

Comparative investigation of the copper(II) complexes of (*R*)-, (*S*)- and (*R,S*)-1-phenyl-*N,N*-bis(pyridine-3-ylmethyl)ethanamine along with the related complex of (*R,S*)-1-cyclohexyl-*N,N*-bis(pyridine-3-ylmethyl)ethanamine. Synthetic, magnetic, and structural studies

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Abstract The interaction of the enantiopure (*R*)- and (*S*)-1-phenyl-*N,N*-bis(pyridine-3-ylmethyl)ethanamine ligands, *R-L*¹ and *S-L*¹, with copper(II) chloride followed by addition of hexafluorophosphate resulted in the isolation of the corresponding enantiomeric complexes [Cu(*R-L*¹)Cl](PF₆) (**1**), [Cu(*S-L*¹)Cl](PF₆) (**2**) and [Cu(*S-L*¹)Cl](PF₆)·0.5Et₂O (**3**), in which dimerization occurs through two long Cu...Cl interactions, the μ -chloro bridges being thus strongly asymmetric. The organic ligand is bound to the metal centre via its N₃-donor dipyridylmethylamine fragment in a planar fashion, such that each copper centre is in a square planar environment (or distorted square pyramidal with a long axial bond length if the additional interaction is considered). When *R,S-L*¹ was employed in a parallel synthesis, the similar racemic complex [Cu(*R,S-L*¹)Cl](PF₆)·0.5MeOH

(**4**) was obtained, in which the *L*¹ ligands in each dimeric unit have opposite hands. In contrast to the complexes of *L*¹, the reaction of Cu(II) chloride with the related ligand, (*R*)-1-cyclohexyl-*N,N*-bis(pyridine-3-ylmethyl)ethanamine (*R-L*²), yielded the mononuclear complex [Cu(*R,S-L*²)Cl₂] (**5**), displaying a distorted square pyramidal coordination geometry. The structure of this product along with its corresponding circular dichroism spectrum revealed that racemisation of the starting *R-L*² ligand has occurred under the relatively mild (basic) conditions employed for the synthesis. A temperature-dependent magnetic studies of the complexes **1**, **2** and **5** indicate that a weak ferromagnetic interaction is operative in each dicopper core in **1** and **2** with $2J = 1.2 \text{ cm}^{-1}$. On the other hand, a weak antiferromagnetic intermolecular interaction is operative for **5**.

Keywords Copper(II) · Chloro-bridged · Crystal Structure · Di(2-picolyl)amine · Optically active

We dedicate this publication to Prof. Len Lindoy in celebration of his 75th birthday.

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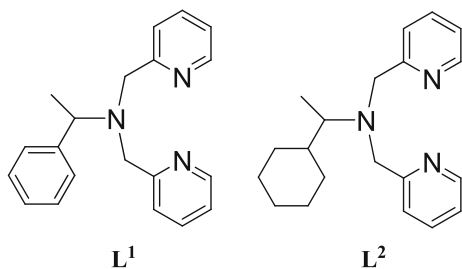
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Introduction

Complex formation by transition and post-transition metal ions with di- and polypyridyl ligands continues to receive much attention, in part reflecting the coordination versatility of such ligands as well as their potential application in a number of biological, catalytic, photoactive and sensor applications [1, 2]. For example, the 'classical' di(2-picolyl)amine ligand (dipic, **1**), together with its secondary nitrogen substituted derivatives, readily yield complexes with a wide range of such metal ion types. Reports of the interaction of dipic with Cu(II) to yield both mono- and bis-ligand derivatives have appeared [3–13]. Similarly, the interaction of Cu(II) with various dipic derivatives containing substitution at the secondary

nitrogen centre has also been widely investigated [14–24]; a number of such complexes are effective reagents for interaction with and oxidative cleavage of DNA [25–38].

We now report the results of further studies involving the interaction of the *N*-substituted di(2-picoyl)amine derivatives (*R*-, *S*- and *R,S*-1-phenyl-*N,N*-bis(pyridine-3-ylmethyl)ethanamine (*R-L*¹, *S-L*¹, *R,S-L*¹) as well as (*R*-1-cyclohexyl-*N,N*-bis(pyridine-3-ylmethyl)ethanamine (*R-L*²) with Cu(II).



Experimental

Physical methods

IR spectra were recorded with a JASCO FT-IR 5300. UV/Vis absorption spectra were measured on a SCINCO S-2100 diode-array spectrophotometer and circular dichroism (CD) spectra on a Jasco 715 spectrometer. Elemental analyses were carried out with a CE Instruments EA-1110 analyser. All samples were dried in air at 60 °C for 48 h before CHN microanalysis; the crystals for X-ray diffraction measurements were used directly without further drying. Magnetic susceptibilities of ground samples were measured on a superconducting quantum interference device (SQUID) magnetometer (Quantum Design MPMS-5S) under external field 5,000 Oe. Samples were put into a gelatin capsule, mounted inside the straw, and then fixed to the end of the sample transport rod.

