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Copper(I) bromide complexes from 1,2-bis(diphenylphosphano) benzene and some heterocyclic thiones

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Abstract

The synthesis, characterization and solid state emission properties of a series of mixed-ligand copper(I)bromide complexes containing 1,2-bis(diphenylphosphano)benzene (dppbz) and some heterocyclic thiones (L) are reported. The complexes are readily synthesized by the addition of the appropriate thione to a CuBr-diphosphane adduct in acetonitrile/methanol or acetone solution. The molecular structures of [CuBr(dppbz)(py2SH)], [CuBr(dppbz)(pymtH)] and [CuBr(dppbz)(imdtH$_2$)] were established by single-crystal X-ray diffraction. Each of these structures features a tetrahedral copper(I) centre with two phosphorus atoms from the chelating diphos ligand, one bromine and the exocyclic sulfur atom of the heterocyclic thioamide unit. Slow decomposition of the mixed-ligand complexes via ligand dissociation occurs when their chloroform solutions are left to stand at room temperature for several weeks. On the basis of elemental analysis, NMR and IR spectra, the resulting coloured crystals are found to contain phosphane-free coordination polymers of composition [CuBr(L)]. At room temperature, some of the molecular complexes in the solid state exhibit strong emission assigned to a metal–ligand charge transfer of type Cu(I) → $\pi^*(PPh_2)$.

Keywords: Copper; Sulfur heterocycles; 1,2-bis(diphenylphosphano)benzene complexes; Crystal structures; Luminescence

1. Introduction

The interaction of heterocyclic thiones with transition metals has attracted much attention in the past, due to the biochemical significance of such thiones [1] and their use as medicinal substances [2,3]. The key feature of these heterocyclic thioamides, with respect to their ligating properties, is based upon the presence of both nitrogen and sulfur as potential donating atoms. Hence, the ability to bind to a metal in several ways is evident and this can produce a rich variety of structural prototypes. However, considering the univalent coinage metals in general and the copper(I) halides in particular, these typical soft acids tend to be coordinated by the neutral thione unit exclusively through the exocyclic sulfur atom, either in a terminal or bridging mode. Our work within this area of research has involved the incorporation of a tertiary arylphosphane as a second bulky soft donor. This produced a large number of mixed-ligand copper(I) complexes with a variety of structures ranging from mononuclear three- or four-coordinate species with trigonal planar and tetrahedral copper(I), respectively, to double bridged dimers [4–10]. Within this theme, our particular interest has been to understand and control the factors which may affect the stoichiometric and geometrical preferences of these complexes. According to the observed characteristics for the copper(I) complexes examined by us so far there are indications that other parameters, apart from the well known extraordinary flexibility of copper(I), are

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also involved. For example, the steric and electronic requirements on the part of the ligands and the reaction conditions (stoichiometry, temperature, solvent) applied might be expected to play a crucial role in determining the preferred geometry in each case [5,6,8]. Sometime ago, we started comparative studies into the substitution of unidentate arylphosphanes with oligomethylene-backboned symmetric diphosphanes of the type $Ph_2P(CH_2)_nPPh_2$ ($n = 1–6$). We demonstrated that, dependent on the nature of the phosphorus donors, it is possible to prepare and isolate diphosphane complexes of copper(I) of different nuclearity and stoichiometry. Recently, we examined the coordination capability of *cis*-1,2-bis(diphenylphosphano)ethene (*cis*-dppet) toward copper(I) halides in the presence of a series of heterocyclic thione donor groups [11]. The results prompted us to consider further chelating rigid diphosphanes, including 1,2-bis(diphenylphosphano)benzene (dppbz), in our investigations. The present study concentrates on derivatives from the reactions of copper(I) bromide with dppbz and various related heterocyclic thiones.

2. Results and discussion

2.1. Preparative investigations

Diphosphanes are by far the most frequently used species for bridging or chelation of low oxidation state transition metal centres. Previously, we attempted to chelate copper(I) using acyclic diphosphanes of the type $Ph_2P(CH_2)_nPPh_2$ and when 1,3-bis(diphenylphosphano)propane (dppp) was used we observed formation of six-membered chelate rings [12]. The bridging mode of coordination was preferred for diphosphanes bearing either a short or a long backbone. Our initial approach to five-membered chelate rings using 1,2-bis(diphenylphosphano)ethane (dppe) failed as the products obtained were found to be diphosphane-bridged dimers [13]. Nevertheless, use of the rigid *cis*-1,2-bis(diphenylphosphano)ethene (dppet) led to the successful chelation of copper(I) [11], and we focused once more on five-membered chelate rings including *cis*-1,2-bis(diphenylphosphano)benzene (dppbz) in our investigations. Note that no copper(I) derivatives of this rigid diphosphane are currently known, although dppbz has already found extensive utilisation as a chelating ligand at many metal centres [14–23].

For the preparation of the new compounds, we followed the synthetic pathways that have already yielded many mixed-ligand copper(I) halide complexes. Thus, copper(I) bromide was first treated with an equimolar quantity of 1,2-bis(diphenylphosphano) benzene (dppbz) to produce an intermediate adduct. This was then allowed to react with one equivalent of the appropriate thione (L) [L = pyridine-2-thione pyrimidine-2-thione, 4,6-dimethyl-pyrimidine-2-thione, tetrahydropyrimidine-2-thione or imidazolidine-2-thione] (Fig. 1) in dry acetonitrile for 2 h at 50 °C. The pure mixed-ligand compounds were generally isolated in good yields as the only product of the reaction. However, in a few cases formation of an amorphous solid was observed during the partial evaporation of the clear reaction solution. This solid could not be identified unambiguously by spectroscopy or by elemental analysis. The composition of the solid depended on the extent of the evaporation, indicating the presence of a mixture of two or more products and attempts to isolate the individual components of such mixtures were only partly successful. In the case of pymtH, the compound that first separated during the initial stages of the evaporation of the diluted acetonitrile mother liquid was a greenish product. This gave analytical and spectroscopic data identical with those of the above copper/diphosphane intermediate.

