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Luminescence and thermal behavior by simultaneous TG/DTG–DTA coupled with MS of neutral copper (I) complexes with heterocyclic thiones

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Abstract Copper(I) halide complexes formulated as $[(L)CuX(\mu_2\text{-}L)_2CuX(L)]$ (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, coupled with MS for the analysis of the gaseous decomposition products, 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 a mixture of Cu_2S and CuX, while at 1,300 °C a mixture of Cu_2S and Cu. In oxygen atmosphere the residues were CuO.

Keywords Copper(I) complexes · Heterocyclic thiones · Luminescence · TG/DTG–DTA · Coupled TG–MS · PXRD

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Introduction

Heterocyclic thiones have attracted considerable interest in the last three decades because of their relevance in biological systems [1, 2]. Specific attention has been given to the study of their binding properties in complexes with closed-shell d^{10} metal ions, mainly 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 almost exclusively in the isolation of pseudo-tetrahedrally coordinated symmetrical doubly bridged dicopper species of the general type $[CuX(thione)_2]_2$, where X = Cl, Br, I [6, 7], or of dinuclear mixed-ligand copper(I) complexes $[CuX(phosphine)(thione)]_2$ [7–9].

It is recently mentioned, however, the preparation and structural characterization of two isostructural tetranuclear complexes $[CuX(pymtH)]_4$, where X = Cl, Br [10]. It is interesting that 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 tetranuclear complex $[CuCl(dmpymtH)]_4$ has also been obtained from $CuCl_2$ with the thione ligand in a molar ratio 1:2 [11].

Much attention has also been paid to emissive copper (I) complexes in view of practical applications in solar-energy conversion systems, chemical sensors, or display devises [12–14]. However, most of the studies about copper (I) complexes with thiones as ligands, are limited to the structural aspects, and reports on their photochemical properties are scarce [10]. The computational (DFT and 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]. Since it is very interesting to reveal the impact of the thione ligands on the luminescence properties of such complexes, four neutral dimeric copper(I) halide complexes, formulated as [(L)CuX(μ_2-L)$_2$CuX(L)], where X = Cl, Br and L = pyridine-2-thione (py2SH), or 4,6-dimethylpyrimidine-2-thione (dmpymtH) were studied.

A further important scope of this article pertains to the study of the thermal properties of the two neutral [CuX(dmpymtH)$_2$]$_2$ complexes (X = Cl, Br), by using the simultaneous TG/DTG–DTA technique in inert and oxidative atmospheres. Simultaneous TG-DTA coupled with MS was used for the analysis of the gaseous decomposition products in argon atmosphere, while 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 mourexide as indicator. Molar conductivities were measured in CH_3CN 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, within the temperature range 30–950 °C, at a heating rate of 10 °C min^{-1}. Mass spectra (MS) of the gaseous evolved moiety during the experiments were recorded since the TG apparatus was coupled with a Quadrupole Mass Spectrometer (QMS) model Thermostar. The TG was linked to a heated gas cell of the MS by means of a heated transfer line, at temperature 180 °C. Data were processed using on-line connected computer system with commercial software Quadstar.

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 1,400 °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 weight, its first derivative, and heat flow were taken.

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

General procedure for the synthesis of the neutral Cu(I) complexes [CuXL$_2$]$_2$ (1–4)

The complexes were prepared according to published procedures [6, 7], in some cases slightly modified. A suspension of 0.5 mmol of copper(I) halide (49.5 mg for CuCl, 71.7 mg for CuBr) in 50 cm^3 of dry acetonitrile was stirred for 2 h at 50 °C. The resulting clear solution was filtered off and then treated with a solution of the appropriate thione (0.5 mmol) dissolved in a small amount (~20 cm^3) of ethanol or methanol, and the new reaction mixture was stirred for additional 30 min at 50 °C. Slow evaporation of the clear solution at ambient temperature afforded a microcrystalline solid, which was filtered off and dried in vacuum. The compounds are moderately soluble in CH_3CN, CH_3COCH_3, and $CHCl_3$.

