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Copper Dithiolene [Cu(SC₆H₂Cl₂S)₂][−] Units Connected to Alkaline/Copper Complexes: From Ionic Assemblies to Discrete Molecular Entities and Coordination Polymers

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Direct reaction between Cu(ClO₄)₂ and 3,6-dichloro-1,2-benzenedithiol (HSC₆H₂Cl₂SH) in the presence of basic salts, *i.e.* NaOH, KOH, Rb₂CO₃ or RbCO₃, leads to a series of bis(dithiolato)cuprate(III) [Cu(SC₆H₂Cl₂S)₂][−] coordination complexes and coordination polymers depending upon the metal counterion used in the process. These compounds clearly show the robustness of the bis(dithiolato)cuprate(III) [Cu(SC₆H₂Cl₂S)₂][−] entities, showing a nearly planar structure which is retained not only when they interact weakly with alkaline cations but also when they do it with more strongly interacting copper(I) ions. In the latter case, the interaction provides one of the few examples so-far reported on Cu^I/Cu^{III} mixed oxidation state compounds. This study also shows that the sulfur and chloro donor atoms of the [Cu(SC₆H₂Cl₂S)₂][−] entity are able to anchor soft-metal cations giving rise to the formation of coordination polymers. A semiconductor behaviour is observed in the polymers {[Rb(OH₂)] [Cu(SC₆H₂Cl₂S)₂]}_n and {[Cs(OH₂)] [Cu(SC₆H₂Cl₂S)₂]}_n.

Introduction

Metal bis(1,2-dithiolene) complexes have gained a considerable research interest due to the important physical properties they may exhibit, as well as the structural diversity and their redox chemistry.^{1–14} As far as we know, most of the copper bis(dithiolene) derivatives are ion pair molecules^{15–16} being scarce the examples concerning the formation of coordination polymers. Thus, it has been reported the syntheses of CPs {[K(CH₃COCH₃)₃][Cu(btddt)₂]}_n, {[K(NCCH₃)₂][Cu(btddt)₂]}_n (btddt = 2,1,3-benzenethiadiazole-5,6-dithiolate)¹⁷ and the PC (porous coordination polymer) Cu[Cu(pdt)₂]₂ (pdt = pyrazine-2,3-dithiolate). On the other hand, it is well-known that the nature of the counter-cation and the coordinating solvents used in the crystallization process among other factors can affect the dimensionality of the polymers.^{17–19} We have previously described^{20,21} a study carried out to evaluate the effect of the size of the alkali countercation as well as of the solvent used in the crystallization process on the resulting structures containing the dianionic entity [Fe₂(SC₆H₂Cl₂S)₄]^{2−}. Herein we report on the one-pot syntheses and detailed structural characterization of

compounds [M(thf)₆][Cu(SC₆H₂Cl₂S)₂] [M = Na (**1**); K (**2**)], {[Rb(OH₂)] [Cu(SC₆H₂Cl₂S)₂]}_n (**3**), {[Cs(OH₂)] [Cu(SC₆H₂Cl₂S)₂]}_n (**4**), 2[(CH₃CN)₃Cu(μ-SC₆H₂Cl₂S)Cu(SC₆H₂Cl₂S)]·[(CH₃CN)Cu(μ-SC₆H₂Cl₂S)Cu(SC₆H₂Cl₂S)]₂·2CH₃CN (**5**), and {[K(OH₂)] [Cu(SC₆H₂Cl₂S)₂]}_n (**6**). Additionally, preliminary electrical characterization has been carried out for compounds **3** and **4** showing a semiconductor behaviour.

Results and discussion

In previous works, it was described the reaction between Na[Cu(pdt)₂]·2H₂O (pdt = 2,3-pyrazinedithiolate) and CuI to yield compound Cu^I[Cu^{III}(pdt)₂].¹⁸ Based on this fact and our results concerning the formation of alkaline iron-dithiolate CPs,^{20,21} we decided to evaluate the possibility of obtaining Cu/Fe dithiolate CPs replacing Cu⁺ by Na⁺ from the precursor {[Na₂(μ-OH₂)₂(thf)₂][Fe₂(SC₆H₂Cl₂S)₄]}_n.²⁰ Thus, the reaction between {[Na₂(μ-H₂O)₂(thf)₂][Fe₂(SC₆H₂Cl₂S)₄]}_n and CuI was carried out under argon atmosphere and continuous stirring for 4 h, the solvent was removed and the residue crystallized in THF/n-heptane. Instead of the expected Cu/Fe polymer, single crystal X-ray diffraction structure elucidation showed the formation of compound [Na(thf)₆][Cu(SC₆H₂Cl₂S)₂] **1**.

This result indicated that a transmetalation reaction, as well as the oxidation of Cu(I) to Cu(III) probably because of the presence of oxygen dissolved in the solvent, had taken place. When this reaction was carried out using an open-air atmosphere instead, compound **1** was obtained in 27% yield. Finally, we have confirmed that compound **1** can be obtained in better yield (90%) by the reaction between NaOH, HSC₆H₂Cl₂SH and Cu(ClO₄)₂·6H₂O in air atmosphere (Scheme 1).

