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New class of Cu(I) complexes with 2-thioxohexamethyleneimine (tclH) and Group V_A donors. Crystal structure of $[Cu(tclH)_2(AsPh_3)Br]$

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Abstract

A new class of mixed ligand complexes, of copper(I) hexamethyleneimine-2-thione (ω-thiocaprolactam, tclH) with triphenylphosphine and triphenylarsine is synthesized and characterized. The complexes may be formulated as $[Cu(tclH)_2(EPh_3)X]$, where $E=P$ or As; $X=Cl$, Br or I. The arsine complexes express a remarkable photostability compared to their phosphine counterparts. Moreover, they do not react with stoichiometric amounts of pyridine which, in the case of the phosphine complexes displaces the thione ligands coordinated to copper. Furthermore, the crystal structure of the complex $[Cu(tclH)_2(AsPh_3)Br]$, which is also discussed is the first one to present a mixed ligand arsine–thione copper(I) complex. The compound crystallizes in the $P2_1/n$ space group, with $a=18.704(1)$, $b=10.855(1)$, $c=15.593(1)$ Å and $\beta=92.70(1)°$. A distorted tetrahedral environment around copper is present, with the two Cu–S bonds almost equivalent (2.310(1) and 2.315(1) Å). The Cu–As bond distance is equal to 2.371(1) Å and the Cu–Br bond length is 2.605(1) Å.

Introduction

The understanding of the stereochemistry and reactivity of copper(I) compounds, especially with sulfur donor ligands is among the major goals of coordination chemistry, in view of the involvement of Cu(I) ions in several bioprocesses [1]. The structural study of mixed ligand Cu(I)–thione compounds has long been a main theme in our work [2], recently expanded [3] to include non-aromatic thione ligands such as ω-thiocaprolactam. The study of the coordination ability of this bulky thione has revealed the existence of a three-coordinated Cu(I) center capable of reacting with labile small molecules and Lewis bases. The study of the coordination of $AsPh_3$ to the above-mentioned Cu(I) center seems interesting since the arsine ligand is softer than the corresponding phosphine, almost equally bulky, and has been found to express interesting features upon coordination to Cu(I) [4].

The crystal structure of the bromine compound is discussed in detail. To our knowledge, this study is among the few so far discussing mixed ligand Cu(I)–arsine complexes [5]. It is certainly the first where the concerted effects of arsine and thione ligands may be investigated by means of X-ray crystal structure studies.

Experimental

Materials and measurements

All the solvents used were of reagent grade. Copper halides as well as triphenylphosphine 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 elemental analyzer. The IR spectra were recorded in KBr discs on a Perkin-Elmer 467 spectrophotometer, while the electronic spectra were obtained by means of a Perkin-Elmer-Hitachi 200 spectrophotometer. For the photolyses, a 200/4 W, Osram high pressure mercury lamp, model HBO 250 was used. An UV–Vis 1 cm cell was used for the study and it was placed parallel to the axis of the lamp. Substrate concentrations of c. 2×10^{-4} M were employed. A Bruker AW-80 spectrometer was used for the recording of the ^1H NMR spectra. The chemical shifts obtained in deu-

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terated chloroform solutions are presented in δ (ppm) downfield from internal TMS standard.

Preparation of the complexes

In a typical preparation, 1 mmol of CuX (X = Cl, Br, I) was suspended in 20 ml hot methanol, followed by the addition of 2 mmol (260 mg) of the thione ligand. After refluxing for 10 min, 1 mmol of the eligible Lewis base (262 mg of PPh_3 or 306 mg of $AsPh_3$) was added and the initial fine suspension formed was dissolved by the addition of *c.* 20 ml toluene. The solution was heated for 30 min, filtered and allowed to cool at room temperature. The microcrystalline products which separated upon cooling, were collected, washed with cold methanol and air-dried. Only in the case of CuCl was prolonged heating (3 h) necessary for the reaction to be completed. Satisfactory elemental analyses consistent with the formula $[Cu(tclH)_2(EPh_3)X]$, except in the case of $[Cu(tclH)(PPh_3)_2I]$, were obtained for the studied compounds.

The crystals of the bromine compound, which were used for the X-ray analysis were obtained by slow evaporation of a methanol–chloroform 1:1 solution of the complex.