(1) **[CuCl(py2SH)$_2$]$_2$**: yellow microcrystalline solid, yield 44.5%. Stoichiometry calculated for $C_{20}H_{20}Cl_2Cu_2N_4S_4$: *C, 37.38; H, 3.13; Cu, 19.78; N, 8.72. Found: C, 37.81; H, 3.14; Cu, 19.87; N, 8.71%.*

(2) **[CuBr(py2SH)$_2$]$_2$**: yellow microcrystalline solid, yield 55.0%. Stoichiometry calculated for $C_{20}H_{20}Br_2Cu_2N_4S_4$: *C, 32.83; H, 2.75; Cu, 17.37; N, 7.65. Found: C, 33.26; H, 3.04; Cu, 17.85; N, 8.11%.*

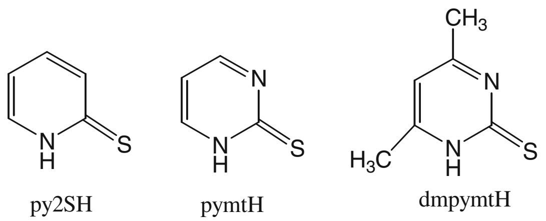
(3) **[CuCl(dmpymtH)$_2$]$_2$**: orange microcrystalline solid, yield 55.0%. Stoichiometry calculated for $C_{24}H_{32}Cl_2Cu_2N_8S_4$: C, 37.99; H, 4.25; Cu, 16.75; N, 14.77. *Found: C, 38.25; H, 4.35; Cu, 16.27; N, 14.82%.*

(4) **[CuBr(dmpymtH)$_2$]$_2$**: orange microcrystalline solid, yield 46.4%. Stoichiometry calculated for $C_{24}H_{32}Br_2Cu_2N_8S_4$: C, 34.0; H, 3.80; Cu, 14.99; N, 13.22. *Found: C, 35.25; H, 3.93; Cu, 14.79; N, 12.85%.*

Results and discussion

General considerations

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



Scheme 1 The heterocyclic thiones with their abbreviations

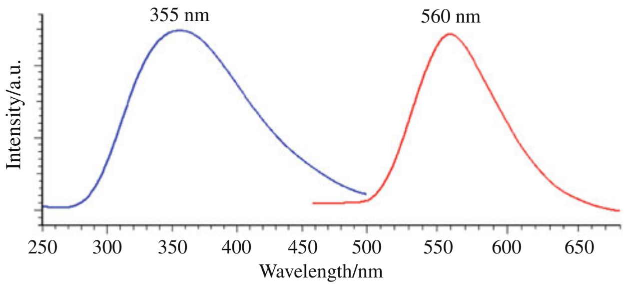


Fig. 1 Room temperature solid state excitation and emission spectra of $[CuCl(py2SH)_2]_2$

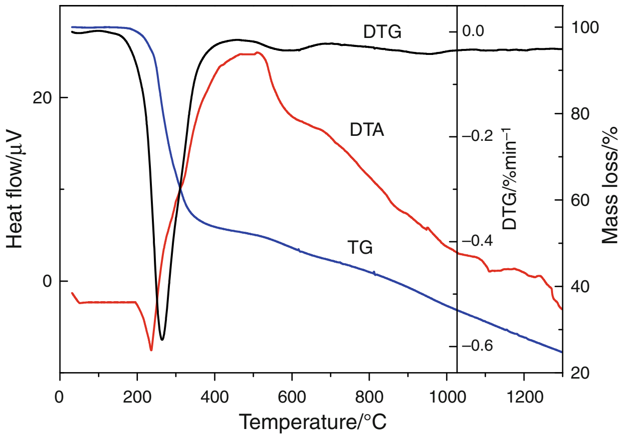


Fig. 2 Thermoanalytical curves (TG/DTG–DTA) of the compound $[CuCl(dmpymtH)_2]_2$ in N_2 atmosphere with heating rate 20 °C min^{-1}

All the complexes are air stable, yellow to orange microcrystalline solids. They were characterized as neutral diamagnetic compounds with the formula $[CuX(thione)_2]_2$ by means of elemental analysis, conductivity measurements (they show no conductance in CH_3CN solutions), and FT-IR spectra. The Powder XRD of all the studied compounds was recorded and their patterns are given as supplementary materials in Figs. 1, 2, 3, 4.