One possible outcome was a mixture containing the Cu/diphosphane intermediate adduct plus the desired mixed-ligand complex and a phosphane-free species. The separation of each of these compounds depended on their relative solubilities in the solvent used. Thus, attempts were made to direct the reaction course towards the exclusive formation of the desired mixed-ligand complexes. These attempts included treatment of the intermediate after isolation by redissolving in appropriate organic solvents or mixtures of them, as well as addition of the components in a reverse sequence. Respective modifications of the original one-pot procedure leading to efficient synthesis are given in the experimental section as an alternative method.

In the solid state, complexes **1**–**5** can be stored at room temperature for several months, but they were found to decompose in solution over the course of a couple of weeks. For example, separation of a dark red microcrystalline solid was obtained from a chloroform solution of [CuBr(dppbz)(py2SH)]. Exposure to daylight clearly accelerated the decomposition, and the microcrystalline solid that was released quantitatively could be spectroscopically identified as a phosphane-free adduct of composition [CuBrL]. No other copper-containing species, apart from the free dppbz, could be identified in the solution, thus, Scheme 1 can be used to show this interesting phenomenon.

To check the photochemical nature of this process, we performed photolytic experiments on degassed chloroform solutions of some mixed-ligand complexes. UV irradiation of these solutions containing **1**, **2** or **3** at $\lambda = 250–300$ nm indeed caused complete decomposition of the complex within 10–30 min. The process was monitored spectroscopically and produced in each case the corresponding phosphane-free polymer, while dppbz was isolated from the solution as the only soluble photoproduct (Fig. 2).

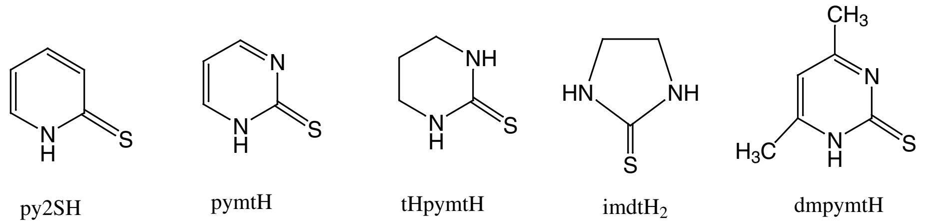
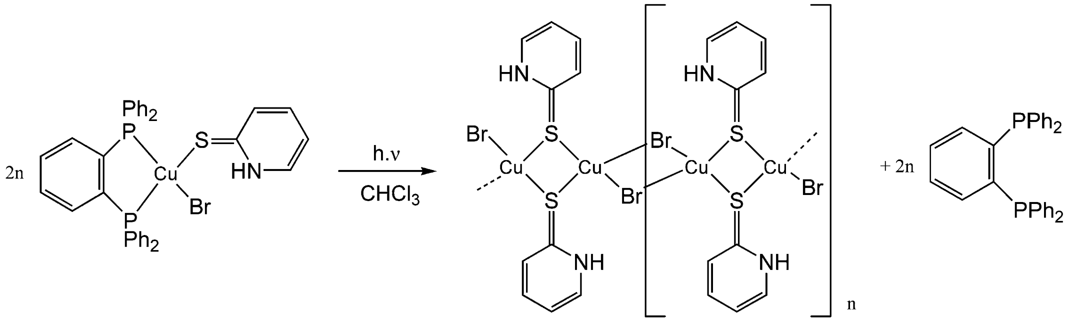


Fig. 1. The heterocyclic thione ligands used with their abbreviations.



1 **6**

Scheme 1. Photochemical decomposition of **1**.

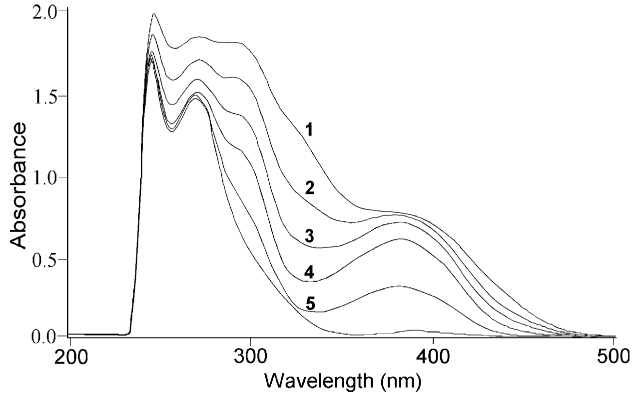


Fig. 2. UV–Vis absorbance changes in the course of the irradiation of a 10^{-3} M chloroform solution of [CuBr(dppbz)(py2SH)]. (1) Spectrum of the initial non-irradiated solution, (2)–(6) after irradiation for 2, 4, 6, 8 and 10 min, respectively.

The above decomposition seemed to be indicative of the inherent lability of the coordinated dppbz and thione ligands in solution and thus prompted us to investigate the possibility of exchanging the chelating diphosphane or thione ligand by other phosphane or thione units. Refluxing reaction mixtures of [CuBr(dppbz)L] with a 3-fold excess of the appropriate thione L in acetonitrile or acetone did lead to some reaction. However, intractable mixtures were normally formed, and only in the unique case of the more basic dmpymtH, was a quantitative replacement of the coordinated thione L achieved. On the other hand, analogous ligand-exchange reactions on complexes **1**–**5** using an excess of triphenylphosphane (PPh_3) in acetonitrile or acetone took place very slowly and could not be driven to completion even after heating under reflux for several days.

