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Synthesis and study of mixed ligand monomer Cu(I) compounds with Cu–As bonds. Crystal and molecular structure of bis(triphenylarsine)-(2-thioxohexamethyleneimine)copper(I) bromide

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Abstract

A new series of mixed ligand coordination compounds with Cu–As bonds is synthesized by the reaction of $Cu(AsPh_3)_3X$, where X = Cl, Br, or $[Cu(AsPh_3)I]_4$ with 2-thioxohexamethyleneimine (ω-thiocaprolactam, tclH) in acetone or by the addition of triphenylarsine to $Cu(tclH)_2X$ in methanol/chloroform. The products of both reactions are formulated as $Cu(tclH)(AsPh_3)_2X$, on the basis of their elemental analyses, IR, ^1H NMR and UV–Vis spectral data. The crystal structure of the bromo compound is reported and discussed with respect to that of $Cu(tclH)_2(AsPh_3)Br$. The compound crystallizes in the monoclinic space group *C2/c*, with $a = 41.981(8)$, $b = 9.961(2)$, $c = 19.087(2)$ Å, $\beta = 101.09(1)°$, 8 discrete molecules being present in the unit cell. The copper environment is a distorted tetrahedron, with two inequal Cu–As bonds, which are 2.411(2) and 2.372(2) Å, respectively. The Cu–Br and Cu–S bond lengths are equal to 2.456(3) and 2.313(4) Å, respectively, while the bond angles around copper vary from 104.4(0)° for As1–Cu–S to 116.1(1)° for As1–Cu–As2.

Introduction

One of the main topics in current inorganic chemistry is the investigation of the stereoelectronic factors governing the stereochemical preferences of copper(I) compounds, since copper(I) is involved in several biologically important redox reactions [1]. Within this field our research has long been directed [2] at the structural characterization of mixed ligand coordination compounds of Cu(I) with heterocyclic thiones, possessing an α-nitrogen heteroatom and triarylphosphines. Recently we have initiated [3] a detailed study aiming at the elucidation of the coordination mode of the saturated and bulky ω-thiocaprolactam, (abbreviated as tclH) both alone and in the concurrent presence of phosphines towards copper(I) centers. In this respect, resonance phenomena induced by the aromatic thiones studied so far are circumvented and the role of the steric factor made more apparent. Furthermore, in view of the unique properties of copper coordinated triphenylarsine [4] and for the sake of comparison with its extensively studied phosphine counterpart, we prepared and communicated the structure and reactivity of a new group of compounds formulated as $Cu(tclH)_2(AsPh_3)X$ [5] where X denotes a halogen atom. The structure of the bromine compound of the series, hereafter denoted as **1**, which is almost the sole fully characterized monomer compound bearing a copper–arsenic bond [6] has been determined and communicated. Therefore, it seemed challenging to investigate the consequences of substituting one thione by one arsine ligand, on both the structure and reactivity of the involved compounds. The proposed substitution may be carried out using either $Cu(tclH)_2X$ or $Cu(AsPh_3)_3X$, where X = Cl, Br, or $[Cu(AsPh_3)I]_4$ as precursors. The results of this study are presently reported and the molecular and crystal structure of $Cu(tclH)(AsPh_3)_2Br$, hereafter denoted as **2** is presented and discussed in connection with the previously described one for **1**.

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Materials and measurements

The solvents used were of reagent grade. Cuprus halides and triphenylarsine (Merck) were used as obtained, while ω-thiocaprolactam (Aldrich) was recrystallized from hot methanol prior to its use.

The elemental analyses for C, H and N were carried out on a Perkin-Elmer 240 B elemental analyzer. The IR spectra were recorded in KBr discs on a Perkin-Elmer 1430 spectrophotometer, while the electronic spectra were obtained by means of a Shimadzu 160 A spectrophotometer. A Bruker AW-80 spectrometer and internal TMS standard were used for the recording of the ^{1}H NMR spectra.

