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Unexpected structural similarity between the chlorocopper(I) unit and the methyllithium and phenyllithium units. First complexes between (−)-sparteine and copper(I) chloride: synthesis and structural characterisation

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Received (in Montpellier, France) 13th February 2004, Accepted 24th March 2004
First published as an Advance Article on the web 9th July 2004

Two complexes containing copper(I) chloride and (−)-sparteine (spa), namely [$Cu_2Cl_2spa_2$] and [$Cu_4Cl_4spa_2$], have been synthesised from the above-mentioned constituents in the CuCl:spa ratios 1:1 and 2:1, respectively. Characterisation by means of crystal-structure determination shows [$Cu_2Cl_2spa_2$] to be a discrete dimer and [$Cu_4Cl_4spa_2$] a discrete complex with an unusual Cu_4Cl_4 ladder-type core. An unexpected structural similarity between the chlorocopper(I) unit and the methyllithium and phenyllithium units, respectively, became apparent during a closer inspection of the relevant structures.

Introduction

There is a general urgency with respect to the search for new chiral metal complexes for use as catalysts in polymerisation reactions or as model substances for the elucidation of mechanisms in biological processes. An early investigation demonstrated that the naturally occurring enantiopure alkaloid, (−)-sparteine, depicted schematically in Fig. 1, formed complexes with first row transition metal halides.[1] Despite the proven efficacy of (−)-sparteine, in the presence of copper(I) chloride or bromide, as a homogeneous catalyst for the atom transfer radical polymerisation of styrene or methyl methacrylate,[2] no information concerning the aggregation states and coordination geometries of copper(I) in such complexes is currently available. Structural information on copper (−)-sparteine complexes appears at present to be limited to dichloro{(−)-sparteine}copper(II)[3] and {(−)-sparteine}-copper(II) diacetate.[4] Owing to our ongoing interest in complexes between copper(I) and hard-donor ligands[5] and, moreover, in the use of various metal complexes containing chiral ligands for organic synthetic applications,[6,7] we embarked on an investigation of those complexes formed in a direct reaction between copper(I) chloride and (−)-sparteine.

We now report the preparation and structural characterisation of two novel complexes between copper(I) chloride and (−)-sparteine. In addition, an unexpected structural similarity between the chlorocopper(I) unit and the methyllithium and phenyllithium units, respectively, which became apparent during a closer inspection of the relevant structures, will be discussed.

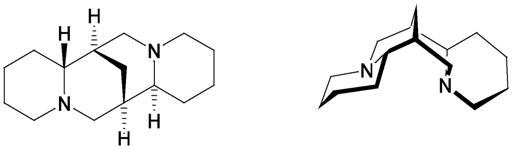


Fig. 1 Schematic drawing of the bidentate (−)-sparteine ligand.

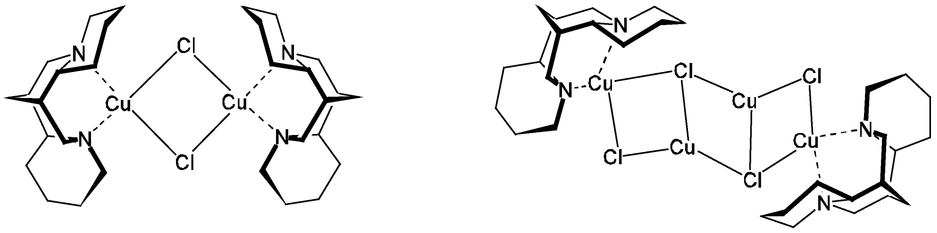
Results and discussion

Direct reaction between copper(I) chloride and (−)-sparteine in equimolar amounts yields a discrete dimer, [$Cu_2Cl_2spa_2$] (**1**). Excess of copper(I) chloride, *i.e.* an initial CuCl:(−)-sparteine ratio of 2:1, results in discrete [$Cu_4Cl_4spa_2$] (**2**), with a laddered Cu_4Cl_4 core. These compounds are depicted schematically in Fig. 2. The reactions proceed cleanly and give solely **1** and **2**, respectively, with no evidence for the formation of mixtures of the two crystalline products or other such by-products. Both compounds are relatively stable and are oxidised slowly on exposure to air, as indicated by a gradual change in colour from yellow to green.

