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Luminescence and thermal behavior of copper (I) complexes with heterocyclic thiones. Part II: cationic complexes

P. Aslanidis · K. Chrissafis · M. Lalia-Kantouri

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Abstract Copper (I) halide complexes formulated as $[(L)_2Cu(\mu_2\text{-}L)_2Cu(L)_2]^{2+}\ 2X^-$, (X = Cl, Br and L = pyridine-2-thione (py2SH) or 4,6-dimethylpyrimidine-2-thione (dmpymtH)) were prepared, and their photoluminescence and thermal properties were investigated. The complexes are strongly emissive in the solid state, with the emissions being dominated by large Stokes shifts (>200 nm), which are depending on both the heterocyclic thione and the nature of the halogen. These emissions can be assigned to MLCT with some mixing of the halide-to-ligand (XL) CT characters. Simultaneous TG/DTG–DTA technique was used for two complexes with the dmpymtH ligand to determine their thermal degradation, which was found to be very complicated. In inert atmosphere the residues at 1,000 °C (verified with PXRD) were mainly Cu_2S, while at 1,300 °C a mixture of Cu_2S and Cu. In oxygen atmosphere the residues were CuO.

Keywords Cationic copper (I) complexes · Heterocyclic thiones · Luminescence · TG/DTG–DTA · PXRD

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P. Aslanidis · M. Lalia-Kantouri (✉)
Laboratory of Inorganic Chemistry, Department of Chemistry,
Faculty of Sciences, Aristotle University of Thessaloniki,
P.O. Box 135, 541 24 Thessaloniki, Greece
e-mail: lalia@chem.auth.gr

K. Chrissafis
Solid State Physics Department, School of Physics, Aristotle
University of Thessaloniki, 541 24 Thessaloniki, Greece

Introduction

The past three decades heterocyclic thiones have attracted considerable interest due to their relevance in biological systems [1, 2]. Specific attention has been given to the study of their binding properties in complexes with copper (I) and silver (I). The metal–ligand interaction in such complexes has been found to be highly flexible, resulting in an extraordinary variety of molecular structures [3–5]. However, our long standing investigations within this field of research resulted in the isolation of pseudo-tetrahedrally coordinated symmetrical doubly bridged dinuclear species of the general type $[CuX(thione)_2]_2$, where X = Cl, Br, I [6, 7] or of mixed-ligand copper (I) complexes $[CuX(phosphine)(thione)]_2$ [7], or of the general type $[Cu_2(thione)_6]^{2+}\ 2X^-$ (X = Cl, Br) [8, 9]. The stoichiometry of these complexes strongly depends on the molecular ratio of the starting materials. Recently, it is also referred the preparation and structural characterization of two polymers with tetrameric structural units $[CuX(pymtH)]_4$, (X = Cl, Br) [10], where the Cu centers have two different coordination environments, that is CuNSCl in a distorted planar trigonal geometry and $CuNS_2Cl$ in a distorted tetrahedral geometry. The mixed coordinated cyclic tetramer $[CuCl(dmpymtH)]_4$ has also been obtained from $CuCl_2$ with the thione ligand in a molar ratio 1:2 [11].

In view of practical applications in solar-energy conversion systems, chemical sensors, or display devises [12–14], attention has been paid to emissive copper (I) complexes with thiones as ligands, although reports on their photochemical properties are scarce [10]. The computational (TD–DFT) methodologies in conjunction with single crystal X-ray studies have been used to explore the relationship between structure and luminescence in thione-S ligated copper (I) complexes bearing tertiary arylphosphanes as bulky spectator ligands [15].

In this study, the photoluminescence properties of four cationic dimeric copper (I) halide complexes, formulated as $[(L)_2Cu(\mu_2\text{-}L)_2Cu(L)_2]^{2+}$ $2X^-$, where X = Cl, Br and L = pyridine-2-thione (py2SH), or 4,6-dimethylpyrimidine-2-thione (dmpymtH) were studied. A further important scope of the present paper was the study of the thermal properties of the two cationic $[Cu_2(dmpymtH)_6]^{2+}$ $2X^-$ complexes (X = Cl, Br), by using the simultaneous TG/DTG–DTA technique in inert and oxidative atmospheres. Powder XRD was used for the verification of the final solid residues.

Experimental section

Materials and instrumentation

Commercially available copper (I) halides were purchased as reagent grade from Aldrich and were used without further purification, while the thione ligands were re-crystallized from hot ethanol prior to their use. All the solvents were purified by respective suitable methods and allowed to stand over molecular sieves.

