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Tetrahalidocuprates(II) – structure and EPR spectroscopy

Part 2: tetrachloridocuprates(II)

Tetrahalidocuprates(II) – structure and EPR spectroscopy. Part 2: tetrachloridocuprates(II)†

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We present and discuss the results of crystallographic and electron paramagnetic resonance (EPR) spectroscopic analyses of five tetrachloridocuprate(II) complexes to supply a useful tool for the structural characterisation of the $[CuCl_4]^{2-}$ moiety in the liquid state, for example in ionic liquids, or in solution. Bis(benzyltriethylammonium)-, bis(trimethylphenylammonium)-, bis(ethyltriphenylphosphonium)-, bis(benzyl-triphenylphosphonium)-, and bis(tetraphenylarsonium)tetrachloridocuprate(II) were synthesised and characterised by elemental, IR, EPR and X-ray analyses. The results of the crystallographic analyses show distorted tetrahedral coordination geometry of all $[CuCl_4]^{2-}$ anions in the five complexes and prove that all investigated complexes are stabilised by hydrogen bonds of different intensities. Despite the use of sterically demanding ammonium, phosphonium and arsonium cations to obtain the separation of the paramagnetic Cu(II) centres for EPR spectroscopy no hyperfine structure was observed in the EPR spectra but the principal values of the electron Zeeman tensor, $g_{\parallel}$ and $g_{\perp}$, could be determined. With these EPR data and the crystallographic parameters we were able to carry out a correlation study to anticipate the structural situation of tetrachloridocuprates in different physical states. This correlation is in good agreement with DFT calculations.

Introduction

In the previously published article "Tetrahalidocuprates(II) – structure and EPR spectroscopy. Part 1: Tetrabromidocuprates(II)"[1] we considered the tetrahalidocuprates(II) in general and focused on tetrabromidocuprates(II). The current article deals with the tetrachloridocuprate(II) complexes which have been investigated over a long period of time, for example by W. M. Dehn[2] in 1926 or by H. Remy and G. Laves[3] in the early 1930s. L. Helmholz and R. F. Kruh published the first crystal structure of such a copper complex with a simple inorganic cation, $Cs_2[CuCl_4]$, in 1952.[4] The variety of cations ranges from simple inorganic cations[4,5–8] to more complex inorganic[9,10] as well as organic cations[5,11–46] which can be aryl- or alkyl-substituted ammonium, phosphonium, pyridinium, sulfonium, and imidazolium ions. N. S. Gill and R. S. Nyholm were pioneers in the syntheses of halidocuprates with a more complex organic cation, *i.e.*, $(As(C_6H_5)_3CH_3)^+$.[17] These authors provided magnetic susceptibility measurements for tetrachloridocuprate(II) complexes and assigned the reduced susceptibilities (1.91 B.M. *vs.* 2.2 B.M. for a perfect tetrahedron) to deviations from perfect tetrahedral coordination in the $[CuCl_4]^{2-}$ moiety. Depending

on the nature of the counter cation these compounds show an impressive structural flexibility between square planar and an almost tetrahedral geometry. This variability of the bond angles in the $[CuCl_4]^{2-}$ anion leads to variable chemical and physical properties of the complexes. As a result, tetrahalidocuprates are interesting for research and technology, such as catalysis. Accordingly, E. Lukevics *et al.* demonstrated the catalytic activity of chloridometallates in the hydrosilylation of phenylacetylene,[47] and E. N. Golubeva and co-workers presented investigations on tetrachloridocuprate(II) complexes as catalyst precursors for C–Cl bond metathesis.[48–50] Furthermore, Y. Iwasawa *et al.* reported an immobilised chloridocuprate(II) ionic liquid including its catalytic performance in the Kharasch reaction,[51] and J. Sundermeyer *et al.* used ionic liquids comprising a chloridocuprate anion for oxidation of trimethylphenol[52] or in oxidative methanol carbonylation.[53] $[CuCl_4]^{2-}$ based ionic liquids have also been used as antimicrobial agents.[54]

In 1974, R. D. Willett *et al.*[55] and R. L. Harlow *et al.*[56] described Cu(II) complexes exhibiting thermochromism. The reversible colour change from green to yellow while increasing temperature is interpreted as a phase transition leading to a change in coordination geometry from square planar to distorted tetrahedral. Further studies on other thermochromic substances followed.[8,35,57–62]

Indeed, tetrachloridocuprates(II) exhibit additional interesting features: thermotropic ionic liquid crystals based on tetra-chloridocuprates with an alkylpyridinium ion with an alkyl chain length of $n \geq 12$ were first reported by F. Neve *et al.* in

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2001.[63] If the alkyl chain length is shorter the compounds are ionic liquids (ILs). Their thermotropic liquid crystalline behaviour and crystal structures have been further investigated using differential scanning calorimetry (DSC), powder X-ray diffraction (XRD) or polarizing optical microscopy (POM).[64–66] Furthermore, tetrachloridocuprates were also used as precursors for inorganic materials like copper sulfide nanoparticles[67] or copper chloride platelets. The latter were obtained from ILs or ionic liquid crystals (ILCs).[68–71]

There is still much interest in structure determination of chloridocuprates(II) because "such a determination, when it is well done, ends speculation and provides us with the starting point for the understanding of every physical, chemical, and biological property of the molecule".[72] Thus, there is an appreciable number of attempts to correlate structural parameters, *i.e.*, the degree of distortion of the $[CuCl_4]^{2-}$ moiety with its spectral parameters using UV-Vis,[29,55,73,74] EPR spectroscopy[75,76] or other methods.[9,77,78] Especially EPR spectroscopy is well suited for the investigation of copper(II) compounds under a variety of conditions. With this method it is possible to study the samples such as tetrachloridocuprates(II) and their electronic situation in various physical states; *i.e.*, liquids and solids (powder, frozen solution, and single crystal), even an investigation of dynamic systems like ionic liquids is possible.[79] Thus, the literature on Cu(II) complexes examined by EPR spectroscopy increases. Some of the work focused on the investigation of single crystals,[44,80–88] powders[43,89–91] or of Cu^{2+} solutions.[48,49,76,92–94] Other authors investigated the photolysis of a $[CuCl_4]^{2-}$ complex by observing a decreasing EPR signal intensity.[50] R. H. Borcherts and co-workers combined EPR measurements with a strain experiment where they observed an increasing intensity of the parallel part *vs.* the perpendicular part in the EPR spectrum of the stressed crystal.[95] The relaxation behaviour of Cu^{2+} in a tetrahedral crystal field was studied by R. A. Vaughan.[96]

The theoretical background of the tetrachloridocuprate system is well investigated.[97–99] Thus, it is also used as a model system for other copper systems.[100]

In addition to the previously described tetrabromidocuprate series[1] we have now examined the tetrachloridocuprate complexes to provide a correlation of their experimental EPR data with the degree of distortion in the $[CuCl_4]^{2-}$ moieties. To that end we synthesised five tetrachloridocuprates(II) and characterised them mainly by X-ray diffraction and EPR spectroscopy. The EPR–X-ray crystal structure correlation was further achieved *via* an extensive comparison with published data trying to answer the question: is there a way to predict or extract structural information on tetrachloridocuprate complexes only from EPR data?

Experimental

Chemicals

The following chemicals were used without further purification: copper(II) chloride dihydrate (99%, Alfa Aesar), potassium bromide (Uvasol, for IR spectroscopy, Merck), benzyltriethylammonium chloride (>98%, Merck), trimethylphenylammonium chloride

(>99%, Merck), ethyltriphenylphosphonium chloride (98%, ABCR), benzyltriphenylphosphonium chloride (99%, Sigma-Aldrich), tetraphenylarsonium chloride (Fluka), hydrochloric acid (37%, A.C.S. reagent, Sigma-Aldrich), *n*-hexane (96%, Riedel-de Haen), diisopropyl ether (>99%, Merck), propan-2-ol (>99%, Fisher Chemicals), methylene chloride (>99%, Merck), and acetone (>99.8%, Roth).

