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PII:	\$0277-5387(14)00350-7
DOI:	http://dx.doi.org/10.1016/j.poly.2014.05.034
Reference:	POLY 10748
To appear in:	Polyhedron
Received Date:	13 March 2014
Accepted Date:	14 May 2014



Please cite this article as: R.J. Davidson, E.W. Ainscough, A.M. Brodie, G.H. Freeman, G.B. Jameson, Structural studies on tris(2-cyanoethyl)phosphine complexes of Cu(I): The sensitivity of the secondary nitrile coordination to the nature of the anion, *Polyhedron* (2014), doi: http://dx.doi.org/10.1016/j.poly.2014.05.034

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 Structural studies on tris(2-cyanoethyl)phosphine complexes of

Cu(I): The sensitivity of the secondary

nitrile coordination to the nature of the anion

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Graphical Abstract

The potentially multidentate ligand, tris(2-cyanoethyl)phosphine (tcep), reacts with copper(I) to give 1:1 salts CuX(tcep) (X = Cl, Br, I and SCN) or 2:1 salts CuY(tcep)₂ (Y = BH₄, CF₃COO, CN and ClO₄). Single crystal X-ray studies show a variety of structural types have been formed with either coordinated or non-coordinated anions.



ABSTRACT

Tris(2-cyanoethyl)phosphine (tcep) reacts with the copper(I) compounds, CuX (X = Cl, Br, I and SCN), in a 1:1 ratio to give 1:1 complexes, CuX(tcep), whereas it reacts with CuY (Y = PF₆, ClO₄, NO₃, BH₄, CN and CF₃COO) in a 2:1 ratio to give the 2:1 complexes, CuY(tcep)₂. Single crystal X-ray structures show that for the anions X = Br and SCN, the complexes are coordination polymers, [CuX(tcep)]_n, with the Cu centres being bridged by the anion, and as well, one nitrile arm per tcep ligand coordinates intermolecularly to the Cu to give tetrahedral 'PBr₂N' and 'PSN₂' coordination spheres respectively. The 2:1 compounds exhibit a variety of structures. For Y = ClO₄, CN and CF₃COO polymeric structures are formed except for Y = BH₄ where the compound is a discrete monomer, [Cu(BH₄)(tcep)₂], with a chelating anion and two monodentate P-

bound tcep ligands. Both the compounds obtained with Y = CN and CF_3COO also contain coordinated anions and are formulated as $[Cu(CN)(tcep)_2]_n$ and $[Cu(CF_3COO)(tcep)_2]_n$ respectively. In the case of Y = CN the anion is bridging and the tcep ligands are only P-bound giving a 'P₂NC' coordination sphere. In contrast, for Y = CF_3COO , the anion is an O-bound monodentate and the tcep ligands bridge to give a 'P₂NO' environment for the copper. In the case of $Y = CIO_4$, the anion is not coordinated but a polymeric structure, $[Cu(tcep)_2]_n(CIO_4)_n$, is formed via bridging tcep ligands linking Cu centres intermolecularly resulting in a 'P₂N₂' coordination sphere.

Keywords: Tris(2-cyanoethyl)phosphine; Copper(I) complexes; X-ray crystallography

1. Introduction

Tris(2-cyanoethyl)phosphine, P(CH₂CH₂CN)₃ (tcep), is potentially a multidentate ligand which can coordinate through the cyano nitrogens as well as the phosphorus. It has been recognized as being a better π -acid than the trialkylphosphines [1] and is stable towards oxidation by oxygen as a result of the electron-withdrawing cyano groups. Its high melting point (97 °C), when compared with alkyl phosphines, which are liquids at room temperature, has been attributed to strong intermolecular dipole-dipole attractions between the polar CH₂-CN groups [2]. On Streuli's scale, where the basicities of phosphines were determined by nonaqueous titrimetry, the pK_a of tcep at 1.37 is lower than for P(CH₂CH₂CH₃)₃ (8.64) and P(C₆H₅)₃ (2.73). In this case, the presence of the cyano groups results in tcep having a low basicity [3]. The cone angle, which is a measure of its steric size, for uncoordinated tcep has been calculated to be 132° [4] which

is the same as for PEt₃; however, for the coordinated ligand in $[Ag(tcep)_2]NO_3$ it is 175° [5], showing that it varies substantially depending on changes in the conformation of tcep which has a site symmetry of C_s in the former [6] and C_3 for the latter [5]. Tcep reacts with soft metals to give complexes in which the ligand is bound through the phosphorus atom only as in Mo(CO)₅(tcep) [1] but with intermediate or hard metals the N atoms may participate as well e.g. red *trans*-NiBr₂(tcep)₂, obtained under kinetic control, exists as a square-planar form with both P atoms bound, but when the solid is heated a blue linear polymer is formed consisting of octahedral Ni(II) centres with Ni-P-CH₂-CH₂-CN-Ni bridges [7,8]. In some complexes the donor set can include two or three nitrile nitrogen atoms per ligand molecule hence giving rise to an array of oligomeric and polymeric structures. The complex $3CoCl_2 \cdot 2(tcep)$ may have a trimeric cage structure containing only Co-N bonds [7]. In contrast, synthesis of the square-planar [Ni(NCS)₂(tcep)₂] complex at room temperature leads to the formation of three conformational polymorphs – polymerization does not occur [9]. Two crystalline polymorphs of AuCl(tcep) have been studied [10] while the corresponding bromo complex exists only in one polymorph [11]. The ability of tcep to allow various conformations may be a factor promoting polymorph formation.

