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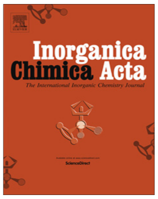

Research paper

Luminescent thione/phosphane mixed-ligand copper(I) complexes: The effect of thione on structural properties

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ABSTRACT

The reactions of tetrameric clusters $[CuX(PPh_3)]_4$ (X = Br or Cl) with a series of small size, five-member ring *N*-heterocyclic thiones, 5-methyl-1,3,4-thiadiazole-2-thione (mtdztH), 5-amino-1,3,4-thiadiazole-3-thione (atdztH) and 4,5-diphenyl-imidazole-2-thione (dpimdztH), in 1:4 molar ratio, in acetonitrile/methanol mixtures, resulted in the isolation of symmetrical, mixed-ligand phosphane/thione-S-bridged dicopper species of the general type $[CuX(PPh_3)(\mu\text{-S-thione})]_2$, with the copper centers being in distorted tetrahedral coordination environments consisting of a PS_2X donor set. In contrast, analogous reactions with the less basic and more sterically demanding 1-phenyl-tetrazole-5-thione (dpimdztH) afforded mononuclear mixed-ligand complexes with the general formula $[CuX(PPh_3)_2(\text{thione})]$, in which the thione acts in a terminal bonding mode. All copper(I) complexes are found to be photoluminescent in the solid state at ambient temperature, with their emission maxima influenced by the type of heterocyclic thione, as well as (to a smaller extent) the halide present in each case.

1. Introduction

The photophysical properties of copper(I) coordination compounds have triggered much research efforts in the perspective of their potential applications as materials for organic light-emitting diodes (OLEDs) and light-emitting electrochemical cells (LECs) [1]. A number of copper(I) complexes, the majority of them being mononuclear or binuclear complexes containing *N*-donor polypyridine [2,3] and/or P-donor phosphane ligands [4–8], have been reported to be luminescent at room temperature either in the solid state or in solution. Recently, mixed-ligand copper(I) complexes incorporating S-donor, *N*-heterocyclic thiones/thiolates in combination with arylphosphanes or polypyridines have also revealed interesting photophysical properties [9–14]. On the basis of both experimental and theoretical data, the emitting state of this type of complexes is assigned to be of MLCT character, while their emission energies were shown to be tunable through suitable thione modification, related to the strength of the Cu—S bond. Furthermore, studies on related luminescent copper-thiolate complexes of different nuclearities and core geometries revealed that the metal core structure has a profound effect on their emissive properties [15].

In general, *N*-heterocyclic thioamides tend to coordinate to copper(I) centers preferably through their soft exocyclic sulfur atom [16], leading to the formation of simple cationic or neutral complexes with a trigonal [17–20] or tetrahedral [21] ligand arrangement. However, when they are combined with tertiary phosphanes in a mixed set of ligands around the copper(I) centers, diverse molecular architectures can be obtained. In our previous studies on reactions of copper(I) halides with various thiones and tertiary arylphosphanes as a second bulky σ-donor/π-acceptor ligand it was reported that, in addition to the usually formed mixed ligand mononuclear species (Scheme 1A), symmetrical binuclear complexes were also frequently formed, containing either the thione ligand coordinated through the exocyclic sulfur atom in a μ-S-bridging mode (Scheme 1C) [22,23], or the halides as bridging ligands in a $Cu_2(\mu\text{-}X)_2$ core structure (Scheme 1B) [24]. On the basis of our observation that halide bridges were preferably formed by the “soft” iodide rather than the “hard” chloride ion, it was initially assumed that the type of structure that is adopted (terminal or bridging thione/halide) is determined by the choice of the halide used in each case [25]. However, there are quite a few examples of related complexes in the literature in which the reverse trend has been observed [26–28]. Consequently, not only the copper(I) halide starting material, but also the nature of the thione should be taken into account.

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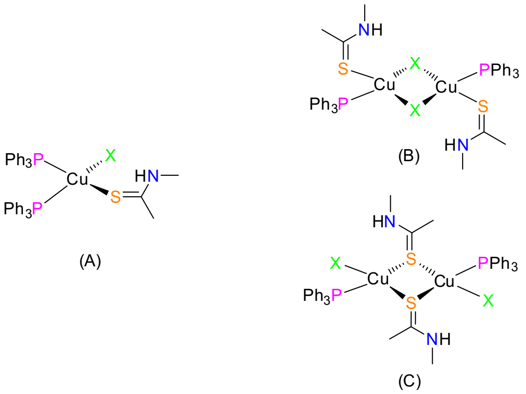


Scheme 1. Common binding modes of *N*-heterocyclic thiones.

Against this background, we decided to further investigate the factors that govern the synthesis of thione/phosphane mixed-ligand copper(I) complexes with specific structures, and to gain more insight into the relationship between their structures and luminescence properties. Herein we report on the coordination behavior of four five-membered ring heterocycles thiones, derived from 1,3,4-thiadiazole, imidazole and tetrazole, in combination with triphenylphosphane, and the study of the photoluminescent properties of the resulting copper(I) compounds.

2. Experimental

2.1. General procedures and chemicals

All manipulations were carried out under atmospheric conditions, unless otherwise mentioned. Solvents were purified according to established methods and allowed to stand over molecular sieves for at least 24 h prior to use. Copper(I) halides, triphenylphosphane, 5-methyl-1,3,4-thiadiazole-2(3H)-thione (mtdztH), 5-amino-1,3,4-thiadiazole-2(3H)-thione (atdztH), 4,5-diphenyl-1H-imidazole-2(3H)-thione (dpimdztH) and 1-phenyl-1H-tetrazole-5(4H)-thione (ptztH) were obtained from commercial sources and used without any purification. The compounds $[CuCl(PPh_3)]_4$ and $[CuBr(PPh_3)]_4$ were prepared according to literature procedures from the respective copper(I) halide and triphenylphosphane in refluxing $CHCl_3$ [29].

2.2. Instrumentation

Infra-red spectra were recorded on a Nicolet FT-IR 6700 spectrophotometer as KBr discs in the region of 4000–400 cm^{-1}. UV–vis electronic absorption spectra were obtained on a Shimadzu 160A spectrophotometer as solutions 1.0×10^{-4} M in $CHCl_3$. Solid-state and solution emission/excitation spectra were obtained on a Hitachi F-7000 fluorescence spectrometer. Elemental analyses were performed on a PerkinElmer 240B elemental microanalyzer.

