Introduction

Bis(dithiolene) transition metal complexes \([\text{M(S}_2\text{L})_2]\) have attracted a great deal of attention in recent decades in different research fields, from molecular conductors to nonlinear optics catalysis or bioinorganic chemistry.[1] The rich redox behaviour of these complexes, which have the capacity to accommodate partial oxidation states, makes them particularly interesting in the field of conducting and magnetic materials.[2] The \([\text{M(S}_2\text{L})_2]\) complexes can be obtained as dianionic, monoanionic, neutral and even cationic species, depending on both the metal M and the ligand. Associated with this variety of oxidation states, and also depending on the transition metal, there is a rich diversity of possible magnetic moments for these complexes; therefore, they are particularly useful for the design of magnetic systems and for studying the effects of specific variations of local magnetic moments.

One important feature of dithiolene ligands is that they are redox-active species that can formally coordinate either as 1,2-enedithiolate dianions, neutral dithioketones or mixed-valence thioketone radical thiolate monoanions; this makes the correct assignment of the metal oxidation state controversial.[3] The description of the electronic structures of these dithiolene complexes and the contributions of the metal and ligand to their frontier orbitals have been debated, and the correct elucidation has been achieved only recently in a few cases by a combination of theoretical and experimental techniques, in particular, sulfur K-edge X-ray absorption spectroscopy.[4]

In terms of coordination geometry, the majority of the homoleptic bis(dithiolate) complexes of transition metals from groups 8 to 11 have a square-planar coordination geometry. Co and Fe complexes are often arranged as dimers with a 4+1 coordination of the metal centres. Fewer complexes present a tetrahedral coordination, and some cases, such as those with cobalt, may even present well-defined trimeric or polymeric structures,[5] and multimetallic cluster arrangements are known for Ni[6] and Cu.[7]

In the solid state, the planar geometry favours face-to-face intermolecular interactions, which, together with the ability of these complexes to accommodate partially oxidised...
ised states, has led to several highly conducting,[8] metallic[9] or even superconducting[10] systems based on bis(dithiolate) complexes. More recently, highly conducting metallic properties have been found in neutral dithiolate complexes, and this had led to a new paradigm of molecular conductors, the so-called single-component molecular metals (SCMMs).[11] One of the first compounds based on a neutral molecule to present very high electrical conductivity was the neutral thiophenedithiolate complex [Au(α-tpdt)$_2$] (α-tpdt = 2,3-thiophenedithiolate), which has a room-temperature conductivity ($\sigma_{RT}$) of 7 S cm$^{-1}$ as a polycrystalline sample.[12] However, neutral complexes with extended dithiolate ligands containing tetrathiafulvalene (TTF) moieties could be better characterised in single crystals as molecular metals.[11,13] Related bis(dithiolate) complexes based on extended ligands with fused TTF and thiophenic moieties also present high electrical conductivity in the neutral state; [Ni(dtdt)$_2$], {dtdt = 2-(5,6-dihydrothieno[2,3-d][1,3]dithiol-2-ylidene)-1,3-dithiol-4,5-dithiolate} has $\sigma_{RT} = 200$ S cm$^{-1}$.[14]

These findings increased the interest in neutral bis(dithiolate) complexes. However, in general, the neutral complexes present a rather low solubility in organic solvents, and in many cases it has not been possible to isolate single crystals suitable for X-ray diffraction and for detailed measurement of physical properties. Despite the recent demonstration of the possibility to metalize polycarbonate films with the single-component molecular conductor [Au(α-tpdt)$_2$][5] by using a modified reticulate doping technique,[15] the processing of SCMMs into suitable forms for technological applications is still generally limited by their poor solubility, which precludes the application of solution-based methods for the deposition of the complexes over large areas.

In principle, the functionalization of the ligands with appropriate substituents should increase the solubility of these neutral complexes. Indeed, high conductivity and even metallic properties under pressure have been found recently in neutral gold complexes with the N-ethyl-2-thioxo-1,3-thiazoline-4,5-dithiolate ligand[16] and in the corresponding selenium analogues,[17] which are fairly soluble as they have peripheral ethyl groups. In this work, we have prepared and characterised a new family of thiophenedithiolene transition metal complexes based on a new ligand, 5-methylthiophene-2,3-dithiolate (α-mtpdt). This new ligand comprises a thiophene ring substituted with a methyl group and affords neutral complexes that are significantly more soluble than the related unsubstituted complexes, although they have lower electrical conductivity.

### Results and Discussion

The complexes based on the α-mtpdt ligand were obtained from the precursor 4,5-bis(propargylothio)-1,3-dithiol-2-thione (1) according to a previously described procedure,[18] as shown in Scheme 1.