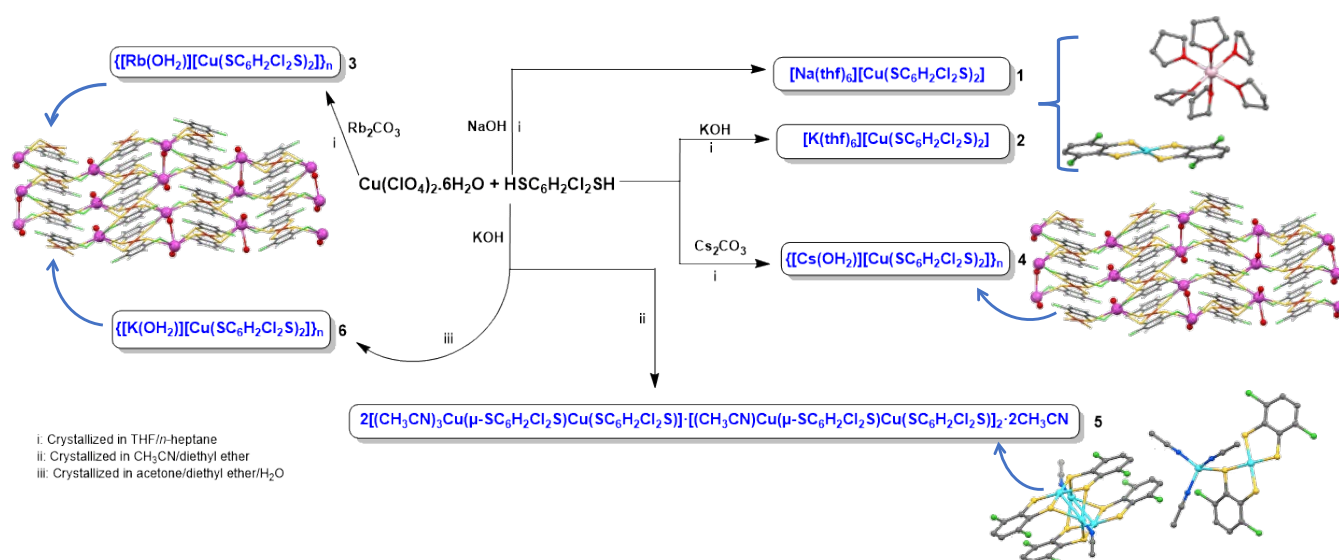
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† Supplementary Information (ESI) available: additional structural information is available free of charge. Files in CIF format for compounds **1–6** are available free of charge [CCDC 1590257–1590262]. See DOI: 10.1039/x0xx00000x



Scheme 1. Summary of the reactions.

This latter synthetic procedure was also employed to obtain compound **2** replacing NaOH by KOH.

As can be seen in Fig. 1, compounds [Na(thf)₆][Cu(SC₆H₂Cl₂S)₂] **1** and [K(thf)₆][Cu(SC₆H₂Cl₂S)₂] **2** comprise ionic structures made up by the anionic entity [Cu(SC₆H₂Cl₂S)₂][−] and [M(thf)₆]⁺ (M: Na⁺ and K⁺) cationic complexes as counterion. It is worth noting that compound **1** is isostructural with the iron derivative [Na(thf)₆][Fe(SC₆H₂Cl₂S)₂].²¹

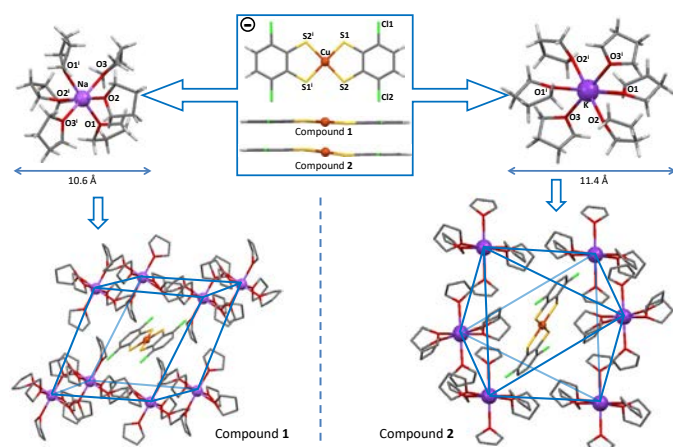


Fig. 1. Building units of the ionic architecture of compounds **1** and **2** showing the arrangement of the [M(thf)₆]⁺ (M= Na⁺ and K⁺) complex cations around the anionic [Cu(SC₆H₂Cl₂S)₂][−] discrete entities.

The Cu atom in the anionic moiety is coordinated to four sulfur atoms corresponding to two chelating dithiolato ligands

affording a square-planar environment, as usual for d⁸ copper(III) metal centres. The sodium/potassium is coordinated to six oxygen atoms of the thf solvent yielding an octahedral geometry around this metal. In both compounds, the two 3,6-dichlorobenzene-1,2-bis(thiolate) ligands coordinated to the metal centre are parallel but not coplanar as they are displaced 0.20 and 0.42 Å for compounds **1** and **2**, respectively.

Consequently, the CuS₄ coordination plane is tilted 3.9° (for **1**) and 8.4° (for **2**) with respect to the 3,6-dichlorobenzene-1,2-bis(thiolate) mean plane. The Cu-S and Na-O distances (Tables S1 and S2), are in the range found for analogous complexes.^{21,22} Despite these apparent similarities between the building blocks, the supramolecular architecture differs significantly. The differences do not seem to come from the presence of strong supramolecular interactions such as hydrogen bonds, aromatic stacking or halide...halide contacts.

Indeed, the presence of that kind of interactions usually leads to lamellar architectures in which layers of alternated cationic and anionic entities. In this case, the assembly of the charged building units comes from the optimization of the electrostatic forces by surrounding each ionic entity by the greatest number of complex entities of opposite charge that can be accommodated considering their size.

