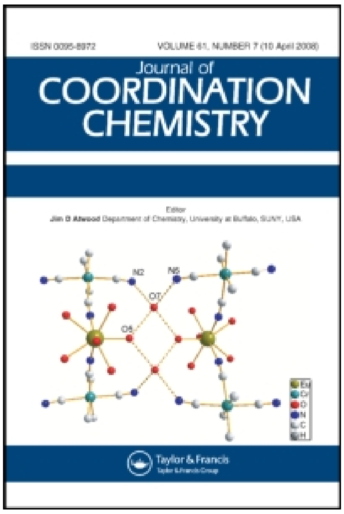
This article was downloaded by:
On: *23 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

Preparation, Crystal and Molecular Structure of (Triphenylphosphino)-Bis(2-Thioxohexamethyleneimine)Copper(I) Chloride

Biserka Kojic-Prodic[a]; Marija Luic[a]; Petros Karagiannidis[b]; Pericles Akrivos[b]; Stefan Stoyanov[c]
[a] Department of Materials Research and Electronics, Rudjer Boskovic Institute, Zagreb, Croatia, Yugoslavia [b] Aristotelian University of Thessaloniki, General and Inorganic Chemistry Laboratory, Thessaloniki, Greece [c] Department of Chemistry, University of Sofia, Sofia, Bulgaria

To cite this Article Kojic-Prodic, Biserka , Luic, Marija , Karagiannidis, Petros , Akrivos, Pericles and Stoyanov, Stefan(1992) 'Preparation, Crystal and Molecular Structure of (Triphenylphosphino)- Bis(2-Thioxohexamethyleneimine)Copper(I) Chloride', Journal of Coordination Chemistry, 25: 1, 21 — 28

To link to this Article: DOI: 10.1080/00958979209407899

URL: http://dx.doi.org/10.1080/00958979209407899

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

J. Coord. Chem. 1992, Vol. 25, pp. 21–28
Reprints available directly from the publisher
Photocopying permitted by license only

© 1992 Gordon and Breach Science Publishers S.A.
Printed in Great Britain

PREPARATION, CRYSTAL AND MOLECULAR STRUCTURE OF (TRIPHENYLPHOSPHINO)-BIS(2-THIOXOHEXAMETHYLENEIMINE)COPPER(I) CHLORIDE

BISERKA KOJIC-PRODIC, MARIJA LUIC

Rudjer Boskovic Institute, Department of Materials Research and Electronics, 41000 Zagreb, P.O. Box 1016, Croatia, Yugoslavia

PETROS KARAGIANNIDIS,* PERICLES AKRIVOS

Aristotelian University of Thessaloniki, General and Inorganic Chemistry Laboratory, P.O. Box 135, GR-540 06 Thessaloniki, Greece

and STEFAN STOYANOV

University of Sofia, Department of Chemistry, 1 I. Antonov. Ave., 1126 Sofia, Bulgaria

(Received January 28, 1991)

Downloaded At: 18:01 23 January 2011

The mixed ligand complex (triphenylphosphino)bis(2-thioxohexamethyleneimine)copper(I) chloride, $Cu(tclH)_2(PPh_3)Cl$, has been synthesized and studied by spectroscopic methods and single crystal X-ray diffraction. It crystallizes in space group $P\bar{1}$, with $a = 11.110(1)$, $b = 11.880(1)$, $c = 11.994(1)$ Å, $\alpha = 98.86(1)$, $\beta = 90.92(1)$, $\gamma = 96.71(1)^\circ$ and $Z = 2$. The final R and R_w values are 0.065 and 0.071, respectively, for 3393 reflections with $I > 3\sigma(I)$. The copper atom is four coordinate, in a distorted tetrahedral environment. The mean value of the two Cu–S bonds is 2.334(3) Å and the Cu–Cl bond distance is 2.394(2) Å; the interbond angles around copper vary from 96.53(9) to 117.28(8)°. A chair conformation of one of the seven membered thione rings is stabilized by an intramolecular hydrogen bond N1–H...Cl (3.192(7) Å); the second analogous ring is disordered, exhibiting transitions from twisted to distorted chair conformations.