Preparative

The title complexes were prepared by two routes (Fig. 1), both of which are summarized below. Refluxing of 1 mmol of CuX (X = Cl, Br) and excess $AsPh_3$ (5 mmol) in 50 ml of chloroform produced a clear solution, which upon cooling deposited white microcrystalline $Cu(AsPh_3)_3X$ or $[Cu(AsPh_3)X]_4$ depending on whether X is Cl, Br or I. These products were subsequently treated with equimolar amounts of tclH in acetone. The clear solutions produced were filtered and evaporated to half of their original volume. The composition of the microcrystalline substances deposited was that expected for $Cu(tclH)(AsPh_3)_2X$. Calc. for $Cu(tclH)(AsPh_3)_2Cl$: C, 59.99; H, 4.92; N, 1.66. Found: C, 59.63; H, 4.73; N, 1.60%. Calc. for $Cu(tclH)(AsPh_3)_2Br$: C, 56.63; H, 4.64; N, 1.58. Found: C, 56.92; H, 4.60; N, 1.65%. Calc. for $Cu(tclH)(AsPh_3)_2I$: C, 54.14; H, 4.43; N, 1.50. Found: C, 54.11, H, 4.57; N, 1.57%.

In an alternative preparation scheme, equimolar amounts (1 mmol) of the thione and CuX in 20 ml methanol were heated until a clear yellow coloured solution emerged. Prolonged heating was necessary in the case of the chlorine complex. A 20 ml chloroform solution of 2 mmol of triphenylarsine was added producing instant decolorization of the solution. The resulting solutions were filtered and evaporation at room temperature produced white crystals identical in composition to those already described.

Crystals appropriate for X-ray analysis were obtained by slow evaporation of a 1:1 methanol:chloroform solution of the title compound at room temperature.

Solution of the structure

Intensities were collected at room temperature, on a CAD4 diffractometer (Mo Kα radiation, graphite monochromator) in the ω–2θ scan mode ($\theta < 25°$). Lorentz and polarization corrections were applied. The structure was solved by direct methods using the SDP software package [7]. Refined parameters were calculated by using anisotropic thermal parameters for non-hydrogen atoms and isotropic factors for all hydrogen atoms.

Cell dimensions along with other experimental conditions and residual factors are listed in Table 1, while main bond distances and angles are given in Table 2.

Spectral characterization

The IR spectra of the complexes are indicative of the thione bonding towards copper(I), since the strong wide band at 3190 cm^{-1} attributed to the –NH stretching is present and only slightly shifted relative to the one observed in the spectrum of the free thione. This serves as an indication for a weak intramolecular hydrogen bond towards the halogen atom, contrary to the observations for **1** and its analogous compounds [5], where it lies about 20 cm^{-1} lower. An intense thioureide band is present at 1575 cm^{-1}, quite close to its position in the free ligand, indicating substantial retainment of the π-character of the C=S bond, which, in other studied compounds was partially delocalized towards the backbone of the thione ligand.

The UV–Vis spectra recorded in chloroform reveal two rather broad bands expressing their maximum absorbance at 260 and 278 nm, respectively. The positions of these maxima are indicative of the presence of both the thione and arsine ligands to copper's coordination sphere. They are almost identical to those observed in $Cu(tclH)_2(AsPh_3)X$ complexes [5], inspection though of their logϵ values verifies the thione:arsine 1:2 ratio since the highest energy band, where both the $AsPh_3$ and the thione ligands contribute is substantially more intense relative to the lower energy one, while in the aforementioned compounds [5] the reverse was observed.

The ratio of the aromatic versus saturated carbon protons (30:11) is also indicative of the presence of

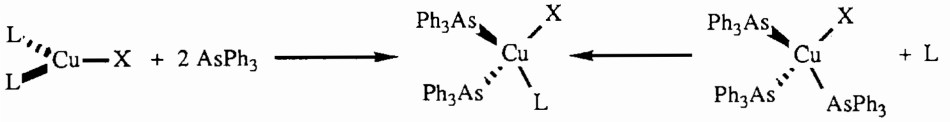

Fig. 1. Schematic representation of the two preparative routes to the discussed compounds; L denotes ω-thiocaprolactam.