Solution of the structure

Complete crystal data and parameters for data collection are reported in Table 1. The space group was determined by preliminary Weissenberg and precession photographs. Unit cell dimensions were derived from a least-squares refinement of the setting angles of 48 automatically centered reflections in the range $11 < 2\theta < 23°$ on a Syntex $P2_1$ diffractometer upgraded by CRUSTAL LOGIC with Nb-filtered Mo Kα radiation. Three standard reflections measured every 100 reflections, showed <3% intensity fluctuation. Lp and absorption corrections were applied. Scattering factors were taken from the International Tables for X-ray Crystallography [6]. The crystal structure was solved by direct methods using the program SIR88 [7]. The refinement was carried out by blocked full matrix least-squares, in which $\Sigma w\Delta^2$ was minimized using SHELX76 [8]. The hydrogen atoms bonded to the carbon atoms were calculated as riding on carbon atoms at 0.96 Å. The non-H atoms were refined using anisotropic and the hydrogens using isotropic temperature factors. Two reflections showing poor agreement were given zero weight during the final refinement cycles.

The fractional atomic coordinates, excluding hydrogen and phenyl ring atoms, with equivalent thermal parameters are listed in Table 2.

TABLE 1. Summary of crystal and intensity collection data

Formula	$CuAsBrS_2N_2C_{30}H_{37}$
Formula weight	708.14
a (Å)	18.704(1)
b (Å)	10.855(1)
c (Å)	15.593(1)
β (°)	92.70(1)
V (Å^3)	3162.4(2)
Z	4
D_{calc} (Mg m^{-3})	1.487
D_{meas} (Mg m^{-3})	1.47
Space group	$P2_1/n$
Crystal dimensions (mm)	0.15×0.35×0.5
Radiation	Mo Kα
μ (cm^{-1})	30.88
Scan speed (°/min)	3.5
Scan range (°)	2 plus a_1–a_2 divergence
Background counting (s)	0.5 of scan time
2θ limit (°)	50.0
Data collected	6068
Data unique	5567
Data used	4213
$F_o\rangle$	3.0 $\sigma(F_o)$
R_{int}	0.0246
Weighting scheme	$1/w = \sigma^2(F_o) + 0.00016F_o^2$
$F(000)$	1440
No. refined parameters	347
$\lvert\Delta/\sigma\rvert_{max}$	0.002
$(\Delta\rho)_{max}$ (e Å^{-3})	0.0461
$(\Delta\rho)_{min}$ (e Å^{-3})	−0.361
S^a	1.36
R^b (obs.)	0.0314
R^b (all data)	0.0552
R_w^c(obs.)	0.0370
R_w^c (all data)	0.0437

$^a S = [\Sigma w(\Delta F)^2/(N-P)]^{1/2}$, where P = number of parameters and N = number of reflections. $^b R = \Sigma|\Delta F|/\Sigma|F_o|$. $^c R_w = [\Sigma w(\Delta F)^2/\Sigma w(F_o)^2]^{1/2}$.

Results and discussion

Characterization of the complexes

The compounds studied are microcrystalline materials of white or pale yellow colour, stable in the air and readily soluble in a variety of common organic solvents e.g. $CHCl_3$, CH_3OH, CH_3CN etc. They do not appear to be electrolytes both in chloroform and in acetonitrile, since their molecular conductivities in these solvents hardly differ from those of the neat solvents.

The two classes of compounds do not present distinctly different IR spectra. Both are dominated by the strong bands of the thione ligand, most characteristic being that at 3190 cm^{-1}, originating from the –NH moiety, which confirms the through-sulfur coordination of tclH. The strong bands attributed to the skeletal deformation vibrations of the triphenylphosphine and triphenylarsine ligands

TABLE 2. Selected final atomic positions and equivalent thermal parameters ($\times 10^4$) of the non-hydrogen atoms of the $Cu(tclH)_2AsPh_3Br$ molecule with e.s.d.s in parentheses