2.3. X-ray crystal structure determinations

Suitable single crystals of all compounds were mounted on thin glass fibers with the aid of an epoxy resin. X-ray diffraction data were collected on a Bruker Apex II CCD area-detector diffractometer, equipped with a Mo Ka (λ = 0.71073 Å) sealed tube source, at 295 K, using the φ and ω scans technique. The program Apex2 (Bruker AXS, 2006) was used in data collection, cell refinement, and data reduction [30]. Structures were solved and refined with full-matrix least-squares using the program Crystals [31]. Anisotropic displacement parameters were applied to all non-hydrogen atoms, while hydrogen atoms were generated geometrically and refined using a riding model. Details of crystal data and structure refinement parameters are shown in Table 1. Molecular plots were obtained by using the program ORTEP-3 [32].

2.4. Syntheses of compounds

Compounds **1a**, **1b**, **2**, **3**, **4a** and **4b** were synthesized according to the following general synthetic procedure. A suspension of 0.125 mmol of $[CuX(PPh_3)]_4$ (0.203 g of $[CuBr(PPh_3)]_4$ for **1a**, **2**, **3** and **4a** or 0.180 g of $[CuCl(PPh_3)]_4$ for **1b** and **4b**) in 30 mL of acetonitrile was heated at 50 °C for 1 h. To the resulting mixture, a solution of 0.5 mmol of the appropriate thione in 30 mL of methanol was added dropwise. The reaction mixture was further stirred at 70 °C for 2 h and then it was filtered off in order to remove a small amount of insoluble material. The filtrate was set aside in dark to evaporate slowly at room temperature and over a period of a few days crystals of the product were obtained, which were filtered off and dried in air.

2.4.1. $[CuBr(PPh_3)(\mu\text{-}S\text{-}mtdztH)]_2$, ***1a***

Yellow crystals. Yield: 0.178 g (66%). Anal. Calcd for **1a**·CH_3CN (%): C, 47.31; H, 3.70; N, 6.27. Found (%): C, 47.20; H, 3.61; N, 6.38. IR (cm^{-1}): 3446 br, 2960 w, 2805 w, 2731 w, 1584 w, 1541 w, 1477 s, 1461 s, 1434 s, 1386 w, 1292 m, 1200 w, 1181 w, 1158 w, 1126 w, 1095 w, 1060 w, 1047 m, 1026 w, 997 w, 858 w, 803 w, 756 s, 748 s, 705 m, 694 s, 626 w, 591 w, 519 w, 505 w, 495 w, 430 w. UV–vis ($CHCl_3$), λ/nm (log ε): 252 (4.41), 310 (4.59).

2.4.2. $[CuCl(PPh_3)(\mu\text{-}S\text{-}mtdztH)]_2$, ***1b***

Yellow crystals. Yield: 0.177 g (71%). Anal. Calcd for **1b**·CH_3CN (%): C, 51.41; H, 4.02; N, 6.81. Found (%): C, 51.29; H, 3.89; N, 6.89. IR (cm^{-1}): 3483 vw, 3049 w, 2958 w, 2778 w, 2715 w, 1667 w, 1585 w, 1541 m, 1471 s, 1434 s, 1387 w, 1297 s, 1200 m, 1181 vw, 1159 s, 1129 s, 1096 m, 1048 s, 1027 m, 997 w, 981 vw, 933 vw, 863 s, 844 vw, 747 s, 694 s, 627 w, 618 w, 593 vw, 520 s, 505 s, 494 s, 431 m. UV–vis ($CHCl_3$), λ/nm (log ε): 251 (4.45), 309 (4.31).

2.4.3. $[CuBr(PPh_3)(\mu\text{-}S\text{-}atdztH)]_2$, ***2***

Yellow-green crystals. Yield: 0.172 g (64%). Anal. Calcd for **2**·CH_3CN (%): C, 45.08; H, 3.51; N, 8.76. Found (%): C, 45.22; H, 3.60; N, 8.65. IR (cm^{-1}): 3276 w, 311 87 w, 3049 w, 2901 w, 2759 w, 1612 s, 1548 s, 1484 s, 1433 s, 1368 m, 1333 m, 1178 w, 1157 s, 1095 m, 1069 m, 1045 s, 997 w, 930 w, 853 w, 745 s, 692 s, 640 w, 618 w, 543 w, 520 s, 503 s, 491 m, 429 w, 401 w. UV–vis ($CHCl_3$), λ/nm (log ε): 250 (4.46), 316 (4.19).

2.4.4. $[CuBr(PPh_3)(\mu\text{-}S\text{-}dpimdztH)]_2$, ***3***

Pale-yellow crystals. Yield: 0.246 g (75%). Anal. Calcd for **3**·2CH_3CN (%): C, 59.17; H, 4.53; N, 4.06. Found (%): C, 59.31; H, 4.40; N, 4.19. IR (cm^{-1}): 3573 w, 3431 w, 3051 w, 1629 w, 1596 w, 1571 w, 1503 s, 1480 s, 1434 s, 1209 w, 1184 w, 1157 w, 1094 m, 1071 m, 1026 w, 998 w, 913 w, 846 w, 762 mw, 744 m, 693 s, 582 w, 545 m, 518 m, 505 m., 434 w. UV–vis ($CHCl_3$), λ/nm (log ε): 252 (4.69), 289 (4.77).

2.4.5. $CuBr(PPh_3)_2(ptztH)$, ***4a***

Off-white crystals. Yield: 0.342 g (81%). Anal. Calcd for **4a** (%): C, 61.03; H, 4.29; N, 6.62. Found (%): C, 60.87; H, 4.16; N, 6.48. IR (cm^{-1}): 3447 br, 3045 w, 2924 w, 1594 vw, 1498 m, 1481 m, 1435 m, 1389 m, 1373 m, 1302 m, 1232 w, 1094 w, 1047 w, 1020 w, 997 w, 765 m, 740 m, 692 s, 559 w, 519 m, 509 m, 487 w, 419 w. UV–vis ($CHCl_3$), λ/nm (log ε): 271 (4.31).

Table 1
Crystal data, data collection and refinement parameters for compounds **1a**, **1b**, **2**, **3**, **4a** and **4b**.