TABLE 1. Summary of crystal and intensity collection data

Formula	$As_2BrCuNSC_{42}H_{41}$
Formula weight	885.1
Space group	$C2/c$
a (Å)	41.981(8)
b (Å)	9.961(2)
c (Å)	19.087(2)
β (°)	101.09(1)
V (Å^3)	7832.2
Z	8
D_{calc} (Mg m^{-3})	1.501
Radiation	Mo Kα
Reflections collected	6880
Reflections with $I > 3\sigma(I)$	2566
No. refined parameters	557
R	0.052
R_w	0.052
$(\Delta\rho)_{max}$ (e Å^{-3})	0.30

TABLE 2. Selected bond distances (Å) and angles (°) of the studied compound

Bond distances			
Cu–S	2.313(4)	Cu–As1	2.411(2)
S–C19	1.665(16)	Cu–As2	2.372(2)
C19–N20	1.322(20)	Cu–Br	2.456(3)
N20–C21	1.461(19)	As1–C1	1.95(1)
C21–C22	1.520(26)	As1–C7	1.97(2)
C22–C23	1.511(27)	As1–C13	1.96(1)
C23–C24	1.488(34)	As2–C26	1.95(1)
C24–C25	1.536(31)	As2–C32	1.94(2)
C25–C19	1.478(21)	As2–C38	1.94(1)
Angles			
S–Cu–As1	106.3(1)	C1–As1–C7	101.1(6)
S–Cu–As2	104.4(1)	C1–As1–C13	100.0(5)
S–Cu–Br	114.7(1)	C7–As1–C13	104.5(6)
As1–Cu–As2	116.1(1)	C26–As2–C32	101.4(6)
As1–Cu–Br	105.9(1)	C26–As2–C38	101.8(6)
As2–Cu–Br	109.7(1)	C32–As2–C38	100.3(6)
C19–S–Cu	109.3(5)	Cu–As1–C1	111.7(4)
N20–C19–C25	115(1)	Cu–As1–C7	118.4(4)
C19–N20–C21	128(1)	Cu–As1–C13	118.3(4)
C21–N20–C22	109(1)	Cu–As2–C26	116.3(4)
C19–C25–C24	115(1)	Cu–As2–C32	116.1(4)
		Cu–As2–C38	118.2(4)

two $AsPh_3$ ligands and one tclH ligand in the complexes, while the signals appear at the same position as previously reported for analogous compounds [3,5], i.e. nitrogen proton resonates at 10.28 ppm(s,1H), thione carbon protons at 3.4(m,2H), 2.8(m,2H) and 1.7–1.9(m,6H) and triphenylarsine ones in the region 7.0–7.9 ppm.

Description of the structure

The positional parameters of the most relevant atoms are reported in Table 3 and a series of selected bond distances and angles are presented in Table 2.

TABLE 3. Positional parameters (e.s.d.s. in parentheses) of the non-hydrogen atoms composing the core of the compound (phenyl carbon atoms are not included)

Atom	x	y	z	B (Å^2)[a]
Cu	0.36304(4)	0.1526(2)	0.89190(9)	3.23(4)
Br	0.32460(4)	0.0097(2)	0.93972(8)	3.83(4)
As1	0.34641(3)	0.1441(1)	0.76386(8)	3.01(4)
As2	0.41693(3)	0.0824(2)	0.93855(8)	2.92(3)
S	0.3621(1)	0.3767(4)	0.9233(2)	4.7(1)
C1	0.3030(3)	0.218(1)	0.7325(8)	3.4(4)
C7	0.3713(4)	0.249(2)	0.7052(9)	4.2(4)
C13	0.3408(3)	−0.032(1)	0.7177(8)	3.0(4)
C19	0.3238(4)	0.426(1)	0.9180(7)	3.7(4)
N20	0.2997(3)	0.340(1)	0.9162(7)	4.4(4)
C21	0.2650(4)	0.368(2)	0.9084(9)	5.4(5)
C22	0.2589(4)	0.438(2)	0.975(1)	6.0(5)
C23	0.2662(6)	0.587(2)	0.978(1)	7.5(6)
C24	0.3014(6)	0.616(2)	0.983(1)	7.2(6)
C25	0.3144(5)	0.569(2)	0.918(1)	7.4(6)
C26	0.4297(3)	0.079(2)	1.0420(7)	3.2(3)
C32	0.4512(3)	0.191(1)	0.9125(9)	3.8(4)
C38	0.4302(3)	−0.095(1)	0.9129(7)	3.2(4)