The solid-state structures of **1** and **2** are illustrated in Figs. 3 and 4, respectively. Complex **1** crystallises as a dimer, with a rhombic Cu_2Cl_2 core of the type often encountered in species between copper(I) chloride and nitrogen donor ligands,[8] as well as in chlorocuprates(I).[9] This core is slightly asymmetric, as is seen from the relevant distances and angles in Table 1, and is planar to within 0.027 Å. The geometry of the (−)-sparteine ligand is unremarkable and differs in no significant way from such ligands in previously reported copper(II) complexes[3,4] or from the two crystallographically different (−)-sparteine molecules in complex **2**. The Cu···Cu distance of 2.6577(7) Å does not suggest the presence of a closed shell attractive interaction between the copper(I) centres.

Complex **2**, on the other hand, has an unusual Cu_4Cl_4 ladder-type core (Fig. 4), in which all four copper(I) centres exhibit different coordination geometries (*cf.* Table 2). Thus, Cu(1) has trigonal/trigonal-pyramidal coordination geometry with a very long [3.151(2) Å] apical contact, while Cu(2) is purely trigonally coordinated (r.m.s deviation of the four atoms from the best plane = 0.009 Å). Cu(3) is essentially

DOI: 10.1039/b402260b



1

2

Fig. 2 Schematic drawings of complexes **1** and **2**.

two-coordinated, with Cu–Cl distances of 2.108(2) and 2.115(2) Å [Cl–Cu–Cl = 160.8(1)°] but has a third long contact of 2.798(2) Å to give a T-shaped coordination polyhedron, and finally Cu(4) has trigonal pyramidal coordination geometry, with an apical bond of 2.714(2) Å. The Cu···Cu distances. 2.649(1), 2.910(2) and 3.031(2) Å, are not indicative of attractive copper(I)–copper(I) interactions.

Perhaps the most curious feature of this investigation becomes apparent when the complexes described in this article are compared with their methyllithium and phenyllithium counterparts.[7] With methyllithium and (−)-sparteine, a dimer completely analogous to **1** is obtained.[7] [$Cu_2Cl_2spa_2$] (**1**) and [$Li_2Me_2spa_2$][7] crystallise with the same unit cell and space group and are almost isostructural, the main difference being that the Li_2C_2 rhombus is more regular than its Cu_2Cl_2 counterpart, in that the bridging Li–C bonds do not differ appreciably from one another. Very recently, dimeric [{*n*-BuLi(−)-sparteine}$_2$] has also been reported.[10]

With phenyllithium and (−)-sparteine a laddered structure, analogous to that of **2**, ensues.[7] The laddered helical Li_4Ph_4 core of [$Li_4Ph_4spa_2$][7] is somewhat more regular than the Cu_4Cl_4 core of [$Cu_4Cl_4spa_2$] in that both outer lithium centres have unambiguous four (distorted tetrahedral) coordination whereas the two inner lithium centres are both three-coordinated (both halves of the molecule are related by a two-fold axis). The similarity between [$Cu_4Cl_4spa_2$] and [$Li_4Ph_4spa_2$] is illustrated in Fig. 5. Owing to the "replacement" of the phenyl groups in the latter compound by chloride in **2**, the helicity of the core of **2** is less pronounced than that of [$Li_4Ph_4spa_2$].

Although the phenyl-bridged lithium dimer, analogous to [$Cu_2Cl_2spa_2$] (**1**), was not obtained in the previous study,[7] there are examples of similar phenyl-bridged lithium compounds in the literature, notably [$Li_2Ph_2(tmeda)_2$][11] and [$Li_2Mes_2(THF)_4$][12] (tmeda = *N*, *N*, *N*′, *N*′- tetramethylethylenediamine, Mes = mesityl). Li_4Me_4, Li_4Ph_4 and Cu_4Cl_4 cubane-type cores have been documented in various compounds, *e.g.* $Li_4Me_4(THF)_4$,[13] $Li_4Me_4(dem)_{1.5}$ (dem = diethoxymethane),[14] $Li_4Ph_4(SMe_2)_4$,[15] and in several chlorocopper(I) instances,[8] of which $Cu_4Cl_4(NEt_3)_4$[16] represents an early example. None of these compounds are, however, mutually analogous with respect to the ancillary ligands, and they are therefore not readily comparable.