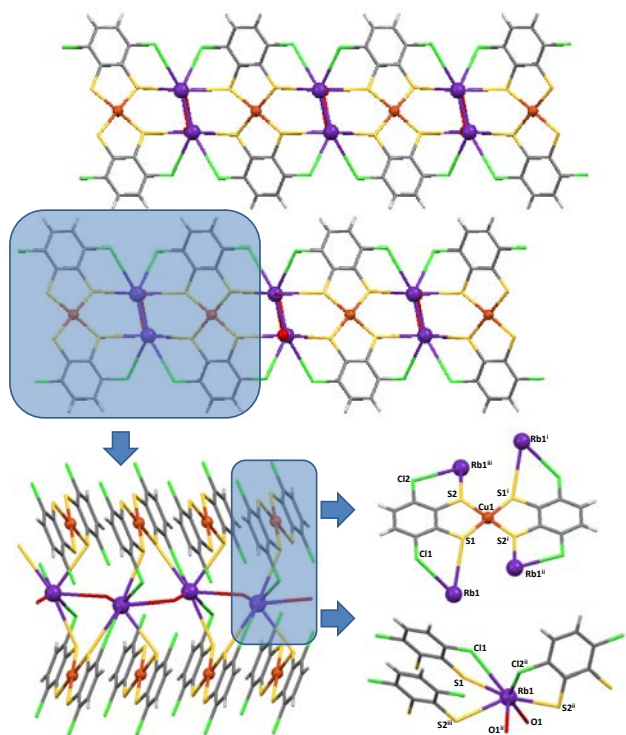


Fig. 2. Details of the 2D coordination architecture of compound **3**, showing the features around the copper(III) and rubidium metal centres. The disorder of the rubidium and water molecules has been omitted for clarity.

In fact, the $[\text{Cu}(\text{SC}_6\text{H}_2\text{Cl}_2\text{S})_2]^-$ entities are surrounded by a different number of cationic complexes depending on the size of the alkali cations, being eight in a pseudo-cubic arrangement for compound **1** (Na) or six in a pseudo-octahedral arrangement for compound **2** (K).

Analogous reactions to those described above for the synthesis of compounds **1** and **2** but using Rb_2CO_3 or Cs_2CO_3 as a base, give rise to the new 2D coordination polymers $\{[\text{Rb}(\text{OH}_2)]\text{Cu}(\text{SC}_6\text{H}_2\text{Cl}_2\text{S})_2\}_n$ **3** (Fig. 2) and $\{[\text{Cs}(\text{OH}_2)]\text{Cu}(\text{SC}_6\text{H}_2\text{Cl}_2\text{S})_2\}_n$ **4** (Fig. 3), respectively. These compounds involve the same square planar $[\text{Cu}(\text{SC}_6\text{H}_2\text{Cl}_2\text{S})_2]^-$ entities but the softer nature of the rubidium and caesium cations apparently promotes their coordination to the sulfur and chloro soft donor atoms of the 3,6-dichlorobenzene-1,2-bis(thiolate) ligands. The steric hindrance generated by the anchorage of the alkali cations to the $[\text{Cu}(\text{SC}_6\text{H}_2\text{Cl}_2\text{S})_2]^-$ entities does not allow the incorporation of the THF molecules into the coordination sphere but the smaller size of the water molecules allow their inclusion within the coordination sphere. Selected distances for compound **3** and **4** are collected in Tables S3 and S4.

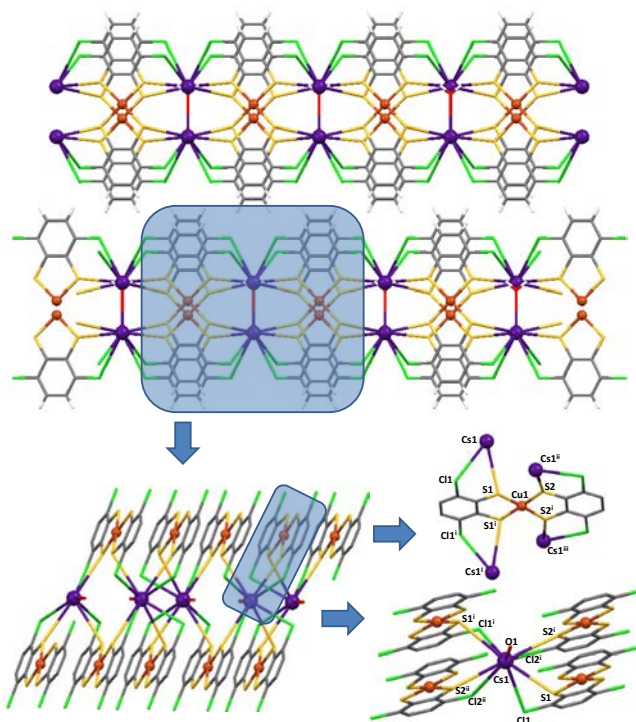


Fig. 3. Details of the 2D coordination architecture of compound **4** showing the features around the copper(III) and caesium metal centres.

As described above, the bulky alkaline cations act as linkers between the copper-dithiolate entities giving rise to 2D coordination polymers. The main difference between both crystal structures (Fig. S1) comes again from the size of the alkali cations that exerts a decisive influence on the number of coordinative interactions that it can establish. In such a way, Rb^+ cation is located in a $\text{RbS}_3\text{Cl}_2\text{O}_2$ environment coordinated to sulfur and chlorine atoms belonging to three $[\text{Cu}(\text{SC}_6\text{H}_2\text{Cl}_2\text{S})_2]$ fragments and two bridging water molecules. At this point, it is worth mentioning that the rubidium atom and the water molecules are disordered between two symmetry related positions (Fig. S2). On the other hand, the bigger Cs^+ cation presents a $\text{CsS}_4\text{Cl}_4\text{O}$ coordination sphere in which the metal centre is coordinated to four $\kappa\text{Cl}, \kappa\text{S}$ -chelating 3,6-dichlorobenzene-1,2-bis(thiolate) ligands from four adjacent $[\text{Cu}(\text{SC}_6\text{H}_2\text{Cl}_2\text{S})_2]^-$ fragments and a terminally coordinated water molecule.

