412(17)
C9–C10	1.457(18)	1.330(20)
C1–C3	1.354(17)	–
C2–C4	1.331(16)	1.567(16)
C3–C4	–	1.250(20)
C5–C7	1.319(18)	1.505(15)
C6–C8	1.349(19)	–
C7–C8	–	1.130(30)
C9–C11	1.349(17)	1.620(19)
C10–C12	1.326(15)	–
C11–C12	–	1.130(12)

Table 5. Selected hydrogen bonds and short contacts in the crystal structure of complexes **4**–**9**.

4	*d* [Å]	Angle [°]
S3···S3[a]	3.492(2)	–
S6···C1	3.436(2)	–
C14–H14···S5	2.815(1)	137
C33–H33···S5	2.980(1)	158
5	*d* [Å]	Angle [°]
C24–H24···S1	2.895(1)	170
C33–H33···S2	2.821(1)	152
C44–H44···S3	2.897(1)	139
6	*d* [Å]	Angle [°]
C22–H24···S5	2.855(3)	141
C64–H64···S6	2.919(6)	148
C36–H36···S8	2.909(4)	137
7	*d* [Å]	Angle [°]
C43–H43···S1	2.851(1)	144
C24–H24···S2	2.940(1)	171
C12–H12···S3	2.942(4)	129
C12–H12···S30	2.798(13)	177
8	*d* [Å]	Angle [°]
C43–H43···S1	2.832(2)	145
C24–H24···S2	2.944(2)	173
C12–H12···S3	2.941(17)	129
C12–H12···S30	2.759(13)	176
9	*d* [Å]	Angle [°]
C22–H22···S2	2.934(5)	135
C94–H94···S5	2.966(4)	124
C53–H53···S6	2.833(6)	160
C75–H75···S7	2.860(4)	147
C86–H86···S9	2.951(10)	120

[a] $-x + 1, -y + 2, -z + 1$.

the $M(xtpdt)_2^{2-}/M(xtpdt)_2^{-}$ couple. These low values are in agreement with the fact that the $Co(tpdt)_2^{-}$ complex was obtained from the dianionic species upon air oxidation and with the previously mentioned fact that $Pt(\alpha\text{-tpdt})_2^{2-}$ changes colour upon air exposure, indicative of oxidation. In spite of not so different oxidation potentials, $Co(\alpha\text{-tpdt})_2^{2-}$ and $Pt(tpdt)_2^{2-}$ do not denote any air oxidation and the monoanionic species could not be isolated, probably because of instability associated with dismutation in the neutral and dianionic species. The Co and Pt complexes also show an irreversible process at more positive potentials, possibly associated with the formation of the insoluble neutral complexes, which could be obtained by chemical oxidation (see below). The Cu complexes also undergo two redox processes, a reversible wave for $Cu_4(tpdt)_3$ at –0.330 V, quasireversible for $Cu_4(\alpha\text{-tpdt})_3$ at about –0.392 V (–0.506, –0.278) and an irreversible oxidation at higher potentials of about 0.18 V.

As suggested by the cyclic voltammetry data, in the case of Pt and Co complexes, the corresponding neutral metal(IV) complexes were easily obtained by chemical oxidation as fine and very insoluble precipitates. The same products, as judged by elemental analysis and IR, were also obtained by electrochemical oxidation from acetonitrile solutions containing the $TPP_y[M(xtpdt)_2]$ salts. Using standard electrocrystallisation galvanostatic conditions with a current density of 1 μA/cm^2 for about 7–12 days, in a two-compartment cell with platinum electrodes, only an equally fine and insoluble microcrystalline dark powder was obtained. The elemental analysis of these products is consistent with the neutral complex. Further characterisation of these products was hampered by the difficulty in the preparation of single crystals because of the large insolubility of these neutral complexes in most solvents. However, the measurements of the electrical conductivity by the four-probe method in compressed powder pellets indicated conductivity lower than 10^{-6} S/cm.

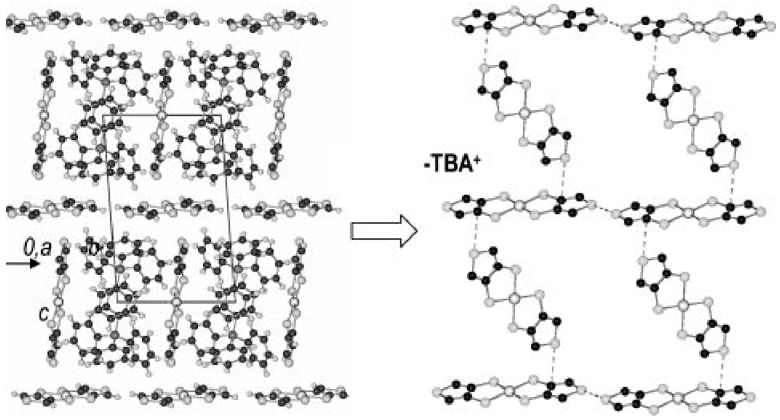


Figure 7. View of the crystal structure of **4** along *a*. On the right side the anionic layer in **4** is shown in detail, emphasising the short S3···S3* and S6···C1 contacts, responsible for the two-dimensional dithiolate network.

