Inorganica Chimica Acta, 202 (1992) 73–77

Preparation and study of three-coordinate mixed ligand copper(I) compounds. Molecular and crystal structure of (tricyclohexylphosphine)(2-thioxohexamethyleneimine)copper(I) iodide

P. D. Akrivos, G. Kapsomenos, P. Karagiannidis*
Aristotle University of Thessaloniki, General and Inorganic Chemistry Laboratory, P.O.B. 135, GR-540 06 Thessaloniki (Greece)

S. Skoulika** and A. Aubry*
Laboratoire de Crystallographie, UA CNRS No. 809, Université de Nancy I, BP 239, 54506 Vandoeuvre les Nancy Cédex (France)

(Received April 10, 1992; revised June 26, 1992)

Abstract

A group of mixed ligand copper(I) coordination compounds with the saturated heterocyclic thione 2-thioxohexamethyleneimine (ω-thiocaprolactam, tclH) and tricyclohexylphosphine (Pcy_3) is prepared and studied. The concerted steric effects of the two bulky ligands result in the formation of three-coordinate copper(I) complexes. The iodo compound is studied by single crystal X-ray diffraction and is shown to crystallize in the $P2_1/n$ space group. Four monomer units with no apparent close contacts between them are present in the unit cell, the dimensions of which are $a=10.306(2)$, $b=15.937(2)$, $c=16.774(2)$ Å, and $\beta=100.06(1)°$. The compound is trigonal planar with the Cu–S, Cu–P and Cu–I bonds equal to 2.243(2), 2.241(2) and 2.564(1) Å, respectively. A computational study is also carried out aiming at the understanding of the factors influencing planar or pyramidal conformation in three-coordinate CuLL′L″ compounds.

Introduction

Copper coordination chemistry provides a connection between spectroscopists, biochemists and inorganic coordination chemists, who have contributed much [1] to the understanding of the metal's involvement in processes related to their topics of activity. The structural preferences of the metal ion *in vivo* are motivated by its environment and affect to a significant extent its activity. Little effort has been placed, though, on the investigation of cuprous model compounds, due perhaps to their instability in aqueous media, relative to their extensively studied cupric counterparts. The main scope of our research has been the monitoring of structural changes in the copper(I) coordination sphere, with respect to the stereoelectronic effects induced by the coordinated ligands. Heterocyclic thiones with an α-nitrogen heteroatom provide nice models for strained thioamide groups, while triarylphosphines and more recently arsines [2] were used to complete the coordination sphere of the studied complexes. In most of the studied compounds, only minor changes were observed in the Cu_2S_2 core of the dimers obtained [3], owing perhaps to the fact that small aromatic thione molecules do not affect drastically the interligand repulsions within it. The relative softness of the ligands seems to be important, since in the case of iodine compounds the core observed was a Cu_2I_2 one [4]. The steric effect of the coordinated phosphines is also important, leading to loosely bound dimers, actually monomer trigonal planar copper(I) compounds in the case of the extremely bulky tri-*o*-tolylphosphine [5]. In view of these observations it seemed appropriate to attempt a more detailed investigation of the thione steric effect as well; for this purpose, ω-thiocaprolactam, combining lack of resonance effect and substantial conformational non-rigidity was chosen. The ligand has already been found to form monomer compounds, even in the case of $Cu(tclH)_2X$ complexes [6]. It was therefore interesting to investigate the concerted effects of this ligand and a substantially bulky phosphine, like tricyclohexylphosphine, avoiding as much as possible the electronic factors involved in the formation of the compounds studied so far. The present study, therefore, is devoted to the preparation and study of three compounds of the general formula $[Cu(tclH)(Pcy_3)X]_n$, where X denotes a halogen atom. The crystal and

---

*Authors to whom correspondence should be addressed.

**Permanent address: Department of Chemistry, Physical Chemistry Sector, University of Ioannina, GR-451 10 Ioannina, Greece.

0020-1693/92/$5.00

molecular structure of the iodo compound is reported and discussed in connection with the previously reported ones of tclH with triphenylphosphine.