Preparation

Tetrachloridocuprate(II) complexes can be made by different procedures.[15,47,57,101–103] For our complexes one synthesis turned out to be very suitable. At first copper(II) chloride dihydrate is dissolved in hydrochloric acid (37% wt). This is followed by addition of the counter ion as a chloride salt dissolved in a suitable solvent (propan-2-ol or methylene chloride). After 30 minutes of heating under reflux the solvent is evaporated until the complex precipitates.[102]

Bis(benzyltriethylammonium)tetrachloridocuprate(II), (BzlEt₃N)₂-[CuCl₄] (1). For complex **1** 2.0 mmol (0.46 g) of BzlEt₃NCl were dissolved in 10 mL of propan-2-ol and mixed with 1.0 mmol (0.17 g) of copper(II) chloride dihydrate, previously dissolved in 1.2 mL of hydrochloric acid. After heating, the solution was slowly evaporated to get orange crystals. A yellow powder was obtained by washing the concentrated solution with acetone.[79]

Melting point: 107–109 °C. Yield: 0.40 g (68%). Elemental analysis calculated for $C_{26}H_{44}N_2CuCl_4$ (590.00): C 52.93, H 7.52, N 4.75 (%), found: C 52.83, H 7.45, N 4.78 (%). IR (KBr, cm⁻¹): 3055 w, 2986 m, 2945 w, 1581 w, 1479 s, 1454 w, 1389 ms, 1209 m, 1154 s, 1008 s, 900 m, 793 s, 753 s, 709 s, 604 w, 537 w, 463 w.

Bis(trimethylphenylammonium)tetrachloridocuprate(II), (Me₃PhN)₂[CuCl₄] (2). This complex was synthesised using the following quantities: 0.5 mmol (0.09 g) CuCl₂·2H₂O dissolved in 0.6 mL of HCl were added to 1.0 mmol (0.17 g) Me₃PhNCl dissolved in 5 mL of propan-2-ol and heated. Afterwards the alcoholic solution was evaporated until a yellow powder precipitated. Yellow crystals were obtained by covering 1 mL of the diluted solution with diisopropyl ether.

Melting point: 164–165 °C. Yield: 0.20 g (83%). Elemental analysis calculated for $C_{18}H_{28}N_2CuCl_4$ (477.79): C 45.25, H 5.91, N 5.86 (%), found: C 45.15, H 5.87, N 5.90 (%). IR (KBr, cm⁻¹): 3059 w, 3033 m, 1594 w, 1492 s, 1462 s, 1409 m, 1298 w, 1167 w, 1121 w, 1030 w, 997 w, 948 ms, 846 m, 766 s, 695 s, 555 m.

Bis(ethyltriphenylphosphonium)tetrachloridocuprate(II), (EtPh₃P)₂[CuCl₄] (3). Complex **3** was prepared by dissolving 0.5 mmol (0.09 g) of CuCl₂·2H₂O in 0.6 mL of hydrochloric acid and 1.0 mmol (0.33 g) of ethyltriphenylphosphonium chloride in 2 mL of propan-2-ol. The latter was added to the copper solution and the mixture was heated. The solution was diluted and covered with diisopropyl ether to obtain orange crystals.

Melting point: 190–191 °C. Yield: 0.28 g (72%). Elemental analysis calculated for $C_{40}H_{40}P_2CuCl_4$ (788.07): C 60.96, H 5.12 (%), found: C 60.89, H 5.10 (%). IR (KBr, cm⁻¹): 3054 w, 2927 w, 2891 w, 1584 w, 1484 w, 1437 s, 1317 w, 1114 s, 1030 wm, 994 m, 735 s, 719 s, 689 s, 531 s, 503 m, 484 m, 460 w.

Bis(benzyltriphenylphosphonium)tetrachloridocuprate(ɪɪ), **(BzlPh$_3$P)$_2$[CuCl$_4$]·2CH$_2$Cl$_2$ (4).** For complex **4** the following quantities were used: 5.0 mmol (0.85 g) of CuCl$_2$·2H$_2$O dissolved in 6 mL of hydrochloric acid and 0.01 mol (3.89 g) of benzyltriphenylphosphonium chloride previously dissolved in 40 mL of methylene chloride. The mixture was heated under reflux for 30 minutes. Yellow crystals were obtained by covering 1 mL of the organic phase with *n*-hexane.

Melting point: 137–139 °C. Yield: 4.83 g (89%). Elemental analysis calculated for C$_{52}$H$_{48}$P$_2$CuCl$_8$ (1082.05): C 57.72, H 4.47 (%), found: C 57.97, H 4.45 (%). IR (KBr, cm^{-1}): 3056 w, 2921 w, 2885 w, 1585 w, 1485 w, 1437 s, 1397 w, 1111 s, 1071 w, 995 wm, 823 w, 786 w, 750 m, 720 m, 689 s, 583 m, 512 s, 496 m, 444 w.

Bis(tetraphenylarsonium)tetrachloridocuprate(ɪɪ), (Ph$_4$As)$_2$-[CuCl$_4$] (5). For this complex 1.0 mmol (0.42 g) of tetraphenylarsonium chloride were dissolved in 10 mL of methylene chloride and then added to 0.5 mmol (0.09 g) of CuCl$_2$·2H$_2$O dissolved in 0.6 mL of HCl. After heating the phases were separated and 1 mL of the organic phase was covered with *n*-hexane to obtain crystals.

Melting point: 209–212 °C. Yield: 0.28 g (72%). Elemental analysis calculated for C$_{48}$H$_{40}$As$_2$CuCl$_4$ (972.03): C 59.31, H 4.15 (%), found: C 58.72, H 4.04 (%). IR (KBr, cm^{-1}): 3050 m, 1640 m, 1575 w, 1477 m, 1437 s, 1312 m, 1390 ms, 1185 m, 1162 m, 1078 s, 1021 w, 994 m, 842 w, 742 s, 687 s, 520 w, 467 s.

Methods

The melting points were determined using a 'Mikroheiztisch Boetius'. Elemental analyses were carried out on an Elementar Vario EL III analyzer. Infrared spectra were recorded on a Perkin-Elmer type 16PC FT-IR spectrophotometer between 4000 and 400 cm^{-1} as KBr-Pellets (reference KBr).

EPR spectra were recorded at 9.4 GHz (X-band) using a Bruker CW Elexsys E 500 spectrometer and at ∼34 GHz (Q-band) using a Bruker EMX spectrometer.

For X-ray structure determinations the crystals were embedded in perfluoropolyalkylether oil and mounted on a glass fibre. Intensity data were collected at 210 K using a STOE Imaging Plate Diffraction System IPDS-2 with graphite monochromatized Mo-Kα radiation (λ = 0.71073 Å) at 50 kV and 40 mA. The data were corrected by numerical absorption correction using the program X-Area (Stoe, 2004) as well as for Lorentz polarisation and extinction effects. The structures were solved by direct methods using SHELXS-97[104] and refined by full-matrix least-squares on F^2 using the program SHELXL-97.[105] All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were calculated in their expected positions and refined with U_{iso}(H) = 1.2 U_{eq}(C). In **4** one of the two solvent molecules and in **5** the [CuCl$_4$]$^{2-}$ moiety are disordered. The unit cell of **5** contains solvent. In spite of several attempts, no reasonable solution could be obtained for the solvent species. PLATON/SQUEEZE[106] calculated a total potential accessible void volume of 84.1 Å and the number of electrons of 29.3 per unit cell. That value roughly correlates with the number of water molecules of 0.75 per asymmetric unit (0.75 × 10 × 4 = 30). The contribution of the disordered solvent species was subtracted from the

structure factor calculations but was included in the overall formula, the formula weight, the density, F(000) and μ. For the visualisation of the structures the graphic program DIAMOND[107] was used.