The crystal structure of the studied compound $[CuCl(dmpymtH)_2]_2$ (**3**) was recently confirmed, by single crystal X-ray diffraction analysis, as dinuclear copper(I) compound, $[(thione)CuCl(\mu_2\text{-}thione)_2CuCl(thione)]$ [16]. Comparison of the experimental XRD pattern of the complex (**3**) with the theoretical one, derived from the crystal analysis, gave good correlation. In this complex, the dmpymtH thione 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). This compound is similar with the $[CuBr(pymtH)_2]_2$ [7], possessing a trans Cu-halide configuration, while in $[CuI(py2SH)_2]_2$ [6] and $[CuI(pymtH)_2]_2$ [10] the Cu–I configuration is cis. This knowledge provides a useful basis, for predicting the structure of the yet unknown analogous complexes.

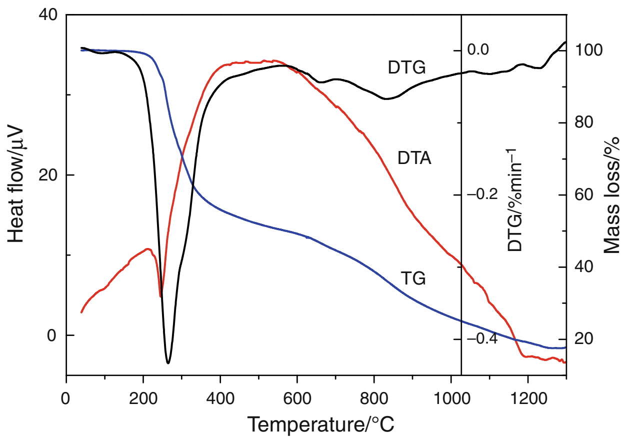


Fig. 3 Thermoanalytical curves (TG/DTG–DTA) of the compound $[CuBr(dmpymtH)_2]_2$ in N_2 atmosphere with heating rate 20 °C min^{-1}

Spectroscopy (UV–Vis and IR)

The electronic absorption spectra of the complexes, recorded in chloroform at room temperature, showed 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, 16].

The infrared spectra, recorded in the range 4,000–250 cm^{-1}, contain the characteristic four “thioamide bands” (1562, 1825, 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.

Luminescence

Room temperature photoexcitation at 350–390 nm of solid samples of the investigated complexes containing py2SH and dmpymtH thiones produces an intense broad emission

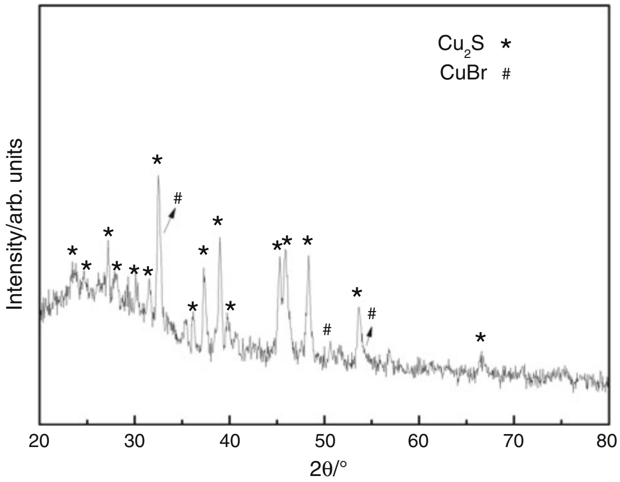
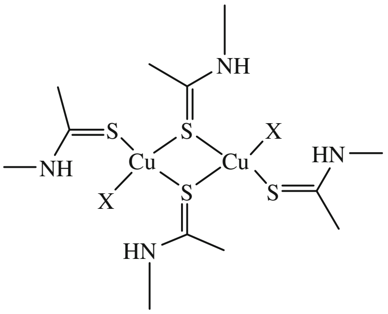


Fig. 4 Powder XRD diffraction pattern of compound $[CuBr(dmpymtH)_2]_2$ under N_2 atmosphere at 1,000 °C. Cu–S phases: PDF #72-1966 ($Cu_{7.2}S_4$), 29-0578 ($Cu_{1.96}S$), 72-1071 (Cu_2S), 65-3816 (Cu_2S), and CuBr phases: PDF #82-2120 (CuBr) [26]



Scheme 2 Structure of the neutral copper(I) complexes $[(L)CuX(\mu_2\text{-}L)_2CuX(L)]$ (X = Cl, Br)

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

Compound	Excitation, λ_{max}/nm	Emission, λ_{max}/nm
1 $[CuCl(py2SH)_2]_2$	355	560
2 $[CuBr(py2SH)_2]_2$	371	545
3 $[CuCl(dmpymtH)_2]_2$	350	572
4 $[CuBr(dmpymtH)_2]_2$	332	546

band with peak maxima for the neutral complexes in the region 545–572 nm (Table 1). The representative excitation and emission spectra of $[CuCl(py2SH)_2]_2$ 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 an 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 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].

