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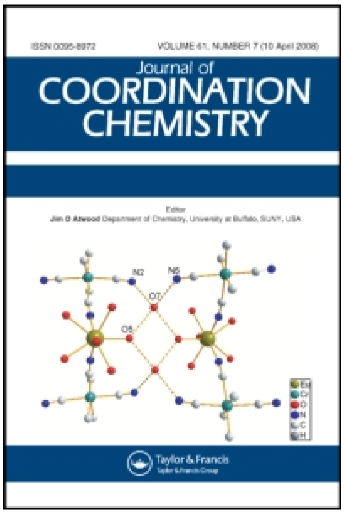

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SYNTHESIS AND REACTIVITY OF TRIGONAL COPPER(I) COMPOUNDS. CRYSTAL STRUCTURE OF BIS(TETRAHYDROPYRIMIDINE-2-THIONE)COPPER(I) BROMIDE

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SYNTHESIS AND REACTIVITY OF TRIGONAL COPPER(I) COMPOUNDS. CRYSTAL STRUCTURE OF BIS(TETRAHYDROPYRIMIDINE-2-THIONE)COPPER(I) BROMIDE

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Reaction of monovalent copper halides with excess tetrahydropyrimidine-2-thione (thpmtH$_2$) in acetonitrile results in the formation of three-coordinate monomer products of formula Cu(thpmtH$_2$)$_2$X. The crystal and molecular structure of the bromo complex is reported and discussed with respect to analogous copper(I) complexes. The compound crystallizes in the tetragonal system, space group, $P4_12_12$ with a = 8.005(1), c = 21.31(1) Å, and Z = 4. The two Cu-S bonds are 2.215(4) Å and the Cu-Br bond distance is 2.405(2) Å, the interbond angles around copper being exactly 360°. Reactivity of the title compound as well as of its iodo counterpart towards Lewis bases was also investigated; the two compounds react readily, in stoicheiometric amounts, with tertiary phosphine and arsine ligands forming monomeric four-coordinate Cu(I) species, the structures of which were deduced by spectroscopic measurements.

KEYWORDS: copper(I), thioamide, X-ray structure, reactivity, NMR spectra

INTRODUCTION

One reason for the investigation of the structure of new monovalent copper compounds is the number and diversity of those already existing. The possibilities of tuning stereoelectronic factors controlling the chromophoric structure of copper(I) compounds are being continuously explored with respect to small model compounds of active enzyme sites.[1] We have studied the coordination to copper(I)

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of thione ligands[2] possessing α-nitrogen heteroatoms, as potential models for thioamido groups which have been found to coordinate to copper in biological media. Particular emphasis has been placed on the determination of the stereochemistry of the metal centre and the coordination mode adopted by the ligands. Investigation of the bonding mode of thioxohexamethyleneimine (ω-thiocaprolactam, tclH) has been undertaken[3] and proved quite interesting, since this bulky thione possesses a saturated and flexible backbone contrary to our previous investigations involving compact, planar thione molecules. The less bulky six-membered ligand tetrahydropyrimidine-2-thione (thpmtH), is therefore the next obvious step in the investigation of ligand effects on copper(I) coordination spheres, since it represents the saturated analogue of pyrimidine-2-thione and a ring smaller than that possessed by thiocaprolactam. The results of its study accompanied by a crystal structure determination of the title compound are presently described.

EXPERIMENTAL

Materials and Measurements

All solvents used were of reagent grade. Copper halides (BDH), triphenylphosphine (BDH), other tertiary phosphines used (Aldrich) and triphenylarsine (Merck) were not subjected to any further purification while tetrahydropyrimidine-2-thione ($thpmtH_2$) (Aldrich) was recrystallized from hot methanol prior to use. Elemental analyses for C, H and N were carried out on a Perkin-Elmer 240 B elemental analyser. IR spectra were recorded in KBr discs on a Perkin-Elmer 1430 spectrophotometer, while electronic spectra were obtained on a Shimadzu 160 A spectrophotometer. A Bruker AW-80 spectrometer was used for recording ^1H NMR spectra, while ^{13}C and ^{31}P NMR were recorded on a Varian VXR-300 spectrometer. Measurements were carried out in deuterated chloroform solutions; ^1H and ^{13}C chemical shifts are reported in ppm relative to $CDCl_3$ and ^{31}P relative to external $(NPCl_2)_3$ standard.

