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Copper(I) complexes with tri-*o*-tolylphosphine and heterocyclic thione ligands. Crystal structures of [(pyrimidine-2-thione)(tri-*o*-tolylphosphine)copper(I) chloride] and [(pyridine-2-thione)(tri-*o*-tolylphosphine)copper(I) iodide]

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Abstract

Copper(I) complexes of the general formula [Cu(totp)(L)X], where X = Cl, I; totp = tri-*ortho*-tolylphosphine; L = pyridine-2-thione (py2SH), pyrimidine-2-thione (pymtH), 1,3-thiazolidine-2-thione (tzdtH), 1-methyl-1,3-imidazole-2-thione (meimtH), benz-1,3-imidazoline-2-thione (bzimtH_2) and quinoline-2-thione (qntH) were prepared and characterized by their IR, UV–Vis and ^{1}H NMR spectroscopic data. The behaviour of the complexes upon photolysis in chloroform solutions has been investigated. The structures of [Cu(totp)(pymtH)Cl] and [Cu(totp)(tzdtH)I] were determined by X-ray diffraction: [Cu(totp)(pymtH)Cl] crystallizes in the trigonal space group $P3$ with $a = 22.433(4)$, $b = 22.433(4)$, $c = 9.526(3)$ Å, $\gamma = 120°$ and $Z = 6$; [Cu(tzdtH)(totp)I] crystallizes in the monoclinic space group $P2_1/n$ with $a = 17.111(2)$, $b = 10.505(1)$, $c = 14.823(1)$ Å, $\beta = 108.30(1)°$, $Z = 4$. In both complexes the coordination around Cu is approximately trigonal planar. Steric protection at the central metal by the three methyl groups neighbouring the donor phosphorus of the phosphine ligand is likely to explain the preferential formation of three-coordinate complexes.

Introduction

There is long standing interest in the preparation and study of Cu(I) complexes with sulfur-containing ligands [1] with the increased awareness of the significance of copper–sulfur interactions in biological systems. A deeper insight into these interactions demands the knowledge of the coordination behaviour of the sulfur donors as well as of the factors which contribute to compound stability.

In our laboratory research has been focused on Cu(I) complexes containing arylphosphines and several heterocyclic thiones as ligands [2]. The presence of two different bulky π-acceptor ligands may allow the study of the influence of each ligand on the coordination geometry of the metal atom. Working on this problem we at first used variations of ring size, along a series of closely related heterocyclic thiones, to induce changes on copper geometry. Our investigations led to the following observations: for monomeric complexes of the type [Cu(PR_3)$_2$(L)X], where X = Cl, Br, I, distortions from the tetrahedral coordination are small and in particular there exist relatively small differences in interatomic distances and bond angles between the complexes formed by different size thione ligands [2a–d]. In dimeric species of the type [Cu(PR_3)(L)X]$_2$, for X = Cl, the exocyclic sulfur atoms of the two thione molecules bridge the metal atoms while the chlorine atoms serve as terminal ligands. For X = I, however, the thione ligands are terminally bonded to copper while the formation of bridges by the iodine atoms is preferred [2e–g]. An explanation for this behaviour could be the hardness of the chlorine and the softness of the iodine base, respectively. Both terminal and

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bridging bonding modes were observed for bromo ligands, [2a, 2h] since bromide lies on the borderline between soft and hard.

Our recent studies have been devoted to the possibility of the phosphine ligand to induce changes in the complex geometry. In the course of these studies it was found that replacement of the triphenylphosphine with tri-*m*-tolyl- or tri-*p*-tolylphosphine does not cause any appreciable structural changes [2e–g], but this fact was not unexpected since the difference in bulkiness between these phosphines is slight.

In contrast, introducing the more bulky tri-*o*-tolylphosphine results in a decrease of the coordination number. In fact, the expected transformation of the coordination geometry of the metal atom from tetrahedral to trigonal planar was observed in the case of [Cu(totp)(tzdtH)Br) [3]. In order to ascertain these arguments we report in this paper the preparation and characterization of novel three-coordinate copper(I) complexes derived from copper(I) chloride and iodide. In addition we describe the X-ray structures of [Cu(totp)(pymtH)Cl] and [Cu(totp)(py2SH)I].

