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Further insight into the coordination of 2,5-dicarbothioamidopyrroles: the case of Cu and Co complexes†

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The coordination chemistry of 2,5-dicarbothioamidopyrrole ligands, namely N2,N5-dibutyl-3,4-diphenyl-1H-pyrrole-2,5-bis(carbothioamide) and N2,N5,3,4-tetraphenyl-1H-pyrrole-2,5-bis(carbothioamide), has been investigated with Cu(II) metal centres by means of X-ray crystallography. This resulted in the formation of the expected planar S,N,S’ coordinated complex for the former ligand and unexpected ring-closure reactions, with formation of benzothiazole sidearms, for the latter. Both Cu(II) and Cu(I), used in large excess, were found to favour the ring-closure reaction, although the structural characterisation of the resulting complexes contained only Cu(II) cations, with varying coordination geometries ranging from square planar and square-based pyramidal to tetrahedral. By repeating the reaction using a slight excess of Cu(II) (2:1) two more different structures were obtained where the metal was coordinated to the original ligand, N2,N5,3,4-tetraphenyl-1H-pyrrole-2,5-bis(carbothioamide), or to the mixed ligand where only one of the thioamide substituents had converted to a benzothiazole. The essential role of Cu for the ring closure reaction was also established by comparing its complex with structural features of the analogous Co(II) complex, the latter revealing no ring closure to give benzothiazole substituents and co-crystallisation of a mixed Co(II)/Co(III) complex. Finally, the structure and photophysical properties of the corresponding 3,4-diphenyl-2,5-bis(benzothiazol-5-yl)-pyrrole ligand, obtained via treatment of the thioamide with K,[Fe(CN)6], were also investigated revealing a blue-centered emission.

Introduction

Pyrrole derivatives such as 2,5-dicarboxamidopyrroles and 2,5-dicarbothioamidopyrroles are well established anion-binding receptors.1 The analogous pyridine derivatives also bind anions,2 but unlike the pyrrole systems, they have a well developed coordination chemistry with cations.3 We recently reported the first structurally characterised examples of metal cation complexes of such pyrrole diamides and dithioamides, with an emphasis on nickel and cobalt complexes.4 As a continuation of this work we decided to investigate the coordination chemistry of Cu2+ with the same ligand systems, in particular N2,N5-dibutyl-3,4-diphenyl-1H-pyrrole-2,5-bis(carbothioamide) and N2,N5,3,4-tetraphenyl-1H-pyrrole-2,5-bis(carbothioamide), referenced as 1 and 2 respectively in Fig. 1. The investigation started with crystallisation studies, using a similar protocol as previously reported.5 In the case of ligand 1 the expected S,N,S’ trischelated complex was obtained, upon deprotonation of the pyrrole NH. It is noteworthy that the deprotonation occurred without the need of added base, which can be explained by the increased acidity of the pyrrole NH due to the presence of two electron withdrawing groups in the positions 2 and 5 of the ring. In contradistinction to these results, using the same conditions, when the ligand 2 was treated with CuCl2, the isolated complex showed that the Cu2+ centre was coordinated to the deprotonated form of ligand 3 (Fig. 1). This result indicated that ring closure and formation of benzothiazole groups occurred on both the phenylthioamide substituents of the pyrrole ring of 2.

Copper promoted ring closure reactions have been reported before for the formation of benzothiazoles, especially catalysed in the presence of Cu(II).6 In this work the same cyclisation seems to be happening even with Cu(II). We have therefore attempted to systematically investigate the formation of the Cu complex with the concomitant ring closure reaction on the ligand...
2. The role of Cu on the benzothiazolisation was also further investigated by treating, under the same conditions, the ligand 2 with CoCl₂ instead of CuCl₂. In addition, as the ligand 3 has not been reported previously, we have attempted its preparation following literature methods. We have also performed structural and preliminary photophysical studies of 3, owing to the typical blue/green emission of the benzothiazole ring.