A range of binary Cu(I) complexes containing tcep has been reported previously, including CuBr(tcep), CuCl(tcep), [Cu(tcep)₂]BF₄ and [Cu(tcep)(CH₃CN)]BF₄ [6,12], but no structural studies. However, single crystal X-ray crystal structures have been determined for the ternary compounds [CuBr(L¹)(tcep)] (L¹ =1,10- phenanthroline, 2,2'bipyridine and dipyrido-[3,2-*d*:2',3'-*f*]-quinoxaline) [13,14], [CuCl(L¹)(tcep)] (L¹ =1,10phenanthroline) [14] and the polymeric compound [Cu(L²)₂)(tcep)₂]_n [L² = dihydrobis(3-

nitro-1,2,4-triazolyl)borate] [15]. The binary compounds above reported by Zanella et al. [12] were evaluated for their cytotoxic activity towards a panel of seven human cell lines. The high uptake shown by CuBr(tcep) in 2008 human ovarian cancer cells may explain its superior cytotoxic and anti- mitochondrial action compared with the others suggesting that cell internalization is an important pre-requisite for drug effectiveness [12]. Similarly, the cytotoxic activities of [CuCl(L¹)(tcep)] [14] and [CuCl(L²)₂(tcep)₂]_n [15] and have been reported.

In this study we further explore the conformational preferences of tcep by synthesizing a series of Cu(I) compounds containing a variety of anions and we determine their structures by single crystal X-ray crystallography. The single crystal X-ray structure of CuBr(tcep) and related 1:1 complexes as well as 2:1 complexes are presented in the current work. All of the determined structures show both the 1:1 and 2:1 complexes to be polymeric, e.g. [CuBr(tcep)]_n, except for the borohydride compound, [Cu(BH₄)(tcep)₂], which is a monomer with both the anion and the tcep ligands coordinated. A feature of a number of the polymeric compounds is the linking of metal centres by bridging µ-tcep ligands which is not common having been found in only a few other cases [15].

2. Experimental

2.1. Materials and instrumentation

Analytical grade solvents were used without further purification [Cu(MeCN)₄]PF₆ was made according to a literature method [16], CuCl, CuBr, CuI, CuCN, Cu(ClO₄)₂·6H₂O, CuSCN, Cu(NO₃)₂·3H₂O, NaBH₄ were purchased from Sigma-Aldrich Chemical Co and tcep was obtained from Strem Chemical Inc. Copper(I) trifluoroacetate Cu(TFA) (TFA = CF₃COO) was prepared by a literature method [17]. All reactions were carried out under nitrogen. Microanalyses were performed by the Campbell Microanalytical Laboratory, University of Otago. IR spectra were run as KBr discs on a Perkin-Elmer FT-IR Paragon 1000 spectrometer and ³¹P{¹H} NMR spectra were recorded at 400 MHz with a Bruker Avance 400 spectrometer. ³¹P NMR chemical shifts were referenced to an 85% H₃PO₄ standard. Electrospray ionisation (ESI) mass spectra were obtained from CH₃CN solutions with a Micromass ZMD spectrometer run in the positive ion mode. Listed peaks correspond to the most abundant isotopomer; assignments were made by a comparison of observed and simulated spectra.

2.2. Syntheses of complexes

2.2.1. $[CuCl(tcep)]_n$

A mixture of 0.052 g (0.52 mmol) CuCl and 0.10 g (0.52 mmol) tcep in 10 mL CH₃CN was refluxed with stirring for 30 minutes and then filtered while hot. The filtrate was allowed to cool to give 0.105 g of white crystals (69% yield). IR (cm⁻¹): 2270 (w, sh), 2246 (m, vCN), 1416 (m). *Anal*. Calc. C₉H₁₂ClCuN₃P: C, 37.00; H, 4.14; N, 14.38. Found: C, 37.12; H, 4.05; N, 14.54%.

2.2.2. $[CuBr(tcep)]_n$

A mixture of 0.075 g (0.52 mmol) of CuBr and 0.10 g (0.52 mmol) of tcep in 25 mL CH₃CN was refluxed with stirring for 30 minutes and then filtered while hot. On cooling 0.103 g of white crystals was formed (59% yield). IR (cm⁻¹): 2267 (w, sh), 2246 (m, vCN), 1418 (m). *Anal.* Calc. C₉H₁₂BrCuN₃P: C, 32.11; H, 3.59; N, 12.48. Found: C, 32.08; H, 3.39; N, 12.57%.

