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COPPER(I) HALIDE COORDINATION COMPOUNDS WITH BENZ-1,3-THIAZOLIDINE-2-THIONE AND TRIARYLPHOSPHINES: THE CRYSTAL AND MOLECULAR STRUCTURE OF [$Cu(PPh_3)_2$(bztzdtH)Cl]CH_3COCH_3

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Abstract—Copper(I) complexes of the general formula [$Cu(PAr_3)_2$(bztzdtH)X] (where X = Cl, Br, I; PAr_3 = tri-*m*-tolylphosphine, diphenyl-*p*-tolylphosphine; bztzdtH = benz-1,3-thiazolidine-2-thione) and [$Cu(PAr_3)$(bztzdtH)X] (where X = Cl, Br; PAr_3 = tri-*o*-tolylphosphine) were prepared and characterized by elemental analysis and their IR and UV-vis spectroscopic data. A single-crystal X-ray diffraction study was carried out on the complex [$Cu(PPh_3)_2$(bztzdtH)Cl]CH_3COCH_3. The complex exhibits a distorted tetrahedral $CuSP_2Cl$ core with Cu—P(1) = 2.278(1) Å, Cu—P(2) = 2.286(2) Å and Cu—Cl = 2.377(1) Å, and bond angles around copper varying from 102.95(5)° for P(2)—Cu—Cl to 122.36(5)° for P(1)—Cu—P(2).

In the past 10 years, copper(I) complexes with heterocyclic thiones have attracted the interest of many researchers.[1] In our laboratory, particular emphasis is being placed on mixed ligand copper(I) complexes with heterocyclic thiones and arylphosphines[2] in order to investigate, amongst other things, the possible influence of these ligands on the coordination geometry of the metal atom. In previous publications we have already noted the preference for trigonal planar geometry instead of the usually favoured tetrahedral[3] when the size of the phosphine ligand is increased as in the case of the bulky tri-*o*-tolylphosphine. Continuing the study of the copper(I) stereochemistry and especially the geometry at the thione site in this family of complexes, in the present paper we describe the synthesis and characterization of nine compounds obtained from the reaction of copper(I) halides with benz-1,3-thiazoline-2-thione and several arylphosphines as well as the crystal structure of [$Cu(PPh_3)_2$(bztzdtH)Cl]CH_3COCH_3.

EXPERIMENTAL

Preparation and physical properties of the complexes

The new complexes were obtained according to a known general procedure for preparing mononuclear mixed ligand complexes of copper(I)

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halides, namely the reaction between the copper(I) salt and a 1 : 2 mixture of the heterocyclic thione and triarylphosphine. Thus, a solution of 0.5 mmol of benz-1,3-thiazoline-2-thione and 1 mmol of the appropriate phosphine in 60 cm^3 acetone or chloroform was added to a 20 cm^3 suspension of 0.5 mmol copper(I) halide in the same solvent. The resulting solution was moderately heated for 2 h and then allowed to cool. Slow evaporation of the solvent at room temperature gave a microcrystalline solid, which was filtered off and dried *in vacuo*.

Using triphenyl-, tri-*m*-tolyl- or diphenyl-*p*-tolylphosphine, the expected tetrahedral complexes of the formula $[Cu(PAr_3)_2(bztzdtH)X]$ were observed, whereas the more bulky tri-*o*-tolylphosphine produced, in the case of CuCl and CuBr, three-coordinate compounds of the formula [Cu(totp)(bztzdtH)X]. Unexpectedly, we were unable to obtain a corresponding copper(I) iodide complex.

All of these complexes are air stable microcrystalline solids soluble in acetonitrile, chloroform, acetone and methanol. The stoichiometry was deduced from the results of the elemental analyses and was confirmed by the X-ray diffraction study in the case of $[Cu(PPh_3)_2(bztzdtH)Cl]CH_3COCH_3$. Room temperature magnetic measurements on several species showed that the central metal ion is diamagnetic copper(I).

The UV-vis spectra of the complexes in chloroform solutions consist of one broad band in the region 260–300 nm with two peaks assigned to intraligand transitions, accompanied by another one at 370–400 nm.

The IR spectra of the compounds, registered in the range 4000–250 cm^{-1}, are in agreement with the X-ray crystal structure analysis given below as far as the monodentate donating character of the thiones is concerned. They are mainly characterized by vibrational absorptions of coordinated bztzdtH and show, apart form the strong phosphine bands, the usual four ‘thioamide’ bands [R] in the regions ~1500, 1320, 1000 and 750 cm^{-1}. The directions of the position shifts of these bands in the spectra are the same, indicating that the binding pattern must be similar. All prepared complexes and some physical properties as well as their elemental analyses are given in Table 1.