Keywords: Copper(I), thiocaprolactam, X-ray structure

INTRODUCTION

The evergrowing interest in Cu(I) complexes with ligands possessing N and S donor atoms is related to the presence of such moieties in a number of potential enzymic sites.[1] Along this line of research, we have investigated a number of mixed ligand Cu(I) complexes with phosphines and thiones as ligands. More recently, the particular features of compounds emerging from complexation of 2-thioxohexamethyleneimine (ω-thiocaprolactam, tclH), to Cu(I) halides[2] has prompted us to investigate further the stereochemical preferences of Cu(I) sites where tclH is already coordinated. The bulky thione is expected to induce low coordination numbers and all the available evidence for its Cu,[2] Rh and Pt[3] complexes indicate its coordination exclusively through sulfur.

---

* Author for correspondence.

In the present study, we report the synthesis, crystal structure determination and reactivity of the complex $Cu(tclH)_2(PPh_3)Cl$.

EXPERIMENTAL

Materials and measurements

All the solvents used were of reagent grade. Copper chloride (Merck) was used as obtained, while ω-thiocaprolactam (Aldrich) was recrystallized from hot methanol prior to use. 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 1430 spectrophotometer, while the electronic spectra were obtained by means of a Shimadzu 160A spectrophotometer. A Bruker AW-80 spectrometer and internal TMS standard were used for recording ^1H NMR spectra.

Preparation of the complex

To a solution of 1 mmol of freshly prepared $Cu(tclH)_2Cl$ in 20 cm^3 methanol, a solution of PPh_3 in 20 cm^3 chloroform was added and the resulting solution was refluxed for 2 h. The resulting clear solution was then filtered and allowed to stand at room temperature for two days, at the end of which a microcrystalline product had deposited. Its elemental analysis was satisfactory for $Cu(tclH)_2(PPh_3)Cl$; in order to obtain crystals appropriate for the subsequent crystal structure determination, an initially obtained sample was redissolved in hot methanol and recrystallized by slow evaporation at room temperature of a methanol : toluene (1 : 1) mixture.

Solution of the structure

The crystallographic data and details of data collection and refinement are listed in Table I. Reference reflections showed a loss of intensity at about 4.4% during data collection. An adequate correction to the intensities was applied. Data reduction was performed by the Enraf-Nonius SDP/VAX package,[4] Lorenz and polarization effects were corrected. Absorption correction was by a Ψ-scan of the $2\,\bar{2}\,\bar{3}$, $1\,\bar{1}\,\bar{2}$, $1\,\bar{2}\,\bar{3}$, $2\,\bar{2}\,\bar{4}$, $2\,\bar{3}\,\bar{4}$, $2\,\bar{3}\,\bar{5}$, and $4\,\bar{4}\,\bar{6}$ reflections; minimum transmission was 0.93.

The structure was solved by direct methods (SHELX-86[5]). Copper scattering factors and anomalous dispersion values were taken from International Tables for Crystallography.[6] For other atoms, the scattering factors were those included in SHELX-76.[7] A difference Fourier map revealed disorder of the N2 → C30 thione ring. Two different locations for N2, C29 and C30 atoms were observed. According to the height of peaks for these atoms in a difference map, occupancy factors were assigned (0.75 and 0.25). It appears that the distorted chair conformation prevails over the twisted one. The results of least-squares refinement agreed with these values for occupancy factors. The structure was refined with a full-matrix least-square procedure. The non-hydrogen atoms were refined anisotropically with exception of N2, N2A, C27, C29, C29A, C30 and C30A, which were treated in the isotropic thermal mode. Hydrogen atom positions were derived on stereochemical grounds and refined under restricted conditions according to the pivot atoms. The N-bonded hydrogen atoms were located by a difference Fourier map and N–H distances adjusted to the theoretical value; hydrogen atoms of the N2 → C30 ring were not found.

Downloaded At: 18:01 23 January 2011

TABLE I
Summary of crystal data.

