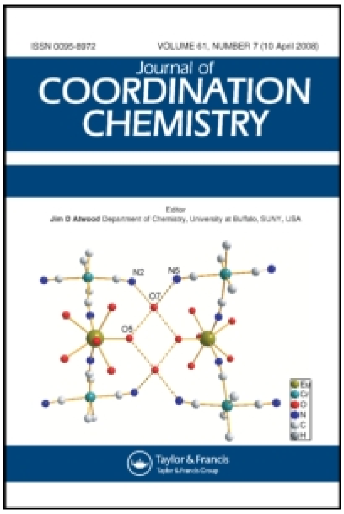

Journal of Coordination Chemistry

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

Copper-sulfur interactions: synthesis and structure of a trigonal planar copper(I) complex with bis(diphenylthiophosphinyl)methane, [CuI(dppmS$_2$)]·MeCN

Tarlok S. Lobana[a]; Gagandeep Singh[a]; Takanori Nishioka[b]
[a] Department of Chemistry, Guru Nanak Dev University, Amritsar - 143 005, India [b] Department of Materials Science, Graduate School of Science, Osaka City University, Sugimoto, Sumiyoshi-ku, Osaka 558-8585, Japan

To cite this Article Lobana, Tarlok S. , Singh, Gagandeep and Nishioka, Takanori(2004) 'Copper-sulfur interactions: synthesis and structure of a trigonal planar copper(I) complex with bis(diphenylthiophosphinyl)methane, [CuI(dppmS$_2$)]·MeCN', Journal of Coordination Chemistry, 57: 11, 955 — 960

To link to this Article: DOI: 10.1080/00958970412331272368

URL: http://dx.doi.org/10.1080/00958970412331272368

J. Coord. Chem., Vol. 57, No. 11, 20 July 2004, pp. 955–960

COPPER-SULFUR INTERACTIONS: SYNTHESIS AND STRUCTURE OF A TRIGONAL PLANAR COPPER(I) COMPLEX WITH BIS(DIPHENYLTHIOPHOSPHINYL)METHANE, [CuI(dppmS$_2$)]·MeCN

TARLOK S. LOBANA[a,]*, GAGANDEEP SINGH[a] and TAKANORI NISHIOKA[b]

[a]*Department of Chemistry, Guru Nanak Dev University, Amritsar – 143 005, India;*
[b]*Department of Materials Science, Graduate School of Science, Osaka City University, Sugimoto, Sumiyoshi-ku, Osaka 558-8585, Japan*

(Received 1 March 2004)

Reaction of copper(I) iodide with 1,1-bis(diphenylthiophosphinyl)methane (dppmS$_2$) in a 1:1 mol ratio in acetonitrile yielded a complex of stoichiometry [CuI(dppmS$_2$)]·CH$_3$CN (**1**) whose X-ray structure determination has shown that the geometry around the copper center is nearly trigonal planar. Acetonitrile is nonbonded. Copper–sulfur bond distances are 2.2470(7) and 2.2591(7) Å, while the copper–iodide bond distance is 2.4937(5) Å. IR and NMR spectroscopic data also show the formation of copper–sulfur bonds. Lack of bridging by iodide led to the formation of a three-coordinate copper complex, as against the expected iodo-bridged dimeric complex with chelating dppmS$_2$.

Keywords: Copper; Phosphine; Trigonal planar; X-ray structure

INTRODUCTION

Tertiaryphosphine sulfides and selenides have been the focus of several investigations for a variety of reasons, ranging from bonding and structural studies of their metal complexes to their extraction and catalytic properties [1–16]. Tertiaryphosphine sulfides generally form monomeric, dimeric or, in a few cases, trimeric complexes [1,2].

Copper(I) has a strong tendency to form covalent bonds with anionic or neutral ligands, and make close Cu···Cu contacts (less than twice the van der Waals radius of Cu, 2.80 Å [17]). This leads to the formation of oligomers and polymers of diverse coordination networks [16]. Reported complexes of copper(I) with monotertiary phosphine sulfides are [Cu(Me$_3$PS)$_3$](ClO$_4$) **2** [18], (Cu(μ-SPMe$_3$)Cl)$_3$ (trimer) **3** [19],

---

*Corresponding author. E-mail: tarlokslobana@yahoo.co.in

ISSN 0095-8972 print: ISSN 1029-0389 online © 2004 Taylor & Francis Ltd
DOI: 10.1080/00958970412331272368