Table 6. Cyclic voltammetry of $[M(L)_2]^{x-}$ complexes.

Compound	$E_{1/2}(M^{I}\rightarrow M^{II})$ [mV]	$E_{1/2}(M^{II}\rightarrow M^{III})$ [mV]	$E_{1/2}(M^{III}\rightarrow M^{IV})$ [mV]	Ref.
$TPP[Co(tpdt)_2]$		–618	+497	this work
$TPP_2[Co(\alpha\text{-}tpdt)_2]$		–591	–257/–175/–8	this work
$TPP_2[Pt(tpdt)_2]$		–253	+416	this work
$TPP_2[Pt(\alpha\text{-}tpdt)_2]$		–519	+69/+152/+278	this work
$TBA[Au(\alpha\text{-}tpdt)_2]$		–1162	+456	[10]
$TBA[Au(tpdt)_2]$		–900	+754[a]/+1319	[10]
$TBA[Ni(\alpha\text{-}tpdt)_2]$		–562	+253	[11]
$TBA_2[Co(mnt)_2]$		–384[a]		[1a]
$TBA_2[Pt(mnt)_2]$		–231[a] (–160)	+853 (+720)	[1a] [b], ([19] [c])
$TPP_2[Cu_4(tpdt)_3]$	–330	+148/+293		this work
$TPP_2[Cu_4(\alpha\text{-}tpdt)_3]$	–506/–278	+182/+430		this work

[a] $M^{III} \rightarrow M^{III/IV}$. [b] In DMF, vs. Ag/AgCl. [c] In acetonitrile vs. Ag/Ag^+.

Summary

New thiophenedithiolate complexes of Cu, Co and Pt with the ligands α-tpdt and tpdt were prepared. The Cu complexes obtained, independently of the metal to ligand ratio, present a tetrametallic Cu^I cluster and three ligands: $[Cu_4(\alpha\text{-}tpdt)_3]^{2-}$ and $[Cu_4(tpdt)_3]^{2-}$. The Co and Pt complexes, with square-planar coordination geometry, are obtained in the dianionic state. In spite of their low oxidation potential, only for $Co(tpdt)_2$ was it possible to isolate the monoanionic complex and in other cases this oxidation state is rather unstable. Further oxidation of these complexes to the neutral state gives an electrically insulating powder material.

Experimental Section

General Remarks: All manipulations were carried out with exclusion of air under dry nitrogen or argon unless otherwise stated. All solvents were purified following standard procedures. Thieno[3,4-*d*]-1,3-dithiol-2-thione (**1**) and 5,6-thieno[2,3-*d*]-1,3-dithiol-2-one (**2**) were synthesised as described previously. Other chemicals were commercially obtained and used without any further purification. Column chromatography was carried out using silica gel (0.063–0.2 mm) from S.D.S. UV/Vis spectra were recorded with a Cary 5G spectrophotometer (Varian). IR spectra were obtained with a Perkin–Elmer 577 spectrophotometer. MALDI mass spectra were obtained in time-of-flight negative linear mode with an apparatus Kratus Kompact Maldi 2 K probe (KRATOS Analytical) operated with pulsed extraction of the ions. Cyclic voltammetry data were obtained by using a BAS C3 Cell Stand. The measurements were performed at room temperature in acetonitrile solutions containing nBu_4PF_6 as supporting electrolyte, with a scan rate of 100 mV/s, platinum wire working and counter electrodes and using a Ag/AgCl as a reference electrode.