2.2.3. $[CuI(tcep)]_n$

A mixture of 0.099 g (0.52 mmol) CuI and 0.10 g (0.52 mmol) of tcep in 30 mL CH₃CN was refluxed for 5 minutes and then 5 mL additions of CH₃CN made until the total volume was 80 mL. The solution was refluxed for a further 15 minutes and then filtered hot and taken to dryness. The precipitate was redissolved in 25 mL of boiling CH₃CN and, after reducing the volume, the white product (0.166 g) appeared on cooling (83% yield). IR (cm⁻¹): 2270 (w, sh), 2253 (w, sh), 2237 (m, vCN), 1422(m). *Anal.* Calc. C₉H₁₂CuIN₃P: C, 28.18; H, 3.15; N, 10.95. Found: C, 28.3; H, 3.21; N, 11.02%.

2.2.4. $[Cu(tcep)_2]_n(PF_6)_n$

A mixture of 0.234 g (0.63 mmol) $[Cu(CH_3CN)_4]PF_6$ and 0.243 g (1.26 mmol) of tcep in 10 mL CH₃CN was refluxed under N₂ with stirring for 1 hour then filtered hot. The filtrate was taken to dryness and the residue dissolved in a mixture of 1 mL CH₃CN and 3 mL acetone. Diethyl ether was diffused into this solution to give 0.31 g of white crystals (83% yield). IR (cm⁻¹): 2276 (w, sh), 2252 (m, vCN), 1426 (m), 844 (s, vPF₆),

558 (m, δPF₆). *Anal*. Calc. C₁₈H₂₄CuF₆N₆P₃: C, 36.34; H, 4.07; N, 14.13. Found: C, 36.88; H, 4.19; N, 14.32%.

2.2.5. $[Cu(tcep)_2]_n(ClO_4)_n$

A mixture of 0.048 g (0.13 mmol) Cu(ClO₄)₂·6H₂O and 0.0088 g (0.14 mmol) copper bronze in 20 mL CH₃CN was stirred at room temperature under N_2 for 2 hours. To the resulting $CuClO_4$ solution was added 0.10 g (0.52 mmol) tcep as a solid and the reaction mixture refluxed under N2 with stirring for 15 minutes then filtered hot. The filtrate was taken to dryness and nitromethane added to solidify the product. The nitromethane was removed in vacuo and 20 mL acetone added to the residue and heated to reflux. Acetonitrile was added slowly until all the solid had dissolved and the resulting solution left to evaporate to dryness at room temperature over two weeks to give small white crystals and a sticky impurity. Nitromethane was added to dissolve the impurity then discarded. The remaining crystals were dissolved in a hot mixture of CH₃CN and nitromethane and the resulting solution left to evaporate at room temperature over two weeks to give 0.056 g white crystals (suitable for X-ray diffraction) (39% yield). The composition of samples of complex varied because of the use of mixed solvents and the rate of precipitation. In this case CH₃NO₂ and H₂O were added to the empirical formula. IR (cm⁻¹): ~ 2270 (w, sh), 2248 (m, νCN), 1421(m), 1090(s, νClO₄), 625 (m, δClO₄). Anal. Calc. C₁₉H₂₉ClCuN₇O₇P₂: C, 36.32; H, 4.65; N, 15.60. Found: C, 36.88; H, 4.38; N, 15.46%.

2.2.6. $[Cu(SCN)(tcep)]_n$

A mixture of 0.063 g (0.52 mmol) CuSCN and 0.10 g (0.52 mmol) tcep in 10 mL CH₃CN was refluxed under N₂ with stirring for 30 minutes then filtered hot. The filtrate was taken to dryness and the oily residue dissolved in a mixture of 5 mL CH₃CN and 3 mL nitromethane and left to evaporate to dryness at room temperature overnight to give 0.091g white crystals (suitable for x-ray diffraction) (56% yield). IR (cm⁻¹): 2270 (w, sh), 2248 (m, vCN), 2103 (s, NCS), 1423 (m). *Anal.* Calc. $C_{10}H_{12}CuN_4PS$: C, 38.15; H, 3.84; N, 17.80. Found: C, 38.36; H, 3.87; N, 17.89%.

2.2.7. $[Cu(tcep)_2]_n(NO_3)_n$

A mixture of 0.032g (0.13 mmol) Cu(NO₃)₂·3H₂O and 0.0088g (0.14 mmol) copper bronze in 20 mL CH₃CN was stirred at room temperature under N₂ for 1 hour. To the resulting CuNO₃ solution was added 0.10 g (0.52 mmol) tcep as a solid and the reaction mixture refluxed under N₂ with stirring for 15 minutes then filtered hot. The filtrate was reduced in volume to 5 mL and diethyl ether diffused into this solution to give 0.101g of white crystals (76% yield). IR (cm⁻¹): ~ 2270 (w, sh), 2240 (m, vCN), 1424(m), 1360(s, vNO₃). *Anal.* Calc. C₁₈H₂₄CuN₇O₃P₂: C, 42.23; H, 4.73; N, 19.15. Found: C, 41.92; H, 4.85; N, 18.89%.