Preparation of $Cu(thpmtH)_2X$

Reaction of CuX (X = Cl, Br or I) with excess thione (1:3 molar ratio) was carried out in acetonitrile with moderate heating for about 20 min. In the case of CuCl, unsatisfactory analysis led to repetition of the reaction under reflux for about 3 h. The clear solutions obtained were allowed to cool and subsequently white precipitates formed. Elemental analyses were satisfactory for $Cu(thpmtH)_2X$. Slow evaporation of a CH_3OH:$CHCl_3$ (1:1) solution of the title complex at room temperature produced crystals appropriate for X-ray diffraction study.

Solution of the structure

Crystallographic data and details of data collection and refinement are listed in Table 1. Data reduction was performed by the Enraf-Nonius SDP/VAX package;[4] Lorentz and polarization effects corrections were performed. Reference reflections showed a loss of intensity at about 4.5% during data collection. The structure was solved by direct methods, using SHELX-86.[5] Copper scattering factors and

Table 1 Crystal Data and Details of the Structure Determination.

a) Crystal Data	
Molecular formula	$Cu_2Br_2S_2P_2N_4C_8H_{16}$
M_r	373.80
a [Å]	8.005(1)
c [Å]	21.31(1)
V[Å^3]	1365.5(1)
D_x [gcm^{-3}]	1.82(1)
Z	4
Crystal system	tetragonal
Space group	$P4_12_12$
Crystal size [mm]	0.4 × 0.3 × 0.1
Linear absorption coefficient [cm^{-1}]	47.82
F (000)	752
b) Data Collection	
Diffractometer	Enraf-Nonius CAD4F
Radiation	MoKα (λ = 0.71073 Å) graphite-monochromator
Temperature [K]	297(3)
θ_{min}, θ_{max} [°] for cell. det.	7,18
No. of reflections used for cell det.	25
θ_{min}, θ_{max}	2,28
ω scan [°]	$\Delta\omega = 1.2 + 0.35 \tan\theta$
hkl limits	(-1,10-1,10;-1,28)
Reflections measured	2603
c) Refinement	
Independent reflections observed with $I>3.5\sigma(I)$	749
No. of parameters	84
Quantity minimized, $\Sigma w\|\|F_o\|-\|F_c\|\|^2$	$w^{-1} = (\sigma^2(F_o) + 0.003 F_o^2)/k$
R, R_w	0.066, 0.070
Max. parameter shift, $(\Delta/\sigma)_{max}$	0.03(C4,z)
Residual electron density, $(\Delta\rho)_{max}$, $(\Delta\rho)_{min}$ [eÅ^{-3}]	1.16, -2.21

anomalous dispersion values were taken from International Tables for Crystallography, Vol. IV[6] while for other atoms the scattering factors were those included in SHELX-76.[7] The H atom coordinates of the tetrahydropyrimidine groups were calculated on stereochemical grounds. The H atom on nitrogen N1 was located in a difference Fourier map and the N-H distance adjusted to the theoretical value. The H atom on N(2) was not located. The structure was refined by full-matrix

Table 2 Final Atomic Coordinates and Equivalent Isotropic Thermal Parameters.

Atom	x/a	y/b	z/c	U_{eq}[Å^2]
Br	0.2423(2)	-0.2423(2)	1/4	0.0604(7)
Cu	0.4547(2)	-0.4547(2)	1/4	0.0442(7)
S	1.2154(5)	0.1127(5)	0.2740(2)	0.0572(14)
N(1)	1.3686(13)	0.3819(14)	0.3145(6)	0.044(4)
N(2)	1.0839(13)	0.3823(12)	0.3280(7)	0.048(4)
C(1)	1.2215(9)	0.308(2)	0.3073(7)	0.042(5)
C(2)	1.3935(18)	0.5483(16)	0.3417(8)	0.054(5)
C(3)	1.2299(13)	0.6429(19)	0.3368(8)	0.050(5)
C(4)	1.0850(18)	0.5413(17)	0.3622(7)	0.055(6)

U_{eq} = 1/3 of the trace of the orthogonalized U tensor.

least-squares methods on the F values;[7] non-H atoms were refined anisotropically and H atoms with individual isotropic thermal parameters. The H-atoms were refined according to the constraints of the pivot carbon atoms. Interatomic distances, bond and torsion angle calculations and analysis of the ring puckering were performed by the EUCLID package of programs[8] and the plot of the molecule by the ORTEP program.[9] Final atomic coordinates and equivalent isotropic thermal parameters are reported in Table 2. Calculations were carried out on the MICROVAX II in the X-Ray Laboratory of Rudjer Boskovic Institute, Zagreb.