Stoichiometric analyses (C, H, and N) were performed on a Perkin-Elmer 240B elemental analyzer. Metal content was determined by EDTA titration after decomposition with nitric acid, using murexide as indicator. Molar conductivities were measured in CH_3NO_2 and CH_3OH solutions, employing a WTW conductivity bridge and a calibrated dip type cell.

Infrared spectra in the region of 4,000–200 cm^{-1} were obtained in KBr disks with a Nicolet FT-IR 6700 spectrophotometer, while a Shimadzu 160A spectrophotometer and a Hitachi F-700 fluorescence spectrometer were used to obtain the electronic absorption and emission/excitation spectra, respectively.

The simultaneous TG/DTG–DTA curves were obtained on a SETARAM thermal analyzer, model SETSYS-1200. The samples of approximately 10 mg were heated in platinum crucibles, in nitrogen or argon atmosphere at a flow rate of 80 ml min^{-1}, within the temperature range 30–950 °C, at a heating rate of 10 °C min^{-1}.

Thermogravimetric analysis was also carried out with a SETARAM SETSYS TG–DTA 16/18. Samples (6.0 ± 0.2 mg) were placed in alumina crucibles. An empty alumina crucible was used as reference. The compounds were heated from ambient temperature to 1,300 °C in a 50 ml/min flow of N_2 or O_2 at heating rate 20 °C min^{-1}. Continuous recordings of sample temperature, sample mass, its first derivative and heat flow were taken.

The structure identification is performed with X-ray diffraction analysis (XRD) using a 2-cycles Rigaku Ultima$^+$ diffractometer (40 kV, 30 mA, CuK_α radiation) with Bragg-Brentano geometry.

General procedure for the synthesis of the Cu(I) complexes $[Cu_2L_6]^{2+}$ $2X^-$ (**1**–**4**)

The complexes were prepared according to the following procedure [8]. A solution of 0.5 mmol of copper (II) chloride or bromide in 10 mL of water was treated with an ethanolic solution of the appropriate thione (2.5 mmol in 20 mL) and the resulting mixture was stirred for 30 min at ambient temperature. The resulting clear solution was kept at 5 °C until a microcrystalline solid was formed, which was filtered off and dried in vacuum. The compounds are soluble in CH_3NO_2, CH_3OH, CH_3COCH_3, and CH_2Cl_2.

$[Cu_2(py2SH)_6]^{2+}$ $2Cl^-$ (**1**): yellow to orange microcrystalline solid, yield 44.5%. Stoichiometry calculated for $C_{30}H_{30}Cl_2Cu_2N_6S_6$: C, 41.65; H, 3.49; Cu, 14.70; N, 9.71. Found: C, 41.80; H, 3.53; Cu, 15.02; N, 10.02%. Conductivity in CH_3NO_2 and in MeOH ($\Lambda = 142.0$ and 183.0 μS/cm, respectively).

$[Cu_2(py2SH)_6]^{2+}$ $2Br^-$ (**2**): yellow to orange microcrystalline solid, yield 55.2%. Stoichiometry calculated for $C_{30}H_{30}Br_2Cu_2N_6S_6$: C, 37.77; H, 3.17; Cu, 13.33; N, 8.81. Found: C, 38.08; H, 3.21; Cu, 13.65; N, 8.70%. Conductivity in CH_3NO_2 and in MeOH ($\Lambda = 145.3$ and 168.0 μS/cm, respectively).

$[Cu_2(dmpymtH)_6]^{2+}$ $2Cl^-$ (**3**): orange to red microcrystalline solid, yield 68.0%. Stoichiometry calculated for $C_{36}H_{48}Cl_2Cu_2N_{12}S_6$: C, 41.60; H, 4.62; Cu, 12.23; N, 16.17. Found: C, 40.99; H, 4.74; Cu, 12.43; N, 15.85%. Conductivity in CH_3NO_2 and in MeOH ($\Lambda = 151.3$ and 194.0 μS/cm, respectively).