2.2.8. [Cu(BH₄)(tcep)₂]

To a suspension of 0.15 g (0.293 mmol) $[CuNO_3(tcep)_2]$ in 15 mL CH₂Cl₂ was added sufficient CH₃CN to give a colourless solution. A solution of 0.015 g (0.40 mmol) NaBH₄ in 5 ml of ethanol was added to the Cu(tcep)₂NO₃ solution and the reaction mixture stirred at room temperature for 3 hours then filtered and the filtrate taken to

dryness. The crude product was dissolved in 5 mL CH₃CN and diethyl ether diffused into this solution to give 0.090 g of crystals (suitable for X-ray diffraction) (66% yield). IR (cm⁻¹): 2952 (m), 2927 (m) and 2855 (w, terminal vBH₄), 2371 (m), 2293(m), 2226 (m) and 2036 (m, bridging vBH₄), 2247 (m, vCN), 1427 (m), 1127 (m, δ BH₄). *Anal*. Calc. C₁₈H₂₈BCuN₆P₂: C, 46.52; H, 6.07; N, 18.08. Found: C, 46.75; H, 5.93; N, 18.16%.

2.2.9. $[Cu(CN)(tcep)_2]_n \cdot 0.5nCH_3CN$

A mixture of 0.0232 g (0.26 mmol) CuCN and 0.10 g (0.52 mmol) tcep in 15 mL CH₃CN was refluxed under N₂ with stirring for 1 hour then filtered hot. The filtrate was allowed to cool to give 0.085 g of white needles (69% yield). IR (cm⁻¹): 2270 (w, sh), 2246 (s), 2100 (s, cyanide ion vCN), 1425 (m). *Anal.* Calc. C₁₉H₂₄CuN₇P₂·½CH₃CN: C, 48.39; H, 5.18; N, 21.16. Found: C, 48.42; H, 5.18; N, 21.26%. Crystals suitable for X-ray diffraction were grown from CH₃CN.

2.2.10. $[Cu(TFA)(tcep)_2]_n$

To a suspension of 0.10 g (0.52 mmol) tcep in a mixture of 10 mL CH₂Cl₂ and 5 mL CH₃CN was added 0.048 g (0.26 mmol) CuTFA as a solid. The reaction mixture was stirred under N₂ at room temperature for 5 minutes then refluxed for 15 minutes and the solvent removed to give 0.122 g of pale blue crude product. Diethyl ether was diffused into a CH₃CN solution of the crude product to give 0.105 g of colourless crystals (suitable for X-ray diffraction) (72% yield). IR (cm⁻¹): 2268 (w, sh), 2239 (m, vCN), 1684 (s), 1209 (s), 1132 (s). *Anal.* Calc. C₂₀H₂₄CuF₃N₆O₂P₂: C, 42.67; H, 4.30; N, 14.93. Found: C, 42.57; H, 4.18; N, 15.00%.

2.3. X-ray Crystallography

All X-ray data were collected at low temperature with a Rigaku-Spider X-ray diffractometer, comprising a Rigaku MM007 microfocus copper rotating-anode generator, high-flux Osmic monochromating and focusing multilayer mirror optics (Cu K radiation, $\lambda = 1.5418$ Å), and a curved image-plate detector. CrystalClear was utilised for data collection and FSProcess in PROCESS-AUTO for cell refinement and data reduction. Crystal refinement data are given in Table 1. The structures were solved by direct methods and refined using both the SHELXTL [18] and OLEX [19] programs. Hydrogen atoms were calculated at ideal positions. Some of the compounds contain solvent molecules in the empirical formulae which are readily lost on standing. Hence in these cases, the number of solvent molecules, as determined by the X-ray structures, in r than t. the lattice is often higher than that determined from the analytical data.

Table 1

Crystal and refinement data.

Compound	[CuBr(tcep)] _n	$[Cu(BH_4)(tcep)_2]$	$[Cu(TFA)(tcep)_2]_n \cdot$ nCH ₂ CN
Molecular formula	C ₉ H ₁₂ BrCuN ₃ P	C ₁₈ H ₂₈ BCuN ₆ P ₂	C ₂₂ H ₂₇ CuF ₃ N ₇ O ₂ P ₂
$M (\text{g mol}^{-1})$	336.64	464.76	603.98
Temperature (K)	153	153	123
Crystal system	Triclinic	Monoclinic	Orthorhombic
Space group	$P\overline{1}$	$P2_{1}/c$	Pbca
<i>a</i> (Å)	7.3679(6)	8.7780(5)	8.10830(10)
<i>b</i> (Å)	7.9416(4)	26.8727(9)	24.7179(5)
<i>c</i> (Å)	12.6707(9)	10.2268(7)	26.8979(19)
α (°)	74.137(5)	90	90
β (°)	89.028(6)	108.698(8)	90
γ (^o)	64.460(5)	90	90
$V(Å^3)$	639.12(8)	2285.1(2)	5390.9(4)
Ζ	2	4	8
μ (Cu K α) mm ⁻¹	7.037	2.791	2.751
$\rho_{\rm calc} ({\rm g cm^{-3}})$	1.749	1.351	1.488
$2\theta_{\max}$ (°)	130.14	130.16	130.14
Number of unique reflections	2146	3835	4574
Data/restraints/ parameters	2146/141/136	3835/6/269	4574/0/336
Final <i>R</i> indices $[I > 2\sigma(I)]$	$R_1 = 0.0732$	$R_1 = 0.0554$	$R_1 = 0.440$
	$wR_2 = 0.1516$	$wR_2 = 0.1255$	$wR_2 = 0.0969$
R indices (all data)	$R_1 = 0.1128$	$R_1 = 0.0750$	$R_1 = 0.0514$
	$wR_2 = 0.2137$	$wR_2 = 0.1489$	$wR_2 = 0.1022$
Goodness-of-fit on F^2	1.070	1.128	1.095

Table 1 continued

Crystal and refinement data.