The fluorescence observed in a number of dimeric or tetrameric complexes of copper(I) halides with metal–metal distances lower than the sum of the van der Waals radii (2.8 Å) has been often assigned to metal–metal bonding interactions [19–21]. The Cu···Cu separation in the studied compounds is clearly above this limit; thus, inter-metallic interactions are quite unlikely to participate in any excited states responsible for the observed emissions.

Thermal decomposition

TG/DTG–DTA in nitrogen

The thermal decomposition for two compounds under investigation $[CuCl(dmpymtH)_2]_2$ and $[CuBr(dmpymtH)_2]_2$, was studied in N_2 and O_2 atmospheres by TG-DTA. The released gaseous products were examined by coupled TG–MS, while the solid residues by powder XRD.

Thermoanalytical curves (TG/DTG–DTA) for the compounds $[CuCl(dmpymtH)_2]_2$ and $[CuBr(dmpymtH)_2]_2$ in nitrogen atmosphere are given in Figs. 2 and 3, respectively.

The shape of the mass loss is very complicated. It presents three different areas of mass loss, and each area 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 (110–470 °C), the compound $[CuCl(dmpymtH)_2]_2$ (Fig. 2) shows sudden mass loss (DTG peak at 264 °C) of 47.5%, which coincides with the release of two thione ligands with a theoretical mass loss of 36.9% plus a moiety that it was not possible to be identified due to the continuing decomposition. The DTA curve shows one sharp endothermic peak at 238 and a broader one (as shoulder) at 290 °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 233–236 °C), while the next one to further decomposition.

Upon increasing the temperature, the unstable intermediates undergo further decompositions with gradually mass loss during the second and third stages (470–790 and 790–1,300 °C) of 27.7%, 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 24.8%), with the calculated value for Cu_2S 21.0% and metallic copper 16.7% denotes that the decomposition of this compound at 1,300 °C was not completed.

For the compound $[CuBr(dmpymtH)_2]_2$ (Fig. 3), in the first stage (120–480 °C) with DTG peaks at 260 and 290(sh) °C, the sudden mass loss of 47.4% coincides with the release of two dmpymtH ligands with a theoretical mass loss of 33.1% plus a moiety that it was not possible to be identified due to the continuing decomposition. The DTA curve shows a sharp endothermic peak at 235 °C, which is attributed to simultaneous melting and decomposition of the compound.

The second and third stages (480–720 and 720–1,300 °C) with mass loss of 36.0% found contribute to the further decomposition of the possible intermediates $[CuBr(dmpymtH)_2]_2$ and $[Cu(dmpymtH)_2]$. The final solid residue at 1,300 °C in nitrogen, estimated from the TG curve (found 17.6.0%) cannot be attributed only to metallic copper (calc. 15.0%) or to Cu_2S (calc. 18.8%), and there is no evidence on the DTA curve for melting of copper at 1,084 °C. On the other hand, there is a small, well-defined endothermic peak at 1,100 °C for both studied copper compounds under nitrogen, which is probably due to the melting point of Cu_2S (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 $[CuBr(dmpymtH)_2]_2$. It was found that the solid material, at 1,000 °C during decomposition in N_2, consists mainly of Cu_2S, while some peaks could also be assigned to CuBr (Fig. 4). Analogous intermediates were found in the literature, according to their TG curves, on complexes of the type $[Cu^{I}XL]_n$ (L = heteroaromatic unit) where the residue above 400 °C corresponds to CuCl [10], while for the Cu(I) complexes of type $[(tpp)Cu(m\text{-}Cl)_2Cu(tppp)]$ (tpp = triphenylophospine) corresponds to metallic copper (Cu^0) at 600 °C [22].

It is also referred, according to XRD measurements, that the residues at 1,200 °C for Cu(I) thiocarbamates in inert atmospheres were consisted from Cu_2S and Cu [23, 24], while a more recent study on mixed valence copper (I, II) salt gave both copper sulfides ($Cu_{1.8}S$ and CuS) [25].