Experimental

Materials and instruments

CuCl, CuI and $P(o\text{-}CH_3C_6H_5)_3$ were purchased from Merck and used as received. All thiones (Merck or Aldrich) used in this work were recrystallized from hot ethanol, while the solvents were of reagent grade and were used without further purification. $[Cu(totp)Cl]_n$ and $[Cu(totp)I]_n$ were prepared by heating equimolar quantities of CuCl or CuI and totp at 50–70 °C in acetonitrile, for about 30 min [2e].

IR, electronic and NMR spectra, conductivities, melting points, magnetic susceptibility measurements and elemental analyses of carbon, nitrogen and hydrogen were performed as described previously [2e]. For the photolyses an Hg lamp manufactured by Sylvania was used. Quantum yields were measured in 1 cm quartz cells using a high pressure HBO 200W/4 Osram lamp, a 2 cm water filter and interference of a monochromator manufactured by Applied Photophysics. All the photochemical work was carried out in the dark.

Preparation of the complexes

The complexes of the formula [Cu(totp)(L)X] (X = Cl, I), were prepared according to the following general procedure. A solution of 0.4 mmol of the appropriate thione in 20 ml of methanol was added to a solution of 0.1 mmol of $[Cu(totp)X]_n$ and an excess totp in 20 ml acetonitrile and the resulting solution was moderately heated for 30 min. Slow evaporation of the solvent at room temperature gave a microcrystalline solid, which was filtered off and dried *in vacuo*.

All prepared complexes and some physical properties as well as their elemental analysis are given in Table 1.

Crystal structure determination

Intensities were collected, at room temperature, on a CAD4 diffractometer (Cu Kα radiation, graphite monochromator) in the ω–2θ scan mode ($\theta \leqslant 70°$). Lorentz and polarization corrections were applied. Only reflections with $I \geqslant 3\sigma(I)$ were retained for the solution of the structure using the SDP software package [4]. Refined parameters were calculated [5] by using anisotropic thermal parameters for non-hydrogen atoms and isotropic factors for all hydrogen atoms. Cell dimensions together with other experimental conditions and residual factors are listed in Table 2. Positional parameters of non-hydrogen atoms are given in Tables 3 and 4. Main bond distances and angles are given in Tables 5 and 6. See also ‘Supplementary material’.

Results and discussion

The reaction of $[Cu(totp)X]_n$ (totp = tri-*o*-tolylphosphine, X = Cl, I) with heterocyclic thiones (L) yields complexes formulated as [Cu(totp)(L)X] on the basis of spectroscopic and analytical data (Table 1). All the complexes are soluble in chloroform, acetone, methanol, ethanol and acetonitrile and exist as microcrystalline, colored air- and moisture-stable solids at room temperature. They are monomeric and non-conducting in chloroform or acetone solutions. As would be expected for d^{10} species, room temperature magnetic susceptibility measurements of the complexes are consistent with the diamagnetic nature of the metal ion Cu(I).

Spectra and photolysis

The IR spectra of the new complexes show the usual four ‘thioamide’ bands [6] in the regions ~1510, 1320, 1000 and 750 cm^{-1} as well as the absence of ν(SH) bands around 2500 cm^{-1}. Further, all the metal-free ligands exhibit absorbances in the 3160–3200 cm^{-1} region corresponding to the N–H stretch; a split of this band at *c.* 3180 cm^{-1} is observed. The directions of the shifts in the position of all bands in the spectra are the same, indicating that the binding pattern in all the complexes must be similar.

The UV–Vis spectra of the complexes in chloroform solutions are dominated by one main broad band in the region 260–300 nm with two or three peaks accompanied by another one at 370–400 nm in the case of conjugated heterocyclic thiones. The higher energy band may be assigned to intraligand transitions of the phosphine and thione ligands, since the spectrum of