A topological analysis of the crystal structure of compounds **3** and **4** was performed with the aid of the TOPOS software,²³⁻²⁵ in which copper bis-dithiolene fragments $[\text{Cu}(\text{SC}_6\text{H}_2\text{Cl}_2\text{S})_2]^-$ and alkaline M^+ metals were taken as nodes, and the coordination bonds between them as linkers, resulted a **sql** uninodal tetraconnected Shubnikov tetragonal plane net with $(4^4.6^2)$ symbol for both compounds (Fig. S3). Additionally, compounds **1-4** were characterized by ^1H and ^{13}C NMR as well as IR spectroscopy. All these compounds are diamagnetic in agreement with a Cu(III) oxidation state located in a d^8 square-planar geometry.

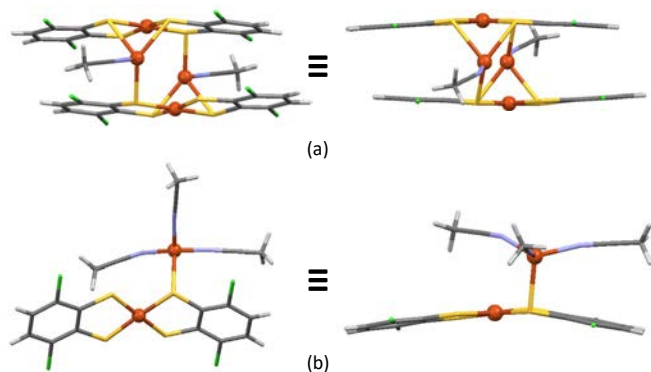


Fig. 4. Discrete tetranuclear (a) and dinuclear (b) entities found in compound 5.

To complete this study, we have considered interesting to evaluate the influence of the use of different coordinating solvents in the crystallization of the potassium containing compound. As it was mentioned before, the use of wet THF/*n*-heptane afforded the ionic compound $[K(thf)_6][Cu(SC_6H_2Cl_2S)_2]$ **2**, but if acetonitrile/diethyl ether was used instead, crystals of a new compound of formula $2[(CH_3CN)_3Cu(\mu-SC_6H_2Cl_2S)Cu(SC_6H_2Cl_2S)] \cdot [(CH_3CN)Cu(\mu-SC_6H_2Cl_2S)Cu(SC_6H_2Cl_2S)]_2 \cdot 2CH_3CN$ (**5**) were obtained in which copper(I) and copper(III) metal centres coexist (Fig. 4). It is worth mentioning that this is one of the few cases in which such coexistence takes place.²⁶⁻³⁰

The presence of copper(I) ions to counterbalance the charge of the $[Cu(SC_6H_2Cl_2S)_2]^-$ fragments generates a substantially different crystal structure. As in compounds **3** and **4**, the soft nature of this cation promotes its coordination to the sulfur donor atoms of the 3,6-dichlorobenzene-1,2-bis(thiolate) ligands. However, the low coordination numbers typical of d^{10} copper(I) metal centres does not promote an extensive polymerization of the $[Cu(SC_6H_2Cl_2S)_2]^-$ entities based on its coordination. In fact, the crystal structure of this compound is comprised of two discrete and one neutral coordination polynuclear entities: a dinuclear complex build up by the anchorage of a $[Cu(NCCH_3)_3]^+$ fragment to a $[Cu(SC_6H_2Cl_2S)_2]^-$ entity through one of the sulfur atoms, and a tetranuclear complex in which two $[Cu(SC_6H_2Cl_2S)_2]^-$ entities are doubly bridged by $[Cu(NCCH_3)_2]^+$ fragments. The copper(I) metal centre in the dinuclear complex adopts a quite regular tetrahedral geometry with a N_3S donor set, but in the tetrameric complex the tetrahedral geometry is more distorted basically due to the fact that its NS_3 donor set involves two sulfur atoms coordinated to the same copper(III) metal centre. This latter feature of the tetrameric entity makes the copper...copper distance (2.690 Å) to be shorter than the sum of the van der Waals radii indicating the presence of some kind of direct interaction between the copper(I) and copper(III) metal centres. This distance is significantly longer for the dimeric complex entity (3.627 Å). Selected distances are collected in Table S5.

On the other hand, $[Cu(SC_6H_2Cl_2S)_2]^-$ fragments retain roughly their square planar geometry but their deviation with respect to the planarity is greater than in the previous compounds (tilt

angle between the 3,6-dichlorobenzene-1,2-bis(thiolate) ligands: 19.0°), probably due to the greater strength of the Cu^I-S bond than the interactions involving the alkali cations that take place in compounds **1-4**.

These discrete polynuclear entities are held together by a complex network of $C-H \cdots S$ hydrogen bonds and chloro...chloro interactions that generate a 3D crystal structure in which crystallization acetonitrile molecules are incorporated.

Finally, all attempts to grow crystals suitable for X-ray diffraction structural elucidation for compound $[K(Cu(SC_6H_2Cl_2S)_2)]_n$ **6** was obtained. Selected distances are collected in Table S6.