Anionic complexes of this ligand with different transition metals were obtained as salts with general formula [Cat]$_{n}$[M(α-mtpdt)$_2$] [M = Au (2), Ni (3), Fe (4), Co (5), Cu (6), Pt (7), Pd (8) and Cat$^+$ = nBu$_4$N, Ph$_3$P and Ph$_3$As] according to a common procedure under strictly anerobic conditions inside a glovebox. The procedure is based on the hydrolytic cleavage of thione 1 with sodium methoxide in methanol. Although 1 is insoluble in methanol, the resulting dithiolate formed in situ rapidly dissolves. This dithiolate in solution immediately reacts with the appropriate metal chloride to yield the anionic complexes [M(α-mtpdt)$_2$]$^{8-}$, as shown in Scheme 2.

By adjusting the ratio of the dithiolate and the metal halide, the monoanionic complexes [nBu$_4$N][Ni(α-mtpdt)$_2$] (3) could be isolated, and its crystal structure was solved by single-crystal X-ray diffraction. The corresponding monoaionic iron complex 4 appears to form in a similar way. However, it was not possible to isolate it as the pure salt [nBu$_4$N][Fe(α-mtpdt)$_2$], because the reaction product cannot be easily recrystallized as it tends to decompose in solution. This is similar to previous observations for the analogous unsubstituted complex [Fe(α-tpdt)$_2$], for which, however, a few pure salts with other cations could be more easily obtained.[19] For M = Co, Pt and Pd, it was not possible to easily control the oxidation states of the corresponding complexes formed, and the elemental analyses of the isolated precipitates under different conditions always indicated mixtures of dianionic and monoanionic salts.

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![Scheme 1. Synthesis of ligand precursor 1](Image)

![Scheme 2. Synthesis of [M(α-mtpdt)$_2$]$^{8-}$ complexes 2-8.](Image)
instance, in the case of platinum, the brown precipitate obtained in the glovebox was expected to correspond to the dianionic complex; however, it gives solutions that readily turn green upon exposure to air, denoting the expected formation of the monoanion. However, the precipitation of the monoanion is difficult, and solvent evaporation returned the solution from green to brown, and a brown precipitate corresponding to the dianion formed. Similar results have been reported for the Pt complex with the unsubstituted ligand \([\text{Pt}(\alpha\text{-tpdt})_2]^{2-}\). The dianionic salts, which appear to be less soluble and easier to precipitate, are often the dominant product, and single crystals of \([\text{Ph}_4\text{As}]_2[\text{Co}(\alpha\text{-mtpdt})_2]\) \((5)\) and \([\text{Ph}_4\text{As}]_2[\text{Pd}(\alpha\text{-mtpdt})_2]\) \((8)\) suitable for X-ray diffraction could be isolated. For \(M = \text{Cu}\), both the elemental analysis and the ESI mass spectra indicate the formation of the four-metal cluster \([\text{Ph}_4\text{As}]_2[\text{Cu}_4(\alpha\text{-mtpdt})_3]^{i}\) in a way similar to that previously observed for thiophenedithiolate analogues based on the \(\text{tpdt}\) and \(\alpha\text{-tpdt}\) ligands.\(^{[7d]}\) Nevertheless, single crystals suitable for X-ray diffraction could not be obtained owing to apparent poor stability of the copper complexes in solution.

Single crystals of \(2\) and \(3\) suitable for X-ray diffraction were obtained by recrystallization from \(\text{CH}_2\text{Cl}_2/\text{n-hexane}\) (1:1) and slow concentration in the presence of air. These compounds were found to be isostructural and to crystallize in the triclinic system in space group \(P\overline{1}\) with two independent half anionic \([\text{M}(\alpha\text{-mtpdt})_2]^\text{−}\) complexes \(A1\) and \(A2\) in the unit cell; the metal atoms are at an inversion centre, and one independent tetrabutylammonium unit is at a general position. The average Ni–S and Au–S bond lengths are 2.1611(7) and 2.3197(14) Å, respectively, which are comparable to those found for \(\alpha\text{-tpdt}\) analogues\(^{[12,20]}\) and in the expected range for monoanionic Ni and Au dithiolenes. In the case of \(2\), complex \(A1\) presents disorder in the position of the thiophene sulfur atoms, which have a 79/21% distribution over two positions, whereas only one position is present in a \(\text{trans}\) configuration in \(A2\), as observed for both anionic units in \(3\) (see Figure 1a). The anionic units are slightly distorted towards a chair configuration. This distortion is more pronounced in \(A1\) than in \(A2\) and in the Au compound. The angles between the central MS₄ plane and the dithiolate plane for \(A1\) and \(A2\) are 6.55(7) and 3.71(7)°, respectively, for \([\text{Ni}(\alpha\text{-mtpdt})_2]^{2−}\) and 10.70(24) and 6.41(13)°, respectively, for \([\text{Au}(\alpha\text{-mtpdt})_2]^{2−}\) (Figure 1b).