Formula	$C_{30}H_{37}N_2S_2ClCu$
fw	619.73
a(Å)	11.110(1)
b(Å)	11.880(1)
c(Å)	11.994(1)
α(deg)	98.86(1)
β(deg)	90.92(1)
γ(deg)	96.71(1)
V(Å^3)	1552.7(3)
Z	2
D_{calcd}(Mg.m^{-3})	1.326(1)
Space group	$P\bar{1}$
Crystal dimensions (mm)	0.2 × 0.2 × 0.1
Linear absorption coefficient (cm^{-1})	9.92
F(000)	648
Radiation	Mo Kα· (graphite monochromator)
Temperature (K)	297 ± 1
θ range (deg) for cell detn.	9, 14
No of reflections for cell detn.	25
θmin, θmax	2, 25
ω/2θ scan (°)	$\Delta\omega = 0.80 + 0.35\tan\theta$
$h\,k\,l$ limits	$-13 \rightarrow 13,\ -14 \rightarrow 14,\ -14 \rightarrow 14$
Reflections collected	10895
Reflections with $I > 3\sigma(I)$	3393
No of refined parameters	311
Weighting scheme $\Sigma w[\lvert F_o\rvert - \lvert F_c\rvert]^2$	$1/w = \sigma^2(F_o) + 0.0012F_o^2$
R, R_w	0.065, 0.071
(Δ/σ)max	0.264 (C17, x)

Interatomic distances, bond and torsion angles and analysis of the ring puckering were calculated by a program for analysis of molecular geometry.[8] Drawings were prepared by the PLUTO program as implemented in the SDP package.[4] Calculations were carried out on the MICROVAX II of the X-Ray Laboratory of the Rudjer Boskovic Institute, Zagreb, Yugoslavia. Final atomic coordinates for the heavy atoms and selected bond lengths and angles are given in Tables II and III.

RESULTS AND DISCUSSION

Characterization of the complex

The main scope of the work reported was to extend our recent studies[2] on the coordination mode expressed by ω-thiocaprolactam towards Cu(I) halides in the presence of triaryl phosphine ligands, as well as the reactivity of these compounds. In every case the relatively ionic character of the Cu–Cl bond makes it neccessary to apply extensive and prolonged heating in order to afford the desired compound.

Downloaded At: 18:01 23 January 2011

Nevertheless, the initially prepared complex Cu(tclH)$_2$Cl, which revealed spectral and physical properties in accordance with those already quoted,[9] proved unstable in solution, especially in the presence of light. Indeed, after two days in dilute chloroform solution a dark yellow microcrystalline product deposited and spectral

TABLE II
Final atomic coordinates and equivalent isotropic thermal parameters (× 10^4).

	x/a	*y/b*	*z/c*	U_{eq} (Å^2)
Cu	0.2747(1)	0.3420(1)	0.2158(1)	569(3)
P	0.2593(1)	0.1750(1)	0.2814(1)	460(5)
Cl	0.4693(2)	0.4445(2)	0.2750(2)	709(7)
S1	0.2431(2)	0.3300(2)	0.0216(2)	790(8)
S2	0.1278(2)	0.4639(2)	0.2693(2)	909(9)
C1	0.2388(5)	0.1888(5)	0.4332(5)	472(21)
C2	0.1624(6)	0.1120(6)	0.4843(6)	585(24)
C3	0.1521(7)	0.1282(7)	0.6003(6)	673(29)
C4	0.2176(8)	0.2205(7)	0.6675(6)	674(30)
C5	0.2973(8)	0.2946(7)	0.6177(6)	754(34)
C6	0.3064(7)	0.2785(6)	0.5011(6)	645(27)
C7	0.1291(6)	0.0747(5)	0.2211(5)	455(22)
C8	0.1288(7)	−0.0422(6)	0.1923(6)	626(27)
C9	0.0278(8)	−0.1119(7)	0.1432(7)	771(32)
C10	−0.0748(8)	−0.0649(7)	0.1226(6)	728(31)
C11	−0.0775(7)	0.0515(7)	0.1521(7)	786(33)
C12	0.0252(7)	0.1198(6)	0.1996(7)	669(30)
C13	0.3874(6)	0.0901(5)	0.2604(5)	489(22)
C14	0.4558(6)	0.1001(6)	0.1678(6)	587(25)
C15	0.5522(7)	0.0380(7)	0.1469(7)	734(32)
C16	0.5820(7)	−0.0349(8)	0.2191(7)	788(31)
C17	0.5124(8)	−0.0457(8)	0.3126(8)	832(38)
C18	0.4173(7)	0.0184(7)	0.3334(7)	699(31)
C19	0.2901(7)	0.4637(6)	−0.0090(6)	642(28)
C20	0.2379(9)	0.5030(8)	−0.1097(7)	842(34)
C21	0.1640(10)	0.6023(9)	−0.0765(9)	1009(49)
C22	0.2332(10)	0.7184(8)	−0.0448(9)	975(45)
C23	0.3163(10)	0.7297(7)	0.0557(9)	912(40)
C24	0.4151(8)	0.6509(6)	0.0431(8)	772(34)
N1	0.3681(5)	0.5333(5)	0.0579(5)	608(22)
C25	0.1660(0)	0.5600(0)	0.3790(0)	954(39)
C26	0.0800(0)	0.6450(0)	0.4240(0)	1194(54)
C28	0.2090(0)	0.7890(0)	0.5670(0)	2215(114)
N2	0.2705(0)	0.5675(0)	0.4240(0)	1577(58)
N2A	0.2340(0)	0.5370(0)	0.4530(0)	419(45)
C27	0.1599(0)	0.7652(0)	0.4428(0)	2099(79)
C29	0.3292(0)	0.7482(0)	0.5425(0)	1397(60)
C29A	0.3114(0)	0.7211(0)	0.5745(0)	418(53)
C30	0.3105(0)	0.6223(0)	0.5391(0)	2709(155)
C30A	0.2620(0)	0.5990(0)	0.5680(0)	549(65)