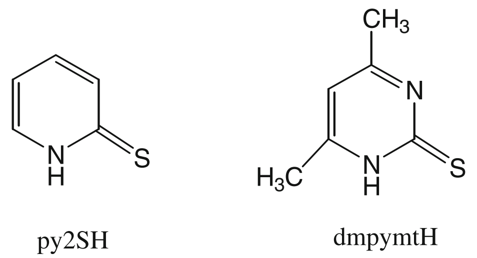
$[Cu_2(dmpymtH)_6]^{2+}$ $2Br^-$ (**4**): orange to red microcrystalline solid, yield 60.6%. Stoichiometry calculated for $C_{36}H_{48}Br_2Cu_2N_{12}S_6$: C, 38.33; H, 4.38; Cu, 11.27; N, 14.90. Found: C, 38.08; H, 3.99; Cu, 11.38; N, 14.67%. Conductivity in CH_3NO_2 and in MeOH ($\Lambda = 148.7$ and 204.0 μS/cm, respectively).

Results and discussion

General considerations

The heterocyclic thiones (pyridine-2-thione (py2SH) and 4,6-dimethylpyrimidine-2-thione (dmpymtH)), are depicted in Scheme 1.

All the complexes are air stable, orange microcrystalline solids. They were characterized as 1:2 electrolytes with the formula $[Cu_2(thione)_6]^{2+}$ $2X^-$ by means of elemental



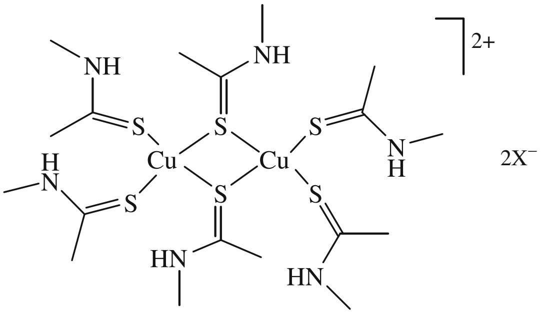
Scheme 1 The heterocyclic thiones with their abbreviations

analysis, conductivity measurements, and FT-IR spectra. The powder XRD of the compounds $[Cu_2(dmpymtH)_6]^{2+}$ $2Cl^-$ and $[Cu_2(dmpymtH)_6]^{2+}$ $2Br^-$ was recorded, and their patterns are given as supplementary materials in Figs. s1 and s2.

The crystal structures of the studied compounds $[Cu_2(py2SH)_6]^{2+}$ $2Cl^-$ (**1**) and $[Cu_2(py2SH)_6]^{2+}$ $2Br^-$ (**2**) were previously confirmed by single crystal X-ray diffraction analysis, as dinuclear copper (I) compound, $[(thione)_2Cu(\mu_2\text{-thione})_2Cu(thione_2)]^{2+}$ [8]. In these complexes, the thione(py2SH) behaves as monodentate ligand, through the exocyclic sulfur, in two coordination modes (as bridging to the two copper atoms and as free neutral thione) (Scheme 2).

Crystal structures of Cu(I) complexes having the molar ratio Cu-thione 1:3, have been early reported as 1:1 electrolytes for $[Cu(py2SH)_3]^+$ NO_3^- [16] and recently for the isomorphous anhydrous monomeric compounds $[Cu(tu)_3]^+$ X^- (tu = thiourea and X = Cl, Br), while as 1:2 electrolytes for the isomorphous hydrated dimeric compounds $[Cu_2(tu)_6]^{2+}$ $2X^-{\cdot}2H_2O$. The structure of the thiourea complexes depends on the molar ratio of copper halide and the sulfur containing ligand, as well as on the number of crystallization water molecules [9].

It is also referred a third isomorphous pair of these complexes with copper-thiourea stoichiometric ratio 1:1, $[Cu(tu)]X{\cdot}0.5H_2O$, behaved as 1:1 electrolyte [9].



Scheme 2 Structure of the cationic copper (I) complexes $[(L)_2Cu(\mu_2\text{-}L)_2Cu(L)_2]^{2+}$ $2X^-$

Spectroscopy (UV–Vis and IR)

The electronic absorption spectra of the complexes, recorded in chloroform at room temperature, show three intense broad bands with maxima in the 227–241, 286–318 and 353–383 nm regions, respectively. With reference to the absorption spectra of the uncoordinated thiones, the two high energy bands can be attributed to intraligand $\pi \rightarrow \pi^*$ transitions on the phenyl groups of the thiones, whereby the lower energy band should be considered as a $\pi \rightarrow \pi^*$ transition located at the C=S bond of the thiones [6, 7].