RESULTS AND DISCUSSION

Description of the structure

The molecular structure of the monomer is presented in Figure 1 and selected bond lengths and angles are listed in Table 3. The figure reveals a three coordinate copper centre, the coordination sphere consisting of two $thpmtH_2$ ligands and a bromine atom. The molecule is symmetrical, the copper and bromine atoms lying on the twofold axis (special position 4*a* of the $P4_12_12$ space group); the Cu-Br bond is 2.405(2) Å, appreciably shorter than those reported for tetrahedral monomers which vary from 2.51(1) to 2.60(0) Å,[10] but exceeding those in linear $CuBr_2^-$ units which range from 2.207(2) to 2.224(2) Å.[11] It is slightly larger than 2.385(1) Å observed in $Cu(tclH)_2Br$, which is the closest analogue of the presently discussed compound.

The Cu-S bond lengths are 2.215(4) Å. They are in close agreement with several reported for trigonal Cu(I) systems, *e.g.*, Cu(*N,N'*-dimethylimidazolidine-2-thione)$_2$Cl,*bis*(2-thiouracil)chlorocopper(I)·dmf, Cu(*N*-ethyl-1,3-imidazolidine-2-thione)$_2$Cl and Cu{1-phenyl-3-(2-pyridyl)-2-thiourea}$_2$Cl,[12] which range from 2.206 to 2.221 Å, and almost midway between 2.228(2) and 2.206(2) Å which have been observed in $Cu(tclH)_2Br$[3b] and in $Cu(thpmtH)_2Cl$,[13] respectively.

The two S-Cu-Br angles are both equal to 119.6(1)°, thus giving rise to a totally symmetric chromophore, with S-Cu-S^i equal to 120.8(2)° (i = 1-*y*, 1-*x*, 1/2-*z*), and being almost identical to 119.7° for $Cu(tclH)_2Br$. The molecule is almost planar, the average deviation from the least squares plane being 0.36(3) Å and the maximum value realized for C(4) (0.82(3) Å).

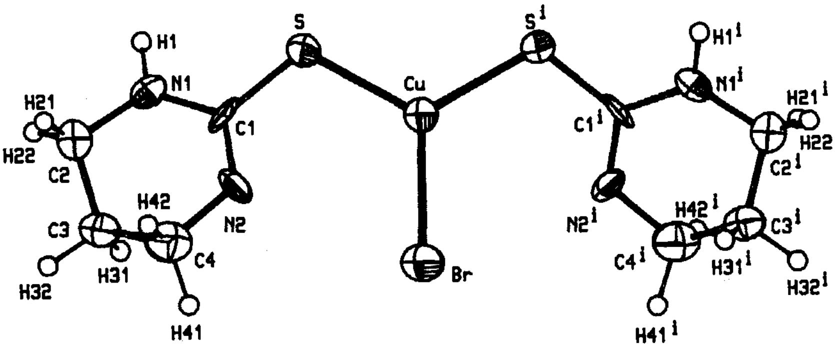

Figure 1 Ortep plot of the trigonal copper(I) complex; symmetry operation *i* is 1-*y*, 1-*x*, 1/2-*z*.

Table 3 Selected Bond Distances (Å) and Angles (°).