**Experimental section**

**General considerations**

Solvents and reagents were purchased from Sigma Aldrich and used as received without any further purification. 3,4-Diphenyl-1H-pyrrole-2,5-dicarboxylic acid,⁷ 1,4 and 2⁴ were prepared according to previously published procedures. ¹H and ¹³C NMR spectra were measured using a Bruker Avance 400 spectrometer (400.1 MHz for ¹H, 100.0 MHz for ¹³C) at room temperature. Chemical shifts were referenced to residual solvent resonances. IR spectra were measured from solid-state samples, on an attenuated total reflectance Perkin Elmer Spectrum 100 FT-IR with a KBr disk. Chemical shifts were referenced to residual solvent resonances. IR spectra were measured using a Bruker Avance 400 spectrometer and a Perkin Elmer Lambda 35 UV/Vis Spectrometer. Emission spectra were measured from diluted solutions using a Hitachi F-4500. Emission spectra were measured from diluted solutions using a Hitachi F-4500. Emission spectra were measured from diluted solutions using a Hitachi F-4500. Emission spectra were measured from diluted solutions using a Hitachi F-4500.

**X-Ray crystal data for complex 4**

Empirical formula C₆₃H₆₃ClCuN₅S₂. Formula weight 547.64. Temperature 120(2) K. Wavelength 0.71073 Å. Crystal system Monoclinic. Space group P2₁/n. Unit cell dimensions a = 14.9200(5) Å, b = 9.0986(3) Å, c = 18.4634(4) Å, β = 90.731(2)°. Volume 2533.37(13) Å³. Z = 4. Density (calculated) 1.436 Mg m⁻³. Absorption coefficient 1.152 mm⁻¹. F(000) 1140. θ range for data collection 3.40° - 27.48°. Index ranges -19 ≤ h ≤ 19, -11 ≤ k ≤ 11, -24 ≤ l ≤ 24. Reflections collected 43572. Independent reflections 5875 [R_ex = 0.1149]. Completeness to θ = 27.48° 99.6%. Absorption correction semi-empirical from equivalents. Max. and min. transmission 0.9034 and 0.8123. Data/restraints/parameters 5785/0/300. Goodness-of-fit on F² is 1.047. Final R indices [F² > 2σ(F²)] R₁ = 0.0505, wR₂ = 0.0997. R indices (all data) R₁ = 0.0844, wR₂ = 0.1141. Largest diff. peak and hole 0.394 and -0.618 e Å⁻³.

**X-Ray crystal data for complex 5**

Empirical formula C₁₇H₁₃ClCuN₅S₂. Formula weight 661.10. Temperature 120(2) K. Wavelength 0.71073 Å. Crystal system Monoclinic. Space group P₂₁/c. Unit cell dimensions a = 12.7475(2) Å, b = 8.48290(10) Å, c = 27.9445(4) Å, β = 101.7920(10). Volume 2958.07(3) Å³. Z = 4. Density (calculated) 1.484 Mg m⁻³. Absorption coefficient 1.090 mm⁻¹. F(000) 1348. θ range for data collection 2.91° - 27.48°. Index ranges -16 ≤ h ≤ 16, -10 ≤ k ≤ 11, -36 ≤ l ≤ 36. Reflections collected 35352. Independent reflections 6752 [R_ex = 0.0532]. Completeness to θ = 27.48° 99.8%. Absorption correction semi-empirical from equivalents. Max. and min. transmission 0.8115 and 0.6596. Data/restraints/parameters 6752/1/375. Goodness-of-fit on F² is 1.022. Final R indices [F² > 2σ(F²)] R₁ = 0.0431, wR₂ = 0.1104. R indices (all data) R₁ = 0.0558, wR₂ = 0.1174. Largest diff. peak and hole 0.490 and -0.721 e Å⁻³.