The infrared spectra, recorded in the range 4,000–250 cm^{-1} contain the characteristic four “thioamide bands” (1,562, 1,825, 985, and 732 cm^{-1}), required by the presence of the heterocyclic thione ligands, with shifts due to coordination indicative of an exclusive S-coordination mode, as well as a broad band in the 3,100–2,900 cm^{-1} region assigned to the ν(NH) stretching vibration, overlapped with aliphatic CH stretching. The FT-IR spectra of the complexes $[Cu_2(py2SH)_6]^{2+}$ $2Cl^-$ and $[Cu_2(py2SH)_6]^{2+}$ $2Br^-$ are given as supplementary material in Fig. s3, while for the complexes $[Cu_2(dmpymtH)_6]^{2+}$ $2Cl^-$ and $[Cu_2(dmpymtH)_6]^{2+}$ $2Br^-$ in Fig. s4. The pair-wise presentation of the spectra shows strong similarities of isomorphous compounds.

Luminescence

Room temperature photoexitation at 350–365 nm of solid samples of the investigated complexes containing py2SH and dmpymtH thiones produces an intense broad emission band with peak maxima for the cationic complexes in the region 540–585 nm (Table 1). The representative excitation and emission spectra of $[Cu_2(dmpymtH)_6]^{2+}$ $2Br^-$ is depicted in Fig. 1. The most characteristic feature of the emission spectra is the large Stokes shifts (>200 nm), much larger than the ones observed for the free thiones. These emissions cannot be considered as one of pure intraligand origin, because of their significant red shifts relative to the solid-state R.T. emission spectra of the free ligands, but appear to be more compatible with a metal-to-ligand charge-transfer (MLCT) excited state of type Cu(I) → halogen. However, the participation of the halogen in the emissive excited states, in the form of a ligand-to-metal charge-transfer (XMCT) or an interligand charge-transfer (XLCT, X → thione) cannot be excluded. In fact, according to recent results [17], a redistribution of charge in terms of transfer from the halogen to the thione unit appears likely in the complexes under investigation. In this respect, there is a dependence of the emission maxima on the kind of the halide present, with a remarkable red shift in the order Br → Cl. The differences in the Stokes shifts observed for the compounds with the same halogen could

Table 1 Solid-state excitation and emission maxima for cationic Cu(I) compounds at R.T.

Compound	Excitation, λ_{max}/nm	Emission, λ_{max}/nm
1. $[Cu_2(py2SH)_6]^{2+}$ $2Cl^-$	330	584
2. $[Cu_2(py2SH)_6]^{2+}$ $2Br^-$	355	576
3. $[Cu_2(dmpymtH)_6]^{2+}$ $2Cl^-$	365	543
4. $[Cu_2(dmpymtH)_6]^{2+}$ $2Br^-$	350	559

be attributed to the electronic properties of the respective thione, which considerably affect the Cu–S bond strength. Recent studies on complexes of the type CuXL (L = heteroaromatic unit) revealed that the emissive excited state strongly depends on the electrophilic character of L [18], while on polynuclear copper (I) complexes with chalcogen ligands the emission at ~570 nm could be ascribed as an LMCT (S → Cu) [10].

Thermal decomposition

TG/DTG–DTA in nitrogen

The thermal decomposition for two compounds under investigation, $[Cu_2(dmpymtH)_6]^{2+}$ $2Cl^-$ and $[Cu_2(dmpymtH)_6]^{2+}$ $2Br^-$, was studied in N_2 and O_2 atmospheres by TG–DTA. The solid residues were examined by powder XRD.

Thermoanalytical curves (TG/DTG–DTA) for the compounds $[Cu_2(dmpymtH)_6]^{2+}$ $2Cl^-$ and $[Cu_2(dmpymtH)_6]^{2+}$ $2Br^-$ in nitrogen atmosphere are given in Figs. 2 and 3, respectively.

The shape of the mass loss is very complicated and resembles the shape of the corresponding neutral compounds $[Cu_2X_2(dmpymtH)_4]$ [19]. Each area of mass loss starts before the ending of the previous one. For this reason it is very difficult to correspond to different areas of mass loss in a specific way of decomposition of the compound. Using mass loss and derivative mass loss plots (TG/DTG) we can conclude that: under nitrogen, in the first stage (120–460 °C), the compound $[Cu_2(dmpymtH)_6]^{2+}$ $2Cl^-$ (Fig. 2) shows sudden mass loss (DTG peak at 257 °C) of 53.5%, which coincides with the release of four thione ligands with a theoretical mass loss of 53.9%. The DTA curve shows one sharp endothermic peak at 227 and a second overlapped one (as shoulder) at 255 °C. The first peak is attributed to simultaneous melting and decomposition of the compound, as it was evidenced with automated melting point capillary tube system in static air (mp. at 225–227 °C), while the next one to further decomposition as the DTG curve implies.