Tetraphenylphosphonium Salt of Cobalt(III) Bis(3,4-thiophenedithiolate), $TPPCo(tpdt)_2$ (4): Whilst stirring, thieno[3,4-*d*]-1,3-dithiol-2-thione (**1**) (100 mg, 5.25×10^{-4} mol) was added to a solution of potassium methoxide in methanol (10 mL, 2 M). The formed yellow solution was filtered and added to a solution (2 mL) of $CoCl_2\cdot6H_2O$ (63 mg, 2.6×10^{-4} mol) in methanol, turning to a green mixture. The inorganic precipitate was removed and the liquor added to 1 mL of a solution of tetraphenylphosphonium bromide (222 mg, 5.25×10^{-4} mol) in methanol giving a green precipitate, **3**. The green solid obtained was dissolved in acetonitrile and stirred under air. Just a few minutes later the solution turned from green to dark blue. After an hour this solution was filtered and evaporated, giving **4** as a blue precipitate. The stirring was maintained, in all steps, only until no visible modifications were observed. The best crystals of **4**, suitable for X-ray measurements, were obtained from crystallisation in acetonitrile/ethyl ether. Total yield: 79%, 142 mg; $C_{56}H_{44}CoP_2S_6$ (**3**) (1030.20): calcd. C 65.29, H 4.30, S 18.67; found C 64.61, H 3.85, S 17.63; $C_{32}H_{24}PS_6Co$ (**4**) (690.81): calcd. C 55.64, H 3.50, S 27.84; found C 56.23, H 3.68, S 26.95. FTIR (KBr) $\tilde{\nu}$ = 3060 (m) (arom. C–H), 1580 (s) (C=C str.), 1480 (s) (C–H, ring C=C str.), 1460 (s) (=C–H, ring C=C), 1310 (s), 1125 (s), 990 (s), 840 (s), 760 (s), 725 (s) (C–S), 690 (s) (C–S), 630 (m) (C–S), 530 (s) cm^{-1}. UV/Vis (CH_3CN) λ_{max} = 1915 nm; m.p. 67 °C dec. MS: *m/z* (%) = 352 (100) [M$^-$].

Bis(tetraphenylphosphonium) Salt of Platinum(II) Bis(3,4-thiophenedithiolate), $TPP_2Pt(tpdt)_2$ (5): The compound was prepared using the same method as for **4**, using $NaPtCl_4\cdot 3H_2O$ instead of $CoCl_2\cdot 6H_2O$. The product was obtained as dark red plate crystals, directly by synthesis, allowing the final solution to rest overnight. Yield: 50%, 152 mg; $C_{56}H_{44}P_2PtS_6$ (1166.36): calcd. C 57.67, H 3.80, S 16.49; found C 56.79, H 3.94, S 16.89; FTIR (KBr) $\tilde{\nu}$ = 3520 (m), 3440 (m) (C–H arom.), 1440 (s) (P-φ), 1300 (s), 1105 (s), 720 (s) (C–S), 690 (m) (C–S), 530 (s) cm^{-1}. UV/Vis (CH_3CN): λ_{max} = 871, 1915 nm; m.p. gradual decomposition 300 °C. MS: *m/z* (%) = 487.5 (100) [M$^-$].

Bis(tetraphenylphosphonium) Salt of Copper(I) Tris(3,4-thiophenedithiolate), $TPP_2Cu_4(tpdt)_3$ (6): The compound was prepared using the same method as for **4**, using $CuCl_2\cdot 2H_2O$ instead of $CoCl_2\cdot 6H_2O$. The product was obtained as a brown precipitate. The best crystals, suitable for X-ray measurements, were obtained by recrystallisation in acetonitrile/ethyl ether. Yield: 62%, 55 mg; $C_{60}H_{46}Cu_4P_2S_9$ (1371.69): calcd. C 52.54, H 3.38, S 21.03; found C 53.88, H 3.52, S 20.66; FTIR (KBr) $\tilde{\nu}$ = 1584 (m), 1482 (m), 1439 (m) (C-φ), 1277 (m), 1109 (s), 997 (m), 839 (m), 755 (s), 726 (s), 689 (s) (C–S), 531 (s) cm^{-1}. UV/Vis (CH_3CN): λ_{max} = 1912 nm; m.p. 120 °C dec. MS: *m/z* (%) = 325 (100) [$C_8H_4S_5Cu$], 209.7 [$C_4H_2S_3Cu$], 693.5 [M$^-$].

Tetraphenylphosphonium Salt of Cobalt(III) Bis(2,3-thiophenedithiolate), $TPP_2Co(\alpha\text{-tpdt})_2$ (7): The compound was prepared using the same method as for **4**. The initial reactive was 5,6-thieno[2,3-*d*]-1,3-dithiol-2-one (**2**). The product was obtained as dark brown crystals after recrystallisation in acetonitrile/ethyl ether. Total yield: 80%, 214 mg; $C_{56}H_{44}CoP_2S_6$ (1030.20): calcd. C 65.29, H 4.30, S 18.67; found C 64.90, H 3.95, S 18.75; $\tilde{\nu}$ = 3440 (m), 3050 (m) (C–H arom.), 1650 (m), 1640 (m), 1590 (s), 1490 (s), 1445 (s) (P-φ), 1310 (m), 1240 (m), 1160 (m), 1110 (s), 1020 (m), 1000 (m), 755 (m), 730 (s), 700 (s), 630 (m), 54 (s) cm^{-1}. UV/Vis (CH_3CN): λ_{max} = 581, 795, 1912 nm; m.p. 117.8–119.5 °C. MS: *m/z* (%) = 144.7 (100) [S_3C_4] [M$^-$].