Experimental

Materials and measurements

All the solvents purchased commercially were of reagent grade. Cuprous salts (Merck) and tricyclohexylphosphine (Aldrich) 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, IR spectra were recorded in KBr discs on a Perkin-Elmer 1430 spectrophotometer, while solution 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 complexes were prepared by a route summarized below. Equimolar amounts (1 mmol in a typical preparation) of the thione and CuX in 20 ml chloroform:acetonitrile 1:1 were heated until a clear pale yellow coloured solution emerged. In the case of the chloro compound, prolonged heating (6 h) was needed. Subsequently a 20 ml chloroform solution of 2 equiv. of the phosphine was added leading to instant decoloration of the solution. Reflux for 15 min was applied, extended to 2 h in the case of the chloro compound. Evaporation at room temperature of the resultant solutions produced white crystals, the elemental analyses of which were in accordance with their formulation as $[Cu(Pcy_3)(tclH)C]_n$.

Anal. Calc. for $Cu(tclH)(Pcy_3)Cl$: C, 54.63; H, 9.13; N, 2.88. Found: C, 54.81; H, 9.27; N, 2.93%. Calc. for $Cu(tclH)(Pcy_3)Br$: C, 52.16; H, 8.02; N, 2.53. Found: C, 51.89; H, 8.09; N, 2.48%. Calc. for $Cu(tclH)(Pcy_3)I$: C, 48.07; H, 7.39; N, 2.34. Found: C, 48.63; H. 7.30; N, 2.19%.

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

Solution of the structure

Intensities were collected at room temperature, on a Enraf-Nonius 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 [8].

Cell dimensions along with other experimental conditions and residual factors are listed in Table 1. Fractional atomic coordinates and equivalent thermal factos are given in Table 2. See also 'Supplementary material'.

TABLE 1. Summary of crystal and intensity collection data

Formula	$CuC_{24}H_{44}INPS$
Formula weight	600.1
Space group	$P2_1/n$
a (Å)	10.306(2)
b (Å)	15.937(2)
c (Å)	16.774(2)
β (°)	100.06(1)
V (Å^3)	2712.6
Z	4
D_{meas} (Mg m^{-3})	1.46
D_{calc} (Mg m^{-3})	1.469
Radiation	Mo Kα
Reflections collected	4760
Reflections with $I > \sigma(I)$	3444
No. refined parameters	395
R	0.050
R_w	0.043
$(\Delta\varrho)_{max}$ (e Å^{-3})	1 (close to I)

Results and discussion

Spectral characterization

The IR spectral data of the compounds studied reveal the presence of S-bonded thiocaprolactam as well as the tricyclohexylphosphine in the coordination sphere of copper; characteristic are the NH– band at *c.* 2300 and the strong multiple band at 2900–3000 cm^{-1} due to the presence of several CH_2– groups. Electronic spectra of the complexes were recorded in methanol, chloroform and toluene. Small shifts were observed with respect to the spectra of the free thione; no comparison was attempted relative to tricyclohexyl phosphine since no band for it appears in the region down to 200 nm.

The complicated pattern observed in the ^{1}H NMR spectra originates from the several $-CH_2-$ groups present in both ligands and corresponds roughly to the superposition of the spectra of the thione and the phosphine ligands; a fact far from unexpected owing to the well-known small effect of Cu(I) upon coordination to these ligands. A small increase of the chemical shift of the imino proton on going from the iodo to the chloro compound is observed, and is in accordance with the expected deshielding effect of the halogen atoms. This also serves as an indication about the

TABLE 2. Positional parameters ($\times 10^4$) of the non-hydrogen atoms and their e.s.d.s