X-ray crystallographic analyses

Crystals of the complex $[Cu(PPh_3)_2(bztzdtH)Cl]CH_3COCH_3$ suitable for data collection were obtained by slow evaporation of an acetone solution of the complex. X-ray diffraction data were collected on a Syntex P3 automatic diffractometer with graphite monochromated Mo-K_α radiation at room temperature. Systematic absences led to space group $P2_1/c$. Unit cell dimensions were calculated by least-squares analysis of measured θ angles of 25 strong reflections in the range $20° < 2\theta < 25°$. The intensities of three standard reflections monitored every 120 reflections showed no significant variation. A total of 5755 reflections were collected, all of them unique and in compliance with the acceptance criterion $I_o > 2\sigma(I_o)$, and were employed in the analyses. In view of the low μ value no correction for absorption was deemed necessary. Details of crystal data, data collection and structure refinement are given in Table 2. The positions of copper, chlorine, sulfur and phosphorus atoms were found by direct methods while the rest of the non-hydrogen atoms were revealed by successive difference Fourier maps using the XTAL3.2 software package.[4] The refinement of the positional and anisotropic thermal parameters of these atoms was carried out by full matrix least-squares analysis with the SHELX93 program package.[5] The atomic scattering factors incorporated in the program were used. A difference Fourier map showed most of the hydrogen atoms at positions very close to calculated ones and the existence of an acetone molecule which

Table 1. Some physical properties and analytical data of the complexes

Compound	Yield (%)	Colour	M.p. (°C)	C (%)	H (%)	N (%)
$[Cu(tmpt)_2(bztzdtH)Cl]$	75	Pale yellow	132	66.8 (67.3)	5.8 (5.4)	1.8 (1.6)
$[Cu(tmpt)_2(bztzdtH)Br]$	80	Yellow	141	63.2 (64.0)	5.2 (5.1)	1.7 (1.5)
$[Cu(tmpt)_2(bztzdtH)I]$	72	Yellow	127	59.3 (60.9)	4.8 (4.9)	1.6 (1.4)
[Cu(totp)(bztzdtH)Cl]	65	Yellow	196	57.2 (58.9)	4.4 (4.6)	2.7 (2.4)
[Cu(totp)(bztzdtH)Br]	65	Yellow	189	55.3 (54.7)	4.3 (4.3)	2.0 (2.3)
$[Cu(dpptp)_2(bztzdtH)Cl]$	75	Yellow	121	65.8 (66.0)	5.0 (4.8)	1.9 (1.7)
$[Cu(dpptp)_2(bztzdtH)Br]$	80	Yellow	118	62.7 (62.6)	4.3 (4.5)	1.6 (1.6)
$[Cu(dpptp)_2(bztzdtH)I]$	80	Yellow	146	58.4 (59.4)	4.7 (4.3)	1.5 (1.5)

Table 2. Crystal data and structure refinement for $[Cu(PPh_3)_2(bztzdtH)Cl]$ CH_3COCH_3

Formula	$C_{46}H_{40}ClCuNOP_2S_2$
Formula weight	847.84
Wavelength (Å)	0.71069
Crystal system	Monoclinic
Space group	$P2_1/c$
Unit cell dimensions	$a = 13.172$ Å $\alpha = 90°$
	$b = 18.713$ Å $\beta = 95.65°$
	$c = 17.357$ Å $\gamma = 90°$
Volume (Å^3)	4257.5
Z	4
Density (calculated) (mg m^{-3})	1.323
Absorption coefficient (mm^{-1})	0.784
$F(000)$	1756
Theta range for data collection (°)	1.90–25.06
Index ranges	$-9 \leqslant h \leqslant 9, 0 \leqslant k \leqslant 22, 0 \leqslant l \leqslant 20$
Unique reflections	5755
Data/restraints/parameters	5755/0/652
Goodness-of-fit on F^2	1.036
Final R indices $[I > 2\sigma(I)]$	0.049
Largest diff. peak and hole (e Å^{-3})	0.387 and -0.612