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

	Complex	Φ_i300*	Colour	Melting point (°C)	Elemental analysis: found(calc.) (%)		
					C	H	N
1	[Cu(totp)(py2SH)Cl]	0.089	bright yellow	127	61.23(60.69)	5.03(5.09)	2.87(2.72)
2	[Cu(totp)(py2SH)I]	0.093	bright yellow	124	52.36(51.53)	4.48(4.32)	2.37(2.31)
3	[Cu(totp)(pymtH)Cl]	0.058	yellow	125	58.27(58.24)	4.55(4.88)	5.65(5.43)
4	[Cu(totp)(pymtH)I]	0.074	yellow	117	49.15(49.47)	4.16(4.15)	4.42(4.61)
5	[Cu(totp)(tztdH)Cl]	0.094	pale yellow	145	54.95(55.16)	5.04(5.01)	2.63(2.68)
6	[Cu(totp)(tztdH)I]	0.025	pale yellow	132	46.62(46.94)	4.23(4.26)	2.22(2.28)
7	[Cu(totp)(meimtH)Cl]	0.086	white	150	57.89(58.06)	5.15(5.26)	5.53(5.41)
8	[Cu(totp)(meimtH)I]	0.036	white	137	50.06(49.30)	4.41(4.47)	4.42(4.60)
9	[Cu(totp)(bzimtH2)Cl]	0.261	white	147	60.78(60.75)	4.55(4.22)	5.04(5.08)
10	[Cu(totp)(bzimtH2)I]	0.116	white	145	52.28(52.14)	3.91(4.91)	4.62(4.35)
11	[Cu(totp)(qntH)Cl]	0.031	red	129	63.88(63.82)	5.01(4.99)	2.42(2.48)
12	[Cu(totp)(qntH)I]	0.036	red	121	53.97(54.92)	4.08(4.30)	1.92(2.13)

Φ_i^{300*} = quantum yields of *i* complex irradiated at 300 nm.

TABLE 2. Details of data collection and structure refinement

Compound	1	2
Formula	$C_{25}H_{24}ClN_2PSCu$	$C_{25}H_{26}INPSCu$
Formula weight	514.5	606.0
a (Å)	22.433(4)	17.111(2)
b (Å)	22.433(4)	10.505(1)
c (Å)	9.526(3)	14.823(1)
β (°)		108.30(1)
γ (°)	120	
V (Å^3)	4152	2529.8
Z	6	4
D_{calc} (Mg m^{-3})	1.23	1.591
D_{meas} (Mg m^{-3})	1.25	1.57
Space group	$P\bar{3}$	$P2_1/n$
Radiation	Cu Kα (λ = 1.54178 Å)	Cu Kα (λ = 1.54178 Å)
Total reflections	4884	4778
Significant reflections ($I > 3\sigma(I)$)	2900	3867
Refined parameters	360	361
R, R_w, *GOF*	0.058, 0.063, 0.85	0.071, 0.083, 1.33
Max. residual density (e Å^{-3})	1	1

the free phosphine consists of two bands at 249 and 279 nm, while these of the free thione ligands show absorptions in the region 280–305 nm.

Room temperature irradiation of the complexes in chloroform at $\lambda_{exit} = 300$ nm causes the decomposition of the complexes within minutes, without evolution of new bands. The decomposition of the complexes yields two photoproducts, as we can estimate according to Coleman's method [7] (Fig. 1). In accordance to our earlier observations in analogous mixed-ligand complexes there is no difference in the decomposition mechanism of the complexes, on the grounds of the lability of the phosphine ligand in solution [2e, 8, 9]. Quantum yields for these complexes have been determined at room temperature and are reported in Table 1.

TABLE 3. Atom coordinates ($\times 10^4$) for [Cu(totp)(pymtH)Cl]

Atom	*x*	*x*	*z*
Cu	2285.6(4)	3703.7(4)	1730.0(4)
Cl	1590(1)	3004(1)	−33(2)
S	1775.6(9)	3531(1)	3804(2)
P	3399.0(8)	4317.3(8)	1127(2)
C(1)	939(3)	2867(4)	3710(8)
N(2)	585(3)	2584(4)	4878(7)
C(3)	−73(5)	2108(5)	4740(10)
C(4)	−426(5)	1879(5)	3500(10)
C(5)	−26(4)	2168(5)	2300(10)
N(6)	632(3)	2642(3)	2454(6)
C(7)	3505(3)	4150(3)	−711(7)
C(8)	3149(3)	4268(4)	−1784(7)
C(9)	2716(5)	4601(5)	−1520(10)
C(10)	3199(4)	4085(4)	−3151(7)
C(11)	3594(4)	3791(4)	−3473(8)
C(12)	3954(4)	3683(4)	−2445(9)
C(13)	3914(3)	3862(3)	−1051(7)
C(14)	3879(3)	5267(3)	1263(7)
C(15)	3826(3)	5588(3)	2460(7)
C(16)	3439(4)	5202(4)	3758(8)
C(17)	4184(4)	6306(4)	2509(9)
C(18)	4570(4)	6688(4)	1408(9)
C(19)	4636(4)	6364(4)	193(8)
C(20)	4292(3)	5663(3)	163(7)
C(21)	3930(3)	4055(3)	2126(6)
C(22)	3687(3)	3362(3)	2415(7)
C(23)	2993(4)	2796(4)	1887(9)
C(24)	4090(4)	3179(4)	3220(8)
C(25)	4705(5)	3666(5)	3760(9)
C(26)	4963(4)	4363(5)	3471(8)
C(27)	4570(4)	4554(4)	2660(7)