Atom	x	y	z	B (Å^2)^a
I	2093.5(4)	841.5(3)	8453.6(3)	4.41(1)
Cu	1395.9(7)	2155.9(4)	9153(1)	3.75(2)
S	−489(2)	2209(1)	9647(1)	5.02(5)
P	2758(1)	3262.6(9)	9324.7(9)	3.06(3)
N	−912(5)	633(3)	9229(3)	4.3(1)
C1	3673(6)	3308(4)	10380(4)	3.6(1)
C2	4455(6)	2505(4)	10589(4)	4.7(2)
C3	5193(8)	2495(5)	11459(5)	6.2(2)
C4	4280(8)	2639(5)	12048(4)	6.0(2)
C5	3479(9)	3422(6)	11849(5)	7.3(3)
C6	2760(8)	3429(5)	10987(4)	5.8(2)
C7	1904(6)	4279(4)	9176(4)	4.9(2)
C8	2662(7)	5067(4)	9323(5)	5.8(2)
C9	1889(9)	5856(5)	9217(6)	8.1(3)
C10	660(9)	5851(6)	8694(8)	10.1(3)
C11	−81(7)	5065(5)	8556(5)	6.0(2)
C12	698(8)	4294(5)	8574(6)	7.5(2)
C13	4040(6)	3215(4)	8689(4)	4.3(2)
C14	5218(7)	3773(5)	8883(5)	6.2(2)
C15	6237(7)	3567(6)	8354(7)	8.1(3)
C16	5690(10)	3544(7)	7488(7)	9.9(3)
C17	4520(10)	2997(6)	7293(5)	8.3(3)
C18	3478(7)	3172(5)	7796(4)	6.0(2)
C19	−1334(5)	1302(4)	9563(4)	3.7(1)
C20	−2578(7)	1231(5)	9883(5)	5.8(2)
C21	−3776(6)	1009(4)	9241(6)	6.4(2)
C22	−3915(7)	98(5)	9038(5)	6.4(2)
C23	−2813(7)	−244(4)	8640(5)	5.6(2)
C24	−1513(6)	−211(4)	9178(4)	4.6(2)

^{a}The isotropic equivalent displacement parameter B is defined as: $(4/3)[a^2B(1,1)+b^2B(2,2)+c^2B(3,3)+ab(\cos\gamma)B(1,2)+ac(\cos\beta)B(1,3)+bc(\cos\alpha)B(2,3)]$.

similarity of structure between the three compounds; because either strong hydrogen bonding or intermolecular interactions would give rise to a different kind of deshielding.

Description of the structure

The molecular structure of the title compound is shown in Fig. 1, while selected bond lengths and angles are reported in Table 3. The chromophore, composed of one S, one I and one P atom directly coordinated to copper is practically trigonal planar as can be seen from the sum of the angles around copper, which is almost 360°.

The Cu–I bond length (2.564(1) Å) is roughly in the middle of the range defined by 2.490(3) [9] and 2.72(1) [10] Å, while it is a little smaller than the 2.590(1) Å observed in the closely related Cu(tclH)$_2$I [6a] complex and almost identical to the 2.563(1) Å reported for Cu(totp)(py2SH)I [5b], where totp = tris-*o*-tolylphosphine and py2SH = pyridine-2-thione. In view of this evidence, it may be stated that this bond is sensitive to the bulk of the ligands attached to copper rather than to their electronic effect.

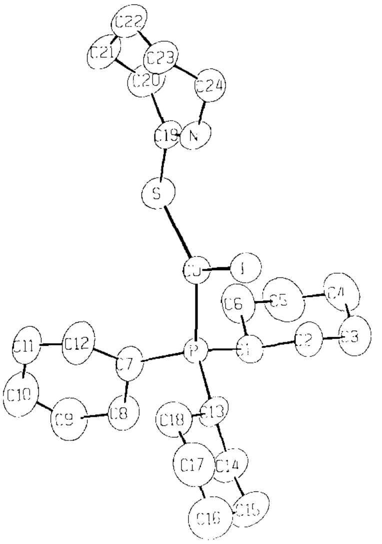

Fig. 1. Molecular structure of the Cu(tclH)(Pcy$_3$)I compound.