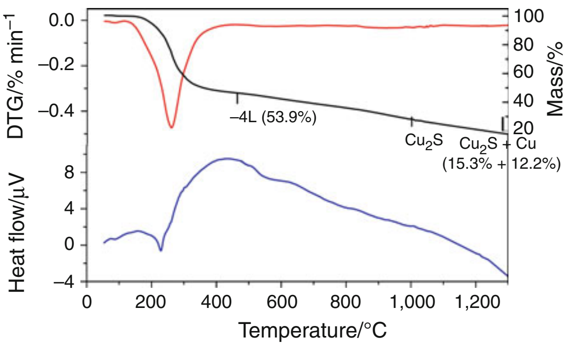


Fig. 2 Thermoanalytical curves (TG/DTG–DTA) of the compound $[Cu_2(dmpymtH)_6]^{2+}$ $2Cl^-$ in N_2 atmosphere with heating rate 20 °C min^{-1}

Upon increasing the temperature, the unstable intermediates undergo further decompositions with gradually and successive mass loss in the temperature range 460–1,300 °C of 28.8%, which could be attributed to further elimination of the remaining thione molecules. Efforts to isolate the intermediates were not successful due to their continuous decomposition, as it was evidenced from the TG curves, while the mass losses at these stages cannot be attributed to certain species. The amount of the solid residue, estimated from the TG curve (found 17.7%), with the calculated value for Cu_2S 15.3% and metallic copper 12.2% denotes that the decomposition of this compound at 1,300 °C was not completed.

For the compound $[Cu_2(dmpymtH)_6]^{2+}$ $2Br^-$ (Fig. 3), in the first stage (130–490 °C) with DTG peak at 264 °C, the sudden mass loss of 49.9% coincides well with the release of four dmpymtH ligands with a theoretical mass loss of

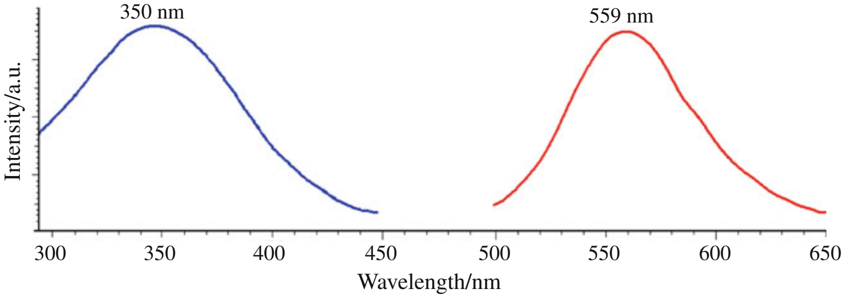


Fig. 1 Room temperature solid-state excitation and emission spectra of $[Cu_2(dmpymtH)_6]^{2+}$ $2Br^-$

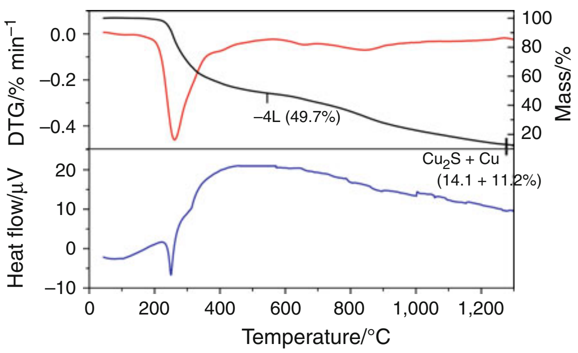


Fig. 3 Thermoanalytical curves (TG/DTG–DTA) of the compound $[Cu_2(dmpymtH)_6]^{2+}$ $2Br^-$ in N_2 atmosphere with heating rate 20 °C min^{-1}

49.7%. The DTA curve shows a sharp endothermic peak at 247 °C, which is attributed to simultaneous melting and decomposition of the compound.