TG/DTG–DTA in oxygen

The shape of mass loss plots is quite different in the two atmospheres, while the decomposition in both atmospheres is very complicated. Thermoanalytical curves (TG/DTG–DTA) for the compounds $[CuCl(dmpymtH)_2]_2$ and $[CuBr(dmpymtH)_2]_2$ in oxygen atmosphere are given in Figs. 5 and 6, 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 (100–445 °C), the compound $[CuCl(dmpymtH)_2]_2$ (Fig. 5) shows sudden mass loss (DTG peak at 300 °C) of 32.4%, which is lower than the release of two thione ligands (calc. 36.9%). The DTA curve shows one small endothermic peak at 235 °C, which is attributed to the melting and further decomposition of the compound.

In the second stage (445–610 °C), the decomposition rate (DTG_{max} at 390 °C) is higher than in N_2 with a sudden mass loss of 35.5% denoting the elimination of two thione ligands. This decomposition is strongly exothermic with DTA peaks at 425 and a doublet at 490, 520 °C, which means that maybe an oxidation takes place along with the decomposition. The residue at 1,300 °C, as it is measured by TG, coincides well with the theoretical amount of CuO (found 20.7%, calc. 20.9%).

The thermal decomposition profile of the compound $[CuBr(dmpymtH)_2]_2$ under O_2 (Fig. 6) is quite similar with the profile of the compound $[CuCl(dmpymtH)_2]_2$. The only difference is that it presents a large plateau in the range

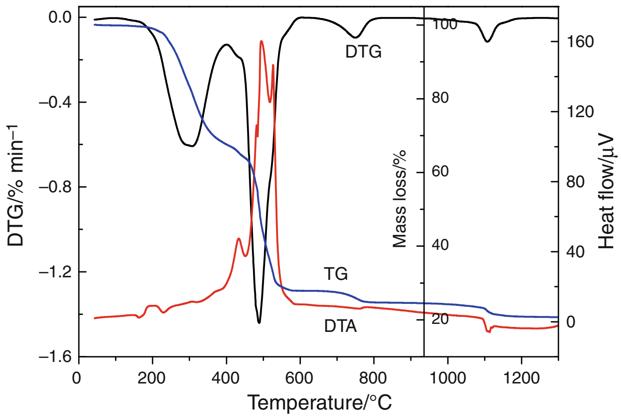


Fig. 5 Thermoanalytical curves (TG/DTG–DTA) of the compound $[CuCl(dmpymtH)_2]_2$ in air with heating rate 20 °C min^{-1}

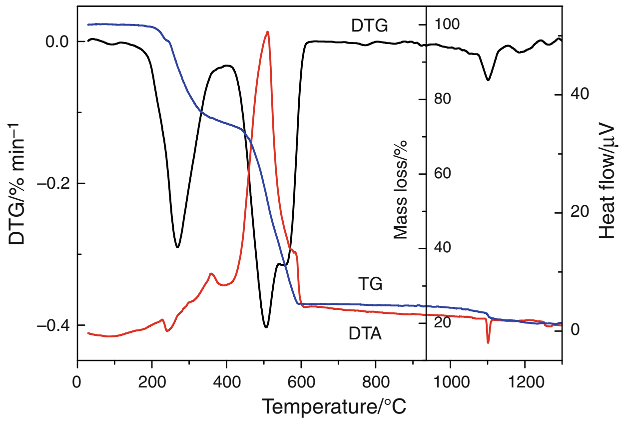


Fig. 6 Thermoanalytical curves (TG/DTG–DTA) of the compound $[CuBr(dmpymtH)_2]_2$ in air with heating rate 20 °C min^{-1}

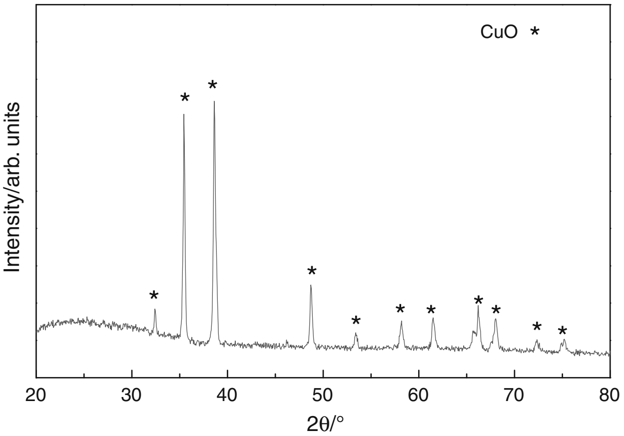


Fig. 7 Powder XRD diffraction pattern of compound $[CuBr(dmpymtH)_2]_2$ under O_2 atmosphere at 1,300 °C. CuO phase PDF #80-1268 (CuO) [26]