Compound	$[Cu(CN)(tcep)_2)]_n$.	[Cu(SCN)(tcep)] _n	$[Cu(tcep)_2]_n(ClO_4)_n$
	nCH ₃ CN		nC ₃ H ₆ O
	$C_{21}H_{27}CuN_8P_2$	$C_{10}H_{12}CuN_4PS$	$C_{21}H_{30}ClCuN_6O_5P_2$
Molecular formula			
M (g mol ⁻¹)	514.98	314.81	607.45
Temperature (K)	123	123	123
Crystal system	Triclinic	Monoclinic	Monoclinic
Space group	$P\overline{1}$	$P2_{1}/c$	$P2_{1}/c$
<i>a</i> (Å)	8.9200(18)	11.750(2)	22.141(4)
<i>b</i> (Å)	12.590(3)	8.9000(18)	8.2450(16)
<i>c</i> (Å)	12.940(3)	13.365(3)	16.104(3)
α (°)	107.34(3)	90	90
β (°)	92.18(3)	104.85(3)	107.48(3)
γ (^o)	109.56(3)	90	90
$V(\text{\AA}^3)$	1291.7(6)	1351.0(5)	2804.1(10)
Ζ	2	4	4
μ (Cu K α) mm ⁻¹	2.558	4.713	3.414
$\rho_{\rm calc} ({\rm g cm}^{-3})$	1.334	1.548	1.439
$2\theta_{\max}$ (°)	130.14	130.16	130.16
Number of unique reflections	4334	2293	4754
Data/restraints/	4334/19/290	2293/0/154	5754/186/320
Final R indices [1/2-(D]	$R_{1} = 0.0600$	$R_{1} = 0.0419$	$R_{\rm c} = 0.0798$
Γ mat Λ more $S[I > 20(I)]$	$M_I = 0.0099$ $WR_2 = 0.1705$	$K_I = 0.0419$ $WR_0 = 0.1051$	$m_{I} = 0.0790$ $m_{R_{0}} = 0.2100$
Rindices (all data)	$W_{12} = 0.1703$ $R_1 = 0.0805$	$WR_2 = 0.1031$ $R_1 = 0.0460$	$W\Lambda_2 = 0.2170$ $R_1 = 0.0837$
r mulees (an uala)	$m_I = 0.0003$ $m_R_2 = 0.2006$	$K_I = 0.0409$ $WR_0 = 0.1207$	$K_I = 0.0037$ $W R_2 = 0.2226$
Goodness of fit	$w_{1} = 0.2090$	$w_{N_2} = 0.1207$ 1 108	$WK_2 = 0.2220$
on F^2	1.100	1.100	1.071

3. Results and discussion

3.1. Syntheses of complexes

The complexes are divided into two stoichiometric types viz. 1:1 CuX(tcep) (X=CI, Br, I and SCN) and 1:2 CuY(tcep)₂ (Y=PF₆, ClO₄, NO₃, BH₄, CN and TFA). All were obtained in moderate yields by refluxing a CH₃CN or a CH₃CN/CH₂Cl₂ solution of the appropriate copper(I) salt with tcep in the appropriate molar ratio, except for Y=BH₄ where the reaction was performed at room temperature. By preparing copper(I) nitrate and copper(I) perchlorate in situ by reduction of the corresponding Cu(II) salts with copper bronze in CH₃CN, the formation of the phosphine oxide, which occurs when tcep is reacted directly with the Cu(II) salts, is avoided. The experimental section has further details. Since the single crystal X-ray structures of six of the complexes show all to be polymeric, except for [Cu(BH₄)(tcep)₂], which is a monomer with coordinated BH₄⁻ ions, it is likely that most of the other complexes are also polymers and therefore are formulated as such. However, they are soluble in solvents such as CH₃CN indicating dissociation in solution.

Positive ion ESI mass spectra of the bis-substituted compounds run in CH₃CN all show peaks at m/z at 449 (relative intensity 100%) assigned to the $[Cu(tcep)_2]^+$ and 297 $[Cu(tcep)(CH_3CN)]^+$ ions (except for the cyano complex for which the latter peak is observed with 25% intensity) and a peak at 256 assigned to the $[Cu(tcep)]^+$ (15-40%) and at 145 assigned to the $[Cu(CH_3CN)_2]^+$ (10-20%). The ESI mass spectra of the 1:1 [CuX(tcep)] compounds display the same mass spectra as above indicating the anions are

removed from the species and that the resulting $[Cu(tcep)]^+$ fragment combines with tcep or CH₃CN in the spectrometer.