**Synthesis of 3,4-diphenyl-2,5-bis(benzothiazol-2-yl)-pyrrole (3)**

Compound 3 was prepared following a previously published literature procedure.⁶ Ethanol (3 ml) was added dropwise to an aqueous mixture of sodium hydroxide (0.05 g, 1.25 mmol) and 2⁴ (0.05 g, 0.10 mmol) until complete dissolution. This was then added dropwise to a vigorously stirred solution of K₂[Fe(CN)₆] (0.14 g, 0.42 mmol) in water (2 ml) and then heated to reflux for 2 h. The mixture was cooled on ice and a yellow precipitate was collected. The precipitate was dissolved in ethyl acetate and insoluble impurities were filtered. The solvent was removed under reduced pressure to yield a yellow crystalline product. This was purified via column chromatography, using silica gel as the stationary phase and a 8:2 hexane/ethyl acetate eluent (second fraction). Single crystals suitable for X-ray diffraction were grown by slow evaporation of an ethyl acetate solution of 3 over 2–3 days. Yield: 0.03 g (53%). Anal. calcd. for 3: C 74.20, H 3.94, N 8.65; found: C 74.09, H 3.84, N 8.61. IR (Diamond ATR): ν = 3442 m, 3427 m, 3341 w, 3059 w, 3025 w, 2955 m, 2924 s, 2853 m, 1566 w, 1539 w, 1503 m, 1457, 1442, 1214 cm⁻¹. H NMR (DMSO-d₆, see numbering in Fig. S4 as a reference for the assignment of the H peaks): δ = 8.03 (2H, d, J = 7.6 Hz, H₁₁a), 7.97 (2H, d, J = 8.0 Hz, H₁₁b), 7.52 (2H, t, J = 7.8 Hz, H₁₁c).
Preparation of the mixture of complex 7 and trimer 8-6-6

An acetonitrile (30 ml) solution of dihydrated CuCl₂ (0.017 g, 0.10 mmol) was added to an acetonitrile (40 ml) solution of 2 (0.025 g, 0.05 mmol). The mixture was heated to reflux for 20 h. Upon cooling to room temperature a dark green precipitate formed. The solid was dissolved in chloroform and vapours of hexane were slowly diffused into the solution. Two crops of crystals were grown over a few days, producing dark green prismatic fragments and block-shaped brown crystals, which were separated by hand picking. Yield 0.012 g (not optimised). Elemental analysis was performed on the batch sample, assuming a solvated (chloroform, eventually forming pale brown plate-like crystals in a couple of days. Yield: 0.02 g (29%). Anal. calcd for 9·0.25HCl: C 58.53, H 3.96, N 6.58; found: C 58.62, H 3.47, N 6.14. IR

Preparation of the mixture of complex 7 and trimer 8-6-6

An acetonitrile (20 ml) solution of hexahydrated CoCl₂ (0.023 g, 0.10 mmol) was added to an acetonitrile (50 ml) solution of 2 (0.025 g, 0.05 mmol). The mixture was heated to reflux for 20 h. The solution was cooled to room temperature, and the solvent removed in vacuo, yielding a green/brown solid. The solid was dissolved in hot ethanol and crystallised by vapour diffusion with chloroform, eventually forming pale brown plate-like crystals in a couple of days. Yield: 0.02 g (29%). Anal. calcd for 9·0.25HCl: C 58.53, H 3.96, N 6.58; found: C 58.62, H 3.47, N 6.14. IR