Quantum yields are exchange reaction constants for the following equilibrium

$$[Cu(PR_3)(L)X]_n \rightleftharpoons [Cu(L)X]_n + nPR_3$$

where $n = 1$ or 2; X = Cl, I; L = thione

TABLE 4. Atom coordinates (×10^4) for [Cu(totp)(py2SH)I]

Atom	x	y	z
I	5918.1(4)	2021.5(6)	5121.0(4)
Cu	5344.8(5)	788.7(9)	3559.9(6)
P	6187.3(8)	−608(1)	3149.8(9)
S	4161.4(9)	1435(2)	2483(1)
C(1)	3731(3)	2702(6)	2864(4)
C(2)	2965(4)	3210(7)	2322(5)
C(3)	2628(4)	4216(7)	2686(6)
C(4)	3026(5)	4721(7)	3562(7)
C(5)	3757(5)	4239(7)	4070(6)
N	4089(3)	3270(5)	3704(4)
C(6)	7264(3)	−423(5)	3901(4)
C(7)	7478(4)	−639(6)	4884(4)
C(8)	8287(4)	−371(8)	5435(5)
C(9)	8865(4)	83(7)	5047(6)
C(10)	8660(4)	265(7)	4076(6)
C(11)	7854(4)	34(6)	3506(5)
C(12)	6900(4)	−1200(7)	5365(5)
C(13)	6003(3)	−2338(5)	3162(4)
C(14)	6657(4)	−3176(6)	3538(5)
C(15)	6520(4)	−4463(6)	3586(5)
C(16)	5745(5)	−4957(6)	3251(5)
C(17)	5086(4)	−4147(6)	2860(5)
C(18)	5195(4)	−2826(5)	2792(4)
C(19)	4461(5)	−2022(8)	2341(7)
C(20)	6224(4)	−330(6)	1942(4)
C(21)	6215(5)	−1358(6)	1354(5)
C(22)	6201(6)	−1169(8)	414(5)
C(23)	6179(5)	45(9)	58(5)
C(24)	6178(4)	1081(7)	631(5)
C(25)	6202(4)	917(6)	1584(4)
C(26)	6254(6)	2084(6)	2176(7)

TABLE 5. Interatomic distances (Å) and angles (°)[a] for [Cu(totp)(pymtH)Cl]