3.2. IR and ${}^{31}P{}^{1}H$ NMR Spectroscopies

Selected bands from the IR and the ${}^{31}P{}^{1}H{}$ NMR spectra are listed in the Experimental section. As well as coordination to copper through the phosphorus atom in a monodentate binding mode, it was anticipated, that for first row transition metals, a second binding mode could occur where tcep binds to copper via P and bridges to another copper via one of its nitrile groups. It has been stated that this latter mode should be indicated by an increase in the C=N stretching frequency to the region 2275-2310 cm⁻¹ (from 2254 cm⁻¹ for the free ligand) if the σ donation from the N is high, otherwise weaker interactions would result in a smaller increase [6]. Apart from $[Cu(BH_4)(tcep)_2]$, for each compound a principal v(C=N) absorption below 2254 cm⁻¹ can be identified with a shoulder at about 2270 cm⁻¹ which points to P-bonded species with bound cyanoethyl groups as confirmed by the single crystal X-ray structures (see Section 3.3). The IR spectrum of the perchlorate, $[Cu(tcep)_2]_n(ClO_4)_n$, is consistent with the anion being noncoordinated as shown by its crystal structure and the spectra of the nitrate and hexafluorophosphate compounds are consistent with those complexes also having noncoordinated anions.

The ³¹P NMR spectra in CD₃CN of $[Cu(tcep)_2]_n(ClO_4)_n$ and $[Cu(tcep)_2]_n(PF_6)_n$ display slightly broadened signals at -13.9 and -14.4 ppm (compared to -25.0 ppm for the free ligand) respectively due to the coordinated tcep while the latter also displays the expected PF₆⁻ septuplet at -145 ppm. For $[Cu(SCN)(tcep)]_n$ a signal appears at -13.4 ppm

suggesting a similar species formed in solution as for the other complexes. Each of the complexes also displays a weak phosphine oxide signal at 43.5 ppm as a result of oxidation of dissociated tcep in solution.

3.3 Molecular Structures

Table 2

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3.3 Molecular Structures				
Table 2				0-
Selected bond lengths (Å) for	r the complexe	s.	ſ	
Complex	Cu-N(tcep)	Cu-P	Cu-X	Cu-Y
[CuBr(toon)]	1.065(0)	$\frac{2}{2} \frac{2}{2} \frac{2}{2} \frac{2}{2} \frac{1}{2} \frac{2}{2} \frac{2}{2} \frac{1}{2} \frac{1}$	2 5012(18)	2 5520(18)
	1.903(9)	2.201(3)	2.3013(18)	2.3329(18)
$\mathbf{X} = \mathbf{Y} = \mathbf{B}\mathbf{r}$				
$[Cu(BH_4)(tcep)_2]$		2.2418(13)	1.83(3)	1.85(3)
X = Y = H		2.2536(12)		
$[Cu(TFA)(tcep)_2]_n \cdot nCH_3CN$	2.012(2)	2.2328(8)	2.099(2)	
X = O		2.2487(8)	3.123(2)	
[Cu(SCN)(tcep)] _n	2.021(3)	2.2184(9)	2.3983(13)	1.994(3)
X = S, Y = N(SCN)	\sim			
$[Cu(CN)(tcep)_2]_n \cdot nCH_3CN$		2.2741(14)	1.000(4)	1.079(4)
$X = Y = C/N(CN^{-})$		2.2813(13)	1.996(4)	1.978(4)
$[Cu(tcep)_2]_n(ClO_4)_n \cdot nC_3H_6O$	1.997(5)	2.2337(16)		
	2.043(5)	2.2349(16)		

3.3.1 $[CuBr(tcep)]_n$

Crystals of [CuBr(tcep)]_n were grown by reacting equimolar quantities of CuBr and tcep in refluxing CH₃CN, filtering hot, and leaving the solution to cool. The structure displayed a ring containing two copper atoms and two bridging bromides. One nitrile group per tcep coordinates to the copper centre forming a coordination polymer

(see Fig. 1), giving a 'PNBr₂' coordination sphere around the copper. The Cu-N bond length of 1.965(9) Å (Table 2) is similar to that of 2.029(1) Å found in $[Cu(L^2)_2)(tcep)_2]_n$ $[L^2 = dihydrobis(3-nitro-1,2,4-triazolyl)borate] [15]$ which also contains the tcep ligand linking copper centres. The two remaining 'free' arms of the tcep fill the cavity between the polymer chains, and show weak interactions between the nitrile nitrogen and the hydrogens of the adjacent alkyl arm (2.613 Å). The Cu-Br bond lengths of 2.5013(18) and 2.5527(18) Å are similar to those found in other 'Cu₂Br₂' systems that have both a P and N ligand bound to the copper (2.47-2.56 Å [21]).



Fig. 1. A polymer segment of [CuBr(tcep)]_n (hydrogens removed for clarity).

The Tolman cone angle around the phosphorus tcep atom in $[CuBr(tcep)]_n$ at 71.4° lies in the range (71-80°) found for all the complexes reported in this study (Table 3).

Table 3

Tolman cone angles.