Br - Cu	2.405(2)
Cu - S	2.215(4)
S - C(1)	1.72(1)
N(1) - C(1)	1.33(1)
N(1) - C(2)	1.47(2)
N(2) - C(1)	1.33(1)
N(2) - C(4)	1.47(2)
C(2) - C(3)	1.52(2)
C(3) - C(4)	1.52(2)
Br - Cu - S	119.6(1)
S - Cu - S^i	120.8(2)
Cu - S - C(1)	110.1(3)
C(1) - N(1) - C(2)	125(1)
C(1) - N(2) - C(4)	123(1)
S - C(1) - N(1)	118.6(9)
S - C(1) - N(2)	121.4(8)
N(1) - C(1) - N(2)	120(1)
N(1) - C(2) - C(3)	108(1)
C(2) - C(3) - C(4)	112(1)
N(2) - C(4) - C(3)	107(1)

^{i}Symmetry operation: 1-*y*, 1-*x*, 1/2-*z*.

The S-C bond length of 1.718(16) Å lies within the range of values observed in analogous complexes, of which representative ones are 1.727(7) Å for $Cu(thpmtH_2)_2Cl$ and 1.691(5) Å for $Cu(tclH)_2Br$. The exocyclic sulfur and N(1), N(2), C(1) and C(2) are coplanar, the six-membered ring exhibiting an overall conformation between half-chair and sofa; this is especially illustrated by the asymmetric displacement of C(3) and C(4) by −0.57(10) Å and 0.13(10) Å respectively. Hydrogen bonds N(1)-H(1)...Br (N1...Br, 3.439(11) Å, H...Br, 2.464 Å, N-H...Br, 169°) connect the molecules into a three-dimensional network.

Spectroscopic studies

IR spectra of the compounds offer evidence of the coordination mode of the ligand, which occurs exclusively *via* the exocyclic sulfur atom, since the characteristic NH stretching vibration is observed at *ca* 3150 cm^{-1}. The shift of these bands relative to that observed in the free thione (3195 cm^{-1}) indicates significant intramolecular hydrogen bonding, confirmed by the structural study. Electronic spectra recorded in methanol are dominated by a sharp band at 223 nm and a broad one with a maximum at 245 nm, accompanied by a shoulder at 265 nm. The latter may be attributed to a MLCT excitation, since no analogous absorption is present in the spectrum of the free ligand. Chloroform solutions of the complexes exhibit a single broad band with a maximum at 260 nm and shoulders at 280 and 290 nm. The ^1H and ^{13}C NMR of the title compound and its iodo counterpart are identical to those already reported.[14]

It is expected that bulky ligands like tclH and $thpmtH_2$, "crowd" the metal environment, thus giving rise to low coordination numbers; it seemed interesting though to investigate the extent of this effect by forcing reactions of the complex with several small molecules as well as some Lewis bases. The results of these studies are presently discussed; both chloroform and methanol solutions (10^{-4} M) of the initial complexes were treated with excess pyridine (final concentration 1 M) and presented a rather sharp peak at *ca* 295 nm in the electronic spectrum of the products, this being indicative of pyridine adduct formation.[4] Slow evaporation of the solvent at room temperature produced the initial compounds, identified by their spectra and thus confirming the reversibility of the bonding of pyridine to the $CuXS_2$ cores of the title complexes. The solutions, upon standing in air, turned bluish-green within a few hours, indicating facile oxidation to divalent copper species.

Reactivity towards Lewis bases

Reactions carried out in stoicheiometric quantities in chloroform solution revealed that the compounds are susceptible to Lewis base attack with formation of complexes of the general formula $Cu(thpmtH_2)_2(base)X$. In a typical preparation, 0.5 mmol of $Cu(thpmtH)_2X$ was dissolved in 5 cm^3 of chloroform. Subsequently, 0.5 mmol of the appropriate ligand (PPh_3, $AsPh_3$, diphenyl-*p*-tolylphosphine, PPh_2(*p*-tol), tricyclohexylphosphine, Pcy_3) dissolved in 4–5 cm^3 of methanol were added and the solution stirred at ambient temperature for about 1 hour. By allowing the solvent to evaporate slowly at room temperature, white microcrystalline products were isolated.

IR spectra of the products are indicative of the formation of the expected products, since they comprise overlapping of the bands attributed to the reactants; in the electronic spectra, the bands of the Lewis bases introduced are also observed. Inspection of the ^1H, ^{13}C and where applicable ^{31}P NMR data conclusively prove

Table 4 Summary of the NMR study of $Cu(thpmtH_2)_2Br$, $Cu(thpmtH_2)_2I$ and their reaction products with Lewis bases. Chemical shifts are reported in ppm downfield from internal TMS standard for ^{13}C and from $(NPCl_2)_3$ for ^{31}P. J P-C couplings where observed are reported in Hz and are presented in parentheses.