[a] $B_{eq} = \frac{4}{3}[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab\cdot\cos\gamma B(1,2) + ac\cdot\cos\beta B(1,3) + bc\cdot\cos\alpha B(2,3)]$.

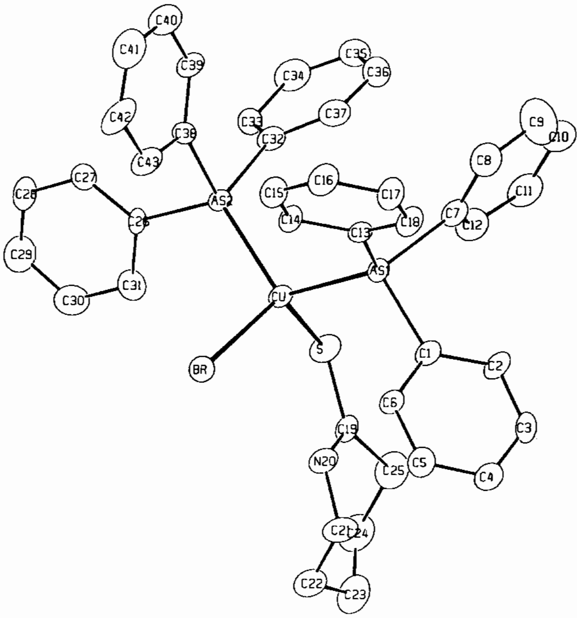

Fig. 2. PLUTO draw of the studied compound.

The coordination around copper is distorted tetrahedral, with one sulfur, two arsenic and one bromine atoms in the vicinity of copper (Fig. 2). In connection with the reported structure for **1**, there exist, besides the many similarities, a few marked differences, which should be commented upon, since they emerge from the substitution of a thione by an arsine ligand. A stereoscopic view is given in Fig. 3.

The copper–sulfur distance observed is 2.313(4) Å. It is shorter than the sum of the tetrahedral single bond covalent radii, predicted to be 2.39 Å for a purely σ bond [8], implying partial involvement of $d\pi$–$d\pi$ bonding as well. It is, though, longer than the corresponding ones observed in trigonal coordinated Cu(I) complexes, a fact attributed to the difference of the metal covalent radius expressed in three-coordinated planar [9] and four-coordinated tetrahedral complexes [10]. Furthermore, though the 2.313(4) Å separating Cu from S represent a mean value of the ones formerly observed, the thione C=S bond retains most of its double bond character, being equal to 1.665(16) Å, that is slightly shorter than the corresponding one in **1**. It should be noted that the adjacent C–N bond gains an almost equal amount in longitude (0.02 Å) relative to the ones observed in the aforementioned compound.

The Cu–Br distance of 2.456(3) Å lies close to the 2.462(0) Å observed in $Cu(PPh_3)_2(py2SH)Br$ [2b], but is shorter than that observed in cubane-like oligomers, such as $[Cu(PPh_3)Br]_4$, $[CuP(t\text{-}Bu)_3Br]_4$ and $[Cu(PEt_3)X]_4$, which are reported to lie between 2.495 and 2.604 Å [11]. It is considerably shorter than 2.605 Å, which is the value in **1**, a difference attributed, partly to the hydrogen bond formed between the bromine atom and the sole NH moiety of the present thione ligand, relative to the two analogous ones in the former complex.