X-Ray crystal data for the dinuclear compound 9

Empirical formula C₆₅H₇₇Cl₂Co₂N₆O₃S₄, [C₆₅H₇₇Co₂N₆S₄, C₄H₄Cl,CoO, CHCl₃]. Formula weight 1366.90. Temperature 120(2) K. Wavelength 0.71073 Å. Crystal system Monoclinic. Space group P2₁/n. Unit cell dimensions a = 17.8652(3) Å, b = 20.1328(3) Å, c = 18.0402(3) Å, β = 108.8240(10)°. Volume 6141.58(17) Å³. Z = 4. Density (calculated) 1.478 Mg m⁻³. Absorption coefficient 0.985 mm⁻¹. F(000) 2796. θ range for data collection 2.97–25.03°. Index ranges −19 ≤ h ≤ 21, −23 ≤ k ≤ 22, −21 ≤ l ≤ 21. Reflections collected 64380. Independent reflections 10813 [Rint = 0.1061]. Completeness to θ = 25.03° 99.9%. Absorption correction semi-empirical from equivalents. Max. and min. transmission 0.9902 and 0.8274. Data/restraints/parameters 10813/1/744. Goodness-of-fit on F² 1.133. Final R indices [F² > 2σ(F²)] Rf = 0.0776, wRf = 0.1364. R indices (all data) Rf = 0.1155, wRf = 0.1528. Largest diff. peak and hole 1.037 and −0.601 e Å⁻³.

Results and discussion

Attempted crystallisation of Cu complexes with ligands 1 and 2

The Cu complex 4 was prepared by treating 1 with hydrated CuCl₂ in acetonitrile at room temperature, according to the scheme reported in Fig. 2. After several days a few dark green crystals appeared from the undisturbed solution, albeit always in very small yield and often contaminated by the co-precipitation of 1. Co-precipitation occurred even if a large excess of metal was used. As the crystals were suitable for X-ray diffraction, we were able to elucidate the structure of the product, which resulted in the trischelated square planar Cu²⁺ complex. Although no base was added to the reaction mixture, the metal centre is bound to the negatively charged deprotonated pyrrole ring.

![Fig. 2 Crystalisation of the Cu complex 4.](image-url)
In a similar procedure, excess hydrated CuCl₂ was added to 2 (Fig. 3). Again, after several days some dark green crystals deposited along with co-precipitation of amorphous ligand 2. X-Ray diffraction studies revealed the formation of complex 5, where a ring closure reaction occurred on the thioamide substituents of the pyrrole ring in the ligand 2. Similar copper-mediated ring closures of thioamides have been reported previously, albeit in ethanol solution rather than acetonitrile. In complex 5 the Cu centre favours a pseudo-tetrahedral geometry via coordination to the ligand 3 in a N',N′ bidentate fashion, an analogous structure to the previously reported CuBr₂ complex coordinated to 2-(2-pyridyl)benzothiazole. Surprisingly, treating ligand 2 with CuCl₂ instead of CuCl₆, resulted in the formation of complex 6 (Fig. 4). In this case the Cu centre is bound to the deprotonated form of ligand 3 via a tridentate N',N,N′ coordination, resulting in a coordination geometry similar to that found in complex 4. Moreover, the metal centre has oxidised (from Cu⁺ to Cu²⁺) during the formation of complex 6.

![Fig. 3] Crystallisation of the Cu complex 5.

![Fig. 4] Crystallisation of the Cu complex 6.

The ring closure that occurred on the ligand 2 was ascribed to the combined oxidation of the phenylthioamide side-arms on the pyrrole ring favoured by the crystallisation in aerobic conditions. On the basis of these results, the formation of the benzothiazole seems to be promoted by the presence of the Cu cations. Moreover in the case of complex 6, Cu⁺ is also likely to be oxidised by O₂ with formation of Cu²⁺. In the latter case, the concomitant reduction of O₂ to H₂O might also be responsible for the deprotonation of the ligand, hence accounting for the structural difference between the complexes 5 and 6 (e.g. deprotonation of the benzothiazole NH bond).

Unfortunately, although in each case single crystals suitable for X-ray diffraction were obtained, the isolation of the Cu complexes 4, 5, and 6 proved particularly challenging due to the consistent co-precipitation of amorphous ligand. Therefore, only the detailed structural studies of these complexes are reported in this work.