[*] The N2→C30 ring is disordered; A denotes the atoms in different locations;
$U_{eq} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* \bar{a}_i \bar{a}_j$

Downloaded At: 18:01 23 January 2011

TABLE III
Selected bond distances (Å) and angles (°) for the complex.

(a) distances		*(b) angles*	
Cu-P	2.234(2)	S1-Cu-S2	96.5(1)
Cu-Cl	2.394(2)	Cl-Cu-S2	107.9(1)
Cu-S1	2.330(3)	Cl-Cu-S1	110.6(1)
Cu-S2	2.339(3)	P-Cu-S2	117.3(1)
P-C1	1.823(6)	P-Cu-S1	115.9(1)
P-C7	1.826(6)	P-Cu-Cl	108.1(1)
P-C13	1.837(7)	Cu-P-C13	117.5(2)
S1-C19	1.709(8)	Cu-P-C7	113.4(2)
S2-C25	1.619(2)	Cu-P-C1	113.8(2)
		C7-P-C13	103.7(3)
		C1-P-C13	103.0(3)
		C1-P-C7	103.8(3)
		Cu-S1-C19	106.0(3)
		Cu-S2-C25	114.6(1)
		P-C1-C6	117.6(5)
		P-C1-C2	124.0(5)
		P-C7-C12	117.2(5)
		P-C7-C8	125.1(5)
		P-C13-C18	123.0(5)
		P-C13-C14	117.8(5)
		S1-C19-N1	120.0(6)
		S1-C19-C20	120.4(6)
		S2-C25-N2A	118.8(1)
		S2-C25-N2	119.5(1)
		S2-C25-C26	120.7(1)

and analytical data confirm its formulation as (CuCl)$_7$(tclH)$_3$. The exceptional stability of the compound with respect to Cu(tclH)$_2$Cl must be attributed to the possible formation of a cubane-like structure probably analogous to those reported for copper(I) and silver(I) tertiary butylthiolates.[10] The IR spectrum of the title complex reveals a split –NH band at *ca* 3180 cm^{-1}, indicative of intramolecular hydrogen bond formation, a phenomenon observed in several analogous compounds.[2] The electronic spectra recorded in chloroform and ethanol reveal two maxima at 288, 245 nm and 278, 221 nm, respectively. They both differ substantially from the spectrum of the thione, thus giving evidence for their MLCT nature. The compound reported proved to be very stable in solution, but reactive upon UV irradiation, a primary report of which has already been communicated.[2b] In the present study, a 6×10^{-5} M solution of the compound was irradiated by a high pressure 200 W/4 Osram lamp at 254 nm. An initial depression of the bands is followed by a shift of the absorption maximum so that an isosbestic point is observed (Fig. 1) at 304 nm, in accord with observations during irradiation by the full spectrum lamp.