	1a·CH_3CN	**1b·CH_3CN**	**2·CH_3CN**	**3·2CH_3OH**	**4a**	**4b**
Chemical formula	$C_{44}H_{41}Br_2Cu_2N_5P_2S_4$	$C_{44}H_{41}Cl_2Cu_2N_5P_2S_4$	$C_{42}H_{39}Br_2Cu_2N_7P_2S_4$	$C_{68}H_{62}Br_2Cu_2N_4O_2P_2S_2$	$C_{43}H_{36}BrCuN_4P_2S$	$C_{43}H_{36}ClCuN_4P_2S$
Formula weight	1116.95	1028.04	1118.93	1380.24	846.25	801.80
Crystal system	Triclinic	Triclinic	Triclinic	Triclinic	Monoclinic	Monoclinic
Space group	P-1	P-1	P-1	P-1	$P2_1/n$	$P2_1/n$
Temperature (K)	295	295	295	295	295	295
Unit cell parameters						
a (Å)	9.2028(4)	9.2116(4)	9.038(3)	10.4050(3)	16.4535(5)	16.3509(12)
b (Å)	11.8572(6)	11.6591(5)	11.417(4)	12.7045(5)	14.2300(5)	14.2672(10)
c (Å)	12.5384(6)	12.5237(5)	12.439(5)	13.9816(6)	18.3630(6)	18.2914(14)
α (°)	111.068(2)	110.458(2)	111.06(2)	112.551(2)	90	90
β (°)	98.927(2)	99.197(2)	100.09(3)	111.236(2)	113.150(2)	113.013(4)
γ (°)	104.711(2)	104.249(2)	102.33(2)	90.765(2)	90	90
Volume (Å^3)	1187.94(10)	1175.81(9)	1124.7(8)	1565.92(11)	3953.2(2)	3927.5(5)
Z	1	4	1	1	4	4
Radiation type, λ (Å)	Mo Kα, 0.71073	Mo Kα, 0.71073	Mo Kα, 0.71073	Mo Kα, 0.71073	Mo Kα, 0.71073	Mo Kα, 0.71073
Absorption coefficient (mm^{-1})	2.86	1.30	3.02	2.12	1.73	0.80
Crystal size (mm)	0.40 × 0.32 × 0.24	0.46 × 0.36 × 0.14	0.28 × 0.19 × 0.13	0.32 × 0.17 × 0.11	0.36 × 0.32 × 0.16	0.33 × 0.27 × 0.21
Diffractometer	Bruker Kappa Apex2	Bruker Kappa Apex2	Bruker Kappa Apex2	Bruker Kappa Apex2	Bruker Kappa Apex2	Bruker Kappa Apex2
Absorption correction	Numerical	Numerical	Numerical	Numerical	Numerical	Numerical
T_{min}, T_{max}	0.40, 0.50	0.63, 0.83	0.56, 0.68	0.70, 0.79	0.57, 0.76	0.81, 0.85
Number of measured, independent and observed [$I > 2.0\sigma(I)$] reflections	15,514, 4815, 3163	24,393, 7179, 4357	19,003, 4502, 3601	24,821, 6996, 4573	28,202, 8108, 4779	80,888, 9641, 5085
R_{int}	0.029	0.024	0.034	0.033	0.045	0.045
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.628	0.718	0.624	0.646	0.628	0.667
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.043, 0.073, 1.00	0.028, 0.049, 1.00	0.039, 0.088, 1.00	0.044, 0.071, 1.00	0.042, 0.062, 1.00	0.042, 0.062, 1.00
No. of reflections	3143	4357	3601	4573	4779	5085
No. of parameters	265	265	265	370	469	469
No. of restraints	2	2	8	6	0	0
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	1.02, −0.74	0.37, −0.36	1.73, −0.96	1.67, −1.05	0.49, −0.54	0.58, −0.51

2.4.6. $CuCl(PPh_3)_2(ptztH)$, **4b**

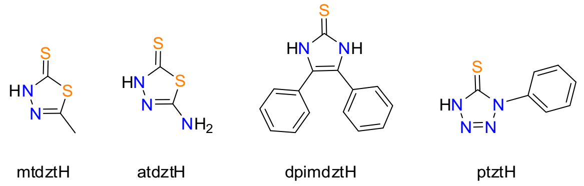
Off-white crystals. Yield: 0.268 g (67%). Anal. Calcd for **4b** (%): C, 64.41; H, 4.53; N, 6.99. Found (%): C, 64.58; H, 4.30; N, 6.78. IR (cm^{-1}): 3448 br, 3047 w, 2925 w, 1595 w, 1498 w, 1481 w, 1435 m, 1390 w, 1373 m, 1301 w, 1233 w, 1186 w, 1095 w, 1046 m, 1020 w, 998 w, 910 w, 847 w, 765 w, 741 m, 692 s, 618 w, 558 s, 520 s, 511 s, 487 m, 435 w, 425 w. UV–vis ($CHCl_3$), λ/nm (log ε): 257 (4.94).

3. Results and discussion

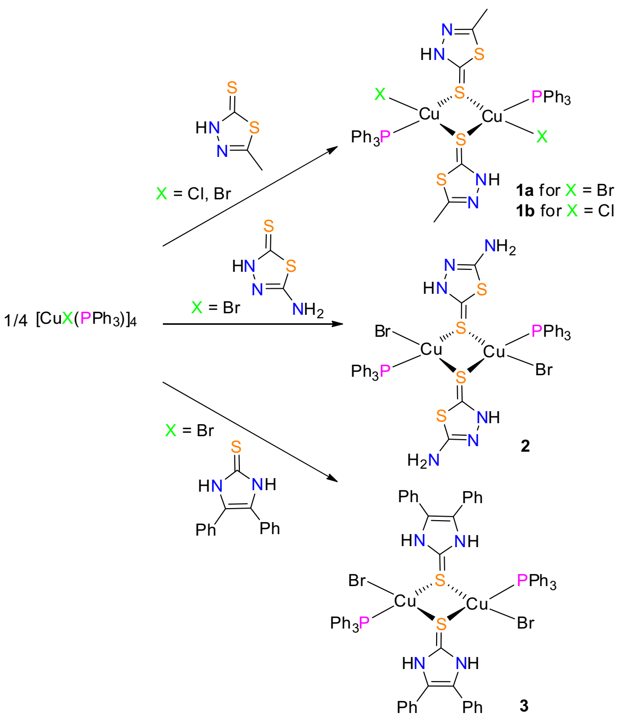
3.1. Syntheses and structures

Among the different synthetic methods that have been reported for the synthesis of thione/phosphane mixed-ligand copper(I) complexes, the most effective one uses a binary acetonitrile/methanol solvent mixture, as acetonitrile is known to stabilize the low oxidation state of the metal, while methanol to facilitate the crystallization of the product. In a typical procedure, a suitable copper(I) halide, dissolved in acetonitrile, reacts with two equivalents of the triarylphosphane to form an intermediate complex, which is then treated with a methanol solution of one equivalent of a thione to give the final product. The complexes isolated by this method are either mononuclear, four-coordinate complexes with the general formula $[CuX(PR_3)_2(thione)]$, or binuclear compounds containing a $Cu_2(\mu\text{-}X)_2$ or a $Cu_2(\mu\text{-S-thione})_2$ core structure (Scheme 1) [21]. More recent studies have shown that by utilizing $[CuX(PPh_3)]_4$ tetrameric clusters as starting material in reactions with four equivalents of a thione under similar experimental conditions, binuclear complexes with a mixed set of thione/phosphane ligands and either μ-X or μ-S bridges are preferably formed.

