Syntheses and Structural Characterizations of Heterometallic Copper(I)/Indium(III) Complexes Containing Phosphine Ligands

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Addition of anhydrous $InCl_3$ to a THF solution of CuCl and dppe (dppe = $Ph_2PCH_2CH_2PPh_2$), or CuCl and PPh_3, resulted in the formation of the crystalline heterometallic copper(I)/indium(III) complexes $[(dppeCu)_2(\mu\text{-}Cl)(\mu\text{-}dppe)][InCl_4]\cdot THF$ (**1**·THF) and $[\{Cu(PPh_3)_2\}_2(\mu\text{-}Cl)_4(InCl)]\cdot THF$ (**2**·THF), respectively, which have been characterized by X-ray diffraction. Compound **1** is composed of a dinuclear copper(I) complex cation and a mononuclear tetrahedral indium(III) complex anion. Complex **2** comprises an indium center in a quasi square-pyramidal chloride-coordination environment connected to two $Cu(PPh_3)_3$ fragments *via* $Cu(\mu\text{-}Cl)_2In$ bridges.

Key words: Synthesis, Crystal Structure, Copper(I) Complex, Indium(III) Complex, Heterometallic Complex

Introduction

Heterometallic copper(I)/indium(III) complexes with chalcogenide ligands have important potential in thin film technology of solar cells [1 – 3]. A typical example is the ternary compound $CuInSe_2$ which can be prepared by a number of physical techniques mainly involving high temperatures [4]. Heterometallic precursor compounds made by chemical synthetic methods have not yet been well developed [5]. Recently, Fenske *et al.* have prepared a series of In-Cu, In-Ag, In-Au and Ga-Au chalocogenide cluster compounds by treatment of mixed metal chlorides with silylated main group element derivatives R-*E*-SiMe₃ (R = organic group; *E* = S, Se, Te) in the presence of a tertiary phosphine PR_3 [6 – 9]. $AgInSe_2$ nanorods have been one-pot synthesized from the precursor compound $[(PPh_3)_2AgIn(SeC\{O\}Ph)_4]$ [10]. To understand the reactive properties of mixed copper(I) and indium(III) chlorides in the presence of phosphine ligands, we have explored the synthesis of this class of heterometallic complexes which should be good sources for the corresponding ternary chalcogenide compounds. In this paper we report the synthesis and structural characterization of the complexes $[(dppeCu)_2(\mu\text{-}Cl)(\mu\text{-}dppe)][InCl_4]\cdot THF$ (**1**·THF) (dppe = $Ph_2PCH_2CH_2PPh_2$) and $[\{Cu(PPh_3)_2\}_2(\mu\text{-}Cl)_4(InCl)]\cdot THF$ (**2**·THF).

Experimental Section

Generals

All experiments were carried out routinely in purified dry nitrogen by standard Schlenk techniques. Solvents were purified, distilled and degassed prior to use. CuCl powder, anhydrous $InCl_3$, dppe and PPh_3 were commercially available. NMR spectra were recorded at r.t. on a Bruker ALX 300 spectrometer for ^1H (relative to $SiMe_4$) and ^{31}P (relative to 85 % H_3PO_4), and mass spectra were performed on a Finnigan TSQ 7000 spectrometer. Elemental analyses were performed with a CHN analyzer.

Syntheses

$[(dppeCu)_2(\mu\text{-}Cl)(\mu\text{-}dppe)][InCl_4]\cdot THF$ (**1**·THF)