[$Cu(Ph_3PS)NS_3$] **4** [20], $Cu_2(Ph_3PS)_2(\mu\text{-}I)_2(CH_3CN)_2$ (dimer) **5** [9]; those with ditertiary-phosphine sulfides are [$CuCl(dppmS_2)$]Me_2CO **6** [21], [$2(CuCl(dppmS_2)) \cdot (CuCl(dppmS_2))_2$] **3** [22], and $(CuCl(dppeS_2))_2$ **8** [23] [$dppmS_2 = Ph_2P(S)–CH_2–P(S)Ph_2$; $dppeS_2 = Ph_2P(S)–CH_2–CH_2–P(S)Ph_2$]. In Complex **8**, the chloride ligand bridges two Cu atoms and $dppeS_2$ is an *S*,*S*-bridging bidentate; in Complex **6**, $dppmS_2$ is an *S*,*S*-chelating bidentate and in Complex **7** it is *S*,*S*-chelating in $CuCl(dppmS_2)$ and *S*,*S*-chelating-*cum*-*S*-bridging in $(CuCl(dppmS_2))_2$.

In this paper, we report the synthesis and structure of a three-coordinate complex of $dppmS_2$ with copper(I) iodide, [$Cu(dppmS_2)I$]$\cdot CH_3CN$ **1**. Interestingly, iodide acts as a bridging ligand in Complex **5**, but is terminal in the three-coordinate Complex **1**; this is an uncommon bonding mode.

EXPERIMENTAL

Materials and Techniques

Oxidation of $Ph_2P–CH_2–PPh_2$, using powdered sulfur (1:1 mol ratio) in benzene formed $Ph_2P(S)–CH_2–P(S)Ph_2$ ($dppmS_2$) [1,2]. Copper(I) iodide was prepared by the reduction of $CuSO_4 \cdot 5H_2O$ with SO_2 in the presence of NaI in water [24]. Bis(diphenylphosphino)methane was purchased from Sigma Aldrich Ltd. C, H, N elemental analyses were measured by the Analytical Center of Osaka City University, Japan. IR spectra were recorded (KBr pellets) on Pye Unicam SP3-300 or FTIR-NICOLET 320 FTIR spectrophotometers in the 4000–200 cm^{-1} range. Proton NMR spectra of the complex were recorded in MeCN-d_3 using TMS as internal reference on a JEOL 300 MHz spectrometer at the Osaka City University, Japan.

Synthesis of the Complex

To a solution of CuI (0.021 g, 0.111 mmol) in dry acetonitrile (10 cm^3) was added a solution of $dppmS_2$ (0.050 g, 0.111 mmol) in dichloromethane (10 cm^3). The mixture was stirred for 4 h and filtered. The product was obtained on slow evaporation of the filtrate at room temperature. Yield, 70%; m.p. 130–132°C. Anal. Calcd. for $C_{27}H_{25}CuINP_2S_2$(%): C, 47.7; H, 3.68, N, 2.06. Found: C, 47.9; H, 3.61; N, 2.00. Crystals were grown from an acetonitrile–dichloromethane mixture at room temperature. Main IR peaks (cm^{-1}): ν(P–S), 500 (s); ν(P–C), 1110 (s); Ligand peaks: ν(P–S), 530 (s), ν(P–C), 1130 (s).

X-ray Crystallography

A colorless, prismatic crystal of **1** was mounted on a glass fiber and used for data collection. Intensity data were collected on a Rigaku/MSC Mercury CCD diffractometer with graphite-monochromated Mo Kα radiation ($\lambda = 0.71070$ Å) at 193 K. Data were processed using the crystal clear program (Rigaku). A symmetry-related absorption correction using the program REQAB (transmission factors 0.61–0.80) was applied. Data were also corrected for Lorentz and polarization effects. All calculations were performed using SGI INDY. The structure was solved by direct methods using the program SIR 92 and refined by full-matrix least-squares techniques against F^2 using

TABLE I Crystal data for **1**

Empirical formula	$C_{27}H_{25}CuINP_2S_2$	Z	4
Formula weight (M)	680.02	D_c ($Mg\,m^{-3}$)	1.626
Temperature (K)	193	Absorption coefficient (mm^{-1})	2.181
Crystal system	monoclinic	F(000)	1352
Space group	$P2_{1/n}$	Crystal size (mm^3)	$0.10 \times 0.20 \times 0.20$
Unit cell dimensions		2θ range for data collection (°)	6.1–55.0
a (Å)	13.461 (2)	Reflections collected	27 094
b (Å)	12.670(2)	Unique reflections	6191 ($R_{int} = 0.035$)
c (Å)	17.067(2)	Goodness-of-fit on F^2	1.01
β (°)	107.423(3)	Reflections with [$I > 2\sigma(I)$]	4680
		R indices (R, wR)	0.030, 0.047
V ($Å^3$)	2777.2(6)	Largest difference peak and hole ($e\,Å^{-3}$)	0.79 and -0.77

the SHELXL-97 and teXsan programs [25–28]. Nonhydrogen atoms were refined anisotropically. Some hydrogen atoms were refined isotropically; the remainder were included in fixed positions. Crystallographic data are summarized in Table I.