3. Characterization of the complexes

All prepared complexes are diamagnetic, air stable microcrystalline solids soluble in acetonitrile and only moderately soluble in chloroform and acetone. The composition of the compounds has been confirmed by elemental analysis. Their solutions in acetone and chloroform are non-conducting. As far as possible, we characterized all of the compounds by elemental analyses, IR, NMR, and mass spectra. The molecular structures of [CuBr(dppbz)(py2SH)], [CuBr(dppbz)(pymtH)] and [CuBr(dppbz)(imdtH$_2$)] were determined by X-ray crystallographic analyses. Room temperature ^{1}H NMR spectra, recorded in deuterated chloroform, exhibit a typical set of complex multiplets due to phenyl/phenylene resonances, as well as signals attributable to the aromatic protons of the thione groups. In some cases, the extent of overlapping does not allow resolution between signals in the phenyl region, thus the corresponding thione resonances were not analyzed further. Nevertheless, the observation of a broad singlet in the ~11–14 ppm region attributed to the NH proton reflects the prevalence of the thione tautomer in the complexes. In the ^{13}C NMR spectrum of **1**, the signal of the thione-S bonded carbon atom, which would be expected to be the most sensitive to coordination, is shifted by about 1.0 ppm to higher fields upon complexation to the metal atom ($\delta = 174.6$ ppm compared with $\delta = 175.6$ ppm for the free py2SH ligand [24]). Shifts of the same order are also observed for the corresponding carbon signals of compounds **2**–**5**, whereas no significant shifts are observed for the other thione or the dppbz carbon atoms. The electronic absorption spectra of the complexes **1**–**5** in chloroform at room temperature show two intense broad bands with maxima in the 243–255 and 285–310 nm regions, respectively. With reference to the absorption bands of the uncoordinated dppbz, the first one can be attributed to intraligand $\pi^* \leftarrow \pi$ transitions on the phenyl group of the phosphane ligand, whereby the lower energy band, which lies in the region where the free thiones absorb, expressing a small red shift as a consequence of the coordination to Cu^I, should be considered as a thione-originating intraligand transition which possesses some MLCT character [25,26]. The presence of the pyridine-2-thione, pyrimidine-2-thione and 4,6-dimethyl-pyrimidine-2-thione units in **1**, **2** and **5** is further associated with absorptions at 465, 450 and 435 nm, respectively. The infrared spectra of compounds **1**–**5**, recorded in the range 4000–250 cm^{-1}, show all the expected strong phosphane bands, which remain practically unshifted upon coordination. Moreover, the spectra of these compounds contain all of the bands originating from the presence of the heterocyclic thione ligands with shifts due to coordination indicative of an exclusive S-coordination mode.

The thermal behaviour of the new compounds was investigated using simultaneous differential thermoanalysis (DTA) and thermogravimetry (TG) in a nitrogen atmosphere. In contrast to their photochemical instability, complexes **1**–**5** proved to be thermally stable to at least 200 °C. On further heating, their DTA/TG curves showed similar decomposition patterns, generally consisting of two main stages. The low temperature initial stage observed in the TG curve at about 200–260 °C was connected with two or three strong endothermic events in the DTA curve and involved overall weight loss indicative of gradual thermal breakdown of the corresponding thione ligand. Subsequent thermal decomposition of **1**, **2** and **5** showed two strong endothermic effects in the temperature range 420–500 °C, which were accompanied by a relative mass loss consistent with burning of the diphosphane ligand. At the same time, the process of dppbz removal in the case of **3** and **4** was accompanied with an intensive exothermic effect, which could be of particular interest but difficult to explain. Although these two derivatives contain non-aromatic thioamide units, it is difficult to envisage any resulting Cu–P bonding situation that would lead to a differentiation in the thermal destruction of the coordination framework. For all the compounds, further heating caused gradual sublimation of the residual CuBr which was completely removed at 980 °C.

The luminescence properties of compounds **1**–**5** in the solid state were investigated at 298 K. Upon excitation at 280 nm, compound **4** emits intensely at 483 nm, whereas compounds **1**–**3** emit weakly with λ_{max} values in the 484–502 nm range which is typical of Cu–P containing chromophores [27–29]. Thus, the excited-state responsible for the luminescence of the monomeric species can be assigned to a metal–ligand charge transfer (MLCT) of the type Cu(I) → π^* (PPh_2).

3.1. X-ray structural investigations

The X-ray crystal structures of [CuBr(dppbz)(py2-SH)] (**1**), [CuBr(dppbz)(pymtH)] (**2**) and [CuBr(dppbz)-(imdtH)] (**4**) (details of crystal and structure refinement are shown in Table 4) corroborate the spectroscopic results discussed above. Tables 1–3 list selected distances and angles of these complexes. Note that the X-ray crystal structure determinations of these three

Table 1
Selected bond lengths (Å) and angles (°) for **1**

Bond length (Å)			
Cu(1)–Br(1)	2.4746(4)	S(1)–C(1)	1.706(3)
Cu(1)–P(1)	2.2534(6)	P(1)–C(6)	1.844(2)
Cu(1)–P(2)	2.2957(7)	C(6)–C(11)	1.406(3)
Cu(1)–S(1)	2.3054(6)	P(2)–C(11)	1.829(2)
Bond angles (°)			
P(1)–Cu(1)–P(2)	86.61(2)	C(1)–S(1)–Cu(1)	105.10(9)
P(1)–Cu(1)–S(1)	113.86(2)	C(6)–P(1)–Cu(1)	101.28(7)
P(2)–Cu(1)–S(1)	109.73(2)	C(11)–C(6)–P(1)	118.07(17)
P(1)–Cu(1)–Br(1)	122.046(19)	C(6)–C(11)–P(2)	117.59(17)
P(2)–Cu(1)–Br(1)	110.980(19)	C(11)–P(2)–Cu(1)	100.96(8)
S(1)–Cu(1)–Br(1)	110.73(2)		
Hydrogen bridge			
N(1)–H(1)	0.8800	Br(1)...N(1)	3.218(2)
NH(1)–Br(1)	2.3400	Br(1)...H(1)–N(1)	174.6°