Ligand and complex synthesis

$[Cu(R-L^1)Cl]_2(PF_6)_2$

NaHCO₃ (13.5 g) was added to a cold solution (0 °C) of 2-picoyl chloride hydrochloride (8.2 g) in water (200 mL) and the mixture was extracted with dichloromethane (3 × 50 mL). The combined reddish brown extracts were washed with water (2 × 50 mL), dried with anhydrous Na₂SO₄ and evaporated under reduced pressure to give a red oil (yield: 5.8 g). The resulting 2-picoyl chloride (5.1 g) in acetonitrile (50 mL) was added to (*R*-1-phenylethylamine (2.4 g) in acetonitrile and K₂CO₃ (5.0 g) was added. The mixture was stirred overnight then heated for

6 h under a nitrogen atmosphere. The solution was allowed to cool to room temperature, filtered and the filtrate taken to dryness under reduced pressure. The residual red oil was dissolved in methanol (100 mL) and CuCl₂·2H₂O (3.4 g) in methanol (50 mL) was added to give a dark green solution. This was stirred for 2 h then evaporated to dryness under reduced pressure. The green residue was dissolved in water (500 mL), the solution was filtered, and then the filtrate was adsorbed onto SP Sephadex (Na⁺ form). After elution with 0.3 mol L⁻¹ NaCl, a fast-moving major blue component was collected and evaporated to dryness under reduced pressure. The residue was extracted with ethanol and evaporated under reduced pressure to give a green powder. Yield: 3.8 g. Addition of NH₄PF₆ to an aqueous solution of this product and slow evaporation of the solution at room temperature yielded blue crystals of [Cu(*R-L*¹)Cl]PF₆ suitable for X-ray analysis. Anal. Calc. for C₄₀H₄₂Cl₂Cu₂F₁₂N₆P₂: C, 43.89; H, 3.87; N, 7.68. Found: C, 43.8; H, 3.93; N, 7.60%. Visible spectrum (in water): λ_{max} (nm) (log ε_{max} M⁻¹ cm⁻¹) 632 (2.06). IR (KBr, cm⁻¹): 3,118–3,030 [w, ν(C–H)_{ar}]; 2,997–2,933 [w, ν(C–H)]; 1,605 (py ring); 1,447 [δ_s (CH₂)]; 837 [vs., ν(P–F)]. CD spectrum (in water): λ_{min/max} (nm) [Δε (M⁻¹ cm⁻¹)] 651 (–0.080), 325 (–0.21).

$[Cu(S-L^1)Cl]_2(PF_6)_2$

This complex was prepared by an identical procedure to that described above starting from (*S*-1-phenylethylamine (*S-L*¹) (2.4 g). Yield: 4.5 g. Anal. Calc. for C₄₀H₄₂Cl₂Cu₂F₁₂N₆P₂: C, 43.89; H, 3.87; N, 7.68. Found: C, 43.9; H, 3.80; N, 7.61%. Visible spectrum (in water): λ_{max} (nm) (log ε_{max} M⁻¹ cm⁻¹) 632 (2.06). IR spectrum (KBr, cm⁻¹): 3,115–3,033 [w, ν(C–H)_{ar}]; 2,997–2,933 [w, ν(C–H)]; 1,607 (py ring); 1,446 [δ_s (CH₂)]; 839 [vs., ν(P–F)]. CD spectrum (in water): λ_{min/max} (nm) [Δε (M⁻¹ cm⁻¹)] 651 (+0.080), 325 (+0.21).

$[Cu(R,S-L^1)Cl]_2(PF_6)_2 \cdot CH_3OH$

This complex was prepared by a similar method to that described for [Cu(*R-L*¹)Cl]₂(PF₆)₂, except that (*R,S*-1-phenylethylamine (2.4 g) was employed for the ligand synthesis instead of (*R*-1-phenylethylamine. Yield: 3.4 g. The crude green complex was dissolved in methanol (10 mL) and NH₄PF₆ (0.1 g in 5 mL water) was added. On standing at room temperature, blue crystals suitable for X-ray crystallography formed. Anal. Calc. for C₄₁H₄₆Cl₂Cu₂F₁₂N₆OP₂: C, 43.70; H, 4.11; N, 7.46. Found: C, 43.7; H, 4.03; N, 7.49. IR spectrum (KBr, cm⁻¹): 3,445 [Br, ν(O–H)]; 3,120–3,064 [w, ν(C–H)_{ar}]; 2,986–2,932 [w, ν(C–H)]; 1,609 (py ring); 1,450 (δ_s [CH₂]); 839 [vs., ν(P–F)].