CCDC 958653 (**1**), 958654 (**2**), 958655 (**3**), 958656 (**4**) and 958657 (**5**) contain the supplementary crystallographic data for this paper.

All quantum chemical calculations were done using the B3LYP hybrid functional together with an aug-cc-pVTZ basis as implemented in Gaussian09.[108] We employed the Gauge-Independent Atomic Orbital (GIAO) method to calculate the magnetic properties.[109] We note that the precise prediction of magnetic properties with hybrid functionals is not very reliable (see *e.g.* ref. 110 and references therein). However, here we focus on general trends for the structure–property relationship and the used methodology seems to work surprisingly well in the present case (see Discussion).

Results

In the following parts we present and discuss the results of the studied tetrachloridocuprate complexes which can be easily achieved by the reaction of copper(ɪɪ) chloride and a chloride salt. We focus on structural information and EPR measurements supported by quantum chemical calculations (DFT) to investigate the structure–EPR relationship for this system.

Single crystal X-ray structures of the complexes

Only the structural features of the tetrachloridocuprate anions and their crystal packing, *i.e.*, hydrogen contacts and Cu···Cu and Cl···Cl distances, are discussed due to possible interactions, because the cations do not provide any new information.

The long hydrogen contacts, *viz.* C–H···Cl, must be considered as weak hydrogen bonds. In the following discussion of the crystal structures hydrogen bonds which were set to the sum of the van der Waals radii[111] minus 0.12 Å (Jeffrey criterion; for H···A 2.83 Å) are given as well as weaker hydrogen contacts generated by the program SHELXL-97[105] (marked with *). Hydrogen bonds whose angle (D–H···A) is lower than 120° were cut off.[112] Possible hydrogen interactions are highlighted (dashed red lines) in the corresponding view of the crystal structure.

The crystallographic data and refinement parameters for the copper complexes **1**–**5** are listed in Table 1.

Bis(benzyltriethylammonium)tetrachloridocuprate(ɪɪ) (1). (BzlEt$_3$N)$_2$[CuCl$_4$] (**1**) crystallises in the non-centrosymmetric space group $P2_1/c$ with four formula units per unit cell. Table 2 lists selected bond lengths and angles of the compound **1**. The shortest Cu···Cu distances are 8.79 and 9.30 Å, the intra-molecular Cl···Cl distances are between 3.42 and 4.11 Å. As expected the tetrachloridocuprate(ɪɪ) moiety shows a distorted tetrahedral geometry. The crystal structure of **1** is stabilised by several hydrogen bonds (Table 3). They occur between the chlorine atoms and the hydrogen atoms of the ethyl–CH$_2$ groups, weaker hydrogen contacts are also observed between Cl and the hydrogen atoms of the benzyl–CH$_2$-group. Fig. 1 provides a stereoscopic

Table 1 Crystallographic data and refinement parameters for the tetrachloridocuprate(II) complexes **1–5**

Compound	(BzlEt₃N)₂[CuCl₄] (**1**)	(Me₃PhN)₂[CuCl₄] (**2**)	(EtPh₃P)₂[CuCl₄] (**3**)	(BzlPh₃P)₂[CuCl₄]·2CH₂Cl₂ (**4**)	(Ph₄As)₂[CuCl₄]·0.75H₂O (**5**)
Empirical formula	C₂₆H₄₄N₂CuCl₄	C₁₈H₂₈N₂CuCl₄	C₄₀H₄₀P₂CuCl₄	C₅₂H₄₈P₂CuCl₈	C₄₈H₄₁.₅O₀.₇₅As₂CuCl₄
M/g mol⁻¹	590.00	477.79	788.05	1082.05	985.54
Crystal colour	Orange	Yellow	Orange	Yellow	Yellow
Crystal size/mm	0.7 × 0.45 × 0.3	0.4 × 0.15 × 0.15	0.48 × 0.4 × 0.35	2 × 0.87 × 0.37	0.6 × 0.48 × 0.4
Crystal form	Block	Block	Prism	Prism	Block
Crystal system	Monoclinic	Triclinic	Orthorhombic	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P1$	$Pccn$	$C2/c$	$P2_1/n$
a/Å	14.607(3)	8.5804(6)	11.9429(3)	40.6863(8)	16.9900(9)
b/Å	11.5592(15)	8.8402(7)	17.3997(5)	13.2243(4)	13.6667(4)
c/Å	17.378(3)	9.0740(7)	18.2717(5)	19.3006(4)	20.1376(10)
α/°	90	65.411(6)	90	90	90
β/°	99.097(15)	63.947(6)	90	100.397(2)	108.961(4)
γ/°	90	69.209(6)	90	90	90
V/Å³	2897.4(8)	549.64(7)	3796.91(18)	10 214.1(4)	4422.2(3)
Z	4	1	4	8	4
$F(000)$	1244	247	1628	4440	1994
Density/mg m⁻³	1.352	1.443	1.378	1.407	1.480
μ/mm⁻¹	1.140	1.484	0.969	0.944	2.255
Θ range/°	2.12–25.00	2.59–24.99	2.07–25.00	1.62–25.00	1.83–25.00
R_{int}	0.1537	0.0230	0.0225	0.1250	0.0476
Refl. measured	36 209	4930	46 132	65 119	28 183
Refl. independent	5106	3282	3340	8992	7780
Parameters	296	227	214	578	515
R_1/wR_2 [$I > 2\sigma(I)$]	0.0342/0.0944	0.0272/0.0745	0.0208/0.0584	0.0454/0.1263	0.0248/0.0615
R_1/wR_2 (all data)	0.0380/0.0968	0.0285/0.0757	0.0235/0.0593	0.0525/0.1318	0.0324/0.0636
Goodness of fit	1.038	1.080	1.061	1.057	1.018
Max. diff. peak/hole/e Å³	0.49/−0.48	0.51/−0.36	0.30/−0.28	1.01/−1.08	0.43/−0.52

Table 2 Selected bond lengths and angles of (BzlEt₃N)₂[CuCl₄] (**1**)

Bond lengths/Å		Angles/°	
Cu1–Cl1	2.2686(7)	Cl1–Cu1–Cl2	100.23(2)
Cu1–Cl2	2.2458(6)	Cl1–Cu1–Cl3	98.35(2)
Cu1–Cl3	2.2578(6)	Cl1–Cu1–Cl4	130.13(3)
Cu1–Cl4	2.2617(7)	Cl2–Cu1–Cl3	130.97(3)
		Cl2–Cu1–Cl4	98.73(3)
		Cl3–Cu1–Cl4	102.98(3)

Table 3 Hydrogen bond geometry (Å, °) for complex **1**

D–H⋯A	D–H	H⋯A	D⋯A	D–H⋯A
C8–H8A⋯Cl3ⁱ	0.97	2.83	3.618(2)	139.0
C10–H10A⋯Cl1	0.97	2.82	3.729(3)	155.7
C10–H10B⋯Cl4*	0.97	2.91*	3.735(3)	143.9
C14–H14A⋯Cl2ⁱⁱ	0.97	2.97*	3.892(2)	160.1
C14–H14B⋯Cl3ⁱⁱⁱ	0.97	2.89*	3.841(2)	166.6
C24–H24A⋯Cl2ⁱⁱ	0.96	2.68	3.622(3)	168.4
C25–H25A⋯Cl2	0.97	2.81	3.468(2)	125.5
C26–H26A⋯Cl2ⁱⁱⁱ	0.96	2.91*	3.826(3)	160.4

Symmetry codes: (i) $1 - x$, $0.5 + y$, $0.5 - z$; (ii) x, $0.5 - y$, $-0.5 + z$; (iii) $-x$, $-y$, $-z$.

view of the crystal packing of **1** including some of the hydrogen contacts.