The second and third stages (490–700 and 700–1,300 °C), with mass loss of 37.6% found, contribute to the further decomposition of the possible intermediates [CuX(dmpymtH)$_2$]. The final solid residue at 1,300 °C in nitrogen, estimated from the TG curve (found 12.5%), could be attributed to metallic copper (calc. 11.2%) but not to Cu_2S (calc. 14.1%). The DTA curves do not clearly show the endothermic peaks due to the melting of copper at 1,084 °C or to the melting of Cu_2S at 1,130 °C.

In order to verify the solid residues, as they deduced and estimated from the TG and DTG curves of the studied copper compounds, powder XRD studies were used in the case of the compound $[Cu_2(dmpymtH)_6]^{2+}$ $2Br^-$. It was found that the solid material, at 1,000 °C during decomposition in N_2 consists mainly of Cu_2S, while at 1,300 °C to metallic copper.

It is known that for Cu(I) complexes of type [(tpp)Cu (μ-Cl)$_2$Cu(tppp)] (tpp = triphenylophospine) the residue at 600 °C corresponds to metallic copper (Cu^0) [20]. It is also referred, according to XRD measurements, that the residues at 1,200 °C for Cu(I) thiocarbamates in inert atmospheres consisted of Cu_2S and Cu [21, 22]. A more recent study on mixed valence copper (I, II) thiosulfate salt gave both copper sulfides ($Cu_{1.8}S$, digenite and CuS, covellite) at about 300 °C range even in flowing air atmosphere [23]. Similarly both sulfides are formed from thiourea solution [24].

TG/DTG–DTA in oxygen

The shape of mass loss plots is quite different in the two atmospheres. Thermoanalytical curves (TG/DTG–DTA) for the compounds $[Cu_2(dmpymtH)_6]^{2+}$ $2Cl^-$ and $[Cu_2(dmpymtH)_6]^{2+}$ $2Br^-$ in oxygen atmosphere are given in Figs. 4 and 5, respectively. The decomposition rate of the compounds under O_2 atmosphere becomes larger than the one under N_2 atmosphere, and at around 600 °C they have lost the major quantity of their mass. In details, in the first stage (120–385 °C), the compound $[Cu_2(dmpymtH)_6]^{2+}$ $2Cl^-$ (Fig. 4) shows sudden mass loss (DTG peaks at 240(sh) and 270 °C) of 36.9%, which is lower than the release of three thione ligands (calc. 40.5%). The DTA curve shows one small endothermic peak at 240 °C, which is attributed to the melting and further decomposition of the compound.

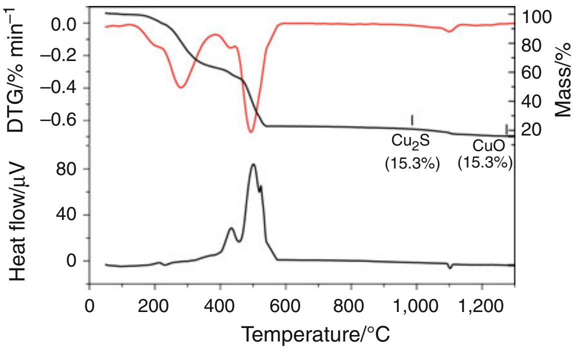


Fig. 4 Thermoanalytical curves (TG/DTG–DTA) of the compound $[Cu_2(dmpymtH)_6]^{2+}$ $2Cl^-$ in oxygen with heating rate 20 °C min^{-1}

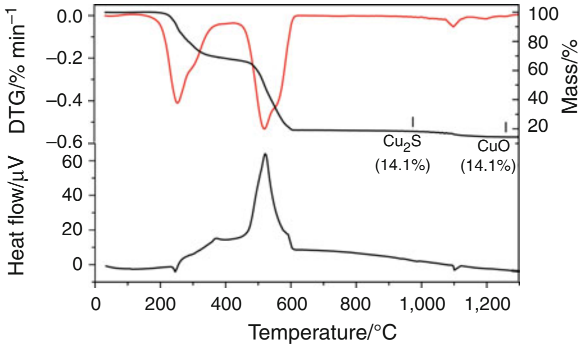


Fig. 5 Thermoanalytical curves (TG/DTG–DTA) of the compound $[Cu_2(dmpymtH)_6]^{2+}$ $2Br^-$ in oxygen with heating rate 20 °C min^{-1}