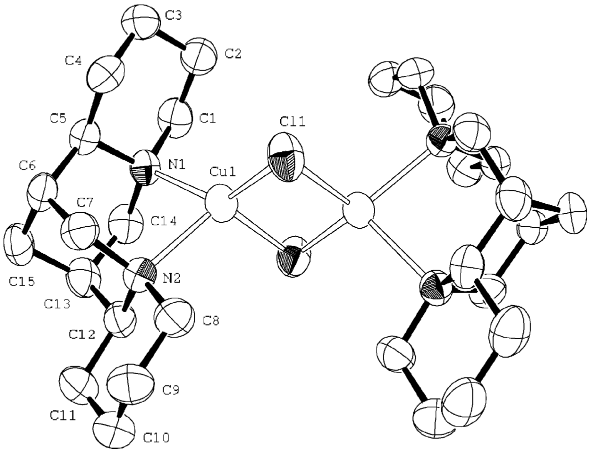


Fig. 3 Complex **1**, showing the crystallographic numbering. The thermal ellipsoids enclose 50% probability. The two halves of the molecule are related by a two-fold axis that runs parallel to the crystallographic *c* axis. For symmetry code see Table 1.

The present investigation provides evidence for structural similarity between the methyllithium and chlorocopper(I) units, and between the phenyllithium and chlorocopper(I) units, in completely analogous compounds. It is not inconceivable that the geometries associated with the atoms comprising the various cores are determined, at least to some degree, by the bulky, chiral (−)-sparteine ligands. Although likenesses between lithium halides with nitrogen base ligands and their copper(I) counterparts were recognised early on,[17] as were likenesses between phenylcopper(I) and phenyllithium,[15] it is, nevertheless, somewhat surprising that there is such close structural similarity between the chlorocopper(I) and organyllithium units. To the best of our knowledge, this likeness between the methyllithium and chlorocopper(I) units, on the one hand, and between the phenyllithium and chlorocopper(I) units, on the other, has not been enunciated previously.

Experimental

Synthesis of compounds 1 and 2

All operations were carried out under nitrogen using standard Schlenk techniques. Solvents were distilled under nitrogen from sodium/benzophenone shortly prior to use. Commercial copper(I) chloride was purified[18] and stored under nitrogen.

[$Cu_2Cl_2spa_2$] (1). Copper(I) chloride (0.32 g, 3.2 mmol) was suspended in THF (4.5 ml) in a Schlenk tube. Upon addition of (−)-sparteine (0.76 g, 3.2 mmol) all the CuCl dissolved. The yellow solution was refluxed for a few minutes and allowed to cool slowly to ambient temperature, yellow prisms of X-ray quality being formed within a few hours. The crystals

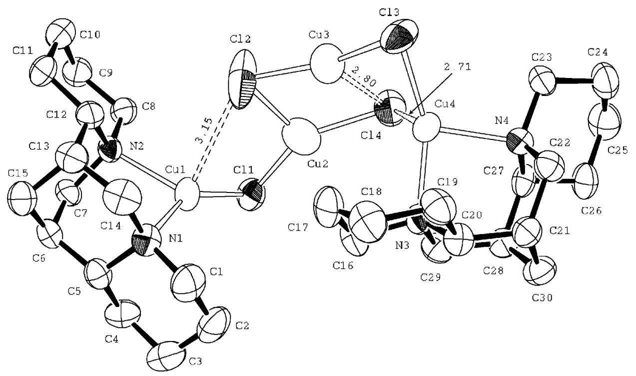


Fig. 4 Complex **2**, showing the crystallographic numbering. The thermal ellipsoids enclose 50% probability.

Table 1 Selected interatomic distances (Å) and angles (°) for [$Cu_2Cl_2spa_2$] (**1**)[a]