Bis(trimethylphenylammonium)tetrachloridocuprate(II) (2). (Me₃PhN)₂[CuCl₄] (**2**) crystallises in the triclinic space group $P1$ with one formula unit per unit cell. The cations of the complex consist of an ammonium centre which is tetrahedrally surrounded by a planar phenyl ring and three methyl groups. The [CuCl₄]²⁻ anion possesses a distorted tetrahedral geometry,
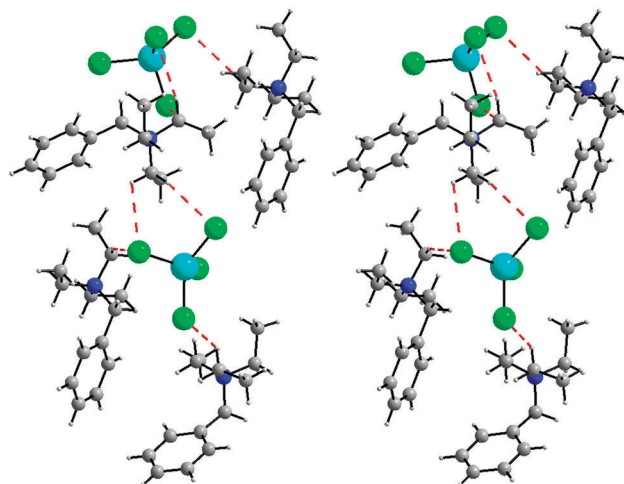
Fig. 1 Stereoscopic view of the crystal packing of (BzlEt₃N)₂[CuCl₄] (**1**).

the corresponding bond lengths and angles are listed in Table 4. The shortest Cu⋯Cu distances are 8.58 and 8.84 Å, the intramolecular Cl⋯Cl distances are between 3.37 and 4.18 Å.

Table 4 Selected bond lengths and angles of (Me₃PhN)₂[CuCl₄] (**2**)

Bond lengths/Å		Angles/°	
Cu1–Cl1	2.2591(9)	Cl1–Cu1–Cl2	99.37(3)
Cu1–Cl2	2.2609(9)	Cl1–Cu1–Cl3	135.17(3)
Cu1–Cl3	2.2402(9)	Cl1–Cu1–Cl4	96.68(3)
Cu1–Cl4	2.2509(9)	Cl2–Cu1–Cl3	98.88(4)
		Cl2–Cu1–Cl4	136.03(3)
		Cl3–Cu1–Cl4	97.87(4)
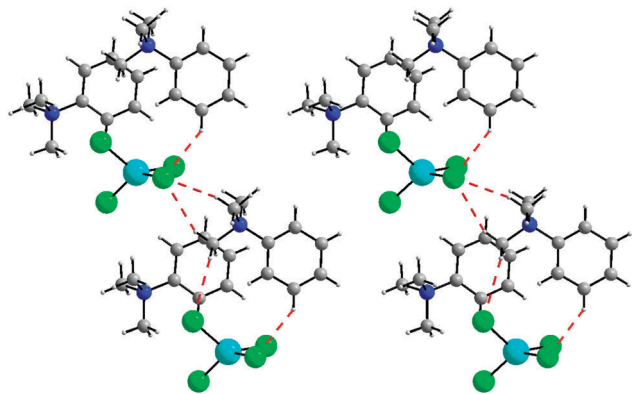
Fig. 2 Stereoscopic view of the crystal packing of (Me₃PhN)₂[CuCl₄] (2).

Fig. 3 Stereoscopic view of the crystal packing of (EtPh₃P)₂[CuCl₄] (3).

The crystal structure of (Me₃PhN)₂[CuCl₄] which is illustrated in Fig. 2 is also stabilised through several hydrogen bonds. The chlorine atom Cl4 for example exhibits three of these bonds which fulfil the Jeffrey criterion for a hydrogen atom of the phenyl ring and for hydrogen atoms of the methyl groups. Moreover, there are two weaker three-centered hydrogen interactions (Table 5).

Bis(ethyltriphenylphosphonium)tetrachloridocuprate(II) (3). (EtPh₃P)₂[CuCl₄] (3) crystallises in the orthorhombic space group *Pccn* with four formula units per unit cell. The phosphonium cation is tetrahedrally surrounded by an ethyl group and three planar phenyl rings. Similar to the previously discussed complexes the complex anion of 3 possesses a distorted tetrahedral geometry (Fig. 3) but shows the highest tendency towards a square planar geometry. The corresponding main bond lengths and angles are given in Table 6. The shortest Cu···Cu distances are 9.14 and 10.76 Å, the intramolecular Cl···Cl distances are between 3.29 and 4.19 Å.

As well as the complexes 1 and 2 the crystal structure of (EtPh₃P)₂[CuCl₄] (3) is stabilised through hydrogen bonds. Stronger bonding occurs between the chlorine atom Cl2 and the hydrogen atom H18 of a phenyl ring (Table 7) and four hydrogen atoms are weakly hydrogen-bonded to chlorine atoms.

Table 6 Selected bond lengths and angles of (EtPh₃P)₂[CuCl₄] (3)

Bond lengths/Å		Angles/°	
Cu1–Cl1	2.2348(4)	Cl1–Cu1–Cl1ⁱ	94.96(2)
Cu1–Cl2	2.2723(4)	Cl1–Cu1–Cl2	99.44(1)
		Cl1–Cu1–Cl2ⁱ	136.77(1)
		Cl2–Cu1–Cl2ⁱ	97.34(2)

Symmetry codes: (i) 0.5 − x, 0.5 − y, z.

Table 7 Hydrogen bond geometry (Å, °) for complex 3

D–H···A	D–H	H···A	D···A	D–H···A
C2–H2···Cl1	0.93	2.96*	3.884(2)	171.1
C8–H8···Cl2ⁱⁱ	0.93	2.90*	3.812(2)	167.1
C18–H18···Cl2ⁱⁱⁱ	0.93	2.70	3.552(2)	152.0
C19–H19A···Cl1ⁱ	0.97	2.84*	3.695(2)	148.1
C19–H19B···Cl2ⁱⁱ	0.97	2.87*	3.662(2)	139.0

Symmetry codes: (ii) x, 0.5 − y, 0.5 + z; (iii) 0.5 − x, y, 0.5 + z.

Bis(benzyltriphenylphosphonium)tetrachloridocuprate(II) (4). (BzlPh₃P)₂[CuCl₄]·2CH₂Cl₂ (4) crystallises in the centrosymmetric space group *C*2/*c* with eight formula units per unit cell. The shortest Cu···Cu distances are 10.39 and 10.61 Å, the intramolecular Cl···Cl distances are between 3.41 and 4.13 Å. Table 8 lists selected bond lengths and angles of the distorted tetrahedral tetrachloridocuprate. Unlike the other complexes two solvent molecules, *i.e.* methylene chloride, are incorporated in the crystal structure of 4.