Atom	x	y	z	U^a
Br	1657.0(2)	142.0(3)	−1085.4(2)	503
Cu	1792.7(2)	2321.0(3)	−397.6(3)	465
As	2983.4(2)	2341.0(3)	194.9(2)	366
S(1)	980.6(5)	2675(1)	646.6(6)	562
C(41)	170(2)	2263(3)	211(2)	422
N(42)	105(2)	1511(3)	−440(2)	464
C(43)	−556(2)	1071(3)	−866(2)	512
C(44)	−973(2)	2088(4)	−1319(3)	610
C(45)	−1376(2)	2905(4)	−729(3)	718
C(46)	−913(2)	3604(4)	−71(3)	698
C(47)	−498(2)	2787(4)	564(2)	551
S(2)	1424.9(5)	3666.1(9)	−1482.7(6)	531
C(51)	1681(2)	3195(3)	−2455(2)	443
N(52)	2069(2)	2215(3)	−2554(2)	530
C(53)	2320(3)	1728(4)	−3356(3)	752
C(54)	1719(3)	1258(4)	−3958(3)	879
C(55)	1296(4)	2267(5)	−4411(3)	1039
C(56)	938(3)	3168(4)	−3838(3)	843
C(57)	1438(2)	3911(3)	−3242(2)	579

[a] $U_{eq} = (U_{11} + U_{22} + U_{33})/3$.

are also in fine agreement with the literature reported positions and patterns [9].

The electronic spectra of the triphenylphosphine compounds are dominated by the well characterized intraligand absorption of PPh_3 which is negligibly shifted relative to its position in the free ligand. The same holds as well for the triphenylarsine complexes for the $AsPh_3$ absorption band at 260 nm while the concomitant shoulder at 275 nm is not well defined in the spectra of the complexes. The bands of the intraligand thione and the Cu–S charge transfer excitations appear in the region 285–295 nm with a clearly defined shoulder near 310 nm.

Reaction of chloroform solutions of the triphenylphosphine complexes with pyridine at a 1:1 molar ratio, produces a new series of complexes, where pyridine has substituted tclH, while the corresponding arsine complexes appear inert to this reaction. The UV–Vis spectra of the former revealed an additional shoulder in the region 325–335 nm, which is regarded as evidence for pyridine ligation to Cu(I) [10]. These facts indicate that pyridine either coordinates to the copper atom in the studied complexes, at the expense of two thione molecules or does not, depending on the relative hardness of the copper core. This in its turn is affected by the coordination of either a phosphine or an arsine ligand.

The NMR spectra of the two series of compounds appear quite akin to one another, expressing a complicated pattern at δ 7.2–7.4 (15H), in accordance with previous observations in triphenylphosphine and triphenylarsine complexes [11]. Regarding the thione protons, the observations also concur with previous investigations of its Cu(I) complexes [3, 13]. The NH– proton is detected in the region δ 10.5–11.0 (2H), dropping to lower δ values as the halogen atomic radius increases (10.97, 10.72 and 10.45 δ in the chlorine, bromine and iodine complex, respectively). The carbon protons of the thione ligands are practically unchanged and appear at 3.40–3.45 (4H), 2.80–2.90 (4H) and 1.75–1.85 (12H), respectively. For the $[Cu(tclH)(PPh_3)_2I]$ compound the same pattern appears as well, though of course, the proton numbers are different due to the reverse ratio of thione versus phosphine molecules ligated to Cu(I).

The arsine complexes express an exceptional photochemical stability compared to their phosphine counterparts. In a comparative study, chloroform solutions of the three arsine complexes were subjected to irradiation using the full spectrum of a UV lamp. The bromine compound proved to be more stable than the other two, which seem to be of equal photoreactivity. This assumption is based upon the time required, for the reduction of the band at λ_{max} of the spectra by 50%. The corresponding times were calculated by interpolating the obtained parabolic absorbance versus time curves to be *c.* 15, 25 and 12 min for the chlorine, bromine and iodine complexes, respectively. Under identical circumstances, the phosphine compounds showed total obliteration within the first 3 min of irradiation. Such a diversity in the behaviour of the two Group VA ligands is by no means unexpected. Triphenylarsine copper(I) complexes, owing to their photostability have proved to be more effective catalysts than their triphenylphosphine counterparts in the photochemical isomerization of norbornadiene [4b].

Description of the structure

Selected bond lengths and angles are presented in Table 3, while an ORTEP stereoview [13] of the molecule in presented in Fig. 1.

The coordination around copper is distorted tetrahedral, with two sulfur atoms, one arsenic and one bromine atom in the vicinity of copper.

The copper–sulfur distances are almost equal (2.310(1) and 2.315(1) Å, respectively) and are shorter than the sum of the tetrahedral single bond covalent radii (2.39 Å). They are, 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 and four-coordinated tetrahedral complexes.