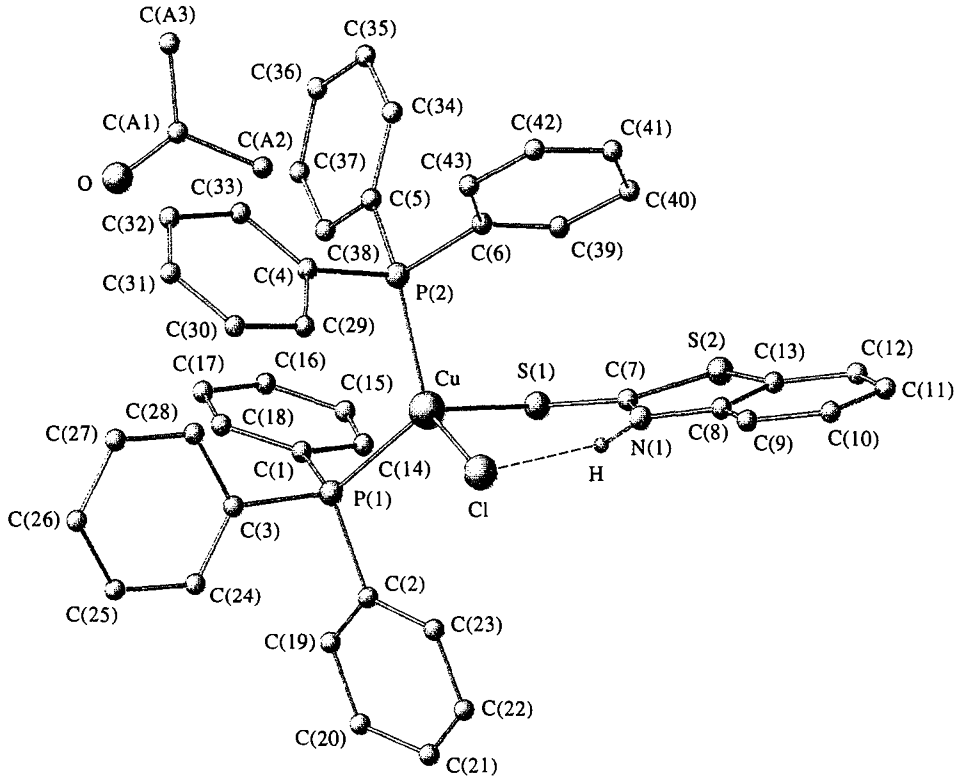

Fig. 1. Clinographic projection of the molecule $[Cu(PPh_3)_2(bztzdtH)Cl]CH_3COCH_3$.

was included in the lattice during the crystallization process. The hydrogen atoms were included in the refinement at positions either calculated on stereochemical grounds (phenyl, imidazole rings) or taken from a ΔF map (methyl groups) with isotropic temperature factors assumed equal to those of the bonded C or N atoms. Their positional and thermal parameters were refined during the last cycle. The function minimized in the least-squares refinement was $\Sigma w(|F_o|-|F_c|)^2$ where $w = 1/[\sigma^2(F_o^2)+(0.1301P)^2+3.03P]$ and where $P = (\max(F_o^2,0)+2F_c^2)/3$. The plot of the molecular structure shown in Fig. 1 and the clinographic projection of the unit cell shown in Fig. 2 were produced with the programs ATOMS[6] and ORTEX[7], respectively. Selected bond lengths and angles together with their standard deviations are listed in Table 3.

DESCRIPTION OF THE STRUCTURE AND DISCUSSION

The structure of $[Cu(PPh_3)_2(bztzdtH)Cl]CH_3COCH_3$ is closely related to those of $[Cu(PPh_3)_2(bzimtH_2)Cl]$, $[Cu(PPh_3)_2(nbzimtH_2)Cl]$[8] and $[Cu(PPh_3)_2(pyzsH)Cl]$.[9] It appears that the exchange of the $bzimtH_2$, $nbzimtH_2$ or py2SH entity with that of bztzdtH produces no significant variation in the $CuSP_2Cl$ core. The coordination geometry about the copper atoms remains distorted tetrahedral with only three of the bond angles close to the ideal tetrahedral value. The rest and especially the P—Cu—P angle deviate considerably from those of a regular tetrahedron.