As seen in Fig. 4 there are also hydrogen contacts formed by the hydrogen atoms of the solvent molecules with the

Table 5 Hydrogen bond geometry (Å, °) for complex 2

D–H···A	D–H	H···A	D···A	D–H···A
C3–H3···Cl4ⁱ	0.93	2.82	3.582(4)	140.5
C7–H7B···Cl4	0.96	2.77	3.676(7)	156.9
C8–H8B···Cl4	0.96	2.83	3.707(7)	153.1
C8–H8C···Cl1ⁱ	0.96	2.94*	3.597(7)	126.6
C9–H9A···Cl1ⁱⁱ	0.96	2.74	3.572(7)	145.6
C11–H11···Cl2ⁱⁱⁱ	0.93	2.93*	3.846(5)	168.9
C16–H16A···Cl4	0.96	2.87*	3.755(5)	153.4
C16–H16B···Cl3ⁱᵛ	0.96	2.78	3.674(5)	155.3
C16–H16C···Cl1ᵛ	0.96	2.92*	3.805(6)	154.6
C16–H16C···Cl2ᵛ	0.96	2.91*	3.615(5)	131.6
C17–H17A···Cl1ᵛ	0.96	2.90*	3.786(6)	154.8
C18–H18C···Cl1	0.96	2.88*	3.601(5)	132.7
C18–H18C···Cl4	0.96	2.87*	3.754(6)	153.2

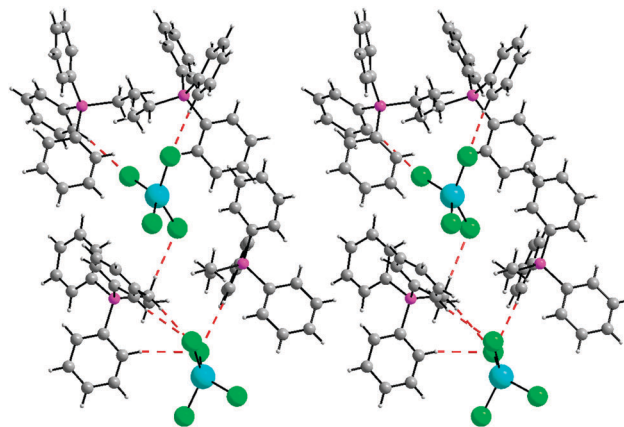Symmetry codes: (i) x, y, 1 + z; (ii) 1 + x, y, z; (iii) x, 1 + y, −1 + z; (iv) −1 + x, 1 + y, z; (v) x, 1 + y, z.

Table 8 Selected bond lengths and angles of (BzlPh₃P)₂[CuCl₄]·2CH₂Cl₂ (4)

Bond lengths/Å		Angles/°	
Cu1–Cl1	2.2722(7)	Cl1–Cu1–Cl2	100.30(3)
Cu1–Cl2	2.2344(8)	Cl1–Cu1–Cl3	100.18(3)
Cu1–Cl3	2.2572(8)	Cl1–Cu1–Cl4	132.09(3)
Cu1–Cl4	2.2498(8)	Cl2–Cu1–Cl3	131.01(3)
		Cl2–Cu1–Cl4	98.98(3)
		Cl3–Cu1–Cl4	99.29(4)
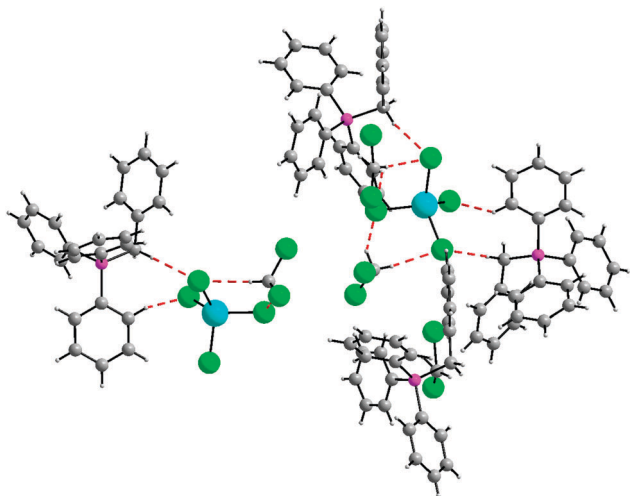
Fig. 4 Part of the crystal packing of (BzlPh₃P)₂[CuCl₄]·2CH₂Cl₂ (4) (disordered equivalent atoms are omitted).

Table 9 Hydrogen bond geometry (Å, °) for complex 4

D–H···A	D–H	H···A	D···A	D–H···A
C1–H1A···Cl1	0.97	2.69	3.658(3)	176.8
C19–H19···Cl1	0.93	2.94*	3.762(3)	148.2
C19–H19···Cl3	0.93	2.87*	3.602(3)	136.7
C26–H26A···Cl4	0.97	2.77	3.705(3)	162.4
C44–H44···Cl2	0.93	2.91*	3.608(3)	133.5
C51–H51A···Cl2^i	0.97	2.58	3.428(5)	145.6
C51–H51B···Cl1^i	0.97	2.94*	3.708(5)	137.0
C52–H52C···Cl4^{ii}	0.97	2.76	3.656(5)	154.0

Symmetry codes: (i) $-x, y, 0.5 - z$; (ii) $x, 1 - y, -0.5 + z$.

$[CuCl_4]^{2-}$ moiety. Additionally two hydrogen bonds, fulfilling the Jeffrey criterion, are observed between the benzyl-CH₂ groups and the chlorine atoms and weaker hydrogen interactions between the less acidic hydrogen atoms of the phenyl rings and the chlorine atoms (Table 9).

Bis(tetraphenylarsonium)tetrachloridocuprate(ɪɪ) (5). (Ph₄As)₂-[CuCl₄] (5) which is demonstrated in Fig. 5 crystallises in the monoclinic space group $P2_1/n$ with four formula units per unit cell. For compound 5 the highest tendency to tetrahedral geometry was determined. This also results in the shortest intramolecular Cl···Cl distances that are between 3.39 and 4.07 Å. The shortest Cu···Cu distances are 10.80 and 11.01 Å, compared to the other four complexes 5 shows the highest value for the copper–copper distance. The corresponding bond lengths and angles are presented in Table 10. Hydrogen bonding interactions between the chlorine atoms and the hydrogen atoms of the cation that are shorter than 2.83 Å are not observed but there are two weak hydrogen contacts with a distance between 2.87 and 2.98 Å where hydrogen atoms of the phenyl rings are bonded to chlorine atoms (Table 11).

EPR spectroscopy

To avoid or minimise line broadening in the EPR spectra, which is due to the magnetic interactions between the paramagnetic copper centres, a separation of these complex $[CuCl_4]^{2-}$ anions
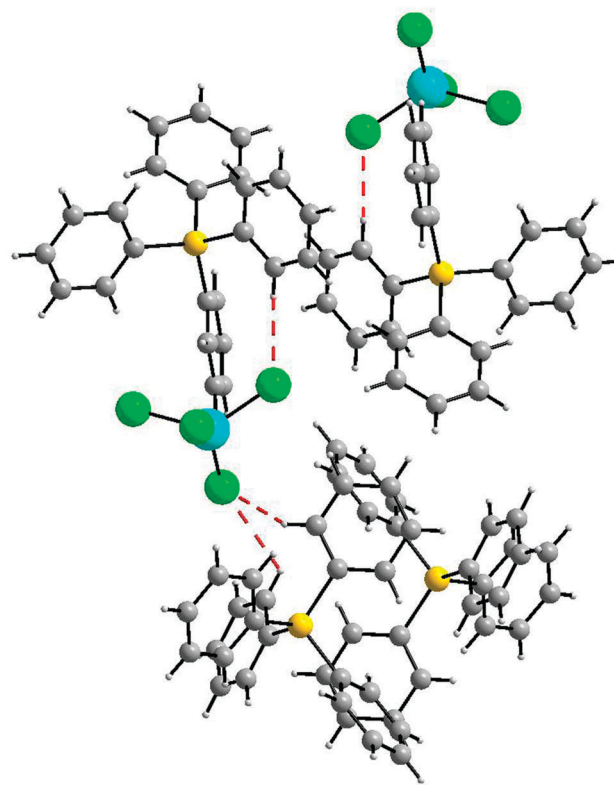

Fig. 5 Part of the crystal packing of (Ph₄As)₂[CuCl₄] (5) (disordered equivalent atoms are omitted).