Description of the structure

The molecular structure of the title complex is shown in Figure 2. The chromophore consists of two sulfur atoms originating from two tclH molecules, the phosphorus

Downloaded At: 18:01 23 January 2011

Downloaded At: 18:01 23 January 2011

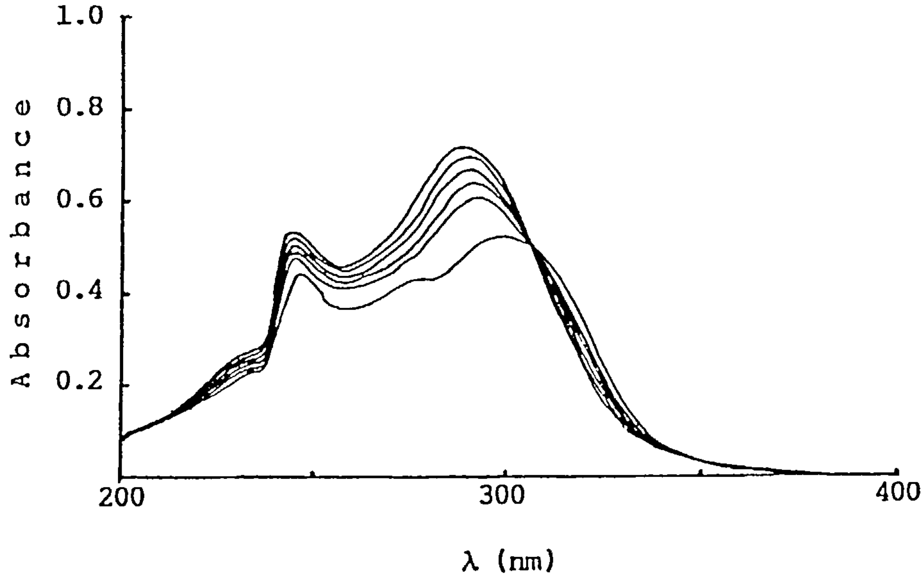


FIGURE 1 Spectral changes during irradiation at 254 nm. Spectra recorded at 0, 5, 10, 15, 20 and 40 min after irradiation.

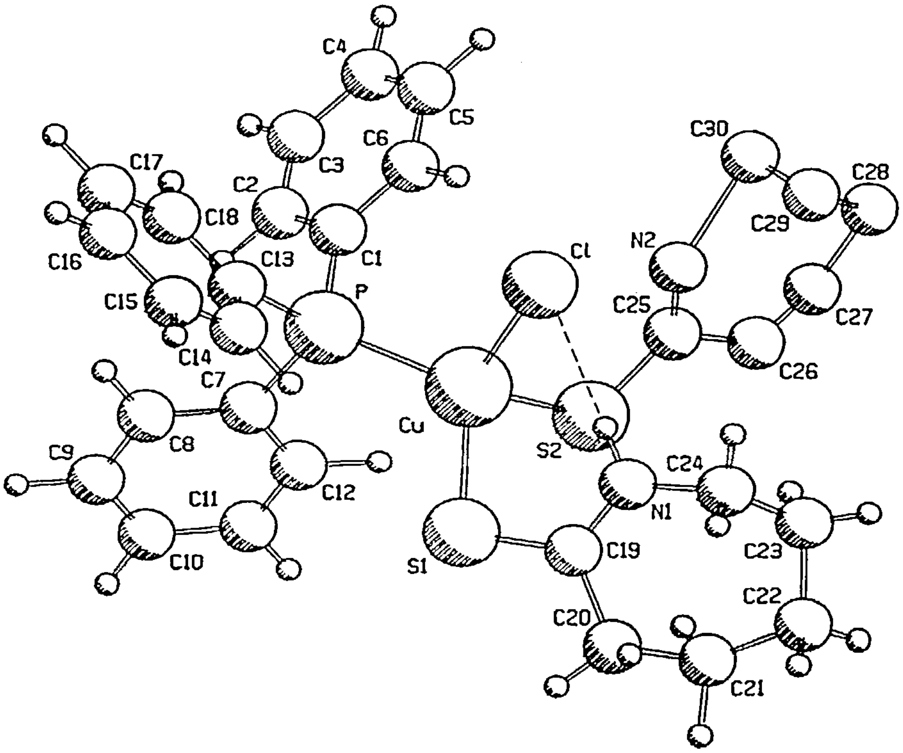


FIGURE 2 PLUTO drawing of the molecule with the atom numbering; the intramolecular hydrogen bond is denoted by a dashed line.

atom of the triphenylphosphine ligand and a chlorine atom, and possesses a distorted tetrahedral arrangement around copper. The dihedral angle between the S1–Cu–S2 and P–Cu–Cl planes is 91.63(7)°.