Cu(1)–N(1)	2.097(2)	Cu(1)–N(2)	2.195(2)
Cu(1)–Cl(1)	2.2439(9)	Cu(1)–Cl(1$^{\mathrm{i}}$)	2.4749(9)
N(1)–C(1)	1.483(3)	C(8)–C(9)	1.511(5)
C(1)–C(2)	1.507(5)	C(9)–C(10)	1.516(5)
C(2)–C(3)	1.510(5)	C(10)–C(11)	1.512(5)
C(3)–C(4)	1.524(4)	C(11)–C(12)	1.536(5)
C(4)–C(5)	1.500(4)	C(12)–N(2)	1.486(4)
C(5)–N(1)	1.482(4)	C(12)–C(13)	1.519(4)
C(5)–C(6)	1.532(4)	C(13)–C(14)	1.527(5)
C(6)–C(7)	1.523(4)	C(14)–N(1)	1.471(4)
C(7)–N(2)	1.468(3)	C(13)–C(15)	1.520(4)
N(2)–C(8)	1.473(4)	C(15)–C(6)	1.520(4)
Cu(1)···Cu(1$^{\mathrm{i}}$)	2.6577(7)		
N(1)–Cu(1)–N(2)	85.53(8)	N(1)–Cu(1)–Cl(1$^{\mathrm{i}}$)	99.55(7)
N(1)–Cu(1)–Cl(1)	135.33(7)	N(2)–Cu(1)–Cl(1$^{\mathrm{i}}$)	137.04(6)
N(2)–Cu(1)–Cl(1)	109.13(7)	Cl(1)–Cu(1)–Cl(1$^{\mathrm{i}}$)	111.58(2)
Cu(1)–Cl(1)–Cu(1$^{\mathrm{i}}$)	68.35(2)		

[a] Symmetry code: (i) $-x+1$, $-y+2$, z.

slowly decompose in air, as indicated by a colour change to green (yield: 0.42 g, 39%).

[$Cu_4Cl_4spa_2$] (2). Copper(I) chloride (0.28 g, 2.8 mmol) was suspended in THF (2.8 ml) in a Schlenk tube. When (−)-sparteine (0.32 g, 1.4 mmol) was added from a syringe all the CuCl dissolved, after which a precipitate started to form. The mixture was heated to reflux until all solids were dissolved, yielding a clear, yellow solution. The solution was allowed to cool slowly to ambient temperature, yellow prisms of X-ray quality being deposited within a few hours. The crystals decompose slowly on exposure to air, as indicated by a colour change to green (yield: 0.45 g, 75%).

Crystal structure determination†

Crystals of **1** and **2** were selected and mounted under nitrogen in glass capillaries at low temperature[19] and transferred to a Rigaku R-AXIS IIc image plate system. Diffracted intensities were measured at ambient temperature, 293(2) K, using graphite-monochromated Mo–Kα radiation ($\lambda = 0.71073$ Å) from a RU200 rotating anode operated at 50 kV and 90 mA. Ninety oscillation photographs with a rotation angle of 2° were collected and processed using the CrystalClear software package. Empirical corrections were applied for the effects of absorption using the REQAB program under CrystalClear. The structures were solved by direct methods (SIR 97)[20] and refined using full-matrix least-squares calculations on F^2 (SHELXL-97)[21] on all reflections, both programs operating under the WinGX program package.[22] Anisotropic thermal displacement parameters were refined for all non-hydrogen atoms and the hydrogen atoms were included using the riding model. Structural illustrations have been drawn with ORTEP-3 for Windows[23] and PLUTON[24] under WinGX.[22]

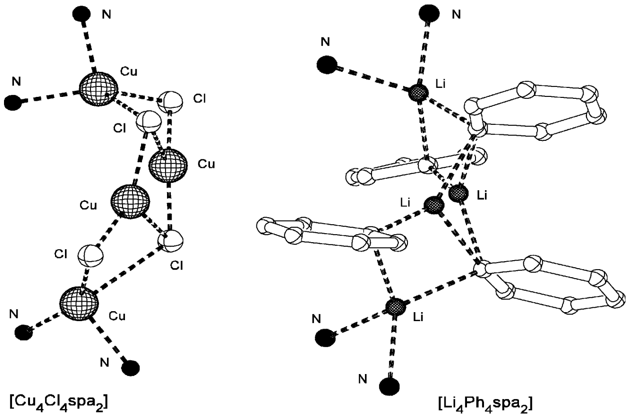


Fig. 5 The similarity between [$Cu_4Cl_4spa_2$] and [$Li_4Ph_4spa_2$].