Table 10 Selected bond lengths and angles of (Ph₄As)₂[CuCl₄] (5)

Bond lengths/Å		Angles/°	
Cu1–Cl1	2.2427(6)	Cl1–Cu1–Cl2	99.93(3)
Cu1–Cl2	2.2233(6)	Cl1–Cu1–Cl3	123.10(7)
Cu1–Cl3	2.365(3)	Cl1–Cu1–Cl4	104.72(7)
Cu1–Cl4	2.187(2)	Cl2–Cu1–Cl3	95.25(9)
		Cl2–Cu1–Cl4	134.84(7)
		Cl3–Cu1–Cl4	101.88(9)

Table 11 Hydrogen bond geometry (Å, °) for complex 5

D–H···A	D–H	H···A	D···A	D–H···A
C8–H8···Cl1^i	0.93	2.87*	3.481(2)	124.7
C38–H38···Cl2^{ii}	0.93	2.98*	3.746(2)	140.4

Symmetry codes: (i) $0.5 + x, 0.5 - y, -0.5 + z$; (ii) $0.5 + x, 0.5 - y, 0.5 + z$.

is necessary. One possibility to realize such a separation is a diamagnetic dilution either by a solvent or by doping into a diamagnetic host lattice. In both cases structural changes might be induced by the dilution. Comparison of the exact structural parameters with the EPR parameters of the solid samples can only be achieved with sterically rather demanding cations, which should result in an adequate separation and with this a minimum of magnetic interactions between the tetrachloridocuprate(ɪɪ) anions as it was already successfully applied to the tetrabromidocuprate series.[1]
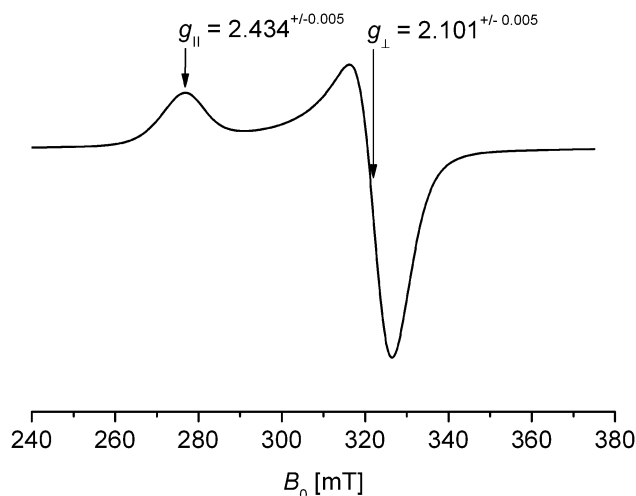
Fig. 6 X-Band powder EPR spectrum of (BzlEt₃N)₂[CuCl₄] (**1**) (*T* = 154 K, *f* = 9.4261 GHz).

$g_\parallel$ = 2.434$^{+/-0.005}$ $g_\perp$ = 2.101$^{+/- 0.005}$

Despite this approach, however, the line broadening results again in a missing hyperfine structure resolution for the copper(II) ion with a nuclear spin for both Cu isotopes (^{63}Cu and ^{65}Cu; nuclear spin I = 3/2 each). The interaction with the four chlorido ligands (^{35}Cl and ^{37}Cl; nuclear spin I = 3/2 each and a natural abundance of 75.76 and 24.24%, respectively) should theoretically result in a superhyperfine pattern which is also not resolved. This is mainly caused by the exchange broadening due to the still incomplete separation of the paramagnetic centres. The distances between the paramagnetic centres in the complexes **1–5** are
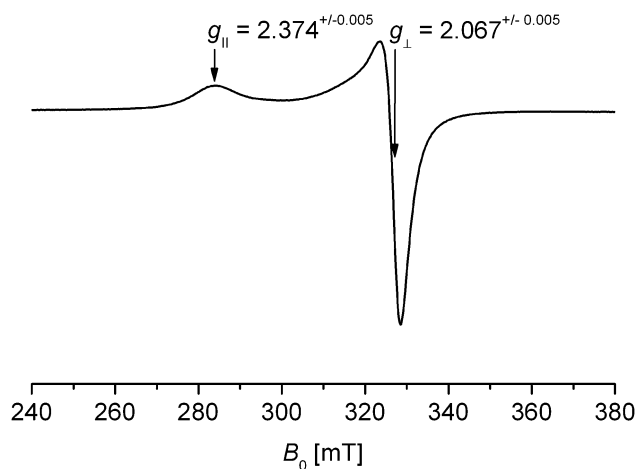

Fig. 7 X-Band powder EPR spectrum of (Me₃PhN)₂[CuCl₄] (**2**) (*T* = 154 K, *f* = 9.4334 GHz).

$g_\parallel$ = 2.374$^{+/-0.005}$ $g_\perp$ = 2.067$^{+/- 0.005}$

between 8.5 and 11 Å. All EPR spectra measured at 9.4 GHz (X-band) of the complexes correspond to an axial *g*-tensor showing broad signals (Fig. 6 and 7). The *g*-parameters, $g_\parallel$ and $g_\perp$, were determined for the five complexes (Table 12), but no coupling parameters could be extracted. For a better resolution these complexes were also measured at $\sim$34 GHz (Q-band), the spectrum of **5** is shown in Fig. 8. The averaged *g*-values (g_{av}) were obtained through the following relationship between the anisotropic parameters of the *g*-tensor, eqn (1):

$$g_{av} = \frac{g_\parallel + 2 \cdot g_\perp}{3} \tag{1}$$

Quantum chemical calculations

We used the same model (Fig. 9) and computational approach to relate average *cis*-angles to g_{av}-values as in the previous study for the tetrabromidocuprates(II).[1] A discussion with further details and the connection to the more sophisticated Continuous Symmetry Measure (CSM) methodology[113–115] can be found in ref. 1.

Fig. 10 shows the energies relative to the minimum as a function of the *cis*-angle and the positions of the minimum are only slightly influenced by the environment. In contrast, the Mulliken charge and the bond lengths *r* are rather different in a solvent, where, however, only minute changes between aceto-nitrile and water can be observed. In the lower right panel of Fig. 10 one can see the clear correlation between the *cis*-angle and the Mulliken spin density on the Cu-ion. As for the tetrabromidocuprates(II),[1] this spin density on the Cu(II) is dominated by a $d_{x^2-y^2}$ contribution (*cf.* the coordinate system in Fig. 9) and thus increases with large *cis*-angles, *i.e.*, when the chloride ions move out of the *xy*-plane (Fig. 11). This is also reflected by the calculated values of g_{av}, shown in Fig. 12, which are also in good agreement with experiment.

Discussion

The coordination geometry of most tetrachloridocuprates is an intermediate between square planar (D_{4h}) and regular tetrahedral (T_d). The geometry does not vary randomly. The factors which have an influence on the degree of distortion can be grouped into five categories: the Jahn–Teller effect, crystal field stabilisation, ligand–ligand repulsion, ligand–lattice interactions, and crystal packing effects. More details about these factors are given in Part 1: tetrabromidocuprates.[1] This structural flexibility is also in good agreement with the results of DFT calculations.