The Cu–Br distance of 2.605(1) Å compares well with those reported for $[CuP(t\text{-}Bu)_3Br]_4$ and

TABLE 3. Relevant interatomic distances (Å) and angles (°) for the Cu(tclH)$_2$AsPh$_3$Br molecule

Bond lengths			
Cu–Br	2.605(1)	N(42)–C(43)	1.456(4)
Cu–As	2.370(1)	C(43)–C(44)	1.507(5)
Cu–S(1)	2.310(1)	C(44)–C(45)	1.505(6)
Cu–S(2)	2.315(1)	C(45)–C(46)	1.514(6)
As–C(11)	1.944(3)	C(46)–C(47)	1.516(5)
As–C(21)	1.946(3)	N(52)–C(53)	1.457(5)
As–C(31)	1.956(3)	C(53)–C(54)	1.519(6)
S(1)–C(41)	1.693(3)	C(54)–C(55)	1.510(6)
S(2)–C(51)	1.690(3)	C(55)–C(56)	1.507(7)
C(41)–N(42)	1.303(4)	C(56)–C(57)	1.519(5)
C(51)–N(52)	1.301(5)		
Bond angles in the vicinity of copper			
As–Cu–Br	103.91(3)	S(2)–Cu–S(1)	103.22(9)
S(1)–Cu–Br	112.69(7)	C(41)–S(1)–Cu	106.3(1)
S(2)–Cu–Br	104.62(7)	N(42)–C(41)–S(1)	121.8(3)
S(1)–Cu–As	111.13(7)	C(51)–S(2)–Cu	112.2(1)
S(2)–Cu–As	121.38(7)	N(52)–C(51)–S(2)	122.5(3)

Hydrogen bonds

A B C	A–B	B–C	A–C	A–B–C
N42–H42···Br	0.80(4)	2.67(3)	3.454(3)	160(3)
N52–H52···Br	0.82(4)	2.55(4)	3.326(3)	160(3)

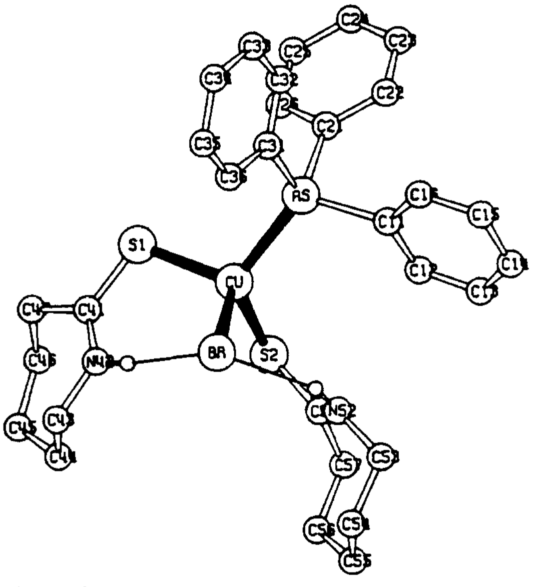

Fig. 1. ORTEP stereoview of the molecule.

[CuPEt$_3$X]$_4$, 2.593 [14] and 2.544 Å [15], respectively. It is, however, significantly longer than 2.515 and 2.495 Å observed for [Cu(PPh$_3$)$_2$(pyrimidine-2-thione)Br] [2] and [Cu(PPh$_3$)Br]$_4$ [15], respectively. Such a weakening of the Cu–Br bond may be regarded as a consequence of two intramolecular hydrogen bonds between Br and the two NH– protons. These non-bonded contacts are about 0.5 Å shorter than the sum of the corresponding van der Waals radii, as in an analogous complex of pyridine-2-thione, namely [Cu(py2SH)(PPh$_3$)Br]$_2$ [2]. The afore-mentioned hydrogen bonds emerge since the two tclH ligands, though in other respects almost identical (see Table 3), express dramatic differences in the angles around the thioketone moiety.

The copper–arsenic distance of 2.371(1) Å is slightly shorter than the sum of the covalent bond radii, viz. 2.38 Å and in good agreement with 2.368 Å in [Cu(AsPhMe$_2$)$_2$Cl]$_2$ [16] and 2.361 Å in [CuAsEt$_3$I]$_4$ [17].