610–1,100 °C, which could be attributed to the intermediate Cu_2S (found 25.1%, calculated 18.8%) or to CuS (calculated 22.5%) or to $CuBr_2$ (calculated 26.4%). Evidence for the presence of Cu_2S gives the small sharp endothermic peak on the DTA curve at 1,100 °C, 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 18.8%, calc. 18.8%) and verified from the results of the powder XRD analysis (Fig. 7), in accordance with the literature findings [23].

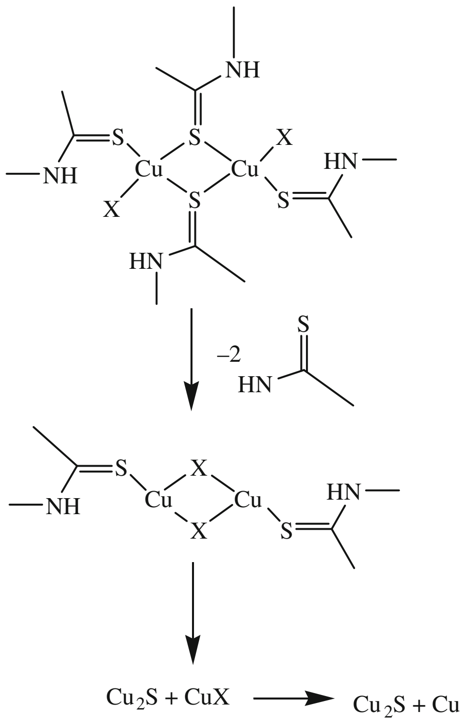
Decomposition mechanism Taking into account the results coming from the TG/DTG measurements and the XRD analysis of the solid intermediate and residue materials, of the thermal decomposition in nitrogen atmosphere, we propose a general decomposition pathway for the complexes under investigation in Scheme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

TG–MS

By the analysis of the evolved gases, performed by on-line coupling an MS spectrometer to the thermobalance, the proposed decomposition stages can be confirmed. Examination of the ionic current profiles during decomposition in inert, under argon atmosphere of the investigated compounds, has shown the presence of small molecules released at the 200–480 and 480–700 °C temperature ranges, which correspond to the decomposition stages I and II, respectively.

In the MS spectra of the thermal decomposition released gases of the copper (I) complexes, the detected masses for the first stage (DTG_{max} 260 °C) with *m*/*z*: 17, 28, 32 and 44 are assigned to ammonia (NH_3), nitrogen (N_2) or ethylene ($CH_2{=}CH_2$), sulfur (S) or hydrazine ($NH_2{-}NH_2$) and carbon monosulfide (CS), respectively. The fragments with *m*/*z*: 16(CH_4) and 42 ($CH_3{-}CH{=}CH_2$) are also detected, giving evidence for the rupture of the bonds inside the dimethyl-pyrimidino thione ligand. All the detected ions derived from the fragmentation of the thione ligands, after the break of the coordination bonds between copper and ligands (Cu–S bonds) and the rupture of bonds inside the ligands, confirmed the proposed fragmentation pattern with the elimination of the ligand molecules, estimated by the mass loss on the TG/DTG curves.

For the second stage (DTG_{max} 690 °C) the masses *m*/*z*: 17, 18, and 28 could be assigned to ammonia, water vapor(H_2O), and nitrogen or ethylene, respectively, giving evidence for the elimination of further fragments of the



Scheme 3 Proposed decomposition pathway in nitrogen atmosphere

ligands. Beyond 790 °C, the detected mass (*m*/*z*: 44), obtained in broad temperature range, is assigned to carbon monosulfide (CS).

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 metal-to-ligand charge-transfer (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 proved by the coupled TG–MS. The XRD gave mainly Cu_2S and traces of CuBr 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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