[Cu(*R,S*-L²)Cl₂]

This compound was prepared by a similar method to that for [Cu(*R*-L¹)Cl]₂(PF₆)₂, except that (*R*)-1-cyclohexylethylamine (1.3 g) was employed for the synthesis instead of (*R*)-1-phenylethylamine. Yield: 2.9 g. The crude complex was dissolved in water and the solution was allowed to stand at room temperature to yield blue crystals suitable for X-ray crystallography. The crystal structure of this product showed that L² was present in the complex as its racemate, indicating that racemisation had occurred during the synthesis in this case (see “Results and discussion”). Anal. Calc. for C₂₀H₂₇Cl₂CuN₃: C, 54.11; H, 6.13; N, 9.47. Found: C, 54.3; H, 5.90; N, 9.50. Visible spectrum (in water): λ_{max} (nm) (log ε_{max} M⁻¹ cm⁻¹) 663 (2.14). IR (KBr, cm⁻¹): 3,067, 3,030 [ν(C–H)_{ar}]; 2,926, 2,851 [ν(C–H)]; 1,609 (py ring); 1,451, 1,442 [δ_s (CH₂)].

Crystallography

The data were collected at 150(2) K on a Nonius Kappa-CCD area detector diffractometer [39] using graphite-monochromated Mo-Kα radiation (λ 0.71073 Å). The crystals were introduced in glass capillaries with protecting “Paratone-N” oil (Hampton Research) coating. The unit cell parameters were determined from ten frames, and then refined on all data. The data (combinations of φ- and ω-scans giving complete data sets up to θ = 25.7° and a minimum redundancy of 4 for 90% of the reflections) were processed with HKL2000 [40]. Absorption effects were corrected empirically with the program SCALEPACK [40]. The structures were solved by direct methods with SHELXS-97 and subsequent Fourier-difference synthesis and refined by full-matrix least-squares on F² with SHELXL-97 [41]. All non-hydrogen atoms were refined with anisotropic displacement parameters. The carbon-bound hydrogen atoms were introduced at calculated positions and were treated as riding atoms with an isotropic displacement parameter equal to 1.2 (CH, CH₂) or 1.5 (CH₃) times that of the parent atom. The absolute configuration in complexes 1–3 was determined from the value of the Flack parameter [42]. Special details are as follows:

Compound 3. Restraints on displacement parameters were applied for some atoms of the counter-ions and the solvent molecule. The inversion centre of pseudo symmetry between the two molecules is not valid for the –CH(CH₃)(C₆H₅) substituent.

Compound 4. The PF₆ ion is disordered over two positions sharing the phosphorus atom, which were refined with occupancy parameters constrained to sum to unity and restraints on bond lengths and angles. The methanol molecule is very badly resolved and was given

an occupancy factor of 0.5 in order to retain acceptable displacement parameters; its carbon atom is further disordered over two positions which were refined with occupancy parameters constrained to sum to 0.5 and restraints on bond lengths and displacement parameters. The methanolic hydrogen atom was not found, nor introduced.

Compound 5. The methyl atom C20 is disordered over two positions, with occupancy parameters first refined to a value close to 0.5, then fixed to this value.

Crystal data and structure refinement details are given in Table 1 and selected bond lengths in Table 2. The molecular plots were drawn with SHELXTL [41].

Results and discussion

Ligand and complex synthesis

The syntheses of *R*-L¹, *S*-L¹ and *R,S*-L¹ were performed using an established general procedure [14] which in the present study involved the condensation of 2-chloromethylpyridine with (*R*)-, (*S*)- or (*R,S*)-1-phenylethylamine in acetonitrile under basic conditions (see Scheme 1). In each case the oil obtained was reacted directly with Cu(II) chloride dihydrate in methanol in the presence of potassium carbonate (as base) to yield a blue solid; this was dissolved in water and, after chromatography on SP Sephadex C-25 (Na⁺ form) and the addition of hexafluorophosphate anion to the eluent, blue crystals were obtained. All three complexes prepared in this manner were characterised by microanalysis, infrared and UV–Vis spectrophotometry as well as by an X-ray crystal structure determination.