The distorted tetrahedral copper(I) geometry with the enlarged P—Cu—P bond angle is the com-

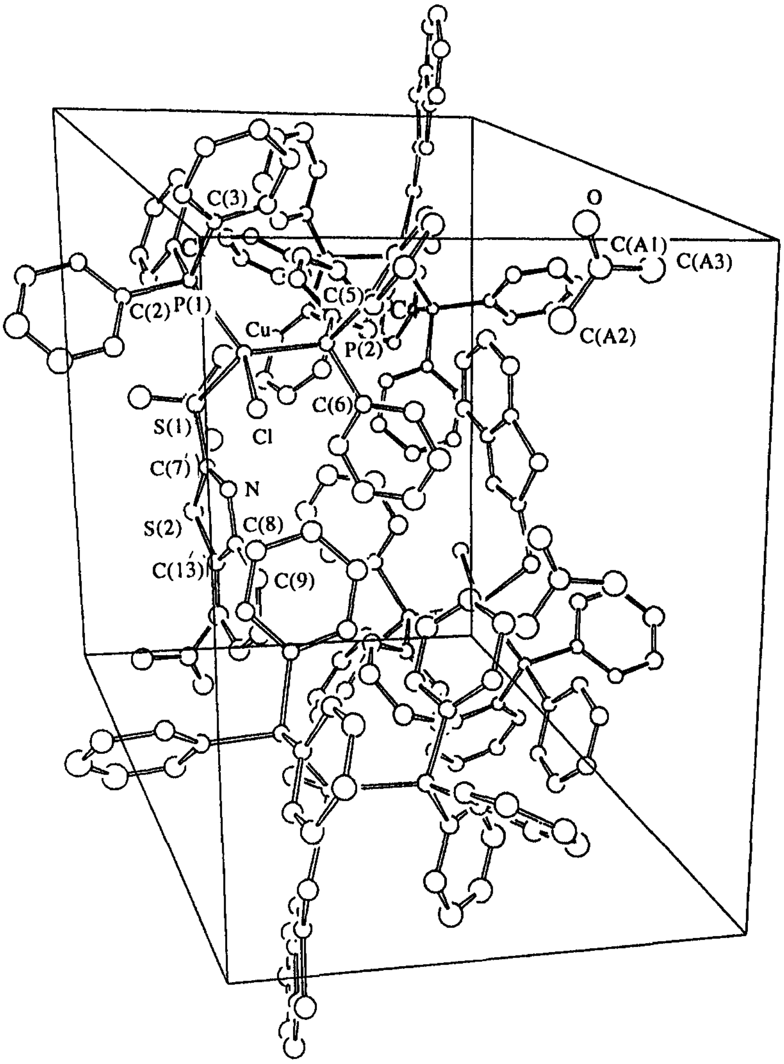

Fig. 2. Clinographic projection of the unit cell of $[Cu(PPh_3)_2(bztzdtH)Cl]CH_3COCH_3$.

Table 3. Selected bond lengths (Å) and angles (°) for non-hydrogen atoms of $[Cu(PPh_3)_2(bztzdtH)Cl]CH_3COCH_3$

Cu—P(1)	2.2787 (13)	P(2)—C(6)	1.832 (5)
Cu—P(2)	2.286 (2)	S(1)—C(7)	1.682 (4)
Cu—Cl	2.3776 (12)	S(2)—C(13)	1.741 (5)
Cu—S(1)	2.3821 (13)	C(7)—N	1.325 (6)
P(1)—C(1)	1.832 (4)	N—C(8)	1.403 (5)
P(1)—C(2)	1.823 (6)	C(8)—C(13)	1.376 (6)
P(1)—C(3)	1.835 (4)	O—C(A1)	1.212 (8)
P(2)—C(4)	1.835 (5)	C(A1)—C(A3)	1.463 (13)
P(2)—C(5)	1.828 (5)	C(A1)—C(A2)	1.488 (12)

P(1)—Cu—P(2)	122.36 (5)	C(5)—P(2)—Cu	118.5 (2)
P(1)—Cu—Cl	112.25 (5)	C(6)—P(2)—Cu	114.8 (2)
P(2)—Cu—Cl	102.95 (5)	C(7)—S(1)—Cu	108.8 (2)
P(1)—Cu—S(1)	103.31 (5)	N—C(7)—S(1)	126.3 (3)
P(2)—Cu—S(1)	107.83 (5)	C(7)—N—C(8)	115.7 (4)
Cl—Cu—S(1)	107.43 (5)	C(13)—C(8)—N	111.8 (4)
C(1)—P(1)—Cu	112.9 (2)	C(8)—C(13)—S(2)	110.4 (3)
C(2)—P(1)—Cu	115.3 (2)	O—C(A1)—C(A3)	124.2 (8)
C(3)—P(1)—Cu	118.5 (2)	O—C(A1)—C(A2)	118.5 (9)
C(4)—P(2)—Cu	112.6 (2)	C(A3)—C(A1)—C(A2)	117.4 (9)