Upon solving the structure of compound **6** it was found to be a 2D coordination polymer, isostructural with compound **3** (displaying the same random disposition of the M^+ and water molecules), and thus with an underlying net of **sql** topology as well. This result also indicates that the incorporation of water molecules into the coordination sphere of the alkali metal is crucial to stabilize the coordination of the latter ones to the sulfur and chloro donor atoms of the $[Cu(SC_6H_2Cl_2S)_2]^-$ entities. The dc electrical conductivity of CPs **3** and **4** have been evaluated. The suitable size of the crystals of compound **4** has allowed their characterization using the two-contacts method at 300 K with graphite paste. All the attempts to perform variable temperature measurements were unsuccessful because of its crystal instability, probably due to partial loss of solvent. The electrical conductivity measured in different crystals gave an average value of *ca.* $10^{-7} \Omega^{-1} \text{cm}^{-1}$ (Fig. S4). The electrical characterization of crystals of compound **3** was hampered due to their small size. In order to perform a suitable comparison of the electrical properties of **3** and **4**, we carried out their electrical characterization using pellets of the two compounds (ESI for experimental details, Fig. S5-S6). The results obtained confirm that both compounds show similar and moderate electrical conductivity, *ca.* $3 \times 10^{-8} \Omega^{-1} \text{cm}^{-1}$, indicating a semiconductivity behaviour.

This study suggests that the presence of rubidium or caesium complex cations produce a similar electronic effect in the electron transmission along their different structures. These values are in the range to those found for related CPs formed by metal-dithiolene entities bridged by alkali complexes.^{20,35-37}

Experimental

All reactions were carried out either under argon or aerobic atmosphere. All reagents and solvents are commercial and were used as received without further purification. Elemental analyses were performed on an LECO CHNS-932 Elemental Analyzer. 1H and ^{13}C NMR spectra were registered on a Bruker Avance III-HD Nanobay 300-MHz. The IR spectra were recorded on a PerkinElmer spectrum 100 spectrophotometer using a universal ATR sampling accessory.

Crystal structure determination of complexes 1-6. Suitable crystals of compounds **1-6** were coated with mineral oil and

mounted on Mitegen MicroMounts. The samples were measured in a Bruker D8 KAPPA series II with APEX II area-detector system equipped with graphite monochromated Mo K α radiation ($\lambda = 0.71073$ Å). The substantial redundancy in data allowed empirical absorption corrections (SADABS)³¹ to be applied using multiple measurements of symmetry-equivalent reflections. Raw intensity data frames were integrated with the SAINT program,³² which also applied corrections for Lorentz and polarization effects. The Bruker SHELXTL Software Package³³ was used for space group determination, structure solution, and refinement. The space group determination was based on a check of the Laue symmetry and systematic absences were confirmed using the structure solution. The structures were solved by direct methods (SHELXS-2014),³⁴ completed with different Fourier syntheses, and refined with full-matrix least-squares using SHELXS minimizing $\omega(\text{Fo}^2 - \text{Fc}^2)^2$. Weighted R factors (R_w) and all goodness of fit S are based on F^2 ; conventional R factors (R) are based on F. All non-hydrogen atoms were refined with anisotropic displacement parameters. All scattering factors and anomalous dispersion factors are contained in the SHELXTL 6.10 program library. Details of the data collection and structure refinement are collected in Table S7, and the structures have been deposited in the CSD with deposit numbers CCDC 1590257-1590262.

Synthesis of compound [Na(thf)₆][Cu(SC₆H₂Cl₂S)₂], 1. A solution of HSC₆H₂Cl₂SH (74 mg, 0.35 mmol) in CH₃CN (3 ml) and 0.52 mL of NaOH_{aq} (5% weight in water) was stirred for 5 minutes. Then, Cu(ClO₄)₂·6H₂O (64 mg, 0.18 mmol) was added and the mixture stirred at room temperature for 2 h in an open-air atmosphere. After that, a change of the solution colour from red to green was observed. Then the solvent was removed to dryness and the residue washed with H₂O and hexane. Crystallization in THF/*n*-heptane at 20 °C yielded crystals of compound [Na(thf)₆][Cu(SC₆H₂Cl₂S)₂] **1** (152 mg, 90 %). Anal. Calcd. (Found) for C₃₆H₅₂Cl₄CuNaO₆S₄: C, 46.37 (46.13); H, 5.48 (5.59); S, 12.51 (13.68). IR (cm⁻¹): $\nu_{(\text{C}=\text{C})}$: 1601, 1542, 1408; $\delta_{(\text{C}-\text{H})}$: 1057, 820; $\nu_{(\text{C}-\text{Cl})}$: 782. ¹H NMR (CD₃COCD₃, 300 MHz) δ (ppm): 7.07 (s, 2H, C₆H₂). ¹³C NMR (CD₃COCD₃, 300 MHz) δ (ppm): 144.3 (C-S), 127.2 (C-Cl), 125.4 (C-H).

Synthesis of compound [K(thf)₆][Cu(SC₆H₂Cl₂S)₂], 2. Following a similar method to obtain compound **1** but using KOH, crystals of compound [K(thf)₆][Cu(SC₆H₂Cl₂S)₂] **2** (147 mg, 78%) were obtained. Anal. Calcd. (Found) for C₂₀H₂₀Cl₄CuKO₂S₄ (2-4thf): C, 35.53 (36.12); H, 3.40 (3.03); S, 17.54 (19.28). IR (cm⁻¹): $\nu_{(\text{C}=\text{C})}$: 1601, 1542, 1408; $\delta_{(\text{C}-\text{H})}$: 1057, 826; $\nu_{(\text{C}-\text{Cl})}$: 780. ¹H NMR (CD₃COCD₃, 300 MHz) δ (ppm): 6.96 (s, 2H, C₆H₂). ¹³C NMR (CD₃COCD₃, 300 MHz) δ (ppm): 144.3 (C-S), 127.2 (C-Cl), 125.4 (C-H).