In the crystal structures of \(2\) and \(3\), the average molecular planes of \(A1\) and \(A2\) make dihedral angles of 44.24 and 43.62°, respectively. The crystal structure of these compounds (as shown in Figure 2 for \(3\)) presents an interpenetration of chains of each anion unit along different directions with cations in the free spaces between the two-chain network. The \(A2\) units are arranged in chains of side-by-side dithiolates connected by short \(\text{S···H–C}\) hydrogen bonds.

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**Figure 1.** (a) ORTEP diagrams with anisotropic displacement parameters (ADPs) at 40% probability level for the \([\text{Au}(\alpha\text{-mtpdt})_2]^{2−}\) and \([\text{Ni}(\alpha\text{-mtpdt})_2]^{2−}\) anions in the crystal structures of \(2\) and \(3\), respectively. (b) Side views of the \([\text{Ni}(\alpha\text{-mtpdt})_2]^{2−}\) and \([\text{Au}(\alpha\text{-mtpdt})_2]^{2−}\) anions.
along \(a\). These chains do not interact directly with each other but are linked by the A1 units, which in turn are arranged in chains along \(a-b\) connected through a pair of S−H−C hydrogen bonds.

\[
\text{Figure 2. Crystal structure of } 3. \text{ (a) View along } a. \text{ Anions A1 and A2 are green and blue, respectively, and the cations are red. (b) Partial view of the anionic layer.}
\]

Single crystals of 5 were collected from the reaction mixture under anaerobic conditions. This compound crystallizes in the triclinic system in space group \(P1\) with two independent tetraphenylarsonium cations, C1 and C2, and one independent \([\text{Co(}\alpha\text{-mtpdt})_2]^{2-}\) dianion in the unit cell. The cobalt atom is found in nearly perfect tetrahedral coordination geometry, which is rare for cobalt bis(dithiolene), and the dithiolate mean planes make an angle of 87.74(15)°. The dithiolate moieties are planar within experimental uncertainty (Figure 3). Among a total of 49 structures of cobalt bis(dithiolene) complexes listed in the CCDC, only four are dianionic, and just one of these displays a tetrahedral coordination, \([\text{Ph}_4\text{P}]_2[\text{Co(dmit)}_2]\) (dmit = 4,5-disulfanyl-1,3-dithiole-2-thionate)\(^{[21]}\) the other dianions are square-planar. The Co−S bond lengths in 5 are 3.294(3) Å, which is similar to those of the above-mentioned tetrahedral complex and slightly larger than those of dianionic square-planar (or square-pyramidal if dimerised) bis(dithiolene) cobalt complexes.

The crystalline arrangement of 5 consists of columns of cations parallel to \(b\), separated by columns of non-interacting \([\text{Co(}\alpha\text{-mtpdt})_2]^{2-}\) units (Figures 4). The cations in each column interact with the adjacent cations through a single weak C−H−C hydrogen bond. Each anion is connected to four C1 units (red) and two C2 units (blue) through several short contacts, but there are no short contacts between the anions.

Single crystals of 8 suitable for X-ray diffraction were obtained after successive recrystallizations in the presence of air. Complex 8 crystallizes in the monoclinic system in space group \(P2_1/n\), and the unit cell contains one half \([\text{Pd(}\alpha\text{-mtpdt})_2]^{2-}\) anion with the metal atom located at an inversion centre and one cationic unit at a general position. The anions present typical disorder of the thiophene sulfur atom, which is distributed 80/20% over two positions (Figure 5).

The crystal packing of 8 is shown in Figure 6, in which the anions are depicted in green. The cations, shown in red, are arranged in columns of pairs along \(a\) that separate the anionic chains. This crystal packing is similar to those found in tetraphenylphosphonium salts of dianionic complexes based on thiophenedithiolate ligands, \([\text{Ph}_4\text{P}]_2[\text{Co(}\alpha\text{-tpdt})_2]\), \([\text{Ph}_4\text{P}]_2[\text{Pt(}\alpha\text{-tpdt})_2]\) and \([\text{Ph}_4\text{P}]_2[\text{Pt(tpdt})_2]\)^{[7d]} There are a number of short contacts between the cations and between the cations and anions, namely, charge-assisted S−H−C hydrogen bonds.