RESULTS AND DISCUSSION

Synthesis and Spectroscopy

The reaction of copper(I) iodide with $dppmS_2$ in $MeCN–CH_2Cl_2$ formed colorless crystals whose analysis supported the composition $[CuI(dppmS_2)] \cdot MeCN$ **1**. In order to understand whether the complex was dimeric or monomeric, suitable crystals of **1** were studied by X-ray crystallography (*vide infra*). The I.R. spectrum of the compound shows that $dppmS_2$ coordinates to Cu via both S atoms [ν(P=S), 500; $dppmS_2$, 530 cm^{-1}]. ^1H NMR spectra of **1** show a triplet for $–CH_2–$ protons at $\delta = 4.2$ ppm ($J = 13.0$ Hz) and this is at low-field relative to free $dppmS_2$ [$\delta = 3.9$ ppm; $J = 13.4$ Hz] [22]. Similarly, phenyl protons, which show signals at $\delta = 7.59$ ppm (2H, o-C_6H_5) and 7.22 ppm (4H, m- and p-C_6H_5) [22], shift to low field and give separate signals for the three types of protons at 7.80 (2H, o-C_6H_5), 7.55 (2H, p-C_6H_5), and 7.47 (2H, m-C_6H_5) ppm. Thus both I.R. and NMR data confirm that both S atoms coordinate to Cu. NMR spectra support the conclusion that there is no other species in solution and that the monomeric structure remains intact.

Crystal structure of 1

The atom numbering scheme of **1** is shown in Fig. 1. Table II lists significant bond lengths and angles. The X-ray study established that the compound is monomeric. There is no coordination by MeCN and also there are no significant intermolecular interactions between monomers.

Two S atoms and one iodine ion coordinate to Cu atom forming a three-coordinate complex. MeCN lies in the crystal lattice nonbonded. The angles around Cu are I(1)–Cu(1)–S(1), 122.73(2); I(1)–Cu(1)–S(2), 119.86(2); S(1)–Cu(1)–S(2), 117.14(3)° and this shows that the geometry is almost trigonal planar; and Cu is only 0.07 Å above the plane defined by the sulfur and iodine atoms. Angles within the six-membered ring formed by Cu, two S, two P and C of CH_2 spacer range from 102 to 119° and the

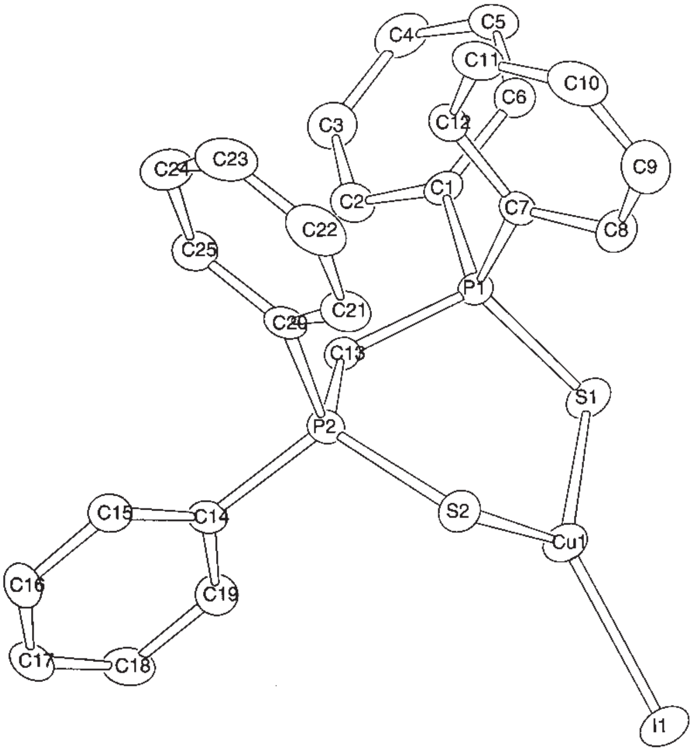

FIGURE 1 Molecular structure of Complex **1** with numbering scheme (hydrogen atoms are omitted for clarity).