Table 2
Selected bond lengths (Å) and angles (°) for **2**

Bond length (Å)			
Cu(1)–Br(1)	2.4588(5)	S(1)–C(1)	1.691(3)
Cu(1)–P(1)	2.2947(6)	P(1)–C(6)	1.839(2)
Cu(1)–P(2)	2.2927(6)	C(6)–C(11)	1.390(3)
Cu(1)–S(1)	2.2965(10)	P(2)–C(11)	1.830(2)
Bond angles (°)			
P(1)–Cu(1)–P(2)	85.28(2)	C(1)–S(1)–Cu(1)	111.99(11)
P(1)–Cu(1)–S(1)	103.9(4)	C(6)–P(1)–Cu(1)	100.78(7)
P(2)–Cu(1)–S(1)	112.83(3)	C(11)–P(2)–Cu(1)	102.13(7)
P(1)–Cu(1)–Br(1)	119.26(2)	C(11)–C(6)–P(1)	116.72(16)
P(2)–Cu(1)–Br(1)	113.51(2)	C(6)–C(11)–P(2)	117.92(16)
S(1)–Cu(1)–Br(1)	115.51(3)		
Hydrogen bridge			
N(1)–H(1)	0.8800	Br(1)...N(1)	3.214(3)
NH(1)–Br(1)	2.3300	Br(1)...H(1)–N(1)	177.7°

Table 3
Selected bond lengths (Å) and angles (°) for **4**

Bond lengths (Å)			
Cu(1A)–Br(1A)	2.4557(4)	S(1A)–C(1A)	1.690(3)
Cu(1A)–P(1A)	2.2577(6)	P(1A)–C(4A)	1.837(2)
Cu(1A)–P(2A)	2.2981(6)	P(2A)–C(5A)	1.827(2)
Cu(1A)–S(1A)	2.3214(7)		
Bond angles (°)			
P(1A)–Cu(1A)–P(2A)	86.58(2)	C(1A)–S(1A)–Cu(1A)	102.51(9)
P(1A)–Cu(1A)–S(1A)	110.58(3)	C(4A)–P(1A)–Cu(1A)	101.16(7)
P(2A)–Cu(1A)–S(1A)	105.90(2)	C(5A)–P(2A)–Cu(1A)	101.16(7)
P(1A)–Cu(1A)–Br(1A)	125.24(2)	C(5A)–C(4A)–P(1A)	117.71(17)
P(2A)–Cu(1A)–Br(1A)	115.96(2)	C(4A)–C(5A)–P(2A)	118.08(17)
S(1A)–Cu(1A)–Br(1A)	109.53(2)		
Hydrogen bridge			
N(1A)–H(1A)	0.8800	Br(1A)...N(1A)	3.543(3)
NH(1A)–Br(1A)	2.7200	Br(1A)...H(1A)–N(1A)	156.1°

complexes are the first to be carried out on copper(I) compounds containing dppbz.

The structures of the three mixed-ligand compounds are similar having a common tetrahedral coordination of the copper(I) centres, which are surrounded by one Br, the S donor of the thione ligand and two P atoms of the chelating dppbz unit. Complex **1** crystallizes in the triclinic space group $P\bar{1}$ with two formula units in the unit cell. Fig. 3 depicts a perspective of the molecule showing the atom numbering. The tetrahedral environment of the copper atom is considerably distorted, with the largest deviation from the ideal geometry being reflected by the P(1)–Cu(1)–P(2) and P(1)–Cu(1)–Br(1) angles whose values of 86.61(2)° and 122.046(19)°, respectively, are markedly different than the ideal tetrahedral value.

As expected, the carbon atoms of the phenylene backbone and the two adjacent phosphorus atoms are coplanar with the lone-pair of electrons of the latter lying on the same side of the plane, thus the CuPCCP five-membered ring is in envelope conformation with the metal atom out of the plane containing the four diphos ligand atoms by −0.999(2) Å. Considering the orientation of the two phenyl rings on each phosphorus atom, they are nearly perpendicular to each other. However, the C(18)–C(23) and C(30)–C(35) phenyl rings have their planes in an almost parallel arrangement with a 3.85 Å π-stacking interaction between them. The two individual Cu–P distances of 2.2534(6)° and 2.2957(7)° are within the limits of the value range expected for tetrahedrally coordinated Cu(I). Within the heterocyclic thione ligand, which exhibits a strictly planar six-membered ring, the bond distances and angles are not altered significantly upon coordination. Finally, the Cu–S and Cu–Br bond lengths lie in the range normally observed for tetrahedrally coordinated copper(I) complexes with terminal bromine and thione-sulfur donors.