The Cu–S distances are quite close (2.330(3) and 2.339(3) Å respectively) and are about equal to the sum of copper and sulfur covalent bond radii,[11] 2.39 Å. They are longer than the corresponding bonds in $[Cu(tclH)_2(AsPh_3)Br]$,[2b] which were found to be 2.310(1) and 2.315(1) Å, and the terminal Cu–S distance of 2.326(3) Å observed in $[Cu(py2SH)_3]_2Cl_2$,[12] where py2SH is pyridine-2-thione. A substantial elongation is however detected with respect to the monomeric compound $Cu(tclH)_2I$,[2a] where the two Cu–S bonds are 2.238(1) and 2.250(1) Å, respectively.

Close analogy was observed between the Cu–P bond length of 2.234(2) Å in the title complex and the value of 2.183(2) Å in $[Cu(Pcyc_3)Cl]_2$[13] and is attributed to the strong overlap between copper and phosphorus, facilitated by the near orthogonality (*vide supra*) of the phosphine ligand towards the thiones. This bond length lies near the lower extreme of Cu–P bond lengths, which have been observed to vary from 2.23 to 2.31 Å.[14]

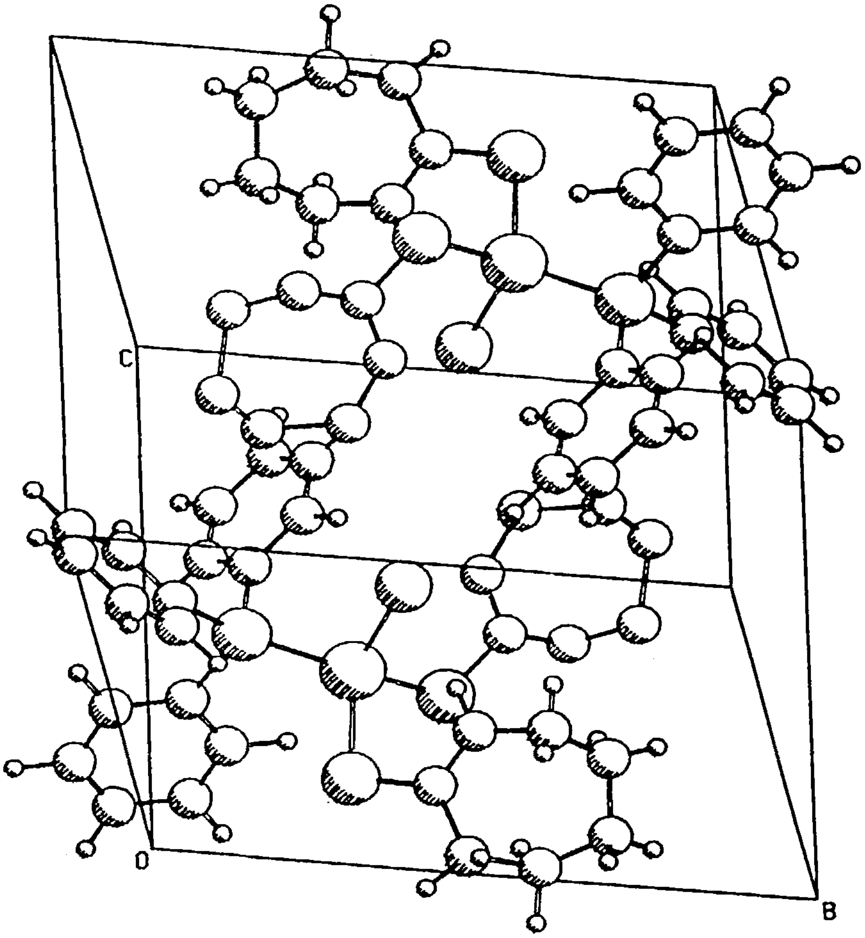


FIGURE 3 Molecular packing in the crystal.

Downloaded At: 18:01 23 January 2011

The Cu–Cl bond (2.394(2) Å) is rather long relative to the value of 2.34 Å assigned to tetrahedral Cu(I),[11] a fact attributed to the competition of Cl and P for the same central metal ion orbital. It is, though, quite similar to that observed for several monomeric $Cu(PPh_3)_2(L)Cl$ compounds, where L is dithiooxamide,[15] 2-thiopyrazole-1,2-dicarboxamide[16] or pyridine-2-thione.[17]

The tclH ligands exhibit differences in their internal geometry. One of them (N1→C24 ring) exhibits a chair conformation,[18] the other one is disordered flopping between twisted and distorted chair conformation. The ring with the well defined chair conformation is involved in an intramolecular hydrogen bond N1–H...Cl, 3.192(7) Å [H...Cl 2.189(3) Å, < N1–H...Cl 178.5(3)°]. Molecular packing is supported by the H...S interaction between molecules related by $\bar{x}$, $\bar{y}$, $\bar{z}$, and $\bar{x}$, $\bar{y}+1$, $\bar{z}$ operations involving a hydrogen atom of a benzene ring [H10...S1, 2.69(1) Å]. These contacts are shorter than the mean H...S van der Waals distance[11] of 3.05 Å.