As expected for a monoanionic nickel dithiolate, complex 4 is paramagnetic; its effective magnetic moment \(\mu_{\text{eff}}\) is 1.773 \(\mu_B\) at room temperature and remains almost temperature-independent upon cooling to 30 K (Figure 7); the magnetic moment is consistent with the calculated value for a system of independent \(S = 1/2\) spins with an average \(g\) value of 2.047. This is in excellent agreement with the EPR signal, which shows a typical rhombic spectrum with \(g_1 = 2.071, g_2 = 2.065\) and \(g_3 = 2.005\) (Figure S1). At temperatures below 30 K, the decrease of the effective magnetic moment upon cooling denotes weak antiferromagnetic (AF) interactions. The presence of dominant antiferromagnetic interactions at low temperatures is further confirmed by the isothermal magnetization measurements at 1.7 K, and the experimental values are well below the calculated Brillouin function (see inset of Figure 7). The presence of dominant AF interactions is a common feature of many bis(dithiolene) nickel complexes with the exception of \([\text{Bu}_4\text{N}]\text{-}[\text{Ni(}\alpha\text{-tpdt})_2]\), for which the dominant interactions are ferromagnetic.^{[20]}

For \(M = \text{Co}\), a pure sample with a mass large enough for magnetic characterisation was obtained only for \([\text{Ph}_4\text{P}]_2[\text{Co(}\alpha\text{-mtpdt})_2]\). This salt is assumed to be isostructural to the \(\text{Ph}_4\text{As}\) salt 5. Its effective magnetic moment \(\mu_{\text{eff}}\) at room temperature is 4.12 \(\mu_B\); \(\mu_{\text{eff}}\) then decreased slowly upon...
Figure 3. ORTEP diagrams with ADPs at 40% probability level for the [Co(α-mtpdt)₂]²⁻ anion in 5.

Figure 4. Crystal structure of 5 viewed along a. Anions are green, and cations C1 and C2 are red and rose, respectively.

cooling to ca. 3.9 μB at 100 K and then more rapidly for lower temperatures (Figure S2). This value is in fair agreement with an \( S = \frac{3}{2} \) system with \( g = 2.035 \), as expected for a d⁶ cobalt ion with tetrahedral coordination.

The copper compound 6 was found to be diamagnetic, as expected for this type of cluster compound. The material resulting from the preparation of the palladium compound was also found to be essentially diamagnetic, in agreement with the crystal structure determined for an isolated crystal of 8; therefore, this diamagnetic dianionic Pd complex is the dominant product. The EPR spectrum of this sample shows a weak signal with \( g \) values of 2.045, 2.172 and 1.960, which is ascribed to contamination with the monoanionic complex.

The redox properties of the [M(α-mtpdt)₂] complexes were studied by cyclic voltammetry. The redox processes observed are comparable to those previously described for the [M(α-tpdt)₂] complexes with the unsubstituted ligand, albeit they are generally at higher oxidation potentials for the unsubstituted ligand. The voltammograms of the Ni and Au complexes are shown in Figure 8, and those of all other complexes are shown in Figure S3. The nickel complex shows two pairs of quasireversible redox waves at –0.923 and –0.185 V versus Ag/AgNO₃,
which are ascribed to the couples \([\text{Ni}(\alpha\text{-mtpdt})_2]^{2-}/[\text{Ni}(\alpha\text{-mtpdt})_2]^{-}\) and \([\text{Ni}(\alpha\text{-mtpdt})_2]/[\text{Ni}(\alpha\text{-mtpdt})_2]^{3+}\), respectively. The corresponding processes for the Ni analogue with the \(\alpha\)-tpdt ligand occur at more positive values of \(-0.562\) and \(0.253\) V[20]. Upon cycling the \([\text{Ni}(\alpha\text{-mtpdt})_2]^{2-}\) complex to more positive potentials above the onset of an oxidation wave at ca. \(0.8\) V, two reductions processes at \(0.383\) and \(0.368\) V become evident and are indicative of the formation of a cationic complex. The gold complex presents one pair of asymmetric waves centred at \(0.121\) V versus Ag/AgNO₃, which are ascribed to the couple \([\text{Au}(\alpha\text{-mtpdt})_2]^{-}/[\text{Au}(\alpha\text{-tpdt})_2]^{0}\) (Figure 8). The asymmetry of the waves is enhanced after successive cycles and suggests that an Au deposition process may occur at ca. \(0\) V. The platinum and palladium compounds present pairs of quasireversible waves, which are ascribed to the \([\text{M}(\alpha\text{-mtpdt})_2]^{2-}/[\text{M}(\alpha\text{-tpdt})_2]^{0}\) couple at \(-0.199\) and \(-0.138\) V, respectively. The close proximity of these potentials to the atmospheric oxygen redox potential explains the previously described difficulty in controlling the oxidation state of these complexes upon recrystallization.