In the case of [CuBr(dppbz)(pymtH)] (**2**), which crystallizes in the monoclinic space group $P2_1/n$ with four formula units in the unit cell, two different orientations were refined for the bromine atoms and the atoms of the pymtH ligand, with an occupancy of 93% for the major and 7% for the minor orientation respectively (Fig. 5). The four-coordinate monomer (Fig. 4) reveals a copper coordination sphere with

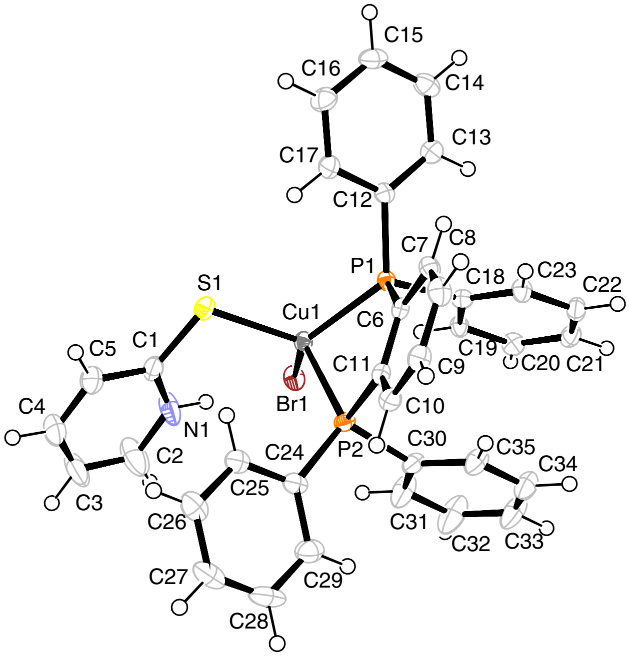


Fig. 3. A view of compound **1** with atom labels. Displacement ellipsoids are shown in the 50% probability level.

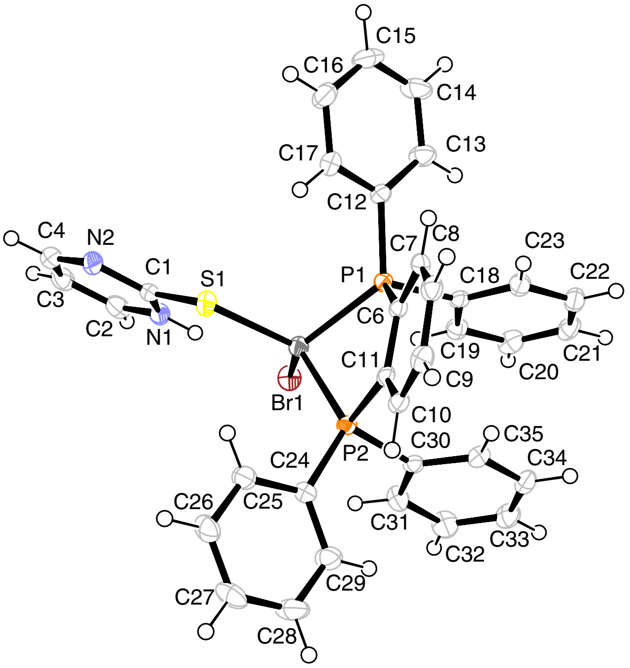


Fig. 4. Molecular structure of **2** with disorder removed to show only the major (93% occupancy) orientation (ORTEP drawing, 50% probability ellipsoids).

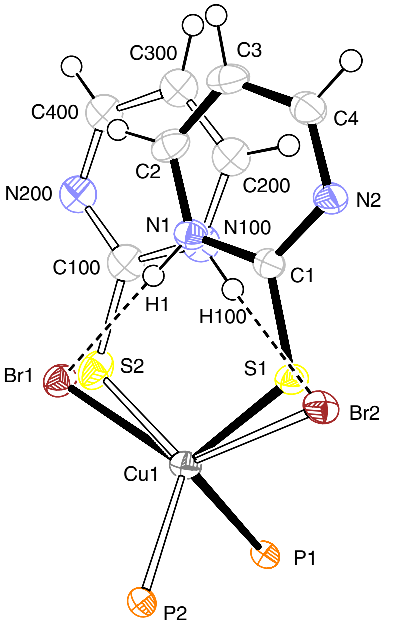


Fig. 5. A section of molecule **2** showing the orientations of the disordered bromine atoms and thione units.

bond lengths in the ranges documented in the literature. As in the structure of **1**, the CuPCCP five-membered ring is in envelope conformation with the metal atom out of the plane containing the four diphos ligand atoms by 1.0463 Å. The two individual Cu–P distances are essentially equal against their remarkable inequality within the structure of **1**. Moreover, comparison of the CuPCCP framework with that of **1** shows a slightly reduced P–Cu–P angle of 85.28(2)° (vs. 86.61(2)° in **1**).

[CuBr(dppbz)(imdtH$_2$)] (**4**) crystallizes in the triclinic space group $P\bar{1}$ with four discrete molecules in the unit cell. The asymmetric unit contains two independent molecules (A and B) with small differences in the bond distances and angles. One of these (molecule A) is depicted in Fig. 6.

Similarly to the structure of **2** and **3**, the PCCPCu five-membered ring is in an envelope conformation with the intraligand P–Cu–P angle 86.58(2) Å in molecule A and 86.61(2) Å in molecule B. The most striking feature between molecules A and B is the inclination of the five-membered imidazoline-ring to the C(22)–C(27) ring. The dihedral angle between mean planes through these two rings is 15.4(2)° in molecule A and 45.6(1)° in molecule B. As a consequence, a 3.78 Å closest contact distance between these two rings in the former molecule is observed.

Likewise, the almost parallel arrangement of two additional phenyl substituents [rings C(16A)–C(21A) and C(28A)–C(33A)] results in a 3.89 Å π-stacking interaction between them. Although these interligand interactions are small, they may be considered to contribute in some degree to the overall stabilization of the molecule.