Distances			
Cu–Cl	2.293(2)	C(10)–C(11)	1.38(2)
Cu–P	2.241(2)	C(11)–C(12)	1.37(1)
Cu–S	2.221(2)	C(12)–C(13)	1.40(1)
P–C(7)	1.831(7)	C(14)–C(15)	1.38(1)
P–C(14)	1.850(6)	C(14)–C(20)	1.39(1)
P–C(21)	1.835(8)	C(15)–C(16)	1.51(1)
S–C(1)	1.718(6)	C(15)–C(17)	1.40(1)
C(1)–N(2)	1.33(1)	C(17)–C(18)	1.36(1)
C1–N(6)	1.35(1)	C(18)–C(19)	1.41(1)
N(2)–C(3)	1.33(1)	C(19)–C(20)	1.36(1)
C(3)–C(4)	1.37(1)	C(21)–C(22)	1.39(1)
C(4)–C(5)	1.40(1)	C(21)–C(27)	1.40(1)
C(5)–N(6)	1.328(9)	C(22)–C(23)	1.52(1)
C(7)–C(8)	1.40(1)	C(22)–C(24)	1.39(1)
C(7)–C(13)	1.40(1)	C(24)–C(25)	1.36(1)
C(8)–C(9)	1.51(2)	C(25)–C(26)	1.40(1)
C(8)–C(10)	1.39(1)	C(26)–C(27)	1.39(1)
Angles			
P–Cu–S	130.9(1)	C(8)–C(7)–C(13)	119.1(6)
P–Cu–Cl	113.5(2)	C(7)–C(8)–C(9)	122.6(7)
Cl–Cu–S	114.7(1)	C(7)–C(8)–C(10)	119.3(9)
Cu–P–C(7)	109.8(2)	C(9)–C(8)–C(10)	118.0(8)
Cu–P–C(14)	121.1(3)	C(8)–C(10)–C(11)	121.2(8)
Cu–P–C(21)	111.9(2)	C(10)–C(11)–C(12)	120.3(8)
C(7)–P–C(14)	104.0(3)	C(11)–C(12)–C(13)	119.9(9)
C(7)–P–C(21)	105.0(3)	C(7)–C(13)–C(12)	120.1(7)
C(14)–P–C(21)	103.6(3)	C(15)–C(14)–C(20)	119.5(6)
Cu–S–C(1)	110.4(3)	C(14)–C(15)–C(16)	123.4(6)
P–C(7)–C(8)	121.0(6)	C(14)–C(15)–C(17)	118.6(6)
P–C(7)–C(13)	119.9(5)	C(16)–C(15)–C(17)	117.9(7)
P–C(14)–C(15)	120.3(4)	C(15)–C(17)–C(18)	121.3(8)
P–C(14)–C(20)	120.1(5)	C(17)–C(18)–C(19)	120.4(7)
P–C(21)–C(22)	120.3(4)	C(18)–C(19)–C(20)	117.8(7)
P–C(21)–C(27)	120.1(6)	C(14)–C(20)–C(19)	122.4(7)
S–C(1)–N(2)	120.2(6)	C(22)–C(21)–C(27)	119.5(7)
S–C(1)–N(6)	120.3(5)	C(21)–C(22)–C(23)	122.1(7)
N(2)–C(1)–N(6)	119.5(5)	C(21)–C(22)–C(24)	119.2(6)
C(1)–N(2)–C(3)	117.5(7)	C(23)–C(22)–C(24)	118.7(7)
N(2)–C(3)–C(4)	126.0(8)	C(22)–C(24)–C(25)	121.2(8)
C(3)–C(4)–C(5)	114.6(7)	C(24)–C(25)–C(26)	121.2(1)
C(4)–C(5)–N(6)	118.6(8)	C(25)–C(26)–C(27)	118.8(7)
C(1)–N(6)–C(5)	123.8(7)	C(21)–C(27)–C(26)	120.6(7)

[a]e.s.d.s given in parentheses.

and depend on both pK_a and steric properties of the phosphine ligands. A quantitative measure of this dependence can be established by comparing quantum yields with the phosphine cone angles [10] which are clearly correlated not only to electronic properties but to the steric size of the phosphines as well. In Table 7 are given quantum yields and cone angles for trigonal monomeric and tetrahedral dimeric complexes, determined by the positional parameters of phosphine, hydrogens and copper atoms. Figure 2 shows the dependence between cone angles and quantum yields of the above complexes.

Description of the structures

The molecular structures of compounds **1** and **2** together with the atom numbering schemes are shown in Figs. 3 and 4, respectively. Selected bond lengths and angles are given in Tables 5 and 6. In both structures, with pyrimidine-2-thione and pyridine-2-thione, the compounds consist of well separated monomeric [Cu(totp)(pymtH)Cl] and [Cu(totp)(py2SH)I] units, respectively. In both complexes the central copper atom is three coordinated to one thione ligand, bonded in a unidentate mode through the exocyclic sulfur atom, one phosphorous atom belonging to the tri-*o*-tolylphosphine molecule and one halogen atom. The coordination geometry about the copper atom is best described as slightly distorted trigonal planar.