Although the processes seen in cyclic voltammetry are indicative of the formation of neutral species, attempts to electocrystallise the Au and Ni neutral complexes were unsuccessful, probably owing to their relatively high solubility. However, these neutral complexes were easily obtained by chemical oxidation of the corresponding anions with iodine. By this means, it was possible to isolate the neutral complexes \([\text{Ni}(\alpha\text{-mtpdt})_2]^{0}\) (9) and \([\text{Au}(\alpha\text{-mtpdt})_2]^{0}\) (10) from acetone solutions of 3 and 2, respectively.
The neutral gold and nickel compounds are both considerably soluble in dimethylformamide and dimethyl sulfoxide and moderately soluble in acetone and acetonitrile. This allowed the recrystallization of 9 to yield single crystals suitable for X-ray diffraction. Compound 9 crystallizes in the monoclinic system in space group $P2_1/c$, and the unit cell contains one [Ni($\alpha$-mtpdt)$_2$] molecule with the nickel atom located at an inversion centre. The [Ni($\alpha$-mtpdt)$_2$] molecule is planar within the experimental uncertainty. As in most crystal structures with thiophene dithiolene ligands, a disorder of the sulfur atom of the thiophene ring over two positions (50/50%) is also observed (Figure 9). This disorder is most likely orientation disorder of molecules in a trans configuration. The Ni–S bond lengths (average value 2.150 Å) are only slightly smaller than the values obtained for the anionic species and comparable to those of the few neutral Ni complexes described to date with unextended dithiolene ligands.[22] However, the ligand bond lengths of the neutral complex 9 are significantly different from those of the monoanionic complex 3 (see Table S8), which clearly indicates that the oxidation from a monoanion to a neutral compound is a ligand-centred process, as has been observed with other ligands such as maleonitrile dithiolate (mnt).[4b,4c] Unfortunately, no firm conclusions can be drawn from a comparison of the bond lengths in the ligand precursor 1 owing to the relatively poor quality of the structure determination.

The crystalline arrangement of 9 consists of parallel and out-of-registry uniform stacks of [Ni($\alpha$-mtpdt)$_2$] along the $a$ axis (Figure 10). The molecules are tilted by ca. 22.95° towards the stacking axis and stack with an Ni over S overlap mode (Figure 11); the distance between molecular planes is 3.508 Å. The shortest intermolecular contact along the stacks is Ni–S1* (* = 1 + $x$, $y$, $z$), which has a distance of 3.517 Å; all others are slightly above the sum of the van der Waals radii. The methyl group prevents very short contacts between neighbouring columns along $c$. However, each molecule is connected to four other units in side stacks along $b$ by S3–H3–C3 hydrogen bonds of 2.656 Å and S3–S3A contacts in the range 3.419–3.571 Å, depending on the possible configuration (see Table S7).

The paramagnetic susceptibilities of the neutral complexes 9 and 10 are plotted as a function of temperature in Figure 12. The neutral Ni complex presents a rather large...
paramagnetism that corresponds to an effective magnetic moment of 1.22 μB at room temperature, gradually decreases upon cooling to 1.1 μB at 25 K, and more rapidly decreases for lower temperatures. Similar magnetic behaviour has been reported for two other neutral Ni bis(dithiolenes) with extended thiophene ligands, namely, [Ni(dtdt)2] with μeff ≈ 1.1 μB and [Ni(α-tdt)2] {α-tdt = 2-(thieno[2,3-d]-[1,3]dithiol-2-ylidene)-1,3-dithiol-4,5-dithiolate} with μeff ≈ 1.5 μB.[14]

The neutral Au complex 10 presents a somewhat smaller paramagnetic susceptibility of ca. 1.5 × 10^{-4} emu mol^{-1}, which is approximately temperature-independent down to 50 K and is reminiscent of a Pauli-type paramagnetism with a small Curie tail of paramagnetic impurities, as is typical for molecular conductors and similar to that described for the neutral gold analogue [Au(α-tpdt)2].[12]

The crystals obtained for 9 and 10 were too small to allow electrical transport measurements of single crystals; therefore, thermopower and conductivity measurements were performed with compressed polycrystalline powder samples. Both compounds are modest semiconductors with a well-defined thermally activated behaviour of the electrical conductivity (Figure 13). The room-temperature conductivity of 9 is 5.2 × 10^{-7} S cm^{-1} with an activation energy of 325 meV, and the gold complex 10 presents a slightly higher conductivity of 8.7 × 10^{-5} S cm^{-1} at room temperature with an activation energy of 287 meV. This semiconducting behaviour was also confirmed by a large room-temperature thermoelectric power of ca. 400 μV K^{-1}, which slightly increases upon cooling for both compounds.