TABLE 3. Molecular structure parameters relevant to the local copper, phosphorous and sulfur environments

Bond lengths (Å)			
Cu–P	2.241(2)	C19–N	1.314(8)
Cu–S	2.243(2)	N–C24	1.477(8)
Cu–I	2.564(1)	C19–C20	1.477(10)
P–C1	1.856(6)	C20–C21	1.531(10)
P–C7	1.839(6)	C21–C22	1.493(10)
P–C13	1.839(7)	C22–C23	1.515(11)
S–C19	1.680(6)	C23–C24	1.480(9)
Bond angles (°)			
P–Cu–S	119.1(1)	Cu–P–C1	110.8(2)
P–Cu–I	118.8(1)	Cu–P–C7	113.7(2)
S–Cu–I	122.0(1)	Cu–P–C13	113.0(2)
C19–S–Cu	113.9(2)	C1–P–C7	104.3(3)
C19–N–C24	126.7(5)	C1–P–C13	104.9(3)
C19–C20–C21	114.0(6)	C7–P–C13	109.5(3)

The Cu–S bond seems also to be sensitive to the coordination environment of copper because it differs from the analogous bonds in tetrahedral copper–thiocaprolactam complexes, where it ranges from 2.310(1) to 2.313(4) Å [2]. The observed bond length is 2.243(2) Å and is almost identical to the one observed in Cu(tclH)$_2$I [6a] (2.244(1) Å). It is also near the mean value of the reported Cu–S distances in trigonal copper compounds, which vary from 2.20 to 2.27 Å [11].

Considering now the Cu–P bond, it is somewhat shorter than the corresponding ones in other Cu(I) complexes of tricyclohexyl phosphine, which range from 2.262(1) for Cu(Pcy$_3$)$_2$ClO$_4$ [12a] to 2.29(1) Å for Cu(Pcy$_3$)$_2$NO$_3$ [12b], but it must be noted that in these compounds copper is four-coordinated, since the counteranions are also coordinated to the metal.

The bond angles around copper are close to the ideal trigonal planar conformation, i.e. near 120°, as in Cu(tclH)$_2$I [6]. The conformation of the thione molecule is irregular, the C–C and C–N bond distances lying in the region of the usual single bond lengths. The environment around P is not ideal tetrahedral and the P–C bonds range from 1.839(6) Å to 1.856(6) Å, being roughly equal to the ones observed in other coordination compounds of tricyclohexyl phosphine [12].

Computational study

In view of the several three-coordinated Cu(I) compounds already prepared by us [4–6] and the almost planar environment of the discussed complex, we carried out a series of computations on model mixed ligand copper(I) compounds, where thioformaldehyde was substituted for the thione and trimethylphosphine for the phosphine ligands. All three halogens (i.e. Cl, Br, I) were taken into consideration In the first step, MNDO level calculations [13], were performed making use of a point charge representation of the central copper ion. The Cu–S, Cu–I and Cu–P bond distances were taken as the mean values of the experimentally observed ones and were not allowed to vary; this was the only restriction to the calculations. Both pyramidal and strictly planar compounds were considered; the dihedral angle, φ, formed between the planes defined by Cu, P, X and Cu, S, X, respectively (Fig. 2) was used as a measure of the pyramidalization of the models studied. Of course, a planar model corresponds to φ equal to 180°. The two forms of each model compound were lying quite close in energy, their ΔH_f not differing by more than 1.3 kcal mol^{-1}; nevertheless, the calculations reveal a preference for the planar geometry in the case of chloro and iodo compounds (lowest energy at $\varphi = 180°$), while the pyramidal one ($\varphi = 164°$) was the more stable in the case of the bromo compound.

This observation is in line with the observations so far made in three-coordinate copper(I) complexes; in the bromo compounds the copper atom is always elevated (up to 0.256 Å) from the plane defined by the remaining three atoms of the chromophore. On the other hand the chloro and iodo Cu(I) complexes are usually planar and even when they are pyramidal, the elevation of Cu is not so pronounced, seldom exceeding 0.130 Å. It should be noted, at this point, that the pyramidal form of the iodo models studied were extremely close to planarity ($\varphi = 176°$), while the bromo ones revealed the most pronounced pyramidalization of all ($\varphi = 164°$).

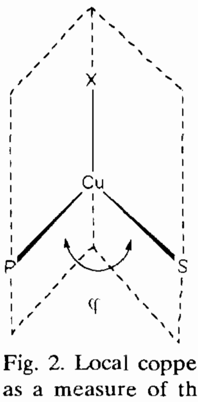

Fig. 2. Local copper environment. The dihedral angle φ is used as a measure of the pyramidalization.