The most significant difference in the bonding between the compounds **1**, **2** and the analogous bromine complex [Cu(totp)(tzdtH)Br] with thiazolidine-2-thione as thione ligand [3] is found in the Cu–S interaction; the values in **1** and **2** (2.221(2) and 2.254(2) Å, respectively), although not statistically different from Cu–S bonds in complexes containing similar coordination [11], are clearly shorter than in [Cu(totp)(tzdtH)Br] (2.290(1) Å). Another feature is that the Cu–P bond lengths in

TABLE 6. Interatomic distances (Å) and angles (°)^a for [Cu(totp)(py2SH)I]

Distances			
Cu–I	2.563(1)	C(8)–C(9)	1.38(1)
Cu–P	2.269(2)	C(9)–C(10)	1.38(1)
Cu–S	2.254(2)	C(10)–C(11)	1.39(1)
P–C(6)	1.840(5)	C(13)–C(14)	1.39(1)
P–C(13)	1.846(5)	C(13)–C(18)	1.41(1)
P–C(20)	1.834(6)	C(14)–C(15)	1.38(1)
S–C(1)	1.701(7)	C(15)–C(16)	1.36(1)
C(1)–C(2)	1.409(8)	C(16)–C(17)	1.39(1)
C(1)–N	1.344(7)	C(17)–C(18)	1.41(1)
C(2)–C(3)	1.39(1)	C(18)–C(19)	1.49(1)
C(3)–C(4)	1.37(1)	C(20)–C(21)	1.39(1)
C(4)–C(5)	1.34(1)	C(20)–C(25)	1.41(1)
C(5)–N	1.36(1)	C(21)–C(22)	1.40(1)
C(6)–C(7)	1.41(1)	C(22)–C(23)	1.38(1)
C(6)–C(11)	1.40(1)	C(23)–C(24)	1.38(1)
C(7)–C(8)	1.40(1)	C(24)–C(25)	1.41(1)
C(7)–C(12)	1.51(1)	C(25)–C(26)	1.49(1)
Angles			
P–Cu–S	120.66(7)	C(7)–C(6)–C(11)	120.1(5)
P–Cu–I	118.2(1)	C(6)–C(7)–C(8)	117.5(6)
I–Cu–S	119.4(1)	C(6)–C(7)–C(12)	123.8(5)
Cu–P–C(6)	111.7(2)	C(8)–C(7)–C(12)	118.6(6)
Cu–P–C(13)	120.6(2)	C(7)–C(8)–C(9)	122.4(6)
Cu–P–C(20)	112.2(2)	C(8)–C(9)–C(10)	120.1(6)
C(6)–P–C(13)	103.9(2)	C(9)–C(10)–C(11)	119.1(7)
C(6)–P–C(20)	103.9(3)	C(6)–C(11)–C(10)	120.7(6)
C(13)–P–C(20)	103.0(3)	C(14)–C(13)–C(18)	119.3(5)
Cu–S–C(1)	112.8(2)	C(13)–C(14)–C(15)	120.9(5)
P–C(6)–C(7)	119.8(5)	C(14)–C(15)–C(16)	121.0(6)
P–C(6)–C(11)	119.9(4)	C(15)–C(16)–C(17)	119.2(6)
P–C(13)–C(14)	120.5(4)	C(16)–C(17)–C(18)	121.8(6)
P–C(13)–C(18)	120.2(4)	C(13)–C(18)–C(17)	117.5(5)
P–C(20)–C(21)	119.5(5)	C(13)–C(18)–C(19)	123.6(5)
P–C(20)–C(25)	120.7.(5)	C(17)–C(18)–C(19)	118.7(6)
S–C(1)–C(2)	121.9(5)	C(21)–C(20)–C(25)	119.6(6)
S–C(1)–N	122.5(4)	C(20)–C(21)–C(22)	120.6(6)
C(2)–C(1)–N	115.6(6)	C(21)–C(22)–C(23)	120.2(7)
C(1)–C(2)–C(3)	119.4(6)	C(22)–C(23)–C(24)	120.0(7)
C(2)–C(3)–C(4)	121.2(6)	C(23)–C(24)–C(25)	120.9(7)
C(3)–C(4)–C(5)	119.0(8)	C(20)–C(25)–C(24)	118.7(6)
C(4)–C(5)–N	119.4(7)	C(20)–C(25)–C(26)	123.4(6)
C(1)–N–C(5)	125.3(5)	C(24)–C(25)–C(26)	117.8(7)

^{a}e.s.d.s given in parentheses.

these three complexes increase almost exactly with the increasing size of the halogen atom.