Bis(tetraphenylphosphonium) Salt of Platinum(II) Bis(2,3-thiophenedithiolate), $TPP_2Pt(\alpha\text{-tpdt})_2$ (8): The compound was prepared from 5,6-thieno[2,3-*d*]-1,3-dithiol-2-one (II) following the same method as in **5**. After recrystallisation the compound was obtained as orange plate-shaped crystals. Yield: 53%, 161 mg; $C_{56}H_{44}P_2PtS_6$ (1166.36): calcd. C 57.67, H 3.80, S 16.49; found C 56.93, H 3.69, S 16.25; $\tilde{\nu}$ = 3054 (m) (C–H arom.), 1578 (m), 1429 (m) (P-φ), 1377 (s), 716 (s) (C–S), 682 (s) (C–S) cm^{-1}. UV/Vis (CH_3CN): λ_{max} = 990, 1912 nm. MS: *m/z* (%) = 487.5 (100) [M$^-$].

Bis(tetraphenylphosphonium) Salt of Copper(I) Tris(2,3-thiophenedithiolate), $TPP_2Cu_4(\alpha\text{-tpdt})_3$ (9): Using as starting material **2** and following the same procedure used for **6**, the product was obtained as golden brown crystals. Yield: 59%, 53 mg; $C_{60}H_{46}Cu_4P_2S_9$ (1371.69): calcd. C 52.54, H 3.38, S 21.03; found C 53.27, H 3.47, S 20.35; $\tilde{\nu}$ = 1482 (m), 1439 (m) (P-φ), 1110 (m), 998 (m), 864 (m), 757 (m), 726 (s) (C–S), 692 (s) (C–S), 601 (m), 514 (s) cm^{-1}. UV/Vis (CH_3CN): λ_{max} = 432, 1418, 1908 nm; m.p. 213.3–214.4 °C dec. MS: *m/z* (%) = 144.9 [$C_4H_2S_3$], 324.8 [$C_8H_4S_5Cu$], 353 [$C_8H_4S_6Cu$].

Cobalt(IV) Bis(3,4-thiophenedithiolate), $Co(tpdt)_2$ (10): A solution of iodine in acetone was added to a solution of **4** in acetone (10 mL, 1.5×10^{-2} M), dropwise in stoichiometric amounts. The fine dark precipitate obtained was isolated by centrifugation, washed by Soxhlet extraction with acetone and dried in vacuo. Yield 32%, 17 mg; $C_8H_4CoS_6$ (351.41: calcd. C 27.34, H 1.15, S 54.74; found C 27.11, H 1.07, S 53.15.

Platinum(IV) Bis(3,4-thiophenedithiolate), $Pt(tpdt)_2$ (11): Using as starting material **5** and following the same procedure used for **10**, the neutral species was obtained as a fine-powdered dark solid. Yield 28%, 20 mg; $C_8H_4PtS_6$ (487.57): calcd. C 19.71, H 0.83, S 39.45; found C 19.03, H 0.95, S 37.14.

Cobalt(IV), Bis(2,3-thiophenedithiolate), $Co(\alpha\text{-tpdt})_2$ (12): Using as starting material **7** and following the same procedure used for **10**, the neutral species was obtained as a fine-powdered dark solid. Yield 45%, 24 mg; $C_8H_4CoS_6$ (351.41): calcd. C 27.34, H 1.15, S 54.74; found C 26.94, H 1.14, S 53.04.

Platinum(IV), Bis(2,3-thiophenedithiolate), $Pt(\alpha\text{-tpdt})_2$ (13): Using as starting material **8** and following the same procedure used for **10**, the neutral species was obtained as a fine-powdered dark solid. Yield 37%, 27 mg, $C_8H_4PtS_6$ (487.57): calcd. C 19.71, H 0.83, N 0.00, S 39.45; found C 19.94, H 1.14, N 0.00, S 35.83.

X-ray Crystallographic Study: The data collection was performed at room temperature for all compounds on an Enraf–Nonius CAD4 diffractometer equipped with a graphite monochromatised Mo-K_α radiation (λ = 0.71069 Å) in the ω-2θ-scan mode, except in the case of compound **5**, where data were collected at 120 K with a Nonius KAPPA CCD using a Mo rotating anode using φ- and ω-scans. Data collection and refinement details are presented in Table 1.

The structures were solved by direct methods using SIR97[14] and refined by full-matrix least-squares methods using the program SHELXL97[15] and the winGX software package.[16] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in idealised positions and allowed to refine riding on the parent C atom. Molecular graphics were prepared using ORTEP 3[17] and SCHAKAL-97.[18] Crystal data and structure refinement are summarised in Tables 5 and 6. Experimental details, atomic coordinates, and bond lengths and angles have been deposited in the Cambridge Crystallographic Data Centre (CCDC). CCDC-263500–263505 for compounds **4**–**9** contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the CCDC via www.ccdc.cam.ac.uk/data_request/cif.

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