To a solution of CuCl (99 mg, 1.0 mmol) and dppe (597 mg, 1.5 mmol) in THF (25 mL) was added anhydrous $InCl_3$ (111 mg, 0.5 mmol). The mixture was stirred at r.t. for 2 h, and a clear yellow solution formed as the solid $InCl_3$ dissolved. The resultant solution was continuously stirred for an additional 1 h and 40 mL of Et_2O was added to result in a yellow precipitate. The yellowish crystalline product was filtered off and washed twice with Et_2O. Yield: 692 mg, 86 %. Recrystallization on a small-scale from THF/Et_2O gave X-ray quality crystals of **1** as orange prisms. – ^1H NMR ($CDCl_3$): δ = 1.75 (m, 4H, THF), 2.14 (br, 6H, PCH_2CH_2P), 2.71 (br, 6H, PCH_2CH_2P), 3.62 (m, 4H, THF), 7.16 – 7.45 (m, 60H, C_6H_5). – ^{31}P NMR ($CDCl_3$): δ = −10.3 (br). – MS (FAB): m/z = 860 $[Cu(dppe)_2+1]^+$, 461 $[Cu(dppe)]^+$. –

Table 1. Crystal data, data collection parameters and details of the structure refinement.

Complex	1·THF	2·THF
Empirical formula	$C_{82}H_{80}OCl_5P_6Cu_2In$	$C_{76}H_{68}OCl_5P_4Cu_2In$
Formula weight	1686.43	1540.33
Color, habit	orange prisms	colorless blocks
Crystal size [mm³]	$0.50 \times 0.50 \times 0.40$	$0.44 \times 0.30 \times 0.26$
Crystal system	monoclinic	triclinic
Space group	$C2/c$	$P\bar{1}$
a [Å]	20.3612(8)	12.6266(7)
b [Å]	20.1280(8)	12.8128(8)
c [Å]	21.5875(8)	25.2589(15)
α [deg]	90	79.202(1)
β [deg]	100.191(1)	84.627(1)
γ [deg]	90	62.488(1)
Volume [Å³]	8708.0(6)	3560.0(4)
Z	4	2
Density (calc.) [g cm⁻³]	1.29	1.44
Absorption coefficient [mm⁻¹]	1.05	1.23
Temperature [K]	293(2)	293(2)
$F(000)$	3448	1568
Radiation	— MoK_α ($\lambda = 0.71073$ Å) —	
Reflections collected	45653	36436
Independent refls	10788	17600)
R_{int}	1.94 %	2.09 %
Reflections with $I \geq 2\sigma(I)$	8253	13168
Weighting scheme $[\sigma^2(F_o^2) + w_2 P^2 + w_1 P]$, $P = (F_o^2 + 2F_c^2)/3$:		
w_2, w_1	0.1379, 5.0642	0.0671, 1.5423
Parameters refined	436	777
Final R indices (all data)	$R1 = 0.0735$, $wR2 = 0.2002$	$R1 = 0.0589$, $wR2 = 0.1250$
Goodness of fit (GoF)	1.03	1.02
Final difference peaks [e Å⁻³]	+1.87, −0.93	+1.01, −0.58

$R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR2 = [\Sigma w(|F_o^2| - |F_c^2|)^2/\Sigma w|F_o^2|^2]^{1/2}$; GoF = $[\Sigma w(|F_o| - |F_c|)^2/(N_{obs} - N_{param})]^{1/2}$.

Anal. for $C_{78}H_{72}Cl_5P_6Cu_2In \cdot C_4H_8O$: calcd. C 58.3, H 4.74; found C 58.1, H 4.69.

[{Cu(PPh₃)₂}₂(μ-Cl)₄(InCl)]·THF (2·THF)

This compound was prepared similarly as described for **1** using PPh₃ (524 mg, 2.0 mmol) instead of dppe. Recrystallization from THF/Et₂O afforded colorless blocks which were suitable for X-ray diffraction analysis. Yield: 470 mg, 64 %. – ¹H NMR (CDCl₃): δ = 1.71 (m, 4H, THF), 3.65 (m, 4H, THF), 7.11 − 7.43 (m, 60H, C₆H_5). – ³¹P NMR (CDCl₃): δ = −2.63 (br). – MS (FAB): *m/z* = 587 [Cu(PPh₃)₂]⁺, 325 [Cu(PPh₃)]⁺. – Anal. for $C_{72}H_{60}Cl_5P_4Cu_2In \cdot C_4H_8O$: calcd. C 59.2, H 4.41; found C 58.8, H 4.40.