	Tolman cone angle (°)		
	P(1)	P(2)	
[CuBr(tcep)] _n	71 A(2)		
(X = Y = Br)	/1.4(2)		
$[Cu(BH_4)(tcep)_2]$	79 24(6)	76 20(6)	
(X = Y = H)	78.34(0)	/0.20(0)	
[Cu(TFA)(tcep) ₂] _n ·nCH ₃ CN	79 21(1)	77 77(4)	
$(\mathbf{X} = \mathbf{O})$	/0.31(4)	//.//(4)	
[Cu(SCN)(tcep)] _n	74 02(0)		
(X = S, Y = N(SCN))	74.23(2)		
$[Cu(CN)(tcep)_2]_n \cdot nCH_3CN$	75 63(9)	76 71(9)	
$(X = Y = C/N(CN^{-}))$	13.02(8)	/0./1(8)	
$[Cu(tcep)_2]_n(ClO_4)_n \cdot nC_3H_6O$	79.91(8)	78.27(8)	

3.3.2 [*Cu*(*BH*₄)(*tcep*)₂]

The crystal structure of $[Cu(BH_4)(tcep)_2]$ shows a discrete molecule consisting of two tcep ligands coordinated to the copper atom and a BH_4^- anion acting in a chelating fashion (see Fig. 2). The Cu-P bond lengths are 2.536(12) and 2.2418(13) Å (Table 2) and the Cu-B distance is 2.222(5) Å. A comparison with $[Cu(BH_4)(PPh_3)_2]$ shows that $[Cu(BH_4)(tcep)_2]$ has longer Cu-P bonds but a shorter Cu-B bond [Cu-P 2.276(1)] and Cu-B 2.184(9) Å] [22].

The arms of the tcep sit in three different positions: two attached to P(1) point away from the complex while the third and one from P(2) sit in the umbrella position. The remaining two arms of P(2) form an inverted umbrella. These positions appear to be

driven by weak interactions between the nitrile nitrogens and hydrogen atoms of other alkyl arms.



Fig. 2. Crystal structure of $[Cu(BH_4)(tcep)_2]$ (all hydrogens except those of BH_4^- have been removed for clarity).

3.3.3. $[Cu(TFA)(tcep)_2]_n \cdot nCH_3CN$

The structure of $[Cu(TFA)(tcep)_2]_n \cdot nCH_3CN$ shows a coordination polymer consisting of one TFA, two tcep (via the phosphorus) and one nitrile group from an adjacent tcep coordinating to the copper centre (see Fig. 3). The Cu-P bond lengths are 2.2328(8) and 2.2487(8) Å (Table 2), similar to all the diphosphine complexes in this study (see Table S1.3), while the Cu-O bond lengths are 2.099(1) and 3.123(1), showing that the TFA is coordinating in a monodentate fashion. As with the other complexes, the remaining 'free' arms of the tcep fill in the cavities between the polymer chains.



Fig. 3. A polymer segment of $[Cu(TFA)(tcep)_2]_n \cdot nCH_3CN$ (hydrogens and an acetonitrile solvate molecule removed for clarity).

3.3.4. $[Cu(SCN)(tcep)]_n$ and $[Cu(CN)(tcep)_2]_n \cdot nCH_3CN$

Both $[Cu(SCN)(tcep)]_n$ and $[Cu(CN)(tcep)_2]_n \cdot nCH_3CN$ feature coordinating bridging anions, but have very different structures. The crystal structure of $[Cu(CN)(tcep)_2]_n \cdot nCH_3CN$ shows a coordination polymer with a $(-Cu-CN-)_n$ backbone (see Fig. 4), with the cyanide nitrogen and carbon being disordered. Two phosphine ligands are also coordinated to the copper centre with bond lengths of 2.2812(13) and 2.2741(14) Å (Table 2). The arms of the tcep are all in an inverted umbrella position showing no interactions with the metal centre, and again only displaying weak interactions between adjacent arms.



Fig. 4. A polymer segment of $[Cu(CN)(tcep)_2]_n \cdot nCH_3CN$ (hydrogens and acetonitrile molecule removed for clarity). Note: crystallographic symmetry causes disorder of the cyano species [atoms labelled C(1)-N(1)].

In contrast, the crystal structure of $[Cu(SCN)(tcep)]_n$ shows a 3-dimensional lattice formed by SCN^- anions acting as bridging ligands between copper centres and one of the tcep arms coordinating to a different copper atom via the nitrile group (see Fig. 5). Although large cavities are formed, the two 'free' arms of the tcep fold to occupy the space. Space filling models offer no suggestions of accessible free space.



Fig. 5. Left: a segment of the $[Cu(SCN)(tcep)]_n$ lattice (hydrogens removed for clarity). Right: a cavity formed within the network (hydrogen and free arms removed for clarity).

3.3.5. $[Cu(tcep)_2]_n(ClO_4)_n \cdot nC_3H_6O$

 $[Cu(tcep)_2]_n(ClO_4)_n \cdot nC_3H_6O$ forms a different structure again with the ClO₄⁻ anion not being coordinated to the copper atom. It remains disordered, as is the acetone molecule, both requiring EADP restraints. Instead, the copper coordination sphere consists of two P-bound tcep ligands and two nitrile groups from other tcep ligands (see Fig. 6). This forms a two-dimensional lattice with two arms of P(1) coordinating while the arms attached to P(2) arranged themselves in an inverted umbrella fashion. The Cu-P bond lengths at 2.23491(16) and 2.2337(16) Å (Table 2) are similar to the other diphosphine complexes in this report. The uncoordinated perchlorate anion sits in-plane of the square formed by the copper atoms while the disordered acetone molecule sits

adjacent to the disordered cyanoethyl arm, comprising atoms C(17), C(18) and N(6), above the plane of the copper square.