The microanalysis data indicated that each complex corresponded to a metal to ligand ratio of 1:1. The infrared spectra of all three products were essentially identical and in accord with the expected structures, while the CD spectra of the first two complexes (Fig. 1) confirmed, as expected, that they are enantiomers (this was important to establish in view of the racemisation behaviour observed for the corresponding complex derived from *R*-L²—see later). The visible spectra of all three products are similar, showing a single broad envelope of *d-d* bands in the visible range, with a λ_{max} of ~632 nm (ε_{max}: log 2.06 M⁻¹ cm⁻¹). The spectra are in accord with the presence of distorted 5- or 6-coordinate Cu(II) centres [43, 44]. All three complexes yielded almost identical IR spectra, except that the complex derived from *R,S*-L¹ also contained an ν(O–H) peak due to the presence of a methanol solvate in the solid state.

Table 1 Crystal data and structure refinement details

| | 1 | 2 | 3 | 4 | 5 |
|---|---|---|--|--|--|
| Chemical formula | C ₂₀ H ₂₁ ClCuF ₆ N ₃ P | C ₂₀ H ₂₁ ClCuF ₆ N ₃ P | C ₂₂ H ₂₆ ClCuF ₆ N ₃ O _{0.5} P | C _{20.5} H ₂₃ ClCuF ₆ N ₃ O _{0.5} P | C ₂₀ H ₂₇ Cl ₂ CuN ₃ |
| <i>M</i> /g mol ⁻¹ | 547.36 | 547.36 | 584.42 | 563.38 | 443.89 |
| Crystal system | Trigonal | Trigonal | Monoclinic | Monoclinic | Triclinic |
| Space group | <i>P</i> 3 ₁ 21 | <i>P</i> 3 ₂ 21 | <i>P</i> 2 ₁ | <i>P</i> 2 ₁ / <i>n</i> | <i>P</i> $\bar{1}$ |
| <i>a</i> /Å | 16.4560(4) | 16.4553(5) | 13.0173(6) | 13.0625(8) | 8.4032(3) |
| <i>b</i> /Å | 16.4560(4) | 16.4553(5) | 14.4482(9) | 14.8215(9) | 10.9260(6) |
| <i>c</i> /Å | 14.5639(3) | 14.5624(3) | 14.7160(10) | 14.4309(8) | 13.1392(8) |
| α /° | 90 | 90 | 90 | 90 | 103.205(2) |
| β /° | 90 | 90 | 115.598(3) | 116.083(3) | 107.843(3) |
| γ /° | 120 | 120 | 90 | 90 | 106.045(3) |
| <i>V</i> /Å ³ | 3415.52(14) | 3414.88(16) | 2496.1(3) | 2509.4(3) | 1036.94(10) |
| <i>Z</i> | 6 | 6 | 4 | 4 | 2 |
| <i>D</i> _{calc} /g cm ⁻³ | 1.597 | 1.597 | 1.555 | 1.491 | 1.422 |
| μ (MoK α)/mm ⁻¹ | 1.208 | 1.209 | 1.109 | 1.100 | 1.320 |
| <i>F</i> (000) | 1,662 | 1,662 | 1,192 | 1,144 | 462 |
| Reflections collected | 105,953 | 59,279 | 106,525 | 69,781 | 33,587 |
| Independent reflections | 4,314 | 4,314 | 9,448 | 6,334 | 3,888 |
| Observed reflections [<i>I</i> > 2 σ (<i>I</i>)] | 4,089 | 3,983 | 8,203 | 4,513 | 3,575 |
| <i>R</i> _{int} | 0.022 | 0.034 | 0.041 | 0.026 | 0.030 |
| Parameters refined | 292 | 292 | 627 | 373 | 244 |
| <i>R</i> 1 | 0.032 | 0.036 | 0.058 | 0.049 | 0.034 |
| <i>wR</i> 2 | 0.086 | 0.093 | 0.164 | 0.143 | 0.079 |
| <i>S</i> | 1.047 | 1.042 | 1.053 | 1.127 | 1.102 |
| $\Delta\rho_{\min}$ /e Å ⁻³ | -0.52 | -0.50 | -0.61 | -0.50 | -0.41 |
| $\Delta\rho_{\max}$ /e Å ⁻³ | 0.50 | 0.44 | 1.10 | 0.84 | 0.27 |
| Flack parameter | 0.004(12) | -0.002(14) | -0.006(14) | - | - |