Crystal structure determination

Single crystals of **1**·THF ($0.50 \times 0.50 \times 0.40$ mm³) and **2**·THF ($0.44 \times 0.30 \times 0.26$ mm³) were mounted in ran-dom orientation on a glass fiber. Diffraction data were collected on a Bruker SMART Apex CCD diffractometer with MoK_α radiation ($\lambda = 0.71073$ Å) at 293 K using an ω scan mode. The collected frames were processed with the software SAINT [11]. The data were corrected for absorption using the program SADABS [12]. Structures were solved by Direct Methods and refined by full-matrix least-squares on F^2 using the SHELXTL software package [13]. All non-hydrogen atoms were refined anisotropically. The positions of all hydrogen atoms were generated geometrically (C_{sp^3} – H = 0.96 and C_{sp^2} – H = 0.93 Å) and included in the structure factor calculations with assigned isotropic displacement parameters, but were not refined. The THF solvent molecules in **1**·THF and **2**·THF were refined isotropically with bond distance restraints due to disorders. The largest peak in the final difference maps with height of 1.87 e Å⁻³ for **1**·THF was in the vicinity of the indium atom. The crystal data, data collection parameters and details of the structure refinement are given in Table 1.
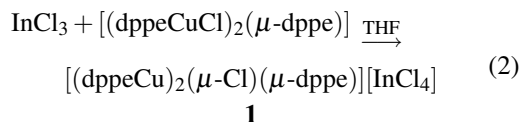
CCDC 631982 and 631983 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

Results and Discussion

The σ donor phosphine ligands are known to stabilize copper(I) species in both the solution and the solid state. Thus, treatment of CuCl powder with 1.5 equivalents of dppe in THF solution at r.t. gave rise to a dinuclear copper(I) complex [(dppeCuCl)₂(μ-dppe)] in nearly quantitative yield (eq. (1)) [14].

$$2\,CuCl + 3\,dppe \xrightarrow{THF} [(dppeCuCl)_2(\mu\text{-dppe})] \quad (1)$$
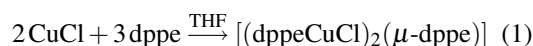
A strict 2 : 3 metal to ligand ratio can prevent formation of 1 : 1, 1 : 2 or 2 : 1 adducts. When anhydrous InCl₃ was dissolved in a THF solution of [(dppeCuCl)₂(μ-dppe)], a color change from colorless to yellow is observed. Attempts to crystallize the yellow product directly from THF solution resulted in the isolation of a complex subsequently characterized as [(dppeCu)₂(μ-Cl)(μ-dppe)][InCl₄]·THF (**1**·THF) (eq. (2)).

$$\begin{aligned} InCl_3 + [(dppeCuCl)_2(\mu\text{-dppe})] &\xrightarrow{THF} \\ [(dppeCu)_2(\mu\text{-Cl})(\mu\text{-dppe})][InCl_4] &\quad (2) \\ \mathbf{1} \end{aligned}$$

As it is well known, InCl₃ is a halide acceptor reagent in solution. In the present reaction, formation of the [InCl₄]⁻ anion gave the [(dppeCu)₂(μ-Cl)(μ-dppe)]⁺
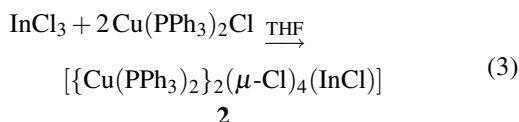
Table 2. Selected bond lengths (Å) and bond angles (deg) for complex **1**·THF.