Substitution of the thione ligand by a more realistic model, namely by S=C(CH$_3$)NH$_2$, did not alter the above picture, in the sense that the iodo compound is predicted to be more stable in a slightly pyramidal form, quite close in energy to the planar one, while a preference of *c.* 3.5 kcal mol^{-1} is evinced for planar conformation of the chloro compound; on the other hand the bromo model does not differ by more than 0.1 kcal mol^{-1} in its two conformations; nevertheless, its pyramidalization is apparently the largest of all three complexes. Calculations at the AM1 level of approximation [14] revealed the same differences as above, the only apparent difference being that the preferred conformations gain in relative stability (differences in ΔH_f of *c.* 5–6 kcal mol^{-1}).

A more detailed study, which might add to the nature of the intramolecular interactions leading to the above observed and calculated structural conformations includes preparation and study of analogous compounds and explicit computations at more sophisticated level, a project that we have initiated [15].

Supplementary material

All the crystallographic material (atomic coordinates, bond lengths, bond angles and equivalent thermal factors) is available from the Cambridge Crystallographic Data Center.

References

1 (a) K. B. Karlin and J. Zubieta (eds), *Copper Coordination Chemistry Biochemical and Inorganic Perspectives,* Adenine, New York, 1983; (b) M. Patch, H. Choi, D. R. Chapman, R. Bau, V. McKee and C. A. Reed, *Inorg. Chem., 29* (1990) 110.

2 (a) P. Karagiannidis, P. D. Akrivos, D. Mentzafos and A. Terzis, *Inorg. Chim. Acta, 181* (1991) 263; (b) P. Karagiannidis, P. D. Akrivos, A. Aubry and S. Skoulika, *Inorg. Chim. Acta, 188* (1991) 79.

3 P. Karagiannidis, S. K. Hadjikakou, P. Aslanidis and A. Hountas, *Inorg. Chim. Acta, 178* (1990) 27.

4 S. K. Hadjikakou, P. Aslanidis P. Karagiannidis, A. Hountas and A. Terzis, *Inorg. Chim. Acta, 184* (1991) 161.

5 (a) S. K. Hadjikakou, P. Aslanidis, P. Karagiannidis, D. Mentzafos and A. Terzis, *Inorg. Chim. Acta, 186* (1991) 199; (b) S. K. Hadjikakou, P. Aslanidis, P. Karagiannidis, A. Aubry and S. Skoulika, *Inorg. Chim. Acta, 193* (1992) 129.

6 (a) P. Karagiannidis, P. D. Akrivos, D. Mentzafos and A. Terzis, *Inorg. Chim. Acta, 180* (1991) 93; (b) P. Karagiannidis, P. D. Akrivos, B. Kojic-Prodic and M. Luic, *J. Coord. Chem.*, in press.

7 *SDP Package.* Enraf-Nonius, Delft, Netherlands, 1977.

8 G. Sheldrick, *SHELX76*, University of Göttingen, Germany, 1976.

9 M. Asplund and S. Jagner, *Acta Chem. Scand., Ser. A, 38* (1984) 297.

10 P. C. Healy, C. Pakawachai and A. H. White, *J. Chem. Soc., Dalton Trans.,* (1983) 1917.

11 (a) E. G. Dance, *Aust. J. Chem., 31* (1978) 2195; (b) C. D. Gamer, J. R. Nicholson and W. Clegg, *Inorg. Chem., 23* (1984) 2148.

12 (a) R. J. Resitvo, A. Costin, G. Ferguson and A. J. Carty, *Can. J. Chem., 53* (1975) 1949; (b) W. A. Anderson, A. J. Carty, G. J. Palenik and G. Schneider, *Can. J. Chem., 49* (1971) 761.

13 M. J. S. Dewar and W. Thiel, *J. Am. Chem. Soc., 99* (1978) 4988.

14 M. J. S. Dewar, E. G. Zoebisch, E. F. Healy and J. J. P. Stewart, *J. Am. Chem. Soc., 107* (1985) 3902.

15 P. Karagiannidis, P. D. Akrivos and G. Kapsomenos, work in progress.