Table 2 Environment of the Cu(II) atoms in compounds **1–5**: selected bond lengths (Å)

| | 1 | 2 | 3^a | 4 | 5 |
|---------------|-----------|-----------|------------------------|-----------|----------------------|
| Cu–N1 | 2.046(2) | 2.044(3) | 2.043(5), 2.070(5) | 2.041(3) | 2.0969(19) |
| Cu–N2 | 1.979(2) | 1.976(3) | 1.995(5), 1.968(5) | 1.976(3) | 1.993(2) |
| Cu–N3 | 1.978(2) | 1.979(3) | 1.987(5), 1.987(5) | 1.988(3) | 1.992(2) |
| Cu–Cl | 2.2472(7) | 2.2468(9) | 2.2500(15), 2.2531(15) | 2.2439(9) | 2.2588(7), 2.5041(7) |
| Cu⋯Cl (axial) | 2.7998(8) | 2.7994(9) | 2.8091(15), 2.8412(15) | 2.7815(9) | |

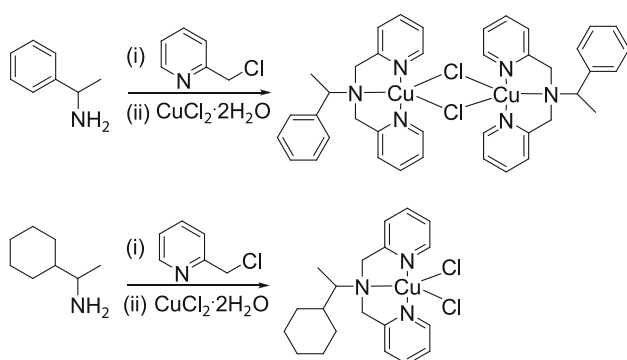
Symmetry codes: see figures

^a The two values correspond to the two independent molecules

Crystal structures

The complexes [Cu(*R*-L¹)Cl](PF₆) (**1**) and [Cu(*S*-L¹)Cl](PF₆) (**2**) crystallize in enantiomorphic space groups, with identical unit cell parameters, and the absolute configuration determined in each case is in agreement with that of the enantiopure ligand used (Fig. 2). In both complexes,

the N₃-donor sequence of L¹ is bound meridionally to the Cu(II) centre, with the remaining coordination site in the plane being occupied by a chlorine atom, with unexceptional Cu–N1, Cu–N2,3 and Cu–Cl bond lengths of ca 2.05, 1.98, and 2.25 Å, respectively (Table 2). Two neighbouring molecules related by a binary axis are connected to one another through two longer axial Cu⋯Cl contacts, at ca



Scheme 1 Synthesis of the complexes; step (i) in each reaction was performed in the presence of sodium hydrogen carbonate as base while potassium carbonate was employed for step (ii)

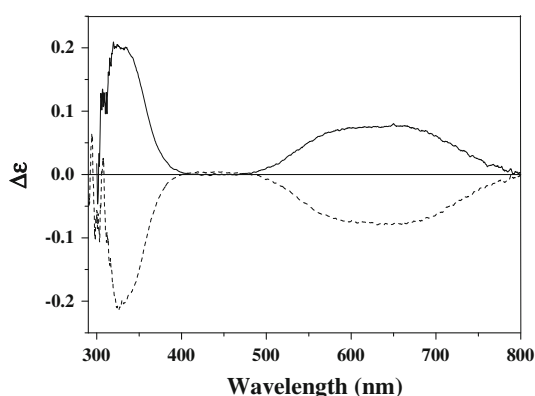


Fig. 1 CD spectra of $[\text{Cu}(\text{R-L}^1)\text{Cl}]_2(\text{PF}_6)_2$ (Dashed line) and $[\text{Cu}(\text{S-L}^1)\text{Cl}]_2(\text{PF}_6)_2$ (Solid line)

2.80 Å, so as to form dimers. The latter value is in the upper range of the distribution of Cu–Cl bonds for structures reported in the Cambridge Structural Database (CSD, Version 5.32) [45], the median of the histogram being ca 2.30 Å, a value in agreement with the in-plane Cu–Cl bond length observed here. The μ -chloro bridges are thus strongly asymmetrical and, while the primary environment of the metal ion is distorted square planar, the overall environment, taking into account the additional interaction, is a much elongated square pyramid.

Complex **3**, $[\text{Cu}(\text{S-L}^1)\text{Cl}](\text{PF}_6) \cdot 0.5\text{Et}_2\text{O}$ (**3**), crystallizes in the chiral space group $P2_1$, and contains the same enantiomorph as complex **2**. Two crystallographically independent molecules comprise the dimeric unit, denoted A and B, both with the same chirality (Fig. 3). In contrast to **1** and **2**, the two molecules possess an inversion centre of pseudo-symmetry, which is accurate for 85% of the atoms, as indicated by PLATON [46], but not for the methyl substituent on the chiral group. In contrast, the complex $[\text{Cu}(\text{R,S-L}^1)\text{Cl}](\text{PF}_6) \cdot 0.5\text{MeOH}$ (**4**) crystallizes in the centrosymmetric space group $P2_1/n$, with unit cell parameters