Cu(1)–P(1)	2.3021(8)	Cu(1)-P(2)	2.2917(8)
Cu(1)-P(3)	2.2710(8)	Cu(1)-Cl(1)	2.3683(5)
Cu(1)#2-Cl(1)	2.3684(5)	In(1)-Cl(2)	2.3507(15)
In(1)-Cl(3)	2.333(2)		
P(3)-Cu(1)-P(2)	122.62(3)	P(3)-Cu(1)-P(1)	121.48(3)
P(2)-Cu(1)-P(1)	90.23(3)	P(3)-Cu(1)-Cl(1)	101.66(3)
P(2)-Cu(1)-Cl(1)	108.10(3)	P(1)-Cu(1)-Cl(1)	112.67(3)
Cu(1)-Cl(1)-Cu(1)#2	134.95(5)	Cl(3)-In(1)-Cl(3)#1	109.90(19)
Cl(3)-In(1)-Cl(2)	106.97(8)	Cl(3)#1-In(1)-Cl(2)	109.95(7)
Cl(3)-In(1)-Cl(2)#1	109.95(7)	Cl(3)#1-In(1)-Cl(2)#1	106.98(8)
Cl(2)-In(1)-Cl(2)#1	113.09(10)		

Symmetry code: #1 $-x+1$, y, $-z+1/2$; #2 $-x$, y, $-z+1/2$.
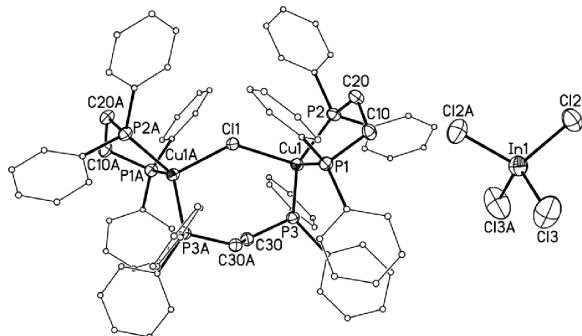
Fig. 1. Molecular structure of the ions [(dppeCu)$_2$(μ-Cl)(μ-dppe)]$^+$ and [InCl$_4$]$^-$ in **1**·THF. Atoms labeled with the suffix A are generated by the symmetry operation $-x$, y, $-z+1/2$ in the [(dppeCu)$_2$(μ-Cl)(μ-dppe)]$^+$ cation and by $-x+1$, y, $-z+1/2$ in the [InCl$_4$]$^-$ anion.

cation with one terminal chloride function converted to a bridging one.

Similarly, anhydrous InCl$_3$ was dissolved in a THF solution of CuCl and PPh$_3$ in a 1 : 2 ratio, in which the complex [Cu(PPh$_3$)$_2$Cl] is present [15], to give complex **2** (eq. (3)).

$$\text{InCl}_3 + 2\,\text{Cu(PPh}_3)_2\text{Cl} \xrightarrow{\text{THF}}$$

$$[\{\text{Cu(PPh}_3)_2\}_2(\mu\text{-Cl})_4(\text{InCl})] \qquad (3)$$
$$\mathbf{2}$$

The ^{31}P NMR resonance of $\delta = -10.3$ ppm for complex **1** is in good agreement with the resonance of [(dppeCuCl)$_2$(μ-dppe)] ($\delta = -10.5$ ppm) [14], while the ^{31}P NMR resonance of $\delta = -2.63$ ppm for complex **2** is slightly down-shifted by comparison with the resonance of [Cu(PPh$_3$)$_2$Cl] ($\delta = -3.6$ ppm) due to the variation of the copper(I) coordination [15]. Both ^{31}P NMR spectra of complexes **1** and **2** at r. t. exhibit a broad signal (width *ca.* 2 ppm), suggesting rapid bond breaking processes in solution. The positive ion

Table 3. Selected bond lengths (Å) and bond angles (deg) for complex **2**·THF.