The Cu–Cl bond length in **1** (2.293(2) Å) is comparable with the value of 2.317(3) Å found in [Cu(tpt)$_2$Cl] (tpt = tetrahydro-1*H*-pyrimidine-2-thione) [12] but somewhat longer than the corresponding bond-distance in [Cu(diditme)$_2$Cl] (diditme = *N*,*N*′-dimethylimidazolidine-2-thione) (2.233(3) Å) [13]. The Cu–I bond length in **2** (2.563(1) Å) is comparable with the value of 2.590(1) found in Cu(tclH)$_2$I (tclH = 2-thioxohexamethyleneimine) [14].

In the nearly trigonal planar CuSPCl and CuSPI cores the values of the angles are very close to the idealized value of 120°. As expected, the largest angle in **1** arises between the two most bulky ligands; the same effect in **2** is practically negligible, in all probability because of the size of the iodine atom. In general, the best rearrangement of the ligands around the copper atom is exclusively influenced by steric interactions.

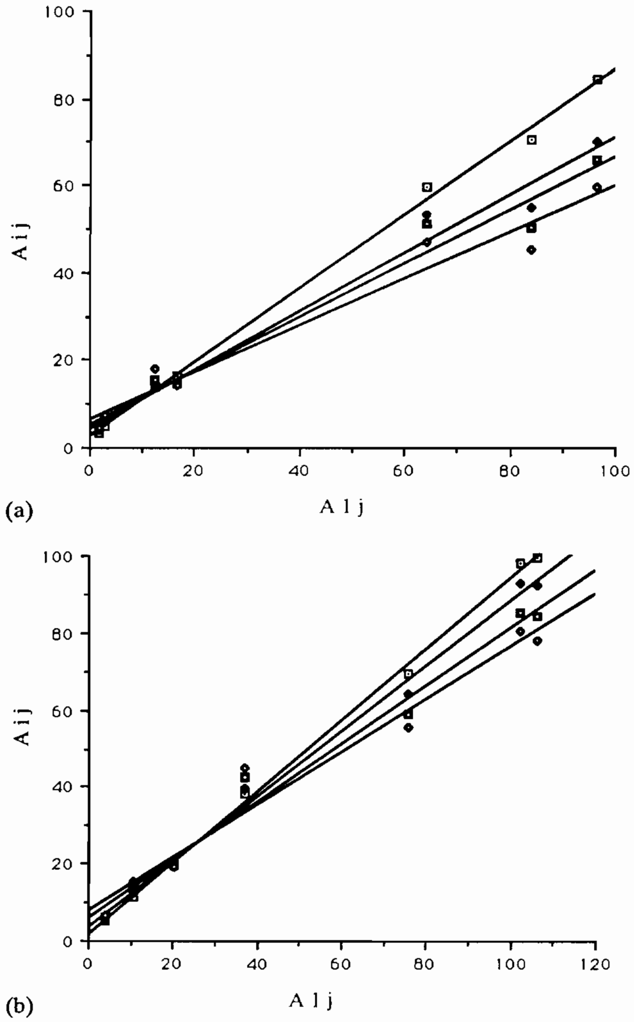

Fig. 1. Plots for graphical matrix method test for two species in the [Cu(totp)(tzdtH)I] (a) and [Cu(totp)(tzdtH)Cl] (b) systems during irradiation in chloroform solutions. A_{ij} is the absorbance of the *j*th (400–200 nm) wavelength after *i* seconds (0, 30, 60, 90, 120) of irradiation with *UV* radiation.

TABLE 7. Cone angles and quantum yields for dimeric and monomeric complexes

Complexes	Cone angle	Φ	Reference
[Cu(tptp)(pmtH)Cl]$_2$	138.7	0.019	2e
[Cu(tmtp)(py2SH)I]$_2$	137.3	0.116	2g
[Cu(tmtp)(bzimtH)Cl]$_2$	149.1	0.014	2h
[Cu(totp)(pmtH)Cl]	181.0	0.058	
[Cu(totp)(tzdH))Br]	164.7	0.030	3
[Cu(totp)(py2SH)I]	176.9	0.058	