The modest conductivity values found certainly reflect the poor intermolecular overlap, which is determined by the position of the methyl groups, and also the effect of disorder on the intermolecular interactions. However, these interactions may significantly increase if the molecules can approach; therefore, the possibility to achieve a higher conductivity and even a metallic regime under pressure, as was observed for ethyl-substituted dithiolenes,[16,17] cannot be excluded and will be the topic of future research work.

Conclusions

A new family of transition metal complexes [M(α-mtpdt)2] with a methyl-substituted thiophenedithiolene ligand and different transition metals (M = Au, Ni, Fe, Co, Pt and Pd) has been prepared as tetraalkylammonium and tetraarylphosphonium or -arsonium salts. The redox behaviour of these complexes was characterized by cyclic voltammetry, and their magnetic properties were investigated by EPR spectroscopy and magnetic susceptibility measurements. The gold, nickel and iron complexes can be easily prepared as monoanionic salts, and the structures of the first two were determined by single-crystal X-ray diffraction. The oxidation state of the Co, Pd and Pt complexes is more difficult to control, and preparations often lead to mixtures of monoanionic and dianionic complexes; however, the crystal structure of the first two as dianionic salts could be solved by single-crystal X-ray diffraction. The cobalt complex has a rare tetrahedral coordination geometry. The complexation of copper by this ligand leads to a distinct structure with a four-metal cluster [Cu4(α-mtpdt)3]^{2–}. The Ni and Au complexes can be obtained in their neutral state as stable compounds and are fairly soluble in organic solvents such as acetonitrile and dichloromethane. However, the methyl groups of the ligands prevent strong intermolecular interactions in the solid state, and the electrical conductivity was also confirmed by a large room-temperature thermoelectric power of ca. 400 μV K^{-1}, which slightly increases upon cooling for both compounds.

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trical conductivities of these neutral complexes are rather modest when compared with those of their unsubstituted analogues.

**Experimental Section**

**General Remarks:** The syntheses of the complexes were performed in a glovebox. Solvents were purified by standard procedures, dried and degassed; methanol was stored with 3 Å molecular sieves. Subsequent manipulations were performed with exposure to air and with standard commercial solvents. Other chemicals were obtained commercially and used without further purification. [Et₄N][Zn(dmit)₂][Zn(dmit)₂] and 4,5-bis(propargylthio)-1,3-dithiol-2-thione were prepared as described previously. IR spectra were obtained with Shimadzu FTIR-8400S and Perkin–Elmer 577 spectrophotometers. Melting points were measured with a Stuart Melting Point Apparatus SMP3 to a maximum temperature of 350 °C. Elemental analyses were performed with a CHNS Carlo Erba apparatus.

**Cyclic Voltammetry:** The cyclic voltammetry data were obtained by using a BAS C3 Cell Stand. The voltammograms were recorded at room temperature at different scan rates with a Pt wire working and counter electrode and an Ag/AgNO₃ reference electrode in a cone-shaped cell containing the unstirred solution. Fresh solutions with a concentration of 10⁻³ M of the analyte and 10⁻¹ M of [nBu₄N][PF₆] as supporting electrolyte were prepared with distilled solvents and usually used in volumes of ca. 10 mL. Under these experimental conditions, E₁/₂ for the ferrocenium/ferrocene couple was 0.199 mV.

**X-ray Diffraction:** The single-crystal X-ray diffraction data were collected with a Bruker AXS APEX diffractometer with a CCD detector by using graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å) in the θ- and ω-scan modes. A semiempirical absorption correction was performed with SADABS.[24] The data collection, cell refinement and data reduction were performed with the SMART and SAINT programs.[25] The structures were solved by direct methods and refined by full-matrix least-squares methods with the SHELXL97 program[27] within the winGX software package.[28] Non-hydrogen atoms were refined with anisotropic thermal parameters, whereas the H atoms were placed in idealized positions and allowed to ride on their parent C atoms. The molecular graphics were prepared with ORTEP 3.[29] CCDC-985397 (for 2), -985398 (for 3), -985399 (for 5), -985400 (for 8) and -985401 (for 9) 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.

**Magnetic Measurements:** Magnetization measurements in the temperature range 2–320 K were performed with an S700X superconducting quantum interference device (SQUID) magnetometer with a 70 kG magnet (Cryogenic Ltd.) with polycrystalline samples inside previously measured gel capsules. The paramagnetic susceptibility was obtained from the experimental magnetization data after a correction for diamagnetism, which was estimated from the tabulated Pascal constants as −369.2 × 10⁻⁶, −627.8 × 10⁻⁶, −163.2 × 10⁻⁶ and −184.2 × 10⁻⁶ emu/mol for 3, 5, 9 and 10, respectively. EPR spectra at 77 K were obtained with a Bruker ESP 300E X-band spectrometer equipped with an ER401KX microwave bridge, a rectangular cavity operating in T102 mode, a Bruker variable-temperature unit, an Oxford Instruments ESR-900 cryostat and an ER 032M field controller system. The modulation amplitude was kept well below the line width, and the microwave power was well below saturation.