The As–C bond lengths are unequal, in line with the general observation of violation of the strict tetrahedral arrangement around As [18]. They range from 1.944 (3) to 1.956(3) Å, lying within the boundaries defined by the analogous bonds in [Ph$_3$AsCo(CO)$_2$NO] [19] and [Mo(diars)$_2$(CO)$_2$I]I [20], which are 1.93(2) and 1.98(6) Å, respectively.

The two S–Cu–As angles are markedly different (111.1(0)° and 121.4(0)°, respectively), both being larger than the regular value of 109.47° connected with a strictly tetrahedral coordination sphere. In view of this irregularity, it is not surprising that the S–Cu–S angle (103.2(1)°) is considerably smaller compared to 117.8(1)° in [Cu(tclH)$_2$I] [3], a fact ascribed to a large steric hinderance induced by the triphenylarsine ligand. 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.

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References

1 (a) T. N. Sorrell and D. L. Jameson, *J. Am. Chem. Soc., 104* (1982) 2053; (b) V. McKee, M. Zvagulus, J. V. Dagdigan, M. G. Patch and C. A. Reed, *J. Am. Chem. Soc., 106* (1984) 4765; (c) M. Patch, H. Choi, D. R. Chapman, R. Bau, V. McKee and C. A. Reed, *Inorg. Chem., 29* (1990) 110.
2 P. Karagiannidis, P. Aslanidis, D. P. Kessissoglou, B. Krebs and M. Dartman, *Inorg. Chim. Acta, 156* (1989) 47, and refs. therein.
3 P. Karagiannidis, P. D. Akrivos, D. Mentzafos and A. Hountas, *Inorg. Chim. Acta, 180* (1991) 93.
4 (a) S. J. Lippard and P. S. Welcker, *Inorg. Chem., 11* (1972) 6; (b) S. Sakaki, K. Ohkubo, H. Fujiwara and A. Ohyoshi, *J. Mol. Catal., 16* (1982) 181.

5 (a) F. H. Jardine, A. G. Vohra and F. J. Young, *J. Inorg. Nucl. Chem., 33* (1971)2941; (b) M. R. Churchill and J. R. Missert, *Inorg. Chem., 20* (1981) 619; (c) M. I. Bruce, P. A. Humphrey, J. M. Patrick, B. W. Skelton, A. H. White and M. L. Williams, *Aust. J. Chem., 38* (1985) 1441.

6 *International Tables for X-ray Crystallography,* Vol. 4, Birmingham, U.K., 1974 (present distributor D. Reidel, Dordrecht, The Netherlands).

7 G. Cascarano, C. Giacovazzo, M. Burla, G. Polidori, M. Camalli, R. Spagne and D. Viterbo, *SIR 88, University of Bari, Italy, 1988.*

8 G. M. Sheldrick, *SHELX76,* program for crystal structure determination, University of Cambridge, Cambridge, U.K., 1976.

9 L. Maier, *Prog. Inorg. Chem., 5* (1963) 27.

10 S. Kitagawa, M. Munakata and A. Higashie, *Inorg. Chim. Acta, 59* (1982) 219.

11 M. M. T. Khan, S. S. Ahamed and R. A. Levenson, *J. Inorg. Nucl. Chem., 38* (1976) 1135.

12 P. Castan, *Transition Met. Chem., 6* (1981) 14.

13 C. K. Johnson, *ORTEP II, Rep. ORNL-5138,* Oak Ridge National Laboratory, TN, U.S.A., 1976.

14 R. G. Goel and A. L. Beauchamp, *Inorg. Chem., 22* (1983) 395.

15 M. R. Churchill, B. G. Deboer and S. J. Mendalc, *Inorg. Chem., 14* (1975) 2041.

16 J. T. Gill, J. J. Mayerle, P. S. Weckler, D. F. Lewis, D. A. Ucko, D. J. Barton and D. Stowens, *Inorg. Chem., 15* (1976) 1155.

17 M. R. Churchill and J. Calabrese, *Inorg. Chem., 13* (1974) 1899.

18 (a) S. J. Lippard and K. M. Melmed, *Inorg. Chem., 6* (1967) 2223; (b) M. R. Churchill and T. A. O'Brien, *J. Chem. Soc. A,* (1968) 2970.

19 G. Gilli, M. Sacendoti and G. Reichenbach, *Acta Crystallogr., Sect. B, 29* (1973) 2306.

20 M. G. B. Drew and J. D. Wilkins, *J. Chem. Soc., Dalton Trans.,* (1973) 2664.