In order to explore the factors that might favor the formation of mononuclear or binuclear structures, or one type of bridge over the other, i.e. μ-X or μ-S, we explored the reactivity of $[CuX(PPh_3)]_4$ (X = Br, Cl) clusters with a series of small size, five-member ring heterocyclic thiones, namely mtdztH, atdztH, dpimdztH and ptztH (Scheme 2), in acetonitrile/methanol mixtures, in 1:4 molar ratio. With the first three thiones, binuclear, thione-S bridged compounds with the general formula $[CuX(PPh_3)(\mu\text{-S-thione})]_2$ (**1a**, **1b**, **2**, and **3**) were isolated in crystalline form (Scheme 3). Views of the molecular structures of these binuclear compounds are shown in Figs. 1–4, while selected bond length and angle parameters are summarized in Table 2. Complexes **1a**, **1b**, **2**, and **3** are centrosymmetric and contain a basic structural unit consisting of two copper atoms and two doubly bridging sulfur atoms of thione ligands that form a four-membered $Cu_2(\mu\text{-}S_2)$ ring. The copper centers are in distorted tetrahedral coordination environments which are completed by a halide, and a phosphane ligand. All compounds exhibit the usual planar, asymmetric $Cu_2(\mu\text{-}S_2)$ core with a short Cu—S distance (ranging from 2.323 to 2.354 Å) and a long Cu—S distance (2.465–2.551 Å) (Table 2). The Cu—P and Cu—halide bond lengths do not differ significantly among the four complexes and they fall in ranges that are normally found for analogous binuclear, halide- or thione-S-bridged copper(I) compounds [18,33,34]. The Cu···Cu interatomic distances in the four binuclear compounds are found to be in the range of 2.754–3.016 Å. The shorter intermetallic distance observed for compound **3**, with the imidazole-based bridging thione, is smaller than the sum of the van der Waals



Scheme 2. *N*-Heterocyclic thiones used in this work.



Scheme 3. Synthesis of compounds **1a**, **1b**, **2** and **3**.

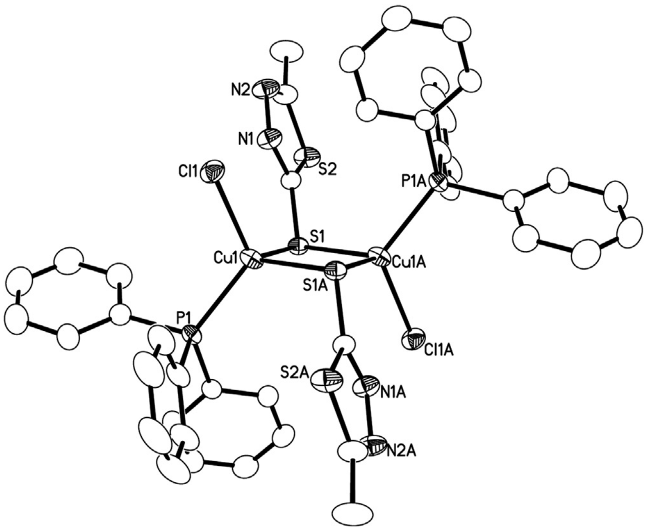


Fig. 2. X-ray structure ORTEP diagram of compound **1b** with displacement ellipsoids drawn at the 35% probability level. All hydrogen atoms have been omitted for clarity.

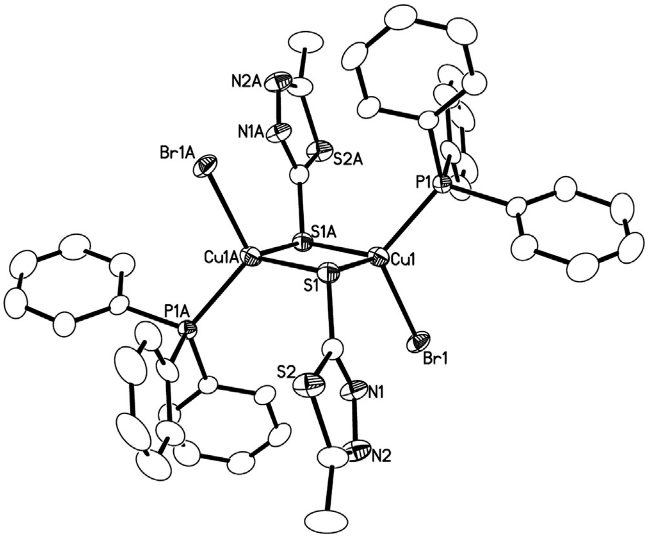


Fig. 1. X-ray structure ORTEP diagram of compound **1a** with displacement ellipsoids drawn at the 35% probability level. All hydrogen atoms have been omitted for clarity.

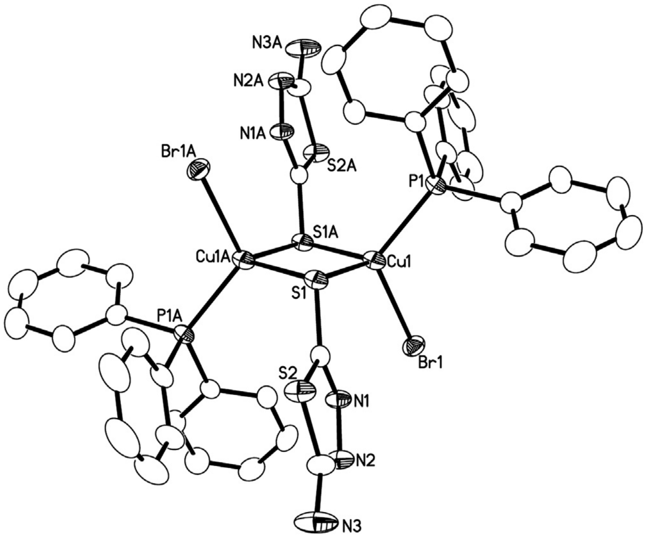


Fig. 3. X-ray structure ORTEP diagram of compound **2** with displacement ellipsoids drawn at the 35% probability level. All hydrogen atoms have been omitted for clarity.

radii of two copper(I) atoms, suggesting a weak bonding interaction between the two closed-shell metal ions. All complexes are further stabilized through the formation of intramolecular hydrogen-bonds between the halide ligand of the copper atoms and the closest NH group of the thione heterocycle Table 2.

In contrast to the abovementioned results, analogous reactions of $[CuX(PPh_3)]_4$ (X = Br, Cl) with the phenyl-substituted tetrazole ptztH, under identical experimental conditions as above, resulted in the isolation of mononuclear complexes with the formula $[CuX(PPh_3)_2(ptztH)]$ (X = Br (**4a**), X = Cl (**4b**)), as shown in Scheme 4. The formulas of the two compounds are not in agreement with the corresponding reaction stoichiometry; however, it has not been possible to identify any other product from the corresponding reaction mixtures. Views of the molecular structures of the two mononuclear compounds are shown in Figs. 5 and 6, while selected bond length and angle parameters are summarized in Table 2. Crystals structures of these two mononuclear compounds have been reported in the past, however, the compounds were obtained from different synthetic routes and exhibit different crystal and structural parameters [35]. The tetrahedral coordination environment around the metal centers, formed by two phosphorus atoms of two triphenylphosphane molecules, a halide ligand, and the exocyclic sulfur atom of the heterocyclic thione, is slightly distorted, with the largest deviations being reflected by the P—Cu—X angles of 101.80° and 103.72° for **4a** and **4b**, respectively. In addition, the Cu—S and Cu—halide distances in these mononuclear compounds are longer than the corresponding distances of the binuclear compounds discussed above.