Ligand L	^{13}C								^{31}P
	thione resonances[a]				L resonances[b]				
X = Br									
PPh_3	18.8	40.0	172.9	134.2(23.1)	133.9(14.9)	128.1(8.7)	129.1		−6.46
$P(p-tol)_3$	19.0	40.2	173.3	130.9(27.1)	133.8(15.4)	129.0(9.6)	139.1	21.3[c]	−7.75
Pcy_3	19.0	40.1	173.0	31.8(14.6)	27.3(11.0)	30.2(3.2)	26.1		14.32
$PPh_2(p-tol)$	18.9	40.0	172.5	133.6(26.6)	134.5(16.0)	128.1(9.3)	130.1	21.3[c]	−5.21
					130.9(14.0)		137.7(8.9)		
X = I									
PPh_3	18.9	40.2	173.0	134.2(24)	134.0(14.3)	128.3(8.9)	129.3		−7.74
$P(p-tol)_3$	18.8	40.1	172.3	130.7(27.8)	133.8(14.6)	128.9(8.2)	139.1	21.2[c]	−8.83
Pcy_3	19.0	40.2	173.1	31.9(14.1)	27.3(10.6)	30.1(3.2)	26.1		12.15
$PPh_2(p-tol)$	18.8	40.1	172.3	133.6(25.4)	134.2(16.2)	128.0(8.4)	130.0	21.2[c]	−7.03
					130.8(14.0)		137.6(8.3)		
$AsPh_3$	19.0	39.9	170.6	139.4	133.6	128.5	126.4		

[a] Thione ligand resonances given in the sequence: methyleno, N-CH_2-, thioketo carbon. [b] Ligand L resonances given in the sequence: C-E(P or As), *ortho*-, *meta*- *para*- carbon. [c] Methyl carbon of the tolylphosphine ligand L. For PPh_2 (*p*-tol) two signals are reported for the carbon atoms which are located at the *ortho*- and *para*- positions in the phenyl and tolyl rings, respectively.

coordination of the Lewis bases to the CuS_2X cores of the initial complexes as can be seen from the summarized results of Table 4.

The solution ^{31}P NMR spectra of the compounds at room temperature present a single resonance signal within a small margin around the value obtained for the free ligands, owing to the small changes in the phosphorus environment upon coordination. In a few instances traces of the corresponding phosphine oxide were detected, as confirmed by the more complicated pattern of ^{13}C NMR shifts and this may be due to the preparation scheme adopted, in which no efforts were made to exclude air and moisture from the reaction medium.

The compounds studied reveal a trend for the phosphorus chemical shift to resonate at higher fields for the iodo compound in accordance with the deshielding effect of the halogens. The differences observed between the members within each group, though small in absolute terms, are indicative of analogous chemical environments in the bromo and iodo complexes respectively, thus providing grounds for assumption of analogous structures.

The shifts of the thione carbon atoms in the ^{13}C NMR spectra are indicative of the ligand complexation by comparison to the corresponding data for the free ligand (see Table 4) and analogous coordination compounds.[14,3c] Of special interest is the high field shift of the thioketo carbon atom by *ca* 5 ppm relative to the resonance observed in the ligand; this shielding is paralleled by a deshielding, of less pronounced magnitude, of the carbon atoms adjacent to the heterocyclic nitrogen (a phenomenon that has been rationalized in terms of reduced polarity of the amido group brought about by steric crowding around the C-N bond). Indeed, in all structures of either $Cu(tclH)_2X$ or $Cu(tclH)_n(EPh_3)_{3-n}X$ the C-S bond seems to partly retain its double bond character, its length varying between 1.66 and 1.71 Å. The adjacent C-N distance lies between 1.29 and 1.31 Å, implying partial delocalization.

SUPPLEMENTARY MATERIAL

Tables of fractional coordinates for hydrogen atoms, isotropic thermal parameters for hydrogen atoms, anisotropic thermal parameters for heavy atoms and observed and calculated structure factors are available from the authors upon request.

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