**Electrical Transport Measurements:** Electrical conductivity and thermoelectric power measurements were performed with compressed pellets of the polycrystalline material of elongated parallel-epipedral shape. The measurement cell was attached to the cold stage of a closed-cycle helium refrigerator to allow measurements in the temperature range 20–320 K. In a first step, the thermopower was measured by using a slow alternating current (ac; ca. 10⁻² Hz) technique[30] by attaching two 60 μm diameter 99.999% pure Au wires (Goodfellow metals), thermally anchored to two quartz reservoirs, with Pt paint (Demetron 308A) to the extremities of the elongated sample as in a previously described apparatus[32] controlled by a computer.[33] The oscillating thermal gradient was kept below 1 K and measured with a differential chromel–AuFe (0.05 atom-% Fe) thermocouple, and the sample temperature was measured with a previously calibrated thermocouple of the same type. The absolute thermoelectric power of the sample was obtained after correction for the absolute thermopower of the Au leads by using the data of Huebner.[32] In a second step, two additional gold wires were attached to the sample, and the electrical resistance was measured by using a four-probe configuration to impose direct and reverse currents well below 0.1 μA through the sample, and the voltage was measured with a Keithley 619 electrometer.

[nBu₄N][Au(α-mtpdt)₂] (2): Compound 1 (100 mg, 4.9 × 10⁻⁴ mol) was added to a solution of sodium methoxide (0.3 M), and the mixture was stirred for 2 h. The resulting yellow solution was filtered and added to a solution of KAuCl₄ (95 mg, 2.5 × 10⁻⁴ mol), and the resulting solution was stirred for 1 h. The golden solution was then filtered and added to a solution of nBu₄NBr (161 mg, 5 × 10⁻⁴ mol) in methanol. A light brown precipitate was collected by filtration, washed with cold methanol and dried under vacuum. Brown single crystals were obtained from recrystallization in CH₂Cl₂/n-hexane (1:1) and slow concentration. Yield: 30% (54.8 mg); m.p. 165 °C. IR (KBr): ν = 370, 398 (s, Au-S), 636 (m, HC=CH arom), 757 (s, C–H aliph), 837, 865 (m, C–S), 1327, 1365, 1394, (s, C–H aliph), 2960–3000 (br., C–H arom) cm⁻¹. MS (ESI): m/z (%) = 516.8 (100) [Au(α-mtpdt)₂]⁺. C₂₆H₄₈AuNS₆ (795.97): calc. C 40.93, H 7.66, N 2.00, S 24.79.

**Crystal Data and Structure Refinement for 2:** C₆H₄AuN₂S₆. M = 759.95 g/mol⁻¹, crystal size: 0.30 × 0.10 × 0.03 mm, triclinic, space group: P1̅1, a = 9.7324(2), b = 10.8836(3), c = 16.1937(4) Å, α = 72.1280(10), β = 79.5370(10), γ = 71.0300(10)°, V = 1537.46(7) Å³, Z = 2, dcalc = 1642 kg m⁻³, μ = 5.208 mm⁻¹, λ = 0.71073 Å, T = 150(2) K, θ range: 2.55–25.68°, reflections collected: 18402, independent: 5768 (Rint = 0.0419), 316 parameters. The structure was solved by direct methods and refined by full-matrix least squares on F²; final R indices [I > 2σ(I)]: R₁ = 0.0321, wR₂ = 0.0691.

[nBu₄N][Ni(α-mtpdt)₂] (3): According to the same procedure described for 2 with NiCl₂·6H₂O (60 mg, 2.5 × 10⁻⁴ mol) instead of KAuCl₄, a dark red solution was obtained. The solution was filtered and added to a solution of nBu₄NI (185 mg, 5 × 10⁻⁴ mol) in methanol. The resulting solution was stirred under air until it turned dark green and formed a dark green precipitate, which was collected by filtration, washed with cold methanol and dried under vacuum. Single crystals were obtained by recrystallization from CH₂Cl₂/n-hexane (1:1) and slow concentration. Yield: 76% (114 mg); m.p. >350 °C. IR (KBr): ν = 663 (m, HC=CH arom), 813 (s, C–H aliph), 841, 862, 679 (m, C–S), 1333, 1431, 1520 (w, C–H aliph), 3020–2980 (br., C–H arom) cm⁻¹. MS (ESI): m/z (%):
Crystal Data and Structure Refinement for 3: C₆₃H₃₂Cu₄P₂S₉ (1146.09 gmol⁻¹, crystal size: 0.34 \(\times\) 0.28 \(\times\) 0.11 mm). Yield: 100% (14.3 mg). IR (KBr): \(\nu = 378, 385\) (s, Au–S), 685 (s, C–H aliph), 763 (s, C–H aliph), 841, 862, 679 (m, C–H aliph), 3020–3080 (br., C–H arom) cm⁻¹. MS (ESI): \(m/z\) (\%): 377.8 (100) [Ni(μ-mdpt)]⁻, C₂H₄OHNiS₆ (379.24) calcd. C 53.52, H 3.71, S 20.41; found C 53.22, H 3.71, S 20.41.