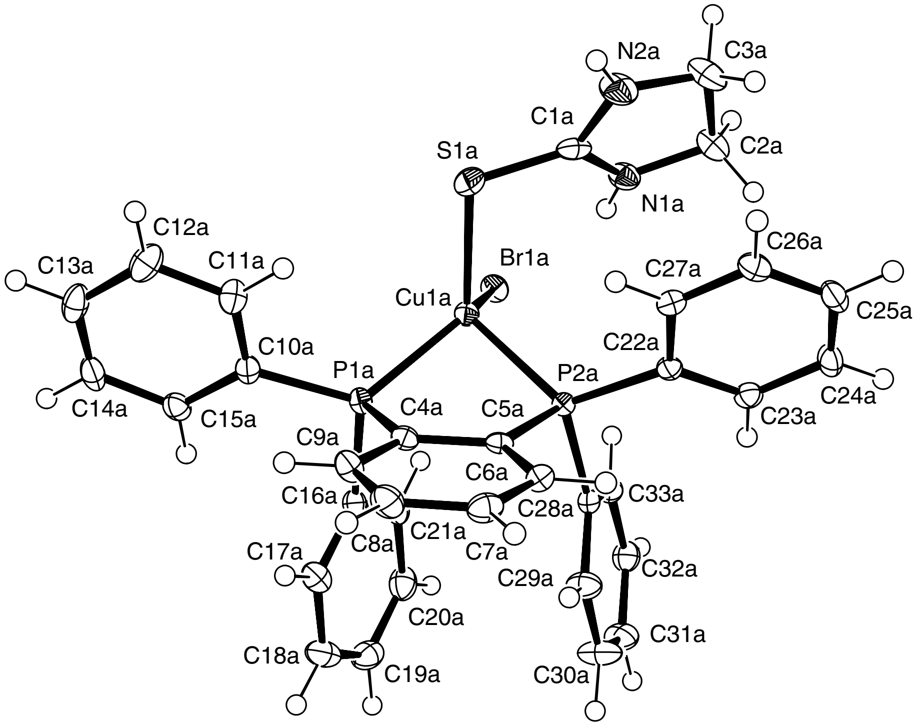


Fig. 6. A view of compound **4** with atom labels. Displacement ellipsoids are shown at the 50% probability level.

4. Conclusion

The aim of this work was the study of the coordination capability of the rigid diphos ligand 1,2-bis(diphenylphosphano)benzene (dppbz) toward Cu(I) bromide. We have found that dppbz readily forms a copper/diphosphane intermediate, which proves to be a good precursor for the preparation of other derivatives; in the course of the present study it was chosen for the synthesis of monomeric complexes which contain, besides the chelating dppbz, some heterocyclic thioamides bonded to the metal via the thione-S atom. These complexes are light sensitive, undergoing slow decomposition when exposed to daylight or intense UV irradiation. The mixed-ligand derivatives exhibit in the solid state at room temperature strong luminescence, the excited-state responsible for the emission assigned to a metal to ligand charge transfer (MLCT) of type Cu(I) → π* (PPh_2).

5. Experimental

5.1. Materials and instrumentation

Commercially available copper(I) bromide and 1,2-bis(diphenylphosphano)benzene were used as received, while the thiones (Merck or Aldrich) were recrystallized from hot ethanol prior to their use. All the solvents were purified by respective suitable methods and allowed to stand over molecular sieves. Infrared spectra in the region of 4000–250 cm^{-1} were obtained in KBr discs with a Perkin–Elmer Spectrum-1 spectrophotometer, while a Perkin–Elmer-Hitachi 200 spectrophotometer and a Perkin–Elmer 350 S10 fluorescence spectrophotometer were used to obtain the electronic absorption spectra and the luminescence spectra, respectively. ^1H NMR spectra were recorded on a Brucker AM 300 spectrometer at 25 °C with positive chemical shifts given downfield from TMS. TGA were performed under dry N_2 using a SETSYS-1200 machine with DTG facility. Sample sizes were in the range 8–10 mg and open Pt crucibles were used. The heating rate was 10°/min. For the photolyses, an Osram high pressure HBO 200 W/4 lamp was used. Melting points were measured in open tubes with a STUART scientific instrument and are uncorrected. Molar conductivities, magnetic susceptibility measurements and elemental analyses for carbon, nitrogen and hydrogen were performed as described previously [6].

5.2. Crystal structure determination

Single crystals suitable for crystal structure analysis were obtained by slow evaporation of acentonitrile/methanol solutions of the complexes at room temperature. X-ray diffraction data were collected on an Enraf-Nonius Kappa CCD area-detector diffractometer. The programs DENZO [30] and COLLECT [31] were used in data collection and cell refinement. Details of crystal and structure refinement are shown in Table 4. The structures were solved using program SIR-97 [32] and refined with program SHELX-97 [33]. Molecular plots were obtained with program ORTEP-3 [34].

*5.3. General synthesis of complexes **1–3***

To a suspension of copper(I) bromide (71.7 mg, 0.5 mmol) in 30 cm^3 of dry acetonitrile, 223.2 mg (0.5 mmol) of 1,2-bis(diphenylphosphano) benzene was added and the mixture was stirred for 2 h at 50 °C during which time a greenish precipitate was formed. To this was added a solution of the appropriate thione (0.5 mmol) in a small amount (~20 cm^3) of methanol and the new reaction mixture was heated under reflux for two hours whereupon the precipitate gradually disappeared. The resulting clear solution was filtered off and left to evaporate at ambient temperature. The microcrystalline solid, which was deposited upon standing for several days, was filtered off and dried in vacuo.

5.4. Alternative method

To a stirred suspension of **4** (236 mg, 0.2 mmol) in 50 cm^3 of dry acetone, a solution of the appropriate thione (0.4 mmol) in 20 cm^3 acetone was added dropwise and the mixture was heated under reflux to clearness. Slow evaporation of the mother liquid over a period of a few days gave the microcrystalline solid which was filtered off and dried in vacuo.