very close to those of complex **3**. The two molecules in the dimeric unit are related here by the inversion centre and are of opposite hands (Fig. 3), in agreement with the use of the racemic ligand as a reagent. In both **3** and **4**, the Cu(II) environment is the same as in **1** and **2**, with Cu–Cl bond lengths of ca 2.24–2.25 Å and axial Cu⋯Cl interactions at ca 2.78–2.84 Å. In all complexes **1–4**, the aromatic ring belonging to the 2-phenylethane substituent is positioned over one of the pyridyl rings such that strong face-to-face π -stacking interactions are present (centroid⋯centroid separations, centroid offsets, and dihedral angles in the ranges 3.60–3.79 Å, 1.19–1.65 Å, and 21.6–25.6°, respectively).

The structures of the complex cations in **1–4** are quite similar to the square pyramidal structures reported previously for the related di- μ -chloro species $[\text{Cu}(\text{L}^3)(\mu\text{-Cl})]_2(\text{PF}_6)_2 \cdot 0.5\text{CH}_2\text{Cl}_2$ [47], $[\text{Cu}(\text{L}^3)(\mu\text{-Cl})]_2(\text{ClO}_4)_2 \cdot 0.33\text{CH}_3\text{OH}$ [48] and $[\text{Cu}(\text{L}^3)(\mu\text{-Cl})]_2(\text{ClO}_4)_2 \cdot 0.67\text{C}_2\text{H}_5\text{OH}$ [49], where L^3 is *N*-benzyl-di(2-picolyl)amine, with each of these complexes containing the same complex cation (but different anions).

For comparison, an attempt was made to prepare the corresponding Cu(II) complex of the closely related, enantiopure cyclohexyl-substituted ligand *R-L*². Accordingly, this ligand was reacted with Cu(II) chloride dihydrate using a similar procedure to that employed for the corresponding complexes of L^1 , except that no hexafluorophosphate was added to the aqueous solution used in the final crystallisation step. The blue complex formed was shown from microanalytical data to have the stoichiometry $\text{Cu}(\text{L}^2)\text{Cl}_2$. The infrared spectrum was quite similar to the spectra obtained for the respective Cu(II) complexes of L^1 . However, somewhat to our surprise the CD spectrum gave no measurable rotation and hence the product is not optically active. In view of this, the crystal structure of this product was also determined (Fig. 4). Complex **5** crystallizes in a centrosymmetric space group, with one molecule in the asymmetric unit, which confirms that L^2 is present in its racemic (*R,S*) form. While the square pyramidal coordination sphere of the copper atom is generally similar to that occurring in the complexes of L^1 , the orientation adopted by the cyclohexyl-containing pendent group differs. Presumably reflecting the absence of the π -stacking of aryl groups found in the complexes of L^1 , the pendent group in the present complex is orientated away from the metal coordination sphere.

Clearly, racemisation has occurred under the (mildly) basic conditions employed for the synthesis in this case. There is literature precedence for related racemisation occurring under mild conditions during the synthesis of Cu(II) complexes of amine-containing ligands [50] and it is assumed in the present case that racemisation occurs via generation of a carbanion at the asymmetric site under the basic conditions employed for the reaction.

Fig. 2 Views of the dimeric assemblies in complexes **1** (left) and **2** (right). Counterions and hydrogen atoms are omitted. Displacement ellipsoids are drawn at the 30% probability level. The long axial Cu⋯Cl interactions are shown as dashed lines. Symmetry codes: **1**: ' = -x, y - x, 1/3 - z; **2**: ' = 2 - x, y - x + 1, 5/3 - z