**X-Ray structure of Cu complex 4**

The structure of the Cu complex 4 is shown in Fig. 5. The complex crystallises into the P2₁/c space group. There is a slightly distorted square planar coordination environment around the Cu centre, with its charge counterbalanced by the negative chloro anion and the deprotonated pyrrole ring. The remaining two coordination sites are occupied by the two S atoms of the butylthioamide substituents. Similar complexes of the related N,N'-dibenzyldihydro-1H-pyrrole-2,5-dicarbothioamide have been reported for nickel and palladium. Unlike these related systems, however, the structure reported here forms dimeric structures within the lattice, as shown in Fig. 6. Within each dimer, both the Cu centres interact with one S atom of the neighbouring complex. The interaction of the metal with the apical S atom is weaker than the Cu–S bond within the square planar complex, as witnessed by its longer distance (Cu–S₃planar ca. 3.2 Å, Cu–S₂planar 2.4 Å). This kind of arrangement has been previously observed in analogous Cu complexes with pyridine 2,6-thioamide ligands. The dimers are arranged in order to form two square based pyramidal Cu complexes. This dimeric arrangement has been reported before in analogous Cu complexes bearing S,N,S′ tridentate pyridine-2,6-dithiocarboxamide ligands (Cu–S₂planar ca. 3.4 Å, Cu–S₃planar 2.3 Å). The two phenyl rings lie twisted at 64° and 56° with respect to the pyrrolido plane.

![Fig. 5] X-Ray crystal structure of complex 4 with thermal ellipsoids drawn at the 35% probability level. Hydrogen atoms omitted.

**X-Ray structure of Cu complex 5**

Complex 5, shown in Fig. 7, crystallises in the monoclinic P2₁/c space group. The Cu²⁺ center is tetracoordinated and bound to two chloro and the pyrrolido ligands, and to a neutral benzothiazolyl nitrogen atom. The overall anionic charge of the copper complex is counterbalanced by the protonation of the non coordinating benzothiazolyl nitrogen atom. This means the complex is neutral in its entirety, albeit assuming a zwitterionic form. The dibenzothiazolylpyrrolido unit is coordinated adopting a N,N-η² mode and forming, along with the other two chlorido ligands, a distorted tetrahedral geometry around the Cu²⁺ cation.

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**Fig. 6** X-Ray crystal structure of complex 4 with thermal ellipsoids drawn at the 35% probability level. Hydrogen atoms omitted.
Fig. 6 Dimeric structures formed by complex 4. Cu...S distance (dashed bond) is 3.159 Å (amide butyl groups removed for clarity).

The two Cu–N bond distances are essentially identical, ca. 2.0 Å, and slightly shorter than the Cu-Cl bonds, ca. 2.2 Å. The distortion from the tetrahedral geometry is consistent with a Jahn–Teller effect, although a hydrogen bonding interaction between one of the chlorido ligands and the N–H bond of the protonated benzothiazole ring is also noted (Fig. 8). The two phenyl rings are again twisted at 79° and 65° with respect to the pyrrolido plane. There is no sign of extensive hydrogen bonding or π stacking. There is one molecule of acetonitrile per asymmetric unit, crystallised within the lattice. The lattice solvent molecule seems to be arranged so that there is a short range interaction, 3.2 Å, between the acetonitrile N atom and the electron deficient S atom of the protonated benzothiazole ring.

X-Ray structure of Cu complex 6

The dimeric structure of complex 6 is shown in Fig. 8. The complex crystallises into the monoclinic \( P_{2}/n \) space group. The \( Cu^{2+} \) cation lies in a distorted square planar coordination environment, with its charge counterbalanced by the negative chlorido anion and the deprotonated pyrrole ring. The dibenzothiazolopyrroldio ligand is coordinated to the metal centre by adopting a \( N,N,N-\eta^{1} \) tridentate mode, with the shortest Cu–N distance belonging to the pyrrolido nitrogen atom (ca. 1.9 Å compared to ca. 2.2 Å of the other two Cu–N bonds). The two phenyl substituents in position 3 and 4 of the pyrrole ring are twisted with respect to the pyrrole plane, respectively by 48° and 41°. The molecule forms a dimeric structure in the solid state, with longer Cu...S distances (3.535 Å) than observed in complex 4, such that the interaction may be better described as π-stacking, than a metal ligand interaction. The protruding aromatic rings of the dimer interact with the equivalent groups in a neighbouring dimer in the crystal, with a p-p interplanar distance of 3.35 Å.