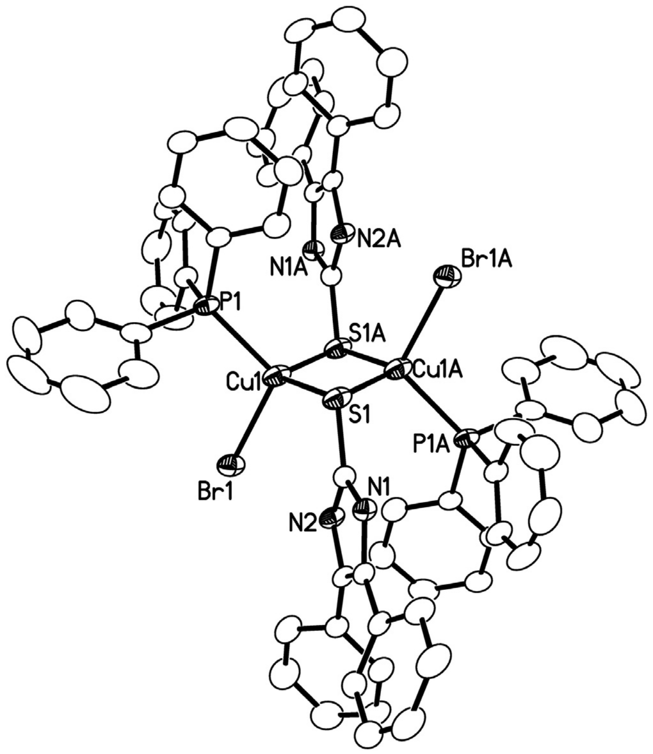
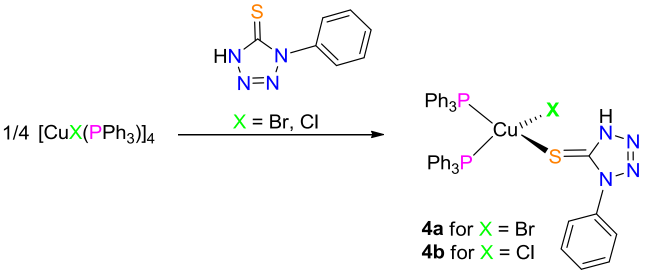


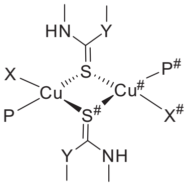
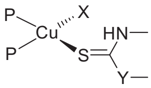
Fig. 4. X-ray structure ORTEP diagram of compound **3** with displacement ellipsoids drawn at the 35% probability level. All hydrogen atoms have been omitted for clarity.



Scheme 4. Synthesis of compounds **4a** and **4b**.

Overall, there is a number of factors that might favor the formation of either binuclear or mononuclear mixed-ligand thione/phosphane/halide copper(I) compounds. Among them, electronic factors determining the thione Lewis basicity as well as stereochemical demands imposed by each of the ligands should primarily be taken into account. As far as the Lewis basicity of the thione-S atom concerns, it seems reasonable to assume that strong thione-S bases tend to bind to more copper centers, favoring the formation of S-bridged dimers. In this context, considering that the basicity of azoles decreases when the number of imino nitrogens increases and when there are substituents with electron withdrawing resonance effects, the low basicity of the thione-S atom in the tetrazole-based thione ligand ptztH (used in **4a** and **4b**) could be responsible for the formation of mononuclear complexes, whereas the increased basicity in the diazole- and imidazole-based thione ligands mtdztH, atdztH, dpimdztH (used in **1a**, **1b**, **2**, and **3**) accounts for the formation of S-bridged dimers. Steric hindrance

Table 2
Selected bond lengths (Å) and angles (°) for the centrosymmetric binuclear compounds **1a**, **1b**, **2**, **3**, and the mononuclear compounds **4a** and **4b**.

						
	1a X = Br Y = S	**1b** X = Cl Y = S	**2** X = Br Y = S	**3** X = Br Y = NH	**4a** X = Br Y = NPh	**4b** X = Cl Y = NPh
Bond distances (Å)						
Cu—P	2.2355(13)	2.2301(5)	2.2211(16)	2.2453(11)	2.2617(10) 2.2861(11)	2.2567(9) 2.2835(9)
Cu—X	2.4512(8)	2.3175(6)	2.4387(10)	2.4962(7)	2.5291(6)	2.3931(9)
Cu—S	2.3394(13)	2.3543(5)	2.3231(14)	2.3318(11)	2.3910(10)	2.3964(8)
Cu—S#	2.4654(14)	2.4713(5)	2.4816(15)	2.5505(14)	N/A	N/A
Cu···Cu#	2.943	3.016	2.983	2.754	N/A	N/A
Bond angles (°)						
P—Cu—X	112.59(4)	116.16(2)	115.94(5)	108.97(4)	101.80(3) 107.24(3)	103.72(3) 107.37(4)
P—Cu—S	112.58(5)	112.14(1)	113.70(5)	116.92(4)	110.53(4) 104.03(4)	109.97(3) 103.36(3)
X—Cu—S	114.97(4)	112.75(2)	113.59(4)	112.21(3)	108.75(3)	107.76(3)
S—Cu—S#	104.50(4)	102.68(2)	103.32(5)	111.50(4)	N/A	N/A
P—Cu—S#	113.64(5)	113.56(2)	111.72(5)	107.67(4)	N/A	N/A
X—Cu—S#	97.39(4)	97.94(2)	96.45(4)	97.80(3)	N/A	N/A
Hydrogen bonding	**1a**	**1b**	**2**	**3**	**4a**	**4b**
N—X	3.234	3.064	3.264	3.274	3.170	3.000
N—H	0.854	0.853	0.855	0.842	0.870	0.856
X—H	2.383	2.223	2.429	2.518	2.320	2.163
N—H—X	174.07	168.61	165.15	149.86	165.29	165.96