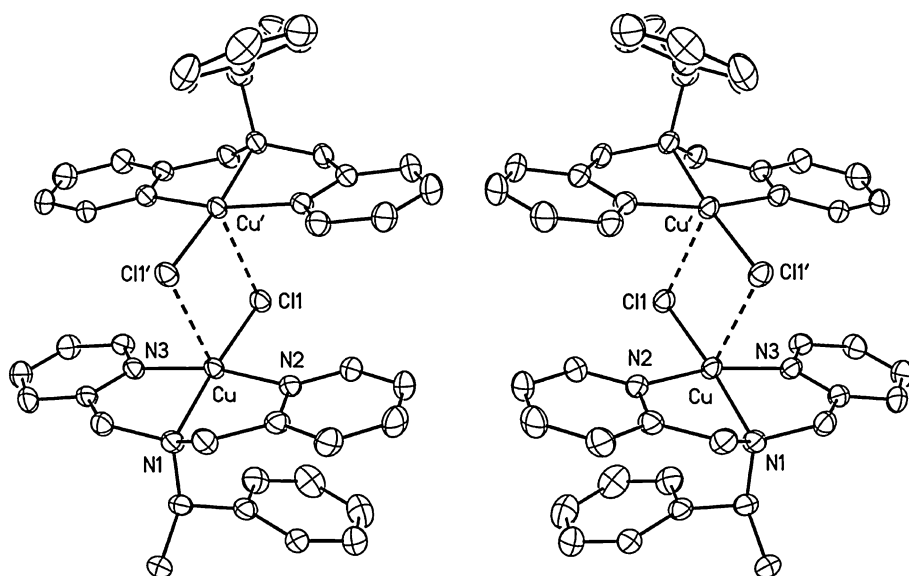
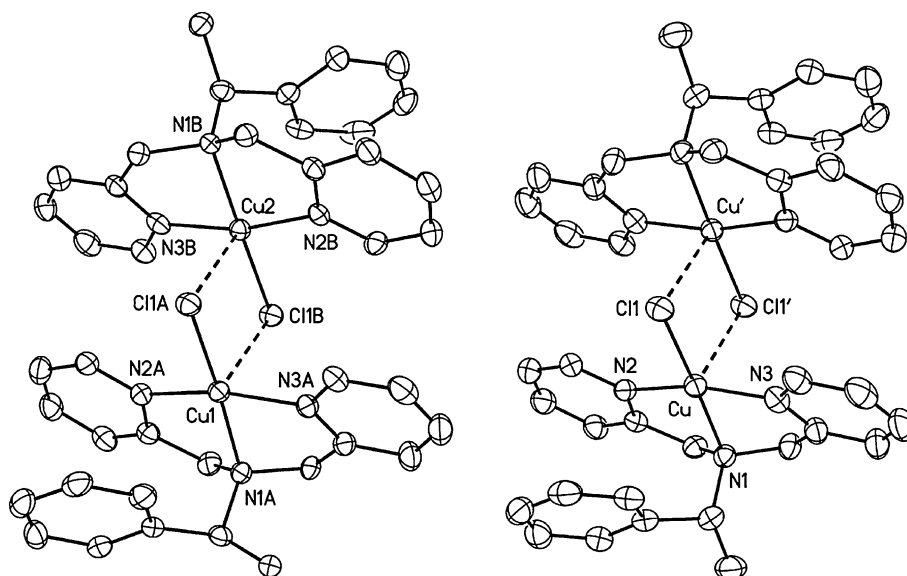


Fig. 3 Views of the dimeric assemblies in complexes **3** (left) and **4** (right). Counterions and hydrogen atoms are omitted. Displacement ellipsoids are drawn at the 30% probability level. The long axial Cu⋯Cl interactions are shown as dashed lines. Symmetry code in **4**: ' = 1 - x, 1 - y, 1 - z



Magnetic studies

The temperature dependencies of magnetic susceptibilities of the ground samples were measured in the temperature range of 2–300 K in the form of the $\chi_m T$ versus T curve, where χ_m is the molar magnetic susceptibility and T the temperature. Complex **1** has $\chi_m T$ value ($\chi_m T = 0.92 \text{ cm}^3 \text{ K mol}^{-1}$) close to the spin-only value for two Cu(II) ions at 300 K but displays an increase below 20 K in $\chi_m T$ versus T profile indicative of ferromagnetic coupling (Fig. 5). The data χ_m versus T were fitted to the Bleaney–Bowers equation (1) ($H = -2J\hat{S}_1 \cdot \hat{S}_2$) (Fig. 5) [51].

$$\chi_m = (1 - \sigma) \frac{N\beta^2 g^2}{k(T - \theta)} \left[\frac{2}{3 + \exp(-\frac{2J}{kT})} \right] + \sigma \frac{N\beta^2 g^2}{4kT} + N\alpha \quad (1)$$

$2J$ is the singlet–triplet splitting, $N\alpha$ is the temperature-independent paramagnetism, θ is a Weiss-like corrective term for weak intermolecular associations [52, 53] and σ represents the fraction of a magnetically dilute impurity. The parameters giving the best fit were obtained using a nonlinear regression analysis with g , J , σ and θ as variables, and $N\alpha$ is fixed at $N\alpha = 60 \times 10^{-6} \text{ cm}^3 \text{ mol}^{-1}$.