Synthesis of the ligand 3

The synthesis of the ligand 3 was attempted following previously published procedures related to the formation of the benzothiazole heterocycle. The first attempt, albeit unsuccessful, was based on a procedure published by Addison et al., starting from 3,4-diphenyl-1H-pyrrole-2,5-dicarboxylic acid and treating it with 2-aminothiophenol in neat polyphosphoric acid at high temperatures (≈180 °C). The reaction did not occur because of the decarboxylation of the pyrrole substrate favoured by the high temperature, as evidenced by recovering the corresponding 3,4-diphenyl-1H-pyrrole. In a second attempt we reacted 2 with \( K_{3}[Fe(CN)]_{6} \), acting as a one electron oxidant, in a 1:1 refluxing alkaline water/ethanol mixture, according to the scheme reported in Fig. 9 and following a methodology published by Wang et al. The reaction was successful in moderate to good yield after purification via column chromatography, as confirmed by NMR data with the disappearance of one of the ortho-H signal of the phenylthioamide, as well as elemental analysis. Moreover, the structure of the ligand 3 was also determined with the use of X-ray crystallography.
X-Ray structure of ligand 3

The structure of ligand 3 is shown in Fig. 10. The compound crystallises into the triclinic P\overline{1} space group, with two crystallographically independent molecules within the unit cell. The major difference between the two units is represented by the torsion angle value of the phenyl rings with respect to the pseudo-plane of the dibenzothiazolylpyrrole unit. These values (ca. 88° and 57° for the first unit and ca. 68° and 38° for the second unit) suggest a lack of interannular conjugation between the phenyl rings and the heterocyclic systems. In both units, the two benzothiazolyl substituents are orientated so that their nitrogen atoms lie in the same direction of the pyrrole NH, thus mimicking a singly protonated 2,2′,5,6′-terpyridine ligand. Throughout the lattice there is no evidence of hydrogen bonding between adjacent molecules. On the other hand, the units are arranged forming antiparallel oriented dimers that are joined together by π stacking, with an average distance between the two planes of ca. 3.5 Å (Fig. 11). The antiparallel orientation is likely to be favoured in order to position the bulky phenyl substituents on the opposite sides of the dimer. The lack of extensive hydrogen bonding and π stacking interaction throughout the lattice, due to the presence of the phenyl rings in substituents on the positions 3 and 5 of the pyrrole ring, is consistent with the highly soluble nature of 3. In fact, analogous unsubstituted compounds, such as the previously reported 2,6-dibenzothiazolylpyrline, proved to be highly insoluble.\(^{13}\)

**Fig. 10** X-Ray crystal structure of the ligand 3 with thermal ellipsoids drawn at the 35% probability level. Only one of the two independent molecules within the asymmetric unit is shown for clarity.