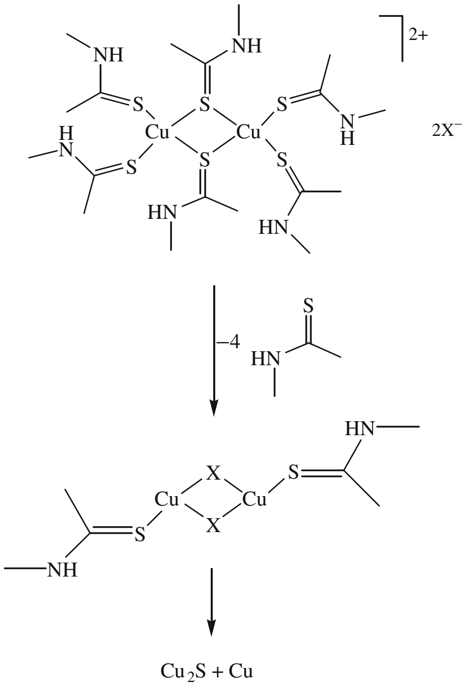
In the second and third stages (385–450 and 450–612 °C), the decomposition rate (DTG peaks at 440 and 490 °C) is higher than in N_2 with sudden mass losses of 6.2 and 34.2%. These decompositions are strongly exothermic with DTA peaks at 440 and 490 °C, which means that maybe an oxidation takes place along with the decomposition. Finally, an endothermic fourth stage takes place (612–1,300 °C) with DTG peak at 1,100 °C. The residue at 1,300 °C, as it is measured by TG, coincides well with the theoretical amount of CuO (found 15.9%, calc. 15.3%). For an analogous copper-thiourea compound $[Cu_2(tu)_6]Cl_2 \cdot 2H_2O$, the main degradation step in static air led to the formation of $Cu_{1.8}S$ (digenite) at 300 °C, while stoichiometric amount of the oxides CuO and Cu_2O was formed at ~1,000 °C, proved by powder XRD [25].

The thermal decomposition profile of the compound $[Cu_2(dmpymtH)_6]^{2+}$ $2Br^-$ under O_2 (Fig. 5) is quite similar with the profile of the compound $[Cu_2(dmpymtH)_6]^{2+}$ $2Cl^-$. The first stage (120–420 °C, with DTG peak at 250 °C) shows sudden mass loss of 32.4%, which is lower than the release of three thione ligands (calc. 37.3%). The DTA curve shows one small endothermic peak at 250 °C, which is attributed to the melting and further decomposition of the compound. The second stage (420–650 °C, with DTG peak at 520 and DTA exothermic peak at 525 °C) shows even larger mass loss of 48.5%. A large plateau in the range 650–1,100 °C with an intermediate solid found 18.0% could be attributed to the intermediate Cu_2S (calculated 14.1%) or to CuS (calculated 16.9%) or to $CuBr_2$ (calculated 19.8%) although the XRD gave only CuO.

The final residue at 1,300 °C as it is measured by TG coincides well with the theoretical amount of CuO (found 14.3%, calc. 14.1%) and verified from the results of the powder XRD analysis, in accordance with the literature findings [21].

Decomposition mechanism

Taking into account the results coming from the TG/DTG measurements and the XRD analysis of the solid intermediate and residue materials, of the thermal decomposition in nitrogen atmosphere, we propose a general decomposition pathway for the cationic complexes under investigation in Scheme 3.



Scheme 3 Proposed decomposition pathway in nitrogen atmosphere for the Cu(I) complexes

Conclusions

The determination of the emissive excited states in the compounds under investigation is a difficult task, with research in this area being yet in the beginnings. The results of this study provide some promising qualitative trends that could be useful as a basis for further investigations. The complexes are strongly emissive in the solid state at ambient temperature, with the emissions being dominated by large Stokes shifts (>200 nm), which are depending on both the heterocyclic thione and the nature of the halogen. The emissions of these compounds can be assigned to MLCT excited states with some mixing of the halide-to-ligand (XL) CT characters. The thermal decomposition of the title compounds under both atmospheres is very complicated giving multi-step TG/DTG curves. The decomposition starts with the elimination of the thione ligands in small fragments. The XRD gave mainly Cu_2S as intermediates at 1,000 °C. The final residue at 1,300 °C is a mixture of Cu_2S and metallic Cu, as it was calculated by TG measurements. In the case of O_2 atmosphere the final residue of all the compounds, as verified from the results of the powder XRD analysis, is CuO, and its value, as it is measured by TG, coincides well with the theoretical amount of CuO.

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