The effect of the hydrogen bonds and/or the molecular packing on the structure of the reported tetrachloridocuprate(II) dianions

Table 12 Experimental EPR parameters ($g_\parallel$- and $g_\perp$-values), averaged *g*-value and *g*-value anisotropy

Compound	$g_\parallel$	$g_\perp$	g_{av}	Δg
(BzlEt₃N)₂[CuCl₄] (**1**)	2.434 ± 0.005	2.101 ± 0.005	2.212 ± 0.005	0.333
(Me₃PhN)₂[CuCl₄] (**2**)	2.374 ± 0.005	2.067 ± 0.005	2.170 ± 0.005	0.307
(EtPh₃P)₂[CuCl₄] (**3**)	2.386 ± 0.005	2.076 ± 0.005	2.179 ± 0.005	0.310
(BzlPh₃P)₂[CuCl₄]·2CH₂Cl₂ (**4**)	2.403 ± 0.005	2.081 ± 0.005	2.189 ± 0.005	0.322
(Ph₄As)₂[CuCl₄] (**5**)	2.431 ± 0.005	2.093 ± 0.005	2.206 ± 0.005	0.338
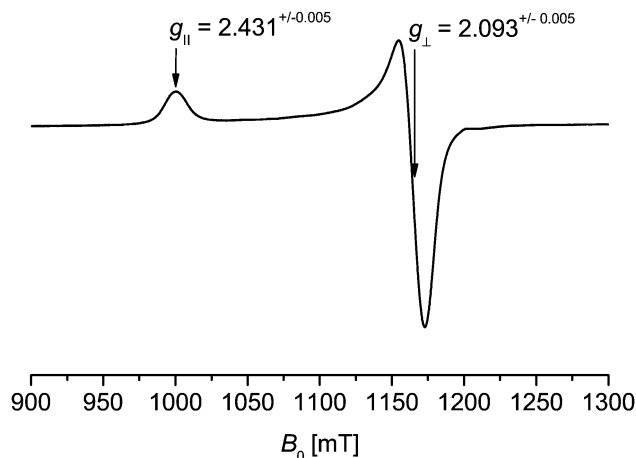
Fig. 8 Q-Band powder EPR spectrum of $(Ph_4As)_2[CuCl_4]$ (5) ($T = 150$ K, $f = 34.038$ GHz).

Fig. 11 Spin density distributions in $[CuCl_4]^{2-}$ in the square planar geometry (left), the optimised structure (middle) and the tetrahedral geometry (right). The spin densities are obtained from the acetonitrile PCM approach.
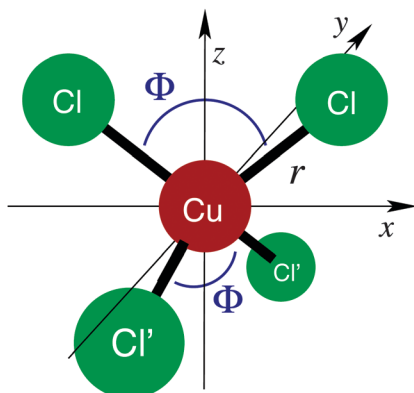

Fig. 9 Sketch of the model: Φ is varied to create different geometries. Here, the (upper) Cl-atoms remain in the xz-plane and the (lower) Cl′-atoms in the yz-plane and all bond lengths r are equal.

Fig. 12 Correlation between averaged cis-angles and averaged g-values for tetrachloridocuprates(II). The black dots reflect the calculated g-values from DFT calculations.
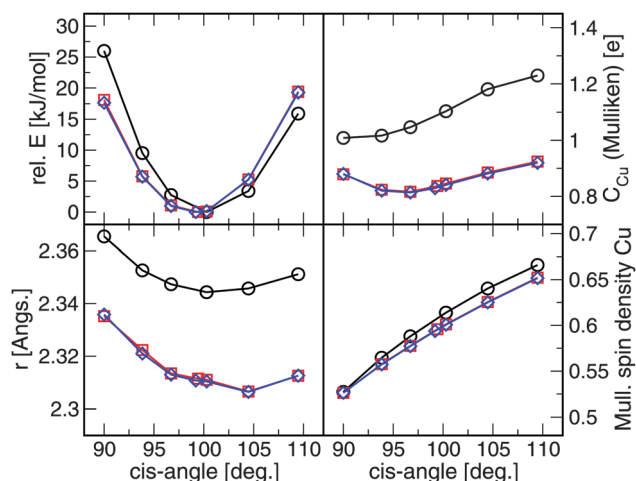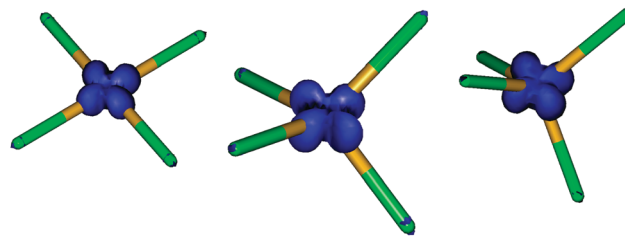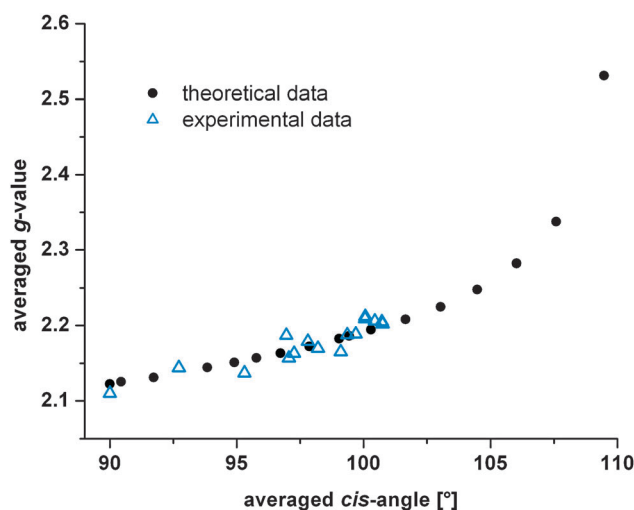

Fig. 10 Electronic energy relative to the minimum (upper left), the Cu–Cl distance (lower left), the Mulliken charge (upper right) and Mulliken spin density as a function of the cis-angle for different solvent models (○ gas phase, □ acetonitrile, and ◊ water).

results in averaged cis-angles Cl–Cu–Cl between $97.80°$ and $100.44°$ for $(EtPh_3P)_2[CuCl_4]$ (3) and $(Ph_4As)_2[CuCl_4]$ (5), respectively. The tendency to a square planar geometry as is the case in complex 3 might be caused by a reduced effective charge on the chloride ions through these hydrogen bonds. If the electrostatic repulsion forces between the chloride ions dominate, a more tetrahedral geometry should be favoured.

In the attempt of S.-K. Kang et al.[76] to correlate the EPR parameters (g_{av}) with the degree of distortion (Φ, i.e. the average of the biggest two angles, the trans-angles) of tetrachloridocuprate(II) complexes the EPR spectra were recorded in frozen glass ($DMF:CH_2Cl_2 = 1:1$), where the structural situation might be totally different, due to the interaction with the solvent and possibly by the freezing process. Nevertheless this study concluded that the larger the trans-angle the smaller is the experimental g-value. Here we correlate the measured EPR data in the pure solid substance with the structural parameters of our five tetrachloridocuprate(II) complexes and some other complexes reported in the literature. In contrast to the study mentioned above, the current study does not use the trans-angle, but the averaged cis-angle (i.e. the average of the smallest four Cl–Cl–Cl angles) in an attempt to increase the accuracy of the degree of distortion.