Synthesis of 2D coordination polymer {[Rb(OH₂)] [Cu(SC₆H₂Cl₂S)₂]}_n **3 and {[Cs(OH₂)] [Cu(SC₆H₂Cl₂S)₂]}_n **4**.** Following a similar method to obtain compound **1** but using Rb₂CO₃ or Cs₂CO₃ as deprotonating agent, compounds {[Rb(OH₂)] [Cu(SC₆H₂Cl₂S)₂]}_n **3** (48 mg, 47%) or {[Cs(OH₂)] [Cu(SC₆H₂Cl₂S)₂]}_n **4** (75 mg, 67.8%) were obtained, respectively. Anal. Calcd. (Found) for C₁₂H₆Cl₄CuORbS₄ (**3**): C, 25.00 (24.63); H, 1.24 (1.03); S, 21.66 (21.91). IR (cm⁻¹): $\nu_{(\text{C}=\text{C})}$: 1601, 1542, 1408; $\delta_{(\text{C}-\text{H})}$: 1057, 826; $\nu_{(\text{C}-\text{Cl})}$: 784. ¹H NMR

(CD₃COCD₃, 300 MHz) δ (ppm): 7.1 (s, 2H, C₆H₂). ¹³C NMR (CD₃COCD₃, 300 MHz) δ (ppm): 144.3 (C-S), 127.2 (C-Cl), 125.4 (C-H). Anal. Calcd. (Found) for C₁₂H₆Cl₄CsCuO₄S₄ (**4**): C, 21.68 (22.78); H, 1.15 (0.96); S, 19.48 (20.27). IR (cm⁻¹): $\nu_{(\text{C}=\text{C})}$: 1601, 1542, 1408; $\delta_{(\text{C}-\text{H})}$: 1057, 826; $\nu_{(\text{C}-\text{Cl})}$: 784. ¹H NMR (CD₃COCD₃, 300 MHz) δ (ppm): 7.11 (s, 2H, C₆H₂). ¹³C NMR (CD₃COCD₃, 300 MHz) δ (ppm): 144.2 (C-S), 127.2 (C-Cl), 125.4 (C-H).

Synthesis of compound 2[(CH₃CN)₃Cu(μ-SC₆H₂Cl₂S)Cu(SC₆H₂Cl₂S))·[(CH₃CN)Cu(μ-SC₆H₂Cl₂S)Cu(SC₆H₂Cl₂S))]₂·2CH₃CN, 5. Following the same method to prepare compound **2**, but using acetonitrile/diethyl ether for crystallization, compound **5** was obtained in trace amounts. IR (cm⁻¹): $\nu_{(\text{C}\equiv\text{N})}$: 2224; $\nu_{(\text{C}=\text{C})}$: 1540, 1407; $\delta_{(\text{C}-\text{H})}$: 1063, 822; $\nu_{(\text{C}-\text{Cl})}$: 798.

Synthesis of compound {[K(OH₂)] [Cu(SC₆H₂Cl₂S)₂]}_n, 6. Following the same method to prepare compound **2** but using an acetone/diethyl ether in addition to a few drops of H₂O provided some crystals of compound **6**. Anal. Calcd. (Found) for C₁₂H₆Cl₄CuKOS₄ (**6**): C, 26.75 (27.70); H, 1.12 (1.49); S, 23.80 (23.35).

Conclusions

One-top reactions carried out under room conditions between Cu(ClO₄)₂ and 3,6-dichloro-1,2-benzenedithiol (HSC₆H₂Cl₂SH) in presence of NaOH, KOH, Rb₂CO₃ or Cs₂CO₃, lead to a series of bis(dithiolato)cuprate(III) [Cu(SC₆H₂Cl₂S)₂]⁻ coordination complexes and coordination polymers depending upon the metal counterion used in the process. The study of the structures of [M(thf)₆][Cu(SC₆H₂Cl₂S)₂] [M = Na (**1**); K (**2**)], {[Rb(OH₂)] [Cu(SC₆H₂Cl₂S)₂]}_n (**3**), {[Cs(OH₂)] [Cu(SC₆H₂Cl₂S)₂]}_n (**4**), 2[(CH₃CN)₃Cu(μ-SC₆H₂Cl₂S)Cu(SC₆H₂Cl₂S))·[(CH₃CN)Cu(μ-SC₆H₂Cl₂S)Cu(SC₆H₂Cl₂S))]₂·2CH₃CN (**5**), and {[K(OH₂)] [Cu(SC₆H₂Cl₂S)₂]}_n (**6**) compounds point out the robustness of the bis(dithiolato)cuprate(III) [Cu(SC₆H₂Cl₂S)₂]⁻ entity. The nearly planar structure of the complex anion is retained not only when interacting weakly with alkaline cations, but also when it shows more strongly coordinative bonds with copper(I). In the latter case compound **5** was obtained, which represents one of the very few examples of Cu^I/Cu^{III} mixed-oxidation state compounds. Some of these compounds indicate that the sulfur donor atoms of the [Cu(SC₆H₂Cl₂S)₂]⁻ entity and even the chloro substituents are able to anchor additional metal centres, specially softer ones, promoting a further polymerization.