Coordination of Cu\(^{2+}\) to the ligand 2

In an effort to systematically control the coordination chemistry of Cu\(^{2+}\) centres with ligand 2, and further understand the role of the metal in the promotion of the ring closure reaction, we have treated a slight excess (2:1) of CuCl\(_2\) with the ligand 2. The reaction was left overnight in refluxing acetonitrile and a dark coloured precipitate formed upon cooling to room temperature. As before, we attempted to purify the product by crystallisation of this dark solid via vapour diffusion of hexanes into a chloroform solution. By inspecting the crystalline sample under an optical microscope, it was immediately evident that two crops of different crystals had formed, one green and the other brown. The crystals were separated by hand with the help of tweezers and their structures were elucidated via X-ray diffraction. Following this procedure a mixture of two new complexes had formed, 7 and 8, with formulations as given in Fig. 12. The green coloured crystals were composed exclusively of the complex 7 along with lattice solvent molecules. On the other hand, the brown crystals involved co-crystallisation of two complexes, the newly obtained 8 and the previously obtained 6. In this case, the two sets of complexes had formed trimeric units of 8·6·6 linked together by two bridging Ìµ\(_i\)-coordinated Cl\(^-\) ligands. The formation of the complex 7 and the trimer 8·6·6, although unexpected, can be viewed as a further confirmation that the O\(_3\) oxidation of the phenylthioamide substituents on the pyrrole ring of the ligand 2 is indeed favoured by the presence of the Cu\(^{2+}\) metal centre. In fact the complexes 7 and 8 can be considered as the first and second reaction intermediates towards the formation of the doubly ring-closed ligand in complex 6, which is only obtained when the reaction is left for prolonged periods of time during the crystallisation stage (several days compared to 48 h to isolate the complex 7 and the trimer 8·6·6). The reaction is probably also influenced by the relative temperature and the extent of excess of starting Cu salt with respect to the ligand 2.

**Fig. 11** The π stacking involving the benzothiazole units in the lattice of 3. The interplanar distance is 3.458 Å. Hydrogen atoms omitted.

**Fig. 12** Structures of the new complexes 7 and 8 obtained with the 2:1 reaction of CuCl\(_2\) with the ligand 2 in refluxing acetonitrile.

X-ray structure of complex 7

Compound 7 crystallises in the triclinic P\overline{1} space group. Its structure, shown in Fig. 13, is analogous to the one of complex 4, with a square planar Cu\(^{2+}\) centre coordinated to the ligand 2, deprotonated on the pyrrole NH bond. The ligand is bound to the metal in a trischelating S,N,S’ fashion. The remaining
coordination site is occupied by a chloro anion. Similarly to complex 4, the complexes are arranged forming dimeric units throughout the lattice, where each of the Cu$^{2+}$ interacts, albeit weakly, with an apical S atom belonging to the neighbouring molecule of the dimer (Cu–S$_{apical}$ ca. 3.1 Å, Cu–S$_{planar}$ 2.4 Å). The two phenyl rings lie twisted at 67° and 60° with respect to the pyrrolido plane. Chloroform molecules are present as lattice solvent. There is no evidence of hydrogen bonding or π stacking between each of the dimeric units.

X-Ray structure of the trimer 8·6·6

The structure of this unprecedented trinuclear Cu$^{2+}$ complex is reported in Fig. 14. It crystallises in the triclinic P1̅ space group, along with chloroform and water molecules throughout the lattice. The trimer is formed by three Cu$^{2+}$ complexes, two of which are coordinated to the deprotonated form of ligand 2 in a similar fashion to that observed for complex 6. The remaining metal centre, shown schematically in Fig. 12 as complex 8, is bound in the same trischelating manner. The “base” of the trimer is composed by the Cl1–Cu1–Cl2–Cu2–Cl3–Cu3 zigzag, with Cl2 and Cl3 bridging between adjacent Cu centres in a µ$_2$-fashion. Cu1 and Cu2 are therefore pentacoordinated and arranged in square-based pyramidal geometry. In each case, the distance between the metal and the base chloro ligand is shorter (= 2.2 Å) than the one involving the apical chloro ligand (= 2.7 Å). On the other hand, Cu3 is square planar. There is no evidence of hydrogen bonding or π stacking between each of the trimeric units.