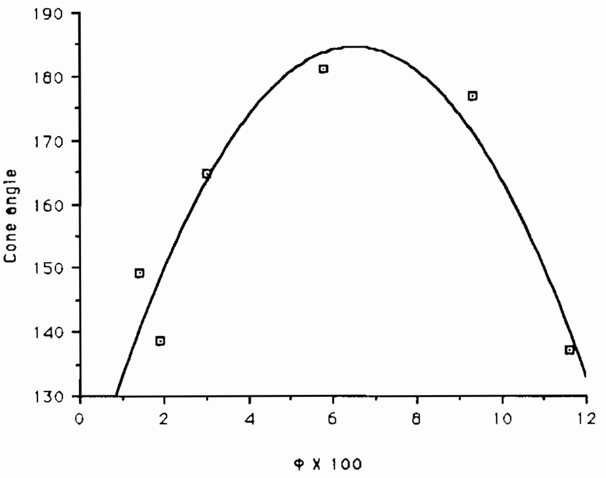

Fig. 2. Correlation between cone angles and quantum yields for some complexes.

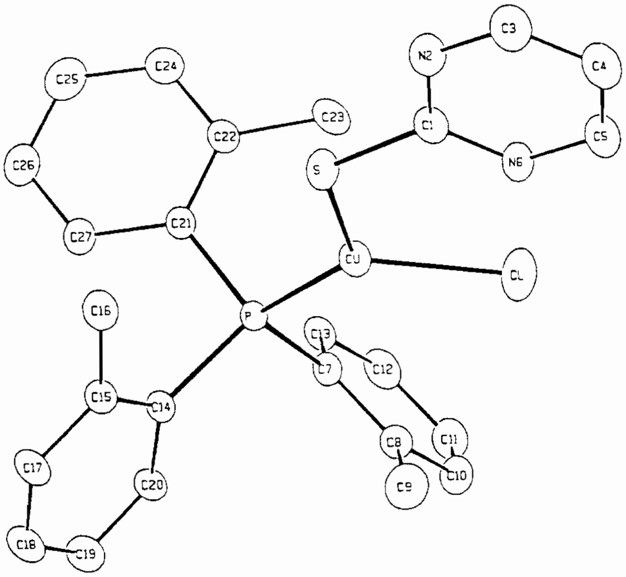

Fig. 3. A view of the complex [Cu(totp)(tzdtH)Cl].

Thus the presence of intramolecular X···H–N hydrogen bonds (Cl···N=3.029(6) and N–H···Cl=155.5(6)° in **1**; I···N=3.435(4) and N–H···Br=160.3(1)° in **2**) appears to be of minor importance.

The displacement of the copper atom from the SPCl plane in **1** and SPI plane in **2** (0.120(4) and 0.175(2) Å, respectively) is comparable to that observed in [Cu(PPh$_3$)(pptu)Cl] (where pptu=1-phenyl-3-(2-pyridyl)-2-thioureal)) which has the copper located 0.14 Å from the SPCl plane [15]. The corresponding value in [Cu(totp)(tzdtH)Br] is significantly greater (0.263 Å). Within the py2SH, pymtH and totp ligands, the bond distances and angles are not altered significantly upon coordination.

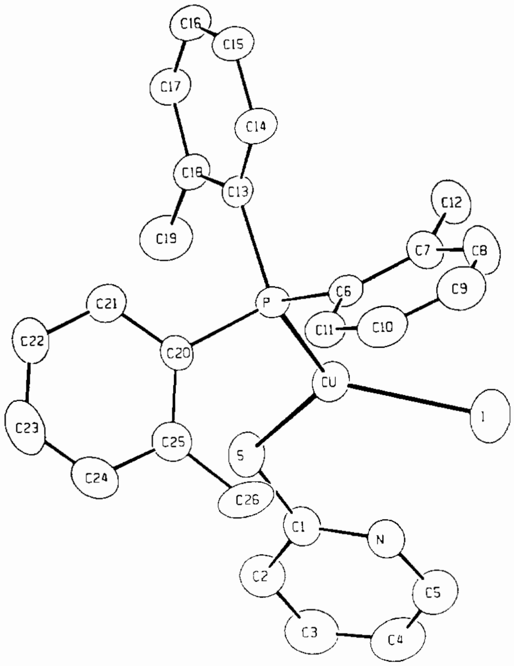

Fig. 4. A view of the complex [Cu(totp)(tzdtH)I].

Supplementary material

List of observed and calculated structure factors, of positional and anisotropic thermal parameters of the H atoms and the positional and equivalent thermal parameters of the phenyl-carbon atoms are available from the authors on request.

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