Crystal Data and Structure Refinement for 4: C₅₈H₄₈AsPdS₆ (1193.56 gmol⁻¹, crystal size: 0.50 \(\times\) 0.30 \(\times\) 0.15 mm). Yield: 36% (6.8 mg). IR (KBr): \(\nu = 3378, 3395\) (m, HC=CH arom), 734, 763, 841, 862, 933, 1221, 1263, 1371, 1373, 1388, 1400, (w, C–H aliph) cm⁻¹. MS (ESI): \(m/z\) (\%): 377.8 (100) [Ni(μ-mdpt)]⁻, C₂H₄OHNiS₆ (379.24) calcd. C 53.52, H 3.71, S 20.41; found C 53.22, H 3.71, S 20.41.

Crystal Data and Structure Refinement for 5: C₅₈H₄₈AsCo₆S₆ (1146.15) calcd. C 53.53, H 3.70, S 22.52; found C 55.21, H 4.45, S 18.02.

Crystal Data and Structure Refinement for 6: CuCl₂·2H₂O (42 mg, 2.5 \(\times\) 10⁻⁴ mol) instead of KAuCl₄ and nBu₄NBr, respectively. An abundant black crystalline precipitate was collected by filtration after the reaction mixture had rested in a glovebox for 1 d. Black needles were selected, and the structure was determined by single-crystal X-ray diffraction. Yield: 25–35% (77 mg); m.p. 95 °C. C₃₅H₂₆AsCo₆S₆ (618.85) calcd. C 50.46, H 7.17, N 2.26, S 31.91; found C 49.95, H 7.90, N 2.42, S 31.57.

Crystal Data and Structure Refinement for 7: [CuCl₂·2H₂O]CuCl₆H₂O (101 mg, 2.4 \(\times\) 10⁻⁴ mol) instead of KAuCl₄ and nBu₄NBr, respectively. The final solution was filtered and exposed to air, whereupon it turned from light brown to grey. The green precipitate was collected after the addition of water. Yield: 3% (101 mg); m.p. 165 °C; C₁₅₃H₄₄AsPdS₆ (1194.44) calcd. C 58.32, H 4.05, S 16.11; found C 58.44, H 4.11, S 22.59.

Crystal Data and Structure Refinement for 8: C₆₃H₃₂Cu₄P₂S₉ (1146.09 gmol⁻¹, crystal size: 0.34 \(\times\) 0.24 \(\times\) 0.06 mm, triclinic, space group: P1, \(a = 11.7973\) (8), \(b = 11.8895\) (7), \(c = 20.6576\) (2), \(\alpha = 92.313(3)^\circ\), \(\beta = 91.296(2)^\circ\), \(\gamma = 113.936(2)^\circ\), \(V = 2643.7(4)^{3}\) \(\AA^3\), \(Z = 2\), \(d_{calc} = 1440\) kg m⁻³, \(\mu = 1.841\) mm⁻¹, \(\lambda = 0.71073\) Å, \(T = 150(2)\) K, \(\theta\) range = 2.75–25.68°, reflections collected: 14018, independent: 5640 (\(R_{int} = 0.0324\)), 311 parameters. The structure was solved by direct methods and refined by full-matrix least squares on \(F^2\); final R indices \(I > 2\sigma(I)\): \(R_I = 0.0393, wR = 0.1092\).


Dithiolene Complexes


5-Methylthiophene-2,3-dithiolene Transition Metal Complexes

Keywords: Dithiolene complexes / S ligands / Coordination chemistry / Cyclic voltammetry / Magnetic properties

A family of transition metal complexes \([M(\alpha\text{-mtpd}t)_2]\) (M = Au, Ni, Fe, Cu, Co, Pt and Pd) with a methyl-substituted thiophenedithiolene ligand (\(\alpha\text{-mtpd}t\)) are synthesised. The Ni and Au complexes can be obtained in their neutral state as stable compounds; they are fairly soluble in organic solvents and have semiconducting properties.