Coordination of Co$^{2+}$ to the ligand 2

To ultimately confirm that the presence of Cu plays a fundamental role in the O$_2$ oxidation of the phenylthioamide substituents in 2, we have repeated the same reaction as for the synthesis of complex 7 and trimer 8·6·6 but using hydrated CoCl$_2$, which is unlikely to behave as an oxidising agent in the same way as copper ions in acetonitrile. The reaction of hydrated CoCl$_2$ with the ligand 2 was attempted before, albeit in different conditions. That time, complete oxidation of the metal centres from Co$^{2+}$ to Co$^{3+}$ occurred and a charge separated dinuclear compound was obtained. The anionic part was composed of [CoCl$_4$$^-$], whereas the countercations was the pseudo-octahedral Co$^{3+}$ coordinated by two deprotonated ligands 2. Following the procedure reported in this work, a very similar compound was obtained. In the present case, however, the charge separated compound 9 was obtained, where the two metal centres are now in different oxidation states, as shown in Fig. 15. While the cationic part is identical to the previously reported Co$^{3+}$ complex, the anionic part is now formed by a pseudo-tetrahedral ethanol solvated [CoCl$_3$]$^-$ anion.

The structure of the isolated complex, where the ligand 2 did not undergo any ring closing reaction albeit in the presence of atmospheric O$_2$; as in the previous cases, confirms that the presence of Cu is required for the formation of the benzothiazole units under the conditions used.

X-Ray structure of the compound 9

Compound 9 (shown in Fig. 16) crystallises in the monoclinic P2$_1$/n space group. Two different complexes are present within the asymmetric unit: i) an anionic pseudo-tetrahedral Co$^{3+}$ bound to three Cl$^-$ ligand and to a neutral ethanol molecule; ii) a cationic pseudo-octahedral Co$^{3+}$ bound to two units of ligand 2 each with
a trischelating $S,N,S'$ fashion. Chloroform and water molecules are also present within the lattice. Apart from the Coulombic force generated by the separation of charge, there is no other evident interaction between the cationic and the anionic complexes. Two adjacent tetrahedral complexes are linked by formation of two symmetrical hydrogen bonds respectively involving the hydroxyl group of the ethanol ligand with the neighbouring chlorido anion (OH $\cdots$ Cl $= 2.0 \text{ Å}$). On the other hand, two of the external phenyl rings of the ligand 2 with respect to adjacent cationic Co$^{3+}$ complexes show some degree of $\pi$ stacking, with an average distance of 3.4 Å between the planes.

**Photophysical properties of the ligand 3**

The steady-state absorption and emission profiles of the ligand 3 are reported in Fig. 17. The spectra were recorded from diluted dichloromethane solutions at room temperature. The absorption spectrum shows structured bands in the 250–400 nm UV region. The higher energy band at 294 nm is tentatively assigned to a $\pi \rightarrow \pi^*$ transition centered on the phenyl substituents. In fact, due to the dihedral angles with respect to the pyrrole plane (as also shown in the crystal structure in Fig. 10), the phenyl rings experience a limited interannular conjugation. On the other hand, the structured band between 340 and 400 nm is assigned to a combination of $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions, which are centered on the planar and conjugated dibenzothiazolylpyrrole unit. Upon excitation at $\lambda_{ex} = 385 \text{ nm}$ a blue coloured emission is observed, which is typical of benzothiazole containing compounds. Supporting the previously reported band assignments, the emission profile is symmetrical with respect to the 340–400 nm absorption band.

**Conclusions**

The coordination chemistry of Cu$^{II}$ cations with 2,5-dicarbothioamidopyrroles has been reported. Several complexes of different geometries were isolated and the tendency of both Cu$^{I}$ and Cu$^{II}$ to promote a ring closing reaction resulting in the formation of benzothiazole was established. Under the same conditions, the ring closing reaction was not observed when Cu$^{II}$ was substituted with Co$^{II}$. The resulting benzothiazole-

**Fig. 16** X-Ray crystal structure of the dinuclear compound 9 with thermal ellipsoids drawn at the 35% probability level. Selected hydrogen atoms and chloroform solvent molecules are omitted for clarity.

**Fig. 17** Absorption (dashed line) and emission (solid line) profiles of a dichloromethane solution of 3. The emission spectrum was recorded at an excitation wavelength of 385 nm, corresponding to the most intense maximum of the absorption spectrum.

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**Notes and references**