Table 13 summarises the data extracted from literature and the new data obtained from our complexes. Fig. 12 reveals a

Table 13 Averaged *cis*-angles and averaged *g*-values of available tetrachloridocuprate(II) complexes

Entry	Formula	*cis*-angle/°	g_{av}	Ref.
1	$K_2[Pd(Cu)Cl_4]$	90.00	2.110	82
2	$(C_6N_2H_{10})[CuCl_4]$	92.72	2.144	85
3	$[HPrz]_2[CuCl_4]$	95.30	2.137	93
4	$[H_2triam][CuCl_4]$	96.95	2.187	90
5	$(MePh_3P)_2[CuCl_4]$	97.05	2.157	15[a]
6	$[H_52,6Acgu_2][CuCl_4]Cl\cdot H_2O$	97.26	2.163	43
7	$(EtPh_3P)_2[CuCl_4]$	97.80	2.179	This work (**3**)
8	$(Me_3PhN)_2[CuCl_4]$	98.20	2.170	This work (**2**)
9	$[H_3Bzgu]_2[CuCl_4]Cl_2\cdot H_2O$	99.10	2.165	43
10	$(BzlMe_3N)_2[CuCl_4]$	99.35	2.188	14[a]
11	$(BzlPh_3P)_2[CuCl_4]\cdot 2CH_2Cl_2$	99.69	2.189	This work (**4**)
12	$(pyH)_2[CuCl_4]$	100.06	2.209	91
13	$(BzlEt_3N)_2[CuCl_4]$	100.07	2.212	This work (**1**)
14	$(Ph_4As)_2[CuCl_4]$	100.44	2.206	This work (**5**)
15	$[H_3Fogu][CuCl_4]$	100.72	2.205	43
16	$(Ph_4P)_2[CuCl_4]$	100.75	2.202	11[a]

[a] For crystal data.

Fig. 14 Correlation between the *cis*-angles and the *g*-value anisotropy from DFT calculations.

direct relationship between the averaged *cis*-angles and the corresponding g_{av}-values, taking again into account that the averaged *g*-values increase as the geometry of the structure of $[CuCl_4]^{2-}$ anions changes from square planar towards distorted tetrahedral. Interestingly the majority of the known examples is grouped around the energy minimum calculated by DFT (Fig. 10, upper left). The complexes with a square planar coordination geometry (*cis*-angle 90°) possess g_{av}-values > 2.10. This is in slight contrast to the analogous tetrabromide complexes that show a general trend to lower *g*-values.[1] Starting from a *g*-value of about 2.12 the $[CuCl_4]^{2-}$ anions show a increasing tendency to a more or less distorted or compressed tetrahedral geometry. This observed trend in increasing *g*-values with increasing *cis*-angles is in a very good agreement with the calculated Mulliken spin density at the copper centre (Fig. 10, lower right) and the trend of calculated *g*-values generated from the DFT calculations (black dots in Fig. 12). The fit of calculated and experimental values is even better than for the bromide series.[1]
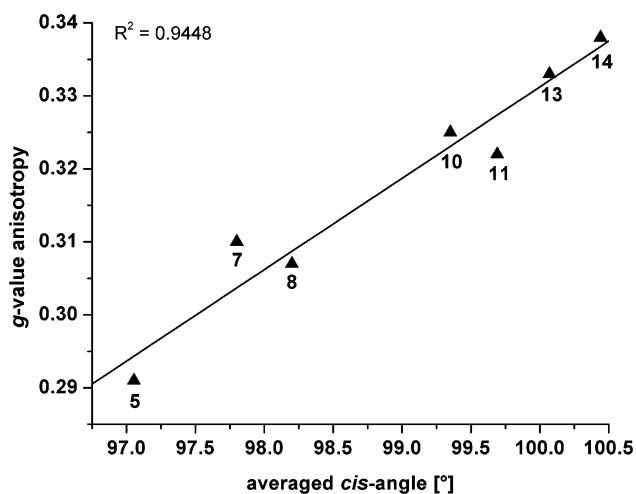
On this basis a correlation with exact structural parameters is possible.

We also correlate the anisotropy of the *g*-value of the investigated compounds **1**–**5** (Δg, Table 12) and a few data from literature where reliable values have been reported with the corresponding *cis*-angles which gives a good correlation ($R^2 = 0.9448$) for the experimental data (Fig. 13). The reason why the correlation of the *g*-value anisotropy is not very useful can be seen in Fig. 14 where the calculated Δg-values from DFT are correlated to the *cis*-angles. The changes in the symmetry of the $[CuCl_4]^{2-}$ moiety result for both, square planar and tetrahedral symmetry, in decreasing Δg-values with a maximum around 104°. Thus, no definite structural information can be extracted.

Conclusion

The aim of this work was, compared to the series of tetrabromidocuprates, the synthesis of a series of new tetrachloridocuprate(II) complexes and the correlation of their structure parameters, in particular the geometry of the $[CuCl_4]^{2-}$ moieties, with the g_{av}-value obtained from EPR measurements of the solid and pure (*i.e.* undissolved) complexes. In order to sufficiently separate the paramagnetic centres from each other sterically quite demanding cations were used. The EPR X-band spectra were again poorly resolved (no hyperfine structure), due to exchange broadening caused by incomplete separation of the paramagnetic centres. The Q-band EPR spectra allowed a more precise determination of the *g*-tensor parameters. The complexes with the cations, benzyltriethylammonium, trimethylphenylammonium, ethyltriphenylphosphonium, benzyltriphenylphosphonium, and tetraphenylarsonium, crystallise as monomeric complexes and the X-ray structures show for all tetrachloridocuprate(II) anions a compressed tetrahedral geometry.

The key finding of this work is that there is a clear relationship between the tetrachloridocuprate geometry and the averaged *g*-value. Tetrachloridocuprates(II) with a geometry close to square

Fig. 13 Correlation between the averaged *cis*-angles and the *g*-value anisotropy (numbers correspond to entries in Table 13).

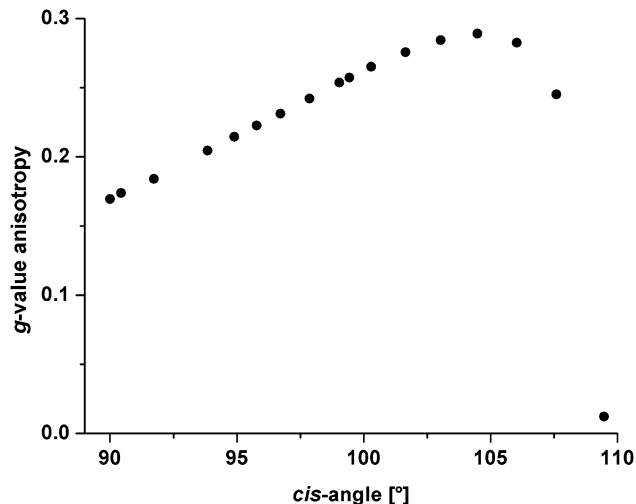planar possess average *g*-values of about 2.12. With increasing distortion towards tetrahedral geometry the averaged *g*-values increase accordingly. For averaged *cis*-angles with values between 90 to 95° and larger than 100.75° unfortunately no complete data (X-ray and EPR) are available in the literature. The aim of this study was also not to achieve best resolution or the use of highly sophisticated EPR techniques but to provide an efficient tool to obtain structure information on tetrachloridocuprates $[CuCl_4]^{2-}$ in liquids (*e.g.* solutions and ionic liquids) or structurally not yet characterised solid samples by cw-X-band EPR spectroscopy. Thus, more investigations are required to fill the remaining gap as well as further refinement of the correlation to make it applicable for the structural characterisation of tetrachloridocuprate(II) complexes in general and those which are ionic liquids in particular. In combination with Part 1 of this study dealing with the analogous tetrabromidocuprates(II) we can now provide tools for both, the $[CuCl_4]^{2-}$ and the $[CuBr_4]^{2-}$ anions.

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