The electrical studies carried out in this work with **3** and **4** CPs as compare with those previously reported for related CPs based on metal-dithiolene entities bridged by alkali complexes,^{20,35-37} suggest that the electrical conductivity is limited to relatively low values, 10⁻⁶-10⁻⁹ σ·cm⁻¹, probably because of the limitation in electric current passes through the group 1 metal complexes. These results indicate that the formation of electrically conductive of CPs based on metal-dithiolene entities require more efficient connectors.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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Notes and references

- Robertson, N.; Cronin, L. Metal Bis-1,2-Dithiolene Complexes in Conducting or Magnetic Crystalline Assemblies. *Coord. Chem. Rev.* **2002**, *227*, 93-127.
- Dithiolene Chemistry: Synthesis, Properties and Applications; Karlin, K. D., Stiefel, E. I., Eds.; Progress in Inorganic Chemistry Vol. 52. John Wiley & Sons, Inc. New York, 2003.
- Muller-Westerhoff, U. T.; Vance, B. In *Comprehensive Coordination Chemistry*; Wilkinson, G., Gillard, R. D. and McCleverty, J. A., Eds.; Pergamon Press: Oxford, U. K., 1987; Vol. 2.
- Clemenson, P. I. The Chemistry and Solid State Properties of Nickel, Palladium and Platinum Bis(Maleonitriledithiolate) Compounds. *Coord. Chem. Rev.* **1990**, *106*, 171-203.
- Ezzaher, S.; Gogoll, A.; Bruhn, C.; Ott, S. Directing Protonation in [FeFe] Hydrogenase Active Site Models by Modifications in their Second Coordination Sphere. *Chem. Commun.* **2010**, *46*, 5775-5777.
- Alcácer, L.; Novais, H. Linear Chain 1,2-Dithiolene Complexes. In *Extended Linear Chain Compounds*. Miller, J. S., Ed.; Springer US: New York, 1983; Vol. Cap. 6, pp 319-351.
- Cassoux, P.; Valade, L.; Kobayashi, H.; Kobayashi, A.; Clark, R. A.; Underhill, A. E. Molecular Metals and Superconductors Derived from Metal Complexes of 1,3-dithiol-2-thione-4,5-dithiolate (Dmit). *Coord. Chem. Rev.* **1991**, *110*, 115-160.
- Sproules, S.; Wieghardt, K. O-Dithiolene and O-Aminothiolate Chemistry of Iron: Synthesis, Structure and Reactivity. *Coord. Chem. Rev.* **2010**, *254*, 1358-1382.
- Garreau de Bonneval, B.; Moineau-Chane Ching, K. I.; Alary, F.; Bui, T. T.; Valade, L. Neutral d⁸ Metal Bis-Dithiolene Complexes: Synthesis, Electronic Properties and Applications. *Coord. Chem. Rev.* **2010**, *254*, 1457-1467.
- Alvarez, S.; Vicente, R.; Hoffmann, R. Dimerization and Stacking in Transition-metal Bisdithiolenes and Tetrathiolates. *J. Am. Chem. Soc.* **1985**, *107*, 6253-6277.
- Ribas, X.; Dias, J. C.; Morgado, J.; Wusrt, K.; Santos, I. C.; Almeida, M.; Vidal-Gancedo, J.; Veciana, J.; Rovira, C. Alkaline Side-Coordination Strategy for the Design of Nickel(II) and Nickel(III) Bis(1,2-Diselenolene) Complex Based Materials. *Inorg. Chem.* **2004**, *43*, 3631-3641.
- Llusar, R.; Uriel, S.; Vicent, C.; Clemente-Juan, J.; Coronado, E.; Gómez-García, C. J.; Braña, B.; Canadell, E. Single-Component Magnetic Conductors Based on Mo₃S₇ Trinuclear Clusters with Outer Dithiolate Ligands. *J. Am. Chem. Soc.* **2004**, *126*, 12076-12083.
- Llusar, R.; Triguero, S.; Polo, V.; Vicent, C.; Gómez-García, C. J.; Jeannin, O.; Fourmigué, M. Trinuclear Mo₃S₇ Clusters Coordinated to Dithiolate Or Diselenolate Ligands and their use in the Preparation of Magnetic Single Component Molecular Conductors. *Inorg. Chem.* **2008**, *47*, 9400-9409.
- Gushchin, A. L.; Llusar, R.; Vicent, C.; Abramov, P. A.; Gómez-García, C. J. Mo₃Q₇ (Q = S, Se) Clusters Containing Dithiolate/Diselenolate Ligands: Synthesis, Structures, and their use as Precursors of Magnetic Single-Component Molecular Conductors. *Eur. J. Inorg. Chem.* **2013**, *2013*, 2615-2622.
- Vicente, J.; González-Herrero, P.; García-Sánchez, Y.; Jones, P. G.; Bautista, B. Copper Complexes with (2,7-Di-tert-butylfluoren-9-ylidene)methanedithiolate: Oxidatively Promoted Dithioate Condensation. *Eur. J. Inorg. Chem.* **2006**, 115-126.
- Mrkvová, K.; Kamenicek, J.; Sindelar, Z.; Kvitek, L.; Mrozinski, J.; Nahorska, M.; Zak, Z. Synthesis, properties and crystal structures of R[M^{III}(bdt)₂] complexes (M=Ni, Co, Cu) *Trans. Met. Chem.* **2004**, *29*, 238-244.
- Bolligarla, R.; Tripuramallu, B. K.; Sreenivasulu, V.; Das, S. K. Synthesis and structural characterization of potassium coordination polymers based on a copper-bis(dithiolato) complex: role of coordinating solvents and counter cation. *Indian J. Chem.* **2011**, *50A*, 1410-1417.
- Takaishi, S.; Hosoda, M.; Kajiwara, T.; Miyasaka, H.; Yamashita, M.; Nakanishi, Y.; Kitagawa, Y.; Yamaguchi, K.; Kobayashi, A.; Kitagawa, H. Electroconductive Porous Coordination Polymer Cu[Cu(pdt)₂] Composed of Donor and Acceptor Building Units. *Inorg. Chem.* **2009**, *48*, 9048-9050.
- Bolligarla, R.; Das, S. K. Dimensionality of coordination polymers decided by the type of hybridization of the central carbon atom of the solvent molecule that coordinates to an alkali metal cation: from discrete to 3D networks based on a gold(III) bis(dithiolene) complex. *Cryst. Eng. Comm.* **2010**, *12*, 3409-3412.
- Benmansour, S.; Delgado, E.; Gómez-García, C. J.; Hernández, D.; Hernández, E.; Martín, A.; Perles, J.; Zamora, F. Coordination Polymers Based on Diiron Tetrakis(Dithiolato) Bridged by Alkali Metals, Electrical Bistability Around Room Temperature, and Strong Antiferromagnetic Coupling. *Inorg. Chem.* **2015**, *54*, 2243-2252.
- Castillo, O.; Zamora, F.; Hernández, D.; Hernández, E.; Martín, A.; Martín, I.; Zamora, F. Structural Diversity of Compounds Based on Iron-Dithiolene with Sodium or Potassium Complexes. *Cryst. Growth. Des.* **2016**, *16*, 5466-5478.
- Cerdeira, A. C.; Belo, D.; Rabaça, S.; Pereira, L. C. J.; Coutinho, J. T.; Simão, D.; Henriques, R. T.; Jeannin, O.; Fourmigué, M.; Almeida, M. Heterodimetallic Structures Based on Cyano-Substituted Bis(dithiolene) Complexes and Ni and Cu Cyclam Cations. *Eur. J. Inorg. Chem.* **2013**, 4612-4618.
- Blatov, V. A. Multipurpose crystallochemical analysis with the program package TOPOS. *IUCr Comp. Comm. Newsletter*, **2006**, *7*, 4-38.
- Blatov, V. A. Nanocluster analysis of intermetallic structures with the program package TOPOS. *Struct. Chem.*, **2012**, *23*, 955-963.
- Blatov, V. A.; Shevchenko, A. P.; Proserpio, D. M. Applied Topological Analysis of Crystal Structures with the Program Package ToposPro. *Cryst. Growth Des.* **2014**, *14*, 3576-3586.
- Maiti, B. K.; Maia, L. B.; Pal, K.; Pakhira, B.; Avilés, T.; Moura, I.; Pauleta, S. R.; Nuñez, J. L.; Rizzi, A. C.; Brondino, C. D.; Sarkar, S.; Moura, J. J. G. One Electron Reduced Square Planar Bis(benzene-1,2-dithiolato) Copper Dianionic Complex and Redox Switch by O₂/HO⁻. *Inorg. Chem.* **2014**, *53*, 12799-12808.
- Ribas, X.; Maspoch, D.; Dias, J.; Morgado, J.; Almeida, M.; Wurst, K.; Vaughan, G.; Veciana, J.; Rovira, C. 2D Layered coordination polymer based on an unusual mixed valence Cu(III)/Cu(I) bis-1,2-diselenolene compound. *Cryst. Eng. Comm.* **2004**, *6*, 589-592.
- García-López, J.; Yañez-Rodríguez, V.; Rocas, L.; García-Granda, S.; Martínez, A.; Guevara-García, A.; Castro, G. R.; Jiménez-Villacorta, F.; Iglesias, M. J.; Ortiz, F. L. Synthesis and Characterization of a Coupled Binuclear Cu^I/Cu^{III} Complex. *J. Am. Chem. Soc.* **2010**, *132*, 10665-10667.
- Coucouvanis, D.; Kanodia, S.; Swenson, D.; Chen, S.-J.; Studemann, T.; Baenziger, N. C.; Pedelty, R.; Chu, M. Mixed-valence coinage metal clusters with 1,1-thioperthio ligands. Syntheses and molecular structures of the copper and gold