Table 2 Selected interatomic distances (Å) and angles (°) pertaining to the core of [$Cu_4Cl_4spa_2$] (**2**). The geometries of the two crystallographically independent (−)-sparteine ligands in **2** differ in no significant way from that of the sparteine ligand in **1**

Cu(1)–N(1)	2.036(5)	Cu(4)–N(3)	2.064(5)
Cu(1)–N(2)	2.131(5)	Cu(4)–N(4)	2.130(5)
Cu(1)–Cl(1)	2.177(2)	Cu(4)–Cl(3)	2.258(2)
Cu(1)···Cl(2)	3.151(2)	Cu(4)–Cl(4)	2.714(2)
Cu(2)–Cl(1)	2.185(2)	Cu(3)–Cl(2)	2.115(2)
Cu(2)–Cl(2)	2.436(3)	Cu(3)–Cl(3)	2.108(2)
Cu(2)–Cl(4)	2.196(2)	Cu(3)···Cl(4)	2.798(2)
Cu(1)···Cu(2)	3.031(2)	Cu(2)···Cu(3)	2.910(2)
Cu(3)···Cu(4)	2.649(1)		
N(1)–Cu(1)–N(2)	89.1(2)	N(3)–Cu(4)–N(4)	88.0(2)
N(1)–Cu(1)–Cl(1)	146.5(2)	N(3)–Cu(4)–Cl(3)	139.0(2)
N(2)–Cu(1)–Cl(1)	119.6(1)	N(4)–Cu(4)–Cl(3)	117.0(1)
Cl(1)–Cu(2)–Cl(2)	111.5(1)	N(3)–Cu(4)–Cl(4)	108.0(1)
Cl(1)–Cu(2)–Cl(4)	140.3(1)	N(4)–Cu(4)–Cl(4)	100.4(1)
Cl(2)–Cu(2)–Cl(4)	108.1(1)	Cl(3)–Cu(4)–Cl(4)	99.2(1)
Cl(2)–Cu(3)–Cl(3)	160.8(1)	Cu(1)–Cl(1)–Cu(2)	88.0(1)
Cu(2)–Cl(2)–Cu(3)	79.1(8)	Cu(3)–Cl(3)–Cu(4)	74.6(1)
Cu(2)–Cl(4)–Cu(4)	105.7(1)		

Crystallographic data for 1. [$Cu_2Cl_2spa_2$]: $C_{30}H_{52}Cl_2Cu_2N_4$, $M_r = 666.7$, orthorhombic, space group $P2_12_12$, $a = 13.306(3)$, $b = 10.422(2)$, $c = 11.153(2)$ Å, $U = 1546.6(5)$ Å^3, $Z = 2$, $D_c = 1.43$ g cm^{-3}, $\mu = 1.410$ mm^{-1}. Yellow prisms, $0.2 \times 0.2 \times 0.2$ mm, 9836 reflections measured, 2651 unique ($R_{int} = 0.069$), 172 parameters, $R_1 = 0.030$ and $wR_2 = 0.073$ for the 1543 reflections for which $I > 2\sigma(I)$, $R_1 = 0.033$ and $wR_2 = 0.075$ for all 2651 reflections; Flack parameter[25] = −0.016(14); maximum and minimum residual electron density: 0.16 and −0.29 e Å^{-3}.

Crystallographic data for 2. [$Cu_4Cl_4spa_2$]: $C_{30}H_{52}Cl_4Cu_4N_4$, $M_r = 864.7$, monoclinic, space group $P2_1$, $a = 8.328(2)$, $b = 16.118(3)$, $c = 12.848(3)$ Å, $\beta = 100.390(8)°$, $U = 1696.3(6)$ Å^3, $Z = 2$, $D_c = 1.69$ g cm^{-3}, $\mu = 2.817$ mm^{-1}. Yellow prisms, $0.2 \times 0.2 \times 0.2$ mm, 10 605 reflections measured, 5899 unique ($R_{int} = 0.040$), 379 parameters, $R_1 = 0.053$ and $wR_2 = 0.142$ for the 5220 reflections for which $I > 2\sigma(I)$, $R_1 = 0.059$ and $wR_2 = 0.146$ for all 5899 reflections; Flack parameter[25] = −0.019(17); maximum and minimum residual electron density: 1.13 and −1.07 e Å^{-3}.

Acknowledgements

Financial support from the Swedish Research Council, Natural and Engineering Sciences, (Vetenskapsrådet, Naturvetenskap och Teknikvetenskap) is gratefully acknowledged.

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† CCDC reference numbers 225051 and 225052 for **1** and **2**, respectively. See http://www.rsc.org/suppdata/nj/b4/b402260b/ for crystallographic data in .cif or other electronic format.

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