Table 4. Cu(I) geometry in similar copper(I) halide compounds

	A	B	C	D	E	F	G	H
Distances (Å)								
Cu—X	2.462 (2)	2.509 (0)	2.519 (1)	2.674 (2)	2.376 (1)	2.384 (2)	2.361 (1)	2.377 (1)
Cu—S	2.302 (4)	2.375 (1)	2.345 (3)	2.338 (4)	2.377 (1)	2.381 (2)	2.374 (2)	2.382 (1)
Cu—P	2.263 (4)	2.268 (1)	2.303 (2)	2.296 (4)	2.278 (1)	2.265 (2)	2.286 (2)	2.278 (1)
	2.267 (4)	2.281 (1)	2.306 (2)	2.303 (4)	2.295 (1)	2.282 (2)	2.301 (2)	2.286 (2)
Angles (°)								
X—Cu—S1	114.9 (1)	112.6 (0)	108.2 (1)	116.5 (1)	106.6 (0)	108.1 (1)	109.2 (1)	107.4 (0)
X—Cu—P1	104.4 (1)	106.7 (0)	108.0 (1)	103.5 (1)	111.5 (0)	110.4 (0)	99.6 (1)	112.2 (0)
X—Cu—P2	105.9 (1)	98.3 (0)	111.0 (1)	103.6 (1)	103.6 (0)	103.7 (0)	111.6 (1)	102.9 (0)
Cl—Cu—P1	104.5 (2)	102.9 (0)	106.5 (1)	105.4 (1)	103.0 (0)	100.8 (1)	111.3 (1)	103.3 (0)
S1—Cu—P2	102.8 (2)	105.3 (0)	110.0 (1)	103.4 (1)	109.6 (0)	108.2 (0)	102.6 (1)	107.8 (0)
P1—Cu—P2	125.0 (2)	130.9 (0)	112.9 (1)	125.3 (1)	121.7 (0)	124.7 (0)	122.4 (1)	122.4 (0)

A $[Cu(PPh_3)_2(py2SH)Br]$.
B $[Cu(PPh_3)_2(meimtH)Br]$.
C $[Cu(PPh_3)_2(pymtH)Br]$.
D $[Cu(PPh_3)_2(pymtH)I]$.
E $[Cu(PPh_3)_2(bzimtH_2)Cl]CH_3COCH_3$.
F $[Cu(PPh_3)_2(nbzimH_2)Cl]$.
G $[Cu(PPh_3)_2(py2SH)Cl]$.
H $[Cu(PPh_3)_2(bztzdH)Cl]CH_3COCH_3$.

mon feature of the molecular structure of the compounds included in Table 4. Apparently this is a consequence of factors of the same nature near the copper coordination sphere which are essentially determined by the steric bulky ligands and the constraints due to intramolecular hydrogen bridging bonds.

The Cu—S bond length of 2.382(1) Å in [Cu $(PPh_3)_2$(bztzdtH)Cl]CH_3COCH_3 is consistent with values found for tetrahedrally coordinated copper(I) with thione-S donors.[9–11] Its difference from the Cu—S bond distances in [Cu$(PPh_3)_2$(pyzsH)Cl], [Cu$(PPh_3)_2$(bzimtH_2)Cl] and [Cu$(PPh_3)_2$(nbzmtH_2) Cl], equal to 8σ, 5σ and 1σ, respectively, decreases as the size of the S-ligand increases. This influence of the ligand size can undoubtedly be seen in the bromide complexes (Table 4). In this case it is obvious that the Cu—S bond length increases as the increasing size of the thione ligand imposes greater steric repulsion around the copper atom.

The Cu—P(1), Cu—P(2) and Cu—Cl bond distances, 2.278(1), 2.286(2) and 2.377(1) Å, respectively, are in good agreement with the values found so far.[9,11–14] In particular, the Cu—P bond lengths fall in the middle of the range 2.306–2.263 Å of values found for the complexes in Table 4. As in all these compounds, the halogen atom in [Cu $(PPh_3)_2$(bztzdtH)Cl]CH_3COCH_3 is hydrogen bonded to the (bztzdtH)—NH atom. This hydrogen bond, HN···Cl = 2.23 Å and N—H—Cl 116.7°, apparently also contributes to the conformational distortion of the $CuSP_2Cl$ core. The interatomic distances and angles within the triphenylphosphine and bztzdtH ligands are the expected ones. The solvent acetone molecule present in the structure is connected with the [Cu$(PPh_3)_2$(bztzdtH)Cl] moiety by a C—H···O hydrogen bond (C(16)—H···O = 2.56 Å).

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