TABLE II Selected bond lengths (Å) and angles (°) for **1**

Cu(1)–I(1)	2.4937(5)	P(1)–C(13)	1.817(3)
Cu(1)–S(1)	2.2470(7)	P(2)–C(13)	1.825(3)
Cu(1)–S(2)	2.2591(7)	P(2)–C(14)	1.807(3)
S(1)–P(1)	1.9854(9)	P(2)–C(20)	1.805(3)
S(2)–P(2)	1.9830(9)	N(1)–C(27)	1.102(6)
P(1)–C(1)	1.803(3)	C(26)–C(27)	1.450(7)
P(1)–C(7)	1.803(3)		
I(1)–Cu(1)–S(1)	122.73(2)	C(1)–P(1)–C(7)	106.1(1)
I(1)–Cu(1)–S(2)	119.86(2)	C(1)–P(1)–C(13)	104.8(1)
S(1)–Cu(1)–S(2)	117.14(3)	C(7)–P(1)–C(13)	107.2(1)
Cu(1)–S(1)–P(1)	102.14(3)	S(2)–P(2)–C(13)	115.12(8)
Cu(1)–S(2)–P(2)	106.37(3)	S(2)–P(2)–C(14)	112.63(9)
P(1)–C(13)–P(2)	119.2(2)	S(2)–P(2)–C(20)	110.8(1)
S(1)–P(1)–C(13)	112.7(1)	C(14)–P(2)–C(20)	108.7(1)
S(1)–P(1)–C(1)	110.19(8)	C(13)–P(2)–C(14)	102.0(1)
S(1)–P(1)–C(7)	115.05(9)	C(13)–P(2)–C(20)	107.0(1)
		N(1)–C(27)–C(26)	177.8(6)

smaller angles are at S atoms. The property of sulfur to adopt a range of angles leads to a large angle at Cu, namely S(1)–Cu(1)–S(2), 117.14(3)°. Further, the angles at P atoms vary in the range 102 to 115°. The N(1)–C(27)–C(26) angle of MeCN, 177.8(6)°, is similar to that in Compound **5** [178.2(7)°] [9], in which it is coordinated; however, C–C and C–N bond lengths are marginally different [**1**, C–C = 1.450(7); C–N = 1.102(6) Å; **5**, C–C = 1.446(7); C–N = 1.122(7) Å [9]].

In Compound **1**, the Cu(1)–S(1) and Cu(1)–S(2) bond distances of 2.2470(7) and 2.2591 (7) Å are somewhat less than those found in related species [*c.f.* Cu–S = 2.344 Å [9]], and in the analogous compound [CuCl(dppmS_2)]Me_2CO [Cu–S = 2.259, 2.321 Å [21]]. The Cu(1)–I(1) bond distance of 2.4937(5) Å is considerably smaller than those in the iodo-bridged dimer **5** [2.6503(8), 2.7196(9) Å [9] and the distance in **1** is much less than the sum of the ionic radii of Cu^+ and I^- (2.97 Å) [17]. The S(1)–P(1) and S(2)–P(2) bond distances of 1.9854(9) Å and 1.9830(9) Å respectively, are shorter than the sum of the covalent radii of the P and S atoms (2.12 Å). The P–C_{Ph} bond distances are shorter than P–C_{Alkyl}, as shown in Table II.

It is appropriate to discuss possible factors which lead to the formation of a trigonal planar, rather than an iodo-bridged dimer. The ligand dppmS_2 with copper(I) chloride in acetone forms a trigonal planar complex, [CuCl(dppmS_2)]Me_2CO **6** [21], and in ethanol it forms a mixture of trigonal planar CuCl(dppmS_2), and an *S*-bridged dimer, [2(CuCl(dppmS_2)) · (CuCl(dppmS_2))$_2$] **7** [22]. In **1**, prepared in MeCN, dppmS_2 chelates as in **6** and does not bridge as in (CuCl(dppmS_2))$_2$. This lack of bridging is not attributable to steric factors. However, lack of bridging with an iodide ligand is unusual, as iodide has good bridging properties as in the $Cu_2(Ph_3PS)_2)(\mu\text{-}I)_2(CH_3CN)_2$ (dimer) **5** [9], and the $\{Cu_4I_4(dppeSe_2)_2\}_n$ polymer **9** [10]. It is possible that MeCN present in the lattice somehow prevents dimer formation, *vis-à-vis* **5**, in which it is coordinated to Cu. The nature of ligand, solvent used in reaction and anion may all play roles in the formation of differently bonded complexes.