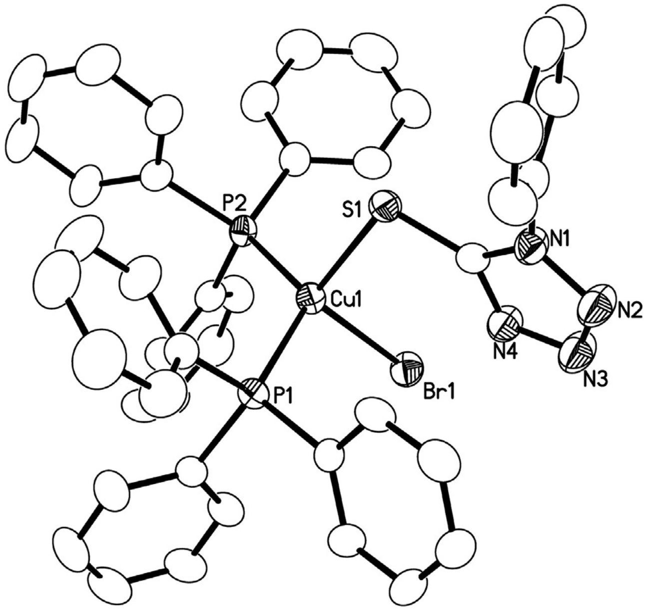


Fig. 5. X-ray structure ORTEP diagram of compound **4a** with displacement ellipsoids drawn at the 35% probability level. All hydrogen atoms have been omitted for clarity.

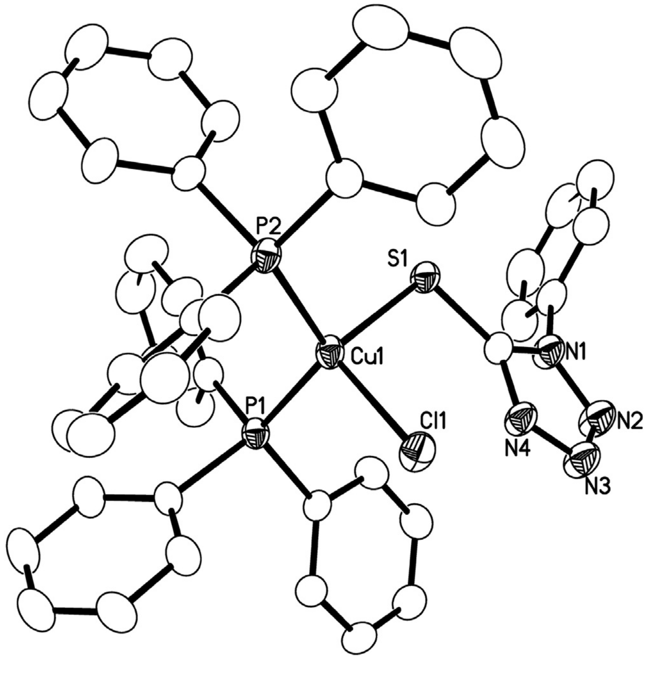


Fig. 6. X-ray structure ORTEP diagram of compound **4b** with displacement ellipsoids drawn at the 35% probability level. All hydrogen atoms have been omitted for clarity.

reasons should not be ruled out as well, since the two mononuclear complexes **4a** and **4b** are obtained only for the more sterically demanding, N1-phenyl substituted ptztH. Last, the solubility of the complexes in the particular solvent mixture might also influence the formation of one type over the other. In particular the isolation of specific solid-state structures of copper(I)/phosphane/halide complexes is heavily influenced by choice of crystallization solvent [36], while in many cases dynamic equilibrium schemes have been proposed to exist in solutions of phosphane-containing heteroleptic copper(I) complexes, which contain species with different solubility properties [37,38].

3.2. Infra-red spectroscopy

Corroborating evidence for the identity of the six copper(I) compounds in bulk form, as well as verification of the coordination mode of the heterocyclic sulfur containing ligands, has been obtained by Infra-red spectroscopy. The IR spectra of all compounds display bands attributed to vibrations of both triphenylphosphane and the corresponding sulfur donor ligands. For example, compounds **1a** and **1b** contain the mtdztH ligand. The IR spectra of free mtdztH, as well as those of the binuclear compounds **1a** and **1b**, do not show any bands in the 2600–2500 cm^{-1} region, where the ν(SH) mode is expected to appear, suggesting that the ligand, either free or in its coordinating mode, exists mainly in its thioketo, instead of the tautomeric thiole, form [39]. The free ligand band at 1550 cm^{-1}, assigned to ν(C=N) mode, is shifted to lower frequency at 1541 cm^{-1} in complexes **1a** and **1b** [40]. On the contrary, the free ligand band at 1268 cm^{-1}, having contributions mainly from the ν(C—N) mode, is shifted to higher frequency at 1296 cm^{-1}, in agreement with the electron shift $H\overset{\rightarrow}{\ddot{N}}{-}C{=}\vec{S}{:}\rightarrow Cu$, upon coordination of the thioketo form of mtdztH through its sulfur atom to the copper center. Accordingly, the frequency shift of the strong band of free thione from 764 to 747 cm^{-1} of the binuclear compounds is associated with the ν(C=S) vibration mode [41]. Analogous conclusions are drawn from the IR spectra of the other compounds.

3.3. Photophysical measurements

The UV–Vis electronic absorption spectra of compounds **1a**, **1b**, **2** and **3**, recorded in chloroform at room temperature, are dominated by two intense bands with maxima in the ~250 and ~290–315 nm regions, while only the broad high energy band at 271 and 257 nm is shown in the spectra of **4a** and **4b** respectively. With reference to the absorption spectrum of free PPh_3, which exhibits absorption bands at 245 nm, the high energy bands can be considered as intraligand $\pi^* \leftarrow \pi$ transitions on the phenyl groups of the phosphane moiety [4]. The lower energy band, which lies in the region where the free thiones absorb, can be attributed to a thione originating intraligand transition.

The photoluminescence properties of compounds **1a**, **1b**, **2**, **3**, **4a**, and **4b** were examined on solid-state samples at room temperature. Complexes **1a**, **1b**, **2** and **3** were found to be emissive with maxima of emission bands in the 430–498 nm range (Table 3 and Fig. 7). At first sight, their emission maxima seem to be slightly dependent on the thione ligand present in each case. In particular, photoexcitation of solid samples of complexes $[CuBr(PPh_3)(\mu\text{-S-mtdztH})]_2$ (**1a**) and $[CuCl(PPh_3)(\mu\text{-S-mtdztH})]_2$ (**1b**) in the 310 nm region results in strong and broad emission bands with maxima located at 498 nm and 493 nm, respectively. These low lying emissions cannot be of pure phosphane originating intra-ligand nature, because of their significant red shift relative to the solid-state emission spectrum of the free PPh_3, which consists of a broad band with maximum at 433 nm [42] after photoexcitation at 335 nm. On the other hand, excitation of a solid state

Table 3
Photoluminescence data for compounds **1a**, **1b**, **2**, **3**, **4a** and **4b**.