In(1)–Cl(1)	2.3595(9)	In(1)–Cl(2)	2.5228(7)
In(1)–Cl(3)	2.4311(7)	In(1)–Cl(4)	2.5361(7)
In(1)–Cl(5)	2.4208(7)	Cu(1)–P(1)	2.2751(8)
Cu(1)–P(2)	2.2767(8)	Cu(2)–P(3)	2.2707(7)
Cu(2)–P(4)	2.2744(7)	Cu(1)–Cl(2)	2.4293(9)
Cu(1)–Cl(3)	2.5692(7)	Cu(2)–Cl(4)	2.3849(7)
Cu(2)–Cl(5)	2.6642(8)		
Cl(1)–In(1)–Cl(5)	116.03(4)	Cl(1)–In(1)–Cl(3)	120.05(4)
Cl(5)–In(1)–Cl(3)	123.90(3)	Cl(1)–In(1)–Cl(2)	93.95(4)
Cl(5)–In(1)–Cl(2)	93.21(3)	Cl(3)–In(1)–Cl(2)	84.40(2)
Cl(1)–In(1)–Cl(4)	92.90(3)	Cl(5)–In(1)–Cl(4)	85.48(2)
Cl(3)–In(1)–Cl(4)	90.53(2)	Cl(2)–In(1)–Cl(4)	172.89(3)
P(1)–Cu(1)–P(2)	123.20(3)	P(1)–Cu(1)–Cl(2)	112.21(3)
P(2)–Cu(1)–Cl(2)	114.07(3)	P(1)–Cu(1)–Cl(3)	107.22(3)
P(2)–Cu(1)–Cl(3)	109.02(3)	Cl(2)–Cu(1)–Cl(3)	83.45(2)
P(3)–Cu(2)–P(4)	125.97(3)	P(3)–Cu(2)–Cl(4)	119.33(3)
P(4)–Cu(2)–Cl(4)	107.12(3)	P(3)–Cu(2)–Cl(5)	106.41(3)
P(4)–Cu(2)–Cl(5)	104.76(3)	Cl(4)–Cu(2)–Cl(5)	83.40(2)
Cu(1)–Cl(2)–In(1)	96.70(3)	In(1)–Cl(3)–Cu(1)	95.44(3)
Cu(2)–Cl(4)–In(1)	97.60(2)	In(1)–Cl(5)–Cu(2)	93.38(3)
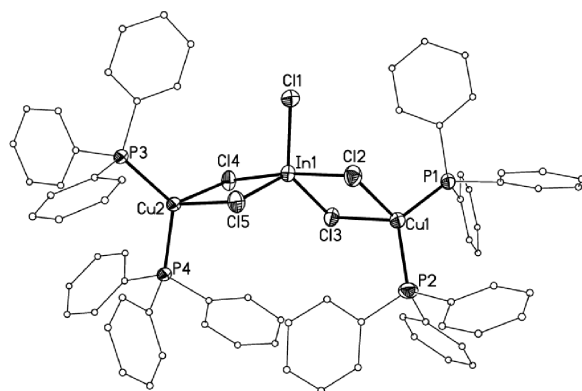
Fig. 2. Molecular structure of **2** with atomic numbering (ORTEP drawing, 40 % probability ellipsoids, hydrogen atoms omitted for clarity).

FAB mass spectra of **1** and **2** show copper(I)-phosphine fragment ions with the characteristic isotopic distribution patterns.

The structures of **1** and **2** were determined by single-crystal X-ray diffraction, and are shown in Figs. 1 and 2, respectively. Selected bond lengths and angles of **1** and **2** are given in Tables 2 and 3, respectively. The structure of **1** contains [(dppeCu)$_2$(μ-Cl)(μ-dppe)]$^+$ and [InCl$_4$]$^-$ ions. Atoms Cl1 and In1 lie on crystallographic two fold axes. In the cation of **1**, two μ-Cl and one μ-dppe bridge two Cu atoms to construct a seven-membered ring. The Cu atoms have a highly distorted tetrahedral geometry with P–Cu–P and P–Cu–Cl angles in the ranges of 90.23(3) – 122.62(3)°