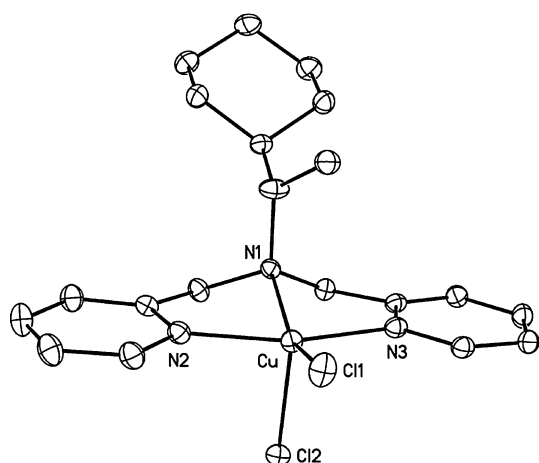


Fig. 4 View of complex **5**. Hydrogen atoms are omitted. Displacement ellipsoids are drawn at the 30% probability level. Only one position of the disordered methyl group is represented

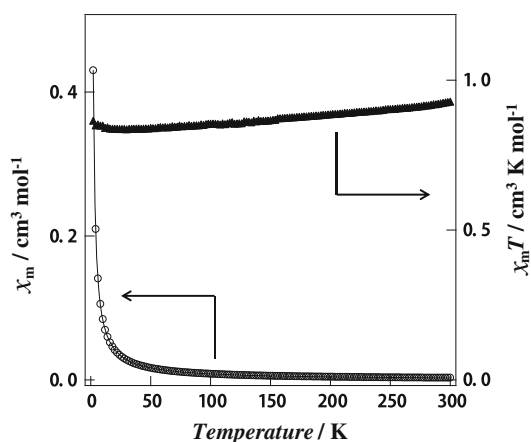


Fig. 5 Temperature dependence of χ_m and $\chi_m T$ for **1** at 5000 Oe. The solid lines correspond to the best-fit curves to Eq. (1)

The solid line in Fig. 5 represents the best-fit situation with $g = 2.09$, $2J = 1.2 \text{ cm}^{-1}$, $\sigma = 0.0028$ and $\theta = -0.4 \text{ K}$. The Cu...Cu distance is 3.4 \AA and the Cu–Cl–Cu angle is 83.9° for **1**. A very weak ferromagnetic interaction is operative in the intramolecular Cu...Cu core. On the other hand, a weak antiferromagnetic interaction is operative in the intermolecules. Complex **2** also shows magnetic behavior which resembled that of **1** very well. The least-squares fitting of the experimental data for **2** has given $g = 2.09$, $2J = 1.0 \text{ cm}^{-1}$, $\sigma = 0.0030$ and $\theta = -0.4 \text{ K}$. The Cu...Cu distance is 3.4 \AA and the Cu–Cl–Cu angle is 83.9° for **2**. Complex **5** is mononuclear, and the magnetic behavior is shown in Fig. 6. The $\chi_m T$ value is $0.42 \text{ cm}^3 \text{ K mol}^{-1}$ in the range of 300–50 K, and the value is closed to the spin-only value for one Cu(II) ion. The $\chi_m T$ value decreases below 50 K on cooling. The weak antiferromagnetic interaction is operative in the intermolecules.

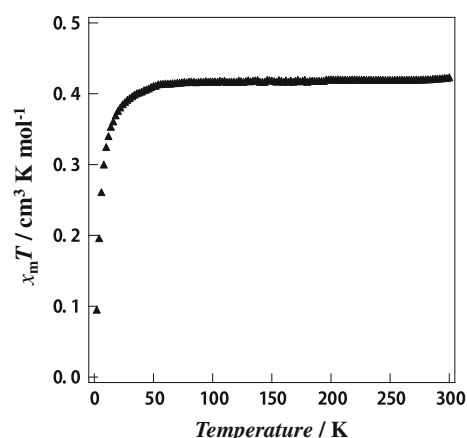


Fig. 6 Temperature dependence of $\chi_m T$ for **5** at 5000 Oe

Concluding remarks

In this paper we report the synthesis and characterisation of new Cu(II) complexes formed from enantiopure *R-L*¹ and *S-L*¹ as well as from racemic *R,S-L*¹. All these complexes have similar four-coordinate coordination geometries with one additional long axial contact about each copper centre, being thus dimeric species with asymmetric di- μ -chloro bridges. In contrast to these structures, the related cyclohexane derivative *R-L*² yields a mononuclear five-coordinate complex incorporating racemic *R,S-L*², thus providing a further example of the facile racemisation of an asymmetric carbon centre present in an amine-containing ligand bound to Cu(II).

Supplementary material

Crystallographic data for the five complexes have been deposited with the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK and are identified by deposition numbers CCDC 833618–833622. Copies of this information can be obtained free of charge on request by e-mail at deposit@ccdc.cam.ac.uk or at <http://www.ccdc.cam.ac.uk>.

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