Compound	λ_{max} (emission), nm
$[CuBr(PPh_3)(\mu\text{-S-mtdztH})]_2$ (**1a**)	498
$[CuCl(PPh_3)(\mu\text{-S-mtdztH})]_2$ (**1b**)	493
$[CuBr(PPh_3)(\mu\text{-S-atdztH})]_2$ (**2**)	488
$[CuBr(PPh_3)(\mu\text{-S-dpimdztH})]_2$ (**3**)	428
$CuBr(PPh_3)_2(ptztH)$ (**4a**)	408
$CuCl(PPh_3)_2(ptztH)$ (**4b**)	404

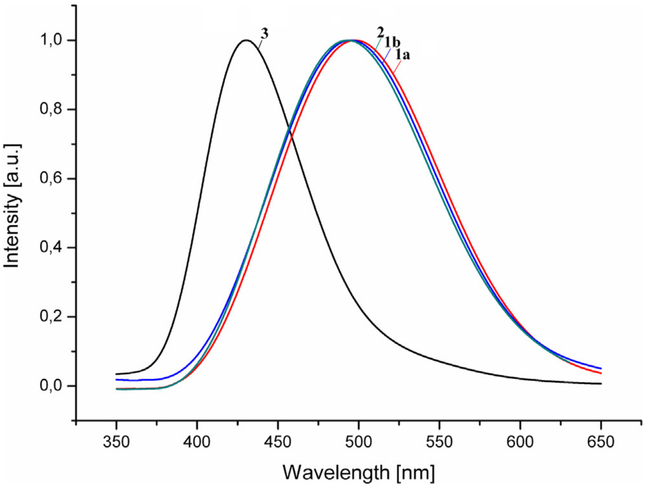


Fig. 7. Normalized emission spectra of compounds **1a**, **1b**, **2** and **3** in solid state at room temperature.

sample of free mtdztH in the UV region produces a rather weak and structured fluorescence emission with a maximum at 470 nm. Thus, based on previous results obtained by TD-DFT calculations on similar systems [6], we tentatively attribute the blue-green emission of these complexes to a mixed MLCT/LLCT excited state composed of a metal-to-ligand charge transfer (MLCT) of the type $Cu^I \rightarrow \pi^*(PPh_3)$ and to an intraligand charge transfer (LLCT) mediated by the copper central metal atom. Regarding the participation of the thione ligand to the emissive excited state, there are controversial views in the literature. Thus, while the case of a $Cu^I \rightarrow S{=}C{-}N(S,N)_{thione}$ MLCT is suggested [43], this possibility is excluded by others, because sulfur is considered to preferentially acts as a reducing ligand [44]. Furthermore, in accordance with previous results from related compounds [8,9,45] a small shift (~10 nm) of the emission energy is observed upon changing the halide ligand, indicating the participation of a halide-to-ligand charge-transfer in the emissive excited sites [46,47]. The characteristics of the emission band of compound **2** are similar to those of complexes **1a** and **1b**, whereby the maximum of the emission band is at slightly higher energy (488 nm) and red-shifted by 30 nm compared to the free ligand's emission.

Excitation of a solid sample of $[CuBr(PPh_3)(\mu\text{-}S\text{-}dpimdztH)]_2$ (**3**) in the 270 nm region results in a very intense blue luminescence with the broad emission band showing a maximum at 428 nm. This emission appears to be red-shifted by 20 nm in comparison to the similarly intense emission band of the free ligand dpimdztH. While the ligand's emission could obviously be due to either $n \rightarrow \pi^*$ or $\pi \rightarrow \pi^*$ transitions, it is difficult to assess its contribution to the overall constitution of the emissive excited state of the complex **3**. However, the quest for the origin of the lowest lying emissive state in this specific case should additionally take into account the possibility of a metal centered state as, unlike in the above-mentioned dicopper complexes, the Cu···Cu separation of 2.754 Å in **3** is indicative of a weak intermetallic bonding interaction.

Solid samples of the mononuclear compounds $CuX(PPh_3)_2$(thione), X = Br (**4a**) and X = Cl (**4b**), upon photoexcitation at 360 nm, display very weak violet luminescence with emission maxima at 408 and 404 nm, respectively. These emissions are significantly blue shifted compared to the ones of the other four compounds; however, this fact is unlikely to be associated with the nuclearity of the complexes, since a contribution of a cluster-centered emission in the dicopper species **1a**, **1b**, and **2** is expected to be negligible due to the large Cu···Cu separation. It would be therefore more appropriate to suppose that these emissions are of thione originating intra-ligand nature, since the solid sample of the free ligand ptztH also shows a very weak fluorescence with maximum at 390 nm. Finally, and not unexpectedly, the emission band of the Br-derivative **4a** is slightly red-shifted compared to that of its Cl-counterpart **4b**, indicating involvement of the halide ligand in the emissive excited state, as in the case of **1a** and **1b**. All the compounds under investigation are also luminescent in dilute dichloromethane solutions, exhibiting emission characteristics similar to the ones in solid state, which might give an indication about their stability in dichloromethane solution.

4. Concluding remarks

Herein, we present the syntheses and solid-state structures of a series of copper(I) complexes containing a mixed set of halide (Cl or Br), PPh_3 and five-membered ring heterocyclic thione ligands. Despite the fact that all complexes were synthesized under identical experimental conditions, their solid state structures reveal two distinct structural motifs: either binuclear, centrosymmetric complexes of the type $[CuX(PPh_3)(\mu^2\text{-}S\text{-thione})]_2$ with two doubly bridging sulfur atoms of a thione ligand, or mononuclear complexes of the type $CuX(PPh_3)_2$(S-thione) with the thione present in a terminal bonding mode. Although there are no clear-cut conclusions to draw from, it seems that a number of factors, including differences in Lewis basicity and steric factors of the heterocyclic thiones used in each case, play an important role in the formation of a specific structure in crystalline form. Furthermore, all complexes are photoluminescent in the solid state at ambient temperature, exhibiting emission maxima in the 400–490 nm range, while their emission properties are strongly affected by the Lewis basicity of the thione-S donor atom of the respective heterocyclic thione, as well as (to a smaller extent) by the halide present in each case.

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Appendix A. Supplementary data

CCDC 1483508–1483513 contain the supplementary crystallographic data for compounds **1a**, **1b**, **2**, **3**, **4a**, and **4b**, respectively. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.ica.2017.01.007.