Acknowledgments

Financial assistance from the CSIR, New Delhi and laboratory facilities for one of us (GS), furnished by the Guru Nanak Dev University, are gratefully acknowledged.

Supplementary Data

The CCDC number for the compound is 224366.

References

[1] T.S. Lobana, *Prog. Inorg. Chem.* **37**, 495 (1989).

[2] T.S. Lobana, In: *The Chemistry of Organophosphorus Compounds*, Vol. 2 (F.R. Hartley, ed. J. Wiley & Sons, Chichester, Ch. 8. 1992).

[3] M.S. Hussain, *J. Crystallogr. Spectrosc. Res.* **16**, 91 (1986).

[4] T.S. Lobana, R. Verma, R. Mahajan and E.R.T. Tiekink, *Z. Kristallogr.* **214**, 513 (1999).

[5] T.S. Lobana, A. Singh, M. Kaur and A. Castineiras, *Proc. Indian Acad. Sci.* (*Chem. Sci.*) **113**, 89 (2001).

[6] L.S.D. Glasser, L. Ingram, M.G. King and G.P. McQuillan, *J. Chem. Soc.* 2501 (1969).

[7] T.S. Lobana, R. Hundal and P. Turner, *J. Coord. Chem.* **53**, 301 (2001).

[8] T.S. Lobana, R. Hundal, A. Singh, A. Sehdev, P. Turner and A. Castineiras, *J. Coord. Chem.* **55**, 353 (2002).

[9] T.S. Lobana, R. Mahajan and A. Castineiras, *Transition Met. Chem.* **26**, 440 (2001).

[10] T.S. Lobana and G. Hundal, *J. Chem. Soc.*, *Dalton Trans.* 2203 (2002).

[11] T.S. Lobana, M.K. Sandhu, M.J. Liddell and E.R.T. Tiekink, *J. Chem. Soc., Dalton Trans.* 691 (1990).

[12] T.S. Lobana, R. Verma, A. Singh, M. Shikha and A. Castineiras, *Polyhedron* **21**, 205 (2002).

[13] E.W. Ainscough, H.A. Bergen and A.M. Brodie, *J. Chem. Soc.*, *Dalton Trans.* 1649 (1976).

[14] K.L. Brown, *Acta Crystallogr.* **B35**, 462 (1979).

[15] J. Novosad, K.W. Tornroos, M. Necas, A.M.Z. Slawin, J.D. Woollins and S. Husebye, *Polyhedron* **18**, 2861 (1999).
[16] T.S. Lobana, A. Castineiras and P. Turner, *Inorg. Chem.* **42**, 4731 (2003), and references therein.
[17] J.E. Huheey, E.A. Keiter and R.L. Keiter, (eds.), *Inorganic Chemistry: Principles of Structure and Reactivity*. (HarperCollins, New York, 1993), 4th ed.
[18] P.G. Eller and P.W.R. Corfield, *J. Chem. Soc. Chem. Commun.* 105 (1971).
[19] J.A. Tiethof, J.K. Stalick and D.W. Meek, *Inorg. Chem.* **12**, 1170 (1973).
[20] G.M. Sheldrick, K.K. Pandey, M. Noltemeyer and H.W. Roesky, *Acta Crystallogr.* **C40**, 1555 (1984).
[21] E.W. Ainscough, H.A. Bergen and A.M. Brodie, *J. Chem. Soc., Dalton Trans.* 1649 (1976).
[22] E.W. Ainscough, A.M. Brodie and K.L. Brown, *J. Chem. Soc., Dalton Trans.* 1042 (1980).
[23] K.L. Brown, *Acta Crystallogr.* **B35**, 462 (1979).
[24] H. Brauer, *Handbook of Preparative Inorganic Chemistry*, Vol. 2. (Academic Press, New York, 1965), 2nd ed.
[25] R. Jacobson, Private Communication.
[26] A. Altomare, M.C. Burla, M. Camalli, M. Cascarano, C. Giacovazzo, A. Guagliardi and G. Polidori, *J. Appl. Crystallogr.* **27**, 435 (1994).
[27] G.M. Sheldrick, *SHELXL-97, Program for the Refinement of Crystal Structures* (University of Göttingen, Göttingen, 1997).
[28] TeXsan: *Crystal Structure Analysis Package* (Molecular Structure Corporation, Houston, Texas, 1985, 1999).