and $101.66(3) - 112.67(2)°$, respectively. The average Cu–P bond length of $2.2883(8)$ Å in **1** agrees well with those in $[(dppeCuX)_2(\mu\text{-}dppe)]$ (X = Cl, Br, I and CN) [14]. The bridging chloride equally binds two copper atoms with a nonlinear Cu–Cl–Cu linkage. The Cu–Cl distance is $2.3684(5)$ Å and the Cu–Cl–Cu angle is $134.95(5)°$. In the $[InCl_4]^-$ anion, the Cl–In–Cl angles lie in the range of $106.97(8) - 113.09(10)°$. The average In–Cl bond length [$2.342(2)$ Å] is significantly shorter that those in the trigonal-bipyramidal $[InCl_5]^{2-}$ anion [av. $2.378(3)$ Å] [9] and in the octahedral complex [$\{1,2\text{-}bis(diphenylphosphanyl)benzene\}_2InCl_2][InCl_4]$ [av. $2.4830(5)$ Å] [16].

Complex **2** crystallizes in the triclinic space group $P\bar{1}$ with two molecules per unit cell. The structure of **2** comprises an indium center in a quasi square-pyramidal chloride-coordination environment connected to two Cu(PPh)$_3$ fragments *via* two Cu(μ-Cl)$_2$In bridges. The terminal chloride atom occupies the apical position. The heterometallic four-membered InCl$_2$Cu rings in **2** are nearly planar, which is typical of the geometry in MCl$_2$M$'$ rings [15, 17, 18]. Each ring contains a pair of long and short In–Cl and Cu–Cl bonds: In(1)–Cl(2) = $2.5228(7)$ and Cu(1)–Cl(3) = $2.5692(7)$ ("long"), In(1)–Cl(3) = $2.4311(7)$ and Cu(1)–Cl(2) = $2.4293(9)$ Å ("short") in the In1–Cl2–Cu1–Cl3 ring, In(1)–Cl(4) = $2.5361(7)$ and Cu(2)–Cl(5) = $2.6642(8)$ ("long"), In(1)–Cl(5) = $2.4208(7)$ and Cu(1)–Cl(4) = $2.3848(7)$ Å ("short") in the In1–Cl4–Cu2–Cl5 ring. The inner ring angles at the chlorine atoms [In(1)–Cl(2)–Cu(1) = $96.70(3)°$ and In(1)–Cl(3)–Cu(1) = $95.44(3)°$, In(1)–Cl(4)–Cu(2) = $97.60(2)°$ and In(1)–Cl(5)–Cu(2) = $93.38(3)°$]

are larger than those at the metal atoms [Cl(2)–In(1)–Cl(3) = $84.40(2)°$ and Cl(2)–Cu(1)–Cl(3) = $83.45(2)°$, Cl(4)–In(1)–Cl(5) = $85.48(2)°$ and Cl(4)–Cu(2)–Cl(5) = $83.40(2)°$]. The terminal In(1)–Cl(1) bond length [$2.3595(9)$ Å] in **2** is slightly longer than those in **1** [av. $2.342(2)$ Å]. The coordination geometry around the copper atom in **2** is highly distorted tetrahedral. The average Cu–P bond length [$2.2742(8)$ Å] in **2** is in good agreement with those in some related Cu-PPh$_3$ complexes [15]. The geometry of the four-membered rings in **2** enforces an average Cu$\cdots$In distance of $3.703(2)$ Å, indicative of no significant electronic interaction.

In summary, we have explored reactions of copper(I) and indium(III) chloride mixtures with phosphine ligands, and isolated and structurally characterized two heterometallic copper(I)/indium(III) complexes, $[(dppeCu)_2(\mu\text{-}Cl)(\mu\text{-}dppe)][InCl_4]\cdot THF$ and $[\{Cu(PPh_3)_2\}_2(\mu\text{-}Cl)_4(InCl)]\cdot THF$. The r. t. ^{31}P NMR spectra of the two complexes exhibit a broad signal due to rapid bond breaking processes in solution, which also suggests that the labile bridging chlorides can also be easily substituted by electron-rich chalcogenide ligands, which may provide further insight into mechanisms of formation of ternary chalcogenide compounds. Investigations in this area are under way.

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