*5.5. [CuBr(dppbz)(py2SH)] (**1**)*

Bright yellow crystals (272 mg, 78%), m.p. 232 °C; *Anal.* Calc. for $C_{35}H_{29}BrCuNP_2S$: C, 59.96; H, 4.17; N, 2.00. Found: C, 59.93; H, 4.07; N, 2.20%. IR (cm^{-1}): 3469m, 3049w, 1618m, 1575vs, 1481s, 1435vs, 1369s, 1180m, 1132vs, 1096s, 992s, 755s, 753vs, 693vs, 518vs, 493s, 482s, 446m. UV–Vis (λ_{max}, log ε), ($CHCl_3$): 290 (4.14), 366 (3.75), 465 (2.11). ^1H NMR ($CDCl_3$, δ ppm): 14.33 (br, 1H, NH_{py2SH}), 7.48 (dd, 1H, H^6_{py2SH}), 7.18–7.34 (m, 24H, $4C_6H_5 + C_6H_4$), 7.29 (overlapping t, 1H, H^4_{py2SH}), 7.29 (t, 1H, H^4_{py2SH}), 6.70 (t, 1H, H^5_{py2SH}). ^{13}C NMR ($CDCl_3$, δ ppm): [128.18, 128.24, 128.30(t)], 129.18, 129.83, 130.28, 132.51, [132.90, 133.10, 133.29(t)], [133.68, 133.77, 133.81, 133.90(q)], 134.00, 134.06, 137.00,137.26, [142.41, 142.80, 143.19(t)], 174.60(s).

*5.6. [CuBr(dppbz)(pymtH)] (**2**)*

Red crystals (151 mg, 43%), m.p. 219 °C; *Anal.* Calc. for $C_{34}H_{28}BrCuN_2P_2S$: C, 58.17; H, 4.02; N, 3.99. Found: C, 58.15; H, 3.90; N, 3.97%. IR (cm^{-1}):

Table 4
Crystal data and structure refinements for (**1**), (**2**) and (**4**)

	1	**2**	**4**
Molecular formula	$C_{35}H_{29}BrCuNP_2S$	$C_{34}H_{28}BrCuN_2P_2S$	$C_{33}H_{30}BrCuN_2P_2S$
Formula weight	701.04	702.03	692.04
Temperature (K)	120(2)	120(2)	120(2)
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system	triclinic	monoclinic	triclinic
Space group	$P\bar{1}$	$P2_1/n$	$P\bar{1}$
Unit cell dimensions			
a (Å)	9.5559(2)	13.4081(3)	13.0253(2)
b (Å)	12.8262(2)	14.1790(3)	15.8994(2)
c (Å)	13.1234(3)	15.9576(3)	16.2348(2)
α (°)	86.773(2)	90	107.5050(10)
β (°)	76.0370(10)	99.2110(10)	112.1780(10)
γ (°)	84.578(2)	90	90.6270(10)
Volume (Å^3)	1553.04(5)	2994.64(11)	2939.56(7)
Z	2	4	4
D_{calc} (mg/m^3)	1.499	1.557	1.564
Absorption coefficient (mm^{-1})	2.186	2.268	2.309
F(000)	712	1424	1408
Crystal size (mm)	0.36 × 0.24 × 0.06	0.30 × 0.26 × 0.22	0.26 × 0.22 × 0.12
θ Range for data collection	3.01–27.46°	2.96–27.49°	3.13–27.53°
Index ranges	$-12 \leqslant h \leqslant 12$, $-16 \leqslant k \leqslant 16$, $-17 \leqslant l \leqslant 16$	$-17 \leqslant h \leqslant 17$, $-18 \leqslant k \leqslant 18$, $-18 \leqslant l \leqslant 20$	$-16 \leqslant h \leqslant 16$, $-20 \leqslant k \leqslant 20$, $-19 \leqslant l \leqslant 21$
Reflections collected	31501	41226	56774
Independent reflections [R_{int}]	7100 [0.0617]	6855 [0.0666]	13439 [0.0552]
Completeness (θ)	99.7% (27.46°)	99.7% (27.49°)	99.3% (27.53°)
Data/restraints/parameters	7100/0/370	6855/19/409	13439/0/721
Maximum and minimum transmission	0.8800 and 0.5067	0.6353 and 0.5494	0.7691 and 0.5851
Refinement method	full-matrix least-squares on F^2	full-matrix least-squares on F^2	full-matrix least-squares on F^2
Goodness-of-fit on F^2	1.020	1.032	1.020
Final R indices [(I) > 2σ(I)]	$R_1 = 0.0352$, $wR_2 = 0.0775$	$R_1 = 0.0339$, $wR_2 = 0.0685$	$R_1 = 0.0351$, $wR_2 = 0.0747$
R indices (all data)	$R_1 = 0.0543$, $wR_2 = 0.0843$	$R_1 = 0.0555$, $wR_2 = 0.0743$	$R_1 = 0.0561$, $wR_2 = 0.0815$
Final weighting scheme	[a]	[b]	[c]
Largest differential peak and hole (e/Å^3)	0.403 and −0.653	0.414 and −0.501	0.476 and −0.748

[a] Calc $w = 1/[\sigma^2(F_o^2) + (0.0451P)^2 + 0.1329P]$, where $P = (F_o^2 + 2F_c^2)/3$.
[b] Calc $w = 1/[\sigma^2(F_o^2) + (0.0280P)^2 + 1.8928P]$, where $P = (F_o^2 + 2F_c^2)/3$.
[c] Calc $w = 1/[\sigma^2(F_o^2) + (0.0402P)^2 + 10.2513P]$, where $P = (F_o^2 + 2F_c^2)/3$.