Fig. 6. Left: a segment of the $[Cu(tcep)_2]_n(ClO_4)_n$ lattice (hydrogens, a solvate species and a disordered, non-coordinated perchlorate ion removed for clarity). Right: a square plane formed within the lattice (hydrogens removed for clarity). Note: the cyanoethyl arm comprising atoms C(17), C(18) and N(6) is disordered.

4. Conclusions

The potentially multidentate ligand, tcep, reacts with the copper(I) compounds, CuX (X = Cl, Br, I and SCN) in a 1:1 ratio to give the1:1 salts CuX(tcep). X-ray crystal structures show for X = Br the copper has a 'PNBr₂' coordination sphere while the sphere is 'PNSN' for X = SCN. In both cases the anions act as bridging ligands and coordination

polymers are formed by one of the tcep arms coordinating to another Cu centre via the nitrile group. In contrast, with CuY ($Y = BH_4$, TFA, CN, ClO₄) tcep reacts to give the 2:1 salts CuY(tcep)₂. For the complex $[Cu(tcep)_2]_n(ClO_4)_n \cdot nC_3H_6O$, the ClO₄⁻ anion does not coordinate with the result that the copper has a P_2N_2 coordination sphere with two arms of one of the tcep molecules binding in an intermolecular fashion to other Cu centres via the nitrile groups to form a two-dimensional lattice. The nitrile arms of the second tcep do not bind to other Cu centres and are arranged in an inverted umbrella fashion. For the other complexes each of the Y anions bind to the copper so fewer arms of the tcep are needed to achieve a coordination number of four. For $[Cu(BH_4)(tcep)_2]$ the anion binds in a chelate fashion and hence copper has a P_2H_2 coordination sphere with no nitrile groups bound, while for $[Cu(TFA)(tcep)_2]_n$ the TFA binds in a monodentate fashion and the copper has a 'P₂ON' coordination sphere with one nitrile from an adjacent tcep bound, and for $[Cu(CN)(tcep)_2]_n$ the CN bridges copper sites to give copper a 'P₂CN' coordination set and no nitrile groups are required. Remarkably all complexes are strictly four-coordinate and closely tetrahedral. The Cu-N(tcep) bond distances range from 1.965(9) in $[CuBr(tcep)]_n$ to 2.043(5) Å in $[Cu(tcep)_2]_n(ClO_4)_n \cdot nC_3H_6O$. Correspondingly the Cu-P bond distances range from 2.201(3) in $[CuBr(tcep)]_n$ to 2.2813(13) Å in $[Cu(CN)(tcep)_2]_n \cdot nCH_3CN$. The Tolman cone angles around the phosphorus tcep atoms in the complexes all lie in the range $71-80^{\circ}$ in contrast to the larger angles of 132° for the free ligand [4] and 175° for the coordinated ligand in [Ag(tcep)₂]NO₃ [5]. These variations are an indication of the ability of the tcep ligands to readily adapt to different environments.

Acknowledgements

We thank the Massey University Research Fund for financial support and a PhD Scholarship (to R. J. D.). We also thank Associate Professor S.G. Telfer and the MacDiarmid Institute for Advanced Materials and Nanotechnology for the use of the Spider Diffractometer. 9^C

Appendix A. Supplementary material

CCDC 986228 - 986233 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 or from the CCDC, 12 Union Road, Cambridge, CB21EZ,UK; E-mail: deposit@ccdc.cam.ac.uk. Supplementary data (bond lengths and angles) associated with this article can be found in the online version at -----.

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Figure Captions

Fig. 1. A polymer segment of [CuBr(tcep)]_n (hydrogens removed for clarity).

Fig. 2. Crystal structure of $[Cu(BH_4)(tcep)_2]$ (all hydrogens except those of BH_4^- have been removed for clarity).

Fig. 3. A polymer segment of $[Cu(TFA)(tcep)_2]_n \cdot nCH_3CN$ (hydrogens and acetonitrile molecule removed for clarity).

Fig. 4. A polymer segment of $[Cu(CN)(tcep)_2]_n \cdot nCH_3CN$ (hydrogens and acetonitrile molecule removed for clarity). Note: crystallographic symmetry causes disorder of the cyano species [atoms labelled C(1)-N(1)].

Fig. 5. Left: a segment of the $[Cu(SCN)(tcep)]_n$ lattice (hydrogens removed for clarity). Right: a cavity formed within the network (hydrogen and free arms removed for clarity).

Fig. 6. Left: A segment of the $[Cu(tcep)_2]_n(ClO_4) \cdot nC_3H_6O$ lattice (hydrogens removed for clarity); Right: A square plane formed within the lattice (hydrogen removed for clarity).

















Graphical Abstract

The potentially multidentate ligand, tris(2-cyanoethyl)phosphine (tcep), reacts with copper(I) to give 1:1 salts CuX(tcep) (X = Cl, Br, I and SCN) or 2:1 salts CuY(tcep)₂ (Y = BH₄, CF₃COO, CN and ClO₄). Single crystal X-ray studies show a variety of structural types have been formed with either coordinated or non-coordinated anions.

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