References

[1] H. Yersin (Ed.), Highly Efficient OLEDs with Phosphorescent Materials, Wiley-VCH, Weinheim, 2008.
[2] D.R. McMillin, K.M. McNett, Chem. Rev. 98 (1998) 1201.
[3] D. Felder, J.-F. Nierengarten, F. Barigelletti, B. Ventura, N. Armaroli, J. Am. Chem. Soc. 123 (2001) 6291.
[4] C. Kutal, Coord. Chem. Rev. 99 (1990) 213.
[5] P.C. Ford, A. Vogler, Acc. Chem. Res. 26 (1993) 220.
[6] V. Pawlowski, G. Knör, C. Lennartz, A. Vogler, Eur. J. Inorg. Chem. (2005) 3167.
[7] E. Gariati, E. Lucenti, C. Botta, U. Giovanella, D. Marinotto, S. Righetto, Coord. Chem. Rev. 306 (2016) 566.
[8] K. Tsuge, Y. Chishina, H. Hashiguchi, Y. Sasaki, M. Kato, S. Ishizaka, N. Kitamura, Coord. Chem. Rev. 306 (2016) 636.
[9] P. Aslanidis, P.J. Cox, K. Kapetangiannis, A.C. Tsipis, Eur. J. Inorg. Chem. (2008) 5029.

[10] M.G. Babashkina, D.A. Safin, A. Klein, M. Bolte, Eur. J. Inorg. Chem. (2010) 4018.
[11] P. Aslanidis, P.J. Cox, A.C. Tsipis, Dalton Trans. 39 (2010) 10238.
[12] I. Papazoglou, P.J. Cox, A.G. Papadopoulos, M.P. Sigalas, P. Aslanidis, Dalton Trans. 42 (2013) 2755.
[13] V.W.W. Yam, C.H. Lam, W.K.M. Fung, K.K. Cheung, Inorg. Chem. 40 (2001) 3435.
[14] A. Gallego, O. Castillo, C.J. Gómez-García, F. Zamora, S. Delgado, Inorg. Chem. 51 (2012) 718.
[15] R. Langer, M. Yadav, B. Weinert, D. Fenske, O. Fuhr, Eur. J. Inorg. Chem. (2013) 3623.
[16] E.S. Raper, Coord. Chem. Rev. 129 (1994) 91.
[17] E.R. Atkinson, D.J. Gardiner, A.R.W. Jackson, E.S. Raper, Inorg. Chim. Acta 98 (1985) 35.
[18] S.C. Kokkou, S. Fortier, P.J. Rentzeperis, P. Karagiannidis, Acta Crystallogr., Sect: C 39 (1983) 178.
[19] F.A. Devillanova, G. Verani, L.P. Battaglia, A. Bonamartini Corradi, Trans. Met. Chem. 5 (1980) 362.
[20] J.M. Bret, P. Castan, G. Jugie, A. Dubourg, R. Roques, J. Chem. Soc., Dalton Trans. (1983) 301.
[21] L.P. Nattaglia, A. Bonamartini Corradi, M. Nardelli, M.E. Vidoni, J. Chem. Soc., Dalton Trans. (1976) 143.
[22] S.K. Hadjikakou, P. Aslanidis, P.D. Akrivos, P. Karagiannidis, B. Kojic-Prodic, M. Luic, Inorg. Chim. Acta 197 (1992) 31.
[23] P. Aslanidis, P.J. Cox, S.K. Hadjikakou, C.D. Antoniadis, Eur. J. Inorg. Chem. (2002) 2216.
[24] S.K. Hadjikakou, C.D. Antoniadis, P. Aslanidis, P.J. Cox, A.C. Tsipis, Eur. J. Inorg. Chem. (2005) 1442.
[25] P. Aslanidis, S.K. Hadjikakou, P. Karagiannidis, B. Kojic-Prodic, M. Luic, Polyhedron 13 (1994) 3119.
[26] T.S. Lobana, R. Sharma, R. Sharma, R.J. Butcher, Z. Anorg. Allg. Chem. 634 (2008) 1785.
[27] T.S. Lobana, R. Sultana, G. Hundal, A. Castineiras, Polyhedron 28 (2009) 1573.
[28] M.A. Tsiaggali, E.G. Andreadou, A.G. Hatzidimitriou, A.A. Pantazaki, P. Aslanidis, J. Inorg. Biochem. 121 (2013) 121.
[29] G. Costa, E. Reisenhofer, L. Stefani, J. Inorg. Nucl. Chem. 27 (1963) 2582.
[30] Apex2, Version 2 User Manual, M86-E01078, Bruker Analytical X-ray Systems, Inc., Madison, WI, 2006.
[31] P.W. Betteridge, J.R. Carruthers, R.I. Cooper, K. Prout, D.J. Watkin, J. Appl. Crystallogr. 36 (2003) 1487.
[32] L.J. Farrugia, J. Appl. Crystallogr. 45 (2012) 849.
[33] S.K. Hadjikakou, P. Aslanidis, P. Karagiannidis, A. Hountas, A. Terzis, Inorg. Chim. Acta 184 (1991) 161.
[34] P. Karagiannidis, S.K. Hadjikakou, P. Aslanidis, A. Hountas, Inorg. Chim. Acta 178 (1990) 27.
[35] S. Shakhatreh, M. Lalia-Kantouri, M. Gdaniec, P.D. Akrivos, J. Coord. Chem. 65 (2012) 251.
[36] K. Chen, J. Shearer, V.J. Catalano, Inorg. Chem. 54 (2015) 6245.
[37] S. De, K. Mahata, M. Schmittel, Chem. Soc. Rev. 39 (2010) 1555.
[38] A. Kaeser, M. Mohankumar, J. Mohanraj, F. Monti, M. Holler, J.-J. Cid, O. Moudam, I. Nierengarten, L. Karmazin-Brelot, C. Duhayon, B. Delavaux-Nicot, N. Armaroli, J.-F. Nierengarten, Inorg. Chem. 52 (2013) 12140.
[39] C.N.R. Rao, Chemical Applications of Infrared Spectroscopy, Academic Press, New York, 1963.
[40] A.C. Fabretti, G.C. Franchini, G. Peyronel, Spectrochim. Acta 36A (1980) 517.
[41] A.C. Fabretti, A. Giusti, Polyhedron 5 (1986) 1927.
[42] L. Maini, D. Braga, P.P. Mazzeo, B. Ventura, Dalton Trans. 41 (2012) 531.
[43] L.R.V. Favarin, P.P. Rosa, L. Pizzuti, A. Machulek Jr., A.R.L. Caires, L.S. Bezzena, L. M.C. Pinto, G. Maia, C.C. Gatto, D.F. Back, Polyhedron (2016), http://dx.doi.org/10.1016/j.poly.2016.10.003.
[44] D.M. Knotter, G. Blasé, J.P.M. van Vliet, G. van Koten, J. Bourassa, Chem. Rev. 99 (1999) 3625.
[45] P. Aslanidis, P.J. Cox, P. Tsaliki, Polyhedron 27 (2008) 3029.
[46] P.C. Ford, E. Cariati, J. Bourassa, Chem. Rev. 99 (1999) 3625.
[47] M. Henary, J.L. Wootton, S.I. Khan, J.I. Zink, Inorg. Chem. 36 (1997) 796.