3468m, 3052w, 1605s, 1570vs, 1472s, 1435vs, 1331vs, 1217s, 1177vs, 1095s, 977s, 744vs, 691vs, 517vs, 493s, 480m. UV–Vis (λ_{max}, log ε), ($CHCl_3$): 243 (3.59), 285.0 (3.56), 328 (3.47), 450.0 (2.60). ^{1}H NMR ($CDCl_3$, δ ppm): 14.75 (br, 1H, NH_{pymtH}), 7.17–7.37 (m, 24H, $4C_6H_5 + C_6H_4$), 7.50 (m, 2H, $H^{4,6}_{pymtH}$), 6.70 (t, 1H, H^5_{pymtH}). ^{13}C NMR ($CDCl_3$, δ ppm):128.31, 128.37, 129.28, 129.92, 130.28, [132.61, 132.80, 133.00(t)], [133.68, 133.77, 133.81, 133.90(q)], 133.97, 134.03, [142.28, 142.70, 143.09(t)], 180.58(s).

5.7. [CuBr(dppbz)(tHpymtH)] (**3**)

Colorless crystals (324 mg, 92%), m.p. 245 °C; *Anal.* Calc. for $C_{34}H_{32}BrCuN_2P_2S$: C, 57.83; H, 4.57; N, 3.97. Found: C, 57.47; H, 4.36; N, 3.81%. IR (cm^{-1}): 3430m, 3175w, 3050w, 1566vs, 1479s, 1435vs, 1366s, 1214s, 1162s, 1096s, 753s, 746vs, 694vs, 516vs, 490s, 418m. UV–Vis (λ_{max}, log ε), ($CHCl_3$): 278 (3.65), 257 (3.69). ^{1}H NMR ($CDCl_3$, δ ppm): 7.93 (s, 1H, NH), 7.25–7.57 (m, 24H, $4C_6H_5 + C_6H_4$), 3.35 (dt, 2H, $H^3_{tHpymtH}$), 1.85 (q, 2H, $H^4_{tHpymtH}$). ^{13}C NMR ($CDCl_3$, δ ppm): 137.29, 133.90, 133.74, 132.51, 132.44, 129.37, 129.27,128.40.

5.8. [CuBr(dppbz)(imdtH$_2$)] (**4**)

Pale green crystals (326 mg, 94%), m.p. 231 °C; *Anal.* Calc. for $C_{33}H_{30}BrCuN_2P_2S_2$: C, 57.27; H, 4.37; N, 4.05. Found: C, 56.81; H, 4.32; N, 4.01%. IR (cm^{-1}): 3428s, 3051w, 1618m, 1522vs, 1500vs, 1479vs, 1435s, 1319s, 1282s, 1188s, 1095s, 1028m, 747vs, 695vs, 518vs, 489vs, 418m. UV–Vis (λ_{max}, log ε), ($CHCl_3$); 251 (3.77), 297 (3.80), 328 (3.69). ^{1}H NMR ($CDCl_3$, δ ppm): 14.75 (br, 1H, NH_{imtH}), 7.17–7.59 (m, 24H, $4C_6H_5 + C_6H_4$), 2.32 (dt, 4H, –$(CH_2)_2$–). ^{13}C NMR ($CDCl_3$, δ ppm):128.20, 128.27, 128.33, 128.62, 128.79, 128.88, [129.13, 129.20, 129.27(t)], [132.25, 132.31, 132.37, 132.43(q)], [133.64, 133.77, 133.86, 133.96(q)], [136.97, 137.13, 137.29(t)].

5.9. Synthesis of [CuBr(dppbz)(dmpymtH)] (**5**)

To a suspension of copper(I) bromide (71.7 mg, 0.5 mmol) in 60 cm^3 of dry acetone, 223.2 mg (0.5 mmol) of 1,2-bis(diphenylphosphano) benzene was added and the mixture was stirred for 30 min at 50 °C during which time a greenish precipitate was formed. To this was added a solution of 4,6-dimethylpyrimidine-2-thione (70.5 mg, 0.5 mmol) in a small amount ($\sim$20 cm^3) of acetone and the new reaction mixture was heated under reflux for 20 min whereupon the precipitate gradually disappeared. The resulting clear solution was filtered off and left to evaporate at ambient temperature. The microcrystalline solid, which was deposited upon standing for two days, was filtered off and dried in vacuo. Orange crystals (305 mg, 84%), m.p. 278 °C; *Anal.* Calc. for $C_{34}H_{32}BrCuN_2P_2S$: C, 59.22; H, 4.42; N, 3.84. Found: C, 59.06; H, 4.64; N, 3.76%. IR (cm^{-1}): 3468m, 3047w, 2905m, 1612s, 1562vs, 1480s, 1434vs, 1228vs, 1186s, 1095s, 980s, 753s, 744vs, 695vs, 518vs, 491s, 462s. UV–Vis (λ_{max}, log ε), ($CHCl_3$): 245 (4.03), 288 (4.01), 328 (3.94), 435 (3.17). ^1H NMR ($CDCl_3$, δ ppm): 14.24 (br, 1H, NH_{pymtH}), 7.37 + 7.19 (m, 24H, $4C_6H_5$+ C_6H_4), 6.38 (s, 1H, H^5_{pymtH}), 2.41 (s, 6H, CH_3). ^{13}C NMR ($CDCl_3$, δ ppm): 111.06, 128.21, 128.27, 129.11, 129.76, [132.77, 132.96, 133.16(t)], [142.38, 142.80, 143.19(t)], 179.55.

6. Supplementary data

CCDC-243704 (**1**), CCDC-243705 (**2**) and CCDC-243706 (**4**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.code.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK, fax: (intrnat.) +44 1223/336 033; e-mail: deposit@ccdc.cam.ac.uk].

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