- [Cu₄L₃]²⁻, [Cu₅L₄]⁻, and [AuCu₄L₄]⁻ anions (L = 1,1-dicarbo-tert-butoxyethylene-2,2-thioperthiolate). A geometrically-locked, charge-separated valence state in the [Cu₅L₄]⁻ anion. *J. Am. Chem. Soc.* **1993**, *115*, 11271-11278.
- 30 Zhang, S.-L.; Bie, W.-F. Ligand-dependent formation of ion-pair Cu^I/Cu^{III} trifluoromethyl complexes containing bisphosphines. *Dalton Trans.* **2016**, *45*, 17588-17592.
 - 31 Sheldrick, G. M., SADABS Version 2.03, Program for Empirical Absorption Correction; University of Göttingen: Germany, 1997–2001.
 - 32 SAINT+NT Version 6.04, SAX Area-Detector Integration Program; Bruker Analytical X-ray Instruments: Madison, WI, 1997–200.
 - 33 Bruker AXS SHELXTL Version 6.10, Structure Determination Package; Bruker Analytical X-ray Instruments: Madison, WI, 2000.
 - 34 Sheldrick, G. M., SHELXL-2014/7: Program for the Solution of Crystal Structures, University of Göttingen, Göttingen, Germany, 2014.
 - 35 Amo-Ochoa, P., Delgado, E., Gómez-García, C. J., Hernández, D., Hernández, E., Martín, A., Zamora, F. Electrical bi-stability around room temperature in an unprecedented 1D coordination magnetic polymer. *Inorg. Chem.* **2013**, *52*, 5943–5950.
 - 36 Delgado, E., Gomez-Garcia, C. J., Hernandez, D., Hernandez, E., Martín, A., Zamora, F. Unprecedented Layered Coordination Polymers of Dithiolene Group 10 Metals. Magnetic and Electrical Properties. *Dalton Trans.* **2016**, *45*, 6696-6701.
 - 37 Castillo, O., Delgado, E., Gomez-García, C. J., Hernandez, D., Hernandez, E., Martín, A., Martínez, J. I., Zamora, F. Group 10 Metal Benzene-1,2-dithiolate Derivatives in the Synthesis of Coordination Polymers Containing Potassium Counteranions. *Inorg. Chem.* **2017**, *56*, 11810–11818.