SUPPLEMENTARY DATA

Full lists of bond lengths and angles, hydrogen atom positions, temperature factors, and observed and calculated structure factors are available from P.K.

Downloaded At: 18:01 23 January 2011

REFERENCES

1. T.N. Sorrell and D.L. Jameson, *J. Am. Chem. Soc.*, **104**, 2053 (1982).
2. (a) P. Karagiannidis, P.D. Akrivos, D. Mentzafos and A. Hountas, *Inorg. Chim. Acta*, 180, 93 (1991); (b) P. Karagiannidis, P.D. Akrivos, D. Mentzafos and A. Terzis, *ibid*, 181, 263 (1991).
3. (a) R.S. Lifsey, M.Y. Charan, L.K. Chau, M.Q. Ashan, K.M. Kadish and J.L. Bear, *Inorg. Chem.*, 26, 577 (1987); (b) P. Dini, J.C.J. Bart, E. Santoro, G. Cum and N. Giordano, *Inorg. Chim. Acta*, **17**, 97 (1976); (c) P. Castan and J.P. Laurent, *ibid*, **51**, 103 (1981); (d) J.M. Bret and P. Castan, *ibid*, **54**, L237 (1981).
4. B.A. Frenz, The Enraf-Nonius CAD4-SDP, in "Computing in Crystallography", Edited by H. Schenk, R. Olthof-Hazenkamp, H. Van Koningveld and G. C. Bassi, (Delft University Press, Holland, 1978), pp. 64–71.
5. G.M. Sheldrick, SHELX86, in "Crystallographic Computing 3", Eds. G.M. Sheldrick, C. Krueger and R. Goddard, (Oxford Univesity Press, Oxford, 1985).
6. *International Tables for X-ray Crystallography*, Vol. IV, Eds. J.A. Ibers and W.C. Hamilton, (Kynoch Press, Birmingham, 1973).
7. G.M. Sheldrick, "SHELX77 Program for Structure Determination", (University of Cambridge, Cambridge, 1983).
8. M. Nardelli, *Comput. Chem.*, **7**, 95 (1983).
9. (a) P. Castan and J.P. Laurent, *C.R. Hebr. Seances Acad. Sci., Ser. C*, **286**, 577 (1978); C.A. **89**: 122,221f; (b) P. Castan, *Trans. Metal Chem.*, **6**, 14 (1981).
10. I.G. Dance, L.J. Fitzpatrick, D.C. Craig and M.L. Scudder, *Inorg. Chem.*, **28**, 1853 (1989).
11. L. Pauling, "The Nature of the Chemical Bond", (Cornell University Press, Ithaca, 1960).
12. (a) G.A. Stergioudis, S.C. Kokkou, P.J. Rentzeperis and P. Karagiannidis, *Acta Cryst.*, **C43**, 1685 (1987); (b) E.C. Constable and P.R. Raithby, *J. Chem. Soc., Dalton Trans.*, 2281 (1987).
13. R.G. Goel and A.L. Beauchamp, *Inorg. Chem.*, **22**, 395 (1983).
14. M.R. Churchill and K.L. Kalra, *Inorg. Chem.*, **13**, 1065 (1974).
15. M.B. Ferrari, G.G. Fava, C. Pelizzi and P. Tarasconi, *Inorg. Chim. Acta*, **98**, L49 (1985).
16. K.K. Pandey, M. Noltenmeyer, G.M. Sheldrick and R. Saheb, *Z. Naturforsch*, **B39**, 586 (1984).
17. (a) T.S. Lobana, P.K. Bhatia and F.R.T. Tiekink, *J. Chem. Soc., Dalton Trans.*, 749 (1989); (b) P. Karagiannidis, personal communication; unpublished results on the same complex prepared in acetone.
18. D. Cremer and J.A. Pople, *J. Am. Chem. Soc.*, **97**, 1354 (1975).