The two copper–arsenic distances are 2.411(2) and 2.372(2) Å, respectively, the former exceeding the sum of the covalent bond radii, viz. 2.38 Å while the latter is in good agreement with 2.368 Å in $[Cu(AsPhMe_2)_2Cl]_2$ [12], 2.361 Å in $[Cu(AsEt_3)I]_4$ [13], 2.370(2)–2.394(3) Å in $[Cu_3(AsPh_3)_3I_4]^-$ [14] and almost identical to 2.371(1) Å observed in **1**.

The inequality of the As–C bond lengths in the triphenylarsine ligands which range from 1.94(1)–1.97(2) Å is by no means unexpected in view of the generally observed violation of the strict tetrahedral arrangement around As.

The bond angles around copper are rather irregular, particularly interesting is the inequivalence of the two As–Cu–Br angles, which are observed to be 105.9(1) and 109.7(1)°, respectively. The two S–Cu–As angles are quite close in value (104.4(1)° and 106.3(1)°, respectively), both being slightly smaller than the regular value of 109.47° connected with a strictly tetrahedral coordination sphere. The As1–Cu–As2 angle (116.1(1)°) is the most deviating from this ideal value, a fact ascribed to a large steric hindrance induced by the arsine ligands. It should be noted that it is somewhat smaller than the 118.0(1)° observed in $[Cu(AsPhMe_2)_2Cl]_2$ [12], where the restricted copper environment and packing forces allow the opening up of this angle. Finally, the arsenic environment is also far from being ideal tetrahedral, the Cu–As–C angles ranging from 111.7(4)–118.4(4)°.

The phenyl rings are planar within experimental error and the average C–C bond distances and bond angles do not differ significantly from the generally accepted values of 1.399 Å and 120°, respectively, for normal phenyl groups.

Conclusions

The non-aromatic bulky thiocaprolactam and triphenylarsine coordinate to copper(I) giving rise to monomer compounds. The two ligands prove to be of similar relative softness as Lewis bases since it has been shown that they readily exchange each other to form two series of compounds, namely

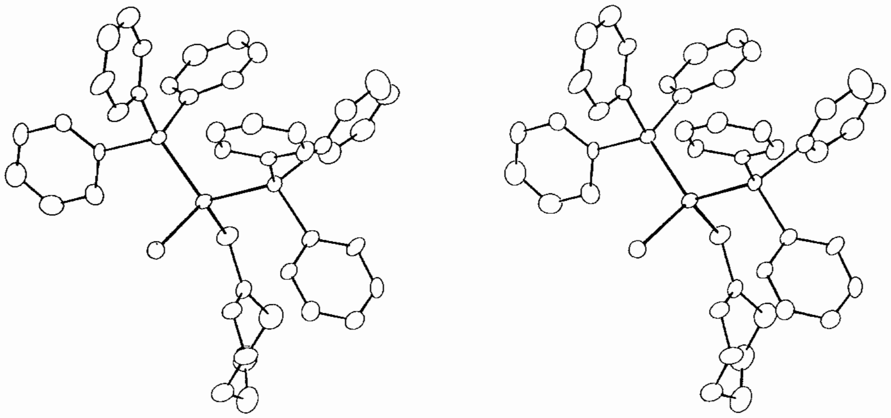

Fig. 3. Stereoscopic view of the studied compound.

$Cu(tclH)_2(AsPh_3)X$ and $Cu(tclH)(AsPh_3)_2X$. In the latter group, the introduction of a second triphenylarsine ligand provokes reorganization of the chromophore since the interligand repulsions must be kept minimum. These repulsions account for the distorted tetrahedral environment around copper, the largest bond angle, in every case, being observed between the pair of similar ligands.

Supplementary material

All the crystallographic material (atomic coordinates, bond lengths, bond angles and equivalent thermal factors) have been deposited with the Cambridge Crystallographic Data Center.

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